Université du Québec
INRS Eau-Terre-Environnement

Sols pollués par les métaux lourds résultant de l'enfouissement de déchets industriels (Montréal, Canada): Géochimie, spéciation des métaux, et décontamination par flottation

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Thèse présentée pour l'obtention du grade
de Philosophiae Doctor (Ph. D.)
en Sciences de la Terre et Environnement

Jury d'évaluation

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Résumé

Les friches industrielles (*brownfields*) polluées par les métaux lourds sont des lieux potentiellement toxiques pour l'environnement. De plus, la présence de ces terrains contaminés en milieu urbain handicape largement l'aménagement du territoire. Dans la ville de Montréal, plus de 200 sites présentent une forte contamination métallique des sols. Dans le cadre de cette thèse, les travaux se focalisent sur un terrain situé à proximité du centre-ville de Montréal et affecté par des déchets minéralurgiques riches en métaux lourds. Le défi actuel est de promouvoir des solutions technologiques pour traiter les sols pollués plutôt que d'avoir recours à des techniques d'enfouissement. Une revue exhaustive de littérature permet de faire un état des lieux de la problématique des sols contaminés par les métaux et fournit l'éventail des techniques conventionnelles et innovatrices pour immobiliser ou extraire les métaux des sols.

Le premier objectif de cette thèse est de déterminer la répartition spatiale des métaux dans plusieurs profils du sol afin d'évaluer leur potentiel de mobilisation dans l'environnement. Le second objectif est d'établir la spéciation et la répartition des métaux dans la phase solide du sol dans une perspective de lavage de sol. Enfin, le troisième objectif est de déterminer l'efficacité de l'enlèvement des métaux par flottation et d'évaluer les principaux paramètres (physiques et chimiques) influençant le processus de séparation.

Le profil du sol est composé d'un horizon superficiel de remblais riches en déchets minéralurgiques reposant sur le sol naturel initial, lequel est composé d'un horizon organique (tourbe) et minéral calcaire (marne et sédiments lacustres). Dans l'horizon anthropique, les teneurs en As, Cd, Cu, Pb et Zn dépassent largement les critères génériques des sols établis par le Ministère du Développement durable, de l'Environnement et des Parcs du Québec (MDDEP, 1999). Les concentrations totales des métaux dans les horizons du sol naturel sont très souvent

inférieures au niveau de fond géologique (critère A) établi par le MDDEP. Cependant, le calcul du facteur d'enrichissement des métaux révèle une forte « contamination » de l'horizon organique par rapport à l'horizon minéral. Cela suggère que la tourbe est contaminée par les métaux provenant d'une lixiviation potentielle des fragments de scories minéralurgiques.

La distribution spatiale des contaminants dans l'horizon anthropique est très hétérogène. La concentration des métaux s'avère indépendante d'une composition géochimique particulière des échantillons de sol. Toute les fractions granulométriques étudiées sont affectées, et ce, même si les particules fines contiennent les plus hautes teneurs. L'étude micro-spectroscopique (microscope électronique à balayage couplé à un analyseur de rayons X par spectrométrie en énergie dispersive) d'environ 150 particules riches en métaux reflète une grande diversité de la spéciation des métaux en phase solide. La forme prédominante du Zn est la sphalérite (ZnS), tandis que le Cu et le Pb sont distribués dans un large panel de formes minéralogiques, particulièrement des oxydes/carbonates. La distribution du Cu, Pb et Zn est aussi évaluée selon la localisation de la phase métallique au sein de la particule (libérée, associée, incluse ou localisée à la surface). En outre, l'étude micro-spectroscopique montre que certaines particules auraient subi des altérations chimiques (*weathering)* importantes et que certaines phases riches en métaux seraient issues d'un processus de re-précipitation (par exemple des phases oxydes/hydroxydes riches en Cu, Pb et Zn sur la surface d'un grain de quartz). Ces observations consolident l'hypothèse de la contamination de l'horizon organique par une mobilisation des métaux dans le profil de sol provenant de l'altération lente des fragments des scories métallurgiques.

Parmi les technologies éprouvées dans le traitement des minerais, la flottation est une alternative intéressante à explorer afin d'extraire les métaux des matrices environnementales. Le rôle de la flottation est de concentrer les particules riches en métal dans un plus petit volume de sol. Les expériences à l'échelle laboratoire ont permis de déterminer l'efficacité et les limites de

cette technologie en intégrant les problématiques spécifiques aux sols à traiter. Le taux d'enlèvement des métaux, ainsi que la sélectivité de la séparation ont été évalués en fonction des paramètres opératoires liés à la technologie de flottation et de la distribution des métaux dans le sol (minéralogie et granulométrie). Le sol subit un prétraitement par broyage afin de traiter toutes les fractions fortement contaminées <10 mm et d'obtenir une granulométrie appropriée (<250 µm). L'influence des conditions chimiques (type et concentration d'agent collecteur, pH, prétraitement chimique, minéralogie) et des paramètres physiques (vitesse d'agitation, taille des particules, mode d'addition du collecteur, ultrasonication) a été évaluée dans le but de mieux comprendre les mécanismes de séparation des particules riches en métal.

En général, la flottation a permis d'enlever suffisamment de métaux pour abaisser la concentration dans le sol résiduel du critère D au critère C. L'utilisation d'un agent tensioactif (collecteur) anionique, le KAX, a permis d'obtenir un bon compromis entre le taux d'enlèvement des métaux (42–52%) et la réduction de volume (>80%). L'utilisation d'un collecteur non ionique (le kérosène) a donné de meilleurs taux d'enlèvement, cependant la séparation est moins sélective. Deux mécanismes contribuent à l'enlèvement des particules riches en métaux : (1) le vrai mécanisme de flottation, basé sur la séparation sélective des particules hydrophobes; (2) l'entraînement mécanique des particules fines qui se fait indépendamment des propriétés des surfaces des particules. L'effet d'entraînement est responsable d'une grande part de l'enlèvement des métaux puisque les particules fines (<20 µm) contiennent une part importante de la contamination et que l'effet d'entraînement est significatif dans les cellules de flottation agitée. La sélectivité de la flottation est améliorée avec un temps de processus inférieur à 5 min et une addition en plusieurs étapes du collecteur. La sélectivité de la flottation est optimale pour la fraction particulaire intermédiaire (20–125 µm).

Remerciements

Je désire remercier mon directeur de thèse, monsieur Mario Bergeron, qui a bien su me guider dans mes travaux, tout en me laissant la liberté d'explorer les voies qui me passionnent. Tous mes remerciements vont également à mes deux co-directeurs, messieurs Marc Richer-Laflèche et Guy Mercier, qui, par leurs précieux conseils et leur enthousiasme à partager leur savoir, m'ont supporté tout au long de mes recherches.

Je souhaite également remercier les examinateurs qui ont gentiment accepté de participer à l'évaluation de cette thèse, madame Catherine Mulligan et messieurs Robert Hausler et Jean-François Blais. Au fil des ans, j'ai pu m'inspirer de leurs nombreux travaux afin d'approfondir mes recherches et d'élargir mes horizons. Je les remercie grandement pour l'intérêt porté à mes recherches.

De plus, cette thèse aurait été impossible à réaliser sans le soutien financier de l'Institut national de recherche scientifique Eau Terre et Environnement (INRS-ETE), ainsi que le support technique, administratif et matériel des techniciens qui y travaillent. Je les remercie sincèrement. Je remercie également monsieur Bruno Boussicault pour son expertise en géophysique.

Je tiens à remercier chaleureusement mes collègues doctorants: Belkacem, Loubna, Edgar, Satinder, Kokou, Amélie, Vladimir, Jorge, Mathieu…Je tiens finalement à offrir mes derniers remerciements à monsieur Angus Calderhead pour ses commentaires pertinents et ses suggestions fort enrichissantes, ainsi qu'à ma famille, mes amis, et ma compagne, Kathrine, pour leur affection et leurs encouragements constants.

Avant-propos

L’ensemble de cette thèse se focalise sur la décontamination des sols pollués par les métaux. Le document suivant s’articule en deux parties distinctes. La première partie (Chapitre 1) permet de faire le point sur la contribution des travaux et des publications dans le domaine du traitement des sols contaminés par les métaux. Elle comprend également des informations complémentaires aux écrits de la partie suivante. La deuxième partie (Chapitres 2 à 7) présente six articles publiés, acceptés ou sur le point d’être soumis à des revues scientifiques avec comité de lecture. Plus précisément, les trois premiers articles offrent un état des lieux de la problématique des sols contaminés par les métaux et fournissent l’éventail des techniques conventionnelles et innovatrices pour immobiliser ou extraire les métaux des sols. Les trois articles suivants synthétisent les résultats obtenus dans le cadre des travaux de terrain et de laboratoire, lesquels s’étendent de la caractérisation pluridisciplinaire du site pollué à la décontamination du sol par la technologie de flottation. Un septième article publié dans le cadre d’une conférence internationale avec comité de lecture complète la caractérisation du site d’un point de vue géotechnique (Annexe A). Bien que cet article fournisse des informations pertinentes sur le sol étudié, les résultats présentés sont considérés comme préliminaires. Par conséquent, ce document n’est pas intégré dans la deuxième partie afin d’éviter certaines répétitions et confusions dans les résultats.

Dans le cadre de sa thèse, l’auteur a pu apporter des contributions pertinentes au domaine choisi à travers : (A) les articles de revues scientifiques publiés ou soumis; (B) les articles et/ou communications réalisés dans le cadre de conférences internationales. Il faut cependant mentionner que les communications sans arbitrage ne sont pas reportées ici. Dans tous les cas, le premier auteur est l’auteur correspondant. En qualité de premier auteur, l’étudiant a rédigé entièrement tous les articles après révisions et suggestions pertinentes du Dr. Mario Bergeron et des autres co-auteurs.

A. Articles de périodique composant la seconde partie :

1. Dermont, G., Bergeron, M., Mercier, G., Richer-Lafleche, M. (2008). Metal-Contaminated Soils: Remediation Practices and Treatment Technologies. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* 12, 188-209.

2. Dermont, G., Bergeron, M., Mercier, G., Richer-Laflèche, M. (2008). Soil washing for metal removal: A review of physical/chemical technologies and field applications. *Journal of Hazardous Materials* 152, 1-31.

3. Dermont, G., Bergeron, M., Mercier, G., Richer-Laflèche, M. Remediation of contaminated soils by metal immobilization technologies. Article soumis à la revue *Environment International* (résumé et plan de rédaction pré-accepté par l'éditeur en chef, Dr. Ruth Alcock, en décembre 2007).

4. Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G. Geochemistry and solid-phase speciation of heavy metals in urban soil contaminated by metallurgical wastes disposal: implications for metal mobilization and soil remediation. Article soumis à la revue *Environmental Pollution*.

5. Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G. Heavy metal removal from contaminated soils by froth flotation: Part 1. Influence of chemical factors. Article soumis à la revue *The Science of the Total Environment*.

6. Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G. Heavy metal removal from contaminated soils by froth flotation: Part 2. Influence of physical factors and contribution of entrainment mechanism. Article soumis à la revue *The Science of the Total Environment*.

B. Communications ou articles de conférences internationales avec comité de lecture :

7. Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G., Boussicault, B. (2006). A multidisciplinary approach to improve characterization and remediation feasibility of urban soils contaminated by heavy metals. *In: 59th Canadian Geotechnical Conference, Canadian Geotechnical Society*, Vancouver, BC, Canada, Sea to sky Geotechnique 2006, 848-855. (article reporté en annexe A)

8. Dermont, G., Bergeron M., Richer-Laflèche, M., Mercier, G. (2005). Caractérisation par une approche multidisciplinaire de sols urbains contaminés par les métaux dans le cadre d'une stratégie de décontamination/ Decontamination strategy : Multidisciplinary approach to Metal-contaminated urban soil, *The International Environmental Technology Trade Show and Conference « Americana », 6th biennial Edition*, April 6-8, 2005, Montreal, QC, Canada.

9. Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G., Boussicault, B. (2006). Caractérisation de sols d'une friche industrielle polluée par les métaux, *Geological Association of Canada, Annual Meeting*, May 14-17, 2006, Montreal, Canada, Volume 31, 37.

10. Dermont, G., Bergeron M., Richer-Laflèche, M., Mercier, G. (2007). Décontamination des sols pollués par les métaux lourds: Revue des technologies novatrices de traitement / Heavy metal contaminated soils: A review of innovative decontamination technologies, *The International Environmental Technology Trade Show and Conference « Americana », 7th biennial Edition*, March 20-22, 2007, Montreal, QC, Canada.

Contribution de l'auteur pour les travaux et la rédaction des articles

La compilation des données et la revue de littérature de toutes les techniques de traitement figurant dans les articles 1, 2, 3 ont été entièrement réalisées par l'étudiant. L'ensemble des travaux décrits dans les articles 4, 5, 6 ont également été réalisés par l'étudiant. Les travaux de terrains ont été effectués ou supervisés par l'étudiant avec la participation des co-auteurs.

L’ensemble des manipulations des échantillons de sol, la mise au point des protocoles opératoires et les expériences de laboratoire ont été réalisés par l’étudiant, de même que la quasi-totalité des analyses chimiques (à l’exception de l’analyse du C et N). Toutes les microanalyses par SEM-EDX ont été effectuées et interprétées par l’auteur. Les analyses XRD ont été réalisées par l’Université Laval (Québec, Canada). Les tomographies de résistivité électrique reportées dans l’article de conférence (Annexe A) ont été réalisées par Monsieur Bruno Boussicault, tandis que les interprétations ont été effectuées sous la direction du Dr. Marc Richer-Laflèche. Les travaux de terrain concernant les sondages géophysiques ont été effectués en étroite collaboration avec Monsieur Bruno Boussicault.

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Partie 1

Chapitre 1: Synthèse

Abréviations utilisées dans la synthèse

AS	Horizon de sol anthropique
BTEX	Benzène, Toluène, Ethylbenzène, Xylène
CEMRS	Centre d'excellence de Montréal en réhabilitation de sites
ETM	Éléments traces métalliques
EXAFS	Extended X-Ray absorption fine structure
HAP	Hydrocarbures aromatiques polycycliques
KAX	Amyle xanthate de potassium
MDDEP	Ministère du Développement durable, de l'Environnement et des Parcs (Québec)
MEDD	Ministère de l'Écologie, de l'Énergie, du Développement Durable (France)
MO	Matière organique
PRM	Particules riches en métaux
SCM	Sols contaminés par les métaux
SEM-EDX	Scanning electron microscopy / Energy dispersive X-ray
S/S	Solidification/Stabilisation
TRNEE	Table ronde nationale sur l’environnement et l’économie (Canada)
USEPA	United States Environmental Protection Agency
XRD	X-ray diffraction

1. Introduction

La présence de friches industrielles (*brownfield*) en milieu urbain est un problème majeur dans les pays industrialisés. Au Canada, 30 000 terrains de ce type seraient concernés (TRNEE, 2003). Au Québec, le MDDEP a répertorié plus de 6000 terrains, dont un grand nombre sont localisés dans la région de Montréal (MDDEP, 2006). Dans le cadre de l'aménagement urbain de Montréal, certaines friches industrielles font l'objet d'un intérêt particulier, car elles sont situées à proximité du centre-ville. Parmi ces sites répertoriés à des fins de réhabilitation, un grand nombre sont affectés par des remblais hétérogènes dont les teneurs en métaux lourds dépassent les critères génériques établis par le MDDEP. La nécessité de la décontamination de ces terrains s'appuie donc sur une double motivation : environnementale et socio-économique. Dans le cas des sols urbains affectés par des métaux issus de déchets industriels, la problématique principale est l'hétérogénéité de la contamination. D'autre part, la connaissance de la spéciation des métaux à l'intérieur des sols est primordiale afin de connaître le potentiel de mobilisation des métaux et d'établir une stratégie de décontamination.

Cette synthèse s'articule autour de quatre axes majeurs: (1) une discussion générale sur la prévision du devenir des métaux dans le sol; (2) un retour sur la problématique des sols contaminés par les métaux (SCM) dans les sites répertoriés et sur les traitements disponibles, accompagné d'une discussion centrée sur le contexte québécois; (3) une présentation des travaux de caractérisation multidisciplinaire d'un sol urbain à Montréal afin d'estimer le potentiel de mobilisation des métaux et la faisabilité de traitement par lavage de sol; (4) l'évaluation de l'efficacité de l'enlèvement des métaux par la technologie de flottation et l'identification des principaux paramètres qui influencent la sélectivité de la séparation et de la récupération des métaux. La gestion des SCM doit évoluer en passant de l'enfouissement vers le traitement. Le choix d'étudier la flottation comme outil de décontamination est pertinent, car il s'agit d'une technique physico-chimique éprouvée en minéralurgie pour récupérer les métaux. Cependant, son application dans le traitement des matrices environnementales hétérogènes, plus complexes que les minerais, a été peu étudiée comparativement aux techniques chimiques de lavage de sol.

2. Prévision du devenir des métaux dans le sol

Dans le domaine de l'environnement, l'expression « métaux lourds », ou par extension « éléments traces métalliques" (ETM), regroupe les métaux de densité supérieure à 5 g/cm^3 et les métalloïdes lourds, comme l'arsenic As (McLean et Bledsoe, 1992). Dans ce document, le terme « métaux » regroupera tous les éléments choisis (As, Cd, Cr, Cu, Ni, Pb et Zn) pour la discussion, lesquels sont les ETM dont la présence a été la plus fréquemment constatée dans les sites répertoriés aux États-Unis (USEPA, 2004), en France (MEDD, 2008) et au Québec (MDDEP, 2007). Bien que le cas du mercure ne soit pas abordé dans cette première partie, quelques procédés de traitement des sols affectés par le Hg sont discutés au fil des Chapitres 2, 3 et 4. Les métaux peuvent affectés les nappes aquifères et sont dangereux pour l'environnement et la santé humaine selon leur spéciation et leur biodisponibilité (Adriano, 2001; Alloway, 1994). La discussion se concentre sur la problématique des sols fortement affectés par des remblais contenant des déchets solides porteurs de métaux lourds. Les solides ciblés sont des déchets métallifères et industriels comme par exemple, des résidus de la métallurgie/minéralurgie (scories, sable de fonderie, mâchefer, fragments de soudures, etc.). La pollution diffuse des métaux dans l'environnement et les conséquences inhérentes ne sont pas l'objet de ce document. Le potentiel de risque de libération des métaux vers les eaux souterraines est brièvement discuté, cependant les techniques de dépollution de la zone saturée et des eaux souterraines ne sont pas abordées.

2.1. Les risques de pollution des métaux issus des déchets solides

Les sols peuvent être affectés par l'enfouissement ou le dépôt de matériaux solides contenant de fortes teneurs en métaux. Ces déchets solides, source potentielle de pollution, peuvent subir différentes altérations physiques et/ou chimiques et libérer peu à peu les métaux dans la phase liquide du sol. Les polluants libérés peuvent être transportés par les eaux d'infiltration vers le sol naturel sous-jacent et les eaux souterraines. La libération des métaux contenus dans les déchets solides vers l'environnement immédiat ne s'effectue pas de manière homogène. La libération des métaux dépend de plusieurs paramètres : (1) les aspects géochimiques des métaux dans le sol (la concentration, la spéciation, le fractionnement et la distribution spatiale); (2) les propriétés physicochimiques du solide porteur (porosité, granulométrie, composition chimique et minéralogique, etc.); (3) les conditions chimiques environnantes (pH, Eh, concentrations des ligands, etc.) ; (4) les caractéristiques pédologiques du sol naturel environnant (capacité d'échange ionique, composants organiques et minéraux, sites d'adsorption, granulométrie, etc.); (5) les conditions hydrogéologiques du site (milieu poreux/non poreux, non fracturé/fracturé, zone saturée/non saturée, etc.).

Dans le cas de l'enfouissement ou du dépôt de déchets solides, la mobilisation des métaux peut s'effectuer par deux vecteurs principaux: (1) l'infiltration des eaux de pluie à travers les horizons anthropiques contenant les solides porteurs (lixiviation potentielle); (2) la dispersion par voie aérienne des poussières de déchets exposés en surface. Dans le premier cas, les polluants sont transportés par l'eau d'infiltration (percolation), tandis que dans le deuxième cas, les polluants sont diffusés sur les sols environnants.

2.2. Facteurs influençant le comportement des métaux dans le sol

Les métaux introduits dans le sol par la décharge de déchets solides peuvent se retrouver, au fil du temps, sous différentes formes chimiques (suite à des processus d'altération) et distribués dans divers locus du sol. Les premiers paragraphes du Chapitre 2 récapitulent les aspects importants de la physico-chimie des métaux dans le sol: (1) la distribution des métaux selon la granulométrie; (2) la répartition des métaux entre la phase solide et liquide du sol; (3) le fractionnement des métaux dans les différentes phases minérales ou organiques de la phase solide; (4) la spéciation dans la phase solide et la solution du sol. Les méthodes analytiques permettant d'appréhender ces différents aspects sont également présentées dans le Chapitre 2. La spéciation est un paramètre essentiel pour évaluer la solubilité, la toxicité et le devenir des métaux dans le sol (Chapitre 2).

La concentration et le degré d'oxydation des ions libres métalliques dans la solution de sol sont régis par un certain nombre de processus chimiques et biologiques: (1) réactions d'adsorption/désorption et échanges d'ions; (2) complexation inorganique et organique, (3) réactions de réduction ou d'oxydation, (4) réactions acido-basiques; (5) réactions de précipitation/dissolution des phases solides minérales; (6) biotransformations (Figure 1). Les composantes physicochimiques et biologiques du sol peuvent interagir avec les métaux. Les métaux peuvent être dans la solution de sol sous différentes formes : (1) ions libres en métal, (2) complexes solubles avec des ligands inorganiques ou organiques, ou (3) associés à des colloïdes inorganiques et organiques (Kalis, 2006; MacLean et Bledsoe, 1992). Dans le cas de phases solides minérales contenant les métaux (tels que des déchets minéralurgiques), la libération du métal dans la solution de sol dépend surtout de la capacité de la phase minérale à se solubiliser, laquelle dépend du produit de solubilité (Kps) des espèces minérales et des conditions chimiques (en particulier pH et Eh).

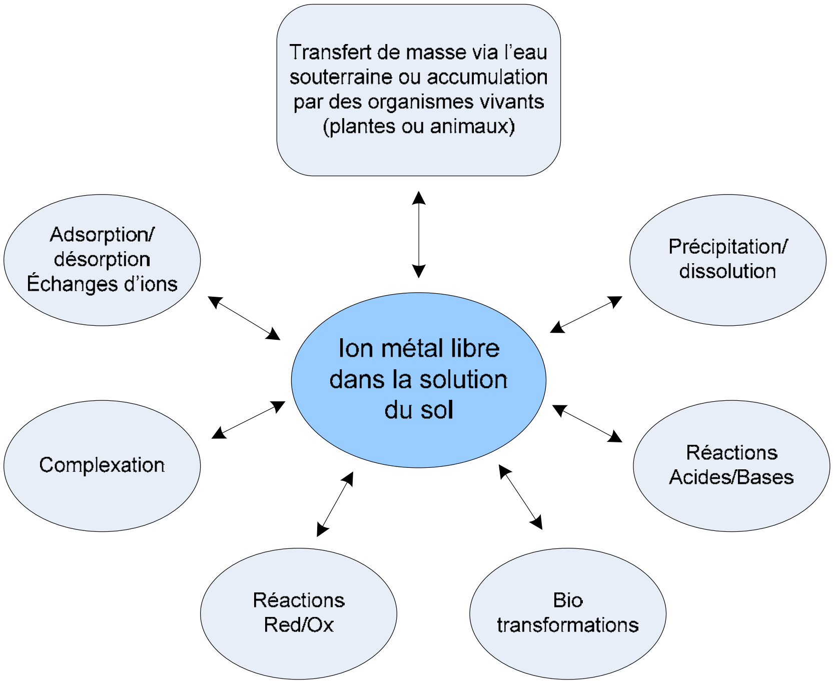


Figure 1. Principaux facteurs et réactions chimiques contrôlant la concentration et le degré d'oxydation des ions libres métalliques dans la solution du sol (d'après Adriano et al., 2004 ; MacLean et Bledsoe, 1992 ; Wang et Mulligan, 2004)

Le coefficient de partage (Kd) entre la phase solide et liquide du sol n'est pas le seul paramètre pour décrire l'interaction des métaux dans le sol, car leurs concentrations dans les phases solides et la solution de sol ne sont pas constantes et dépendent des conditions chimiques de la phase liquide concernée (pH, Eh, autres ions ou complexes en solutions) et des capacités d'adsorption du sol par les sites d'échanges d'ions ou par chimiosorption (oxyhydroxydes de Fe/Al/Mn, les argiles, la MO,...) ou biosorption (microorganismes, plantes,…). Le comportement et la réactivité chimique des métaux cationiques (Cd, Cu, Pb, Ni et Zn) diffèrent nettement du comportement des oxyanions du Cr et du métalloïde As. Selon Adriano et al. (2004), l'ordre d'affinité des cations divalents métalliques pour l'adsorption par la MO est : $Cu^{2+} > Cd^{2+} > Pb^{2+} >$

Ni^{2+} > Zn^{2+}. En plus des composantes physicochimiques du sol, les réactions biochimiques causées par les microorganismes présents dans le sol peuvent jouer un rôle prépondérant dans le devenir des métaux et peuvent être utilisées à des fins de restauration des sols (*bio-stabilisation* ou *bio-immobilisation*), en particulier pour changer la valence des espèces du Cr ou de As [réduction du Cr(VI) et oxydation de As(III)] ou pour les précipiter (Gadd, 2004; Wang et Mulligan, 2006).

Les diagrammes Eh-Ph, ainsi que différents modèles basés sur les paramètres thermodynamiques sont généralement utilisés pour prévoir la prédominance des espèces (Adriano et al., 2004). Le pH est souvent considéré comme l'un des facteurs les plus importants. Les réactions de précipitation pour les cations métalliques de Cd, Cu, Pb et Zn prédominent pour des pH >6–7 en présence d'anions tels que des sulfates, carbonates, hydroxydes et phosphates (Adriano et al., 2004). En milieu alcalin, les mécanismes de précipitation/dissolution et d'adsorption/désorption des espèces anioniques de As et Cr sont fortement dépendants de leur spéciation (en particulier de leur degré d'oxydation), ainsi que de la présence d'autres ions (par ex : Ca^{2+} , SO_4^{2-}, Fe^{2+}, Mg^{2+}) (Cornelis et al., 2008). Généralement, l'adsorption diminue pour la plupart des espèces cationiques des métaux quand le pH de la solution diminue. Au contraire, l'adsorption des espèces anioniques des métaux tels que les oxyanions du métalloïde As ou Cr(VI) diminue quand le pH augmente. La présence simultanée des espèces anioniques et cationiques en métal qui ont des comportements chimiques différents dans le sol peut être un handicap à leur éventuel traitement.

3. Les sites pollués et les solutions de traitement

3.1. La prépondérance des métaux dans les sites répertoriés

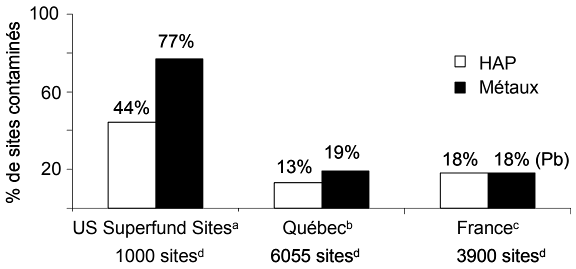
De nombreux sites répertoriés pour leur réhabilitation en Amérique du Nord et en Europe sont contaminés par les métaux (Chapitre 2). En terme d'occurrence, les 3 principaux métaux discernés dans les 1000 sites prioritaires aux États-Unis (sites *Superfund*) sont As, Cr et Pb (USEPA, 2004); dans les 7600 sites répertoriés au Québec sont Pb, Cu et Zn (MDDEP, 2007); dans les 4000 sites répertoriés en France sont Pb, Cr et Cu (MEDD, 2008). Aux États-Unis, la fréquence de contamination par les métaux dans les principaux programmes de réhabilitation est souvent plus importante que celle causée par les produits organiques (Tableau 1).

Tableau 1. Comparaison de la fréquence de contamination par les métaux et les composés organiques pour les principaux programmes de réhabilitation de sites aux États-Unis (sources : USEPA, 2004)

Programme de réhabilitation	Nbr. Total de sites	Fréquence Métaux	Fréquence COV	Fréquence COSV
NPL (*Superfund*)	1 000	77%	78%	71%
U.S. DOD (Défense)	9 000	72%	64%	57%
U.S. DOE (Énergie)	5 000	55%	38%	38%

COV= Composés Organiques Volatils (ex: COV halogénés, BTEX, HAP)

COSV= Composés Organiques Semi-Volatils (ex: PCB, phénols)



HAP= Hydrocarbures Aromatiques Polycycliques

[a] USEPA, 2004

[b] MDDEP, 2006

[c] MEDD, 2008

[d] Nombre total de sites répertoriés dans le cadre des programmes de réhabilitation

Figure 2. Comparaison du pourcentage de sites contaminés par les HAP et les métaux pour les programmes de réhabilitation aux États-Unis, au Québec et en France.

Les inventaires récents des sites contaminés par les agences environnementales du Québec et de la France indiquent que la fréquence de contamination par les métaux est comparable à celle des HAP (Figure 2). Cependant, les hydrocarbures pétroliers sont les polluants les plus fréquents en France (MEDD, 2008) et au Québec (MDDEP, 2006). Aux États-Unis, la plupart des sites sont affectés par une contamination mixte : pollution simultanée par des métaux et des composés organiques (Chapitre 2).

3.2. La gestion des SCM aux États-Unis et en Europe

Malgré les efforts fournis au cours des vingt dernières années dans le développement des technologies de traitement des SCM, l'enfouissement/confinement demeure l'option de gestion la plus utilisée en Amérique du Nord (Chapitre 2). L'enfouissement/confinement n'est pas une solution environnementale satisfaisante, alors que la gestion par le traitement s'intègre dans une politique de développement durable. Contrairement aux polluants organiques, les métaux ne peuvent pas être dégradés ou détruits. Les procédés sont limités à deux principes d'action: (1) l'immobilisation (fixation; isolation; ou réduction de la mobilité/toxicité des métaux); (2) l'extraction (séparation des métaux de la matrice du sol).

La Figure 3 résume ces différentes stratégies et les technologies pertinentes pour traiter spécifiquement les SCM. Le Chapitre 2 de ce document récapitule les différents avantages, inconvénients, limites d'utilisation et efficacité selon la forme des métaux pour chaque technologie de dépollution. L'utilisation des traitements ex-situ se révèle pertinente pour la décontamination des sites urbains, car les terrains à réhabiliter sont souvent de petite taille et doivent être rapidement disponibles (poussée immobilière, échéance de projets de revitalisation, etc.). Aux États-Unis, la solidification/stabilisation (S/S) ex situ est énormément utilisée pour traiter les SCM (Chapitre 3 et Chapitre 4). L'association canadienne du ciment (ACC) relate également quelques applications récentes de la S/S au Canada, en particulier en Colombie-Britannique et en Ontario (ACC, 2008). La S/S est encore peu employée en Europe pour gérer les sols contaminés, son utilisation concernant surtout les déchets (Chapitre 2 et Chapitre 4). La S/S ex situ ne résout pas définitivement le problème de la contamination, car le procédé débouche sur l'enfouissement.

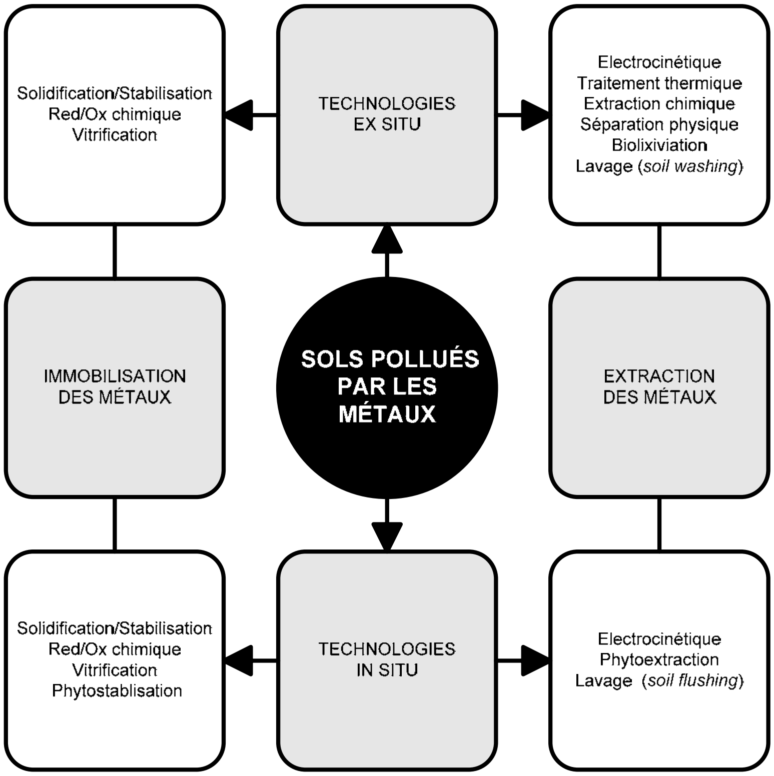


Figure 3. Schéma synthétique des technologies de traitement des sols pollués par les métaux

Les technologies alternatives d'extraction telles que les méthodes biologiques ou physicochimiques de lavage de sol sont parmi les plus prometteuses, mais la production des résidus de traitement peut engendrer une augmentation des coûts de dépollution et d'autres nuisances environnementales (Chapitre 3). Une revue exhaustive des travaux de recherche et des applications réelles des méthodes de lavage des sols (physiques et chimiques) a permis d'actualiser la synthèse des connaissances acquises au cours des 15 dernières années et de préciser la pertinence des différentes techniques en fonction de la spécificité des métaux et des caractéristiques du sol (Chapitre 3). Les technologies de lavage de sol ont été peu employées dans le cadre des projets de décontamination en Amérique du Nord comparativement aux méthodes d'enfouissement ou d'immobilisation (Chapitre 2 et Chapitre 4). Les procédés de lavage de sol sont plus intensément utilisés en Europe du Nord, principalement aux Pays-Bas, en Allemagne, en Norvège et en Suède (Chapitre 3). La combinaison des technologies doit être privilégiée, car une seule technologie ne suffit pas à décontaminer efficacement le sol.

Les méthodes d'extraction in situ (la phytoextraction et la décontamination électrocinétique, lavage de sol in situ ou *soil flushing*) sont appropriées aux formes adsorbées, ioniques ou facilement extractibles des métaux. La phytoextraction est en plein développement surtout aux États-Unis où elle est disponible à l'échelle commerciale (Chapitre 2). L'utilisation in situ d'agents de chélation est souvent requise afin d'améliorer les taux d'extraction des métaux (fraction disponible) par les plantes hyper accumulatrices (Cooper et al., 1999; Lestan et al., 2008; Liu et al., 2008). L'utilisation du traitement électrocinétique in situ est limitée à la restauration des sols saturés et argileux (Chapitre 2). La technologie électrocinétique a permis de décontaminer 10–15 sites en Europe (surtout aux Pays-Bas), tandis que cette technique a été peu utilisée aux États-Unis, et ce, malgré une dizaine de projets pilotes supervisés par le Département de la Défense (Chapitre 2).

Dans le cas où l'extraction des métaux est techniquement difficile ou peu rentable économiquement, les techniques de stabilisation in situ des métaux (utilisant des plantes, des microorganismes, des stabilisants biologiques et/ou chimiques) peuvent être employées pour réduire efficacement et durablement la mobilité, la toxicité ou le potentiel de lixiviation des métaux (Chapitre 4).

3.3. La gestion des SCM au Québec

La gestion des sols contaminés au Québec repose sur l'utilisation de critères génériques de sol. Le règlement sur la protection et la réhabilitation des terrains fixe les valeurs limites (critères A, B, C) pour une gamme de contaminants et détermine les catégories d'activités acceptables pour l'utilisation du site et du sol (MDDEP, 1999). En plus des critères génériques, une valeur limite pour l'interdiction d'enfouissement a été introduite plus récemment afin de limiter l'importation de sols contaminés. Les valeurs limites établies par le MDDEP pour les métaux sélectionnés dans la discussion sont présentées dans le Tableau 2.

Il importe de noter qu'il y a peu d'informations sur la gestion des SCM au Québec pour plusieurs raisons. D'une part, seulement 19% des sites répertoriés sont affectés par les métaux dont 11% présentent une contamination mixte (MDDEP, 2006). D'autre part, l'enfouissement sécurisé semble être le mode de gestion le plus utilisé pour les SCM. Il n'est donc pas étonnant de constater que, au Québec, les 2/3 des dépôts de sols et de résidus industriels sont affectés par les métaux (MDDEP, 2006). De plus, la pratique de la S/S n'est pas généralisée sur les SCM bien que la technologie soit disponible (ACC, 2008; Stablex, 2008). Le CEMRS, localisé à Montréal, a permis la démonstration de diverses technologies de décontamination pour enlever les métaux de sols en milieu urbain: la phytoextraction et deux procédés de lavage de sol (CEMRS, 2008). La phytoextraction, ainsi que les techniques électrocinétiques ne sont pas utilisées au Québec. La phytoextraction a été testée à travers plusieurs projets pilotes sur le terrain (Biogénie, 2000; Inspec-Sol, 2004), mais les résultats de ces expériences sont mitigés (la fraction non disponible des métaux peut être importante et l'utilisation d'agents chélateurs augmentent les coûts de traitement). Les techniques de lavage de sol ne sont pas employées dans les projets de réhabilitation, bien que différentes technologies aient été testées à l'échelle pilote ou à l'échelle commerciale (6 applications reportées dans le Chapitre 3).

Tableau 2. Critères génériques pour les sols et valeurs limites d'enfouissement établis par le MDDEP

Métaux	Critère A[a]	Critère B[a]	Critère C[a]	Critère D[b]
As	6	30	50	250
Cd	1.5	5	20	100
Cr	85	250	800	1500
Cu	40	100	500	2500
Ni	50	100	500	2500
Pb	50	500	1 000	5000
Zn	110	500	1 500	7500

A : Teneur de fond

B : Limite maximale acceptable pour des terrains à vocation résidentielle, récréative et institutionnelle.

C : Limite maximale acceptable pour des terrains à vocation commerciale et industrielle.

D : Limite maximale acceptable pour l'enfouissement du sol

[a] Critères génériques pour les sols (MDDEP, 1999)

[b] Valeurs limites d'enfouissement (MDDEP, 2008)

4. Cas d'étude d'une friche industrielle en milieu urbain

4.1. Le contexte du canal Lachine à Montréal

Le secteur du canal Lachine, situé dans le Sud-ouest de l'île de Montréal, fut l'un des principaux centres de production manufacturière au Canada depuis les débuts de l'industrialisation au milieu du 19ième siècle jusqu'au milieu du 20ième siècle. Le canal Lachine a engendré la plus grande concentration industrielle au Canada, 600 sociétés environ s'étant succédées pendant près d'un siècle, sur ses berges. Ces activités industrielles ont laissé une kyrielle de déchets, contenant souvent des concentrations élevées en substances toxiques pour l'environnement, tels que des métaux lourds.

En date du 1 décembre 2007, près de 250 terrains contaminés (concentrations au-dessus du critère B, incluant les sites déjà réhabilités) par différents métaux ont été répertoriés par le MDDEP, dans la municipalité de Montréal (Figure 4). Les métaux les plus fréquemment constatés dans le sol comme milieu récepteur sont : Pb, Cu et Zn (Figure 4). Parmi cette liste, de nombreux terrains sont situés sur les abords du canal Lachine, lesquels sont affectés par des remblais hétérogènes générant une pollution mixte en métaux et en substances organiques (Pilon, 2004).

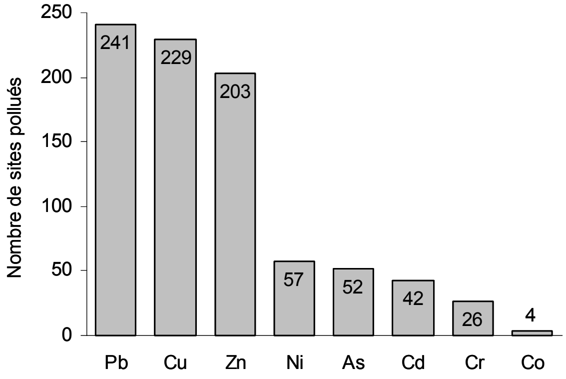


Figure 4. Principaux métaux identifiés dans les sites répertoriés (le sol comme milieu récepteur) pour leur réhabilitation dans la municipalité de Montréal, Canada (MDDEP, 2007)

Dans le cadre de l'aménagement urbain de Montréal, ces sites font l'objet d'un intérêt particulier, car ils sont situés à proximité du centre-ville. La nécessité de leur réhabilitation s'appuie donc sur une double motivation : environnementale et socio-économique. Depuis 1997, les berges du canal Lachine sont dans un processus de revitalisation afin de développer des projets tels que la création de nouvelles entreprises, de parcs verts récréatifs et de quartiers résidentiels.

4.2. Description et historique du site étudié

Le site à l'étude est localisé du côté nord du canal Lachine, au coin du chemin de la côte St-Paul et de la rue Ste Ambroise, dans une zone résidentielle (Figure 5a). Le terrain, considéré comme une friche industrielle (*brownfield*), est situé le long de la piste cyclable (longeant le canal) gérée par Parcs Canada (Figure 5a). Ce terrain, appartenant à la ville de Montréal, est actuellement vacant et couvre une superficie d'environ 20 000 m^2. Il est prévu que ce terrain soit utilisé à des fins de développement industriel ou récréatif. La totalité du terrain est affecté par des remblais hétérogènes présentant une forte contamination par les métaux lourds. Selon SNC Lavalin (1996) et les présents travaux, la profondeur de la nappe d'eau se situe entre 2.25 et 3.5 m selon les secteurs et les variations saisonnières. La caractérisation de l'eau souterraine n'est toutefois pas l'objet du présent document.

L'historique spécifique de l'utilisation de ce terrain n'est pas très évident à cerner, car les informations sont rares et imprécises. Selon Parcs Canada, l'usine « Frothingham and Workman Co. » (quincaillerie), une des plus importantes du genre en Amérique du Nord, était située près de l'écluse Côte-Saint-Paul, probablement sur le site de 1872 à 1940 (Parcs Canada, 2008). Plus récemment, selon Tecsult (1994), le long du chemin de la Côte Saint-Paul, un marchand de ferraille était implanté, tandis qu'une cimenterie était localisée du côté Est. Cependant, le rapport reste imprécis sur les dates et sur la durée des activités et indique seulement que le démantèlement des installations remonterait entre 1984 et 1988. Tecsult (1994) indique également que ce terrain a reçu des remblais illicites, mais il ne précise pas la date de ces événements. Depuis plus de 10 ans, ce terrain est utilisé comme site de dépôt de la neige usée (SNC Lavalin, 1996).

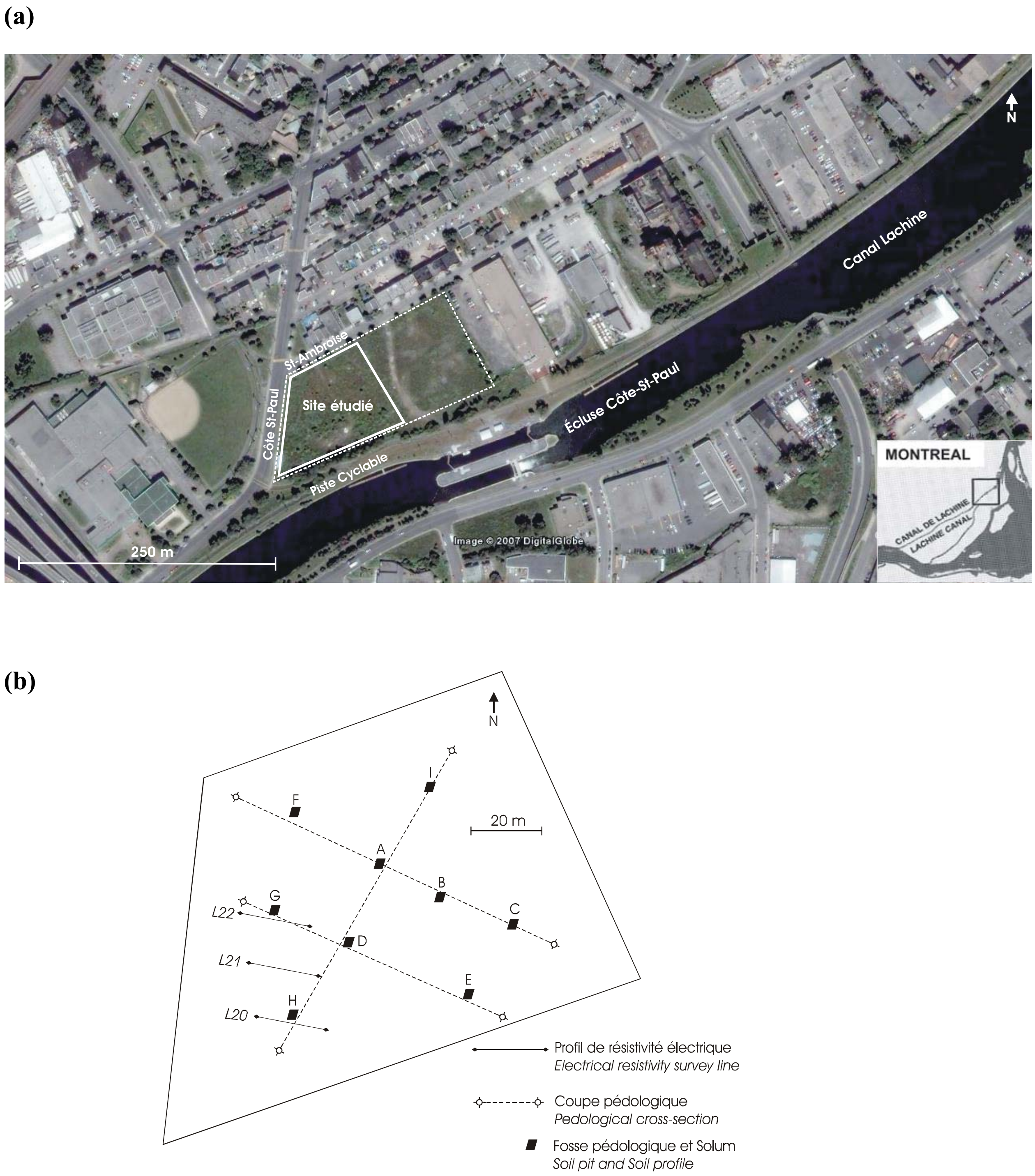


Figure 5. (a) Localisation du site étudié; (b) Localisation des fosses pédologiques (échantillonnage sur les profils A, B, D et G), des coupes pédologiques et des sondages géophysiques (profil de résistivité électrique L20, L21, L22).

Plusieurs campagnes de caractérisation géotechnique impliquant des forages, sondages et fosses d'exploration ont été réalisées à l'échelle du terrain afin de déterminer les zones les plus affectées en vue de l'excavation des sols (SNC Lavalin, 1996; Tecsult, 1994). Les analyses des sols ont porté notamment sur des échantillons composites sur l'ensemble du site, sans tenir compte réellement de la stratification des remblais et du sol sous-jacent. Ces travaux ne comprenaient ni une étude exhaustive de la distribution des métaux tels que la spéciation, la distribution granulo-chimique, la minéralogie des matériaux, les profils verticaux, ni une étude géochimique du sol sous-jacent pour estimer le risque de pollution des déchets.

4.3. Travaux de terrain et échantillonnage

Les travaux réalisés dans le cadre de cette thèse se focalisent sur le secteur considéré comme le plus contaminé par les études géotechniques antérieures, lequel couvre environ la moitié du terrain (Figure 5b). L'autre secteur (secteur est) est surtout affecté par des remblais grossier dont des gravas de construction, de briques, de morceaux de ferrailles, etc. Les photographies de l'environnement du terrain (Figure 6) montrent un panorama qui contraste entre l'héritage industriel du site (friche industrielle) et l'environnement urbain, dans lequel se trouvent actuellement : résidences, écoles, terrains de jeux, pistes cyclables de Parcs Canada et industries récentes.

Quatre phases de sondages et d'échantillonnages ont été organisées entre 2003 et 2005. La caractérisation s'appuie sur une approche pluridisciplinaire : pédologie, géophysique, géochimie et minéralogie. Les différentes fosses pédologiques explorées (3 m de profondeur maximum), ainsi que les lignes de sondages de résistivité électrique sont localisées sur la Figure 5b. L'échantillonnage (environ 70 échantillons de sol et de morceaux de déchets) a été réalisé sur la paroi (*le solum*) des fosses pédologiques A, B, D et G, selon une méthodologie conventionnelle

(Baize et Jabiol, 1995). Des renseignements complémentaires à la collecte et à la préparation des échantillons de sols sont reportés dans le Chapitre 5. La méthodologie et les interprétations des sondages géophysiques (profils de résistivité électrique du sol) figurent dans l'Annexe A. En outre, une grande section tomographique de résistivité électrique (Longueur=160 m) permettant de visualiser le substrat rocheux et l'ensemble des dépôts meubles (Profondeur sondée= 25 m) composant le terrain étudié, est reportée dans l'Annexe A.

Figure 6. Photographies du terrain étudié et de son environnement (été 2005)

Bien que les remblais contiennent des déchets de bouilloires de charbon dans le secteur à l'étude, des analyses chimiques préliminaires des échantillons ont montré que la concentration en polluants organiques tels que des hydrocarbures pétroliers C_{10}–C_{50} ou des HAP ou des BTEX n'est pas significative en regard des critères établis par le MDDEP (Bergeron et al., 2000).

4.4. Description du profil du sol

Trois coupes pédologiques (longueur : 80 à 100 m ; profondeur : 3 m) couvrant le secteur étudié ont été extrapolées à partir de la stratigraphie observée dans les différentes fosses (Annexe B). En résumé, le profil de sol est composé d'une couche de remblais hétérogène de 1.5 m d'épaisseur en moyenne (sous divisée en deux horizons anthropiques principaux, AS1 et AS2) recouvrant un sol naturel composé d'un horizon organique (tourbe, *peat*) et d'un horizon minéral calcaire (marne, *marl*) (Annexe B). La description des horizons de sols naturels repose sur la comparaison entre l'observation in situ et les informations tirées de la carte des dépôts meubles de l'île de Montréal (CGC, 1975). Le Chapitre 5 donne une description détaillée des principaux horizons de sol (AS1, AS2, tourbe et marne). Selon la nouvelle typologie du système de classification internationale des sols (FAO, 2006), le sol urbain étudié est un *Spolic Technolosol* (détail de la description dans le Chapitre 5).

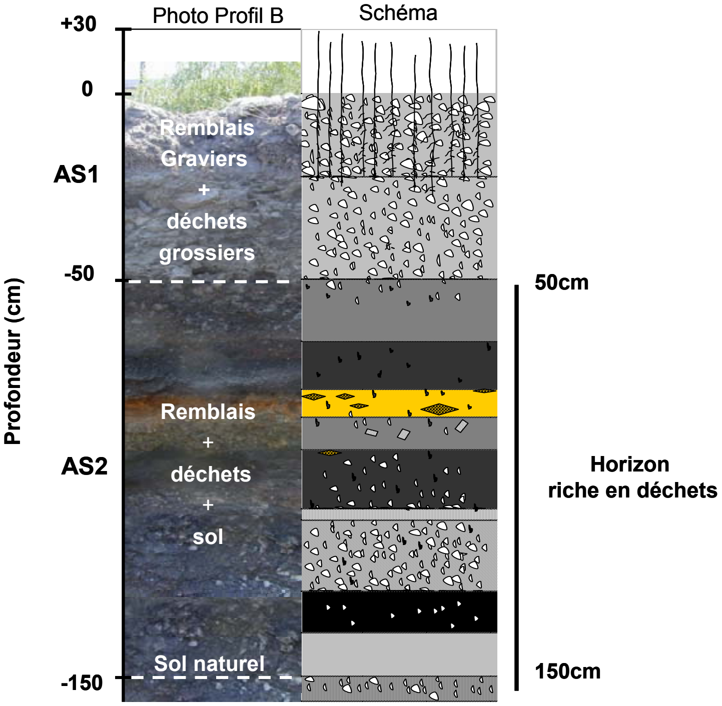


Figure 7. Exemple de profil de sol (profil B) observé sur le site de Montréal

Une description sommaire du profil du sol anthropique (horizons AS1 et AS2 du profil B) est représentée sur la Figure 7. Les déchets métallurgiques (lesquels représentent 25–30% du volume des horizons AS1 et AS2) retrouvés sur le site montrent une grande disparité dans leurs propriétés physicochimiques (densité, aspect, composition chimique et minéralogique, porosité). Quelques exemples de fragments grossiers de déchets sont illustrés sur la Figure 8. En résumé, deux catégories de déchets se côtoient : (1) des résidus de la métallurgie/minéralurgie (Figure 8a, b, c, d, e) lesquels représentent environ 75–90% (en volume) des déchets; (2) des résidus de la combustion de charbon (bouilloires de charbon) qui représentent 10–25% des déchets (Figure 8f).

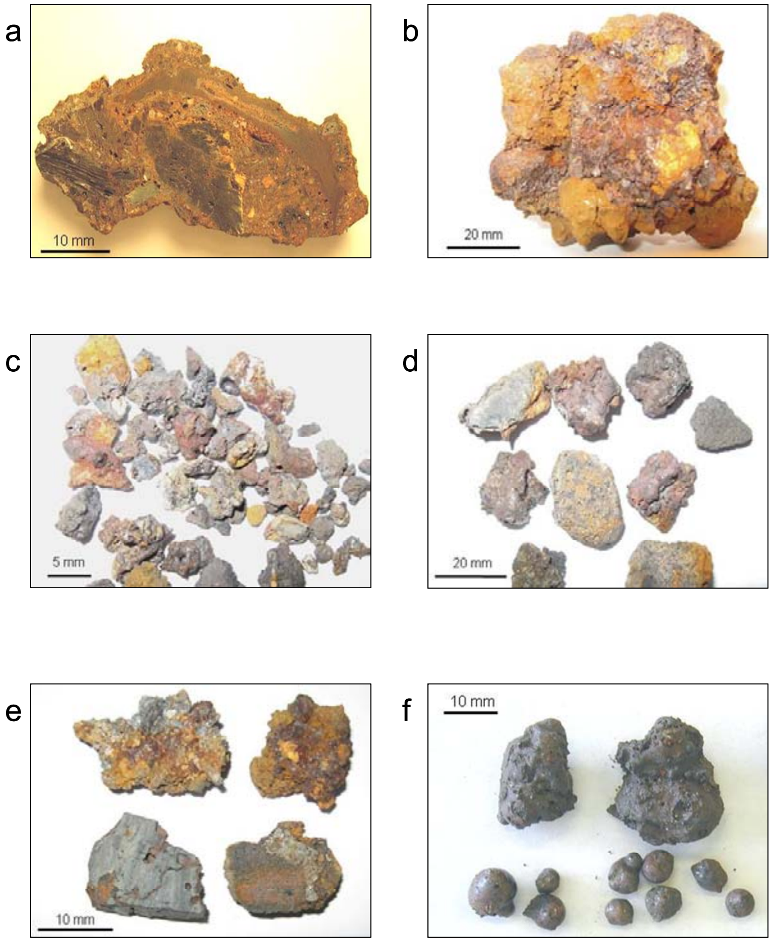


Figure 8. Photographies de fragments de déchets minéralurgiques (a b, c, d, e) et résidus de bouilloires de charbons (f) retrouvés dans l'horizon de sol anthropique du site de Montréal

4.5. Principaux aspects géochimiques étudiés

L'évaluation de la distribution spatiale des métaux à l'échelle du profil du sol (4 profils étudiés) et à l'échelle particulaire (150 particules étudiées pour établir la spéciation en phase solide des métaux et les aspects morphologiques) s'inscrit dans une double stratégie: (1) évaluer le potentiel de mobilisation des métaux dans le profil du sol; (2) offrir une caractérisation exhaustive de la matrice du sol et des contaminants en vue de son traitement par une technique physicochimique de lavage de sol. Pour chaque échantillon de sol, les paramètres physiques et chimiques suivants ont été analysés :

- Les éléments majeurs (Al, Ca, Fe, K, Mg, Mn, Na, P, Si et Ti) et le Scandium (Sc)
- Carbone, Carbone organique, Souffre, Azote
- Les métaux (As, Cd, Co, Cr, Cu, Ni, Pb et Zn)
- La granulométrie

Pour l'échantillon composite du sol anthropique AS2, les facteurs suivants ont été évalués:

- La minéralogie du sol et des différents déchets (à l'aide de XRD, SEM-EDX)
- La distribution des métaux (Cu, Pb et Zn) selon leur forme minéralogique (SEM-EDX)
- La distribution des métaux (Cu, Pb et Zn) selon la morphologie des PRM (SEM-EDX)
- La distribution des métaux (As, Cd, Cu, Pb et Zn) dans 11 fractions granulométriques

Ces données ont facilité la réalisation de profils verticaux, de diagrammes ternaires, et le calcul de coefficients de corrélation afin de comparer la distribution des éléments majeurs et des métaux dans le sol. De plus, le facteur d'enrichissement en métal (As, Cd, Cu, Pb et Zn) a été évalué pour les horizons du sol naturel en fonction de 3 éléments pris comme référence (Si, Ti et Al) et des valeurs correspondantes de la croute terrestre (normalisation usuelle pour le calcul des facteurs d'enrichissement des métaux; la formule est décrite dans le Chapitre 5), et ce, afin d’appréhender une éventuelle « contamination métallique» causée par l’altération des déchets de la couche de remblais. La méthodologie des travaux et des analyses est précisée dans le Chapitre 5. L’annexe C présente le contrôle qualité des analyses chimiques réalisé avec des matériaux géologiques de références (2 sols contaminés de références NIST 2710 et NIST 2711).

4.6. Résumé des résultats et discussion

Les résultats des analyses physicochimiques des échantillons de sols pour les profils A, B, D et G sont présentés dans l’annexe D (éléments majeurs et caractéristiques pédologiques) et dans l’annexe E (concentrations des éléments traces métalliques). Les résultats de la distribution verticale des éléments sont spécifiquement discutés dans le Chapitre 5. Cette section propose d’en donner un bref résumé. Dans l’horizon riche en déchets (AS2), les teneurs en métaux (As, Cd, Cu, Pb et Zn) dépassent largement le critère générique C du MDDEP. La distribution en métaux dans les remblais reflète une grande hétérogénéité spatiale et géochimique. Les métaux sont aléatoirement distribués dans toutes les fractions granulométriques, et ce, bien que les particules fines soient les plus affectées. L'étude micro-spectroscopique indique que la forme géochimique prédominante du Zn est la sphalérite (ZnS), tandis que le Cu et le Pb sont distribués dans diverses formes, principalement des oxydes/hydroxydes et des carbonates. La composition chimique et minéralogique de certaines phases riches en métaux suggère un processus probable d’altération physicochimique. L’altération des résidus de déchets et la libération des métaux impliquerait deux étapes principales: (1) une altération physique (émiettement des résidus, et production de fines particules colloïdales riches en métaux); (2) une altération chimique impliquant une dissolution lente de certaines phases (libération d’ions métalliques) ou des changement de phases (par ex : oxydation des sulfures, carbonatation des oxydes, etc.). Les facteurs d’enrichissement élevés des métaux dans l'horizon organique situé juste sous les remblais confirment cette hypothèse. Cependant, les conditions chimiques dans le profil du sol semblent peu favorables à leur mobilité : (1) pH >6 et présence de Fe-oxides, sulfates, et carbonates dans AS2 ; (2) horizon de tourbe riche en MO. La variabilité des formes minéralogiques des métaux est un handicap pour l'application des procédés de décontamination par lavage de sol.

5. Enlèvement des métaux par flottation

5.1. Un outil pertinent de traitement

La flottation est une méthode éprouvée depuis près d'un siècle pour concentrer sélectivement les minerais métalliques, en particulier les sulfures (Bouchard, 2001; Fuerstunau, 2007). Sa simplicité et sa technologie largement répandue dans l'industrie minéralurgique impliquent un coût d'utilisation relativement faible comparativement à d'autres méthodes de séparation physique ou hydrométallurgique. Dans le domaine environnemental, la flottation peut s'intégrer dans un schéma de traitement de type lavage de sol afin de concentrer les PRM dans un plus petit volume de sol. Elle peut être utilisée en combinaison avec d'autres techniques minéralurgiques (hydrocyclones, tamisage, séparation gravimétrique, séparation magnétique, etc.) ou chimiques (lixiviation à l'aide d'acides, d'agent complexant, etc.) en fonction des caractéristiques de la matrice à traiter et des métaux concernés. La flottation a été peu étudiée pour enlever les métaux comparativement à d'autres techniques de lavage de sol, en particulier, les méthodes purement chimiques ou biologiques (Chapitre 3). La revue de littérature révèle moins de dix articles publiés dans les revues internationales portant spécifiquement sur l'enlèvement des métaux par flottation depuis les années 1995 (Chapitre 6). C'est pourquoi la flottation est un outil potentiellement intéressant à explorer pour récupérer les métaux des sols pollués.

Spécifiquement dans le cadre du traitement du sol étudié, l'utilisation de la flottation s'avère pertinente comparativement aux autres techniques de lavage de sol pour les raisons suivantes : (1) la séparation conventionnelle par la taille particulaire (argile/silt vs. sable/gravier) serait inefficace puisque toutes les fractions granulométriques du sol initial (0–10 mm) présentent une forte teneur en métaux (Chapitre 5); (2) la séparation gravimétrique peut être efficace pour concentrer sélectivement les particules riches en plomb (à cause de la densité élevée des phases minérales contenant du Pb comparativement au principaux minéraux composant le sol étudié, tels que calcite, hématite, gypse, silicates, etc.) mais elle serait inefficace pour la séparation des particules riches en Zn et Cu dont la densité n'est pas très différente des Fe-oxides présents dans le sol (conclusion du Chapitre 5); (3) les techniques de lavage chimiques (acides, agents complexant, oxydant, tensioactifs, etc.) ne sont pas particulièrement adaptées pour traiter une contamination de type particulaire (Chapitre 3).

5.2. Le principe de la flottation en cellule agitée

Le principe du procédé de flottation consiste à séparer sélectivement les particules sur la base de leurs propriétés physicochimiques de surface. Dans le domaine du lavage de sol, la flottation propose de séparer les PRM, lesquelles sont le plus souvent rendues hydrophobes par l'adsorption en surface de molécules d'agents chimiques tensioactifs, appelés collecteurs. Les particules hydrophobes sont transportées par des bulles d'air injectées dans la pulpe (mélange de sol et d'eau) en suspension, tandis que les particules peu hydrophobes restent dans la pulpe (Figure 9). En conséquence, et si la dimension de la bulle le permet, les particules collectées lévitent au sein de la pulpe pour enfin être concentrées dans une mousse qui surnage en surface. La mousse peut ensuite être récoltée par raclage. Généralement, les sulfures (plus hydrophobes) sont plus faciles à flotter que les sulfates, les oxydes, et les carbonates (Bouchard, 2001).

Cependant, le processus (idéal) de séparation sélectif des particules hydrophobes (Figure 9) n’est pas le seul mécanisme de transport des particules qui intervient dans la cellule de flottation. En plus des propriétés de surface, les conditions hydrodynamiques dues à l’agitation de la pulpe jouent un rôle majeur dans la séparation. En conséquence, la flottation des particules dépend donc de la probabilité : (1) de la collision entre les particules et les bulles; (2) des processus d’attachement et de détachement du couple particule-bulle (taille des bulles, vitesse d’ascension, stabilité de la mousse, etc.). Il est reconnu que dans les cellules agitées mécaniquement, les particules fines (généralement <20 µm) sont prioritairement collectées dans la mousse par l’intermédiaire d’un phénomène d’entraînement dans la couche d’eau inter bulles, et ce, indépendamment de leur différence d’hydrophobicité (Chapitre 6; Cilek et Yilmazer, 2003; Koh et Schwarz, 2006; Vanthuyne et Maes, 2007).

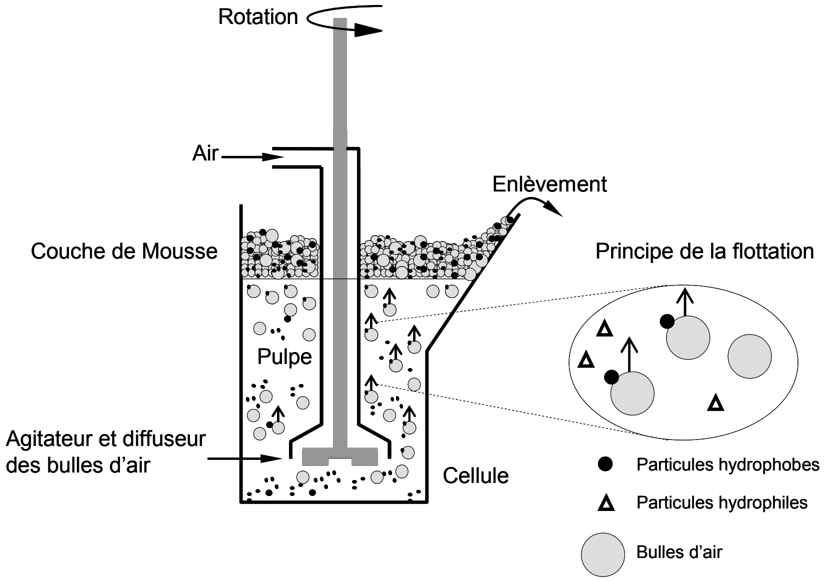


Figure 9. Schéma simplifié de la cellule de flottation de type Denver D1 et du principe de flottation

Bien que ce phénomène soit généralement considéré comme nuisible dans l’industrie du traitement des minerais, il peut être bénéfique dans le domaine de la décontamination des sols puisque que les particules fines (<20 µm) contiennent généralement une très forte concentration en métaux (Chapitre 6). L'entraînement hydraulique des particules fines contribue néanmoins à réduire la sélectivité globale de la séparation. En résumé, dans le cas des systèmes de flottation en cellule agitée, la récupération des PRM résultera donc de la combinaison du vrai processus de flottation (sélectif) et de l'entraînement des particules fines (non sélectif).

5.3. Les applications dans la décontamination des sols

La flottation est avant tout un procédé de séparation particulaire, par conséquent cette technique est pertinente pour traiter des résidus de minéralurgie ou de déchets miniers. Par rapport aux concentrateurs gravimétriques conventionnels (séparation par liquide dense, jig, spirales et tables à secousses), la flottation peut traiter les particules <63 µm et sa simplicité implique un coût d'utilisation plus faible comparativement aux concentrateurs gravimétriques spécifiques aux particules fines tels que le séparateur de type Mozley (Chapitre 3). L'application de la flottation est limitée par un intervalle granulométrique dont les limites dépendent de la technologie utilisée (appareillage et conditions opératoires) et des caractéristiques intrinsèques de la matrice à traiter. En générale, la flottation est applicable pour les particules <200–300 µm (Bouchard, 2001). En ce qui a trait à la flottation en cellule, la sélectivité de la séparation est moins efficace pour les particules <20 µm (Fuerstunau, 2007).

Plusieurs études en laboratoire et applications à grande échelle ont été réalisées depuis les années 1990. Les performances dans l'enlèvement des métaux obtenues par divers systèmes de flottation à l'échelle pilote ou à grande échelle, en Europe et aux États-Unis, sont discutées en détails dans le Chapitre 3, ainsi que dans Vanthuyne et al. (2003). La plupart des expériences de laboratoire utilisant les cellules de flottation, ainsi que les résultats obtenus dans l'extraction des métaux sont reportés en détail dans le premier tableau du Chapitre 6. La plupart des travaux, accomplis en Belgique et aux Pays-Bas sont axés sur le traitement des sédiments anoxiques contaminés par les métaux de transition (Cd, Cu, Pb et Zn), lesquels se retrouvent sous formes de sulfures.

Néanmoins, son efficacité dans le cas des matrices environnementales est inférieure à celle observée dans les applications minéralurgiques (Chapitre 6). L'emploi de la flottation est conditionné par les caractéristiques du sol à traiter, ainsi que par les conditions opératoires de la flottation (réactifs chimiques et paramètres hydrodynamiques). Dans le cas du traitement des SCM, les paramètres à surveiller sont : (1) la teneur en matière organique (acides humiques); (2) la proportion des particules <20 µm; (3) la spéciation géochimique des métaux; (4) la distribution des métaux selon la taille des particules.

5.4. Stratégie de lavage de sol par broyage et flottation

Dans le cadre de cette thèse, la technologie de flottation (cellule de laboratoire conventionnelle de type Denver, Figure 9) a été étudiée comme technique de décontamination dans le but d'enlever les métaux (As, Cd, Cu, Pb et Zn) du sol anthropique (AS2) provenant de la friche industrielle de Montréal préliminairement caractérisée. Étant donné les concentrations élevées dans toutes les fractions granulométriques du sol s'étendant de 0 à 10 mm (Chapitre 5), la stratégie du lavage de sol est basée sur un broyage préliminaire des fractions granulométriques supérieures à 250 µm (Figure 10).

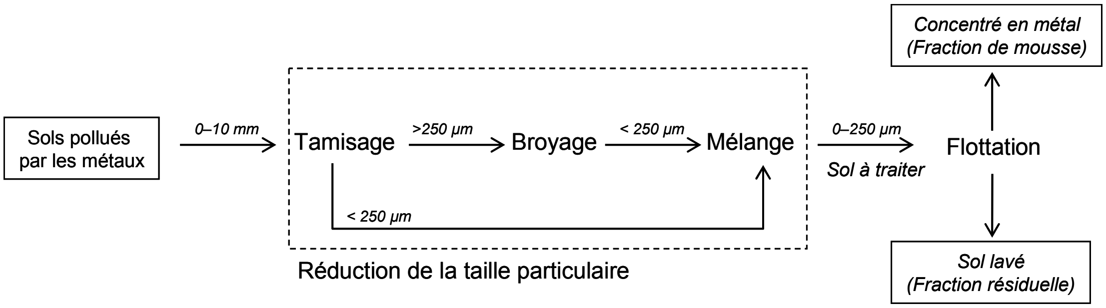


Figure 10. Schéma de principe du lavage de sol utilisé pour enlever les métaux

Cette préparation mécanique à plusieurs objectifs : (1) permettre le traitement de la totalité des fractions granulométriques contaminées; (2) obtenir une taille particulaire appropriée pour le processus de flottation; (3) augmenter le degré de libération des phases minérales à flotter (Bouchard, 2001). Le principe du degré de libération (pour des phases solides particulaires) est expliqué en détail dans le Chapitre 3. L'utilisation d'une étape de broyage évite ainsi l'utilisation d'un circuit complexe de lavage de sol. En effet, l'usage des appareils de séparation physique (en particulier les concentrateurs gravimétriques) est limité pour un intervalle très restreint de taille particulaire (Chapitre 3).

Cependant, une étape de broyage contribue à produire des particules fines, souvent non désirées dans les circuits de flottation (*les schlamms;* Bouchard, 2001). Avec la préparation du sol par un broyage approprié, la part des particules très fines <5 µm n'a pas augmenté, mais la part des particules 5–20 µm a doublé (Annexe F). La distribution relative des métaux (As, Cd, Cu, Pb et Zn) dans les différentes fractions granulométriques, avant et après le broyage, sont reportées dans l'Annexe G.

5.5. Les essais de flottation et les paramètres étudiés

L'étude comporte deux parties distinctes (Chapitre 6 et Chapitre 7) : l'une est consacrée à l'influence des paramètres chimiques sur la sélectivité de la flottation et la récupération des PRM, tandis que l'autre propose d'étudier la sélectivité de la flottation et l'effet d'entraînement en fonction des paramètres de nature physique. L'objectif principal est d'évaluer quel mécanisme parmi les deux principaux (le vrai processus de flottation ou l'effet d'entraînement) intervient dans la récupération des PRM en fonction des différents paramètres opératoires, des caractéristiques du sol et de la distribution des métaux. La méthodologie des différents essais de flottation et la description des paramètres permettant d'appréhender les performances de récupération des métaux et de la sélectivité de la flottation sont détaillées dans les Chapitres 6 et 7. L'efficacité de la flottation a été étudiée en fonction des paramètres opératoires chimiques suivants :

- Le type de collecteur de flottation (kérosène et KAX) et la concentration de collecteur
- Le pH de la pulpe pour les deux types de collecteur
- L'ajout d'une étape chimique d'activation (sulfuration)

L'efficacité de flottation a été étudiée en fonction des paramètres opératoires physiques suivants:

- La vitesse d'agitation
- Le temps de flottation
- Le mode d'addition du collecteur (flottation en plusieurs étapes)
- L'utilisation d'un prétraitement par ultrasons

L'efficacité de la flottation a aussi été étudiée selon les caractéristiques du sol et des métaux :

- La distribution des éléments majeurs et des métaux dans 5 fractions granulométriques
- La taille des particules
- La spéciation en phase solide des métaux (Cu, Pb et Zn)
- Le degré de libération des phases minérales contenant les métaux (Cu, Pb et Zn)
- Les index de sélectivité Zn/Ca et Zn/Fe

Parmi les facteurs chimiques impliqués dans le processus de flottation, le collecteur joue un rôle primordial en modifiant les propriétés physico-chimiques des surfaces et des interfaces (Bouchard, 2001). Le collecteur est adsorbé à l'interface solide-liquide. Les mécanismes d'adsorption dépendent du type de collecteur et de la nature minérale des surfaces des particules (Bouchard, 2001; Fuerstunau, 2007). Les collecteurs sont généralement divisés en trois classes, lesquelles diffèrent par leurs propriétés physico-chimiques: (1) non-ionique et non polaire ; (2) anionique ; (3) cationique.

Le choix d'un collecteur ne repose pas seulement sur la nature du minéral (ou phase métallifère) que l'on désire flotter, mais sur la considération de nombreux facteurs tels que les conditions chimiques de la pulpe (pH, Eh, présence d'autres réactifs), les caractéristiques du sol à traiter, la sélectivité du collecteur, la cinétique de flottation, le pouvoir moussant du collecteur, les possibilités de réactions chimiques avec d'autres substances, etc. Dans le cadre de nos travaux, les deux collecteurs sélectionnés concernent les deux premières catégories de collecteurs : l'un est non-ionique (le kérosène, impliquant surtout des alcanes à longue chaîne) et l'autre est anionique (le potassium amyl xanthate ou KAX, appartenant à la famille des sulfhydryles). L'utilisation d'un collecteur cationique (impliquant usuellement une fonction amine) n'est pas pertinente pour notre cas d'étude puisque que les collecteurs cationiques sont généralement utilisés à des pH acides pour flotter les oxydes de Fe/Al (ex : hématite et alumine) et silicates (Fuerstunau, 2007). Le choix et les propriétés des collecteurs sont discutés en détails dans le chapitre 6.

Le kérosène est typiquement utilisé dans l'industrie minéralurgique pour la flottation des minéraux qui présentent intrinsèquement une bonne hydrophobicité. En outre, plusieurs études ont montré que le kérosène offre une bonne efficacité d'enlèvement des métaux lors du traitement des sédiments pollués en comparaison aux collecteurs spécifiques aux sulfures comme les xanthates (impliquant généralement des mécanismes de chimiosorption) (Chapitre 6). Parmi les réactifs sulfhydryles à base d'ions xanthates ($R{-}O{-}C{-}S_2^-$), le choix du KAX est approprié dans notre cas d'étude, car la relative longue chaîne R du KAX (groupement R= Amyl = $-C_5H_{11}$) privilégie la puissance de collection pour les sulfures de Cu, Pb et Zn plutôt qu'une sélectivité restreinte à un sulfure d'un métal en particulier (Chapitre 6). Aussi, le KAX permet une possible flottation des oxydes/carbonates/sulfates de Cu, Pb et Zn (par adsorption physique) (Chapitre 6). De plus, la collection des sulfures par le KAX est la plus employée après un prétraitement chimique de la pulpe par sulfuration, laquelle permet de recouvrir la surface des oxydes/carbonates de Cu, Pb et Zn d'un enduit sulfuré (Chapitre 6).

5.6. Résumé des résultats et discussion

Les résultats des expériences de flottation sont spécifiquement discutés dans les Chapitres 6 et 7. Ce paragraphe propose de résumer les points les plus pertinents. Des résultats satisfaisants pour l'enlèvement des métaux (42–52%), la sélectivité de la flottation (facteur de concentration >2.5) et la réduction de volume (>80%) ont été obtenus avec le collecteur KAX. Bien que la sélectivité de flottation ait été moins efficace avec le kérosène, ce collecteur se révèle une bonne alternative aux agents de type xanthate puisque son utilisation a permis d'obtenir de meilleurs taux d'enlèvement des métaux (45–60%). Les mécanismes de transport impliqués dans le procédé de séparation (c'est-à-dire, la flottation vraie et l'entraînement mécanique) sont évalués par les conditions chimiques de la pulpe (pH, type de réactif, implication d'une étape d'activation chimique), la spéciation des métaux, la distribution des métaux dans les fractions granulométriques et les index de sélectivité de séparation de Zn/Ca et de Zn/Fe. Une grande proportion des PRM a été récupérée dans la fraction de mousse par le mécanisme d'entraînement plutôt que par le véritable processus de flottation.

Le mécanisme non sélectif d'entraînement des particules fines (<20 µm) se produit lorsque le processus se déroule sur un long laps de temps (>5 min) et lorsqu'une dose élevée de collecteur est ajoutée à la pulpe en une seule étape. La sélectivité de flottation est meilleure pour la fraction granulométrique intermédiaire (20–125 µm).

6. Conclusions et perspectives

Caractérisation du site et profil du sol

Le profil de sol d'une friche industrielle, localisée le long du canal Lachine à Montréal (Canada), a été étudié afin d'en déduire la distribution des métaux. Des remblais anthropiques riches en déchets recouvrent un sol naturel composé de tourbe et de marne d'épisode de marais. Dans l'horizon riche en déchets (AS2), les teneurs en métaux (As, Cd, Cu, Pb et Zn) dépassent largement le critère générique C du MDDEP. La distribution de ces polluants dans les remblais reflète une grande hétérogénéité spatiale et géochimique. Les métaux sont aléatoirement distribués dans toutes les fractions granulométriques, et ce, bien que les particules fines soient les plus affectées. Un fort enrichissement en métaux est mesuré dans l'horizon organique (tourbe) comparativement à l'horizon minéral (marne) bien que les teneurs concernées des métaux dans les horizons du sol naturel soient basses (souvent en dessous du critère A du MDDEP). Cet enrichissement suggère l'hypothèse d'une mobilisation des métaux dans le profil du sol et donc, une possible lixiviation des déchets dans la couche de remblais. Les travaux portant sur 150 particules ont montré que :

- La forme géochimique prédominante du Zn est la sphalérite (ZnS)
- Le Cu et le Pb sont distribués dans diverses phases géochimiques dont les plus abondantes sont des oxydes/hydroxydes et des carbonates.
- La composition morphologique des PRM présente également une grande diversité bien que la majorité des phases solides riches en métaux subsistent en tant que particules libres ou forment des associations complexes de plusieurs phases métalliques.
- Les composition chimiques et minéralogiques de certaines phases riches en métaux suggèrent un processus probable d'altération des résidus métallurgiques (émiettement, co-

précipitation, altération de sulfures en sulfates, d’oxydes en carbonates ou hydrocarbonates, etc.).

Cependant, les conditions chimiques du sol anthropique se révèlent peu propices à la mobilisation, à la fois pour des espèces cationiques de Cd, Pb, Cu et Zn (pH 7–8) et anioniques de As (forte présence de calcite, de gypse, d’oxyde/oxyhydroxyde de Fe, Al et Mn) susceptibles de « piéger » les espèces anioniques de As(V) et As(III) (Cornelis et al., 2008). L’adsorption de l’arsenic est étroitement liée aux conditions chimiques du milieu (pH et Eh, anions compétiteurs, etc.) et à son degré d’oxydation. La présence d’anions compétiteurs dans la solution de sol tels que HCO_3^- et SO_4^{2-} peut réduire significativement l’adsorption de l’arsenic (Wang et Mulligan, 2006). Pour des pH alcalins, As(V) va avoir tendance à être piégé en plus grande quantité sur les phases de type oxyhydroxyde de Fe que As(III) (Cornelis et al., 2008; Wang et Mulligan, 2006). L’évaluation de la spéciation de l’arsenic est nécessaire si l’on veut prévoir le transfert de cet élément dans la solution de sol. En considérant que des espèces dissoutes d’arsenic atteignent l’horizon de tourbe, As(III) et As(V) sont susceptibles d’être immobilisés (complexation) par les acides humiques et fulviques contenus dans la tourbe, laquelle présente un pH de 5–6.

Les microanalyses par SEM-EDX n’ont pas permis l’indentification des formes géochimiques des phase solides de As et de Cd. Étant donné le caractère généralement toxique de ces éléments à faible dose, il serait intéressant d’évaluer leur spéciation. Par exemple, il serait pertinent d’étudier la spéciation en phase solide du Cd par spectroscopie EXAFS. La caractérisation des échantillons de sol montre une corrélation forte entre le Zn, le Cd et le S. Cela suggère que le Cd intervient en tant qu’impureté dans la phase de sphalérite. L’étude de la spéciation des métaux (en phase solide et liquide) dans l’horizon de tourbe pourrait également être intéressante afin d’évaluer la mobilisation des métaux. L’hypothèse de l’altération des déchets métallurgiques et de la lixiviation des métaux dans le profil du sol (anthropique et naturel) peut être confirmée ou démentie par l'utilisation des rapports isotopiques du Pb. Les résultats préliminaires (non publiés dans ce document) confirmeraient la contamination de l'horizon organique sous-jacent par les métaux des déchets. Les compositions isotopiques du Pb des échantillons de tourbe sont « encadrées » par deux pôle majeurs, lesquels correspondent à deux type de déchets grossiers situés dans les remblais (à confirmer).

Lavage de sol par flottation

Le lavage de sol par flottation a été étudié pour l'enlèvement des particules riches en As, Cd, Cu, Pb et Zn de ce sol fortement pollué, après un broyage des fractions granulométriques supérieures à 250 µm. Les mécanismes de transport impliqués dans le procédé de séparation (c'est-à-dire, le vrai processus de flottation et l'entraînement mécanique) sont évalués par : (1) les conditions chimiques de la pulpe (pH, type de réactif, concentration des réactifs, implication d'une étape d'activation chimique); (2) les conditions physiques (vitesse d'agitation, temps de flottation, mode d'addition des réactifs et utilisation d'une étape de traitement par ultrasons); (3) les caractéristiques de la contamination (la spéciation des métaux et la distribution des métaux dans les fractions granulométriques); (4) les index de sélectivité de séparation de Zn/Ca et de Zn/Fe. Une grande proportion de particules riches en métaux a été récupérée dans la fraction de mousse par le mécanisme d'entraînement plutôt que par le véritable processus de flottation. L'utilisation du xanthate comme agent collecteur a donné de meilleurs résultats en terme de sélectivité de séparation des PRM comparativement à l'utilisation du kérosène. Cependant, les propriétés liées aux surfaces des particules (environnement chimique de la pulpe et minéralogie des PRM) ne permettent pas d'expliquer clairement la différence de la réponse de flottation observée entre le kérosène et le xanthate.

Dans notre cas, l’effet d’entraînement mécanique des fines particules n’est pas dû à une vitesse d’agitation excessive puisque l’augmentation de 1000 à 1350 tours/min n’a pas provoqué la baisse de la sélectivité de séparation. Le mécanisme d'entraînement des particules <20 µm est mis en évidence par l’étude de la réponse de flottation en fonction de 5 fractions granulométriques. L’effet d’entraînement se produit particulièrement avec: (1) l’utilisation du collecteur kérosène; (2) un long laps de temps de flottation (>5 min); (3) une flottation en une seule étape avec une dose élevée de collecteur. La sélectivité de flottation est meilleure pour la fraction granulométrique intermédiaire (20–125 µm). L’utilisation de la méthode de flottation en plusieurs étapes successives permet d’améliore la sélectivité de séparation par flottation.

Le lavage de sol par flottation serait amélioré en traitant de façon indépendante les fractions fines (<20 µm), intermédiaires (20–125 µm) et grossières (>125 µm) par des systèmes spécifiquement adaptés (par exemple le traitement par le système de flotation à air dissout pour les fines; Chapitre 3) mais cela compliquerait techniquement le procédé de traitement. Le dosage de l’agent de sulfuration Na_2S employé dans le Chapitre 6 pourrait être optimisé avec un contrôle du potentiel Eh de la pulpe à l’aide d’électrodes spécifiques (Fuerstunau, 2007). Si la priorité de la décontamination est d’enlever le Zn (lequel est le principal contaminant en terme de concentration totale, dépassant largement le critère D), le traitement préalable de la pulpe par du sulfate de cuivre ($CuSO_4$) pourrait améliorer la flottation des particules de sphalérite qui flottent moins facilement, comparativement aux autres sulfures métalliques (Bouchard, 2001). En combinant les étapes suivantes, la récupération des métaux, en particulier du Zn, pourrait être significativement améliorée: (1) prétraitement par ultrasons de la pulpe; (2) étape de l’activation chimique des surfaces de sphalérite par l’ajout d’ions Cu^{2+}; (3) étape de sulfuration optimisée par contrôle du Eh; (4) flottation en multi-étapes (<5 min) avec le KAX comme collecteur.

Le but de cette étude n'est pas une optimisation d'un procédé de lavage de sol mais une démonstration à l'échelle laboratoire des principaux facteurs qui influencent les performances de la flottation en cellule pour le traitement des sols contaminés par les métaux. Dans la perspective d'une optimisation et d'une application à plus grande échelle du procédé, il serait pertinent de promouvoir l'utilisation de réactifs de flottation (collecteur et moussant) non nocifs pour l'environnement (des tensio-actifs biodégradables). Bien que les concentrations des réactifs utilisés soient faibles, la présence de kérosène ou de xanthate dans les eaux de procédés pourrait poser des problèmes de toxicité pour l'environnement aquatique. Les eaux de procédés doivent être recyclés pour plusieurs cycles de flottation.

7. Les aspects innovateurs de la thèse

Cette partie récapitule les contributions significatives apportées par la thèse dans l'avancement des connaissances dans le domaine des sciences de l'environnement :

Géochimie des métaux, des sols urbains pollués et des technosols:

- Une caractérisation exhaustive et multidisciplinaire (pédologie, géophysique, minéralogie et géochimie) contribuant à une meilleure compréhension de la problématique des friches industrielles en milieu urbain et de la gestion des sols contaminés par les métaux;
- Une analyse géochimique et minéralogique détaillée des phases métallifères permettant d'appréhender le potentiel de mobilisation des métaux issus de la disposition de déchets métallurgiques/minéralurgiques dans les sites urbains.

Réhabilitation des sites contaminés et génie environnemental:

- Une revue détaillée présentant l'éventail des techniques conventionnelles et innovantes d'immobilisation ou d'extraction des métaux pour le traitement des sols pollués;

- Une revue critique exhaustive des pratiques de lavage de sol (méthodes de lixiviation chimique et de séparation physique) exécutées au cours des 25 dernières années en discutant à la fois des performances des méthodes testées en laboratoire et celles appliquées à l'échelle du terrain;
- Une étude exhaustive des phases métallifères et de la spéciation des métaux permettant d'améliorer la sélection et l'application d'une technologie de traitement des sols pollués.

Lavage des sols et enlèvement des métaux par flottation:

- Une contribution scientifique incontestable dans le domaine de l'enlèvement des métaux des sols pollués par flottation, car seulement une dizaine d'études sur ce sujet sont référées dans les journaux scientifiques depuis les années 1990;
- Une analyse exhaustive des performances de flottation par l'utilisation d'indices de sélectivité et de graphiques inédits;
- Les performances de flottation sont discutées en fonction de deux mécanismes de transport des particules (le vrai mécanisme de flottation et le processus d'entrainement) alors que la contribution de l'entrainement dans les essais de décontamination par flottation est rarement examinée;
- L'analyse des performances est discutée en fonction de trois groupes de paramètres: (1) la distribution et la spéciation des phases métallifères dans la matrice du sol, (2) les composants principaux de la matrice du sol; (3) les paramètres physiques et chimiques propres à la technologie de flottation (l'influence de ces trois groupes de facteurs est rarement abordée dans une même étude);
- L'analyse microscopique par SEM-EDX est plus appropriée pour expérimenter la technologie de flottation que les méthodes chimiques traditionnelles.

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Partie 2

Chapitre 2: Remediation practices and treatment technologies

Résumé

Dans les pays industrialisés, les métaux lourds sont présents dans de nombreux sites répertoriés pour leur réhabilitation et posent de sérieux risques pour les systèmes écologiques. Aux Etats-Unis, les métaux lourds ont été identifiés dans les trois quarts des sites prioritaires nationaux (sites NPL ou *Superfund*) et les sites appartenant au département de la défense (USDOD). Cependant, jusqu'à ce jour, relativement peu de projets portant sur le traitement des sols pollués ont traité les métaux comparativement à ceux qui se sont penchés sur les contaminants organiques. La décontamination des sols contaminés par les métaux (SCM) constitue un défi important en raison de l'énorme quantité et de la complexité de ces sols. Cet article propose tout d'abord un retour sur la problématique des SCM. L'objectif principal est de présenter un récapitulatif sur les options de décontamination et des technologies permettant le traitements des SCM, puis un retour sur l'application de ces techniques aux Etats-Unis au cours des 25 dernières années. La discussion se concentre sur les différentes alternatives aux méthodes ex situ de solidification/stabilisation (S/S), et ce, à travers l'étude de 128 cas. Une comparaison entre les pratiques de traitement des SCM employées en Europe et aux Etats-Unis est également présentée. Les techniques de lavage des sols, de phytorestauration, d'électrorestauration, ainsi que les techniques in situ de stabilisation fournissent une alternative efficace aux options conventionnelles de S/S et de disposition des sols. La poursuite des recherches est nécessaire afin d'améliorer la compréhension de la phytorestauration et des procédés in situ de stabilisation des métaux.

Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management,
ASCE, Vol. 12, No. 3, pp 188-209, 1 July 2008

Remediation practices and treatment technologies

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Received 1 May 2007; approved on 14 August 2007.

Abstract

Heavy metals have polluted many sites in industrial countries and pose risks for ecological systems. In the United States, metals are present at about three-quarters of Superfund and Department of Defense sites. Further, there are relatively few soil treatment projects that have treated metals compared to organic contaminants. The enormous quantity and the complexity of metal-contaminated soils (MCS) constitute an important challenge for their remediation. This paper provides: (1) A summary of the remedial options and treatment technologies for MCS; (2) a review of the field applications of the treatment technologies performed in the United States over the past 25 years. The discussion focuses on the alternatives to ex situ solidification/stabilization (S/S) through a review of 128 case studies. Additionally, a comparison of the practices used in Europe and in the United States relating to the treatment of MCS is also presented. Soil washing, phytoremediation, electrokinetics and in situ stabilization techniques provide an effective alternative to conventional S/S and disposal options. Further research is needed to improve understanding of the phytoremediation and in situ metal stabilization processes.

CE Database subject headings: Heavy metals; soil pollution; soil treatment; United States; Europe.

1. Introduction

Metal contamination of soil and groundwater at a number of locations is causing a serious threat to the environment and human health (Adriano 2001; Cameron 1992). Moreover, the presence of contaminated sites in populated areas is a major concern for urban development. Soils can be highly contaminated by metals as a result of direct contact with plant waste discharges, landfills, and leachates. The "hot spots" of metal contamination in soils are primarily due to industrial and military activities (USEPA 1995a; Williford and Bricka 2000). The elements selected for discussion in this paper are heavy metals and metalloids (As, Cr, Pb, Zn, Ni, Cd, Cu, and Hg) most frequently found at contaminated sites. The term "metals" will be used to include all the elements under discussion.

The first part of this paper presents the extent of the problem of metals at contaminated sites and the physical/chemical aspects of metals in the soil matrix (heterogeneity, fractionation, and speciation). Unlike organics, the remediation of metals in soils is more difficult to achieve (nondegradable and heterogeneity of metal forms). Despite the fact that 77% of the US National Priority List (NPL) sites are affected by metals, a mere 25% of the soil treatment projects address metal contaminants (USEPA 2004a,b). Hence, there is a great need to promote effective soil treatment methods relevant to the metals. An overview of the technologies applicable to remediation of metal-contaminated soils (MCS) is presented.

The main purpose of this paper is to provide a review of the remediation practices performed in the United States for treating the MCS, over the past 25 years. The discussion focuses on the alternatives to ex situ solidification/stabilization (S/S) through a compilation of 128 field applications. Additionally, a comparison of the remediation practices used in Europe and in the United States relating to the treatment of MCS is also presented. This paper is not intended to provide in-depth detail for any one technique or strategy, but rather to present an overview for remedy alternatives.

2. Extent of the Problem of Metals at Contaminated Sites

Many sites are highly contaminated with hazardous substances across North America and Europe (Table 1). Soils and groundwater are the most prevalent affected media. The metals account for much of the contamination present at identified hazardous sites (Table 1). In the United States, metals are prevalent at numerous sites targeted by major remediation programs such as the NPL or Superfund sites, Department of Defense (DOD), and Department of Energy (DOE). Metals appear less frequently at contaminated sites in European countries and Canada, however the percentages are significant.

In the identified sites under U.S. remediation programs, metals are often the most important group of pollutants, more so than organic chemicals such as PAH (polynuclear aromatic hydrocarbons) or BTEX (benzene, toluene, ethylbenzene, xylene) (USEPA 2004a). The Superfund program shows that for sites requiring priority remedial action, metal contamination represents a major concern. The extent of this problem has increased: 65% of the sites were polluted with metals in 1994 (USEPA 1996) and 77% in 2003 (USEPA 2004a). Over the last ten years, the estimated quantities of materials (soil, sludge, or sediment) affected by metals have been multiplied by a factor of 3, at the NPL sites (Fig. 1). The affected volume was 50×10^6 m^3 in 2003 (Fig. 1). The metals most frequently found in the identified hazardous sites under Superfund and DOD remediation programs are: As, Cr, Pb, Zn, Ni, Cd, Cu, and Hg (USEPA 2004a; Williford and Bricka 2000).

3. Complexity of Metals in Soils: Implications for Soil Treatment

The management of soils polluted with metals is complicated because: (1) The contamination is frequently heterogeneous at the macroscale (vertical and horizontal distributions of metals on site) and/or microscale (physical or chemical aspects of metals within the soil matrix); (2) the metals cannot be degraded or destroyed; (3) the variability of metal forms and the soil matrix influence the environmental risk assessment and the soil treatment feasibility. Metals are discharged into the soils in a wide array of physicochemical forms (ions, salts, particles, etc.). The soil-metal interactions (e.g., bonding, partitioning, chemical reactivity, and mobility) depend on the specific metal forms and soil characteristics such as particle size, CEC, pH, soil mineralogy, and organic content.

The knowledge of total metal concentration is not sufficient for assessing the environmental risks and selecting remediation strategy. Although, the Toxicity Characteristic Leaching Procedure (TCLP) test is typically used to verify the efficiency of the metal immobilization techniques, it offers no insight in the environmental risk and in the development of remedial methods (McGeer et al. 2004). This chapter presents several aspects that influence the behavior of metals in soil and the treatment procedures. It does not aim to provide an exhaustive discussion on bioavailability or toxicity assessment of metals (for a recent review of these aspects, see: Adriano 2001; Caruso et al. 2006; Kalis 2006; McGeer et al. 2004).

3.1. Mixed Contamination

At Superfund sites, the metals are largely present in combination with organic pollutants (Fig. 1). The presence of organic compounds influence metal mobility in the soils (Galvez-

Cloutier and Dube 2002) and can be problematic for the physical/chemical treatment of metals (USEPA 1995a). For instance, volatile organic compounds affect the solidification/stabilization process, whereas organic substances with high viscosity affect the soil washing techniques. In these cases, the organic pollutants must be removed prior to treatment of metals.

3.2. Metal Distribution According to Particle Size

The metal distribution according to particle size ranges is often the key influencing parameter for soil remediation, such as soil washing technologies (USEPA 1995a). Metals can be concentrated in a particular particle size fraction or distributed over all fractions, depending to contamination sources, metal forms, and metal-soil interactions. Metals, in ionic form, predominantly associate with fine particles (clay and silt) that are more potentially reactive as they have a higher surface area than coarser particles. However, metals, in particulate form may be distributed within all particle size fractions with no specific location (Venditti et al. 2000a; Williford et al. 1999; Yarlagadda et al. 1995). Moreover, metal concentrations may be high in sand fractions > 1-2 mm, especially for brownfield soils (Dahlin et al. 2002; Dermont et al. 2006; Mercier et al. 2001) and firing range soils (Williford and Bricka 2000).

3.3. Chemical Speciation and Fractionation of Metals in Soils

In the soil, metal contaminants may be found in one or several "pools" as summarized by McLean and Bledsoe (1992): (1) Dissolved in the soil solution; (2) occupying exchange sites on inorganic soil constituents; (3) associated via adsorption with inorganic soil constituents; (4) associated via complexation or adsorption with insoluble soil organic compounds; (5) precipitated as pure or mixed mineral solids; and (6) present in the primary or secondary mineral structure.

Specific chemical species of metals can differ according to, e.g., conformation, electronic and oxidation states, or in chemical nature of their complexed or covalently bonded substituents (Templeton et al. 2000). In the soil solution, the chemical form of metal determines the bioavailability and chemical reactivity (e.g., precipitation/dissolution, sorption/desorption, complexation), whereas the binding form in solid phase is related to the kinetics and equilibrium of metal release (Tack and Verloo 1995). In soil treatment, the removal efficiency of the metals is significantly influenced by their chemical forms and their affinity (adsorption capacity) to the soil matrix.

In this paper, the use of the terms “speciation” and “fractionation” is in conformity with IUPAC recommendations (Templeton et al. 2000). Approaches of chemical speciation and fractionation aspects include analytical process and theoretical considerations. In many cases, mathematical thermodynamic equilibrium models and soil-solution speciation analysis are difficult to apply with contaminated soils where chemistry aspects (reactivity, thermodynamic and kinetics) of multiple metals in the soil matrix are complex (MacGeer et al. 2004; Tack and Verloo 1995). Simple fractionation based on sequential extraction procedures are therefore often used to investigate the chemistry of metals in the contaminated soils.

Solid-Solution Partitioning and Soil-Solution Speciation

Geochemical models based on measurable soil parameters and on theoretical thermodynamic data have been used to predict soil-solution partitioning and soil-solution speciation of metals in contaminated soils (Balasoiu et al. 2001; Sauve et al. 2000a). A good review of these models is provided by Caruso et al. (2006), and Lumsdon and Evans (1995).

In the soil solution, metals may be complexed with organic or inorganic ligands, and/or occur as free hydrated metal ions. Free metal species are generally recognized as the principal parameter that controls the toxicity of metals in the soil solution (Kalis 2006). The quantification of free metal ions can be relatively well determined (Kalis 2006; Sauve et al. 1997a). A large number of analytical techniques (e.g., ion selective electrodes; anodic stripping voltammetry; and chromatography separation with detection by ICP-MS) are available to identify and quantify the individual species of metals in soil solution (Caruso et al. 2006; Kalis 2006; Mach et al. 1996; Sauve et al. 1997a,b, 2000b; Tack and Verloo 1995; Templeton et al. 2000).

Chemical Fractionation of Metals by Sequential Extraction Procedures

The most commonly used methods for investigating the chemical forms of metals in contaminated soils are the sequential extraction procedures, which determine metal fractionation according to bonding with specific soil substrates. The methods are mostly based on the approach proposed by Tessier et al. (1979) involving the following fractions: (1) Exchangeable; (2) carbonates; (3) iron and manganese oxides; (4) organic matter; and (5) residual (silicates and other refractory minerals). This method can help in assessing the potential mobility and solubility of metals in contaminated soils (Berti et al. 1995). However, this analytical procedure determines neither specific chemical forms of a metal, nor the speciation of metals in the soil (Templeton et al. 2000).

Sequential extraction may be helpful for selecting, monitoring and improving the soil treatment processes, especially for metal removal: soil washing/leaching methods (Ko et al. 2005; Peters 1999; Yarlagadda et al. 1995), froth flotation (Cauwenberg et al. 1998; Vanthuyne and Maes 2002), and electrokinetics (Kim and Kim 2001; Reddy et al. 2001). The relevance of the use of this "indirect" chemical procedure has been criticized (D'Amore et al. 2005; Sheppard and Stephenson 1995); especially for assessing heterogeneous soils contaminated with high concentrations of metals (Dahlin et al. 2002; Kennedy et al. 2002).

Solid Phase Speciation by Direct Physical Methods

Metals, in the particulate phase can occur as a single component or within a complex particle of multiple components. Solid phase speciation of metals in the soil matrix can be investigated directly through spectroscopy and microscopy instrumental methods (D'Amore et al. 2005). Scanning electron microscopy (SEM) coupled with energy dispersive x-ray (EDX) is usually used (Kennedy et al. 2002; Langmi and Watt 2003). Also, finer techniques have been applied for the speciation of Pb and Zn, e.g., transmission electron microscope (TEM) coupled with EDX (Buatier et al. 2001); x-ray absorption fine structure (XAFS) and x-ray absorption near edge structure spectroscopy (Manceau et al. 2000; Roberts et al. 2002; Welter et al. 1999).

These instrumental techniques can provide information on the metal forms (primarily for Cu, Zn, and Pb), geochemical associations, and internal particle structure. The SEM-EDX system may evaluate: (1) Metal occurrences in the soils solid phase; (2) morphology, elemental composition, and association degree (enclosed/cemented/liberated nature) of the metal-bearing phase and carrier phase. XAFS spectroscopy is a selective analytical method that determines the chemical binding forms of metals in different soil organic or mineral components (Kennedy et al. 2002; Welter et al. 1999).

The direct acquisition of compositional characteristics of metal-bearing particles provides information for understanding the relationship of the metals and their environment (McGeer et al. 2004) and for the development of the remediation strategy (Kennedy et al. 2002). SEM-EDX is a particularly suitable tool for predicting the treatment efficiency based on physical separation (Mercier et al. 2001). The complementary use of the sequential extraction procedure and the SEM-EDX provides a very useful tool for understanding chemistry aspects of metals in soils (Dahlin et al. 2002; Kennedy et al. 2002; Venditti et al. 2000a,b; Yarlagadda et al. 1995).

4. Overview of the Remedial Options and Technologies

This section seeks to present the remedial options to treat MCS. It contains a description of the key elements for selecting soil remediation technologies. The discussion excludes groundwater treatments. The notion relating to the selection of a numerical criteria-based approach or a risk-based approach for managing soil at contaminated sites will not be discussed in this paper as there are ample discussions elsewhere (Adriano et al. 1995; CLARINET 2002b; Environment Canada 2000).

Remediation technologies can be classified according to: (1) The nature of action that is applied on the metals (immobilization or extraction); (2) the location where the process is applied (in situ or ex situ); (3) technology type, i.e., containment/disposal methods, or chemical, physical, thermal, and biological treatments, or monitored natural attenuation. The concepts of remedial options and existing technologies for MCS are summarized in Fig. 2.

4.1. Treatment versus Containment/Disposal

The methods of isolation (i.e., in situ containment) or relocation (i.e., off-site disposal) of the contaminated soils are used to prevent migration of metals to groundwater or to other environmental media. Between 1982 and 2002, 55% of remedy action of Superfund sites in the United States have implemented the containment/disposal techniques (USEPA 2004a). In the late 1980s, the number of approaches that included treatment began to increase because of environmental legislation and policies encouraging permanent solutions (USEPA 1996). However, soil disposal (with or without S/S pretreatment) is still often used for soil contaminated with metals (USEPA 2000b).

The containment or disposal approaches are not, rigorously speaking, remediation technologies because they do not directly treat the metal contaminants. Containment technologies are most likely to be applicable to metal contaminants for which mobility must be reduced as a temporary measure to mitigate risk until a permanent solution can be tested and implemented (USEPA 1997b). Interest in remediation treatment has been driven by the demand for technologies that are cost effective alternatives to containment options and suppress the long-term liability incurred with soil disposal.

4.2. Monitored Natural Attenuation

The remediation of a contaminated site can involve an alternative approach favoring the natural attenuation processes, which must be regularly monitored; this approach is commonly called "monitored natural attenuation" (MNA). Natural attenuation is an intrinsic process and it is not an “active treatment” technology because it does not involve any unit operations to treat the metals. MNA will be regarded as a “passive treatment” of metal stabilization. MNA is primarily applicable for the remediation of soil and groundwater affected by organic contaminants (AFCEE 2007; Mulligan and Yong 2004).

MNA may be appropriate for some metals when the valence state of a metal changes resulting in the immobilization or toxicity reduction of that metal: e.g., reduction of Cr(VI) to Cr(III) or oxidation of As(III) to As(V) (FRTR 2007a; Wang and Mulligan 2006). Metal ions can be retained in the soil by sorption, precipitation, complexation, or redox reactions with soil components (mineral or organic substrates, or microorganisms), via physicochemical or biological processes (Adriano et al. 2004; Wang and Mulligan 2006).

However, MNA alone may be insufficient for the remediation of metals in soils (very slow processes) and must be enhanced or assisted by engineering actions (Adriano et al. 2004; Wang and Mulligan 2006). The intrinsic metal stabilization processes in soil can be accelerated by using: (1) addition of mineral stabilizers such as lime, phosphates, fly ashes (i.e., in situ chemical stabilization); (2) addition of biosolids or the use of microbial processes (i.e., in situ biological stabilization); and (3) growing vegetation (i.e., phytostabilization). MNA can also be used after an “active” remedial treatment (FRTR 2007a).

4.3. Immobilization versus Extraction Treatment

Unlike organic substances, metals cannot be degraded or destroyed. Consequently, the treatment of metals is limited to two main strategies: Immobilization or extraction. Immobilization or extraction technologies may be used separately or in combination to remediate metal-contaminated soils. Immobilization techniques aim at sequestering or stabilizing metals (minimize the leaching characteristics of the soil matrix and/or change metals to less soluble, toxic, or bioavailable forms) in soil to reduce the risks for human health and the environment. No immobilization treatment technology is permanently effective as metals remain in the soil matrix. However, metal immobilization treatment provides an effective alternative to containment approach.

Extraction methods refer to processes that can separate metals from soil, reduce the concentration of metals, or reduce the volume of the entire contaminated medium. Extraction treatments aim at completely decontaminating the site by removing metals from the soil matrix. The ideal goal of an extraction strategy is to recover metals for reuse and resale, however, metal recovery is often not practicable for projects that lack economic viability or technical feasibility for the extraction and recovery processes. When metal contamination and the soil matrix are highly heterogeneous or when metals are strongly bound with soil matrix, metal extraction is highly difficult. In many cases, extraction methods are used to reduce the metal concentrations to an acceptable level or to considerably reduce the volume of contaminated soil.

4.4. Ex Situ versus In Situ Treatment

The advantages and disadvantages of ex situ or in situ treatments differ according to the use of metal extraction and immobilization methods (Table 2). Ex situ techniques, which require excavation of the contaminated material before carrying out the treatment, involve two options: (1) Remediation on site by using mobile treatment unit and (2) remediation off site in fixed facilities that requires the transport of contaminated material. Although the ex situ option of electrokinetics exists (Lageman et al. 2005; Zagury et al. 1999), the in situ electroreclamation is more interesting from an environmental point of view and is most common (Virkutyte et al. 2002).

Martin and Ruby (2004) indicated three objectives typically accomplished by in situ remediation: (1) Reduce metal leaching; (2) reduce toxicity of metals; and (3) promote vegetation of the site. Although in situ treatments are receiving greater acceptance as a reliable technology by site managers and other remediation professionals, the generalization of an in situ method is difficult because often each site shows unique characteristics. Further, the in situ extraction methods present many disadvantages (Table 2). The center for soil treatment “Service Center Ground” from Dutch environmental agency, with over 20 years of experience in soil remediation concludes that in situ methods cannot compete with ex situ technologies (Honders et al. 2003).

Selection of remedial approach is contingent upon several factors such as: Hydrogeological conditions, environment situation (whether the site is an industrial, urban, rural, woodland, etc.), site size, affected horizon type (saturated or unsaturated zone), and soil characteristics. In urban environments where the site must be quickly available, the ex situ remedial measures are more suitable as soil excavation eliminates the contamination from the site. Conversely, for a large site such as a vast mine sites, an in situ approach would be preferable over an ex situ remediation procedure.

4.5. Description, Advantages, Disadvantages, and Applicability of Technologies

Table 3 provides a brief description, and summarizes the main advantages, disadvantages and limitations for metal immobilization technologies. Likewise, Table 4 presents the same information for metal extraction technologies which have a specific applicability that differ according to metal forms, concentration ranges, and soil type.

4.6. Treatment Train

Generally, no single technology can remediate an entire site or accomplish a sufficient extraction/immobilization of metals. Therefore, in many cases, several treatment technologies are combined to form what is known as a "treatment train" (USEPA 2004b). Further, treatment processes, especially extraction technologies, generate either solid or liquid residual products that must be further treated or disposed. Table 5 summarizes the typical processes used as pretreatment, posttreatment, and the residuals management for each technology type.

5. Review of Remediation Case Studies in the United States

This section provides a review of field-scale projects performed in the United States for the remediation of soils affected by metals, over the last 25 years. This review includes Superfund remedial actions, full-scale applications and pilot/field-scale demonstration projects that have been completed (for the period 1982-2006) or that are currently in operation. Some Canadian projects have also been reported. The discussion covers a wide array of treatment technologies, excluding MNA and disposal/containment options. The review remains restricted to field-scale projects; thus, emerging technology research and laboratory tests are not included. Doubled case studies (i.e., when the same project has been reported by several documents) have been avoided.

The writers have identified 275 projects from over 3,000 projects searched in various databases or reports, primarily FRTR (2006), USEPA (1995a), USEPA (2000a), USEPA/ASR (2007), and USEPA/CLU-IN (2007). The number of soil treatment projects that attempt to treat metals is low compared to the total number of remedial actions recorded in the various documents. That is explained by several points: (1) Many remediation projects aim at treating groundwater (e.g., 50% of Superfund remedial actions); (2) a large majority (75%) of soil remediation projects address organic contaminants; (3) the searches do not include the pre-selected projects (with EPA status: "in design" or "design completed/being installed"), which represents 25% of Superfund projects recorded in the ASR database (USEPA 2004b).

The S/S technology has been commonly selected to treat soils from metal-contaminated sites (Fig. 3). At this time, the S/S technology continues to be the favored technology for metals, although its selection has declined over the past ten years. This study distinguishes ex situ S/S from in situ S/S approaches. The ex situ S/S is a well established method (147 projects, with 115 Superfund remedial actions), whereas the in situ S/S is considered as an innovative technology (21 projects, with 16 Superfund remedial actions). The ex situ S/S, which represents more than half of the projects, is therefore regarded as the conventional treatment technology, whereas the other technologies constitute a treatment alternative (Fig. 3).

5.1. Conventional Technology: Ex Situ S/S

Within the framework of the Superfund program, ex situ S/S technology represents 80% of remedial actions selected at sites contaminated with metals (USEPA 2000b, 2004b). A large majority of ex situ S/S projects are based on cement immobilization processes, involving

Portland-type cements and pozzolanic materials (USEPA 2000b). The main advantage of S/S technologies is their ability to treat a wide variety of soil types and metal forms. However, ex situ S/S treatment is not a good long-term solution because: (1) Metal contaminants are not removed from the soil matrix; (2) the ex situ cement-based S/S process significantly increases the volume of material (FRTR 2007a); (3) the solidified/stabilized material is off-site disposed or landfilled (USEPA 2000b); (4) limited data are available on long-term stability and integrity of solidified/stabilized material (USEPA 2000b); (5) re-vegetation of the site is not encouraged; (6) backfilling the excavated areas with clean fill is necessary when processed soil is disposed off-site. Consequently, ex situ S/S technology could be less extensively used and the development of alternative/innovative technologies (including in situ S/S option) must be encouraged.

5.2. Alternative Technologies

The authors have collected 128 field scale remediation projects involving alternative technologies to ex situ S/S for the treatment of MCS. The appendix to this paper summarizes site description, technology type, treated metals, date demonstration, and reference for the 128 case studies. The five metals frequently treated are: Pb, Cr, As, Cu, and Cd (Fig. 4). Since the early 1990s, the number of U.S. government-sponsored field demonstrations of alternative remediation technologies has significantly grown.

Fig. 5 shows the number of projects versus alternative technology type, which include: In situ S/S (cement-based process or in situ chemical stabilization), vitrification, chemical Red/Ox, phytostabilization, biological stabilization, soil washing (physical separation and/or chemical extraction), thermal treatments, biological extraction (bioleaching or use of biosurfactants), electrokinetics, phytoextraction, and soil flushing. The alternative technologies specifically applicable for in situ treatment (e.g., phytoremediation and electrokinetics) are used slightly more than the ex situ options (Fig. 5). In addition, the technologies based on an extraction approach represent 60% of remedial actions (Fig. 5).

The alternative technologies mostly selected in the United States for treating metals in soils are: Physical/chemical techniques of soil washing followed by phytoremediation, in situ S/S, vitrification and electroreclamation (Fig. 5). Phytotechnology is principally based on the metal extraction approach (19 phytoextraction projects versus 4 phytostabilization projects, and 6 phytotechnology projects involving both approaches) (Fig. 5). Many in situ innovative remediation techniques currently being developed focus on exploiting or altering soil chemistry to reduce metal solubility and bioavailability. Some of the more promising site stabilization alternatives include phytostabilization and biological stabilization. These techniques are often combined with the addition of chemical stabilizers such as phosphates, carbonates, silicates, pH modifiers and fertilizers (in situ chemical stabilization). The main advantage of these techniques compared to conventional cement-based S/S processes is the revegetation of the site with sufficient metal stabilization to reduce the environmental risk.

In Situ S/S Technologies

In situ S/S includes a wide variety of processes such as cement-based S/S (widely used) and stabilization procedures (few used). Conventional cement-based technique aims at sequestering the metals in a strongly modified soil matrix (changes physicochemistry, permeability, structure, and increases volume of soils), whereas in situ stabilization attempts to reduce the bioavailability and solubility of metals without strong alteration of soil properties (ITRC 1997a; Martin and Ruby 2004). Unlike cement-based technique, the in situ stabilization approach may promote revegetation of the site.

In this study, the in situ cement-based S/S process is considered as an alternative technology to ex situ S/S because this one avoids soil excavation and off-site disposal. In situ S/S has a cost advantage over ex situ applications for larger volumes and it is more suitable if volatile or semivolatile organic compounds are present (USEPA 1997a,b). However, mixing of reagent during the in situ process is less effective compared to ex situ applications (USEPA 1997a).

In situ chemical stabilization is an emerging technology that is still in the research and development stage. The soil amendments involved are less significant in quantity compared to those of S/S methods. The main stabilizer agents used are mineral compounds, such as phosphates, lime, fly ashes, and aluminosilicates (ITRC 1997a). Stabilization based on phosphate additives is the most investigated technique to decrease bioavailability and solubility of metals (primarily Pb, Cd, and Zn) (Adriano et al. 2004; Berti and Cunningham 1997; Hettiarachchi and Pierzynski 2002; Ruby et al. 1994); however few large-scale applications have been performed (Martin and Ruby 2004).

Biological Stabilization

In situ stabilization enhanced by bioremediation appears suitable for the treatment of soils contaminated with mining tailings. These techniques involve biosolids amendments, or enhanced-biological activity to promote the formation of less toxic and less soluble metal forms, by either creating ambient conditions (that will cause such species to form), or acting directly on the metal to change their valence state (USEPA 2004b). Metal immobilization mechanisms involving microorganisms may include: (1) Biosorption and intracellular accumulation; (2) metal-binding biomolecules; (3) metal precipitation by metal-and sulfate-reducing bacteria; (4) bacterial and fungal oxidation; (5) oxalates and carbonates produced by microorganisms (Gadd 2004). Hobman (2001) reported the three best understood mechanisms for immobilization of metals are:

Bioaccumulation, biosorption, and biomineralization. In 1999, USEPA conducted a field demonstration of in situ bioremediation/chemical stabilization (biosolids and lime addition) at California Gulch Superfund site, in Leadville, Colo. (Appendix). In addition, the USEPA/ASR (2007) database informs that two remedial Superfund actions have been preselected (predesign status) at the Palmerton Zinc Pile, P. (soils contaminated with Cd, Pb, and Zn) and at the Upper Tenmile Creek Mining Area, Mont. (soils contaminated with As, Cd, Pb, and Zn).

Phytostabilization

Phytostabilization is an emerging technology that uses plants to prevent metal migration and to immobilize them by: (1) Soil stabilization with root systems that minimizes erosion and percolation; and (2) metal stabilization via biochemical processes occurring in roots or within the root neighborhood (Pivetz 2001). Phytostabilization has been used at field scale to stabilize As, Cd, Cu, or Pb (Appendix).

Chemical Red/Ox

Chemical Red/Ox is first and foremost used as a pretreatment prior to S/S in order to reduce hexavalent chromium Cr(VI) to trivalent chromium Cr(III). This chemical treatment (reduction reaction) is necessary for two main raisons: (1) Cr(VI) ion is considered far more toxic than Cr(III) and (2) Cr(III) may be readily precipitated to hydroxide form over a wide range of pH values (USEPA 1995a). This chemical procedure has been used at four Superfund sites (Appendix). Chemical Red/Ox has been performed both ex situ and in situ (Fig. 5).

Vitrification

Vitrification is mainly used in the United States to remediate soils contaminated with heavy metals mixed with radioactive metals from DOE sites. The vitrified product, enclosing metals, is more leach resistant and chemically stable for long periods of time compared to material resulting from reagent-based S/S process. Two main heat sources can be employed to melt and vitrify the soils: (1) Thermal energy by using combustion of fossil fuels; (2) electrical energy by using joule effect, electric arc, induction, or plasma processes (Colombo et al. 2003). The ex situ vitrification (ten projects) has been used more compared to in situ application (two projects) (Fig. 5). Under the Superfund Innovative Technology Evaluation (SITE) program, vitrification has been completed at three sites (Appendix).

Phytoextraction

Phytoextraction has been applied across the United States at various types of sites contaminated with metals such as: Battery manufacturing facilities, smelter sites, military sites, landfills, and residential areas (Appendix). Although four full-scale projects are reported, the majority of phytoextraction projects are limited at pilot-scale applications. The most targeted metals in phytoextraction projects are Pb and As (Appendix). Phytoextraction technology is available at commercialscale. For instance, Phytotech has conducted several successful field trials of phytoextraction under the SITE Demonstration Program: e.g., at the Magic Marker site in Trenton, N.J. (Pb from a former battery facility is the target contaminant, with initial concentrations up to 1,400 μg/g); at a former metal-plating facility in Findlay, Ohio (where soil is contaminated with Cr, Cd, Ni, Zn, and Pb) (USEPA 2007).

Electrokinetics

Electrokinetics is an in situ promising technology to extract metal ions from saturated soils or clay soils. Numerous bench-scale and pilot-scale laboratory studies involving the feasibility of removing heavy metal ions from soils have been completed (ITRC 1997b). At the field scale, electroreclamation has mostly been used in the United States for demonstration purposes at military installations (conducted by Louisiana State University/Electrokinetics, Geokinetics International, Lynntech, and Sandia National Laboratory) and the targeted metals were Cr and Pb (Appendix). Under the SITE Demonstration Program, two field tests have been completed; however, at this time, no large-scale application has been selected for treating metals at Superfund sites.

Soil Flushing

Soil flushing has been employed at a limited number of sites affected by metals. Soil flushing appears appropriate when the soil (ideally, coarse soils with relatively high hydraulic conductivity) and groundwater are contaminated by water-soluble metals such as Cr(VI) ions. Water flushing is more environmentally suitable rather than reagent flushing technique because addition of chemical agents may contaminate the soils and aquifer (USEPA 1997a).

Soil Washing

The soil washing method uses mostly physical separation, which is based on mineral processing technologies such as size separation, gravity concentration, froth flotation, attrition scrubbing, and magnetic separation. Physical separation can be used alone or combined with chemical leaching (Dermont et al. 2008). Physical separation is well established for removing Pb from soils of arms firing range (ten applications reported in the Appendix). Chemical extraction often uses acid leaching or hydrometallurgical processes for metal recovery. Physical separation is primarily applicable when metal contaminants are under particulate forms (ideally liberated particle), whereas chemical extraction is primarily suitable for ionic forms (free ions or adsorbed on soil, salts). Although, soil washing is available at commercial scale in the United States, it has had limited use under the Superfund program compared to conventional S/S techniques. At, the present time, soil washing has been performed at only two Superfund sites contaminated with metals: At King of Prussia, N.J. and at Vineland Chemical, N.J. (Appendix). In addition, recent pilot plant studies of soil washing processes have been successfully performed in Canada (Bergeron 2005; Mercier et al. 2007).

Thermal Treatments

Thermal treatments are principally used to extract volatile metal Hg via thermal desorption. For instance, commercial applications have been performed by the mercury recovery services system (PMET 2006). Pyromettalurgical technologies include high temperature thermal desorption (HTTD) and high temperature metal recovery techniques; the HTTD method is the most widely used. Theses technologies are exclusively applied ex situ and mobile units are available to treat soils on site.

Biological Extraction

Biological extraction includes, in this review, bioleaching techniques and the biosurfactant-enhanced solubilization methods. Although, bioleaching of metals from low-grade ores (principally sulfide minerals) is well established in the mining industry (Olson et al. 2003), no field-scale application of bioleaching in soil treatment for extracting metals has been reported. Various bioleaching methods (e.g., autotrophic leaching via iron-oxidizing bacteria or sulfur-oxidizing bacteria, and heterotrophic leaching via fungus Aspergillus niger) have been broadly tested at laboratory/pilot scale to extract metals from sewage sludges (Blais et al. 1992, 2004; Chan et al. 2003), mining tailings (Mulligan and Galvez-Cloutier 2003), sediments (Löser et al. 2001), and soils (Zagury et al. 2001). Also, several laboratory studies showed that metals under cationic forms can be extracted from soils by anionic biosurfactant solutions; however, this technique has not yet been performed for large-scale remediation projects (Mulligan et al. 1999; Mulligan 2005).

6. Comparison of Practices in the United States and in Europe

This section provides a comparison of the remediation practices employed in Europe and in United States for treating soils contaminated with metals. The possibility of direct landfilling or disposal of contaminated soils is more restricted in Europe compared to North America. Consequently, the development status and the frequency of use of the treatments differ in Europe compared to North America (Table 6).

6.1. Immobilization Technologies

S/S is a well established technology in the United States. For soil remediation, this technique has not been frequently implemented in European countries (UKEA 2004). For example, in The Netherlands, the quantities of soil treated by immobilization were 4 times less significant than that of the volume processed by the soil washing technology for the year 2001 (Honders et al. 2003).

Amongst emerging in situ metal stabilization methods, the phytostabilization technology has been well demonstrated at field-scale in Europe and in the United States (USEPA 2005; Van der Lelie et al. 2001). In Europe, the addition of chemical stabilizer is often used in conjunction with phytostabilization (Van der Lelie et al. 2001). In general, in situ chemical stabilization is still at the development stage in Europe and the United States. Several field tests have been reported in Europeans countries and in the United States, which mostly use phosphate compounds, lime, or/and coal ashes (Adriano et al. 2004; Martin and Ruby 2004). In the United States, biostabilization in conjunction with chemical stabilization has been tested at field-scale. In Europe, metal stabilization in soils by biological approach is at the research and development phase (CLARINET 2002b; Diels et al. 2002).

6.2. Extraction Technologies

The soil washing technology is available at commercial scale in both Europe and the United States; however, its use is not yet extensive in the United States compared to certain Europeans countries (FRTR 2007a). Soil washing based on physical separation, is mainly used in The Netherlands, Belgium, Germany, Norway, and Sweden to treat MCS (CLARINET 2002b). The Netherlands are a pioneering country for the use of the soil washing technology and Dutch firms have contributed to its development in the United States (Mann 1999). In 2001, 21 stationary and 4 mobile plants were operational in The Netherlands, and 855 kt/year had been treated between 1991 and 2001 (Honders et al. 2003).

Electrokinetics has been more widely applied in Europe compared to the United States. For instance, Holland Millieutechniek reported 13 commercial applications in The Netherlands involving treatment of soil and groundwater contaminated with heavy metals (Holland Milieutechniek 2007). Geokinetics International, Inc. (origin of The Netherlands) has successfully demonstrated electrokinetics at 5-10 sites in Europe (Lageman et al. 2005). Although, several tests have been performed, there have been few, if any, commercial applications of electrokinetics in the United States (FRTR 2007a). Phytoextraction of metals has been successfully demonstrated at field scale both in the United States and in Europe; however, its application is more developed in the United States (at commercial scale) (USEPA 2005; Van der Lelie et al. 2001).

7. Conclusions

In the United States, the ex situ S/S technology is usually selected to remediate metal-containing wastes and continues to be the favored technology to treat metals, although its selection has declined in the last ten years. In Europe, S/S is not extensively used for soil remediation. Although, the development and demonstrations of innovative technologies have increased since the 1990s, the field applications of alternatives for treating metals are still limited.

Metal extraction technologies such as soil washing, phytoextraction, and electrokinetics provide a cost effective and environmentally proactive alternative to S/S and disposal options. The soil washing technology is relevant for ex situ extraction, whereas electrokinetics and phytoextraction are relevant for in situ extraction. At the present time, soil washing and electroreclamation have been used more in European countries compared to the United States. Phytoextraction appears more developed in the United States where this technology has been used at commercial scale in several sites. However, phytoextraction is still an emerging technology in the development phase. Before an intensive use, the phytoextraction technology requires: (1) More research for understanding fundamental mechanisms; (2) more tests at the field-scale for optimizing the extraction processes; and (3) more reflection to select an appropriate management of the residual biomass, ideally for metal recovery, and avoiding the disposal option (Pivetz 2001; Van der Lelie et al. 2001).

Overall, the efficiency of metal extraction technologies is strongly influenced by soil type and chemical forms of the metals to be treated. For instance, chemical soil washing is more suitable for removing metals bound to exchangeable/carbonate/reducible Fe-Mn oxide fractions of soils, whereas froth flotation is more applicable for separating the metal sulfide particles from the soil matrix. The metal extraction efficiency decreases significantly with complexity of the soil matrix and the variability in metal forms. The metals, which strongly bond to the soil particles, are technically difficult to remove from soils.

When metal extraction is not feasible or if the site is very large, in situ stabilization (or "in place inactivation") is an interesting approach to reduce environmental risk to acceptable levels. Phytostabilization alone or in combination with chemical stabilization is one of the most promising alternative technologies for stabilizing metals in soils and reducing their bioavailability. More research is necessary for understanding fundamental mechanisms of phytostabilization and in situ stabilization of metals.

Future practices must promote a strategy of combining several techniques (treatment train). The alternative technologies to excavation-immobilization-disposal practice must be encouraged by government agencies. Further efforts are also needed to develop theoretical models for helping in the selection of a remedial solution and for predicting in situ treatment processes.

Acknowledgements

The first writer is thankful to the "Institut National de la Recherche Scientifique Eau Terre et Environnement" (INRS-ETE) for financial support. The writers would also like to thank Angus Calderhead and Kathrine Gauvin for their useful comments.

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Tables

Table 1. Number of potentially contaminated sites and percentage of sites contaminated with metals in selected regions/countries

Region/Country	Number of potentially contaminated sites	Percentage of sites contaminated with metals
United States	500,000 - 1,000,000[a]	69[e]
Europe	1,000,000[b]	31[f]
Canada	30,000[c]	21[g]
Quebec	6,240[d]	19[d]
France	250,000[b]	18[h]

[a] USEPA (1996; 2004a; 2006).

[b] CLARINET (2002a).

[c] NRTEE (2003).

[d] MDDEP (2006).

[e] Average value based on data from 7,500 sites (NPL, RCRA, DOD and DOE program), USEPA (2004a).

[f] Based on data from 32,000 sites, EEA (2005).

[g] Average value based on data from 6,156 federal sites, TBCS (2005).

[h] Value for only Pb, based on data from 3,900 sites, MEDD (2007).

Table 2. Advantages and disadvantages of ex situ and in situ remediation technologies for metal-contaminated soils

	Advantages	Disadvantages/ Limitations
Ex situ	Fast remediation of the site Nearly independent of geology of the site Process optimization and final results can be easily controlled Potential of metal recovery (Extract.) Potential re-use of "cleaned" soil fraction (Extract.) Efficiency of processes can be easily verified Treatment by S/S is usually relatively simple and efficient Usually independent of the type of the metals (Immob.) Potential of re-use for vitrified materials	Risks exposure for workers and the environment during excavation operations Requires transport if treatment off-site Requires heavy equipments Difficult to use when existing infrastructure is complex Influenced by type, mineralogical/chemical forms of metals (Extract.) Requires fixed facilities or transportable treatment unit Usually high costs with metals
In situ	Requires no excavation, no transport, no fixed facilities off-site Minimize exposure to humans and the environment Requires usually no heavy equipment Usually appropriate for a large site (except vitrification) Usually more cost effective Reduce metal leaching, mobility (Immob.) Reduce metal bioavailability to ecological receptors (Immob.) Possible groundwater treatment Possible re-vegetation of the site (except for vitrification and S/S)	Difficult to verify efficiency of process Influenced by site-specific conditions Limited by subsurface heterogeneities Limited by the contamination depth Concern with long term integrity of the site Long term maintenance is required Require access control of the site/limitation of future re-use of the site Long treatment time is usually required Requires addition/injection of chemical reagents to mobilize metals (Extract.) Potential contamination of the aquifer from residual flushing solution (Extract.) Limited with low soil permeability (Extract.) Influenced by type/chemistry/structure of soils (Extract.) Influenced by concentration, fractionation and speciation of metals (Extract.) Concern for biomass management (Phytoextract.) Limited to low metal concentrations and shallow depth (Phytoextract.) Requires subsequent treatment of extraction fluid (electrokinetics, soil flushing)

Table 3. Description, advantages and disadvantages of metal immobilization/isolation technologies

Technology	Description	Advantages	Disadvantages / Limitations
In-situ Containment (Capping and Barriers)	Isolation structure that aims to prevent the movement of groundwater or surface water infiltration in order to avoid the migration of metals.	Can limit the potential for contact of the underlying contamination by people, fauna and flora. Applicable to a broad range of soil types. Can reduce disturbance of the contamination source.	The toxicity/solubility of metals is not reduced. The long term performance of capping and barrier system is unproven and monitoring may be required.
Off-site disposal	Contaminated soils are excavated and transported to authorized hazardous waste landfilling sites.	Relatively short time scale. Effectively removes the sources of many environmental risks from the site.	The toxicity/solubility of metals is not reduced. Off-site disposal is strictly restricted and regulated.
Monitored Natural Attenuation (MNA)	Intrinsic remediation process. Stabilization and toxicity reduction of metals via natural processes (biological/chemical reactions involving valence change or sorption, etc.) with subsurface materials.	Less generation or transfer of remediation wastes. Few surface structures are required. Overall cost will likely be lower than "active" remediation technique.	May not be sufficient for remediation of metals. Not appropriate where imminent site risks are present. Longer time frames may be required. Long term monitoring and associated costs.
S/S and in situ chemical stabilization	S/S (mostly based on cement process) aims at sequestering the metals in a strongly modified soil matrix. In situ chemical stabilization aims to reduce metal bioavailability/solubility without affecting soil matrix.	S/S is applicable to a wide range of mixed contaminants and soil types. In situ stabilization may promote site revegetation and can be applied for a large site.	S/S process increases the volume of treated material. Presence of interfering compounds such as organics (S/S). Concern with long term integrity (S/S).
Vitrification	Vitrification (ex situ or in situ) refers to the immobilization process that uses high temperatures to melt the soil, and to stabilize the metal contaminants after cooling within a solidified vitreous mass.	Permanent remedy with good long term effectiveness. Potential volume reduction of materials. Products have potential reuse options.	Off gases may be created and must be treated. Expensive pilot-scale testing is required. The cost is very high.
Chemical Red/Ox	Chemical Red/Ox (ex situ or in situ) converts mobile/toxic metal compounds to chemical forms that are more stable, less mobile or less toxic.	This technique is often used as pre-treatment prior S/S to reduce Cr(VI) to a less toxic form Cr(III).	This technique requires the input of chemical agents which can be both expensive and hazardous.
Phytostabilization	In situ emerging technology that uses plants to prevent soil erosion (by wind and rain), to stabilize metals in order to avoid metals migration to groundwater.	Potentially applicable for many metals. Large area can be treated. No disposal of contaminated biomass required.	Applications limited to depth of the root zone. Remaining liability issues, including maintenance for an indefinite period of time. Requires controlling of site use.
Biological stabilization	In situ emerging technology that uses biosolids or microbial activity to reduce metals toxicity or bioavailability for the environment. This technology is often associated with chemical stabilization.	Metal bioavailability for human and biological receptors is reduced. Potential revegetation of the site.	Requires more pilot studies to evaluate the efficiency. Remaining liability issues, including maintenance for an indefinite period of time.

Notes: S/S= Solidification/Stabilization; Information extracted from Adriano et al. (2004), FRTR (2007a), Martin and Ruby (2004), Smith et al. (1995), USEPA (1995a).

Table 4. Description, applicability, advantages and disadvantages of metal extraction technologies

Technology	Description	Applicability (Form[a] – Conc[b])	Advantages	Disadvantages / Limitations
SW/Physical separation	Ex situ techniques based on mineral processing technologies (separation by size, gravity, flotation, attrition, magnetism) to remove the metals.	P – H	The clean, larger fraction can be returned to the site for continued use. The treatment duration is short to medium-term.	Difficulty with soils that contain high clay content, high humic content, organic contaminants with high viscosity. Requires a large equipments and large space.
SW/Chemical extraction	Ex situ technique that uses an extracting aqueous fluid containing chemical agents (acids, bases, surfactant, or chelating agents) to extract metals from soils.	I – H	The treatment duration is short to medium-term. Potential to metal recovery.	Difficulty with soils that contain: high clay content and high humic content. Use of chemical agents which can be both expensive and hazardous.
Biological extraction	Ex situ technique (usually slurry phase process) that uses microorganisms to aid the mobilization of metals (bioleaching techniques).	P/I – M	Non-toxic character of the biological agents compared to chemical agents.	No performance data available for completed full-scale applications.
Thermal extraction	Ex situ technique that aims to separating volatile metal (e.g., Hg). Includes Thermal Desorption (TD) and High Temperature Metal Recovery (HTMR).	V – H	TD is one of the rare methods effective to extract Hg. Potential of metal recovery.	Requires air emissions treatment and specialized facilities. Pre-treatment with mixing/fluxing agents to assist melting. The cost is very high.
Electro-kinetics	Technique that uses electrochemical processes to remove metals from (saturated) soils. In situ option is more interesting rather than ex situ approach.	I – M	Metals can be effectively removed from soils via in situ approach. Potentially applicable for broad types of metals.	Applicable only to saturated and partially saturated (clays and silt-clay) soils. Multi-metals contaminated sites pose problems.
Phyto-extraction	In situ technique that uses plants hyper accumulative to extract metals from the soils. Can require reagent addition (EDTA) to enhance the process.	PA – L	Large area can be treated. Good public acceptance. Does not involve excavation, treatment, and disposal.	Process duration is long. Limited by depth of the root zone and number of harvest required. Concern for management of the biomass that contain high metal content.
Soil flushing	In situ technique that uses an injection of water (water flushing), or aqueous fluid containing a chemical agent (reagent flushing) to enhance metals solubility into the soil in order to extract them by groundwater pumping.	I – M	The treatment duration is short to medium-term. May mobilize a wide range of organic or inorganic contaminants from coarse-grained soils.	Associated risk of contamination of underlying aquifer with under covered flushing solution that contains the metals. The reagent flushing may affect the soil properties.

Notes: SW= Soil Washing; Information extracted from FRTR (2007a), Smith et al. (1995), and USEPA (1995a; 1997a,b).

[a] Forms of metals most suitable for the treatment (P= Particulate forms; I= Ionic forms, or easily dissolvable/exchangeable with acid/alkaline/redox/chelating processes, or salts forms; V= Volatile metals; PA= Phytoavailable forms

[b] Concentration level that can usually be treated with the technology (H= High; M= Medium; L= Low)

Table 5. Potential pre-treatment and post-treatment for metal remediation technologies

Technology	Pre-treatment	Post-treatment/ residuals managements
In-situ Containment[a] (Capping and Barriers)	Chemical Red/Ox, S/S, vitrification	Groundwater monitoring; potential re-vegetation; controlling of site use
Off-site disposal[a]	Chemical Red/Ox, S/S, volume reduction by physical separation/soil washing	Capping
Stabilization/Solidification (S/S)[a]	Chemical Red/Ox, volume reduction by physical separation/soil washing; barriers (I)	Off-gas treatment; off-site disposal and capping (E); controlling of site use (I)
In situ chemical stabilization	-	Biological stabilization; Phytostabilization; Controlling of site use
Vitrification[a]	Volume reduction by physical separation/soil washing or thermal extraction; barriers (I)	Off-gas treatment; vitrified material can be re-used as construction aggregates, paving blocks, clean fills (E). Capping; controlling of site use (I)
Chemical Red/Ox[a]	Barriers (I)	S/S, disposal and capping
Phytostabilization	In situ chemical stabilization (amendment of silicates, phosphates, lime, mineral fertilizers, etc.) and biological stabilization	Controlling of site use
Biological stabilization	In situ chemical stabilization	Phytoremediation; controlling of site use
SW/Physical separation[a]	Oversize reduction (crushing or declumping)	Water treatment; S/S and disposal of concentrated fraction; disposal (on site or off site) of soil processed; metal recovery by chemical/thermal extraction
SW/Chemical extraction	Volume reduction by physical separation	Washwater treatment; disposal of solid residuals; metal recovery from extraction fluid by aqueous processing (e.g., electrowining and ion exchange)
Biological extraction	-	Metal recovery from extraction fluid by aqueous processing (e.g., electrowining and ion exchange)
Thermal treatments[a]	Volume reduction by soil washing	S/S; off-site disposal; metal recovery and metal recycling
Electrokinetics[a]	Addition of reagents/fluid to mobilize metals	Disposal or treatment of liquid/solid residuals
Phytoextraction	Addition of reagents/fluid to mobilize metals	Further management of biomass is required (disposal, incineration, or metal recovery)
Soil flushing[a]	Barriers; addition of reagents/fluid to mobilize metals	Treatment of flushing fluid; off-site disposal of liquid processes; Groundwater treatment

Notes: SW= Soil Washing; I= In situ application; E= Ex situ application

[a] Information extracted from USEPA (1995a).

Table 6. Development status, implementation frequencies in the US and in Europe, and estimated cost range for remediation technologies in treating of MCS

Technology	Development Status[a]	Implementation frequency[a]	Estimated cost range[b]
In-situ Containment (Capping and Barriers)	Full-scale	Commonly used in Europe and the US	\$175k – 225k/acre
Off-site disposal	Full-scale	Commonly used in Europe and the US	\$300 – 510 /m^3
Solidification/Stabilization	Full-scale	Widely used in the US; not extensively used in Europe	\$128[c] – 248[d] /m^3 (E) \$50 – 330 /m^3 (I)
In situ chemical stabilization[e]	Pilot/field-scale	In development phase in both Europe and the US (Few used)	\$40[e] – 65[e] /m^3
Vitrification	Full-scale	Specific applications (Not often used)	\$375 – 425 /ton (I)
Chemical Red/Ox	Full-scale	Moderately used in the US; no data for Europe	\$190 – 660 /m^3 (E)
Phytostabilization	Full-scale	In the development phase in both Europe and the US (Few used)	\$147[c]– 2,322[d] /m^3
Biological stabilization	Pilot/field-scale in US; R&D in Europe	Limited applications	NA
Soil washing (PS/CE)	Full-scale	Not extensively used in the US; commonly used in Europe	\$70[c] – 187[d] /m^3 (PS) \$358[c] – 1,717[d] /m^3 (CE)
Biological extraction	Bench-scale	Not demonstrated at full-scale	NA
Thermal treatments	Full-scale	Specific applications	\$250[f] – 560[f] /m^3
Electrokinetics	Full-scale	Not often used in the US; moderately used in Europe	\$50 – 117 /m^3
Phytoextraction	Full-scale	In development phase; more used in the US rather than in Europe	\$147[c]– 2,322[d] /m^3
Soil flushing	Full-scale (water flushing); Limited research (reagent flushing)	Limited applications in the US; no data for Europe	\$33 – 327 /m^3

Notes: PS= Physical Separation; CE= Chemical Extraction; I= In situ; E= Ex situ

[a] FRTR (2007a) and CLARINET (2002b).

[b] Data (in US \$) extracted from FRTR (2007a) except for in situ chemical stabilization and thermal treatments.

[c] For a large site and easy remedial action.

[d] For a small site and difficult remedial action.

[e] Martin and Ruby (2004); [f] USEPA (1997b).

Figures

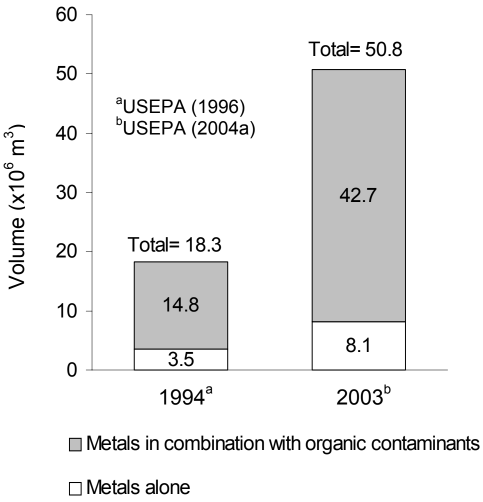
Fig. 1. Estimated quantities of materials (soils, sludges or sediments) contaminated by metals in 1994 and in 2003 for approximately 1,000 National Priority List (NPL) sites in the US

Fig. 2. Schematic diagram of existing remediation technologies for metal-contaminated soil

Fig. 3. Conventional and alternative treatments for metal-contaminated soils in the US: Percentage of projects by technology type for the period 1982-2006

Fig. 4. Frequencies of metals treated in 128 alternative technologies projects

Fig. 5. Alternative treatment technologies for metal-contaminated soils in the US: Number of projects by technology type for the period 1982-2006



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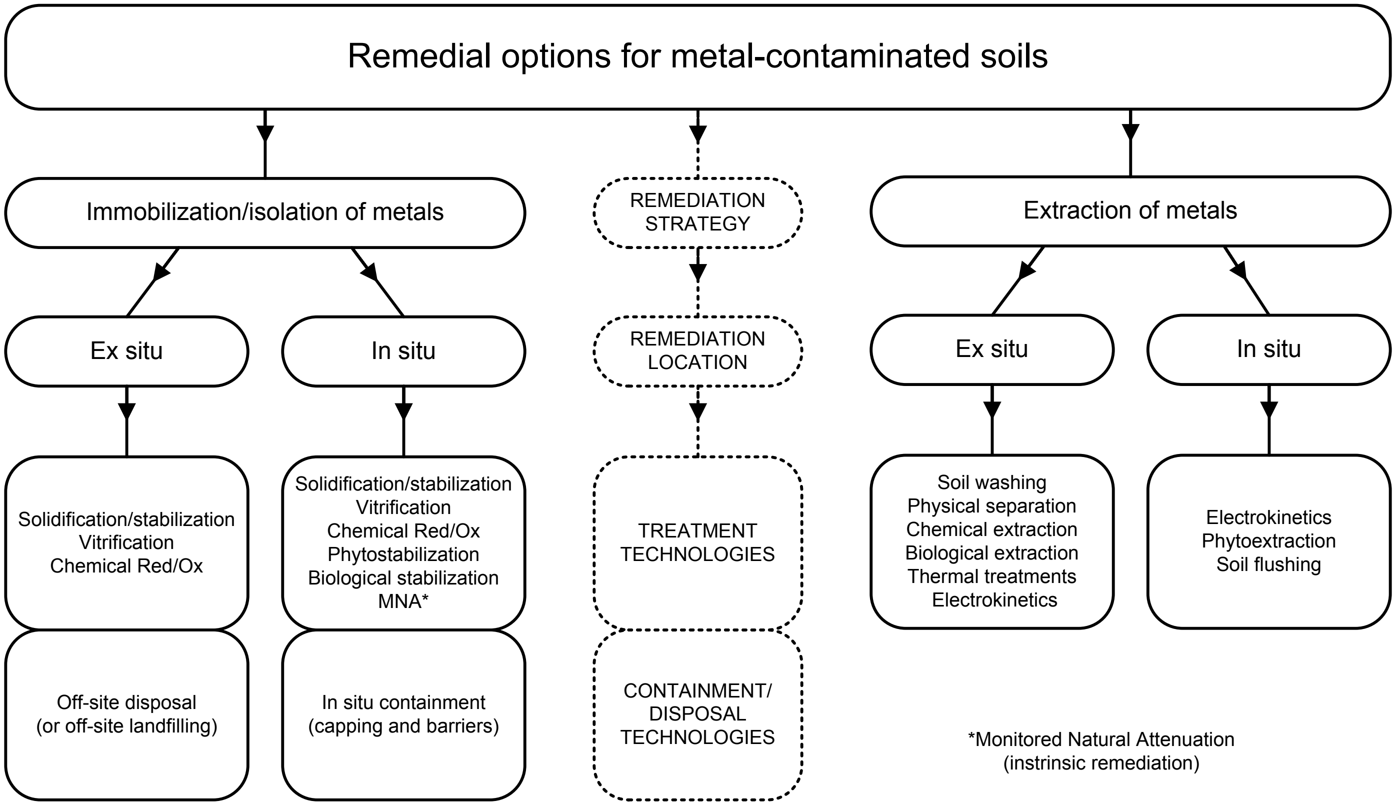

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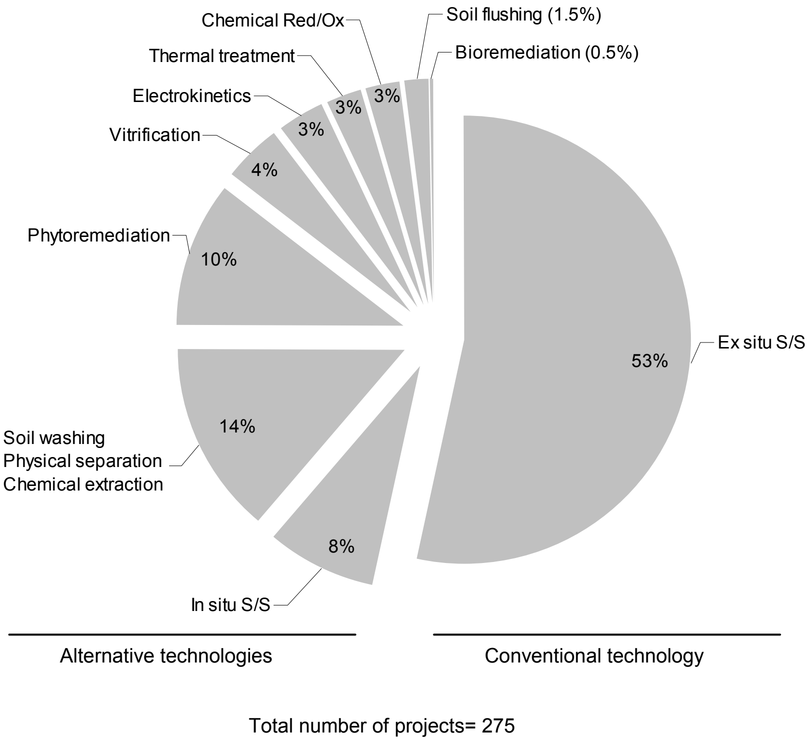

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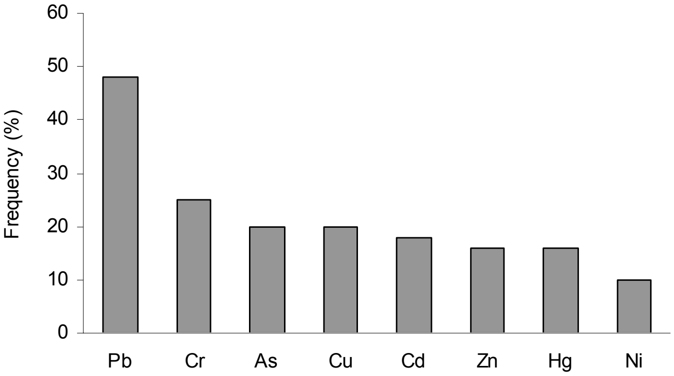

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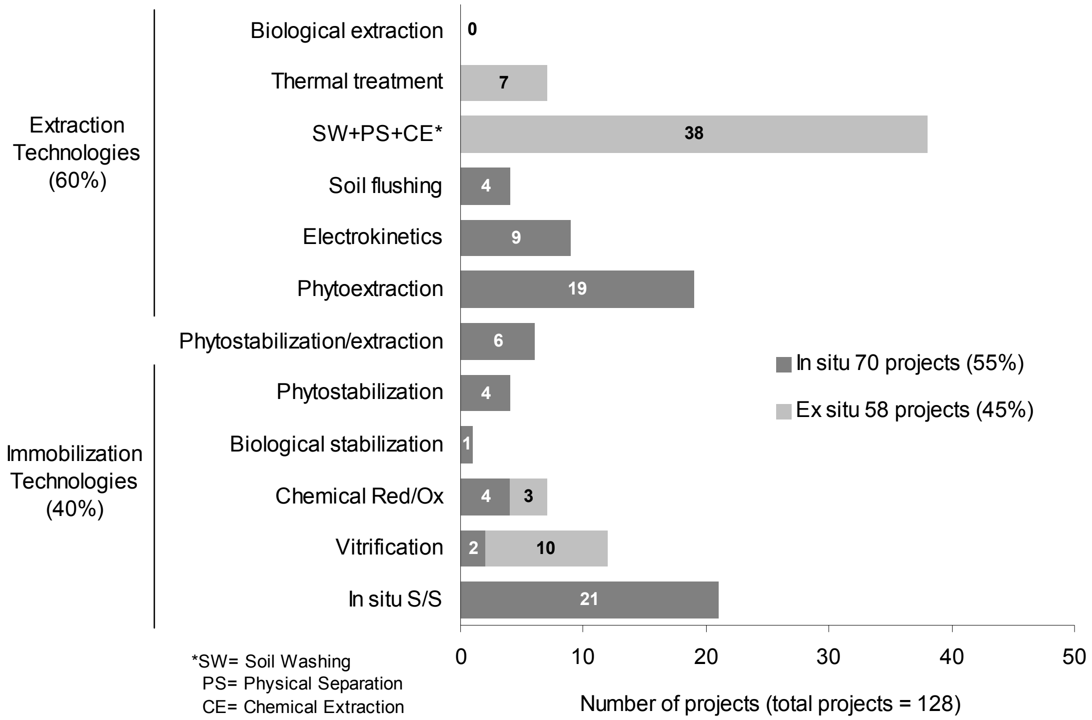

Fig. 5. Alternative treatment technologies for metal-contaminated soils in the US: Number of projects by technology type for the period 1982-2006

Appendix . Summary of 128 case studies involving alternative technologies for the treatment of metal-contaminated soils

	Site/Name demonstration	Technology	Media treated	Main metals treated	Date[a]	Reference
1	Pilot/Field scale Phytoremediation at Green Island and Panchena Point in British Columbia, Canada	Phytoextraction	Soils	Cd, Cu, Pb, Hg, Zn	OP	USEPA/CLU-IN 2007
2	Pilot/Field scale Phytoremediation at a firing range, Chilliwack, BC, Canada	Phytoextraction	Soils	Cu, Pb	2001	USEPA/CLU-IN 2007; USEPA 2005
3	Pilot/Field scale Phytoremediation at an arsenic-contaminated residential site in Austin, TX	Phytoextraction	Soils	As	2003	USEPA/CLU-IN 2007; USEPA 2005
4	Pilot/Field scale Phytoremediation at an unknown lead-contaminated site in Dorchester, MA	Phytoextraction	Soils	Pb	1998	USEPA/CLU-IN 2007; USEPA 2005
5	Pilot/Field scale Phytoremediation at an unknown lead-contaminated site in Bayonne, NJ	Phytoextraction	Soils	Pb	NA	USEPA/CLU-IN 2007; USEPA 2005
6	Pilot/Field scale Phytoremediation at Argonne National Laboratory West in Idaho Falls, ID	Phytoextraction	Soils	Cr, Hg	2002	USEPA/CLU-IN 2007; USEPA 2005
7	Pilot/Field scale Superfund Remedial at U.S. DOE Idaho National Engineering And Environmental Laboratory (operation unit 21), Idaho Falls, ID	Phytoextraction	Soils	Hg, Zn, Cr	OP	USEPA/ASR 2007
8	Pilot/Field scale Phytoremediation at Spring Valley, DC	Phytoextraction	Soils	As	OP	USEPA 2005
9	Pilot/Field scale Phytoremediation at Savannah River Site in Aiken, SC- Project 2	Phytoextraction	Soils	Cd	1992	USEPA/CLU-IN 2007; USEPA 2005
10	Pilot/Field scale Phytoremediation at the Former Army Ammunition Site in Washington, DC	Phytoextraction	Soils	As	OP	USEPA/CLU-IN 2007
11	Full-scale Phytoremediation at the former Orchard Site, Picatinny Arsenal, NJ	Phytoextraction	Soils	As	OP	USEPA/CLU-IN 2007; USEPA 2005
12	Full-scale Phytoremediation at the Magic Marker site in Trenton, NJ	Phytoextraction	Soils	Pb	1998	USEPA/CLU-IN 2007; USEPA 2005
13	Full-scale Phytoremediation at the Small Arms Firing Range 24, Fort Dix, NJ	Phytoextraction	Soils	Pb	2002	USEPA/CLU-IN 2007; USEPA 2005
14	Pilot/Field scale Phytoremediation at the Twin Cities Ammunition Plant in Minnesota/St-Paul, MN	Phytoextraction	Soils	As, Cr, Pb	1998	USEPA/CLU-IN 2007; USEPA 2005
15	Pilot/Field scale Phytoremediation at Copper-, chromium- and arsenic-contaminated sites, Quincy and Archer, FL	Phytoextraction	Soils	As, Cr, Cu	OP	USEPA/CLU-IN 2007
16	Demonstration and Validation of the Range Safe Systems on Native American Lands, Small Arms Firing Range, Adak Naval Air Station, Adak, AK	Phytoextraction	Soils	Pb	NA	USEPA 2000a
17	Phytoremediation Project: Technology to Remove Heavy Metal from Landfill, Augusta-Richmond County Landfill, Augusta, GA	Phytoextraction	Soils	HM	NA	USEPA 2000a
18	Full-scale Phytoremediation at Metal Plating Facility, OH	Phytoextraction	Soils	Pb	OP	USEPA 2005
19	Pilot/Field scale Phytoremediation at East Palo Alto, CA	Phytoextraction	Soils	Pb	OP	USEPA 2005
20	Pilot/Field scale Phytoremediation at an unknown arsenic- and lead-contaminated site in Gary, IN	Phytostabilization and Phytoextraction	Soils	As, Pb	2002	USEPA/CLU-IN 2007; USEPA 2005

Appendix A.(Continued)

21	Pilot/Field scale Phytoremediation at 317/319 Area, Argonne National Laboratory, Lemont, IL	Phytostabilization and Phytoextraction	Soils	As, Pb, Zn	OP	USEPA/CLU-IN 2007; USEPA 2005
22	Pilot/Field scale Phytoremediation at Open Burn and Open Detonating Area, Ensign-Bickford Company in Simsbury, CT	Phytostabilization and Phytoextraction	Soils	Pb	1998	USEPA/CLU-IN 2007; USEPA 2005
23	Full-scale Phytoremediation at Tibbetts Road in Barrington, NH	Phytostabilization and Phytoextraction	Soils	As	OP	USEPA/CLU-IN 2007; USEPA 2005
24	Pilot/Field scale Phytoremediation at Whitewood Creek at the Homestakes Gold Mines in Whitewood Creek, SD	Phytostabilization and Phytoextraction	Soils	As, Cd, Cu	1998	USEPA/CLU-IN 2007; USEPA 2005
25	Pilot/Field scale Phytoremediation at an unknown metal-contaminated site in Galena, KS	Phytostabilization and Phytoextraction	Soils	Cd, Pb, Zn	2000	USEPA/CLU-IN 2007; USEPA 2005
26	Pilot/Field scale Phytostabilization at an unknown metal-contaminated site in Dearing, KS	Phytostabilization	Soils	Cd, Pb, Zn	1998	USEPA/CLU-IN 2007; USEPA 2005
27	Full-scale Phytoremediation at an unknown metal-, nitrate- and sulfate-contaminated site in Anderson, SC	Phytostabilization	Soils	Cd, Pb	OP	USEPA/CLU-IN 2007; USEPA 2005
28	Pilot/Field scale Phytoremediation at an unknown metal-contaminated site in Port Colborne, Ontario, Canada	Phytostabilization	Soils	As, Ni, Cu	2003	USEPA/CLU-IN 2007; USEPA 2005
29	Full-scale Phytoremediation at the Anaconda Smelter Site in Anaconda, MT	Phytostabilization	Soils	As, Cd, Cu	OP	USEPA/CLU-IN 2007; USEPA 2005
30	SITE demonstration of the Bergmann USA transportable unit (in coordination with the Toronto Harbour Commissioners) for volumetric remedial operations at Toronto Harbour, ON, Canada	Soil Washing (Physical separation)	Sediments	Cu, Pb, Zn	1992	USEPA 1995b
31	SITE demonstration performed by Alternative Remediation Technologies (ART) at King of Prussia Superfund site, NJ	Soil Washing (Physical separation)	Soils and sludges	Cr, Cu, Ni	1993	USEPA 1995c
32	SITE Demonstration of BESCORP (Brice Environmental Service Corp) volume reduction plant system at the Alaskan Battery Enterprises site in Fairbanks, AK	Soil Washing (Physical separation)	Soils	Pb	1993	USEPA 1995d
33	Demonstration of physical separation to remove Hg from soils, conducted by MRSDI for Energy and Environmental Research Center (EERC)	Soil Washing (Physical separation)	Soils	Hg	1994	USEPA 1995a
34	Full-scale demonstration performed by Cannonie Environmental at Gould Battery site, Portland, OR (reported in 1995)	Soil Washing (Physical separation)	Soils	Pb	1995	USEPA 1995a
35	Full-scale application performed by ART and CINTEC for remediation of soils from Montreal, Qc, Canada	Soil Washing (Physical separation)	Soils	Cu, Pb, Zn	1996	Mann 1999; ART 2007
36	Field demonstration of Biotrol soil treatment system at Cape Fear Wood Preserving Site, Fayetteville, NC	Soil Washing (Physical separation)	Soils	As, Cr, Cu	1992	USEPA 1992
37	Field demonstration of physical separation techniques for remediation of soils from small arms ranges, conducted by US Bureau of Mines (site name is not provided)	Soil Washing (Physical separation)	Soils	Pb	1993	USEPA 1995a
38	Field-based Pilot scale remediation (DESRT program) of Tallon's physical separation technology at Dickson site, Bombardier Inc., Montreal, QC, Canada	Soil Washing (Physical separation)	Soils	As, Cu, Pb	1993	DESRT 1995
39	SITE demonstration of the Bergmann USA transportable unit at the USACE, confined disposal facility in the Saginaw Bay, MI	Soil Washing (Physical separation)	Soils and sediments	Cu, Pb, Zn	1993	USEPA 1995b
40	Full-scale application of BESCORP's Particle Separation System, performed on Pb-contaminated soils from small arms firing range sites at range 24, Fort Dix, NJ	Soil Washing (Physical separation)	Soils	Pb	NA	BESCORP 2005
41	Full-scale application of BESCORPP's Particle Separation System, performed on soils from small arms firing range sites at Massachusetts Military Reservation (MMR), Cape Cod, MA	Soil Washing (Physical separation)	Soils	Pb	NA	BESCORP 2005

Appendix A.(Continued)

42	Pilot demonstration project of BESCORP's Particle Separation System, performed on three ranges at the small arms range complex (Marine Corps Air Ground Combat Center) at 29 Palms, CA	Soil Washing (Physical separation)	Soils	Pb	NA	BESCORP 2005
43	Full-scale demonstration performed by ART at Former Skeet Shooting Range Site, Lordship Point in Stratford, CT	Soil Washing (Physical separation)	Soils and sediments	Pb	NA	ART 2007
44	Pilot project of Particle Separation System performed by BESCORP on firing range soils at Fort Ord, CA	Soil Washing (Physical separation)	Soils	Pb	NA	BESCORP 2005
45	Remediation (by physical separation) of Mercury-Contaminated Soils from a Natural Gas Metering Site, NM (Development and Testing of Technologies by Energy & Env. Research Center (EERC))	Soil Washing (Physical separation)	Sandy Soils	Hg	1993	USEPA 2000a
46	Iron Mountain Mine Superfund Site, Redding, CA	Soil Washing (Physical separation)	Soils	HM	1992	USEPA 2000a
47	Commercial Mercury Remediation Demonstrations (Physical Separation) at Mercury Recycling Facility, Bedford, OH (by Environmental Technologies International (ETI) Shillington, PA)	Soil Washing (Physical separation)	Soils	Hg	1994	USEPA 2000a
48	Remediation of soils from small arms firing range, Marine Corps Base Quantico, VA (by U.S. Bureau of Mines)	Soil Washing (Physical separation)	Soils	Pb	1994	USEPA 2000a
49	Demonstration and Validation of the Range Safe System on Native American Lands at Small Arms Firing Range, Adak Naval Air Station, Adak, AK (by ARDEC Industrial Ecology Center Picatinny Arsenal, NJ)	Soil washing	Soils	HM	NA	USEPA 2000a
50	Field-scale remediation of soil washing coupled with chemical treatment (chromium reduction in aqueous waste from soil washing) at Palmetto Wood Preserving, SC (supervised by USEPA and completed in 1989)	Soil washing	Soils	As, Cr	1989	FRTR 2007b
51	Field-scale remediation demonstration at Sacramento Army Depot, CA (supervised by US. Army and completed in 1992)	Soil washing	Oxidation lagoon soils	Cd, Ni, Pb, Cu	1992	FRTR 2007b
52	Soil Washing Treatment for Heavy Metal Contaminated Soils (Metal scrap yard) (reported by Washburn & Gillis Associates, Ltd.)	Soil washing	Soils	HM	1992	USEPA 2000a
53	Pilot-scale demonstration of mobile soil washing unit (volume reduction unit) at Escambia wood treating company, Pensacola, FL (performed by Risk Reduction Engineering Laboratory and supervised by USEPA in 1992)	Soil Washing	Soils	HM	1992	FRTR 2007b; USEPA 1995a
54	SITE demonstration of Toronto Harbour Commissioners (THC) Soil Recycle Treatment Train, Toronto, ON, Canada (completed in 1992)	Soil washing (Physical separation and Chemical leaching)	Soils	Cu, Pb, Zn	1992	USEPA 1993
55	SITE Demonstration of BESCORP system coupled with COGNIS TERRAMET leaching process at Twin Cities Army Ammunition Plant Site F in New Brighton, MI	Soil washing (Physical separation and Chemical leaching)	Soils	Cd, Cr, Cu, Pb, Hg, Ni	1994	USEPA 1997c
56	Pilot demonstration of soil washing process developed by Alex-Sol Inc and INRS (environmental research center, university of Quebec) for remediation of soils and sediments from Quebec city, Montreal, and Trois-rivieres, QC, Canada	Soil washing (physical separation, chemical leaching, bioleaching)	Soils and sediments	Cu, Cd, Pb, Zn	1995	Alex Sol and INRS 1999
57	Full-scale demonstration of BESCORP soil washing technology at Joint Small-Arms Range 5, Fort Polk, Leesville, LO	Soil washing (physical separation, chemical leaching)	Soils	Pb, Cu, Zn	1996	ESTCP 1997
58	Full-scale demonstration of ContraCon Northwest soil washing technology at Joint Small-Arms Range 5, Fort Polk, Leesville, LO	Soil washing (physical separation, chemical leaching	Soils	Pb, Cu, Zn	1996	ESTCP 1997
59	USDOE project demonstration of enhance soil washing with soil selective extraction/dissolution process, performed by Clemson Technical Center, SC	Soil washing (physical separation, chemical extraction)	Soil and debris	HM	1996	FRTR 2007b; USEPA 1995a
60	Field-demonstration (Pilot-scale) of soil washing system of Tallon Metal Technologies, Inc. at, Longue Pointe site in Montreal, QC, Canada (reported in 1998)	Soil washing (physical separation, chemical extraction)	Soils	Pb	1998	NATO/CCMS 1998

Appendix A.(Continued)

61	Field-demonstration (Pilot-scale) of soil washing system of Tallon Metal Technologies, Inc. at Ataratiri site in Toronto, ON, Canada (reported in 1998)	Soil washing (physical separation, chemical extraction)	Soils	Cd, Cu, Pb, Zn	1998	NATO/CCMS 1998
62	Full scale demonstration of Soil Washing System at Hunter's Point Shipyard, San Fransisco, CA	Soil washing (physical separation, chemical leaching)	Soils	Cu, Cr, Pb, Zn	2000	USEPA 2000a
63	Full-scale demonstration of ART's process (under contract to Sevenson Environmental Services) at Vineland Chemical (Pesticide manufacturing) Superfund site (project in progress)	Soil washing (physical separation, chemical extraction)	Soils	As	OP	ART 2007
64	Demonstration of "Soil Washing System Employs Aggressive Conditions" at Hunter's Point Shipyard, San Francisco, CA	Soil washing (Physical separation/chemical leaching)	Soils	Cu,Cr, Pb, Zn	NA	USEPA 2000a
65	Remediation of soils contaminated with Metal Finishing and refinery products, performed by Toronto Harbor Commissioners (Soil Recycling Treatment Train), Toronto, ON, Canada	Soil washing (Physical separation/chemical leaching)	Soils	Pb	1992	USEPA 2000a
66	Remediation (chemical extraction) of Mercury-Contaminated Soils from a Natural Gas Metering Site, NM (Development and Testing of Technologies by Energy & Env. Research Center (EERC))	Soil washing (Chemical extraction)	Sandy Soils	Hg	1993	USEPA 2000a
67	Remediation (chemical extraction) of Mercury-Contaminated Soils from Clay Soil from a Mercury Recycling Facility in Bedford, OH (Development and Testing of Technologies by Energy & Env. Research Center (EERC))	Soil washing (Chemical extraction)	Clay soils	Hg	1993	USEPA 2000a
68	Graphite Furnace demonstration, Idaho National Engineering and Environmental Laboratory, ID	Vitrification (ex situ)	Debris/Slag with RMW	HM	1997	FRTR 2006
69	STAR Center, ID (Plasma Process)	Vitrification (ex situ)	Debris/Slag with RMW	HM	1993	FRTR 2006
70	Hazen Research Center and Minergy GlassPack Test Center, WI	Vitrification (ex situ)	Sediment	HM	2001	FRTR 2006
71	SITE demonstration: Babcock & Wilcox Cyclone Furnace, Alliance Research Center, OH (Combustion based heating)	Vitrification (ex situ)	Soils	Cr, Cd, Pb	1992	USEPA 2000a
72	SITE demonstration: Cold Top system (Joule heating), Geotech's pilot plant in Niagara Falls, NY (Joule heated melter)	Vitrification (ex situ)	Soils	Cr		USEPA 2000a
73	Pilot-Scale Activities with Mercury Contaminated Sludges Integrated Defense Waste Processing Facility Melter, Savannah River, SC	Vitrification (ex situ)	Sludges with RMW	Hg	NA	USEPA 2000a
74	Transportable Vitrification System Pilot Demonstration with Surrogate Oak Ridge WETF Sludge, Clemson University ESED Vitrification Facility	Vitrification (ex situ)	Sludges, soils with RMW	Cd, Cr, Pb, Ni	1996	USEPA 2000a
75	Field-scale demonstration (USDOE) of transportable JHM system (Joule heating), Oak Ridge National Laboratory (ORNL) East Tennessee Technology Park (ETTP)	Vitrification (ex situ)	Soils with RMW	HM	1997	USEPA 2000a
76	Field-Demonstration of Retech, Inc. Plasma Centrifugal Furnace (Plasma Arc Vitrification) (DOE test Facility)	Vitrification (ex situ)	Soils	HM	1991	USEPA 2000a
77	U.S. Department of Energy, Hanford Site, WA, Oak Ridge (TN) and Others	Vitrification (in situ)	Sludges, soils with RMW	HM	1997	FRTR 2006
78	Field-Demonstration of In Situ Vitrification - Geosafe Corporation at Chemical Process site contaminated with PCB, dioxins and Metals	Vitrification (in situ)	Soils	HM	1994	USEPA 2000a
79	SITE demonstration at Parsons Chemical Superfund Site in Grand Ledge, MI (Traditional ISV; GeoMelt ISV)	Vitrification (in situ)	Soils	Hg, Pb	NA	USEPA 1997a; USEPA 2000a
80	Electrokinetics demonstration at Alameda Point, CA	Electrokinetics (in situ)	Soil	HM	1997	FRTR 2006
81	Electrokinetics demonstration Beach Haven Substation, Pensacola, FL	Electrokinetics (in situ)	Soil	As	1998	FRTR 2006

Appendix A.(Continued)

82	Electrokinetics demonstration at Camp Stanley Storage Activity Area, San Antonio, TX (by Lynntech Inc.)	Electrokinetics (in situ)	Soils	Cr, Cd	1996	ITRC 1998; USEPA 2000a
83	Electrokinetics demonstration at Radford Army Ammunition Plant, VA (by Lynntech Inc.)	Electrokinetics (in situ)	Soils	Pb, Zn, Cu, Cd, Cr	1996	ITRC 1998; USEPA 2000a
84	Field Demonstration Old TNX Basin, Savannah River Site, Aiken, SC (Westinghouse Savannah River Company)	Electrokinetics (in situ)	Soils	Hg (nitrate), Cr, Pb	1995	USEPA 2000a
85	In situ Electrokinetic Extraction System Demonstration (SITE program) at the Unlined Chromic Acid Pit, Albuquerque, NM (by Sandia National Laboratory, NM)	Electrokinetics (in situ)	Soils	Cr (VI)	1996	USEPA 2000a
86	Evaluation of In Situ Electrokinetic Remediation for Metal Contaminated Soils at Naval Air Weapons Station, Point Mugu, CA (by USAEC, US Army Waterways Experiment Station (USAWES) and Lynntech Inc.)	Electrokinetics (in situ)	Soils	Cr, Cd, Ni, Cu	1998	ITRC 1998; USEPA 2000a
87	Demonstration of In Situ Electrokinetic Remediation for Metal Contaminated Soils at Naval Facility Pearl Harbor, HI (by Geokinetics)	Electrokinetics (in situ)	Soils	HM	1999	USEPA 2000a
88	Demonstration of In Situ Electrokinetic Remediation (SITE program) for Metal Contaminated Soils from small arms firing range at Fort Polk, LA (by USAWES and Electrokinetics, Inc., Baton Rouge, LA)	Electrokinetics (in situ)	Soils	Pb	NA	ITRC 1997b; USEPA 2000a
89	SITE demonstration at National Smelting and Refining Company, Atlanta, GA, 1991 (Flame reactor technology by Horsehead Resource Development (HRD) Company, Inc., PA)	Thermal treatment (HTMR)	Soils	As, Cd, Pb, Zn	1991	USEPA 2000a
90	Thermal desorption (mobile unit) at Natural Gas Metering Sites in NM (by Mercury Recovery Services (MRS) system, Pittsburgh Mineral & Environmental Technology, Inc. (PMET), PA)	Thermal treatment (TD)	Soils	Hg	1994	PMET 2006; USEPA 2000a
91	Thermal desorption (mobile unit) at Mercury Recycling Facility in Bedford, OH (by Mercury Recovery Services (MRS) system, Pittsburgh Mineral & Environmental Technology, Inc. (PMET), PA)	Thermal treatment (TD)	Clay Soil	Hg	1993	PMET 2006; USEPA 2000a
92	"SepraDyne-Raduce" high vacuum and high temperature systems, Brookhaven National Laboratory, NY	Thermal treatment (TD)	Mixed wastes	Hg	NA	USDOE 2002
93	X-Trax system by Chemical Waste Management Inc. and currently marketed by RUST/OHM remediation services, Inc., OH	Thermal treatment (TD)	Soils, sediments	Hg	1995	Mulligan et al. 2001
94	Fort Ord, CA	Thermal treatment (TD)	Debris/Slag	HM	2002	FRTR 2006
95	Pilot-scale Thermal Treatment of Lower East Fork Poplar Creek Floodplain Soils, ORNL, Oak Ridge, TN	Thermal treatment (TD)	Soils	Hg	NA	USEPA 2000a
96	In situ Chemical reduction of Cr (VI) at Valley Wood Preserving, Inc. Superfund Site, Turlock, CA	Chemical Red/Ox (in situ)	Soils	As, Cr	2004	USEPA/ASR 2007
97	In situ Chemical reduction of Cr (VI) Morses Pond Culvert, MA	Chemical Red/Ox (in situ)	Soil	Cr (VI)	2001	FRTR 2006
98	In situ Chemical reduction of Cr (VI) at White Sands Missile Range, SWMU 143, NM	Chemical Red/Ox (in situ)	Soil	Cr (VI)	1998	FRTR 2006
99	In situ Chemical reduction of Cr (VI) at Frontier Hard Chrome Superfund Site, WA	Chemical Red/Ox (in situ)	Soil; GW	Cr (VI)	2003	USEPA/ASR 2007; FRTR 2006
100	JFD Electronics/Channel Master (Electroplating Solvent Recovery Facility) Superfund Site, Oxford, NC (2000)	Chemical Red/Ox (ex situ)	Soils, Sludges	Cr (VI), Ni	2000	USEPA/ASR 2007
101	Palmetto Wood Preserving Superfund Site, Dixiana, SC	Chemical Red/Ox (ex situ)	Soils	Cr (VI)	1989	USEPA/ASR 2007
102	Remediation of Cr (VI)-contaminated soils from Drum Storage Area at Bakersfield , CA (by Versar)	Chemical Red/Ox (ex situ)	Soils	Cr (VI)	1991	USEPA 2000a

Appendix A.(Continued)

103	Lipari Landfill Superfund Site (Industrial Landfills Municipal Landfills), Pitman, NJ	soil flushing	Soils, wastes	Cr, Hg, Ni, Pb	OP	USEPA/ASR 2007
104	Soil flushing in conjunction with pump-and-treat at United Chrome Products Superfund Site in Corvallis, OR	soil flushing	Soils	Cr (VI)	OP	USEPA/ASR 2007
105	Cross Brothers Pail Recycling Superfund Site (Drum Storage/Disposal Manufacturing Process), Pembroke Township, IL	soil flushing	Soils	Pb	1996	USEPA/ASR 2007
106	Ormet Corporation Superfund Site (Manufacturing Process), Hannibal, OH	soil flushing	Soils	As	OP	USEPA/ASR 2007
107	62nd Street Dump (Battery Recycling/Disposal) Superfund Site, Tampa, FL	in situ S/S with Portland cement.	Soils	Cd, Cr, Pb	1995	USEPA/ASR 2007
108	American Cyanamid Co.(Chemical Manufacturing) Superfund Site, Bound Brook, NJ	in situ S/S	Soils, sludges	Cr, Cu, Pb, Ni, Zn	2005	USEPA/ASR 2007
109	Caldwell Trucking (Surface Impoundment/Lagoon) Superfund Site, Fairfield, NJ	in situ S/S with cement	Soils	Cd, Pb	1997	USEPA/ASR 2007
110	Chemical Control Superfund Site, Elizabeth, NJ	in situ S/S	Soils	As	1994	USEPA/ASR 2007
111	Fernald Environmental Management Project, Formerly The Feed Materials Production Center (Munitions Manufacturing) Superfund Site, Fernald, OH	in situ S/S with cement	Soils	As, Pb	1999	USEPA/ASR 2007
112	Fourth Street Abandoned Refinery Superfund Site, Oklahoma City, OK	in situ S/S	Soils	Pb	1996	USEPA/ASR 2007
113	French Limited Superfund Site, Crosby, TX	in situ S/S	Soils	As	1994	USEPA/ASR 2007
114	Geiger (C&M Oil) Superfund Site, Rantowles, SC	in situ S/S with cement and sulfur	Soils	Cr, Pb	1994	USEPA/ASR 2007
115	Hercules 009 Landfill Superfund Site, Brunswick, GA	in situ S/S with cement	Soils	As	1999	USEPA/ASR 2007
116	Industrial Waste Control Superfund Site, Fort Smith, AR	in situ S/S	Soils	Cr, Pb, Ni	1990	USEPA/ASR 2007
117	Jacksonville Naval Air Station Superfund Site, Jacksonville, FL	in situ S/S	Soils, sludges	Cd, Cr, Pb, Ni,	1997	USEPA/ASR 2007
118	Oronogo - Duenweg Mining Bell Superfund Site, Jasper County, MO	in situ S/S with phosphates	Soils	Pb	2002	USEPA/ASR 2007
119	Pesses Chemical Co., Superfund Site, Fort Worth, TX	in situ S/S with Fly ashes	Soils	Cd, Ni	1992	USEPA/ASR 2007
120	Rhone-Poulenc/Zoecon, Superfund Site, East Palo Alto, CA	in situ S/S with Proprietary additives	Soils	As, Cd, Pb	2000	USEPA/ASR 2007
121	Wyckoff/Eagle Harbor Superfund Site, Bainbridge Island, WA	in situ S/S encapsulation	Soils	As, Cu, Pb, Hg, Zn	1997	USEPA/ASR 2007
122	Sulfur Bank Mercury Mine, Lake County Superfund Site, CA	in situ S/S (Pilot-scale)	Soils	Hg	OP	USEPA/ASR 2007
123	Field demonstration (SITE EPA program) at Crooksville/Roseville Pottery Area of Concern (CRPAC), OH (Injection Soil Amendment)	in situ S/S (stabilization)	Soils	HM	1998	USEPA 2000a; FRTR 2006

Appendix A.(Continued)

124	Fiel demonstration (SITE program) at Mike Horse Mine (Mining Wastes Metals), MT (grouting technique by STG technologies and USEPA-NRMRL)	in situ S/S	Soils	HM	1996	USEPA 2000a
125	Field demonstration (DESRT program, Canada) by Bovar Environnemental Services at Pacific Place Site (Railroad Equipment) in Vancouver, BC, Canada	in situ S/S	Soils with cyanide	HM	1992	USEPA 2000a
126	Field demonstration (DESRT program, Canada) by Ogden/Chemifix Technologies, Inc. at Pacific Place Site (Railroad Equipment) in Vancouver, BC, Canada	in situ S/S	Soils with cyanide	HM	1992	USEPA 2000a
127	Field demonstration by WT/Geo-con, Inc., Monroeville, PA	in situ S/S (stabilization)	Soils	HM	1988	USEPA 2000a
128	Field demonstration of In situ Biosolids and Lime addition at California Gulch Superfund Site, OU 11 (Metal Ore Mining and Smelting) in Leadville, CO	Bioremediation in situ / Stabilization	Soils (mining tailings)	Zn, Pb, Cu, Cd	1999	USEPA/CLU-IN 2007; FRTR 2006

Notes: NA= Not Available; OP= Project in Operation; HM= Heavy Metals (when the type of heavy metal treated is not provided); RMW= Radioactive Mixed Wastes; S/S= Solidification/Stabilization; [a]Demonstration date or completion date

Chapitre 3: Soil washing for metal removal: A review of physical/chemical technologies and field applications

Résumé

Le lavage de sol est l'une des rares alternatives à la stabilisation/solidification qui permet d'enlever efficacement les métaux des sols contaminés. Cet article donne une revue exhaustive des différents types de technologies de lavage de sol et des applications effectuées dans le cadre de larges projets de réhabilitation de terrains contaminés par les métaux lourds. Les procédés de séparation physique, les méthodes d'extraction chimique et les techniques combinant la séparation physique et l'extraction chimique sont discutés séparément. De plus, cet article récapitule les principes de base, l'applicabilité, les avantages et les limitations, les méthodes de prédiction et d'amélioration des performances de chaque technologie. La discussion est basée sur une revue de 30 études récentes réalisées à l'échelle laboratoire, ainsi que sur 37 applications de terrain de systèmes de lavage de sol accomplis majoritairement aux États-Unis pendant la période 1990-2007. Finalement, cet article étudie et compare les différentes approches des technologies de lavage de sol aux États-Unis, au Canada et en Europe.

Journal of Hazardous Materials 152 (2008) 1–31
Review

Soil washing for metal removal: A review of physical/chemical technologies and field applications

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Received 14 June 2007; received in revised form 11 October 2007; accepted 11 October 2007
Available online 22 October 2007

Abstract

Soil washing is one of the few permanent treatment alternatives to remove metal contaminants from soils. This paper reviews the various technology types and pilot/full-scale field applications of soil washing applicable to soils highly contaminated with heavy metals. The physical separation technologies, the chemical extraction processes and the integrated processes that combine both physical and chemical methods are discussed separately. This paper reviews basic principles, applicability, advantages and limitations, methods of predicting and improving performance of each physical/chemical technology. The discussion is based on a review of 30 recent laboratory investigations and 37 field applications of soil washing systems which have been undertaken, mostly in the US, for the period 1990-2007. This paper also examines and compares the status of soil washing technology for remediation of soils contaminated with metals in the US, in Canada and in Europe.

Keywords: Heavy metals; Soil washing; Physical separation; Chemical extraction

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1. Introduction

In the United States, heavy metals are prevalent at almost all sites targeted by major remediation programs. For instance, metals are present in 77% of the Superfund sites (National Priorities List), in 72% of the Department of Defense (DOD) sites and in 55% of the Department of Energy (DOE) sites [1]. The USEPA estimates that over 50 million cubic meters of soil at current NPL sites are contaminated with metals [1].

The remediation of metal-contaminated sites has traditionally involved excavation of the contaminated soils, followed by the immobilization of metal contaminants by solidification/stabilization (S/S) technology prior to disposal of the materials treated in a permitted landfill site or on-site [2,3]. The remedial actions based on S/S technology are no longer considered a permanent environmental solution because of: (1) the metals are not removed from contaminated media; (2) the need for future monitoring of heavy metals on site; (3) questionable longevity of the solidified/stabilized materials; (4) the long term management of the solidified/stabilized materials is based on landfilling and requires soil caps to prevent erosion problems. Hence, there is a great need to promote effective soil treatment technologies that attempts to remove the metals from the soils. Soil washing, which uses physical or chemical processes, is one of the few permanent treatment alternatives to separate the metals from soils.

This paper provides a review of the soil washing methods (ex situ techniques) for soil contaminated with arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). Although arsenic is a metalloid, the term “metals” will be used to include all the elements under discussion. The discussion focuses on the remediation of soil matrices highly affected by industrial and military activities (e.g., soil contaminated by tailings/slags, brownfields, battery recycling site, shooting range site). Soil washing processes related to organic contaminants and radioactive metals are not discussed here. Also, the discussion does not include in situ treatment (soil flushing). In this review, soil washing includes the following options: (1) physical separation based on mineral processing technologies; (2) chemical extraction based on leaching or dissolving process; (3) combination of physical separation and chemical extraction.

This paper is organized in five sections: (1) soil washing background; (2) physical separation; (3) chemical extraction; (4) combination of physical separation and chemical extraction; (5) status of soil washing in the US, in Canada and in Europe. The first purpose of this review is to present a technical description of the various technologies: principle, applicability, methods of predicting and improving performance are discussed. Several recent laboratory studies involving physical separation (7 examples) and chemical extractions (24 examples) are summarized. The physical separation technologies, the chemical extraction processes and the integrated processes that combine both physical and chemical methods will be discussed separately. The second purpose of this paper is to provide a review of the field applications of soil washing systems involved in the treatment of the metal contamination. The discussion is based on a collection of 37 case studies of pilot/full-scale remediation projects performed, mostly in the US, for the period 1990-2007. The third purpose of this paper is to review the implementation degree of soil washing technology relevant to the treatment of metal-contaminated soils, in the US, in Canada and in Europe.

2. Soil washing background

Soil washing, as discussed in this paper, refers to ex situ techniques that employ physical and/or chemical procedures to extract metals contaminants from soils. Fig. 1 presents a schematic diagram of typical options used in soil washing processes: (1) physical separation; (2) chemical extraction; (3) combination of both. Physical separation (PS) concentrates metal contaminants into a smaller volume of soil by exploiting differences in certain physical characteristics between the metal-bearing particles and soil particles (size, density, magnetism, hydrophobic surface properties). Chemical extraction (CE) relates to techniques that try to solubilize the metal contaminants from the soil with an extracting aqueous fluid containing chemical reagents such as acids or chelating agents.

Soil washing systems are quite flexible in terms of number, type, and order of processes involved and other names are used for soil washing technologies: “soil separation”, “soil recycling”, or “volume reduction”. The definition and use of the terms “soil washing”, “physical separation” and “chemical extraction” can differ according to the authors. The degree to which chemical agent or physical separation techniques are used may affect the nomenclature to describe the washing process. In the US and in Europe, soil remediation processes based on mineral processing technologies are often referred as the broad term “soil washing” [4-6] although the term “physical separation” appears more accurate [7-9]. The term “soil washing” is also used in the literature for describing processes that involve chemical extraction processes [10-13]. FRTR [4] distinguishes “soil washing” from “chemical extraction”: « soil washing generally uses water or water with wash-improving additives and differs from chemical extraction, which uses an extracting chemical ». Confusion resulting from these misnomers often contributes to the propagation of misconceptions about the soil washing technology.

In the present paper, physical separation is primarily considered as a particle separation process while chemical extraction can be considered as a metal desorption/solubilization process. In general, physical separation is primarily applicable when metal contaminants are under particulate forms (ideally liberated particle), while chemical extraction is primarily suitable for ionic forms adsorbed on soil or non-detrital metals. Specific comments relating to these aspects are provided in the corresponding sections of each technique.

The authors collected information on full-scale and significant pilot/field demonstrations of soil washing projects conducted in the US and Canada for treating metal contaminants. Also, some pilot projects performed in Europe and Korea are gathered. Table 1 recapitulates 37 field application case studies: 16 projects involved PS technologies, 18 projects involved both PS and CE processes, and 3 projects involved CE procedures. About one third of the reported projects have been performed since the year 2000. The metals most frequently treated are: Pb (78% of the projects), Cu (43%), Zn (41%), and As (27%). For each project, Table 1 summarizes the following data: (1) the project description (location, site name, the matrix type treated and completion date); (2) the basic principle and an exhaustive description of the process; (3) the metal concentrations in the initial soil and the cleaned soil; (4) the removal efficiencies of the treated metals; (5) the volume capacity of the process; (6) the treated volume; (7) the quantities of the recovered metals/concentrates, the management of the recovered metals and washing residuals, and volume reduction efficiency. These data are used as support for the overall discussion.

3. Physical separation technologies

The general approach in physical separation is to use technologies generally applied in mining and the mineral processing industry to extract the desired metal-bearing particles from mineral ores. Mineral processing techniques are well established: implementation is relatively simple; operation is often inexpensive; equipments and processes involved are well described in the literature [14,15]. In the context of soil remediation, mineral processing technologies were reviewed particularly to separate metal contaminants from the soil [8,9,16,17]. Table 2 summarizes the main classes of technologies according to the separation principles used. The operation units involved are: mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, electrostatic separation, and attrition scrubbing.

Three aspects about physical separation for remediation of metal-contaminated soils will be separately discussed: (1) the applicability of physical separation technologies according to forms of metal contamination and characteristics of soil matrix; (2) a review of each technology class; (3) integrated processes of physical separation. The discussion focuses first and foremost on gravity concentration and froth flotation technologies because they are the most important separation methods used in a soil remediation context. The arguments are often based on the assessment of the field-scale applications (Table 1) and recent laboratory investigations (Table 3).

3.1 Applicability and limitations of physical separation

Physical separation techniques are primarily applicable to particulate forms of metals: discrete particles or metal-bearing particles. Physical separation is generally not appropriate for treating the sorbed forms of metals although attrition scrubbing can significantly improve metal desorption in chemical leaching process. The knowledge of the degree of liberation of the mineralogical phase containing heavy metals is significant to predict the applicability of physical particle separation methods [16,18]. The liberation degree depends on the mineralogical aspects of metal contaminant particles (shape, morphology and mineralogical association). Liberation degree refers to the release availability of the “metal phase” according to various associations with the “carrying phase” or the soil particles. The term “metal phase” refers to the mineral form under which the metal is present. The term “carrying phase” refers to another mineral phase (Fe-oxides, carbonates, silicates, etc.) with which the “metal phase” can be associated. Fig. 2

summarizes some examples of various potential states of the metal phase (particulate forms): (a) included in the volume, (b) associated, (c) weakly bounded on surface, (d) liberated or free. Liberation degree and applicability of particle separation, by gravity concentration and froth flotation, are briefly discussed for each state of metal phase (Fig. 2). The mineralogical aspects and solid phase speciation of metal-bearing particles can be investigated by microscopy and spectroscopy technologies such as scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDX).

The efficiency of physical separation depends on several soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, humic content, heterogeneity of soil matrix, difference in density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface [8,9]. The treatment is difficult or unfeasible for the following cases: (1) the metal contaminants are strongly bound on soil particles; (2) the difference in density or surface properties between metal-bearing particles and soil matrix are not significant; (3) high variability of chemical forms of metals; (4) the metals are present in all particle size fractions of contaminated soil; (5) the soil contains silt/clay content in excess of 30 to 50%; (6) the soil contains high humic content; (7) the soil contains organic compounds with high viscosity.

Particle size of feed material is one of the most significant parameters that affect applicability of physical separation technologies because the contaminated soils usually contain a wide range of particle sizes, and the technology performance is often restricted to a specific particle size range (Fig. 3). Usually, most of the hydroclassifiers and gravity concentrators have a good applicability for the sand fraction (63–2000 μm). The standard gravity concentrators (jig, shaking table, and spiral) are usually not suitable for fine particles (<63 μm). Depending upon the technology, there is a point at which the percentage of fine particles will be a limiting factor.

Physical separation is mainly appropriate and more cost effective for soils with sand content in excess of 50 to 70% [19,20]. However, a process combining attrition scrubbing (which can be enhanced by chemical additives) and wet screening or hydrocyclones may be used for the remediation of fine-grained matrices such as sediments [10]. Likewise, froth flotation may be effective for treating relatively fine particles (20–63 μm).

The selection of the physical separation technologies strongly depends on the soil and site types to be treated. These techniques are primarily applicable to "anthropogenic" soils located in urban or industrial areas (e.g., brownfields, mine spoils/tailings/slags from mining/smelting sites, shooting range site) (Table 1). These soils are greatly affected by human activity (industrial artifacts, disposal, landfills, etc.) and are typically composed of mixture of toxic wastes and natural/anthropogenic landfills. On the other hand, physical separation techniques are not appropriate for treating the "natural" soils or agricultural soils affected by a diffuse contamination because: (1) the metals are mostly present in sorbed forms; (2) the metal concentration levels are relatively low; (3) these soils typically have a high content of silt/clay and organic matter. Since metals present in soils are mostly in sorbed forms as opposed to discrete particles, physical separation is often associated with chemical procedures to enhance metal removal.

3.2 Hydrodynamic classification

Hydrodynamic classification, also called "hydroclassification" , involves separation of particles based upon the velocity with which particles fall through water flow (involving sedimentation, elutriation, and fluidization) or separation by centrifugal force into water flow (hydrocyclone) [8,16]. The main goal is separation by size particle. Hydrodynamic classification technologies principally include three technology classes: (1) technologies based on centrifugation such as hydrocyclones; (2) technologies based on elutriation such as elutriation column and fluidized-bed classifier; (3) mechanical classifiers such as screw classifier. Hydrocyclones were widely implemented in soil washing process to separate the fine soil from larger sand particles. The centrifugal force is more powerful than the force due to gravity; thereby, the operating time to achieve separation is significantly reduced [16]. Hydrocyclones have low capital and operational costs compared to other classification equipment [9]. Screw classifiers and hydroclassifiers based on elutriation can also be implemented in a soil remediation context [16,21,22]. Moreover, new more efficient technologies of fluidized-bed separator such as the CrossFlow classifier and the HydroFloat separator have recently been developed for the mineral processing industry [23].

3.3 Gravity concentration

Theses techniques exploit the difference in gravity of particles in slurry to separate the metal-bearing particles from soil matrix. Settling is due to density, size, shape and weigh of particle; however, density is the key factor. Gravity separation is inefficient when used to treat particles that have either a wide size distribution or a narrow density distribution [9]. Gosselin et al. [16] report that density difference must be greater than 1g/cm^3 for sufficient separation . The effectiveness of density separation can be estimated by the "concentration criterion" from Taggart [8,14]. The gravity concentrators such as jig, shaking table and spirals can be affected by particle size effect during the separation process [8]. For this reason, it is necessary to classify by size the soil to be treated before performing gravity concentration. If the density difference between the soil and contaminant particles is significant, the gravity concentration technologies should be particularly suitable for particle separation. The volume capacities of gravity concentrators are 100–500 t/h, 25 t/h, 4 t/h, 5 t/h for Dense Media Separation (DMS), mineral jig, spiral, shaking table, and MGS-Mozley respectively [14,16]. The particle size range conditions are reported on Fig. 3.

The most common gravity concentrators, used for soil treatment at large-scale, are jigs, shaking tables and spirals (Table 1). Mineral jigs are commonly used to treat coarse sand fractions (800−2000 µm) or gravel fractions (2000−6000 µm) while shaking tables and spirals are more suitable to treat fine to medium/coarse sand fractions (63−2000 µm) (Table 3). Silt/clay (<63 µm) and very fine sand (63−125 µm) fractions can be processed with MGS-Mozley. Bergeron et al. [22] reported the following results for long-term trials in remediation project of brownfield soils from Montreal, Canada: (1) 75% of Cu removal efficiency (823 µg/g of Cu in initial soil) obtained with the use of two jigs (in series) from the 1700−6400 µm fraction; (2) 54% of Cu removal efficiency (1025 µg/g of Cu in initial soil) obtained with the spiral method from the 106−1700 µm fraction; (3) 47% of Cu removal efficiency (924 µg/g of Cu in initial soil) obtained with MGS-Mozley from the <106 µm fraction.

Since Pb is a dense element, gravity concentration may be used for remediation of soils contaminated with particulate forms of Pb (e.g., Pb-based old paint debris, battery manufacturing/recycling sites, and smelting/mining sites). Density separation with jigs is a well established method to remove Pb from small arms firing ranges (SAFR) where Pb is mostly present in the form of spent bullets (Table 1, project #10-13, 15, 16, 20-23, 29, 30).

3.4 Froth flotation

Froth flotation is a physicochemical technique that exploits difference of hydrophobic properties to separate metal-bearing particles from the soil matrix. The separation principle is based on the affinity of a particle's hydrophobic surfaces for air bubbles injected in the slurry of soil. The separation process involves three steps: (1) attachment of the desired metal-bearing particles to the air bubbles; (2) the bubbles are gathered in a foam portion; (3) the foam fraction, which floats up slurry, is removed. The surface of metals-bearing particles is often rendered hydrophobic by the use of a surfactant agent (collector). The froth flotation is widely used in the mineral industry, and metal sulfides are easier to separate than carbonates and oxides [14]. There are different types of flotation systems including flotation cells and a flotation column.

Froth flotation has been successfully used to remove metals (primarily Cd, Cu, Pb, and Zn) from sediments and soils [24-31]. Some examples of metal removal efficiency obtained with flotation systems are described in Table 3. However, the use of froth flotation as a remediation technique is still less used than other soil washing technologies. Froth flotation appears to be a relevant technique for treating fine-grained matrices, especially anoxic dredged sediments (best separation efficiency in the 20−50 μm range) where heavy metals are mostly present under sulfide forms [25,26].

In soil the remediation context, major factors influencing the floatability of metal-bearing particles are: (1) the heterogeneity of the metal compounds; (2) the metal distribution over the different particle size fractions; (3) the presence of high contents of organic matter; (4) the proportion of the very fine particles <10μm [26,29]. Since sulfide minerals are more floatable than carbonates or oxides, chemical pre-treatment by sulfidisation has been investigated (Table 3) [24,30]. The efficiency of flotation columns is usually much higher than that of flotation cells in the finer portion of the grain size range [16,27]. The selective flotation of metal-bearing particles from the particle size fraction <10 μm is problematic in most mechanical flotation cells because of various phenomena of entrainment and entrapment of the fine hydrophilic undesirable gangue particles [31,32]. The Dissolved Air Flotation (DAF) system, which can produce very small bubbles, is promising to improve the selective flotation for the fine particles range [29]. The conventional flotation systems are less effective in floating large particles (>200–300 μm) due to the inability of bubbles to carry coarse and heavy particles [14]. Compared to conventional flotation technologies, the Separation In Froth (SIF) technology is more suitable for separation in the coarser particle size range [14]. Attrition scrubbing is often used prior to the flotation process in order to disaggregate the small particles bound on coarse particles and to remove the coating of a particle's surface. Also, power ultrasound can be used instead of attrition conditioning [33].

In full-scale application, flotation was mostly combined with hydroclassification, and gravity concentration (Table 1). In the 1980s, Dutch companies like Jaartsveld, Mosmans and Heidemij pioneered the flotation technique for soil cleaning with Metso (Swedish company) as a major equipment supplier [34]. The most significant example of full-scale froth flotation use in the US, for metal removal from contaminated soils, is the project performed at King of Prussia Superfund site in 1993 (Table 1, project #3).

3.5 Magnetic separation

Particles present in soil have magnetic susceptibilities which vary from negative (organic), intermediate (paramagnetic minerals, organometallics) to largely positive ferromagnetic minerals) [35]. Ferromagnetic material can be attracted by a low intensity magnetic field, while separation of paramagnetic material requires a high intensity magnetic field [18]. Low intensity magnetism separation (LIMS) has been used to recover spent munitions debris at military sites [36] or ferrous/metallic debris material containing high heavy metals concentrations in brownfields [37]. The magnetic separation of heavy metals from the soil matrix is based on the fact that metal contaminants are associated with the ferromagnetic materials. Rikers et al. [35] showed that wet high intensity magnetism separation (WHIMS) is suitable for removing Cr, Cu, Ni, Pb, and Zn from several soils. If the heavy metals are not associated with a ferromagnetic phase, separation is not efficient. When the soil matrix is heterogeneous, as in the case of brownfields, magnetic separation is not significantly efficient to remove metal contaminants from soils [17].

3.6 Electrostatic separation

The use of electrostatic separation for soil remediation appears limited and is rarely used. One example of an electrostatic separation application at full-scale is the PMET's Lead-Base Paint Chip Separation and Recovery technology [38]. This process uses a final step of electrostatic separation after size classification, ferromagnetic separation and gravity separation steps [39].

3.7 Attrition scrubbing

Typical attrition scrubbers use an intense opposing flow generated by twin impellers in soil slurry with a very high solid content (70–80%) to provide mechanical particle-to-particle scrubbing in order to accomplish two main effects: scouring and breaking [9,40]. The scouring effect involves the removal of coating or film from individual grains. The breaking effect involves the dispersion/separation of silt and clay bonded to sand and gravel particles, and the disintegration of soil agglomerates. Soil scrubbing is accomplished mostly by particle-to-particle attrition, but also by the interaction between the paddles and the particles [41].

Williford et al. [42] showed that preconditioning by attrition scrubbing enhanced size hydroclassification. Marino et al. [43] showed that mechanical attrition increases the removal efficiency of metal on the Wilfley table (gravity concentration). Scrubbing effect produces fresh and clean grain surfaces (by removing oxidized coating), and thus can enhance subsequent froth flotation processes [14]. Attrition scrubbers can also be used to improve the chemical extraction of superficially-bound contaminants (adsorbed metal cations) from solid particles [44]. Ko et al.

[45] have used a drum-type scrubber (pilot-scale) chemically enhanced by acid leaching to extract metals (As, Ni, and Zn) from soils (Table 1, project #32).

3.8 Integrated process train of physical separation

Table 1 shows that most of the large-scale applications of PS process trains (16 projects reported) primarily exploit the differences in particle size (hydroclassification) and density (gravity concentration). Froth flotation is moderately used. Attrition scrubbing is often employed as a pre-treatment to improve the separation process. Magnetism and electrostatic separators are not often used. In field applications, typical treatment train of physical separation process includes: (1) a preliminary size classification step using mechanical screening to isolate oversized material; (2) a hydroclassification step preceded or followed by attrition scrubbing to provide suitable particle size range for further treatments; (3) the treatment of the sand fraction by gravity concentration or froth flotation; (4) the treatment of the fine fraction; (5) the management of the generated residuals.

Many physical separation processes were based on simple particle size separation because the fine fraction (clay and silt) is often considered as contaminated and the coarse fraction (sand) is considered as uncontaminated. However, metal contamination can be distributed throughout the various particle size fractions of soils and concentrations can be high in sand fraction, especially for urban or industrial soils polluted by heterogeneous waste disposal [46,47,48]. If metal contamination is of particulate nature and is abundant in all particle size fractions, separation only based on size cannot accomplish a sufficient separation of metal contaminants. In this case, the separation based on density or floatability must be investigated. The physical separation treatment train can require crushing, desliming, dewatering, and water treatment. Physical separation can be used as a stand-alone volume reduction process or as pre-treatment prior to metal recovery (Table 1). In certain cases, Pb and Hg may be recovered under a saleable form. In remediation projects of shooting range soil, the Pb concentrates were usually sent to smelter for metal recycling (Table 1).

3.9 Advantages/disadvantages of physical separation technologies

This section provides general comments for the integrated processes, specially large-scale applications. The advantages and disadvantages for each technology type were specifically discussed in the preceding paragraphs. Physical separation presents many advantages: (1) this technology can treat both organic and metal contaminants in the same treatment system; (2) the volume of soil to be further treated (for metal recovery) or to be disposed of off-site are considerably reduced; (3) the soil processed can be returned to the site at low cost; (4) the metal recovered may be recycled in certain cases (e.g., sent to smelting facility); (5) the treatment train systems are easily modular and some mobile unit systems are available at full-scale for on site remediation; (6) the technologies are well established in the mineral processing industry and the operational costs are usually low.

On the large scale applications, the soil treatment by physical separation presents some disadvantages: (1) this treatment system requires a large equipments and large spaces for soil treatment; (2) the volume of soils to be treated must be large to be cost effective (>5000 tons for treatment on site); (3) washwater treatment and off-site disposal of residual solids may be required, thus significantly increases the cost [8,20].

4. Chemical extraction technologies

Chemical extraction uses an extracting fluid containing a chemical reagent (acids/bases, surfactants, chelating agents, salts, or redox agent) to transfer the metals from the soils into an aqueous solution. In extractive metallurgy, the chemical extraction procedures, referred to by the term “hydrometallurgy”, are extensively employed for recovery of the metals from ores, concentrates, and recycled or residual materials [49]. In the soil remediation context, solubility enhancement can be accomplished by leaching solutions in which the metal contaminants are dissolved; or by converting the metal compounds into forms that are more soluble (e.g., conversion to soluble metal salts by valence change). In this review, the use of five leaching solution types will be separately discussed: (1) acids; (2) salts and high-concentration chloride solutions; (3) chelating agents; (4) surfactants; (5) reducing or oxidizing (redox) agents.

Table 4 summarizes the soil types, the treated metals (initial concentrations), the leaching methods, the studied factors in leaching process, the overall results and conclusions of 24 laboratory investigations (18 studies involved EDTA; 3 studies compared EDTA versus other chelating agents; 7 studies compared EDTA versus acids; 6 studies involved the chloride salt solutions, 4 studies compared several acids). Generally, acids rely on ion exchange and dissolution of soil components/discrete metal compounds to extract metals. The use of high-concentrations chloride salt solutions at low pH conditions combines the acid leaching action and the formation of metal chloro-complexes to extract metals from soils. Chelating agents solubilize metals through complexation. Surfactants target desorption of metals from soil interface. The redox manipulation aims to enhance metal solubilization through a valence change. The choice of the extracting reagent depends on the metal type, metal concentration, metal fractionation/speciation and soil characteristics (Table 4). Strong acids such as hydrochloric acid (HCl) and chelating agents such as ethylenediaminetetraacetic acid (EDTA) are commonly investigated to extract heavy metals from soils.

4.1 Applicability and limitations of chemical extraction

Metal removal efficiency by the chemical extraction process depends on the soil geochemistry (e.g., soil texture, cation exchange capacity, buffering capacity, and organic matter content); metal contamination characteristics (type, concentration, fractionation and speciation of metals); dosage and chemistry of extracting agent; and processing conditions (solution pH, residence time, number of successive extraction steps, mode of reagent addition, liquid/solid ratio, etc.) (Table 4). Several experimental results of metal removal efficiency according to the leaching methods, the reagent types (EDTA, HCl, and salts solutions) and the soil characteristics are reported in Table 5.

The speciation (distribution of chemical species) and fractionation (fractions according to bonding with specific soil substrates) of metals in soils are important parameters for determining the metal removal efficiency by chemical treatment. The metal speciation analysis can be complicated (especially when the soil is contaminated with a complex mixture of metal compounds) and the metal fractionation according to soil substrates is often applied. The partitioning of metals according to their association with the soil substrates is usually determined by the sequential extraction procedure [47,48]. The analytical protocols used generally involve 5 fractions: (F1) exchangeable, (F2) acid soluble/carbonate bound; (F3) reducible/Fe-Mn bound; (F4) oxidizable/organic matter and sulfide bound; (F5) residual [50] (Table 4). Van Benschoten et al. [51] have studied metal partitioning for up to 10 fractions.

The fractions most amenable to metal removal by chemical leaching are: (1) exchangeable; (2) associated with carbonates; (3) associated with reducible Fe-Mn oxides of soils [52] (Table 4). However, extraction of metal bound to exchangeable and carbonate fractions was faster compared to extraction of metal bound to Fe-Mn oxides [53,54]. In describing leaching with EDTA and HCl, Van Benschoten et al. [51] reported that non-detrital Pb (i.e., associated with water soluble, carbonates and organic) was removed from soils, while Pb bound to the Fe-oxides, sulfide and residual fractions was not removed. Organically bound metals can be extracted along with the target organic contaminants by the solvent extraction method [4]. The removal efficiency of metals from the distinct fractions depends on the extracting reagents used (Table 4). For instance, due to dissolution effects, certain acid leaching processes may partially remove metals from the crystalline lattice [55]. Nevertheless, the metal fractionation data does not always clearly explain metal removal efficiency because removal efficiency also depends on other factors such as metal concentration and soil geochemistry [56].

In addition, removal efficiency depends on the metal type to be extracted and the valence of the element. Generally, the extractability of most cationic heavy metals (e.g., Cd, Cu, Pb, and Zn) increases when the solution pH decreases. Indeed, at low pH, adsorption onto soil of the cationic heavy metals decreases and the dissolution of metal compounds increases. On the other hand, the solubility of oxyanions of the metalloid As increases when the solution pH increases [57]. In addition, the adsorption of chromium Cr(VI) anionic species is enhanced at low pH [58]. Hence, the simultaneous treatment of both anionic and cationic metal species that have dissimilar chemical behavior in aqueous solution, can be ineffective. Furthermore, Isoyama et al. [58] reported that HCl leaching was relatively efficient for chromate (CrO_4^{2-}) removal from non-allophanic soils but it was inefficient for removal of trivalent chromium Cr^{3+}, particularly from soils having high cation exchange capacity (CEC) and organic matter content (due to complexation by humic substance and adsorption via cation exchange reactions).

If metal is not under an adsorbed form, the removal efficiency depends on solubility of metal compounds in the washing fluid, which are governed by the solubility product (Ks.p.)

values. The treatment of particulate forms of metals is more difficult to achieve compared to the adsorbed ionic forms [59].

Factors that may limit the applicability and effectiveness of the chemical process include: (1) high clay/silt content; (2) high humic content; (3) high content of Fe and Ca element; (4) high calcite content or high buffering capacity; (5) simultaneous contamination of both cationic or anionic heavy metals; (6) high heterogeneity of soil; (7) metals associated with residual soil fraction, imbedded in the mineral lattices, or discrete particle forms. The fine-grained soils may require longer contact times and may reduce chemical extraction efficiency [60,61]. Nevertheless, Table 5 reports several leaching processes that have treated soils having a high clay/silt content (>50%). High humic content can inhibit metal extraction because COOH groups (adsorption sites) on humic substances have high affinity for heavy metals [62]. The corresponding cations of major element Fe and Ca may interfere with chelating process [63,64,65]. High calcite content or high buffering capacity may decrease the acid leaching efficiency [60]. High heterogeneity of soils can affect formulations of extracting fluid and may require multiple process steps.

4.2 Acid extraction

Acid extraction is a proven technology to treat soils, sediments, and sludges contaminated by metals and commercial-scale units are in operation [4]. The pH of the washing fluid plays a significant role in the extractability of heavy metals from soils. Several mechanisms contribute to the extraction of metals from soil using an acid solution: (1) desorption of metal cations via ion exchange; (2) dissolution of metal compounds; (3) dissolution of soil mineral components (e.g., Fe-Mn oxides) which may contain metal contaminants [61,66]. At low pH, the protons (H^+) added can react with soil surface sites (layer silicate minerals and/or surface functional groups including e.g., Al-OH, Fe-OH, and COOH groups) and enhance desorption of metal cations, which are transferred into the washing fluid [62]. Kuo et al. [66] showed that acid leaching with 0.1 M HCl contributes to a significant dissolution of Fe and Al oxide surfaces, and phyllosilicates. At pH <2, this dissolution process replaces ion exchange in metal extraction [66].

Acid leaching may involve strong mineral acid such as hydrochloric (HCl), sulphuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4) or weak organic acid such as acetic acid. While, acetic acid has been used in field demonstrations at Fort Polk in Leesville, LO (Table 1, project #23), the nuisance of odors and its relative low strength limits its efficiency [21]. The removal efficiency of different mineral acid types strongly depends on the metal type, the soil geochemistry, and the reagent concentrations (Table 4). Moutsatsou et al. [67] showed that the extraction of metals (As, Cu, Pb and Zn) from soils, highly contaminated by metallurgical materials, was more effective with HCl compared to H_2SO_4 and HNO_3. On the other hand, Ko et al. [45] showed that: (1) the extraction of Zn and Ni (cationic) was similar in the use of HCl, H_2SO_4 and H_3PO_4; (2) the extraction rate of As (anionic) was higher for the use of H_2SO_4 and H_3PO_4 compared to HCl. Unlike HCl, the use of H_2SO_4 or H_3PO_4 acids, which involve competitive oxyanions (PO_4^{3-} or SO_4^{2-}), may decrease the re-adsorption of As anionic species on reactive surfaces of soil [57].

Many experimental and field test results have shown the efficiency of the HCl leaching process for extracting heavy metals from non-calcareous soils. HCl is often used for chemical leaching at full-scale (Table 1). The co-dissolution of soil components by acid leaching is a critical parameter from an environmental and an economic point of view. Acid leaching strongly affects soil structure and causes an important losses (up to 50%) of the soil mineral substances [61] and organic matter [57]. Co-dissolution of the soil matrix increases the consumption of acid reagent and the complexity of the wastewater treatment [61]. Furthermore, acid leaching causes a high increase in acidity of the treated soil [57]. Acid leaching may be ineffective for soils that have a high buffering capacity such as calcareous soils [60]. Although acid leaching is efficient in extracting metals from the soils, its large-scale application has numerous disadvantages: (1) strong acids may destroy the basic nature and the soil structure, thus affecting soil microbiology and fertility; (2) wastewater and processed soils need to be neutralized; (3) neutralization of wastewater creates enormous amount of new toxic residues; (4) disposal of solid/liquid residues and processed soil may be problematic; (5) cost markedly increases with wastewater processing and soil neutralization.

4.3 Salt solutions and high-concentration chloride solutions

The use of diluted acid solutions containing chloride salts (such as $CaCl_2$) may be an effective alternative to the acid leaching at high concentrations. The processed soil is practically unaffected by the saline leaching with diluted acid. Indeed, the co-dissolution of the soil matrix is less significant and the pH of the final soil is not significantly lower compared to initial soil [61]. Kuo et al. [66] reported that the removal efficiency of Cd from rice soils with a 0.001 M HCl and 0.1 M $NaCl_2$ solution was similar to the removal efficiency obtained with the acid leaching using a 0.01 M HCl solution. The increase in the removal of cationic metals (such as Pb^{2+} and Cd^{2+}) with $CaCl_2$ addition in the acid leaching results from two processes: (1) ion exchange of Ca^{2+} with Pb^{2+}/Cd^{2+} on the reactive surface sites of soil matrix; (2) formation of stable and soluble metal chloro-complexes with chloride ions Cl^{-} (e.g., $Cd^{2+} + yCl^{-} \Leftrightarrow CdCl_y^{2-y}$) [61,66]. Isoyama et al. [62] reported that a second washing step with 0.1 M $CaCl_2$ (after a 1 M HCl leaching step) was used to prevent a re-adsorption of the extracted Pb on cation exchange sites of silicate layer minerals having a permanent negative charge. The destruction of a soil's physico-chemistry and microbiology is minimized by using successive leaching steps with a solution of $CaCl_2$ at low-concentrations (0.1 M) and slightly acidified [66,68].

Several researchers investigated the use of chloride salt solutions at high-concentrations (>1 M) and acidic conditions for removing high Pb concentrations from soils (Table 4). The chloride ions Cl^- at high concentrations form soluble chloro-complexes with Pb^{2+} such as $PbCl^{3-}$ and $PbCl_4^{2-}$ [69]. However, Eh and pH parameters must be monitored for obtaining the optimum thermodynamic conditions and preventing the formation of an insoluble compound $PbCl_2$ [70]. In high ionic strength solutions, the sodium cation Na^+ (of the concentrated NaCl solutions) may play a significant role in Pb extraction via ion exchange [69]. The acidified NaCl solutions were more efficient (or comparable) than conventional extractants (EDTA and HCl) for removing Pb from clayey or fine-grained soils (Table 5).

Unlike the leaching with concentrated HCl, the concentrated NaCl solution is effective in removing Pb from calcareous soils without a high Ca extraction [71]. The leaching with an acidified 2 M NaCl solution (enhanced with an oxidant agent) has been tested at pilot-scale for the remediation of highly Pb-contaminated soils (Table 1, project #29-30). The free chloride ions are often recycled and the extracted metals are recovered by (1) chemical precipitation with addition of sulfide, hydroxide, carbonate compounds or (2) electrochemical coagulation/reduction (Table 4). Meunier et al. [72] showed that the electrochemical coagulation treatment was more effective than chemical precipitation for removing the dissolved metals from acidic and saline leachate; however its cost is higher.

4.4 Chelant extraction

Since chelating agents have the ability to form stable metal complexes, their use offers a promising approach for the extraction of metals from contaminated soils. There are five major factors in the selection of chelating agents for metal extraction from soils: (1) chelating agents should be able to form highly stable complexes over a wide pH range; (2) the metal complexes that are formed should be non adsorbable on soil surfaces; (3) the chelating agents should have a low biodegradability if the reagents is to be recycled for reuse in the process; (4) the reagents used should be cost effective; (5) metal recovery should be cost effective [11,52,56,63]. The main advantage of the use of chelating agent (such as EDTA) compared to strong acids (such as HCl) is that chelating agents cause less destruction of the soil structure. However, EDTA presents two main disadvantages compared to HCl: (1) the chemical products are more expensive; (2) EDTA may pose a serious ecological threat if it is not recycled or destroyed in the washing process because EDTA has a low biodegradability degree (resistant to chemical and biological degradation) and has the potential for remobilizing heavy metals in the environment [73,74].

Many chelating agents have been tested and compared (Table 4). Peters [52] showed that EDTA, nitrilotriacetic acid (NTA) and acid citric were effective, while other chelating agents such as gluconate, oxalate, Citranox, ammonium acetate were ineffective in removing Cu, Pb, and Zn from Aberdeen Proving Ground soils. Carboxilic acids such as EDTA and NTA are chelating agents hydrolytically stable at high temperature and pH levels [75]. However, NTA is not recommended for use in soil remediation because it is hazardous for human health [74]. Moreover, EDTA forms more stable complexes with most of the heavy metals when compared to NTA [75].

EDTA is recognized as the most effective synthetic chelating agent to remove heavy metal (especially Pb, Cd, Cu, and Zn) from soils because of: (1) EDTA has a strong chelating ability for cationic heavy metals; (2) EDTA leaching process can treat a broad range of soil types; (3) EDTA is recoverable and reusable (low biodegradability degree) [56,64,73,76]. The EDTA leaching process has been well demonstrated through many laboratory studies to extract metal cations bound on soil particles (Table 4). On the other hand, EDTA appears ineffective for extracting anionic metal As (Table 5).

Metal removal efficiency with EDTA highly depends on soil characteristics and metal fractionation (Table 6). In general, EDTA is effective in removing metal cations bound to exchangeable, carbonate and organic fraction, while EDTA is less efficient in extracting metals bounds to reducible/Fe-Mn oxide fraction [11,54,65]. Elliott and Shastri [53] have demonstrated that oxalate was more effective than EDTA to remove the metals associated with Fe-Mn oxides of soil (attacks the hydrous oxides). The metals bound to residual fraction are not extracted by EDTA (Table 6). Unlike acid leaching (low concentration), the EDTA complexing process may be efficient in treating calcareous soils [54,60]. However, EDTA may contribute to the co-dissolution of calcite, thus reducing removal efficiency of metals [65].

The low selectivity of EDTA causes high consumption of the reagent due to the potential chelation with other cations, such as Ca^{2+} and Fe^{3+}, dissolved in the washing solution [64]. Competition in the metal-EDTA system is controlled by dissolved metal concentrations, reaction kinetics and certain soil parameters. Factors affecting the stability of metal chelate include: (1) the size and number of rings; (2) ligand substituents on the rings; (3) the nature of the metal; (4) pH of the washing solution; (5) high content of calcite ($CaCO_3$) in the soil [75]. The concentration of Fe^{3+} in the washing solution is a crucial parameter for the stability of metal-EDTA complexes because Fe^{3+} may form more stable complexes with EDTA (log K= 26.5 at 25°C and ionic strength= 0.01) compared to the most heavy metals such as Cu (log K= 19.7), Pb (19), Zn (17.5), Cd (17.4) [56,63]. The complexation interference of Ca^{2+} appears less problematic (thermodynamically) because Ca^{2+} forms much less stable complexes with EDTA (log K= 10.65) than Cd, Cu, Pb, and Zn [63]. On the other hand, a recent study [64] showed that Ca^{2+} is the main competitive cation because $CaCO_3$ is strongly dissolved in the EDTA leaching solution at pH 4-5, thus concentrations of Ca^{2+} in the leaching solution is very high compared to the targeted heavy metal for the chelation with EDTA. Furthermore, complexation competition between heavy metals (such as Zn vs. Pb) may occur in leaching process [77].

Metal extraction also depends on the combination of many parameters such as EDTA/metal molar ratio, leaching method (batch vs. column/pile leaching), mode of reagent addition (single step vs. successive extraction steps with low reagent dosage), solution pH, liquid/solid ratio, and extraction time (Table 4). Multiple-step procedures with a low EDTA dosage gave best results compared to the single-step mode with a high dosage [78]. Leaching with EDTA is usually performed at pH 4-8 (Table 4 and Table 6). At low pH values, the EDTA-metal complexes can be re-adsorbed on soil surface sites [74].

EDTA regeneration is a crucial parameter to the leaching process in order to avoid the release of EDTA into the environment. EDTA must be recycled in order to keep treatment costs at a reasonable level [76]. Several procedures have been proposed for EDTA regeneration (or degradation) and the removal of the metals from the leaching solution: (1) metal precipitation and EDTA regeneration via addition of the chemical agents; (2) electrochemical procedures; (3) ion exchange resin; (4) nano-filtration; (5) degradation of EDTA by oxidation and metal recovery by absorption (Table 4). For instance, Lim et al. [73] have proposed a protocol of regeneration and metal-precipitation using 3 steps: (1) metal substitution with Fe^{3+} to form Fe-EDTA + Me^{2+}; (2) metal precipitation with Na_2HPO_4 to form metal phosphate; (3) Fe precipitation and EDTA regeneration with NaOH addition to form Na_2-EDTA + $Fe(OH)_3$. With this process, the metal recovery was 85%, 89%, and 90% of the extracted Pb, Cd, Ni respectively. Reused EDTA was slightly less efficient compared to fresh EDTA in metal removal [73].

4.5 Surfactant-enhanced solubilization

Although the use of surfactants is more suitable for the treatment of organic contaminants, the removal of metals from soil by surfactants is also an interesting chemical procedure to be investigated. Recently, the use of surfactants has been studied to enhance the EDTA leaching process for metals mobilization from soils [76]. The surfactant addition in washing solution aims at assisting desorption or/and dispersion of contaminants from soils. When the metals are closely associated with organic contaminants, washing by surfactants can be more effective. Association between metal and soil substrates, and acidic or basic conditions are important parameters for soil washing success with surfactants. Mulligan et al. [79] indicates that a caustic surfactant could be used for removing the organically-associated metals while acidic surfactant could be employed for extracting the metals bound to carbonate and oxide. Several laboratory studies showed that cationic forms of metals can be extracted from contaminated soils and sediments by anionic biosurfactant solutions [80-83]. However, the metal extraction by biosurfactants has not yet been performed for large scale remediation projects [84].

4.6 Reducing and oxidizing agents

Reducing and oxidizing agents provide yet another option to enhance solubilization of metals since chemical oxidation/reduction can convert metals to more soluble forms. USBOM and USEPA have conducted laboratory research on Pb extraction involving redox manipulations and valence changes to promote solubilization and recovery of various Pb compounds from synthetic contaminated soils [75]. Some laboratory studies showed that the addition of reducing agents can enhance metal mobilization by EDTA [11,51,52]. The use of reducing agents contributes to the dissolution of Fe-Mn oxides, thus enhancing metal removal bound to Fe-Mn fraction in the EDTA leaching process [51].

Several oxidant agents are also used to enhance the removal of metals [701,707]. Lahoda and Grant [85] proposed the use of an oxidizing agent to enhance the solubilization of metals from fine particles into a soil washing process comprising particle separation, metal solubilization, and metal precipitation. Lin et al. [70] used sodium hypochlorite (NaClO) as an oxidizer agent in the chloride-based leaching process (2M NaCl at pH 2) to extract metallic Pb-particles (smaller than 0.15 mm) and other Pb-species from highly contaminated soils (washing results are reported in Table 1, project #29-30). Reddy and Chinthamreddy [86] reported that complete removal of Cr from clayey soils (artificially contaminated) was achieved with the leaching process using a 0.1 M potassium permanganate ($KMnO_4$) solution.

4.7 Integrated process train of chemical extraction

On large scale operations, leaching methods are classified into two main classes: (1) percolation leaching such as heap/pile leaching or vat leaching; (2) agitated leaching based on batch step or continuous procedure [49]. In the heap leaching process, soil is piled in a heap and the leach solution is sprayed over the top of the heap, and allowed to percolate downward through the heap [49]. The agitated leaching method is performed under turbulent flow conditions. For soil treatment at commercial-scale, heap/pile leaching appears more cost effective [61,63,78]; however the extraction processes can be slow and metal concentrations must be relatively high. Agitation leaching is an interesting method for soil treatment because it can allow aggressive and effective extraction of the metal contaminants from soils [44]. The column washing tests resulted better metal removal efficiency rather than batch tests [11,78]. Abumaizar and Smith [11] reported that the continuous flow in the column promoted the flushing of the reaction reagent/metal complex and minimized the re-adsorption of complex on the soil surface.

After dissolution of the metal compounds, it is necessary to separate the leaching solution from the residual solid phase of soil. The resulting solution containing metals can be treated by various aqueous processes such as precipitation, sedimentation, complexation, electrochemical techniques, liquid ion exchange, resin ion exchange, or membrane technologies to recover metals (Table 4). Solvent extraction techniques make it possible to selectively transfer certain ionic metal species present in an aqueous washing solution to an organic liquid phase if the extracted metal compounds are preferentially soluble in the organic phase [49]. The washed soil is usually rinsed with water to remove the residual extracting agents from the soil. Depending on the soil characteristics and reagents used, the resulting 'clean' soil fraction can be returned to the site or must be disposed off-site.

4.8 Advantages/disadvantages of chemical extraction technologies

The advantages/disadvantages significantly diverge according to the reagents and extraction method used. Specific comments were discussed in the preceding sections. Generally, the principals advantages of chemical procedures compared to physical separation are: (1) the sorbed metal forms can be treated; (2) certain metal compounds can be dissolved; (3) the fine-grained soils may be treated in certain cases; (4) the extracted metals may be easily recovered by a wide variety of methods. Chemically enhanced soil washing can become attractive if the chemical reagents are recycled, detoxified or not hazardous.

The large-scale application of chemical extraction processes presents numerous disadvantages: (1) the use of chemical agents significantly increase processing costs; (2) the processed soil may be inappropriate for re-vegetation and on-site disposal because the physico-chemical and microbiological properties have been affected; (3) the presence of toxic chemical agents in the final soil or the residual sludge may be problematic for disposal; (4) the presence of certain chemical agents in the wash fluid can complicate water recycling and treatment, thus increasing cost of the overall process; (5) the treatment of sludges rich in metal can be difficult. The chemical agents involved may cause other environmental problems. For instance, the soil treated by EDTA leaching may potentially be hazardous to reuse if a part of the chelating agent remains in the soil. Wastewaster treatment may produce large amounts of toxic sludges that must be carefully managed.

5. Combination of physical separation and chemical extraction

Table 1 reports 18 processes combining physical and chemical procedures. The complementary use of the physical particle separation and chemical leaching procedures provides a very useful tool for decontaminating the soils affected with metals. The typical combination uses physical separation (primarily by size, density or floatability properties) to concentrate particulate forms of metals into a small volume of soil, followed by chemical extraction of this concentrated fraction to dissolve the metals (Table 1, project #17-27, 29, 30, 33). For example, a combination of the BESCORP physical separation technology and the COGNIS-Terramet Pb extraction process has been efficient at Superfund site in New Brighton, MN (Table 1, project #20). In this case, the sand fraction is treated by density separation (jig), while fine fractions are treated by chemical leaching. The Pb removal efficiency for the fine fractions ranged from 65 to 77%. Lead concentrates were delivered to a Pb smelting facility.

Many soil washing processes are based on simple particle size separation using hydroclassification and attrition scrubbing with water-based fluid. Particle size separation is often used before chemical extraction, with the assumption that the fines contain most of the metal contamination. Since metal concentrations are usually high in the fine fraction, the practice of direct disposal is inappropriate. Chemical extraction may be used for the decontamination of the fine fractions and can allow metals recovery in a saleable form or concentrated form.

Soil washing systems may involve other combination types depending on the soil matrix characteristics, metal speciation and type of metal to be treated. The combination of PS/CE can be reversed (e.g. chemical leaching followed by wet screening) or may involve a simultaneous process of PS/CE methods. For instance, certain processes use attrition scrubbing chemically enhanced with acids, surfactants or chelating agents followed by a wet screening/hydrocycloning stage to separate the fine particles/washing solution (containing the pollutants) from the clean fraction (Table 1, project #28, 31, 32). The grinding and crushing process of soil particles may be a pre-treatment option for enhancing the efficiency of the chemical extraction treatment. The use of ultrasounds may accelerate the surface cleaning of soil particle and improve the leaching of metals [87-89]. The influence of ultrasounds contributes through several mechanisms (not fully understood) such as the micro-fragmentation of particles, and disturbance of solid/liquid interface by cavitation [87].

The soil washing treatments aim at completely decontaminating the site by removing metals from the soil matrix. Table 1 reports the treatment efficiency for total metal concentrations. However, the aspect of reduction in metal leachability to below standard TCLP is also important in the quality results of soil washing. The ideal goal of an extraction strategy is to recover metals for reuse and resale, however, metal recovery is often not practicable for projects that lack economic viability or technical feasibility for the extraction and recovery processes. The generated toxic sludges (containing metals), which are recalcitrant to a metal recovery treatment, may require a stabilization/solidification process prior to disposal. In many cases, soil washing is used to reduce the metal concentrations to an acceptable level or to considerably reduce the volume of contaminated soil.

6. Status of soil washing technology

This section provides a discussion about the use, at large scale, of soil washing for the remediation of sites polluted by metals. The discussion focuses on the status of soil washing systems employed in the US, Europe and Canada (Table 1). Soil washing based on physical separation (SW-PS) is more employed than processes that use chemical extraction (SW-CE). Chemical extraction is more expensive ($ 358–1,717 /m^3) compared to physical separation ($ 70–187 /m^3) [4].

6.1 Soil washing in Europe

SW-PS is relatively well established in Northern Europe, primarily in the Netherlands since the mid 1980's [4,90]. The Netherlands are a pioneering country for the implementation of the SW-PS technology in a soil remediation context. For instance, Heidemij (now ARCADIS), has used a SW-PS technology since 1983 [91]. Soil washing systems used in the Netherlands is particularly appropriate to treat metal contaminants and typically involve attrition scrubbing, hydrocyclones, upstream columns, spirals and froth flotation cells [90]. A literature review revealed that many Dutch environmental companies offer soil washing system such as: ARCADIS (http://www.arcadis-global.com); A&G Milieutechniek (http://www.aengbedrijven.nl); Boskalis Dolman (http://www.boskalisdolman.nl) [5]. In 2001, 21 stationary and 4 mobile soil washing plants were operational; and 855 kton/year were treated between 1991 and 2001 [90]. Environmental Dutch firms have introduced and promoted the development of SW-PS in the United States in the early 1990's and in Japan in the early 2000's [92,93].

The SW-PS technology is also well established in Germany, Sweden, Norway and Belgium [5,7,19,91] to treat metal-contaminated soils. Ten Swedish companies and 3 Norwegian companies offer treatment by soil washing applicable to metal-contaminated soils [5]. Metso, a Swedish based company, has been a major supplier of physical separation technologies for European soil washing processes since the 1980's [34]. Metso was the equipment's supplier for the first US project of soil washing, conducted by ART [34].

6.2 Soil washing in the USA

Griffiths [7] reported two soil washing systems developed by USEPA in the 1980's: the Mobile Soil Washing System (MSWS) based on chemical extraction, and the Volume Reduction Unit (VRU) based on size separation. According to USEPA [8], the significant applications of SW-PS for remediation of metal-contaminated soils in the United States began in the early 1990's and the first applications were focused on treating Pb-contaminated soils of abandoned small-arms firing ranges (SAFR). For instance, in 1991 US Bureau of Mines presented a conceptual physical separation process train for the remediation of SAFR, which included Pb recovery [9,94]. Since the mid 1990's, Brice Environmental Services Corporation (BESCORP) has had extensive experience for SAFR remediation (Pb removal by density separation) and has also applied physical separation for the remediation of a battery manufacturing site in 1995 (Table 1). Soil washing systems have also been used since the early 1990's for treatment of soils from wood preserving sites contaminated by a mixture of metals (Cu, Cr and As) and organic contaminants [8]. For example, the BioTrol Soil Washing System has been employed at the MacGillis and Gibbs Company site in New Brighton, MN in 1992 [95]. In the mid 1990's, the US Army Corps of Engineers (USACE) and the USEPA reviewed physical separation technologies and concluded that these techniques, coupled with chemical extraction, offered the most promising method for metal remediation in soils [9].

The co-operation with Dutch environmental firms has contributed to the establishment and the development of soil washing in the United States [92,96]. In the early 1990s, the firms Geraghty & Miller, Inc., USA and Heidemij Realisatie of The Netherlands formed a joint venture (now called ARCADIS) and were incorporated as Alternative Remedial Technologies (ART) to introduce the Heidemij soil washing system to the US market [92]. The first project contracted under this arrangement was the large-scale remediation of the King of Prussia Superfund site, NJ performed in 1993 [6].

The number of soil washing technologies available at commercial-scale for the treatment of metals in the US is difficult to estimate. ITRC [20] compiles a list of 16 soil washing technologies available in the US for full-scale applications. The REACH-IT database [97], which compiles 500 remediation technologies, reports only 7 vendors of soil washing technology and 1 vendor of an acid extraction process. On the other hand, FTRT [98] compiles 20 vendors of soil washing or acid extraction technologies. The main US vendors of soil washing technologies, presented in Table 1 are: BESCORP; ART Engineering LLC; Eddy and Metcalf; and Biogenesis. Various soil washing systems have been tested to remove metals from soils in the framework of Superfund Innovative Technology Evaluation (SITE) demonstration program (Table 1).

Although the soil washing technology is available at commercial-scale in the US, its use has been limited for remediation of Superfund sites when compared to the conventional solidification/stabilisation technology. The Annual Status Reports (ASR) database [99] indicates that the soil washing method has been implemented at only two Superfund sites contaminated with metals: at King of Prussia, NJ (completed) and at Vineland Chemical Co., NJ (in operation) (Table 1). Table 7 reports several cases of soil washing projects that have failed in the framework of the Superfund program and give the principal reasons for soil washing failure in the remediation of metals.

6.3 Soil washing in Canada

Table 1 reports some examples of soil washing systems performed at pilot-scale or full-scale in Canada such as: (1) Tallon Metal Technology in Montreal and Toronto; (2) Toronto Harbour Commissioner (THC) treatment train in Toronto; (3) pilot demonstration by Alex-Sol and INRS; (4) pilot demonstration by Dragage Verreault and INRS. Holbein [100] reported on the soil washing process of Tallon Metal Technology (Guelph, Ontario) for mixed contaminants; the soil treatment involved physical separation to treat the coarse fraction, and a chemical process to treat the fines. Three large-scale applications of Tallon's treatment system have been applied. Researchers from INRS ETE (University of Quebec) have tested several pilot-scale soil washing systems for the decontamination of brownfield soils located in urban environment [22,101,102].

7. Conclusions

Soil washing is a technology particularly relevant for the remediation of metal-contaminated soils. The majority of projects are based on physical separation technologies which are cost effective and well established in the mineral processing industry. From the economic and environmental point of view, soil washing may be an effective alternative to solidification/stabilization and landfilling. The soil washing technology presents many advantages: (1) the processes attempt to permanently remove metals from soils and can allow recycling of metal in certain cases; (2) the volume of contaminated soil is markedly reduced; (3) the processed soil can be returned to the site; (4) the process duration is typically short to medium-term compared to other metal extraction methods. However, the success of the soil washing process requires: (1) an exhaustive soil characterization; (2) a study of metal speciation and fractionation; (3) an understanding of the relationship between the soil matrix and metals. The complementary use of the sequential extraction procedure and the SEM-EDX provides a very useful analytical tool for understanding chemistry aspects of metals in soils and predicting the soil washing treatment efficiency.

Soil washing can be used independently or in conjunction with other treatment technologies. While frequently used in Europe, the soil washing method has not been used extensively in the US and in Canada. Soil washing has been performed successfully in Europe, due in part to regulatory actions taken to drastically restrict landfilling options. The soil washing technology is often used for reducing the volume of soils and residues placed in landfills. Soil washing in Europe is mostly performed in fixed facilities, while mobile soil washing plant appears to be more common in the US and Canada.

Acknowledgements

G. Dermont is thankful to the "Institut National de la Recherche Scientifique Eau Terre et Environnement" (INRS-ETE) for their financial support. We would also like to thank Angus Calderhead for his useful comments.

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Tables

Table 1. Field applications of soil washing technologies

Table 2. Summary of physical separation types

Table 3. Laboratory investigations of physical separation technologies

Table 4. Laboratory investigations of chemical extraction technologies

Table 5. Examples of experimental results in metal removal efficiency according to the leaching method and the soil characteristics

Table 6. Examples of metal removal efficiency with EDTA according to the soil characteristics and metal fractionation

Table 7. Examples of deselected soil washing projects in Superfund program

Table 1. Field applications of soil washing technologies

#	Project description (status, location, remediation sponsor/vendor, and completion date)	M/F[a]	Type[b]	Technology description	Metal	Initial[c] (µg/g)	Final[c] (µg/g)	RE[d] (%)	Cap.[e]	Vol.[f]	Metal recovery/recycling, Management of the processed soil and washing residuals	Ref.
1	Pilot-scale demonstration of transportable unit at PPG Canada Inc. site in Beauharnois, QC, Canada (1992)	M	PS	Screening, gravity concentration, hydrocyclone, froth flotation	Hg	> 1000	624	25-50	3 m^3/h	5000 m^3	Hg recycling (1.3 t of Hg were recovered)	[103]
2	Pilot-scale demonstration (Environment Canada program) of Tallon's physical separation unit at Dickson site, Montreal, QC, Canada (1993)	M	PS	Vibrating screen, magnetic separation, attrition scrubbing, froth flotation	As Cu Pb	27-52 115-366 248-336	14-21 100-347 188-327	50-60 <25 <25	300 t/d	-	-	[37]
3	Full-scale application performed by Alternative Remediation Technologies (ART) at King of Prussia Superfund site, NJ (1993)	M	PS	Wet screening, hydrocyclones, attrition scrubbing, froth flotation	Cr Cu Ni	500-5500 800-8500 300-3500	73 110 25	>90 >90 >90	30 t/h	19200 t	85% of soil was re-deposited on site; Revegetation; Sludge cake (2000-6000 µg/g of metals) was disposed off-site	[6,104]
4	SITE demonstration of BESCORP (Brice Environmental Service) plant system at the Alaskan Battery Enterprises site, Fairbanks, AK (1993)	F	PS	Wet screening, attrition scrubbing, density separator	Pb	5600	200	65-85	20 t/h	56000 t	Disposal; Pb recycling (Pb smelter)	[105]
5	SITE demonstration of physical separation coupled with thermal desorption system (Harbauer GmbH & Co. KG, Berlin) for remediation of soils from Marktredwitz site, Germany (1996)	F	PS	Crushing, screening, attrition scrubbing, hydroclassification	Hg	780-1080	17	98	4-20 t/h	63 t	Hg recovery: thermal desorption (vacuum-distillation)	[106]
6	Field application performed by Metcalf & Eddy for remediation of Naval Weapons Station Earle Pistol Range, NJ (1996)	M	PS	Size and density separation	Pb	>20000	14-92	>90	-	1500 t	Pb recycling (10 t of recovered bullet); 70 t of clay fines required recycling at an asphalt batch plant	[21]
7	Full-scale application performed by ART and CINTEC for remediation of soils from seven brownfields in Montreal, Qc, Canada (1996)	F	PS	Screening, hydrocyclones, froth flotation	Cu Pb Zn	200-10000 700-3000 1000-5000	-	-	30 t/h	22300 t	Some site soils, which were not feasible for treatment by soil washing, were disposed directly at the Cintec landfill	[6,107]
8	Pilot-scale demonstration of the physical separation process (INRS and Dragage Verreault Inc.) for remediation of brownfield soils from Montreal, QC, Canada (2000)	F	PS	Screening, fluidized-bed separation, gravity separators (jigs, spiral conc., MGS-Mosley), froth flotation	Cu Pb Zn	675-950 466-994 1869-2293	321-419 399-466 1483-1793	52-56 26-60 21-22	-	10 t	Soil fraction <6 mm was treated; The cleaned soil fraction was 85% of initial soil	[22]
9	Several full-scale applications of Kuryluk Mineral Separator (KMS) concentrator (Phase Remediation Inc.) in Europe (2000)	-	PS	Gravity separator (KMS concentrator)	Cu Pb Zn	-	-	-		-	-	[108]
10	Full-scale application of BESCORP's Particle Separation System, performed on Pb-contaminated soils from the SAFR site at range 24, Fort Dix, NJ (1999)	M	PS	Grizzly, vibrating wet screen, hydrocyclone, gravity separation by jig	Pb	5300-38000	396	93	-	3600 t	Recovering spent bullets and Pb recycling (21 t of Pb 95% purity) for Pb-smelter; 100% of soil suitable for reuse	[109,110]

11	Full-scale application of BESCORP's Particle Separation System, performed on soils from the SAFR site at Massachusetts Military Reservation (MMR), Cape Cod, MA (1999)	M	PS	Screening, hydrocyclone, gravity separation by jig	Pb	>4820	<TCLP	98	-	6200 t	Pb recycling (50 t of spent bullet) for manufacturing batteries; 601 t of residual soil was stabilized; 90% of soil suitable for reuse; Revegetation	[109,110]
12	Full-scale application of BESCORP's Particle Separation System at the SAFR complex of Marine Corps Air Ground Combat Center, 29 Palms, CA (1998)	M	PS	Screening, hydrocyclone, gravity separation by jig	Pb	20000	1600	89	250 t/d	12000 t	Pb recycling (240 t of Pb 94% purity); 100% of soil suitable for reuse	[109,110]
13	Full-scale application of ART's Process at Former Skeet Shooting Range Site (soil and sediment), Lordship Point in Stratford, CT (2000)	M	PS	Vibrating wet screen, hydrocyclones, gravity separation jig	Pb	-	-		100 t/h	30000 m^3	Pb shot recovered (90% purity) was treated in off-site facility for Pb recycling; Revegetation	[107]
14	NATO/CCMS Pilot Test on Decontamination of Mercury-Polluted Site (267-445 t of Hg in 222.740 m^3 of soil) in Ústí nad Labem, Czech Republic (2000)	F	PS	Hydrocyclone, wet gravity separation	Hg	100-100000	< 10	-	-	2 t	Hg recycling	[111]
15	Pilot-scale demonstration of BESCORP's Particle Separation System at the SAFR site, Fort Ord, CA (period 2001-2005)	M	PS	Grizzly, vibrating wet screen, hydrocyclone, gravity separation by jig	Pb Cu	2000 -	227 <100	95	400 t/d	400 t	Metal recycling	[109,110]
16	Full-scale application of ART's Process at Former Bend Trap Club Skeet Range, Bend, OR (2007)	M	PS	Screening, gravity separation by jig	As Pb	-	<400	~90	50 t/h	23800 t	Pb recycling (110 t of upgraded Pb shot); 90% of soil was disposed on-site	[107]
17	SITE demonstration of Toronto Harbour Commissioners (THC) / Bergmann USA for the remediation of the contaminated fine particles of soil from a former auto/metal salvage site, Port Industrial District, Toronto, ON, Canada (1992)	F	PS/CE	(1) PS: screening, hydrocyclones, attrition scrubbing, density separation; (2) CE: solubilization by acid leaching followed by ion exchange chelating resin	Cu Ni Pb Zn	1223 469 1687 3072	169 84 211 211	86 82 87 93	50 t/h	820 t	Metal recovery in metallic forms by electrowinning	[112]
18	Field demonstration of physical separation techniques for remediation of soils from SAFR, conducted by US Bureau of Mines (1993)	-	PS/CE	(1) PS: screening, hydrocyclone, gravity concentration (jig, spirals conc., Bartles-Mozley table); (2) CE: heap acid leaching	Pb	100000	-	>90	-	-	Pb concentrate can be sent to Pb smelter; No data about % of cleaned soil	[8]
19	Field demonstration of physical separation to remove Hg from soils, conducted by MRSDI for Energy and Environmental Research Center (EERC) (1994)	-	PS/CE	(1) PS: vibrating screen, gravity concentration (Neffco concentrator and spirals); (2) CE: acid leaching	$Hg(s)^g$ $Hg(c)^g$	15370 920	10 33	80-99* 30-96*	-	-	*RE are given for PS and CE respectively; Hg recycling (600 g of Hg element was recovered)	[8]
20	Field-scale application of BESCORP and COGNIS systems at Twin Cities Army Ammunition Plant, Site F in New Brighton, MI (1994)	M	PS/CE	(1) PS: BESCORP process (trommel and wet classifier, density separation by jigs); (2) CE: COGNIS Terramet® (acid) leaching process for fine particles	Pb	380-86000	<200	>75	15 t/h	400 t	PS process reduced the Pb load to the CE process by 39% to 63%; Pb concentrates from jigs and CE processes were transported to Pb smelter	[113]
21	Pilot plant demonstration (Environment Canada and MCEBR program) of a metal-separation process developed by Alex-Sol Inc. and INRS for remediation of soils and sediments from Quebec city, Montreal, and Trois-rivieres, Canada (1995)	F	PS/CE	(1) PS: density separation, magnetism separation and froth flotation; (2) CE or bioleaching	Cu Cd Pb Zn	117-7533 1020 1202-2595 1521-22800	34-402 <5 591-877 333-791	48-98 99 51-69 68-99	-	45 t	Potential for reuse of processed soil or sediments; Potential for recovery of extracted metals	[114]

22	Field demonstration of BESCORP's soil washing process at Joint Small-Arms Range 5, Fort Polk, Leesville, LO (1996)	M	PS/CE	(1) PS: attrition, size screening, hydrocyclones, density separation by jig; (2) CE: acid leaching (HCl)	Pb Cu Zn	4117 - -	165 - -	90 97 89	6 t/h	835 t	67% and 32% of soil suitable for reuse after PS and CE respectively; Pb recycling (9 t) by Pb-smelting	[41]
23	Field demonstration of ContraCon Northwest's soil washing process at Joint Small-Arms Range 5, Fort Polk, Leesville, LO (1996)	M	PS/CE	(1) PS: attrition, size screening, hydrocyclones, density separation by jig; (2) CE: acetic acid leaching	Pb Cu Zn	2828 - -	122-1443 - -	93 93 77	3 t/h	263 t	The processed soil was unsuitable for return to the site (due to inadequate neutralization and failed TCLP) and was sent to a landfill	[41]
24	Pilot-scale demonstration of soil washing performed by Metcalf & Eddy at explosives manufacturing, location unknown (1996)	M	PS/CE	(1) PS: size/density separation; (2) CE: acid leaching	As Pb	97-227 3500-6300	7-142 10-306	34-93 95-99	-	200 t	-	[115]
25	Full-scale application of soil washing system of Tallon Metal Technologies Inc. at the Longue Pointe site in Montreal, QC, Canada (reported in 1998)	M	PS/CE	(1) PS: screening, gravity and magnetic separation; (2) CE: hydrometallurgical extraction and Vitrokele™ adsorption	Pb	11800 max	<1000	93	600 t/d	150000 t	95% of processed soil suitable for reuse; Potential recycling of Pb concentrates	[100,116]
26	Pilot-scale demonstration of soil washing system of Tallon Metal Technologies at the Ataratiri site in Toronto, ON, Canada (reported in 1998)	M	PS/CE	(1) PS: screening, gravity and magnetic separation; (2) CE: hydrometallurgical extraction and Vitrokele™ adsorption	Cd Cu Pb Zn	4 950 2112 2535	<1 290 898 286	90 70 57 67	600 t/d	35 t	Potential recycling for recovered metal; 85% of soil was recovered for reuse	[100,116]
27	Field demonstration of the soil washing system at Hunter's Point Shipyard, San Fransisco, CA (1998)	-	PS/CE	(1) PS: fluidized bed separation; (2) CE: acid leaching	Cu, Cr Pb, Zn	-	-	-	-	-	-	[117]
28	Full-scale application (results of pilot demonstration) of Biogenesis Sediment Washing Technology for remediation of dredged materials (90% silt/clay) from the New York/New Jersey Harbor (1999-2001)[h]	-	PS/CE	(1) Washing with high pressure water and surfactants/chelating agents (metal separation) in collision chamber; (2) hydrocyclone and wet screen	As Cd Pb Zn Hg	12.3 3.1 157 279 3.9	7.8 1.2 68 131 0.3	36 61 57 53 92	30 m^3/h	200000 m^3/year	Potential reuse of decontaminated sediment; Further treatment of washing solution (metal precipitation)	[118]
29	Pilot soil washing/leaching test for remediation of soils from battery-breaking site in Fairbanks, AK (2001)	M	PS/CE	(1) PS: size separation, density separation by jig; (2) CE: leaching with chloride solution (NaCl, 2M; HCl, pH 2) and oxidant (NaOCl)	PS: Pb[i] CE: Pb[i]	750 2300	87-117 84	84-88 96	-	40 t	85% and 5% of soil was cleaned with PS and CE respectively (VR= 90%); Jig concentrate was 2.7 t; Metal recovery by PbS precipitation; PbS cake can be sent to smelter	[70]
30	Pilot soil washing/leaching test for remediation of soils from SAFR site, DE (2001)	M	PS/CE	(1) PS: size separation, density separation by jig; (2) CE: leaching with chloride solution (NaCl, 2M; HCl, pH 2) and oxidant (NaOCl)	PS: Pb[i] CE: Pb[i]	5721 830	139-342 81	94-98 90	-	13 t	29% and 62% of soil was cleaned with PS and CE respectively (VR= 91%); Jig concentrate was 1.2 t; Metal recovery by PbS precipitation; PbS cake can be sent to smelter	[70]

31	Pilot-scale demonstration of the BioGenesis Sediment Decontamination Process for remediation of dredged materials from the lagoon of Venice, Italy (2005)[h]	F	PS/CE	(1) Washing with high pressure water and surfactants/chelating agents in collision chamber; (2) Hydrocyclone and wet screen	As Cd Cu Pb Zn Hg	16-73 6-41 95-375 40-531 115-531 3-10	6-15 1-9 17-39 27-138 84-630 0.5-2	6-85 0-83 60-91 0-74 0-72 75-93	15 m^3/h	330 m^3	Precipitation of metals from washing solution; Fine fraction of treated sediment, which has higher metal concentrations, was disposed to a landfill site	[119]
32	Pilot-scale study for remediation of contaminated soils from mining area, Seoul, Korea (2006)	M	PS/CE	(1) Attrition scrubbing chemically enhanced by acid leaching (HCl, H_2SO_4, or H_3PO_4) in drum-type scrubber; (2) Separation of fine soil+wastewater and sand soil	As Ni Zn	43 340 68	10-15 140-145 50-55	63-75 59-60 38-45	Batch (40 kg)	0,5 t	VR= 51-98% (vary according to particle size fraction); The fine soil fraction (highly contaminated) requires further treatment	[45]
33	Pilot plant demonstration for remediation of urban contaminated soil from Québec city, Canada (2007)	M	PS/CE	(1) PS: size separation (screening, spiral, hydrocyclone); (2) CE: acid leaching (HCl, pH 2-3)	Cu Pb Zn	202-350 2030-2200 870-960	40-234 69-848 111-941	44 60 52	-	30 t	The process produced 91% of a non-contaminated soil and 9% of metallic residue and heavily contaminated soil	[101]
34	Full-scale application of the ART's process at Vineland Chemical (Pesticide manufacturing) Superfund site, NJ (project in progress)	F	PS/CE	(1) PS: size screening, hydrocycloning; (2) CE: leaching and precipitation	As	20-5000	<20	-	70 t/h	350000 t	Off-site disposal for filter cake residue containing high concentrations of As	[107,120]
35	Full-scale project of soil washing coupled with chemical treatment (chromium reduction) at Palmetto Wood Preserving, SC (1989)	M	CE	Batch washing process using sodium metaphosphate to lower pH to 2.0 and extract the chromium from the soil	As Cr	2-6200 4-6200	<1 627	99 90	-	10000 m^3	Chemical treatment of leachate: reduction of Cr(VI) to precipitate in Cr(III) form; Disposal of soil and sludges residual	[121]
36	SITE demonstration (bench- and pilot-scale) performed by Center for Hazardous Materials Research for remediation of 4 soils from US Superfund Sites (1995)	F	CE	Acid leaching (HCl, pH < 2)	As, Cd Cr, Cu Pb, Zn	Variable	Variable	50-95*	5-10 t/h	-	*RE is most lower for As; Metals are concentrated in a form potentially suitable for recovery	[96]
37	NATO/CCMS Pilot test of the CACITOX™ process to remediate soils with high clay and silt content, United Kingdom (1998)	F	CE	Mild leaching and extraction (oxidants, complexing agents, and organic acids)	Cr, Cu, Zn, Pb, Cd, As	1000-22500	<Dutch B levels*	50-70	10-100 kg/h	-	*As and Cd > targeted levels; Metal recovery by precipitation/ion exchange	[116]

-= Not Available; SAFR= Small Arms Firing Range; SITE= Superfund Innovative Technology Evaluation of USEPA; MCEBR= Montreal Centre of Excellence in Brownfields Rehabilitation; VR= Volume Reduction; [a]M= Mobile system suitable for remediation on-site; F= The project has been performed in fixed facilities; [b]Basic principle of process: PS= Physical Separation; CE= Chemical Extraction; [c]Metal concentration: mean value or range, which may vary according to the tested samples or the particle size fractions that have been treated; [d]Removal Efficiency of metal (the value is calculated from the concentrations or the recovered metal mass); [e]Capacity in tonnes metric per hour (t/h) or per day (t/d), cubic meters per hour (m^3/h); [f]The treated volume; [g]The study distinguishes the treated soil fractions (s= sand, c= clay); [h]The description does not include the remediation process of the organic contaminants, which were destroyed by cavitation/oxidation after separation with surfactants; [i]The study distinguishes the performances of the PS and CE processes

Table 2. Summary of physical separation types

Operation unit	Basic principle	Description and main objectives	Comments	Typical technologies implemented
Mechanical screening	Separation based on particle size	Mechanical screening uses size exclusion through a physical barrier to provide suitable dimensions for treatment	Widely used. Fine screens are fragile.	Vibrating grizzly; barrel trommel; vibrating or gyratory screens
Hydrodynamic classification	Separation based on settling velocity	Hydrodynamic classification separates the particles by difference of settling velocity or by centrifugal force into a water flow. These methods are often used for size separation.	Widely used. Difficult when clay and humic soils are present.	Hydrocyclones, elutriators, mechanical classifiers (screw classifier)
Gravity concentration	Separation based on density of particles	The gravity concentration technologies separate high density from low density minerals or particles in a slurry of water and soil (relatively high solid content).	Widely used. Difficult when clay and humic soils are present.	Spiral concentrator, shaking table, jig, MGS-Mozley, dense media separation (DMS)
Froth flotation	Separation based on hydrophobic properties of the surface of particles	The differences in hydrophobic properties of particle surfaces are exploited to separate certain minerals from soil by attachment to air bubbles injected in a pulp (low solid content).	Widely used. Chemical additives are required.	Flotation in cell or in column (agitation or non agitation system)
Magnetic separation	Separation based on magnetic properties of particles	Mineral particles are separated according to their different magnetic susceptibilities.	Moderately used. High capital and operating costs.	Dry or wet separators using high intensity (HIMS) or low intensity (LIMS)
Electrostatic separation	Separation based on electrical conductivity properties of particles	The separation is based on the difference in the surface electrical conductivity of the particles to be separated.	Rarely used. Materials must be completely dry.	Electrostatic and electrodynamic separators
Attrition scrubbing	Mechanical particle-to-particle scrubbing	Attrition scrubbing uses high energy agitation of soil slurry (high solid content) to remove coating of particle surface and to disperse soil aggregates.	Widely used. Pre-treatment that improves separation process.	Various types of scrubbers

Table 3. Laboratory investigations of physical separation technologies

Examples of studies	Study objective	Technologies (treated soil fractions)	Metal	Conc. (µg/g)	RE%^{a} (technology or operating conditions)	VR%^{b}	Ref.
Magnetic separation (HIMS) on six soils in the Netherlands (results with soil "L")	Use of magnetic separation as stand-alone remediation technique	High intensity magnetic separation (HIMS) with dry and wet separators (63-2000 µm)	Cu Cr Pb Zn	126 244 121 598	83 77 46 79	87-93	[35]
Attrition scrubbing in conjunction with a shaking table on a soil from an Army small arms training range, USA	Improvement of density separation (shaking table) by the use of attrition scrubbing	Wemco attrition scrubber, Wifley shaking table	Pb	40000	96	80	[43]
Evaluation of physical separation technologies for remediation of six browndfield soils (polluted by landfilling of various wastes in Quebec City, QC, Canada (results with soil "A1", 90% of sand)	Study of various physical separation technologies for an integrated soil washing process	Wet magnetic separator (63-2000 µm), Attrition scrubbing, gravity concentration: shaking table (63-850 µm); jig (850-2000 µm)	Cu Pb Zn	7458 4893 3535	52 (jig) / 89 (shaking table) 61 (jig) / 67 (shaking table) 58 (jig) / 54 (shaking table)	NA	[18]
Gravity separation to remediate two shooting range soils contaminated by Pb-containing shotgun pellets in Finland (results with Utti soil)	Study of applicability of gravity separation to remove bullet fragments	Shaking table, heavy liquid separation (DMS)	Cu Pb	113000 24000	73 (DMS) / 85 (DMS+ shaking table) 88 (DMS) / 91 (DMS+ shaking table)	80-90	[122]
Evaluation and analysis of soil washing for seven Pb-contaminated soils from Netherland	Evaluation of gravity separators in an integrated soil washing process	Shaking table (74-840 µm); jig (840-4760 µm)	Pb	500-2195	22-93^c (jig+ shaking table)	NA	[51]
Froth flotation as a remediation technique for heavily polluted sediment in Belgium	Evaluation of froth flotation as stand-alone remediation technique. The influence of the particle size distribution and metal speciation on the froth flotation efficiency	Denver laboratory cell (grain size: 70% <50 µm)	Cd Cr Cu Pb Zn	13 267 128 721 3200	60 at pH 8 48 53 60 60	80	[25,26]
Froth flotation on a soil in Tienen, Belgium	Improvement of froth flotation by sulfidisation pre-treatment	Sulfidisation with Na_2S, Denver laboratory cell (0-2000 µm)	Cd Cu Pb Zn	8 68 142 357	25 (without sulfi.) / 47 (with sulfi.) 30 (without sulfi.) / 45 (with suldi.) 30 (without sulfi.) / 42 (with suldi.) 30 (without sulfi.) / 42 (with suldi.)	70-80	[28]

[a] Removal Efficiency; [b] Volume Reduction of contaminated soil; [c] Range value, according to soil types

Table 4. Laboratory investigations of chemical extraction technologies

Soil type	Metals (µg/g)	Leaching method	Reagent	Studied factors in leaching process	Overall results and conclusions	Leachate treatment	Ref.
Calcareous soils polluted by mining and smelting activities in Lavrion, Greece	Cd (20-130) Pb (500-34800) Zn (700-20200)	Batch	EDTA	Test with 7 different soil samples; Successive steps (1 to 2) with Na$_4$-EDTA vs. Na$_2$-EDTA; EDTA dosage (0.2 to 1 M), i.e., EDTA/ΣMe molar ratio (1 to 23); S/L (10 to 36%); Study of EDTA/Ca vs. EDTA/Me molar ratio.	Pb RE varied for the different samples (50 to 98%). Cd and Zn RE was <50%. Best results were obtained with two steps, high conc. of Na$_2$-EDTA (0.25 M, i.e., EDTA/ΣMe molar ratio was >20) and low S/L ratio (10%). EDTA may contribute to the co-dissolution of CaCO$_3$.	-	[65]
Calcereous soil from the battery site, Canada	Pb (24600) Cd (27) Zn (241) Cu (43) Ni (120)	Batch	EDTA	EDTA dosage (0 to 0.2 M); pH (4 to 8); extraction kinetic; Extraction mechanism (two-reaction models); MF (6 fractions).	Removal of Cu/Cd/Ni/Zn was less effective than removal of Pb. RE of Pb was 99% with high EDTA dosage (0.2 M) and within 12 h of the leaching. Extraction of Pb bound to carbonates and exchangeable fractions was faster compared to extraction of Pb bound to oxides.	Nano-filtration for Pb-EDTA complex recovery (98%)[a]	[54]
Artificially contaminated sandy soil	Cu (1230)	Batch	EDTA	EDTA/Cu molar ratio (1 to 12.5); L/S ratio (5 to 25); pH (4.8 to 6.56); Extraction time (0 to 25 h); Extraction mechanism of Ca^{2+}, Fe^{3+} and Cu^{2+}.	Cu RE= 80-90% within 5h of the leaching. Cu RE strongly depended on L/S ratio and EDTA/Cu ratio. Best results were obtained with L/S= 12.5 and EDTA/Cu= 12.5.	-	[64]
Four soils from mining and smelting site in Slovenia	Pb (1136-4424) Zn (288-5489)	Batch/ Heap	EDTA	EDTA dosage (0.00375 to 0.06 M); pH (4.5 to 9); Successive steps (1 to 10); Interference of major cations (Ca, Fe) with Pb/Zn-EDTA complexation; Laboratory simulation of soil heap leaching (time= 0-72 h).	Increasing EDTA conc. did not produce a proportional gain in RE. Multi-steps using low EDTA dosage gave best results compared to single-step mode. Fe^{3+} interfered more strongly with Pb/Zn EDTA-complexation when single step mode was used. The interference of Ca^{2+} was less important.	-	[63]
Soil from Pb-smelting site in Mezica Valley, Slovenia	Pb (1243) Zn (1190)	Batch/ Heap	EDTA	Small-scale heap leaching; Successive steps (1 to 6) with EDTA/Pb molar ratio (0.42-6.67) and EDTA/Zn molar ratio (0.14-2.2); Extraction time (0-96 h); MF study (6 fractions).	Multi-step using low EDTA dosage gave best results compared to single-step mode. EDTA extracted more Pb than Zn (Zn bound to the residual soil fraction).	Degradation of EDTA by ozone/UV treatment and absorption of metals	[78]
Four soils (mining activity) in UK and France	Cd (49-380) Cu (42-1350) Pb (265-9430) Zn (1920-30260)	Batch / Column	EDTA	(1) Batch tests (L/S= 5): EDTA dosage (0.01 M); EDTA/ΣMe ratio for initial/final soil; (2) Column tests: effect of the mode of EDTA addition (continuous and pulse mode); EDTA dosage (0.01 to 0.025 M); (3) MF study (5 fractions) before and after treatment.	(1) Batch tests: EDTA extracted the metals similarly. (2) Column tests: EDTA extracted the metals differently. The results showed that metal removal occurs differently in batch and column leaching.	-	[56]
Artificially contaminated soil	Pb (1399) Zn (752)	Batch	EDTA	Extraction time (0.5 to 4 h); EDTA/Pb ratio and EDTA/Zn ratio (1 to 2); pH (5 to 9); Initial Pb and Zn conc. in soil; Study of competition between Zn and Pb.	Optimal conditions for EDTA leaching were: extraction time= 2 h; EDTA/Pb ratio=2 and pH 7 for Pb; EDTA/Zn ratio= 1 and pH 9 for Zn. Metals RE increased with an increases of initial metals conc. (with a fixed EDTA/Me ratio). There is competition between Zn and Pb under different EDTA dosage. Pb RE was higher than Zn RE with low EDTA dosage.	-	[77]
Artificially contaminated soil	Cd (269) Pb (2510) Ni (605)	Batch	EDTA	L/S ratio= 20; EDTA dosage (0.001 to 0.01 M), i.e., EDTA/ΣMe ratio (0.8 to 8); pH (4.7 to 8); Extraction times (15 to 240 min); Tests with fresh EDTA and recycled EDTA; MF study (5 fractions).	Optimum condition for metals RE depends on soil geochemistry and MF. The order of RE was Cd> Pb> Ni. EDTA appeared capable for extracting the Cd/Pb/Ni bound to the exchangeable, acid soluble, reducible and part of the oxidizable fractions.	EDTA regeneration (84%) and metal phosphates precipitation (89-95%)[a]	[73]

Soil contaminated by metals and PCB in Montreal, Canada	Cd (56) Cr (436) Cu (2726) Ni (364) Pb (17944) Zn (8940)	Batch	EDTA + Surfact.	Tests with EDTA (0.002 M), EDTA+Surfactant (anionic and non-anionic) with various ultrasonication times (3, 5, 10, 30 min); Tests with fresh and recycled EDTA. Study of Fe, Mg, and Fe removal.	The use of surfactants improved EDTA leaching. RE with EDTA+surfactant (non-anionic) was effective for Pb (73%) and moderately effective for Cu (49%), Cd (36%) and Zn (44%). RE was ineffective for Cr and Ni (mainly associated with residual soil fraction).	EDTA regeneration and metal precipitation by addition of $Ca(OH)_2$ and Mg^0 (73-96%)[a]	[76]
Artificially contaminated soil	Cd (603) Cr (1231) Pb (742) Zn (624)	Batch / Column	EDTA + Red.	(1) Batch tests: EDTA (0.01 and 0.1 M) and/or reducing agent $Na_2S_2O_5$ (0,1 M); L/S ratio (5,12.5,25); pH (3.9 to 6.3); Extraction time (2 to 90 h); (2) Column tests: EDTA (0.01 M) and/or $Na_2S_2O_5$ (0.1 M).	RE depended on the dissolution of metal-mineral bond, and the dispersion of metal in the washing solution. RE of Cr was low compared to RE of Cd, Pb, Zn. The use of reducing agent improved the EDTA leaching. L/S ratio had less effect. Column tests resulted better metal RE rather than batch tests.	-	[11]
Two metal-polluted soils from Indianapolis, IN and Palmerton, PA	Cd (197-280) Pb (812-210000) Zn (521-2700)	Batch	EDTA Oxalate	EDTA (1 M) vs. Oxalate (1 M) (time= 24h); pH (3 to 10); Study of Fe-oxides removal; MF (5 fractions).	MF was a major factor. EDTA was efficient to extract metal associated with non detrital and organic fractions. EDTA was less efficient to extract metals bound to oxide fraction. Oxalate was efficient to extract metals associated with oxide fraction.	-	[53]
Two urban soils in Montreal, Canada	Cd (1-6) Cu (130-700) Pb (269-800) Zn (360-2650)	Batch	EDTA HCl	HCl (0.001 M) vs. EDTA (0.00274 M) (time= 24 h); Successive steps (1 to 12) with EDTA; EDTA dosage (0.00684 to 0.0274 M); pH (4 and 8.5).	Acid washing with low HCl conc. was ineffective because the soils had high buffering capacity. EDTA was more effective. RE depended on EDTA dosage (best result with high conc.). High silt/clay content affected metal RE.	Anion exchange resin for EDTA-metal complex recovery (90-99%)[a]	[60]
Artificially contaminated soil	Pb (5000)	Column	EDTA HNO_3	Tests with 10 Pb-compounds (adsorbed Pb^{2+}, carbonate, sulfate, oxide, dioxide, sulfide, elemental forms of Pb, Pb-compound from paint); Tests with HNO_3 at various pH (1 to 6); Tests with EDTA (0.0003 and 0.001 M, i.e., EDTA/Pb ratio= 1 and 3) at pH 6.	Best results of acid leaching is obtained at pH 2. RE of adsorbed, carbonate, sulfate, oxide forms was effective and RE of sulfide, dioxide, Pb from paint, and elemental forms was ineffective. RE with EDTA (EDTA/Pb ratio= 3) was effective for adsorbed, carbonate, sulfate, oxide, dioxide forms, while was ineffective for other tested forms of Pb.	-	[12]
Seven Pb-contaminated sandy soils in the US	Pb (1394-11933)	Batch	EDTA HCL $HClO_4$ H_2SO_4 Red.	Acids vs. EDTA (0.01 M) at pH (1,2,3); Temperature (25, 50 °C); L/S ratio (5,10,20); The use of reducing agent NH_2OH-HCl (0.4 M); Extraction kinetic; MF study (10 fractions).	HCl was effective for Pb RE at low pH. RE and kinetic mainly depended on pH. The use of EDTA (0.1 M) improved Pb RE at pH 3 and not at pH 1. L/S ratio and temperature had less effect. Pb not removed by acids/EDTA leaching was associated with Fe-oxides, sulfide and residual. The use of reducing agent improved removal of Pb bound to Fe-oxides.	-	[51]
Soil polluted by battery recycling and Pb-smelting operation, IN	Pb (65200)	Batch	EDTA ADA PDA HCL	HCl (0.1 to 1 M) vs. Chelatants (0.0225 to 0.075 M) Extraction time (1 to 5 h); Successive steps (1 to 3); MF study (5 fractions).	The order of Pb RE: EDTA> ADA> PDA> HCl. The order of Cd RE: HCl> ADA≈ PDA≈ EDTA. RE depended on EDTA dosage. Three-step leaching (1 h) improved RE. Cd was removed from the crystalline lattice by HCl leaching.	Metal hydroxides precipitation by addition of Ca^{2+} and NaOH (72-93%)[a]	[55]
Soil polluted with slags and sulphur compounds in Lavrion, Greece	As (7540) Cu (4100) Pb (64195) Zn (5590)	Batch	EDTA HCl HNO_3 H_2SO_4	Tests with HCl (1,2,3,6 M), H_2SO_4 (6 M), HNO_3 (6 M), Na_2-EDTA (0.1 M); Study of extraction kinetic for HCl (1 M) and Na_2-EDTA (0.1 M) leaching; Mineral analysis by XRD of metal compounds.	RE highly depended on the metal forms. HCl resulted best RE compared to other acids. RE was improved with increasing HCL dosage and at long extraction time (4 h). EDTA was more effective at low leaching time (<1 h). HCl 1 M (4 h leaching) presented better RE compared to EDTA 0.1 M (1 h leaching). HCL 1 M strongly affected soil matrix. RE of As was ineffective with EDTA.	-	[67]
Artificially contaminated soil	Cd (49) Pb (294) Cr (270)	Batch	EDTA NTA DTPA HNO_3 $CaCl_2$	Single-step at pH 7; Extraction time (15 to 300 min); Tests with EDTA/NTA/DTPA (0.001 to 0.01 M); Comparison of EDTA/NTA/DTPA (0.005 M), HNO_3 (pH 2-3), and $CaCl_2$ (0.5 M); MF study (5 fractions).	The order of Pb RE: EDTA≈ NTA≈ DTPA> HNO_3>$CaCl_2$. The order of Cd RE: EDTA>NTA>DTPA> HNO_3>$CaCl_2$. Chelating agents were ineffective in removing Cr (mainly associated with oxidizable and residual fraction).	-	[74]

Soil from mining area located in Korea	As (41) Ni (88) Zn (335)	Batch	HCl H_3PO_4 H_2SO_4	Tests with HCl, H_3PO_4, H_2SO_4 at pH 2-3; Study of RE vs. particle size fractions (0.841-2, 0.420-0.250, <0.074 mm); Extraction time (10 to 25 min) and MF (4 fractions).	Acids with oxyanions (H_3PO_4, H_2SO_4) was effective for removing As and Zn. HCl was less effective in As removal. Acid leaching of Ni was less efficient (residual fraction). Acid leaching caused a loss of OM (50%) and an increase of acidity (7.6 to 3.3) of the treated soil.	-	[57]
Two contaminated rice soils in Taiwan	Cd (4) Cr (720) Cu (800) Ni (850) Pb (1849) Zn (1222)	Batch	HCl + $CaCl_2$	Study of the relation of soil suspension pH with the amount of H^+ added and the loss of H^+ from solution; Study of the dissolution of Fe and Al oxides by HCl; Effect of $CaCl_2$ dosage (0 to 0.1 M) and HCl dosage (0.001 to 0.01M) in RE of Cd with HCL+ $CaCl_2$ solution at various pH (1 to 7).	The use of $CaCl_2$ increased RE in diluted HCl (<0.01 M) for Cd removal. Fe-Al oxides are attacked by HCl with dosage >0.01 M.	-	[66]
Three artificially contaminated soils	Pb (995-1078)	Batch	HCl + $CaCl_2$	Three soil types: kaolinitic, smectitic and allophonic soil Successive steps (1 to 10) using HCl (1 M) followed by $CaCl_2$ (0.1 M) washing; Study of Pb bioaccessibility after the soil washing; MF study (3 fractions).	The successive batch washing with HCL (1 M) + $CaCl_2$ (0.1 M) was effective in removing Pb. RE depended on soil properties (buffering capacity, CEC, humic substance content, and clay mineral content).	-	[62]
Two soils from abandoned Pb-Battery recycling sites, TX and FA	Pb (14400-67400)	Batch	NaCl HCl EDTA	Tests with 7 chloride solution types NaCl, $CaCl_2$, HCl, $MgCl_2$, NH_4Cl, KCl, LiCl (Cl^-= 4.3 M); Successive steps (1 to 6, time= 30 min) using HCl (0.3 M) + NaCl (4.3 M); L/S ratio (5 to 50); Tests with HCl (0.2 M) + NaCl (4.3 M) vs. EDTA (EDTA/Pb ratio: 4.6 to 40) and pH (2 to 10); Tests with HCl (0.1 to 4.3 M) vs. acidified NaCl (4.3M) solutions; Mineral analysis (Pb species) by XRD; Kinetic and mechanism extraction.	Best results (RE= 97%) were obtained with successive two-step extraction (L/S= 7, time= 1 h) using acidified (pH 4) NaCl solution (4.3 M to saturated 6 M). Kinetic study suggested that Pb removal mechanism is composed of 3 stages: (1) extraction of free-Pb precipitates (quick process: <1 min); (2) cation exchange of Pb located on soil surface (30 sec-5 min); (3) Removal of Pb located within soil structure (slow process Pb after 5 min)	-	[69]
Soil from Pointe-aux-Lievres, Canada.	Pb (2730)	Batch	NaCl + HCl	NaCl dosage (0 to 6 M); pH (2 to 4); Soil pulp density (5 to 30%); Extraction times (0 to 1 h).	Pb RE (65-75%) was more effective with high Cl^- conc. (5.5 M), pH 2 and at 30% soil pulp density. Pb RE was independent of acid type, but depended on the pH (best result at low pH).	Electrochemical reduction/ coagulation for Pb recovery (95%)^a	[123]
Calcereous soil from the battery site in St-Jean-sur-Richelieu, Canada	Pb (2730)	Batch	NaCl + HCl	NaCl (8 M); Successive steps (1 to 6); Study of Ca removal; Extraction kinetic; MF study (5 fractions).	Six steps with NaCl (8 M) was effective (RE= 93%); RE increases with extraction time (RE> 80% after 90 h). Extraction appeared to be controlled by a first-order rate (Pb extraction from carbonate and exchangeable soil fractions).	Regeneration of Cl^- and metal precipitation with addition of $NaCO_3$, $CaCO_3$; or lime (90-98%)^a	[71]
Fine-grained soil from Montevecchio, Italy	Cd (34) Zn (3600) Pb (16000)	Column/ Pile	HCl + $CaCl_2$	Column tests: 3 successive steps with HCl (0.2 M)+ $CaCl_2$ (1.9 M) at pH<0.5 followed by 7 successive steps with $CaCl_2$ (2 M) at pH 6.5. Study of Mn, Fe, Al, Mg removal; Particle size distribution vs. metal concentration before and after treatment.	Chloride solution with $CaCl_2$+HCl was effective in metal removing from soil (poor in calcite). The treated soil matrix was sensibly unaffected (total weight loss= 3.5%; initial pH= 5.6; final pH=5.15).	Regeneration of Cl^- and metal precipitation with $CaCl_2$ at pH 9-12 (70-94%)^b	[61]

EDTA= ethylenediaminetetraacetatic acid; ADA= N-2acetamidoiminodiacetatic acid; PDA= pyridine-2,6-dicarboxylic acid; NTA= nitrilotriacetatic acid; DTPA= diethylenetriaminepentaacetic acid; M= mol/L; RE= Removal Efficiency; L/S= Liquid/Solid; MF= Metal Fractionation; Surfact.= Surfactants; Red.= Reducing agent; ΣMe= Molar sum of metals; OM= Organic Matter; CEC= Cation Exchange Capacity; ^{a}Removal efficiency of the dissolved metals from the leaching solution (varies according to the metal types or the processing conditions) ; ^{b}Removal efficiency for the whole process (leaching+precipitation)

Table 5. Examples of experimental results in metal removal efficiency according to the leaching method and the soil characteristics

Leaching method	Reagents (mol/L)	Soil description	Soil pH	CEC[a] (cmol/kg)	Texture[b] S/S/C (%)	OM[c] (%)	Ca (%)	Metal	Conc. (µg/g)	RE[d] (%)	Ref
Batch 1h, 3 steps, pH 4.5 (Chelation)	EDTA (0.0225)	Soil contaminated by smelting and battery recycling operations	7.4	14.3	68/17/15	8.2	-	Pb	65200	56	[55]
								Cd	52	37	
Batch 24h, 12 steps, pH 7-8 (Chelation)	EDTA (0.00275)	Urban soil contaminated by industrial activity	8.03	12.8	69/24/7	2.8[e]	18	Cd	6.3	53	[60]
								Cu	700	49	
								Pb	800	76	
								Zn	2650	84	
Batch 1h, 1 step, pH 6 (Chelation)	EDTA (0.1)	Soil contaminated with slags and metallurgical wastes	7.0	-	-	-	6.2	As	7540	13	[67]
								Cu	4100	41	
								Pb	64195	44	
								Zn	55900	38	
Batch 22 h, 2 steps (Chelation)	EDTA (0.25)	Calcareous soil (S1) contaminated by mining and smelting activities	8.3	-	42% <63 µm	-	11.6	As	1200	8	[65]
								Cd	100	37	
								Pb	32000	71	
								Zn	15000	49	
Batch 1h, 2 steps, pH 4 (Acid leaching + Cl^- complexation)	HCl + NaCl (4.3)	Soil from battery recycling site	7.0	9.5	51/36/13	3[e]	30	Pb	67400	>97	[69]
Batch 1h, 1 step, pH 4 (Acid leaching + Cl^- complexation)	HCl + NaCl (5.5)	Fine grained fraction of industrial soil	-	-	100% <20 µm	-	5.7	Pb	2730	65	[123]
Column: 3 steps with HCl (0.2 M) + $CaCl_2$ (1.9 M) at pH <1 followed by 7 steps with $CaCl_2$ (2 M) at pH 6.5. (Acid leaching + Cl^- complexation + ion exchange with Ca^{2+})	HCL + $CaCl_2$	Fine grained soil contaminated by mining activities	5.6	-	43/29/28[f]	-	0.7	Cd	34	75-80	[61]
								Zn	3600	75-80	
								Pb	16000	90-95	
Batch 1h, 3 steps, pH 4.5 (Acid leaching)	HCL (1)	Soil contaminated by smelting and battery recycling operations	7.4	14.3	68/17/15	8.2	-	Pb	65200	35	[55]
								Cd	52	56	
Batch 1h, 1 step, pH 4 (Acid leaching)	HCl (2)	Soil contaminated with slags and metallurgical wastes	7.0	-	-	-	6.2	As	7540	92	[67]
								Cu	4100	42	
								Pb	64195	57	
								Zn	55900	67	

[a]Cation Exchange Capacity; [b]Sand/Silt/Clay; [c]Organic Matter content; [d]Removal Efficiency; [e]Organic Carbon content (%); [f]The soil was agglomerated before the soil leaching treatment

Table 6. Examples of metal removal efficiency with EDTA according to the soil characteristics and metal fractionation

		Soil Characterization							Metal Fractionation[c] (%)						
Leaching method (EDTA dosage)	Soil description	Soil pH	CEC[a] (cmol/kg)	Sand/Silt/Clay (%)	OM[b] (%)	Ca (%)	Metal	Conc. (µg/g)	F1	F2	F3	F4	F5	RE[d] (%)	Ref.
Batch leaching 24h 1 step, pH 4 (0.2 mol/L)	Soil from battery site, St-Jean-sur-Richelieu, Canada	7.6	-	-	0.7	6	Cd	27	10[e]	26	23	22	20	<10	[54]
							Pb	24600	2[e]	47	43	5	2	98	
							Zn	241	2[e]	12	48	21	17	58	
Batch leaching 30 min, 1 step (0.02 mol/L)	Soil from storage facility, Montreal, Canada	7.5	9.5	52/33/16	12.5	-	Cd	56	<1	36	9	7	48	35	[76]
							Pb	17944	<1	60	19	2	18	66	
							Zn	8940	<1	40	50	<1	9	42	
							Ni	364	4	8	21	8	59	15	
Heap leaching, 24 h, 4 steps (0.04 mol/kg)	Soil from mining site, Mezica Valley, Slovenia	7.1	23.3	56/32/11	9.3	-	Pb	1243	<1[e]	24	<1	56	8	80	[78]
							Zn	1190	<1[e]	8	2	15	61	19	
Batch leaching, 30 min, 1 step, pH 7 (0.002 mol/L)	Artificially contaminated soil	4.7	52	42/33[f]	2.4	0.1	Cd	269	80	7	11	2	0	>95	[73]
							Pb	2510	39	38	19	4	0	>95	
							Ni	605	23	7	4	61	4	40	
Batch leaching, 24 h, 1 step, pH 6 (1 mol/L)	Soil from smelter site, Palmerton, PA	-	-	-	-	-	Cd	280	26	12	22	38	2	53	[53]
							Pb	812	17	7	44	26	6	<10	
							Zn	2700	20	8	38	6	28	28	

[a] Cation Exchange Capacity; [b] Organic Matter content; [c] F1= Exchangeable, F2= Acid soluble/Carbonate bound, F3= Reducible/Fe-Mn oxides bound, F4= Oxidizable/Organic matter bound, F5= Residual; [d] Removal Efficiency; [e] Water soluble + Exchangeable fractions; [f] Sand/Silt+Clay

Table 7. Examples of deselected soil washing projects in Superfund program

Site location and description	Media	Metals	Reasons of soil washing failure	Alternative selected technology
Sacramento Army Depot, oxidation lagoons, OU4, CA	Soil	Cr, Pb	Costs	Solidification/stabilization; Off-site disposal
Zanesville Well Field, OH	Soil	As, Cr, Hg, Pb	Soil volume was much smaller that originally projected; Determined to be too expensive	Off-site disposal
Ewan Property, OU 2, NJ (Industrial waste dumping)	Soil	Cr, Cu, Pb	Soil volume was much smaller that originally projected	Off-site disposal
Gould Inc., Portland, OR (battery site)	Soil	Pb	Soil washing was shown to be ineffective due to varying site conditions	Capping the landfill
United Scrap Lead/SIA, OH (Lead battery recycling)	Soil/sediments	As, Pb	Costs	Soil disposed off-site if Pb levels above 1550 µg/g; Containment of soil below this level
Myers Property, NJ (Pesticide Manufacturing)	Soil/sediments	Cu, Cd, Pb, As	Soil washing treatment was not successful for As during treatability study	Off-site disposal

Data extracted from [124,125]

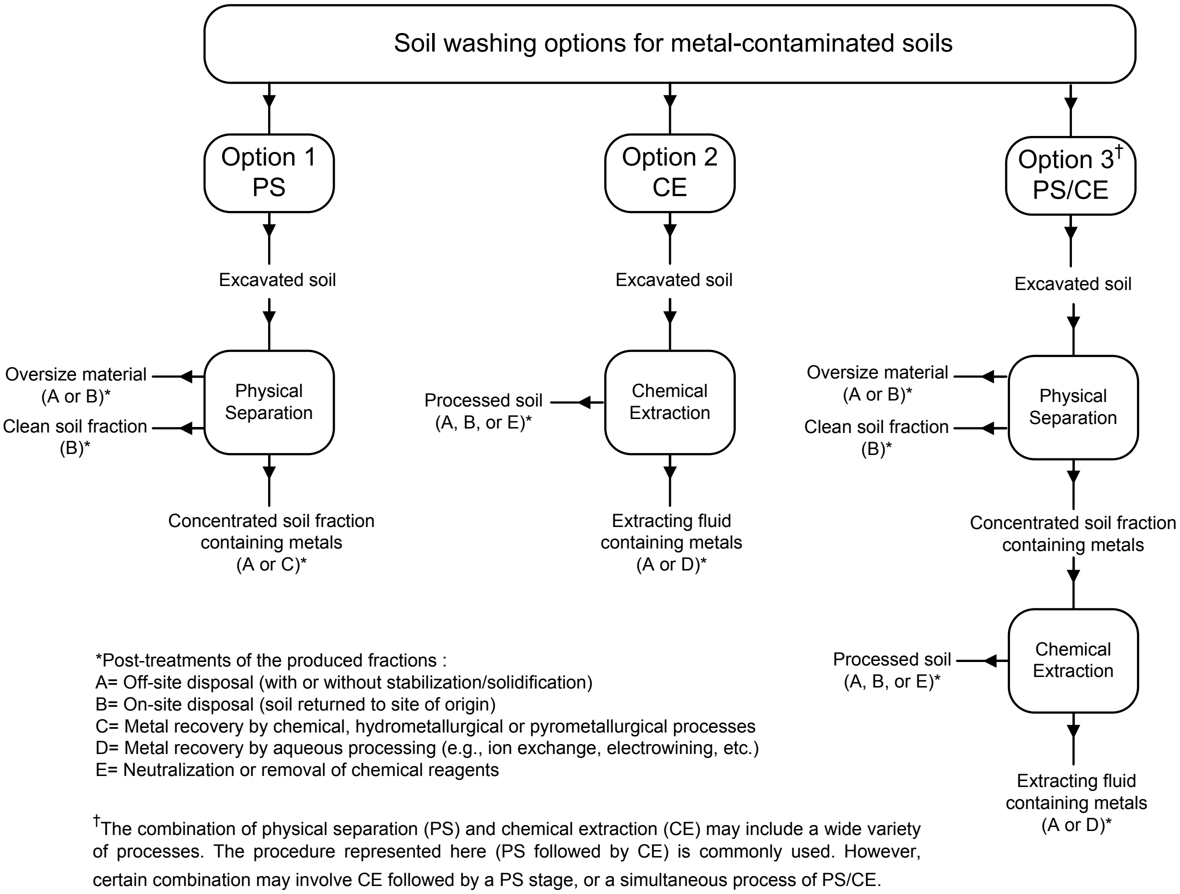
Figures

Fig. 1 Schematic diagram of typical options used in soil washing processes.

Fig. 2. Applicability of physical separation according to liberation degree of the metal phase for the particulate forms.

Fig. 3. Feed particle-size range for application of physical separation techniques. Adapted from [9,14-16,126].

Fig. 1. Schematic diagram of typical options used in soil washing processes.



*Post-treatments of the produced fractions :
A= Off-site disposal (with or without stabilization/solidification)
B= On-site disposal (soil returned to site of origin)
C= Metal recovery by chemical, hydrometallurgical or pyrometallurgical processes
D= Metal recovery by aqueous processing (e.g., ion exchange, electrowining, etc.)
E= Neutralization or removal of chemical reagents

†The combination of physical separation (PS) and chemical extraction (CE) may include a wide variety of processes. The procedure represented here (PS followed by CE) is commonly used. However, certain combination may involve CE followed by a PS stage, or a simultaneous process of PS/CE.

Fig. 2. Applicability of physical separation according to liberation degree of the metal phase for the particulate forms.

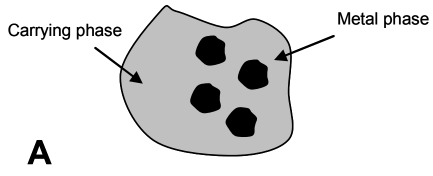
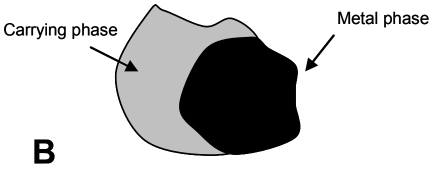
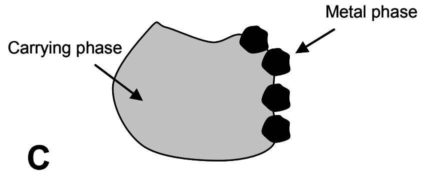
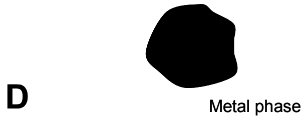
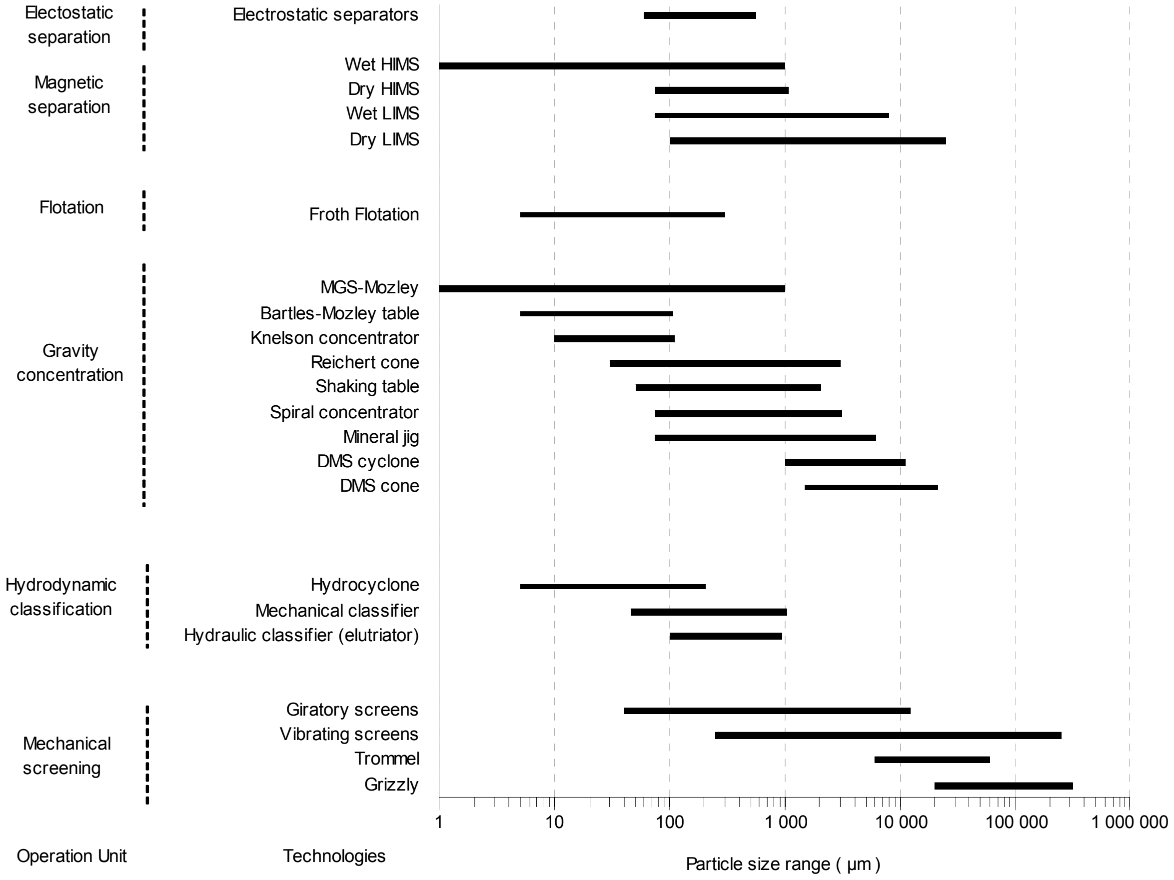
	Metal phase included in volume • Liberation degree is very low • Density depends primarily to minerals of carrying phase • Surface properties are constant but depend to carrying phase • Physical separation is very difficult or impossible • Crushing is required
	Metal phase associated • Liberation degree is medium • Density depends to minerals of metal phase and carrying phase • Surface properties are not constant • Physical separation can be applicable (gravity concentration)
	Metal phase weakly bounded on surface • Liberation degree is medium • Physical separation can be applicable if metal phase particles are liberated by e.g., attrition scrubbing
	Metal phase liberated or free • Liberation degree is very high • Density depends only to minerals of metal phase • Surface properties are constant • Physical separation is applicable (e.g., gravity concentration, froth flotation)

Fig. 3. Feed particle-size range for application of physical separation techniques. Adapted from [9,14-16,126].



DMS= Dense media separation; HIMS= High intensity magnetic separation; LIMS= Low intensity magnetic separation; MGS= Multi gravity separator

Chapitre 4: Remediation of contaminated soils by metal immobilization technologies

Résumé

Cet article fournit une revue des technologies de traitement de sol qui visent à séquestrer ou stabiliser les métaux lourds et les métalloïdes (As, Cd, Cr, Cu, Hg, Ni, Pb et Zn) fréquemment détectés dans les sols contaminés aux emplacements dangereux répertoriés en Amérique du Nord et en Europe. La discussion se focalise sur : (1) les technologies bien établies telles que la solidification/stabilisation (S/S) et les techniques chimiques Red/Ox; (2) les techniques innovatrices telles que la stabilisation chimique et/ou biologique in situ, la phytostabilisation, et la vitrification. Aux États-Unis, la technologie généralement employée pour le traitement des sols contaminés par les métaux sur les sites « Superfund » est la S/S ex situ (80% des projets de réhabilitation). Puisque la gestion à long terme des sols traités par les techniques conventionnelles de S/S ex situ est l'enfouissement, les technologies de stabilisation in situ (stabilisation chimique/biologique in situ et phytostabilisation) sont des alternatives intéressantes. Les principes de base, l'applicabilité, la fréquence d'utilisation, le statut de développement, les avantages et limitations, les traitements exigés avant et après l'application de chaque technologie sont décrits et comparés. La discussion est majoritairement basée sur une revue des applications significatives, à l'échelle pilote sur le terrain, employées aux États-Unis et en Europe pendant la période allant de 1990 à 2007. La principale combinaison des différentes méthodes utilisées est également discutée. Aussi, un bref exposé de la gestion par atténuation naturelle est présenté.

Submission to Environment International

Remediation of contaminated soils by metal immobilization technologies

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Abstract

This paper provides an overview of the remediation technologies that aim at sequestering or stabilizing the heavy metals and metalloids (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) frequently found in contaminated soils at the identified hazardous sites across North America and Europe. The discussion focuses on: (1) the established technologies such as solidification/stabilization (S/S) and chemical Red/Ox; (2) the innovative techniques such as in situ chemical/biological stabilization, phytostabilization, and vitrification. The basic principles, applicability, frequency of use, development status, advantages and limitations of each technology are described and compared. The discussion is mostly based on a review of pilot-scale and field applications performed in the US and Europe for the period 1990-2007. The combination of the different methods is also discussed. A synopsis of monitored natural attenuation (MNA) is also presented.

Keywords: Contaminated soil; Remediation technologies; Metal immobilization; Stabilization

1. Introduction

There are many sites highly contaminated by heavy metals across the United States and Europe (USEPA, 2004a; Dermont et al., in press). For instance, metals are present in 77% of the Superfund sites (National Priorities List), in 72% of the Department of Defense (DOD) sites and in 55% of the Department of Energy (DOE) sites (USEPA, 2004a). Remedial actions for soils affected by metals are a major concern. Though many sites are contaminated with metals, few soil treatment projects address metal contaminants (Dermont et al., in press).

This paper provides a review of the immobilization techniques (ex situ or in situ) for soil contaminated with arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). Immobilization techniques aim at sequestering or stabilizing metals in soil matrix by reduction of their solubility/bioavailability/toxicity in order to reduce the risks for human health and the environment.

Prior to the 1990s, the largest part of contaminated sites in Europe and the United States was managed by disposal and containment options (without pre-treatment) as a result of high treatment costs and the absence of a reuse policy. For instance, between 1982 and 2002, 55% of remedial action of Superfund sites in the United States implemented containment/disposal options (USEPA 2004a). In the late 1980s and early 1990s, the number of approaches that included treatment began to increase because of environmental legislations and policies that promote the use of permanent solutions in Europe (CLARINET, 2002) and in the United States (USEPA, 2004a). Containment and disposal options are not rigorous remediation technologies because they don't directly treat the metal contaminants. The interest in remediation treatment has been driven by the demand for technologies that are cost effective and suppress the long-term liability that is incurred by direct disposal of contaminated soils.

The discussion will specify established treatment technologies of immobilization (S/S and chemical Red/Ox methods) and emerging technologies such as phytostabilization, in situ chemical or biological stabilization, and vitrification. The technologies can be distinguished in two categories (Fig. 1): (1) the technologies that use an intensive treatment (i.e., the soil properties are strongly modified) such as S/S, vitrification, and chemical Red/Ox; (2) the in situ methods that use a non-intensive or passive treatment (i.e., the soil matrix is not strongly modified) such as in situ chemical or biological stabilization, phytostabilization, or MNA.

The treatment technology, commonly selected for metal-contaminated soils at US Superfund sites, is the ex situ solidification/stabilization (USEPA, 2000b; USEPA, 2004b; USEPA, 2007). Since long-term management of soils processing by conventional ex situ S/S is the disposal option (USEPA, 2000b), in situ immobilization technologies (in situ chemical stabilization, phytostabilization and biological stabilization) are an interesting alternative approaches (USEPA, 1997a; ITRC, 1998; Diels et al., 2002). When the excavation is impractical or when the site is very large, in situ immobilization techniques are particularly suitable to reduce environmental risks to acceptable levels (by changing the metal contaminant to a less soluble or less toxic form). The discussion provides a description and examples of field-scale applications for each treatment technology. Treatment and containment options can be used independently or in combination to achieve sufficient site remediation. Typical combinations are specified in the discussion for each technique.

2. Monitored Natural Attenuation (MNA)

The remediation of contaminated site can involve an alternative approach privileging the natural attenuation (NA) processes, which must be regularly monitored; this approach is commonly called “monitored natural attenuation” (MNA). Natural attenuation is an intrinsic process and it is not, strictly speaking, a treatment technology because it doesn't involve any unit operations to treat the metals. MNA will be regarded as a "passive treatment" of metal stabilization process. MNA is primarily applicable for remediation of soil and groundwater affected by organic contaminants (AFCEE, 2007; Mulligan and Yong, 2004). MNA may be appropriate for some metals when process results in a change in the valence state of metal that results in immobilization or toxicity reduction: e.g., reduction of Cr(VI) or oxidation of As(III) (FRTR, 2007; Wang and Mulligan, 2006). Metals ions can be retained in the soil by sorption, precipitation, complexation, or redox reactions with the soil components (mineral or organic substrates, or microorganisms), via physicochemical or biological processes (Adriano et al., 2004; Wang and Mulligan, 2006).

However, MNA alone may be insufficient for the remediation of metals in soils (very slow processes) and must be enhanced or assisted by engineering action (Adriano, 2004; Wang and Mulligan, 2006). The intrinsic metal stabilization processes in soil can be "accelerated" by using: (1) addition of mineral stabilizers and/or biosolids (i.e., in situ bio/chemical stabilization) or the use of microbial processes (i.e., enhanced-bioremediation); (3) establishment of vegetation (i.e., phytostabilization). MNA can also be used after an "active" remedial treatment.

3. Solidification/stabilization (S/S)

3.1. General description

The term solidification/stabilization (S/S), as used in this review, refers to processes that utilize treatment reagents (called reagent-based S/S process) to modify the physical/chemical characteristics of contaminated materials and to change metals to less mobile/soluble forms in order to minimize their leaching potential and to sequester them in a stabilized/solidified matrix. The present discussion excludes vitrification technologies (thermal-based S/S process), these will be addressed in a following section. In addition, the emerging techniques that use in situ (chemical) stabilization only will be discussed separately in a following section. The discussion focuses first and foremost on cement-based S/S for which ex situ application is commonly used to immobilize the metals.

Solidification refers to processes in which the metal contaminants are physically bound or enclosed within a stabilized/solidified matrix (by a chemical reaction between the contaminated materials and binding reagents or by mechanical processes). The aim of solidification processes is to change the physical characteristics of the contaminated materials by producing a stabilized material (crystalline or polymeric material) in order to: increase the strength capacity of the material, limit the contact between transport fluids and metal contaminants by reducing the permeability of materials, and decrease the exposed surface area across which leaching of metals may occur (USEPA, 1997b). Solidification of fine particles is referred to as microencapsulation, while solidification of a large block is referred to as macroencapsulation.

Stabilization involves chemical reactions that are induced between the stabilizing agent and the contaminants to reduce the mobility, solubility, or potential toxicity of metals by the formation of immobile or insoluble forms (adsorbed species, complexes, or precipitates) or by the change of the valence states.

The metals are converted into a solid compound and encapsulated in a solidified matrix that is resistant to leaching. The mechanism by which metals can be immobilized in binding agents involves the precipitation of hydroxides, silicates, carbonates, phosphates, sulfates, or sulfides within the solid matrix. Silicates, which form chemical complexes with metals, often have a greater insolubility than those of hydroxides, carbonates or sulfates precipitates (USEPA, 1995a). S/S projects use primarily inorganic binders to immobilize heavy metals. In general, inorganic binders are less expensive and easier to use than organic binders. Examples of inorganic binders include cements, pozzolanic materials, fly ashes, lime, phosphates, carbonates, silicates and sulfur-based binders (Dermatas and Meng, 2003; USEPA, 1997a, 2000b; Wang et al., 2001). Recently, Malviya and Chaudhary (2006) summarized the main physical and chemical factors affecting the S/S processes: strength of the S/S product, setting time, hydratation, carbonation, pore volume, and volume of the material treated.

3.2. Cement-based S/S

Cement-based S/S is typically appropriate for metal contaminants. This technology involves the mixing of soils with Portland-type cements and/or pozzolanic materials. Portland cement is a mixture of calcium silicates, aluminates, aluminoferrites, and sulfates. Pozzolanic materials are small spherical particles that are formed in combustion of coal (fly ash) or lime and cement kilns. The American Society for Testing and Materials (ASTM) defines pozzolan as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties". Portland cement and pozzolanic reagents chemically react with water to form solid cement and raise the pH of water which may help precipitate and immobilize some metal contaminants (FRTR, 2007). Cement-based S/S reduces the mobility of metal compounds by formation of insoluble hydroxides, carbonates, or silicates; substitution of the metal into a mineral structure; sorption; or physical encapsulation (USEPA, 1997b).

There are many potential interferences in cement-based processes such as coating of particles by organics, excessive acceleration or retardation of set times; excessive heat of hydration; pH conditions (USEPA, 1997b). Soil having high clay content or significant debris may be difficult to mix (USEPA, 1997a). Oversize reduction can be necessary to prepare the waste material before the S/S process. If volatile compounds or dust are present, off-gas treatment may be required. The presence of organic contaminants, especially volatile compounds, can be problematic in a cement-based S/S. Mixing and heating associated with binder hydration may release organic vapors. Pre-treatment may be used to remove the volatile organic compounds. The addition of silicates, modified clays, activated carbon to the binder system may improve S/S performance with organic compounds (USEPA, 1997a, 1997b).

Trivalent arsenic As(III), hexavalent chromium Cr(VI) and Hg are particularly difficult candidates for cement-based S/S. Hg is a metal that does not have low-solubility hydroxides. Cr(VI) and As(III) ions are difficult to stabilize in cement due to the formation of anionic species that are soluble at a high pH (USEPA, 1997b). However, Hg, As(III) and Cr(VI) can be pre-treated by multi-steps processes (e.g., chemical Red/Ox) that will produce an acceptable product for cement-based S/S. For example, hexavalent chromium Cr(VI) can be reduced to trivalent chromium Cr (III), which does form insoluble hydroxides. Trivalent arsenic As(III) can be treated by oxidation to pentavalent As(V) to co-precipitate with Fe. Hg can be treated by lime and sulfide (USEPA, 1997b). S/S of multiple metals can be difficult to address because chemical conditions (e.g. pH) for producing low mobility species for each metal may be different. For instance, the relatively high pH conditions that favor Pb immobilization would tend to increase mobility of As. On the other hand, the various metal species in a multiple metal waste may interact in the immobilization process (USEPA, 1995a).

3.3. Other reagent-based S/S processes

S/S by polymer microencapsulation is a thermoplastic process that involves heating (130°C to 230°C) and mixing the waste material with thermoplastic resin, such as bitumen or polyethylene, in an extrusion machine to encapsulate the metals (USEPA, 1995a). Department of energy (DOE) of the United States has demonstrated the feasibility to treat mixed wastes (radioactive wastes mixed with heavy metals) by a polyethylene encapsulation process at the bench scale (FRTR, 2007). Polymer microencapsulation has been mainly used to treat low-level radioactive wastes and appears applicable to certain metal wastes (particularly water soluble salts such as chlorides or sulfates) that are difficult to immobilize via cement-based S/S (USEPA, 1997b).

There is also a S/S technology that doesn't use physical binders (such as cement or pozzolans) or physical binding principle (e.g., adsorption, absorption, or encapsulation). For instance, the MAECTITE® process employs a chemical reaction that alters the structure of the wastes by chemical bounding to yield mineral compounds in leaching resistant molecular forms (Sevenson, 2007). The MAECTITE® technology creates crystal forms (mineral-suite forms in the barite and apatite mineral groups) that cannot be degraded physically or by the most adverse chemical conditions found in environmental settings (Sevenson, 2007). This technology has been applied in many remedial projects in the United States (under SITE program in 1992), Italy, Canada and Mexico (USEPA, 1995b).

3.4. Ex situ versus in situ techniques

S/S technologies can be performed ex situ or in situ, however ex situ applications represent about 90% of the S/S projects at Superfund sites (USEPA, 2000b). Ex situ S/S requires excavation of the soils to be treated, and the resultant material must be disposed on-site or off-site. In situ S/S uses auger systems and injector systems to add and mix reagents to the contaminated soil without excavation, leaving the resultant material in place (USEPA, 1997a). In situ application can be considered as innovative technology.

Ex situ S/S mixers can treat 75 to 150 m^3 of contaminated soil per day (USEPA, 1997b). Mobile and fixed treatment plants are available. In situ process can be typically performed to depth of 6 m in relatively homogeneous soils (FRTR, 2007) and has been demonstrated to depth of 9 m (USEPA, 1997b). The achievable depth is limited under certain heterogeneous conditions of soils; therefore, depth of contaminants may limit some types of in situ application processes.

Advantages of in situ S/S are: (1) off site disposal is avoided; (2) in situ S/S has cost advantage over ex situ applications for larger volumes; (3) in situ S/S is more suitable if volatile or semi-volatile organics are present (USEPA, 1997a, 1997b). In situ S/S has several disadvantages: (1) reagent delivery and the processing rate are less effective than for ex situ applications; (2) difficulty to verify if the mixing is sufficient; (3) in situ implementation depends on specific site conditions; (4) chemical agents addition to the soil may cause a pollution problem in itself, and may be subject to additional requirements under the land disposal restrictions; (5) future usage of the site is limited since contaminants remain on the site (FRTR, 2007; USEPA, 1997a).

3.5. Long-term management of S/S materials

Several physical and chemical tests are used to measure the potential of stabilized/solidified materials to release metals in the environment and to assess the performance of the binder. The toxicity characteristic leaching procedure (TCLP) test is typically performed to measure the effectiveness of the immobilization of metals. Strength capacity is often measured by the unconfined compressive strength (UCS) test (USEPA, 2000b). The permeability of final products must generally be less than $1\text{x}10^{-6}$ cm/sec (USEPA, 1997a). S/S techniques can be used alone or combined with other treatments to yield products or materials suitable for land disposal or, in other cases, solid products that can be applied for beneficial use. The in situ S/S technique requires often barriers systems during the process and capping systems after the treatment (NATO/CCMS, 2002). These techniques have been used as both final and interim remedial measures.

Long-term management options for the S/S remedial projects at Superfund sites include on-site disposal and off-site disposal with or without capping (USEPA, 2000b). S/S is not a long-term remediation solution because of: (1) the metal contaminants are not removed from the soil; (3) S/S processes may increase up to double the original volume of material; (3) limited data is available on long-term performance of S/S (FRTR, 2007). The long-term environment and conditions to which the solidified/stabilized material is exposed can affect their stability and provoke their degradation (USEPA, 2000b).

3.6. Field applications

The S/S technology is well-established in the USA, Canada, Japan and some European Union member states for treating a variety of wastes and contaminated soils (UKEA, 2004). However, there have been few S/S applications related to soil treatment in Europe (UKEA, 2004). CLARINET (2002) reports that implementation of S/S is available at the commercial-scale in France, Austria, Finland, Greece, Italy, Norway, and Spain. UKEA (2004) reports that S/S is currently carried out principally in Austria, the Netherlands, France, Portugal and S/S has been primarily developed in relation to the disposal of industrial wastes to landfill sites.

S/S technologies are extensively used for the treatment of soils contaminated with metals in the United States. USEPA (2007) indicates that the S/S applications (180 projects) represent 80% of remedial actions selected at Superfund sites contaminated with metals (for the period 1982-2005). S/S technologies are used almost exclusively for metal waste remediation. A comprehensive study about the use of S/S at Superfund sites indicates that the S/S was used to treat metals alone in 56% of the projects, and used to treat metals alone or in combination with other contaminants at 90% of the sites (USEPA, 2000b).

4. Vitrification

4.1. General description

Vitrification technologies refers to the thermal-based processes that use high temperatures (>1000°C) to melt the soil and to immobilize the metal contaminants in a vitrified matrix after cooling. Vitrification treatment aims at primarily reducing the mobility of metals by their incorporation into a molten glass material. Metals are enclosed within a vitrified product showing the following properties: hard, monolithic, chemically stable, leach resistant, amorphous or crystalline (USEPA, 1997b). The composition of the soil to be vitrified may also affect the strength properties of the vitrified material. Borosilicate and soda-lime are the principal glass formers and provide the basic matrix of the vitrified product (FRTR, 2007). Organic contaminants are pyrolysed (in situ) or oxidized (ex situ). Pollutant gases such as volatile compounds and products of combustion can be produced during the vitrification process. These gases must be collected and treated. Low cost materials such as sand, clay, or native soil may be added to improve certain characteristics of the final vitrified product.

The main advantages of the vitrification process compared to reagent-based S/S methods are: (1) the vitrified product, enclosing metal contaminants, is leaching resistant and chemically stable for a long period of time (USEPA, 1997b); (2) the vitrified product (ex situ applications) may be recycled and reused for construction of roads, pavements, and embankments; (3) the volume of vitrified product is typically smaller than the initial material volume (Colombo et al., 2003; Smith et al., 1995). The cost of vitrification is influenced principally by the energy requirements related to the melting process (USEPA, 1997a, b).

Table 1 summarizes the various vitrification technologies that can be used to treat metal wastes. Two main heat sources can be employed to melt and vitrify the soils at high temperatures: thermal or electrical energy. In the thermal processes, heating is carried out by combustion of fossil fuels in various combustion based melters (e.g., tank melters, cyclone melters, submerged combustion melters, rotary kiln melters or fluidized bed melting systems) (Colombo et al., 2003). There are many types of electric heating processes applicable for vitrification such as joule, electric arc, induction, plasma or microwave heating processes (Table 1). Plasma arc technology uses electricity to create a form of artificial lightning capable of reaching temperature exceeding 7,000°C (USEPA, 1992a). Such temperatures are higher than those attainable by combustion heating or joule heating. USDOE has tested the arc vitrification process, which is capable of melting hard structural metals from melted slag (silica and metal oxides) (FRTR, 2007). In this application, tests of the resultant slag showed more leach resistance compared to those obtained from high-level borosilicate glass. The main advantage of microwave heating is that the heat is produced directly and solely in the mass of the material to be heated. Another advantage is high power density (USEPA, 1992a). Vitrification may be performed in situ or ex situ. The main advantage of ex situ applications is a better control of the processing parameters (USEPA, 1997b). In the United States, ex situ applications have been more used than in situ options.

4.2. Ex situ technologies

Ex situ vitrification involves excavation, mixing, melting and vitrification of soils, off-gas treatment, forming and cooling of the vitrified product. Table 1 summarizes existing technologies. Before the melting stage, size reduction of the soils may be required to achieve homogeneous melt, especially for materials containing large debris or refractory compounds such as quartz or alumina (USEPA, 1997b). However, for arcing or plasma technologies that use extremely high temperature, size reduction is not required (USEPA, 1997b). Ex situ vitrification is normally considered a stand-alone technology. The obtained glassy products can be disposed of in landfills without problems or may be reused as clean fill, aggregate, embankment materials (Colombo et al., 2003).

Ex situ vitrification is limited (can become technically difficult or show an increasing cost) for (1) soils containing > 25% moisture content which cause excessive energy consumption; (2) soils containing volatile metals, particularly As, Cd and Hg, these metals will vaporize and therefore must be captured and treated separately; (3) soils containing metal concentrations exceeding their solubility in glass (e.g., Cr and Hg have low glass solubilities: 1 to 3% for Cr, and < 0.1% for Hg); (4) soils containing refractory compounds; (5) soils containing high content of chlorides; (6) soils containing coarse materials and debris that require size reduction and classification (except for plasma processes) (USEPA, 1995a; USEPA, 1997b).

4.3. In situ technologies

More than 170 tests of in situ vitrification at various scales have been performed on a broad range of waste types in soils and sludges (FRTR, 2007). However, this discussion is limited to vitrification technologies or remedial projects that specifically concern the treatment of soils containing metal contaminants (can also involve mixed wastes of radioactive materials and heavy metals). The discussion presents traditional and emerging technologies of in situ vitrification (ISV): (1) traditional ISV using joule heating (called GeoMelt traditional ISV), which has been used at full-scale; (2) non-traditional ISV using joule heating (called GeoMelt Planar ISV), which is currently in development; (3) ISV using plasma torch (in situ plasma vitrification, ISPV), which has been demonstrated at field-scale; (4) ISV using microwave energy, which is limited to preliminary investigations (Table 1).

4.3.1. Traditional ISV

Traditional ISV developed by Geosafe Corporation (GeoMelt technology) uses joule heating and the “top-down” procedure to heat and melt contaminated soils (USEPA 1995b). An electrical current is passed through the soil by using an array of electrodes inserted vertically into the contaminated soil. The maximum treatment depth has been demonstrated to be about 6 m (USEPA, 1995b). ISV by joule heating is limited by the following factors: (1) soils which contain organic content greater than 7 to 10%, metal content in excess of 25%, inorganic contaminants greater than 20%; (2) contaminated soil depth <1.8 m and >6 m below the ground surface; (3) presence of aquifers with high hydraulic conductivities; (4) presence of conductive materials such as pieces of metals in soils that can cause short circuiting with the inserted electrodes; (5) presence of buried liquid wastes and large debris (USEPA, 1995c; USEPA, 1997 a, b). The major factors affecting cost of in situ application are the moisture content, energy used, scale of operation (large site) and depth of treatment (USEPA, 1997a).

4.3.2. Innovative ISV technologies

Geosafe Corporation has also developed a new ISV method (called “non-traditional ISV” or “GeoMelt Planar ISV”) using the same power system (joule heating) but showing differences in the application of electrical current and in the starter-path configuration for subsurface melting (Thomas and Treat, 2002; Thomson et al., 2001). The demonstration project of subsurface Planar ISV technology at Los Alamo National Laboratory has showed higher melting efficiency and has the potential to extend at great depth (>6 m) when compared to the conventional ISV (Thomson et al., 2001). However, the non-traditional ISV option is a newer and much less tested technique by comparison to the traditional ISV.

Circeo et al. (1994) and Georgia Tech Research Institute have developed a new ISV technology that utilizes a plasma arc torch. This technology, called "In Situ Plasma Vitrification" (ISPV), requires a bottom to top in situ vitrification procedure and uses plasma torches inserted into boreholes at given depth to treat contaminated soils or landfill waste (Fox et al., 2001). It is recognized that ISVP has the potential to treat a variety of buried mixed wastes such as soils contaminated with heavy metals (Fox et al., 2001). ISPV overcomes all known deficiencies inherent to the joule-heated in-situ technologies (e.g. soil composition, depth of contamination, the presence of buried liquid wastes, conductive material and groundwater) (Fox et al., 2001). Advantages of ISPV compared to traditional ISV by joule heating are: (1) performance is independent of soil/rock conditions; (2) broad range of contaminants can be remediated; (3) remediation can be conducted at great depth; (4) "hot spots" can be selectively remediated; (5) contaminated soils/rocks and landfill deposits can be remediated, even in saturated soils or below the water table; (6) no other in situ technologies can achieve the temperatures, power levels or energy densities of ISPV; (7) plasma arc technology may reduce original landfill materials volume by as much as 90% (Fox et al., 2001). Although ISPV shows numerous advantages over the top-down approach employed by the Geosafe ISV applications, ISVP presents some disadvantages: (1) the very high operating temperatures generated by plasma process may result in much higher volatilities of waste substances, thereby increasing the problems on the off-gas treatment; (2) the limitation in the application of energy only to the walls of the bored holes rather than within the mass of waste materials, thereby heat is transferred into the waste by the slow process of conduction rather than by convective mixing of the molten glass (occurring in

ISV by joule heating), consequently the mixing of the molten glass is much less homogeneous (Thomas and Treat, 2002).

Abramovitch et al. (2003) have conducted preliminary investigations on the use of microwave energy for in situ vitrification of soil contaminated with metal ions such as Cr (VI). The soil was partially vitrified when this process was applied.

4.4. Field applications

Although vitrification has been demonstrated at full-scale, this technology is not often applied at US Superfund sites for metal-contaminated soils because vitrification is usually expensive compared to conventional reagent-based S/S. Vitrification can be used when reagent-based S/S process is unfeasible. The vitrification technique is mostly used at USDOE sites for remediation of soils contaminated with “mixed wastes” (mixture of radioactive wastes and heavy metals) (USEPA, 2000a; FRTR, 2006). According to CLARINET (2002), vitrification technology is rarely used in Europe for metal-contaminated soils remediation. The ex situ vitrification technologies have been operated for test and field demonstrations at the pilot scale and at full scale on about 10 metal-contaminated sites in North America. Traditional ISV has been commercialized, as GeoMelt™, by Geosafe Corporation. For specific remediation of soils contaminated with metals, traditional ISV, has been implemented at full-scale at one Superfund site (Table 2). The ISPV process was demonstrated at a large scale at the USDOE sites to vitrify soils contaminated with metals and radioactive wastes (Table 2).

5. Chemical Red/Ox

5.1. General description

Chemical Red/Ox method (ex situ or in situ) changes valence states (by reduction or oxidation) of metal contaminants to form species that are less toxic, more stable, less mobile, and/or inert. In soil remediation context, this chemical procedure is used for reduction of hexavalent chromium Cr(VI) to trivalent chromium Cr(III) prior to S/S process when soil is polluted by Cr(VI) ions. This chemical treatment is necessary for two main raisons: (1) Cr(VI) ion is considered far more toxic than Cr(III); (2) Cr(III) may be readily precipitated to hydroxide form over a wide range of pH values. Arsenic may be treatable by chemical oxidation since arsenate As(V) is less toxic than arsenite As(III). However no example (at field-scale) of the As(III) oxidation process is reported for soil remediation. Chemical treatment can be performed ex situ or in situ. However, in situ chemical agents must be carefully selected so that they do not further contaminate the treatment area. The primary problem associated with chemical treatment is the non-specific nature of the chemical reagents. Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions.

5.2. Field applications

Table 3 summarizes seven case studies of chemical reduction of Cr(VI) performed ex situ or in situ. This chemical procedure has been used at 4 Superfund sites: e.g., at Frontier Hard Chrome Superfund site, WA to treat source area soil (approximately 16,000 m^3). The sulfur-based reagents are often used: e.g., sodium metabisulfate and calcium polysulfide (Table 3).

6. In situ chemical stabilization

6.1. General description

In situ chemical stabilization is an emerging technique that uses the application of soil amendments (addition of mineral or organic compounds) to form less mobile, less toxic, and less bioavailable species of metals in order to reduce environmental risk (ITRC, 1997). In situ stabilization, which is also called "in place inactivation", differs from conventional S/S technologies. Conventional S/S technologies aim at sequestering or encapsulating the metals (reduction of solubility and leaching) into a hardened or solidified monolithic mass, while in situ stabilization aims at reducing the bioavailability or toxicity of metals without alteration of soil matrix properties (Martin and Ruby, 2004). Traditional S/S technologies strongly modify the physico-chemistry, permeability, structure and volume of soil treated. On the contrary, in situ stabilization does not cause a significant alteration of the soil properties because the chemical amendments involved have very low concentrations compared to those of S/S techniques (Martin and Ruby, 2004). Thus, unlike conventional S/S processes, in situ stabilization can promote revegetation of the site. The in situ stabilization strategy in soil does not actually reduce the pollutant concentration; however, environmental risks can be reduced to acceptable levels. In situ stabilization is particularly suitable for remediation of large sites.

In situ stabilization focuses on a chemical change of the metal species to reduce their toxicity or bioavailability for humans and other ecological receptors. Incorporation of chemical stabilizer agents such as phosphates and other mineral stabilizers can change metal speciation (by complexation or precipitation). The two main objectives of in situ chemical stabilization are: (1) the reduction of soil toxicity, and metal bioavailability for humans and biological receptors; (2) the improvement of soil quality in order to promote vegetation development.

Main chemical stabilizer agents involved for soil amendment are: phosphorus-based amendment, lime, fly ashes, various materials containing carbonates, iron and manganese in a variety of forms (iron oxyhydroxides, steel shot, manganese oxide, etc.), zeolites and aluminosilicates, or magnesium oxides (Adriano et al. 2004; Chlopecka and Adriano, 1997; ITRC, 1997; Martin and Ruby, 2004; Garcia et al., 2004). For example, the addition of a paper mill sludge (that contains mainly of carbonates, silicates and organic matter) to a metal-contaminated soil may decrease the mobility and the bioavailability of metals (Calace et al., 2005; Battaglia et al., 2007). The carbonate or kaolinite content in the paper mill sludge contribute to the chemical stabilization of metals and consequently in a decrease of toxicity of soil.

6.2. Phosphate stabilization

Phosphate-based soil amendment is the most investigated option to significantly decrease bioavailability of metals (primarily Pb, Cd and Zn). Much of the research in this technique has involved Pb-contaminated soils (Berti and Cunningham, 1997; Hettiarachchi and Pierzynski, 2002; Laperche et al., 1997; Rabinovitch, 1993; Ruby et al., 1994). The phosphate stabilization of Pb involves the formation of insoluble complex or mineral precipitates (Adriano et al., 2004). For instance, Maenpaa et al. (2002) showed that high phosphorus treatments (such as triple phosphate fertilizer and KH_2PO_4) significantly reduced Pb, Zn, and Cd bioavailability for earthworms, probably due to the formation of metal-phosphate complexes. USEPA (1997a) reported that trisodium phosphate (metal-chelating agent and buffering agent) forms a complex with Pb that is insoluble in water. However, the same report indicates that these fine Pb-phosphate particles are toxic by inhalation. In this case, solidification or encapsulation processes of Pb-phosphate are required to prevent air borne particulates and to provide a barrier to acids or alkaline solutions which could solubilize the Pb-phosphate (USEPA, 1997a). In addition, FRTR (2007) reported soluble phosphate processes that use the addition of various forms of phosphate and alkali agents (for pH control) to form low-solubility complex metal molecules in order to immobilize the metals over a wide pH range.

6.3. Field applications

In situ chemical stabilization is an emerging technology that is still in the research and development stage. The literature review revealed few field-scale demonstrations. The in situ stabilization by phosphates has been demonstrated at pilot/field studies for treating heavy metals, primarily Pb, Cd and Zn in soils (Adriano et al., 2004; ITRC, 1997; Martin and Ruby, 2004; NATO/CCMS, 2002). A significant example of a field-scale application is the project involving Pb-phosphate stabilization at the Joplin National Priority List (NPL) Site, MO where soils were contaminated by smelting activities (ITRC, 1997). This project has been conducted by the Inplace Inactivation and Natural Ecological Restoration (IINERT) Action Team, which is part of the USEPA Remediation Technologies Development Forum (RTDF). This field study indicated that Pb bioavailability/bioaccessibility for human receptors and Pb phytotoxicity can be reduced via addition of 1% by weight phosphoric acid plus 0.05% potassium chloride (USEPA, 2004c). Cao et al. (2003) performed a pilot-scale field study of metals-immobilization using phosphates amendment in contaminated soils located in the urban area of Northwest Jacksonville, FL. For this study, the authors conclude that phosphate amendment is more effective for Pb immobilization than Cu, Zn or Cd; and phosphate amendment resulted in a decrease of Pb phytoavailabilities. Also, pilot-and field-scales studies on stabilizing heavy metals in soil have been conducted in Europe. For example, in situ chemical stabilization was tested on several soils at Lavrion in Greece and at Motevecchio in Italy (NATO/CCMS, 2002). In this field test, stabilizers that were tested are phosphates, alumina red mud stabilized with gypsum, fly ash, compost. The goals that were targeted in this in situ chemical stabilization include reduction of Pb, Zn, Cd solubility, reduction of phytotoxicity, and development of vegetation on treated soils.

7. Biological stabilization

7.1. General description

In situ biological stabilization, as used in this review, refers to the in situ techniques that utilize biological transformations via the use of microorganisms to decrease mobility, solubility, or bioavailability of heavy metals in the contaminated soils. Bioremediation has been broadly studied to remediate metal contamination by removing metals from contaminated liquid (groundwater, wastewater, waste stream, mine drainage, etc.) (Gadd, 2000; Lovley and Coates, 1997). Those treatments are not included in this discussion. Unlike organic compounds, bioremediation cannot degrade metals. USEPA (2006) concluded that bioremediation techniques are not effective for metals (except in the case of the constructed wetlands for treating liquids). In addition high metal concentrations may have adverse effects on certain biological treatment of organic contaminants (USEPA, 2006; FRTR, 2007).

Gadd (2004) has reviewed a number of processes for metal immobilization mechanism involving microorganisms: (1) biosorption and intracellular accumulation; (2) metal-binding biomolecules; (3) metal precipitation by metal- and sulfate-reducing bacteria; (4) bacterial and fungal oxidation; (5) phosphatase-mediated metal precipitation; (6) oxalates and carbonates produced by microorganisms. Hobman (2001) reported the three best understood mechanisms for immobilization of metals: bioaccumulation, biosorption, and biomineralization. In addition, Hobman (2001) indicated other mechanism of metal immobilization: microbial reduction of metals to less soluble forms, the complexation of metals by fungal hydroxamate siderophore and the precipitation of metals by oxalic acid secreted by filamentous fungi.

Relatively few applications concern soil treatment to stabilize metals. Biological stabilization is a promising technique for stabilizing metals in soil; however, it is still largely experimental (FRTR, 2007). These techniques involve biological activity to promote the formation of less toxic and less soluble metal forms, by either creating ambient conditions (that will cause such species to form), or acting directly on the metal to change their valence state. In this review, the discussion focuses first and foremost on the treatment of the non-saturated zone. Metal immobilization in the saturated zone will be briefly described.

7.2. Biological stabilization of metals in the non-saturated zone

In situ metal stabilization enhanced by biological treatment may involve various chemical reactions such as precipitation, sorption, valence states changes, or another transformation of the metal contaminants. These treatments are limited to shallow horizons of soil. Metal stabilization in non-saturated zone uses indigenous or select microorganisms for forming less mobile species of metal. Physico-chemical stabilization methods (addition of mineral binders) markedly reduce solubility and mobility of metals but don’t completely decrease metal bioavailability for plants (Diels et al., 2002). The chemical amendments can be combined with biological procedure, which includes the use of microbial activity to reduce metal toxicity/bioavailability in soil. A main advantage of biological stabilization compared to traditional S/S using cements or mineral binders is to promote microbial and biogeochemical activity in order to re-establish vegetation.

Biomineralization uses a microorganisms activity to bind metals with ligands; this results in the formation of insoluble compounds such as metal phosphates, sulfides, hydroxides and carbonates (Hobman, 2001). Pintail System Inc. (PSI) has evaluated the use of biomineralization process for in situ stabilization of heavy metals in mine wastes under Superfund Innovative Technology Evaluation (SITE) Program (USEPA, 1995b). PSI indicates that this process can be applied to sites affected by battery recycling, or metal production activities (USEPA, 1995b).

Biosorption using microorganisms has also been studied as a remediation technique for metal immobilization. Biosorption involves the process of enhancing the metal immobilization by simulating the growth of microorganisms to “biosorb” heavy metals (Lovley and Coates, 1997). Valentine et al (1996) have studied at small-scale the biosorption of Cd and Ni by a *Bacillus simplex* strain to remediate soils contaminated with mine wastes. Bagot et al. (2006) have investigated, at laboratory-scale, biosorption of Cd for remediation of agricultural soils in order to avoid the transfer of this metal from soils to plants. The authors conclude that biosorption of heavy metals appears as a promising alternative remediation of contaminated agricultural soils because these soils are characterized by low level metal contamination and wide affected areas (Bagot et al., 2006).

7.3. Biological stabilization of metals in the saturated zone

Metal stabilization in the saturated zone, presented in this review, involves precipitation or formation of less mobile forms of metal contaminants via microbial process. For instance, sulfate reducing bacteria (SRB) is used to avoid the migration of metal contamination to groundwater by the formation of low soluble metal forms (Diels et al., 2002). Sulfate reducing bacteria (SRB) reduce metal sulfates to metal sulfide forms, which precipitate, resulting immobilization of metals. This process is primarily used to remove metals from the aqueous matrix (wastewater, industrial metal-bearing effluent or contaminated groundwater) (Gavrilescu, 2004; Zouboulis et al., 2004).

Metal immobilization using SRB has been studied at laboratory-scale to treat soils (saturated zone) contaminated with Cu, Pb and Zn (Diels et al., 2002; Groudev et al., 2001) but this method has not been demonstrated at full-scale. This technique requires an injection of an aqueous fluid containing organic compounds as a carbon source to enhance bacterial activity. Sulfate reducing bacterial systems can be used to indirectly reduce Cr (VI) to less mobile form Cr (III) (Gadd, 2004; Lovley and Coates, 1997). Also, this method can be used to remediate the abandoned hard-rock mine site where acid production is occurring with associated metal mobility, resulting from extensive sulfide mining activities (Gadd, 2000).

8. Phytostabilization

8.1. General description

Phytostabilization of metal-contaminated soils is an emerging technology that uses plants to prevent metal migration and to immobilize them by: (1) soil stabilization with root systems that minimizes wind and water erosion, percolation, and soil dispersion; (2) metal stabilization via biochemical processes occurring in roots or within the roots neighborhood (Pivetz, 2001; USEPA, 1997a). Unlike phytoextraction technology, phytostabilization is not intended to remove metal contaminants from the soil. The use of phytostabilization is more suitable at sites with shallow contamination and with a relatively low concentration levels (USEPA, 1997a).

The first purpose of phytostabilization is to re-establish a vegetative cover by using certain plant species that are tolerant to high levels of metal contamination. The vegetation cover with a dense root system mechanically stabilizes the soil matrix and reduces the erosion of soil from wind and water, thus preventing dispersal of the contaminant in runoff or fugitive dust emissions (Pivetz, 2001).

The second purpose of the phytostabilization is to achieve a sufficient reduction of the metal bioavailability to human and biological receptors. The metal stabilization process by vegetation is limited in the root zone and involves changes of soil microbiology and chemistry in this zone. The metal containment mechanism occurs through several biochemical processes: (1) absorption and accumulation onto roots; (2) precipitation within the root zone of plants; or (3) binding into humic (organic) matter through the process of humification (Pivetz, 2001). Phytostabilization involves changes valence states and complexation of metal within the roots and within the root zone (Chaney et al., 1997). Stabilization of metals also includes the non-biological process of surface sorption, due to chelation, ion exchange, and specific adsorption (Salt et al., 1995).

Plant species that have been used at field-scale phytostabilization include grasses, Indian mustard, sunflowers, tall fescue, and soybeans (USEPA, 2005a). Many other plant species are also studied for phytostabilization of metals. For instance, application of arbuscular mycoorhizas appears to be a promising solution for phytostabilization of Zn-contaminated soils (Christie et al., 2004). Environment Canada has developed a database (PHYTOREM) of 775 plants with capabilities in stabilizing or accumulating the metals (McIntyre, 2003). Phytostabilization of metals can be applied with conventional in situ stabilization that uses chemical additives (mineral stabilizers such as lime, phosphates, silicates, and fly ashes, or fertilizer).

Advantages of phytostabilization are: (1) soil removal is not required; (2) disposal of hazardous materials (eventually contaminated biomass) is not necessary; (3) establishment of the vegetative cover enhances ecosystem restoration; (4) vegetation cover minimizes soil erosion by wind and rain; (5) metal mobility is reduced within root zone to prevent metal migration to groundwater; (6) this technology is usually cost-effective for the treatment of a large site compared to solidification/stabilization methods (Pivetz, 2001; USEPA, 1997a).

Disadvantages of phytostabilization are: (1) this method is not intended to remove metals from soil; (2) metal stabilization is limited to the roots zone; (3) long-term maintenance of the vegetation is necessary since the contamination remains in place; (4) future releases of the metals and leaching must be prevented; (5) efficiency of metal stabilization must be verified because the degree of metal immobilization may be less than with other more vigorous soil stabilization technologies such as physical/chemical stabilization; (6) translocation of metals to the aboveground plant portion should be avoided to prevent the transfer of metals to the food chain; (7) research is required to study the chemical processes of metal immobilization in root zone and "binding" by the plant roots; (8) field-scale studies are required to evaluate the efficiency of processes at a large scale (Pivetz, 2001; USEPA, 1997a). A plant system that produces a permanent stabilization process is preferred, but immobilization efficiency must be verified. In certain cases, phytostabilization may to be considered as an interim containment measure (USEPA, 1997a).

8.2. Field applications

Overall, the phytostabilization technology is less applied than phytoextraction. However, phytostabilization of metal-contaminated soils has been performed in many sites at pilot/field scale and full-scale in Europe (Van der Lelie et al., 2001) and the United States (USEPA, 2005a). Table 4 summarizes some examples of projects implemented in the US, Canada and in Europe. Phytostabilization can typically be used to contain metals in soils at military sites (e.g., artillery and small arms impact area), industrial sites (e.g., abandoned smelter site), or landfills (USEPA, 2005a). Phytostabilization may be a successful way to prevent the formation of acid mine drainage (AMD) and stabilize the metals in the mine tailings (Tordoff et al., 2000). For mining site remediation, chemical or chemical stabilization is required prior to phytostabilization process

(Jennings and Krueger, 2000; Zehner et al., 2000). Recently, USEPA (2005) identified 10 field-scale applications of phytostabilization used in the United States and Canada that involved treatment of soil contaminated with heavy metals: 4 projects using phytostabilization and 6 projects simultaneously studying phytostabilization and phytoextraction procedures. Green and Hoffnagle (2004) compiled a meticulous phytoremediation field study database.

9. Combination of "non-intensive" in situ stabilization methods

The combination of soil amendments (chemical stabilizers) with biological stabilization and/or phytostabilization offers a promising alternative for remediation and revegetation of the sites affected by mining wastes. The soils affected by mine wastes were typically characterized by low pH, high acidity, low fertility, high future acid generation potential, and high concentration of soluble heavy metals. In the case of soils associated with mine wastes and acid generating mine wastes, in situ stabilization/inactivation (conventional chemical and/or biological stabilization) can be combined with phytostabilization for mining sites remediation (Jennings and Krueger, 2000; Zehner et al., 2000). Chemical stabilization aims to increasing pH and reducing metal mobility, while the main goals of biological stabilization are to increase carbon and organic matter contents, and to promote microbial activity in order to re-establish vegetation and to reduce metal bioavailability.

For instance, Zehner et al. (2000) reported a field demonstration of metal immobilization that successively combines: (1) chemical stabilization; (2) mineral fertilizer and biological amendments; (3) phytostabilization to remediate mill tailing from the Pinos Altos mining district in Grant County, NM. In this application, chemical amendment (tripe super phosphate, calcium hydroxide, and lime) was used to neutralize potential acidity of the mill tailings and to bind soluble heavy metals. Fertilizer and biological amendments (mycorrhizal fungi inoculum) were used to facilitate the phytostabilization process.

Chemical stabilization and bioremediation have been demonstrated at California Gulch Superfund Site, in Leadville, CO to treat soil contaminated with mine tailing deposits containing heavy metals such as Cd, Cu, Pb, and, Zn (USEPA, 2005b). In this field demonstration, in situ biosolids and lime addition have been used to reduce metals bioavailability, increase the pH of the tailings, and promote vegetation. The results of the one-year study indicated that this treatment (1) reduced the bioavailability of metals; (2) reduced soil toxicity; (3) improved soil quality and fertility to promote plant development and microbial activity in soil (USEPA, 2005b). Vegetation was established at the site treated with lime and biosolids. However, USEPA indicated that additional investigation will be needed to evaluate the long-term effectiveness of this treatment (USEPA, 2005b).

Van der Lelie et al. (2001) reported several successful examples of metal immobilization using soil additives (coal fly ash or zeolites) combined with phytostabilization conducted in Europe: e.g., at Maatheide in Belgium (soil contaminated with Zn and Cd); and at Prescot in United Kingdom. Using these soil amendments strongly reduces the metal availability for plant uptake and limits metal phytotoxicity, allowing revegetation of the site (Van der Lelie et al., 2001).

10. Comparison of the applicability and performance of methods

Table 5 compares efficiency of metal mobility/bioavailability reduction; the limitations relating to soil matrix to be treated, and the remediation applicability of large sites for all immobilization technologies. S/S and in situ stabilization are distinguished in this discussion. The effect on volume of material treated, metal mobility reduction and metal bioavailability for human and the environment are reported for each technology. For example, S/S technologies markedly reduce mobility and toxicity of metals but the volume of produced materials is increased. Certain technologies can treat a broad range of soil types, while others are limited by certain characteristics of the soil matrix. Overall, in situ stabilization via chemical or biological procedures and phytostabilization, are well adapted for remediation of large site, compared to conventional treatment by vitrification or S/S technologies.

Table 6 provides information on the applicability of each treatment technology according to the type of metals and mode of metal contamination (ionic/adsorbed form, particulate form and high concentration). Overall, S/S and vitrification technologies can treat high metal concentrations and broad forms of metal contamination (ionic/adsorbed and particulate forms), compared to biological stabilization and phytostabilization. However, vitrification of soils containing As, Hg, or Cr can be more difficult compared to other metals, because their compounds have low solubilities in silicates glass (USEPA, 1995a). In addition, As-compounds are often present under volatile forms, thus requiring off-gas treatment during vitrification (USEPA, 1995a). The cement-based S/S processes of Hg, As(III) and Cr(VI) compounds can also be difficult. Chemical Red/Ox pre-treatment is often applied to reduce Cr(VI) prior to S/S process.

Table 7 summarizes the pre-treatments and post-treatments that can be required for each immobilization technology. The technologies can be combined to form a “treatment train” in order to achieve complete site remediation. The material treated by conventional S/S technologies is disposed off-site or redeposited on-site.

Table 8 recapitulates frequency of use and development status in the United States. The table primarily provides a discussion on the implementation of each technology for remedial action at Superfund sites. The estimated costs, extracted from FRTR (2007), are also indicated for each technology.

11. Conclusions

Heavy metal contamination in soils is widespread at almost all sites targeted by major US remediation programs, primarily the Superfund program. The alternative treatment technologies that address metals in soils are limited. The management of metal-contaminated soils is often based on metal immobilization and/or isolation of contaminated materials (off-site disposal and in situ containment). In the United States, a large proportion of the metal-contaminated soils are excavated, treated by cement-based S/S to reduce metal mobility and then disposed (on-site or off-site). Ex situ S/S technologies are almost exclusively used at Superfund Sites contaminated with metals. In situ S/S is an alternative option that has not been extensively used yet. When Cr (VI) is present, the chemical reduction process is used as a pre-treatment module prior to conventional S/S process.

Ex situ S/S treatment is not a long-term remediation solution because: (1) metal contaminants are not eliminated; (2) volume of material is often markedly increased (up to double the original volume); (3) the long-term management of solidified/stabilized material is often off-site (or on-site) disposal; (4) limited data is available on long-term stability and integrity of solidified/stabilized material; (5) re-vegetation is not promoted; (6) backfilling with clean fill of the excavated areas is necessary if solidified/stabilized material is off-site disposed. Vitrification technology appears more suitable for treating metals mixed with radioactive materials. In situ immobilization alternatives must be encouraged instead of the use of “ex situ S/S and disposal” or “direct disposal” that are no longer considered a permanent environmental solution.

In situ containment is an emergency measure while waiting for the decision-making of a possible soil remediation procedure. When the site is very large, in situ immobilization techniques are particularly suitable to reduce environmental risk to acceptable levels (by changing metal contaminants to a less soluble or less toxic form). In general, in situ stabilization methods are often capable of providing cost savings, when compared to traditional treatment methods, and are now selected more frequently. Among in situ stabilization techniques, phytostabilization alone or in combination with chemical stabilization of soil (phosphates, silicates, and lime or mineral fertilizer additions) is one of the most promising alternative technologies for reducing metal bioavailability for human receptors but do not permit the reuse of the soil for residential occupation (residential garden, school, etc.). Phytostabilization is a proven technology that has been applied in the US and in Europe. In situ stabilization enhanced by biological treatment is a promising method for remediation of the soils affected by mining wastes. However, more field-scale tests are required to evaluate long-term integrity.

Acknowledgements

G. Dermont is thankful to the research institute “Institut National de la Recherche Scientifique Eau Terre et Environnement” (INRS-ETE) for financial support and Angus Calderhead for reviewing the article.

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Figures

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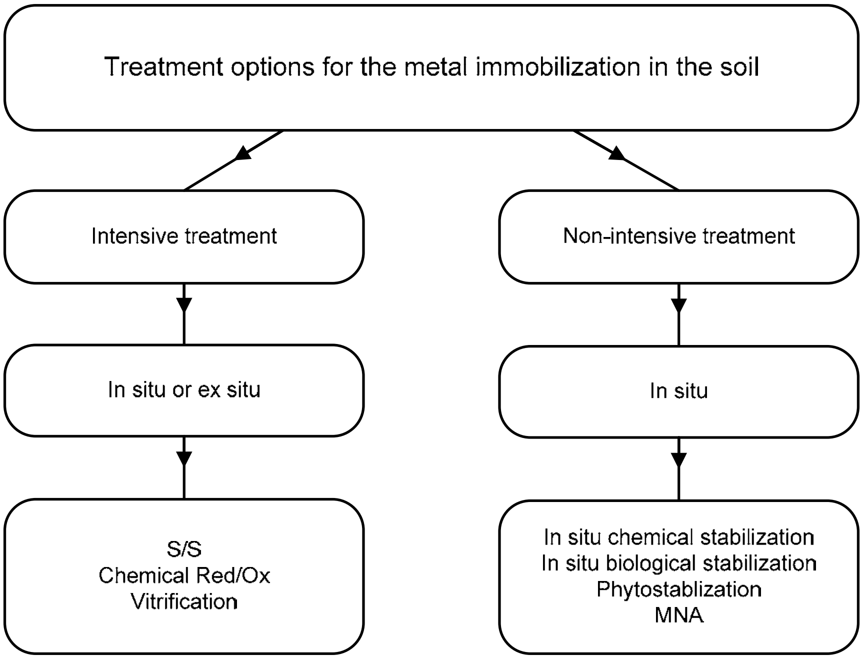
Figure 1. Immobilization methods for remediation of metal-contaminated soils



MNA= Monitored Natural Attenuation (intrinsic remediation)
S/S= Solidification/Stabilization

Tables

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Table 1. Summary of existing vitrification technologies

Heating process	Energy source	Ex situ vitrification technologies	In situ vitrification technologies
Combustion of fossil fuels (coal, natural gas, and oil)	Thermal	Combustion based melters (cyclone furnace, submerged combustion, rotating surface, fluidized bed melting systems)[a,b]	-
Joule heating	Electrical	Joule heated melters (JHM)[a,b] Transportable JHM[a]	Traditional ISV (GeoMelt ISV)[a,b,c] Non-Traditional ISV (GeoMelt Planar ISV)[c]
Electric arc heating	Electrical	Electric arc furnaces[a,b]	-
Induction heating	Electrical	Cold-crucible induction melters (CCIM)[a]	-
Plasma heating	Electrical	Plasma arc torches[a,b]	In Situ Plasma Vitrification (ISPV)[c,d]
Microwave heating	Electrical	Microwave systems[b, f, g]	ISV by microwave[e,f]

[a] Colombo et al., 2003.

[b] USEPA, 1992a.

[c] Thomas and Treat , 2002.

[d] Fox et al., 2001.

[e] Abramovitch et al., 2003.

[f] Jones et al., 2002.

[g] Jou et al., 2006 for the technical description of technologies.

Table 2. Examples of vitrification applications at full-/pilot-/laboratory-scale for metal-contaminated soils

Site/Name demonstration	Technology description	Media and metals treated	Reference
SITE demonstration: Babcock & Wilcox Cyclone Furnace, Alliance Research Center, OH	Thermal heating, cyclone furnace (ex situ)	Soil contaminated by mixed wastes with Cr, Cd, Pb	USEPA, 1992b
SITE demonstration: Cold Top system, Geotech's pilot plant in Niagara Falls, NY	Joule heating, electric resistance furnace (ex situ)	Soil contaminated with Cr	USEPA, 1999
Field-scale demonstration for USDOE, Oak Ridge National Laboratory (ORNL)	Transportable Joule heated melters (JHM) system (ex situ)	Mixed wastes with heavy metals	USDOE, 1998
SITE demonstration at Parsons Chemical Superfund Site in Grand Ledge, MI	Traditional ISV (GeoMelt ISV)	Soils contaminated with Hg, Pb	USEPA, 1995c, 1997a
Field-scale demonstration for USDOE at Los Alamos National laboratory	Non-Traditional ISV (GeoMelt Planar ISV)	Mixed wastes	Thompson et al., 2001
Commercial full-scale systems, Westinghouse Science Technology Center, Pittsburgh, PA	Plasma arc torches (ex situ)	Sediments contaminated with Hg, Cd, Pb	Mulligan et al., 2001b
Field-scale demonstration for USDOE at Savannah River Site soils, SC	In Situ Plasma Vitrification (ISPV)	Soils contaminated with mixed wastes	Blundy et al., 1996
Various demonstration tests (bench-scale)	In Situ Plasma Vitrification (ISPV)	Various metal wastes	Fox et al., 2001
Laboratory experiments	Microwave systems (ex situ)	Soils contaminated with Pb(II)	Jou, 2006
Laboratory experiments	Electric arc furnaces (ex situ)	Residues contaminated with Cr, Ni, Pb, and Zn	Hollander et al., 1996
Laboratory experiments	ISV by microwave	Soils contaminated with metal ions, primary Cr (VI)	Abramovitch et al., 2003

Note: SITE: Superfund Innovative Technology Evaluation program; Mixed wastes: wastes that contain heavy metals and radioactive metals; ISV: In Situ Vitrification

Table 3. Examples of chemical Red/Ox applications for metal-contaminated soils

Site/Name demonstration	Technology description (reagents used)	Associated technology (post-treatment)	Media treated	Metals treated	Date	Reference
Palmetto Wood Preserving Superfund Site, Dixiana, SC	Ex situ reduction (sodium metabisulfate)	Ex situ S/S	Soils	Cr (VI)	1989	USEPA/ASR, 2007
Ex situ Field-scale demonstration (drum storage area) at Bakersfield, CA	Ex situ reduction	NA	Soils	Cr (VI)	1991	USEPA, 2000a
JFD Electronics/Channel Master (Electroplating Solvent Recovery Facility) Superfund Site, Oxford, NC	Ex situ reduction (ferrous sulfate)	Ex situ S/S	Soils, sludges with sulfides	Cr (VI)	2000	USEPA/ASR, 2007
Field-scale demonstration at White Sands Missile Range, SWMU 143, NM	In situ reduction	NA	Soils	Cr (IV)	1998	FRTR, 2006
Field-scale demonstration by EPA at Morses Pond Culvert, MA	In situ reduction (calcium polysulfide)	NA	Soils	Cr (VI)	2001	FRTR, 2004
SITE field-scale demonstration at Frontier Hard Chrome, WA	In situ reduction (sulfur-based reagent)	Stabilization	Soils and GW	Cr (VI)	2003	FRTR, 2005
Valley Wood Preserving, Inc. Superfund Site, Turlock, CA	In situ reduction (calcium polysulfide)	Disposal of residuals; Groundwater treatment	Soils	Cr (VI)	2004	USEPA/ASR, 2007

Note: SITE: Superfund Innovative Technology Evaluation program; NA: not available

Table 4. Examples of phytostabilization projects at field-scale in the US, Canada, and Europe

Site/Name demonstration	Vegetation type	Media treated (site size in ha)	Metals treated	Date	Reference
Pilot/Field scale demonstration at metal-contaminated site in Dearing, KS	Hybrid poplar	Soil (0.4 ha)	Cd, Pb, Zn	1998	USEPA, 2005a
Full-scale demonstration at metal-, nitrate- and sulfate-contaminated site in Anderson, SC	Grasses, Hybrid poplar	Soil (7 ha)	Cd, Pb	OP (1993)[a]	USEPA, 2005a
Pilot/Field scale demonstration at metal-contaminated site in Port Colborne, Ontario, Canada	Corn, Soybeans, Radish, Oats, Alyssum	Soil (0.14 ha)	As, Ni, Cu	2003	USEPA, 2005a
Full-scale demonstration at the Anaconda Smelter Site in Anaconda, MT	Grasses	Soil (0.8 ha)	As, Cd, Cu	OP (1995)[a]	USEPA, 2005a
Field-scale demonstrations at contaminated playing ground Overpelt, and zinc smelter site, Lommel, Belgium (Limburgus University)	Grasses	Soil (NA)	Zn, Cd, Pb, Cu	NA	Van der Lelie et al., 2001

Note: OP: in operation; NA: not available

[a] Planting date

Table 5. Summary of the applicability and the efficiency of the immobilization technologies for metal-contaminated soils

Technology	Effect on volume of material	Effect on solubility of metals	Effect on bioavailability of metals	Potential revegetation	Applicability according to the soil type	Applicability for large sites
Solidification/Stabilization (S/S)	HI	HR	HR	No	Limitations with soils containing high clays content, large debris and high (volatile) organics content	Not adapted. Cost expensive
Vitrification	HR	VHR	VHR	No	Limitations with soils containing high moisture content, refractory compounds (alumina, quartz), debris	Not adapted. Cost very expensive
Chemical Red/Ox	NE	AR	LR	No	Limitation with soils containing coarse material and organic contaminants	Not adapted. Cost expensive
In situ chemical stabilization	NE	AR	HR	Yes	Broad range of soil types can be treated, primarily soils of mining sites	Good
Biological stabilization	NE	AR	AR	Yes	Broad range of soil types can be treated, primarily soils of mining sites	Good
Phytostabilization	NE	AR	AR	Yes	Broad range of soil types can be treated.	Very good

Note: NE= no effect; LR= low reduction; AR= average reduction; HR= high reduction; VHR= very high reduction; HI= high increase.

Table 6. Immobilization treatment technologies versus type of metals, contamination form and concentration level

Technology	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	Ionic forms[a]	Particulate forms	High Conc.
Solidification/Stabilization	◒	●	●	◒	●	●	●	◒	●	●	●
Vitrification	○	●	●	◒	●	●	●	◒	●	●	●
Chemical Red/Ox	●	○	○	●	○	○	○	○	●	○	●
In chemical situ stabilization	–	●	●	–	–	●	●	–	●	◒	◒
Biological stabilization	●	●	●	●	●	●	●	–	●	○	○
Phytostabilization	●	●	●	–	●	●	●	–	●	○	○

●	Good applicability
◒	Average applicability
○	Low applicability
–	Few data

[a] Ionic forms, or adsorbed forms (easily dissolvable/exchangeable)

Table 7. Pre-treatments and post-treatments for each immobilization technologies

	S/S	Vitrification	Chemical Red/Ox	In situ chemical stab.	Phyto-stab.	Biological stab.
Pre-treatment that may be required						
Volume reduction by physical separation/ soil washing	E	E				
Chemical Red/Ox if presence of mobile metals such as Cr (VI)	I,E					
Conversion of metal to less volatile forms (e.g., As compounds)		E				
Treatment to remove or destroy organics	E					
Dewatering and drying for wet materials		E				
In situ chemical stabilization (soil amendments)					I	I
In situ containment (barriers)	I	I	I			
Post-treatment or Residuals management						
Solidification/Stabilization			I,E			
Off-site disposal	E	E	E			
On-site disposal	I,E	E				
Capping	I,E					
Reuse of immobilized products	E[a]	E				
Off-gas treatment	I,E	I,E				
Groundwater monitoring	I	I	I			
Potential revegetation or phytoremediation				I		I

Note: Adapted from USEPA (1997b); I= in situ application; E= ex situ application

[a] For certain cases

Table 8. Status, implementation frequency and estimated cost range in the US for metal immobilization technologies

Technology	Development Status	Implementation frequency	Applications at Superfund sites contaminated with metals	Estimated cost range[a]
Solidification/Stabilization (S/S)	Full-scale	Widely used	>175 full-scale projects	\$128[b] – 248[c] /m^3 (E) \$50 – 330 /m^3 (I)
Vitrification	Full-scale	Not often used	3 applications under the SITE Demonstration Program	\$375 – 425 /ton (I)
Chemical Red/Ox	Full-scale	Moderately used	4 full-scale applications	\$190 – 660 /m^3 (E)
In situ chemical stabilization	Pilot/field-scale	In development phase; Not often used	1 pilot/field project (phosphates) and 2 pilot/field project in combination with biostabilization	NA
Biological stabilization	Pilot/field-scale	Limited applications	1 pilot/field demonstration and 2 selected projects (in pre-design)	NA
Phytostabilization	Full-scale	In development phase; Not often used	No applications at Superfund sites	\$147[b]– 2,322[c] /m^3

Note: SITE= Superfund Innovative Technology Evaluation; (I)= in situ; (E)= ex situ.

[a] Data (in US \$) extracted from FRTR (2007).

[b] For a large site and easy remedial action.

[c] For a small site and difficult remedial action.

Chapitre 5: Geochemistry and solid-phase speciation of heavy metals in urban soil contaminated by metallurgical wastes disposal: implications for metal mobilization and soil remediation

Résumé

L'étude d'un sol urbain (localisé à Montréal, Canada) pollué par les déchets métallurgiques a permis d'évaluer la mobilisation potentielle des métaux. De plus, la caractérisation du sol s'inscrit dans une perspective de décontamination par lavage du sol dans le but d'enlever les métaux. Le profil du sol (*solum*) se compose d'un horizon anthropique (remblais hétérogènes composés de sol et de déchets industriels) recouvrant un horizon de sol naturel composé de tourbe et de marne. La distribution en métal dans l'horizon de sol anthropique reflète une grande hétérogénéité spatiale et géochimique. Les métaux (As, Cd, Cu, Pb et Zn) sont aléatoirement distribués dans toutes les fractions granulométriques, et ce, bien que les particules fines soient les plus affectées. L'étude micro-spectroscopique de plus de 150 particules indique que la forme géochimique prédominante du Zn est la sphalérite, tandis que le Cu et le Pb sont distribués dans diverses formes, principalement des oxydes/hydroxydes et des carbonates. La composition chimique et minéralogique de certaines particules suggère un processus probable d'altération physico-chimique. Les facteurs d'enrichissement élevés des métaux dans l'horizon organique situé juste sous les remblais confirment cette hypothèse. Cependant, la mobilisation des métaux semble très limitée. La variabilité des formes minéralogiques des métaux est un handicap pour l'application des procédés de décontamination par lavage de sol.

Submission to Environmental Pollution, April 2008

Geochemistry and solid-phase speciation of heavy metals in urban soil contaminated by metallurgical wastes disposal: implications for metal mobilization and soil remediation

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"Capsule": Although metals appear to be speciated for the most part as insoluble geochemical forms in the landfills, the high enrichment factors of metals in the native soil suggest that the metallurgical slags were subject to the weathering processes.

Abstract

An urban soil (from Montreal, Canada) contaminated by metallurgical slags was investigated in order to assess the potential metal release and the remediation feasibility by a soil washing method. The soil profile is composed of heterogeneous landfills overlying peat and marl layers. The metal distribution in the anthropogenic soil reflected a large spatial and geochemical heterogeneity. The metals (As, Cd, Cu, Pb, and Zn) were in particulate forms and randomly distributed in all the particle-size fractions. The spatial distribution and speciation of Cu, Pb and Zn were evaluated by SEM-EDS on more than 150 metal-containing particles. This study revealed that the predominant form of Zn was sphalerite, whereas the Cu and Pb were speciated in various forms, primarily oxides and carbonates. The mineralogy of the metal-bearing particles reflected a probable weathering process. This assumption is confirmed by the high enrichment factors of metals in the organic horizon located just under the landfills. Variability in both the soil matrix and the geochemical forms of metal are a technical handicap for the potential remediation.

Keywords: Urban soils; Metallurgical slags; Heavy metals; Speciation; Enrichment factors

1. Introduction

The urban environment geochemistry of metal contaminants is an important scientific issue today (Wong et al., 2006). The presence of polluted soils in populated areas is a major concern for both risks to human health and urban development. More than 200 sites contaminated by heavy metals (primarily Cu, Pb, and Zn) were identified at Montreal, Canada by the environmental protection agency of Québec (MDDEP, 2008a). These contaminated soils are often located in sectors showing a good restoration potential of the urban environment. These sites, which are often referred to as 'brownfields', may be decontaminated, bringing economic benefits to local communities. However, the management of brownfield or urban soils polluted by metals is complicated because: (1) the contamination is frequently heterogeneous at the macro-scale (vertical and horizontal distribution of metals on site) and/or micro-scale (physical or chemical aspects of metals within the soil matrix); (2) unlike organic contaminants, metals cannot be degraded or destroyed; (3) the variability of metal forms and the soil matrix influence the environmental risk assessment and the soil treatment feasibility (Dermont et al., 2008a).

Urban soils can become contaminated by metals as a result of direct contact with industrial landfills, particularly metallurgical waste materials. Generally, metallurgical landfills (such as slags and tailings) are considered chemically inert and are therefore often assimilated with materials that are not very hazardous because the solubility and bioavailabilty of metals from metallurgical materials are low (Remon et al., 2005; Tarzia et al., 2002). Furthermore, several studies on urban contaminated soils at Montreal showed that heavy metals from the top layer (0–15 cm) were mainly in stable forms and their bioavailability was extremely low (Ge et al., 2002; Kennette et al., 2002) due to the chemical characteristics (alkaline pH or high organic matter content) of soils.

However, several studies have shown that metal-containing phases from metallurgical dumps, mining, smelting, or metal processing are not as inert as originally believed (Ettler et al., 2004; Piatak et al., 2004). For instance, the leaching tests carried out on the surface of polished sections of metallurgical slag fragments showed that acid rain may mobilise mainly Cd and Zn (Kucha et al., 1996). The leached metals from weathering of metallurgical slags may easily be re-precipitated into a new secondary geochemical/mineral phase such as metal oxides, carbonates, and sulfates (Ettler et al., 2004). In soil, weathering processes may radically alter metal-bearing particles and therefore obscure the nature of the source.

The present study has been chosen to investigate metal distribution with respect to the soil profile and the site zone, the particle-size fractions, their geochemical forms, and the morphology of the metal-bearing particles in order to assess the potential metal release and the remediation feasibility by the soil washing process. The potential release of metal contaminants was also assessed by determining the metal enrichment factor (metals/Sc, metals/Ti, metals/Al in relation to typical values in the upper crust) of the native soil located just under the landfill horizon.

Metal contaminants are frequently present in brownfield soils in various mineralogical and geochemical forms. The mobility of metals in soil depends on their geochemical forms and the nature of their interactions with solid constituents. The knowledge of the chemistry, mineralogy, and morphology of the particles containing the heavy metals is crucial in assessing the environmental risks and selecting a proper soil remediation technology. There are different methods to examine the geochemical forms of metals in the soil's solid phase: (1) chemical fractionation methods based on sequential extraction procedures (Tessier, 1979) and (2) direct approaches of solid phase speciation (particle-by-particle study) using microscopic and spectroscopic analytical techniques (see D'Amore et al., 2005 and Szaloki et al., 2004 for a review of the various instrumental methods). Metals, in the particulate phase can occur as a single component or within a complex particle of multiple components. Many recent studies specific to metal-contaminated soils focused on the assessment of the solid phase speciation of metals by spectroscopy and microscopy analytical techniques (Kennedy et al. 2002; Langmi and Watt, 2003; Manceau et al., 2000; Matera et al., 2003; Piatak et al., 2004; Roberts et al., 2002; Terzano et al., 2007; Venditti et al., 2000; Welter et al., 1999).

For this study, microscopic investigations using SEM-EDX (scanning electron microscopy/energy dispersive x-ray) were applied to identify the mineralogical forms of metals and their distribution in the solid phase of the soil matrix. The direct acquisition of compositional characteristics of metal-rich particles provides information for understanding the relationship of the metals with their environment. Also, SEM-EDX is a particularly suitable tool for predicting the treatment efficiency based on soil washing technologies (Dermont et al., 2008; Yarlagadda et al., 1995), especially physical separation (Mercier et al., 2001). Microanalyses were used to detect the presence of heavy metal contaminants and to assess elemental composition in the targeted section of the particles. The metal distribution according to the degree of mineral liberation (discrete particle, mineralogical association, inclusion, or localization of metal-bearing phase on particle surface) was also investigated.

2. Materials and methods

2.1. Site description

The study site, considered as a brownfield, occupies a surface of approximately 20 000 m^2 in a residential environment, along the Lachine Canal, Montreal, Canada. The Lachine Canal area, located in the south-east sector of the island of Montreal, was one of the main manufacturing production centres in Canada from the beginning of industrialization in the middle of the 19th century until the middle of the 20th century. The industrial activities in the surrounding area of the Lachine Canal left behind waste material, which often contains high concentrations of hazardous substances such as heavy metals. At the present time, the Lachine Canal district is undergoing a major revitalization. The urban soil under study has been strongly influenced by industrial activities, primarily metal processing industry. In addition, a wide variety of materials such as construction debris and industrial wastes (primarily slags and tailings from metal processing industries, ash, and kiln dust) have illicitly been dumped and buried at the site.

2.2. Pedological investigations

The previous in-situ observations obtained from several excavated soil pits and the soil survey with electrical resistivity tomography (ERT) provided the soil stratigraphy on the sampling area (Dermont et al., 2006). In general, the soil profile (until 3 m depth) is mainly composed of four master horizons: two anthropogenic horizons and two native horizons (Fig. 1). The native soil includes an organic horizon (O horizon; peat) overlying a mineral calcareous horizon (A horizon; marl) (Fig. 1). The map of surficial geology of Montreal island (Geological Survey of Canada, 1975) confirms that the upper native soil in the investigated sector is composed of mucky peat and marl (bog and pond episode) and of lake deposits (early St-Lawrence river episode; not represented here). The anthropogenic soil is a mixture of various solid wastes and soil material. The electrical resistivity cross-section displayed that the landfill layer reflects a great heterogeneity in its composition (Dermont et al., 2006).

Soils dominated or strongly influenced by human-made material have been recently classified in a new key reference group (*Technosols*) in World Reference Base for soil resources (FAO, 2006). Since the topsoil has an large amount (more 20% in volume) of artifacts and human-transported soil material within 150 cm of the soil surface, the brownfield soil studied may be referred as *Technosol* (FAO, 2006). The AS1 horizon (Fig. 1) contains brick fragments, building rubble, paving stones and crushed/dressed stones. The uppermost anthropogenic soil horizon may also contains some synthetic solids (plastic strips, metallic pieces, etc.) and mineralogical waste materials. However, the amount of potentially toxic industrial materials (slags, tailing, and ashes) appears less abundant in the AS1 compared to the AS2. The vegetation roots may penetrate at a shallow depth (20 cm). The AS2 horizon (Fig. 1) contains 20% or more (by volume) of artefacts mostly composed of industrial waste materials (metallurgical slags, tailings, and kiln ashes, etc). The AS2 horizon is characterized by a high heterogeneity and can be subdivided into several layers whose characteristics depend on the studied sector. In the International Union of Soil Sciences (IUSS) classification system, this urban soil can be classified as *Spolic Technosol* (FAO, 2006).

2.3. Sample collection

More than 40 soil samples were collected in order to define the vertical distribution of metals, major elements, and general soil parameters. The soil samples (2–5 kg) were collected from four soil profiles (A, B, D, and G; 3 m depth maximum) at a distance of 25 m between each soil pit on a square basis. Several samples of waste materials were also collected from each pit wall. After collection, soil samples were air-dried at ambient temperature and the coarse fragments >10 mm were removed and noted.

2.4. Particle-size distribution

The 0–2 mm and 2–10 mm fractions were separated and weighed. The soil texture of the <2 mm fraction was determined on a composite sample of each master horizon by wet sieving and a laser diffraction particle size analyzer (for <63 µm). The Wentworth scale (Carver, 1978) was used for the definition of all boundaries for textural classes except the silt-clay boundary, which is set at 2 µm, following the USDA classification system (USDA, 1993). Further, the distribution of metal contaminants (As, Cd, Cu, Pb, and Zn) and major elements (Al, Fe, Si, S, Corg, and Ca) were determined in eleven different particle-size fractions (0–20, 20–38, 38–63, 63–125, 125–250, 250–500, 500–1000, 1000–2000, 2000–4000, 4000–8000, 8000-10 000 µm) of a representative soil sample of AS2 (from the profiles A and B). The various soil particle-size fractions were divided by wet sieving with vibratory sieve shaker "Analysette 3" (Fritsch GmbH, Germany). After sieving, the fraction samples were dried, weighed and pulverized for analytical purposes.

2.5. Chemical analysis procedures

Except where indicated, the chemical analysis was performed on the <2 mm fraction of soil samples. For the chemical analysis (except for the pH), representative samples (15 g) were ground with a Brinkman agate crusher to get a fine powder (<40 µm). The results of soil chemical analysis were reported on the basis of oven-dry (105 °C) soil mass.

Total carbon (C), organic carbon (C_{org}), and nitrogen (N) contents were determined with a Leco CHNS-932 autoanalyzer. Organic carbon content (C_{org}) was measured after carbonate dissolution. The detection limits for C and N were about 0.1 wt.%. Total sulfur (S) concentration was measured with the analytical method used for the determination of trace metal concentrations.

The major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti) and Sc were analyzed by ICP-AES-radial (Perkin Elmer Optima 3000) after complete sample decomposition. The sample decomposition was done using soil fusion (200 mg of sample) with lithium metaborate ($LIBO_2$) in platinum crucible at 1025°C, followed by dissolution of fusion product with a diluted acid solution (10% v/v HNO_3 and 0.5% v/v HCl) at ambient temperature.

Total concentration of metals (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) was analyzed by ICP-AES-axial (Varian Vista AX) after a complete sample decomposition, which was carried out in two stages: (1) calcination of sample to remove organic matter (at 450°C 2 h and at 600°C 2 h); (2) multi-acid digestion on 200 mg of calcined sample in the Teflon® PFA containers. The mixed acid digestion procedure consisted of: (a) closed digestion with 1.5 mL HCl, 0.5 mL HNO_3, 2 mL HF at 125°C, 24 h; (b) digestion with $HCLO_4$ followed by the removal of the HF and $HCLO_4$ (fumes) until dry residue; (c) final dissolution of the dry residue with 5% v/v HNO_3, followed by a centrifugation step. High quality trace metal grade acids and Milli-Q® water (>18 MΩ cm) were used for the digestion procedures.

The analytical method was monitored with two NIST (National Institute of Standards and Technology, Gaithersburg, MD, U.S.) certified reference soils: SRM 2710 (highly metal-contaminated soil) and SRM 2711 (moderately metal-contaminated soil). In addition, scandium (Sc) determination accuracy was monitored with USGS (U.S. Geological Survey) reference geological materials BHVO-2 and AGV-2. The metal determination accuracy was very satisfactory, since the recovery efficiencies were between 94% and 99% for low and high metal contents of the two standard reference soils. The experimental precision was also very satisfactory since the relative standard deviations (RSD) for major elements were below 1% and for trace metals were below 5%.

2.6. Mineralogical investigations of the anthropogenic soil

The mineralogical study was performed on the 0–2 mm and 2–10 mm fractions of the AS2 (composite sample from the soil profiles A and B) in order to provide an overview of the soil components and the various metallurgical waste materials (such as metallurgical slags, ash, coal, tailings, glass silicates, metallic, alloy, solder fragments, etc.). Mineralogical identification was realized by powder X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) coupled with X-ray energy-dispersive system (EDS).

The powder X-ray diffraction was conducted with a Siemens D-5000 diffractometer at Laval University, Quebec, Canada. XRD analysis was performed on a powdered soil sample (<40 µm) with CuKα radiation at 30 mA and 40kV. The sample was scanned from 4° to 60° 2θ with a step size of 0.02° 2θ and a scan rate of 1.2s by step. XRD is a qualitative analysis to identify major mineral materials (well crystallized phases) that are present in proportion of >3–5 Wt% in the soil sample. XRD analysis cannot detect non-crystalline (amorphous) phases that could be present in the contaminated soil. Optical microscopy (reflected, polarized and natural light) and SEM-EDS investigations were carried out at the National Institute of Scientific Research (INRS-ETE, Université du Québec), Quebec, Canada. Petrography studies were conducted on polished thin section (coated with gold for SEM study) from the representative soil sample of AS2.

2.7. Microanalysis of the metal-bearing phases

The particle-by-particle study with the SEM-EDS instrumental technique provide data data on the mineralogy and chemistry of metal contaminants in the soil particulate phase of AS2: (1) identification of the mineralogical/geochemical forms of metal-bearing phases (MBP); (2) evaluation of the occurrence of these forms in the soil; (3) determination of the range of metal content in each MBP identified; (4) evaluation of the mineralogical association involving the MBP and the morphology of the metal-containing particles in order to assess the liberation degree of the MBP.

Liberation degree refers to the release availability of the “metal-bearing phase” according to the mineralogical association with the “carrying phase” (particulate forms). The term “metal-bearing phase” (MBP) refers to the geochemical form under which the metal under consideration

(Cu, Pb, and Zn) is present in the particle. The term “carrying phase” (CP) refers to another mineral or amorphous phase (Fe oxides, carbonates, silicates, glassy slag, etc.) with which the MBP can be associated. The knowledge of the liberation degree of the MBP is useful to assess the release of heavy metals and to predict the applicability of remediation methods. A classification based on 5 morphological classes was proposed (Fig. 2): (1) MBP is liberated (i.e., free particle); (2) one MBP is associated with CP, which involves a simple association; (3) several MBPs and CPs compose a complex association in the same particle; (4) MBP is included in the volume of CP; (5) MBP is specifically located on the surface of CP. In the cases (2), (4), (5), the CP occupies more than 50% of the particle volume.

The SEM-EDS investigations were primarily conducted on the following particle-size fractions: clay/silt fractions (0–20 μm and 38–63 μm) and sand fractions (63–125 μm and 125–2000 μm). To prepare each thin section, a representative dry sample was impregnated with epoxy and polished with diamond powder as the polishing agent. Polished thin sections were coated with gold for backscattered electron imaging, chemical analyses, and morphology observations.

Microanalysis was undertaken on back-scattered electron (BSE) images on a Zeiss EVO-50 scanning electron microscope (SEM) interfaced with an Oxford Instruments INCA X-ray energy-dispersive system (EDS). The whole surface was slowly scanned with the BSE detection mode (using brightness contrast) to locate the particles containing the MBP. The microanalysis was done on a large number of particles (~150) in order to estimate the solid-phase speciation of heavy metals (Cu, Pb, and Zn). SEM spectra were collected using an accelerating voltage of 20 kV and a beam current of 1–10 nA. The elemental composition of the MBP and the CP were noted. The dimension and morphological class of the particles containing MBP were also noted.

EDX analyses were treated by the Oxford Instruments INCA software to give wt.% for the various element Z ≥6 detected (C, O, F, Na, Al, Si, S, P, Cl, K, Ca, Mn, Mg, Fe, Ba, Ti, As, Cu, Cr, Ni, Pb, Zn, Sn, and Sb). Various standard reference materials were used for the EDX calibration in order to provide the elemental composition. In general, accuracy for the EDX microanalysis is about 1% and the detection sensitivity down to 0.1 wt.%. Correction procedures for atomic number Z, absorption, and fluorescence effects (ZAF) were applied in the calculation. The hydroxide species cannot be identified by EDX analysis because hydrogen (H) is not detected.

3. Results and discussion

3.1. Characterization of soil horizons

Table 1 presents the arithmetic mean and the value range of the chemical and physical characteristics for AS1, AS2, peat, and marl horizons. The particle size distribution of the landfill material strongly differs from native soil. The AS1 and AS2 horizons have a high content (30–45 %) of gravel material (2–10 mm fraction) (Table 1). The <2 mm fraction of the AS1 and AS2 reflects a sandy loam texture whereas the marl horizon has a texture of loam (according to the texture class triangle diagram; USDA, 1993) (Table 1). The organic horizon is a material intermediate between muck (sapric) and peat (fibric).

It can be seen in Table 1 and Fig. 3a that the chemical characteristics of anthropogenic soil and native soil are markedly different. The anthropogenic soil is mainly rich in Si, Fe, Al, and organic carbon. The high content of Fe may be taken as an indication of soil contamination by industrial metallic wastes. The C_{org} content includes both humus carbon (e.g., in the peat) and technogenic carbon derived from materials such as coal, ashes, or asphalt. The high content of organic carbon in the anthropogenic soil (especially AS2) is mainly due to technogenic carbon. This assumption is confirmed by the high value of C/N ratio of the AS2 horizon compared to native soil (Table 1 and Fig. 3a). Calcium content is usually low in the anthropogenic soil except for the uppermost horizon (AS1) (Table 1). The pH in the anthropogenic soil from the profile D and G is ranged from 7 to 8 (Fig. 3a). The peat bog horizon is characterized by high C_{org} content, C/N ratio <20, high LOI, high moisture content, relative low level of Ca, slightly acidic pH (from 5.6 to 7), and high sulfur content (Table 1 and Fig. 3a). The marl horizon principally contains calcareous minerals, such as calcium carbonate ($CaCO_3$) resulting from shell accumulation.

3.2. Metal concentrations in the native soil versus the anthropogenic soil

Table 1 reports the metal concentrations (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn), which may be compared with reference values established by Quebec environmental legislation (Table 2). Generally, the anthropogenic soil (AS1 and AS2) does not meet the soil quality level for residential and recreational use (i.e., the values exceed criteria B) for As, Cd, Pb, and Zn (Table 1 and Table 2). Further, the mean concentrations of Cu, Pb, and Zn in the AS2 greatly exceed the level allowed to commercial and industrial use (criteria C). Consequently, site remediation is required (Quebec's Soil Protection and Rehabilitation of Contaminated Sites Policy, MDDEP, 1999).

Fig. 3b shows an abrupt change in vertical distribution of As, Cd, Cu, Pb, and Zn between anthropogenic soil and native soil from the profiles G and D. In general, the order of metal concentration levels in the soil profile is: AS2 >> AS1 >> Peat > Marl (Table 1). The metal contents in the native soil (Table 1) are usually lower than the recommended background levels (Table 2). Unlike the distribution in the anthropogenic soil, the vertical distributions of As, Cd, Cu, Pb, and Zn concentrations do not show a high variability in the peat and marl horizons (Fig. 3c).

3.3. Spatial heterogeneity of metal contamination

The metal contamination shows a great spatial heterogeneity in the anthropogenic soil according to depth, the sector, and metal elements involved. Particularly, the AS2 horizon reflects a large concentration range of As, Cd, Cu, Pb, and Zn (Table 1). The vertical distribution of contaminants in the anthropogenic soil from profiles D and G shows a great variability in the concentration levels and the metal types involved, whereas the distribution of major elements such as S, Fe, Ca and Corg reflects few variability (Fig. 3a, b). The average concentrations of Cu, Pb, and Zn versus the two anthropogenic soil horizons in the four brownfield sectors (Fig. 4) show that: (1) the metal contamination in the AS1 horizon strongly diverges from AS2 on the same soil profile; (2) the order for metal contamination (exceeding the criteria C) in AS1 is: Cu≈ Pb > Zn; (3) the order for metal contamination in AS2 is: Zn > Pb > Cu; (4) the A and B sectors are the most affected. The sectors A and B are predominantly affected by Cu, Pb, and Zn (Fig. 4).

3.4. Geochemical heterogeneity of the landfill materials

The soil samples from AS1 and AS2 have been plotted on three ternary diagrams: Si-Ca-Fe, Si-Ca-Al, and C_{org}-Ca-Fe system (Fig. 5). In addition, the sum of Cu, Pb, and Zn concentrations of these soil samples have been reported on the same ternary diagrams according to four concentration classes (Fig. 5). The soil samples from AS1 and AS2 horizons can be slightly distinguished by their relative content of Fe, Ca, Si, Al, and C_{org}. The soil samples from AS2 have a high relative proportion of Si-Fe, Si-Al, Corg-Fe versus Ca proportion compared to samples from AS1 horizon. This suggests that AS2 horizon generally contains more Si-Fe-Al slags and coal ashes than AS1. Fig. 5 confirms that AS2 horizon contains the highest metal concentrations of Cu, Pb, and Zn. However, Fig. 5 shows that the soil samples containing the highest metal concentrations are not selectively distributed in a particular region of the ternary diagram. This suggest that the heavy metals are not associated to a specific geochemical or mineralogical phase. The mineral composition of solid waste materials containing Cu, Pb, and Zn are therefore miscellaneous and heterogeneous. The heavy metal contaminants appear rather randomly distributed in the anthropogenic soil along with alternations of variously affected zones containing a mixture of waste materials.

The cross-correlation coefficients from chemical analysis of the bulk soil samples (AS2 horizon) reflect few relationships between metal contaminants (As, Cd, Cu, Pb, and Zn) and major elements (Al, Ca, Fe, S, Si, and Corg), excepting Cd and Zn concentrations that show strong correlation (>0.9) with S content (Table 3). Zn and Cd are probably associated in a sulfide or sulfate phase. As concentrations show a medium correlation with Corg and S content. Metal concentrations show poor correlation (<0.5) with Fe, Si, Ca, Al contents. This suggests that no particular element appears to be a major controlling factor on As, Cu, and Pb distributions in the AS2 horizon.

3.5. Metal distribution versus particle-size

The distribution of metal contaminants (As, Cd, Cu, Pb, and Zn) and certain major elements (Al, Fe, Si, S, C_{org}, and Ca) was determined for 11 particle-size fractions of the AS2 soil matrix : 3 clay/silt fractions (<63 μm), 7 sand fractions (63–2000 μm), and 3 gravel fractions (>2000 μm). The study was performed on a composite sample from the A and B profiles. The distribution of major elements and soil mass is displayed in Fig. 6a and the distribution of metal contaminants is reported in Fig. 6b. In addition, the metal concentrations are compared with certain threshold values (criteria C and D) (Fig. 6b). The Ca amount in the gravel fractions was higher than that contained in the sand and silt/clay fractions (Fig. 6a). The amount of organic C and S in the fine particle-size fractions was higher than those contained in the gravel fractions

(Fig. 6a). The distributions of Al, Fe, Si, S, Corg, and Ca were relatively similar to the soil mass distribution, whereas the distribution of metals were markedly different from the soil mass distribution.

Fig. 6b clearly shows that the metal contamination is not limited to the fine particle-size fractions, but it is abundant in all particle size fractions. This suggests that the metal contamination is mainly in a particulate form, resulting from the disposal of various solid waste material. The materials involved (such as metallurgical slags, ash, tailings, etc.) reflect a large range of textures. Some metallurgical slag fragments may have a tendency to crumble. The resulting slag dust may be easily subject to weathering and chemical alteration. The metal concentrations were systematically higher in the 0–20 µm fraction: 311, 38, 3513, 3894, and 17 930 µg/g respectively for As, Cd, Cu, Pb, and Zn (Fig. 6b). This suggests that weathering of the metallurgical slags may have occurred in the anthropogenic soil, causing release of some fine particles of metallurgical slags containing the metal-bearing phases.

The distribution of contaminants within the particle-size fractions strongly differs according to the metal type (Fig. 6a). For instance, the metalloid As is predominantly located in the finest particle-size fraction, while the percentage of Cu in the gravel fraction is significant and comparable to the percentage found in the clay/silt fraction. The concentration of metalloid As increases when particle size decreases, whereas the Cd, Cu, Pb, and Zn concentrations do not show a relationship with particle size (Fig. 6b). The heavy metals (Cd, Cu, Pb, and Zn) were generally found in high concentrations within the entire size spectrum. In summary, the silt/clay fraction (25% of the soil) contains 32%, 34%, 43%, 45%, and 60% of Cu, Cd, Zn, Pb, and As respectively (Fig. 6b). The sand fraction (44% of the soil) contains 29%, 31%, 32%, 38%, and 42% of As, Zn, Cu, Cd, and Pb respectively. The gravel fraction (31% of the soil) also contains 11%, 14%, 26%, 27%, and 36% for As, Pb, Zn, Cd, and Cu respectively (Fig. 6b). However, the concentrations and the relative weight proportion of metal contaminants are less in the 8000–10 000 µm fraction compared to other gravel fractions.

3.6. Mineralogy overview of the anthropogenic soil

For the purpose of this study, the term “metallurgical wastes” includes a wide variety of materials: melted material, mineralogical slags, glassy slags, metallic object, metallic alloy and solder fragments, and metal sulfide particles. The metallurgical waste materials of the 2000–10 000 µm soil fraction (AS2 soil from the profiles A and B) reflects a great heterogeneity in colour, structure types (iridescent, glassy, blocky, vesicular, or rind surface), density, and magnetism characteristics. About 1/3 of the 2000–10 000 µm waste fragments was magnetic and composed of dense and multicoloured slag, whereas 2/3 was non magnetic and composed of coloured glassy slags and black porous particles rich in carbon. Two types of waste materials can be distinguished according to the density: (1) “heavy” material, which includes metallurgical slags; (2) “light” waste material composed of porous particle, glassy silicate slag and coal/graphite/anthracite material.

Slag pieces generally show an aggregation of various components dominated by a rust/brown coloration. The density of slag depends on the chemical composition (relative proportion of Fe oxides and silicate compounds) and the porosity (gas bubbles that have been enclosed into the slag material). The most dense fractions were mostly composed of particles having a high content of Fe oxides. Particles of intermediary density were composed of various proportions of Fe oxides, silicate compounds, and carbon material. Since many gas bubbles were included in the matrix of slag or ashed material, the apparent density of porous particles was generally low. However, the Fe/metal-phases included in a porous particle had a density greater than the bulk density of the particle.

The main mineral species (in proportion >3–5 wt.%) identified in the 0–2 mm and 2–10 mm fractions by powder X-ray diffraction (XRD) analysis were calcite ($CaCO_3$), gypsum ($CaSO_4$, $2H_2O$), hematite (αFe_2O_3), and silicate minerals: quartz (SiO_2), albite ($NaAlSi_3O_8$), mullite ($Al_6Si_2O_{13}$), and microcline ($KAlSi_3O_8$). The presence of mullite may confirm a significant occurrence of the blast-furnace slags and smelted materials in the brownfield soil under study. The presence of gypsum in AS2 horizon may result from the weathering of the pyrite and metal sulfides (Horckmans et al., 2006). No phyllosilicate materials have been detected by XRD in the contaminated soil. In addition, no heavy metals-bearing phases have been identified by XRD analysis. Optical microscopy observations (with reflected, polarized, and natural light) confirm the occurrence of Fe-oxide compounds, calcite, silicate minerals (quartz and feldspars) and indicate the presence of many fragments of metallurgical slag, metallic alloys, and coal/graphite/anthracite material.

The SEM-EDX analysis have also indicated a significant amount of Fe oxides such as magnetite (Fe_3O_4) and hematite (Fe_2O_3), barite ($BaSO_4$), Fe-Cr alloy, various metallic parts and solder/alloy fragments and coal/graphite/anthracite material. Several studies have shown that barite was often a product (secondary precipitates) from the experimental and natural alteration of metallurgical slags (Ettler et al., 2004). The microanalysis of the silicate-based slag fragments reflected a great variability in their chemical composition. The silicate slag groups involved were: Fe-silicates (may be fayallite, Fe_2SiO_4), Al-silicate, Al-K silicate, Mg silicate (may be forsterite Mg_2SiO_4), Fe-Mg silicate (may be olivine [$(Mg,Fe)_2SiO_4$]), and Ca-Fe silicate. It was difficult to strictly differentiate the material types (slags, alloy, solder, metallic pieces, etc.), which have often been affected by various weathering alterations (morphological aspects and chemical composition). A significant proportion (10–25 vol.%) of the waste materials found in the soil were the graphite-rich material resulting from the coal combustion process: blast-furnace slag or smelting furnace (dense material) and the ashed fraction (light material). The SEM-EDX study also indicated that the coal/anthracite/graphite material often contains Fe sulfides such as pyrrhotite, [$Fe_{1-x}S$] and pyrite [F_2S], but theses particles do not contain heavy metals in significant proportion (<1 wt.%).

3.7. Mineralogy of the metal-containing particles

This study was done on a representative sample of the AS2 horizon (composite sample from soil pit A and B). The various geochemical particulate phases (crystalline or amorphous) containing Cu, Pb, and Zn have been identified from elemental composition given by energy dispersive X-ray (EDX). However, EDX microanalyses may provide one spectrum corresponding to the mixture of several species containing the metals even at the micro-scale resolution of this technique. Moreover, EDX microanalysis does not provide any direct information about the identification of the atoms that are bounded to metals (metal binding), the metal valence, the atoms of the coordination sphere, the adsorption of the metal to oxyhydroxides or hydroxides. The EDX microanalysis was not adapted in our case to determine geochemical phases containing As and Cd due to their relative low concentrations in the sample. The metalloid As was sometimes detected in certain Pb-bearing phases at low concentrations (<1 wt.%). The identification was often complex due to chemical heterogeneity of slags and metal-bearing phases, or possible transformations of particular mineral species. Consequently, EDX microanalysis did not indicate well-defined phases or simple stoichiometry for all the Cu/Pb/Zn-bearing phases.

The distribution for the various Cu, Pb, and Zn-bearing phases observed in the 0–63 µm and 63–2000 µm size fractions are shown at Table 4. The distribution is estimated on a total of about 160 metal-bearing phases (MBP) containing >5 wt.% of Cu, Pb, or/and Zn. A significant part of the chemical composition of MBP corresponds to a mean value from several measures on the same MBP. Further, a significant part of the analyzed particles contains several MBP, thereby the number of investigated particles was less than 160. The classification reported in Table 4 involves different groups of geochemical metal-bearing phases (MBP): 9 copper-bearing phases (CBP), 12 lead-bearing phases (LBP), and 7 Zinc-bearing phase (ZBP). The wt.% range of Cu, Pb, and Zn are also reported for each class of geochemical phase. In this classification, the term "oxides" refers to all oxides [MO_x], hydroxides [$M(OH)_x$], and oxyhydroxides [MO_xOH_y] of a metal [M] since these chemical species cannot be distinguished with SEM-EDX study (H is not detected). Likewise, the term "oxide/carbonate" is used since it was difficult to rigorously differentiate with elemental composition the metal oxide and carbonate compounds. The distribution of CBP, LBP, and ZBP differs in the clay/silt (<63 µm) and sand (>63 µm) fractions (Table 4); however, it was difficult to clearly explain the difference of metal distributions between particle-size fractions.

Some examples of elemental composition of MBP are reported in Table 5. The presented data concern specifically the liberated MBP (i.e., discrete metal-containing particles). The data are classified according to the wt.% of Cu, Pb, and Zn in the particles; range from 24 to 86% for Cu, from 33 to 91% for Pb, from 25 to 72% for Zn. The probable mineral species are reported if the chemical composition corresponds to the stoichiometry of known mineral compounds reported in literature. In order to facilitate the comparison, Table 6 summarizes the distribution data of Cu, Pb, and Zn according to seven main mineralogical classes and five morphological classes. Several examples of metal-bearing particles involving the morphological classes (2), (3), (4), and (5) are reported in Fig. 7 and Fig. 8, whereas the Table 7 summarizes the different EDX analyzes performed on these particles.

3.7.1. Copper-bearing phases

The mineralogical/geochemical forms of CBP identified in the soil include (in order of occurrence): oxides, oxides/carbonates, silicates, sulfides and alloy/metal (Table 6). A significant proportion (about 18%) was unclassified. The probable Cu-oxide forms involved include: tenorite (CuO) and cuprite (Cu_2O) that contain 79.9 wt.% and 88.8 wt.% of Cu respectively, or mixture of both (CuO-Cu_2O) (Table 4). The Cu carbonate phase was possibly malachite [$Cu_2(CO_3)(OH)_2$]), which ideally contains 57.5 wt.% of Cu (Table 5). Copper (in variable %) was often associated with Zn and/or Sn in oxidized alloy, solder or slag particles (Table 4 and Table 5). Some fragments of brass alloy (Cu 69% - Zn 27%) and particles of oxidized Cu-Fe sulfides (probably a chalcopyrite [$CuFeS_2$]) were identified (Table 4 and Table 5). A significant content of Cu was also speciated in various compounds such as Fe oxides, silicate slags, Sn-Pb silicates or oxides, and unclassified Si-Fe-C-O slag matrix (Table 4). Although the copper-bearing particles were mostly isolated, a significant proportion of CBP was involved in simple or complex associations or located on surface of the particle (Table 6).

3.7.2. Lead-bearing phases

The geochemical forms of LBP were very diverse: oxides, carbonates, oxide/carbonates, oxides/fluorides, sulfides, silicates, and other unclassified phases (Table 5 and Table 6). No particular geochemical phase was preponderant. However, Pb oxides and Pb oxides/carbonates were the most abundant mineralogical forms found in the Montreal brownfield soil (Table 4 and Table 5). The Pb carbonates, which were also classified in the "oxides/carbonates" class, probably involved cerussite [$PbCO_3$] and/or hydrocerussite [$2PbCO_3 \bullet Pb(OH)_2$], which ideally contain 77.5 wt.% and 75.4 wt.% of Pb respectively (Table 4). For instance, Fig. 7a shows a particle (<20 μm) composed of Pb oxide/carbonate (75 wt.% of Pb) associated with Fe oxide.

The occurence of mixture of oxide, carbonate and hydrocarbonate forms of Pb in the AS2 horizon may be due to the alteration of oxide form of Pb such as litharge (PbO) by the following sequence: litharge → hydrocerussite → cerussite (Vantelon et al., 2005). Lead in variable wt.% was often chemically associated with Sn/Sb in oxide or oxide/carbonate phases, which probably resulted from the weathering of alloy or solder fragment. Several free particles of galena (PbS) and slightly oxidized sulfide phase (mixture of PbS and $PbSO_4$) were identified (Table 5), suggesting the weathering process (oxidation) of galena particles. About 62% of the LBP were often liberated (discrete particles) (Table 6). The LBP can be associated with other MBP or a non-metallic CP, which was often Fe-oxide and various silicate phases. For instance, Fig. 7b shows a particle composed of Pb-Al-Fe-Ca silicate (occupying 20% of particle) associated with Fe oxide.

3.7.3. Zinc-bearing phases

Zn was primarily in discrete sphalerite/wurtzite particles [(Zn,Fe)S] (~70%) (Table 4). The proportion of free particles for the ZBP was elevated (77%) compared to those of Cu and Pb (Table 6). The EDX analysis revealed that numerous sphalerite particles studied may have a significant Fe content (4–8 wt.%) and a low Mn content (0–2 wt.%) (Table 5). Despite strong correlation of Zn, Cd, and S in the bulk soil sample (Table 3), Cd was not found in the sphalerite particles. EDX microanalysis was not precise enough to detect a low Cd concentration in the particle (<0.1 wt.%). Some phases analyzed may involve a mixture of sphalerite [(Zn,Fe)S] and zincite [(Zn,Mn)O] or hydroxides species [$Zn(OH)_2$]. In addition, many sphalerite particles observed were strongly altered in their morphology, thus confirming weathering processes in the soil. For instance, Fig. 7d displays a partly decomposed sphalerite particle cemented with a Si-C-Ca-Fe-O phase containing Pb (9%) and Zn (6%). In addition, Fig. 7d shows Zn sulfate filled fractures in the sphalerite particle. In contact with the atmosphere, oxidation of ZnS phase may release Zn into the soil solution which may be partly retained in the soil solid phase by Fe and Mn oxy-hydroxide compounds that are present in the soil (Manceau et al., 2000; Roberts et al., 2002). Moreover, at alkaline soil pH values (pH 7–8 in the AS2 horizon), Zn solubility may be primarily influenced by the precipitation of Zn hydroxides [$Zn(OH)_2$], Zn carbonates [$Zn(CO_3)$] and Zn-Fe oxides [$Zn(Fe_2O_4)$] (Roberts et al., 2002). Approximately 20% of Zn was speciated in various oxide compounds (mainly associated phases) and Cu-Zn alloy (free particles) (Table 6). No Zn oxide/carbonate phases such as smithsonite [$Zn(CO_3)$] were detected in the AS2 horizon. Zn, in variable wt.%, may be chemically associated with Pb, Sb, Sn, or Fe in oxide phases. For instance, Fig. 7e illustrates a partly eroded particle of Zn oxide intermixed with Zn-Fe alloy with a Pb-Zn oxide phase located on the surface. Fig. 7f shows a Sn oxide fragment with Sn-Zn-Cu oxide/silicate/carbonate phase located on the surface. Moreover, Sn-Zn oxide/carbonate (with Cu 2–3 wt.%) filled certain fractures in the Sn oxide part (Fig. 7f), suggesting a dissolution process of the Zn-bearing phase and re-precipitation in Zn oxide/carbonate phase. The occurrence of Fe-Zn oxide, possibly franklinite ($ZnFe_2O_4$) was low in the studied soil (10% of Zn-bearing phases) (Table 4).

3.7.4. Association of Cu, Pb and Zn

The occurrence of the metal-bearing phases containing simultaneously Cu, Pb, and/or Zn (i.e., chemical association or mixture of mineral phases) were evaluated. The Pb-Zn association involved 50% of the cases (Fig. 7c, e, and Fig. 8c) followed by the Cu-Zn association (25% of the cases; e.g., Fig. 7f) and Cu-Zn-Pb association (25% of the cases; e.g., Fig. 8a, d). The Cu-Pb chemical association was not often observed. For the Pb-Zn association, the %Pb was often greater than the %Zn and occured in Fe-Si, Al-Si or Al-K-Si compounds (slags). For instance,

Fig. 8c shows a complex particle (50–60 µm) composed of multiple Pb-Zn or Pb-bearing phases included in a Si-Al-K-Ca-Fe-O slag. Fig. 7c shows a particle composed of Pb-Zn-Ba silicate associated with a Mg silicate. For the Cu-Zn association, the %Zn is largely greater than the %Cu (Fig. 7f).

3.7.5. Morphological classes of the metal-bearing particles

The distribution summary of morphological classes of particles involving the MBP is reported in Table 6. In general, the majority of MBP were liberated (i.e., discrete particles). Simple association represented less than 10% of the metal-bearing particles. For the morphological classes (2), (3), and (4) (Table 6), the composition of CP was (according to their occurrence): Fe oxides, Sn oxides, Al-Mg silicate slags and Si-Fe slags, or another MBP. For class (5) (Table 6), the composition of CP was Sn oxides (alloy or solder fragment), quartz, and ilmenite ($FeTiO_3$). A significant proportion of metal-containing particles was represented by a complex association involving several Cu/Pb/Zn-bearing phases and carrying phases (Table 6, Fig. 7e, and Fig. 8c).

Numerous particles involving metal-sulfides and alloy/solder/metallic-slag particles are altered respectively to sulfates and oxides/hydroxides or carbonates. Thus, a zone of alteration may be present on their surface. In addition, the microanalysis showed weathering processes involving dissolution and reprecipitation reactions of metal-bearing phases. For instance, Fig. 8a shows a particle (75–85 µm) of ilmenite ($FeTiO_3$) with an important degradation layer of Pb-Ti-Fe-Cu-Zn-Ca oxide, suggesting a substitution or precipitation processes involving divalent ions such as Ca^{2+} and $Metal^{2+}$ on the surface of the ilmenite grain. Fig. 8b shows a quartz grain (65–80 µm) finely coated by a multi-metallic phase (Pb, Cu, Zn, and Fe), suggesting a precipitation of secondary mineral phase (probably mixture of oxyhydroxides, hydroxides, and/or carbonates) on the surface of the quartz grain. Furthermore, the MBP can be incorporated in the CP. For instance, Fig. 8d displays a Pb-Cu oxide phase included in a mineralogical phase composed of Fe oxide and silicate. The occurrence of the morphological classes (4) and (5) was not significant compared to other morphological states (Table 6).

3.8. Metal enrichment factors in the native soil

Despite a high total concentration in the upper anthropogenic soil, the metal contamination level in the native soil was generally below the background values reported by Quebec legislation for this geological area (Fig. 3c). This suggests that there was not much metal mobilization from the landfill layer to the peat and marl horizons. In addition, the heavy metals (Cu, Pb, and Zn) appear to be speciated for the most part as insoluble geochemical particulate forms (Table 4 and Table 6). However, some examples of micrographs (Fig. 7d, f and Fig. 8a, b) and chemical composition of metal-bearing phases (Table 7) reflected a probable weathering process of the initial particulate compounds containing Cu, Pb, and Zn.

The interpretation of the metal enrichment factors may help to assess a possible "contamination" for the native soil horizons. The values of the elements in the upper crust (Wedepohl, 1995) provide a useful point of reference, and normalizing metal/Sc, metal/Ti, metal/Al ratios to these values is a common convention (Reimann and Caritat, 2005; Shotyk et al., 1996). Metal/Sc, metal/Ti, metal/Al ratios were divided by these corresponding ratios in typical crustal material to yield the EF for each metal (Eq. 1).

$$Metal\ \mathrm{EF}(X) = \frac{(Metal\,/\,X)_{\text{Sample}}}{(Metal\,/\,X)_{\text{Upper Crust}}} \quad \text{(Eq. 1)}$$

With

$Metal =$ Concentration of metal under consideration (As, Cd, Cu, Pb, and Zn)

$X =$ Concentration of the chosen "reference element" (Sc, Ti, and Al)

Table 8 clearly shows that metals EFs were high in peat horizon compared to the marl horizon. Depending on what reference element is chosen (i.e., Sc, Ti, or Al), the “contamination” effects may appear to be more or less significant. Particularly, metals EFs (Sc) were approximately 8–25 times higher in the peat horizon compared to the metals EFs (Sc) in the marl horizon (Table 8). The Pb EFs appeared insignificant when compared to the As, Cd, Cu, and Zn EFs. The EFs order according to metal type was Cd >> Cu ≈ As > Zn > Pb. The higher metals EFs in the peat may be due to weathering and leaching process of the solid waste material overlying the peat horizon. Although EFs are often used to discriminate lithogenic or anthropogenic sources of metal contaminants in peat and soils, EFs cannot be used as sensitive tools to prove an anthropogenic impact on the environment (Reimann and Caritat, 2005).

3.9. Potential mobilization of metal contaminants

The potential anthropogenic sources of metals in the peat horizon at the studied area may include: (1) direct contamination by toxic discharges during the intense industrial development in the Lachine Canal area (1850–1950); (2) indirect contamination by the leached metals from the landfill materials, which were disposed over the peat horizon (recent episode, after 1950); (3) the snow collected from the city streets that was dumped on the site (practice on the site since several decades), which may contain heavy metal and high salt content; (4) metal contamination due to atmospheric deposition. In addition, horizontal groundwater flow may transport metal ions or soluble metal-complexes in the saturated horizon (groundwater level is located between 2.5 and 3 m in the study area).

Although metal concentrations measured in the peat are very low, the enrichment of metals (As, Cd, Cu, Pb, and Zn) in the native soil suggests that the metallurgical slags in the upper layer landfill were subject to the weathering processes. The weathering of metallurgical waste materials may involve several episodes (slow processes): (1) liberation of the very fine metal-rich particles by crumbling of metallurgical waste fragment; (2) chemical alteration (e.g., oxidation, carbonation, etc.) and dissolution of the mineral phase containing the metals, thus releasing the free metal ions in soil solution. For instance, the metal sulfides may be oxidized by weathering processes (slow processes). Ramos Arroyo and Siebe (2007) showed that the relative oxidation rate of sulfides (from tailings) followed the order: $PbS > ZnS > CuFeS_2$.

In the soil solution, metals may be complexed with organic or inorganic ligands, and/or occur as free hydrated metal ions. Free metal ions species are generally recognized as the principal parameter that controls the toxicity of metals in the soil solution. The resulting metal ions may be retained by the mineral, organic or biological components of the AS2 horizon via precipitation, adsorption, ion exchange, red-ox, acid-base reactions, or complexation, processes (Adriano et al., 2004). The chemical condition in AS2 (pH>6; the presence of the Fe, Al and Mn oxides, sulfates and carbonates) should be unfavorable for the mobilization of the metal cations such as Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}. In these conditions, the dissolved metal cations may be precipitated in hydroxides, sulfate, carbonate, or hydrocarbonate forms. Furthermore, the presence of Ca^{2+} ions from calcite and gypsum in the soil solution AS2 should be favourable to immobilize oxyanions of As, although the competitions of other anions HCO_3^- and SO_4^{2-} may be reduce the As immobilization process (Cornelis et al., 2008; Wang and Mulligan, 2006).

Peat horizon could play an adsorbent role for the eventual leached metals from the upper landfill layer. The peat, rich in organic matter (OM), is generally considered as a material that immobilizes ionic and aerosol forms of heavy metals (such as Cd, Cu, Ni, Pb, and Zn) and metalloid As (Jackson et al., 2004; Rausch et al., 2005; Shotyk et al., 1996). Adriano et al. (2004) reported the general order of affinity of divalent metal cations for OM: $Cu^{2+} > Cd^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+}$. Under oxygen-free, "reducing" conditions in peat, certain bacteria (sulfate-reducing bacteria) use sulfate in their metabolism, produce hydrogen sulfide as a by-product and acidify the medium by oxidation of the reduced S compounds. Hydrogen sulfide is very reactive with dissolved metals and will quickly form highly insoluble metal sulfides in the peat when present in sufficient concentrations. Other processes such as the complexation/adsorption of metal ions by the organic components or the admixing of mineral phases with the peat may also be important in influencing the distribution of metals in the peat horizon.. Furthermore, oxyanions of the metalloid As may be easily immobilized in peat horizon by metal complexation with humic and fulvic acids (Wang and Mulligan, 2006). The cationic metals in the peat horizon can be leached in certain conditions, specially in acidic conditions (Rausch et al., 2005). However, the pH condition in the anthropogenic soil (from 7 to 8) and in the peat horizon (from 5.6 to 6.4) was not favourable for mobilizing metals in the soil profile (Fig. 3c). The dissolved organic carbon (DOC) may also play an important role in the mobilization and transport of dissolved metals in the peatland systems due to strong complexation potential of certain metals with DOC (Rothwell et al., 2007).

In addition, SNC Lavalin Environnement (1996) indicates that the studied area is usually used as a dumping site of used-snow. Zinger and Delisle (1988) have showed that in the city of Montreal the used-snow may contain a high content of heavy metals (mostly Pb), which are present in fine particles (<63 µm). Moreover, the discharge of de-icing chloride salts with Na, Ca, Mg, and K ions from the deposits of used-snow on the site may increase the mobilization of certain toxic metal ions by saturation of the cationic exchange capacity (CEC) of soil, this effect being particulary important for peat. In addition, the presence of the chloride anions Cl^- (from de-icing salts) having complexing properties may reduce the sorption capacity and binding strength of organic matter (peat horizon) for metal ions (Twardowska and Kyziol, 2003).

3.10. Soil remediation feasibility

The soil characteristics, metal concentration, metal fractionation, and metal speciation are important influencing factors for soil remediation. In addition, the selection of remedial approach for metal-contaminated soils is contingent upon several factors such as: future use of site, hydrogeological conditions, site size, environment situation (whether the site is an industrial, urban, rural, woodland, etc), remediation cost, and time allowed. The remediation of metal-contaminated soils traditionally involves soil excavation followed by the solidification/stabilization (S/S) and/or disposal methods. The treatment technologies alternative to conventional ex situ S/S include soil washing, phytoremediation, in situ chemical stabilization (using soil amendments such as phosphates, Fe oxides, carbonates, clays, bio-solids, etc.) and electrokinetics methods (Dermont et al., 2008a; Kumpiene et al., 2008; Lebeau et al., 2008; Lestan et al., 2008).

Electrokinetic remediation is applicable only to saturated and partially saturated soils (Lageman et al., 2005). Although the phytoremediation is a promising technology for treating urban soils affected by heavy metals (Wong et al., 2006), it is not appropriate for the restoration of the urban site under study because of: (1) the process duration is too long versus the time allowed for the area revitalization; (2) the application is limited to depth of root zone (topsoil); (3) the metal concentrations are high; (4) the metal geochemical forms involved are not relevant for the phytoextraction (even with chelant-enhanced or bioaugmentation-assisted methods). When the excavation is impractical or when the polluted site is very large, in situ metal immobilization techniques including soil amendments and phytostabilization are particularly suitable to reduce environmental risks to acceptable levels by changing the metal contaminant to a less soluble or less toxic form (Adriano et al., 2004; Kumpiene et al., 2008). However, in the urban environment where the brownfield must be quickly revitalized (municipal development and revitalization plan), the ex situ remedial options such as soil washing technologies are more suitable as soil excavation permanently eliminates the contaminated materials from the site.

Soil washing methods include a wide array of physical, chemical, or biological procedures for the removal of metals from soils (Dermont et al., 2008b; Mulligan, 2005; Mulligan and Wang, 2006). In general, physical separation is primarily applicable when metal contaminants are in particulate forms (ideally liberated particle), while chemical extraction is primarily suitable for ionic forms adsorbed on soil or non-detrital metals (Dermont et al., 2008b). The gravity concentration may be efficiently used for separating Pb-rich particles from the brownfield soil because the Pb minerals (such as galena and cerussite) reflect a high density (from 6.5 to 7.5 g/cm^3) compared to the main minerals composing the AS2 horizon such as calcite, gypsum, quartz, feldspar, and hematite (from 2.5 to 5.3 g/cm^3). On the other hand, the separation of Zn-bearing particles from soil matrix by gravity concentration will be ineffective because of low density of sphalerite (4.0 g/cm^3) compared to Fe oxides such as hematite (5.3 g/cm^3). Froth flotation is a selective process that exploits difference in surface properties of mineral particles. Usually, the metal-sulfide minerals (such as sphalerite, galena, chalcopyrite, etc.) are easier to concentrate by flotation than the oxide-type minerals because the surfaces of sulfides are more hydrophobic. A pre-treatment by sulfidization of the soil pulp may be used before the flotation process to form a sulfide film on the surface of metal oxide/carbonate particles (Vanthuyne et al., 2003). The common gravity concentrators (jigs, shaking tables, and spirals) are mainly appropriate for sand-sized soil. Since gravel fraction contains a significant contamination, a grinding step should be applied to obtain an appropriate particle-size range. The separation selectivity with mechanical cell flotation is usually not effective for very fine particles <10 µm (Vanthuyne et al., 2003).

4. Conclusions

The metal distribution in an urban soil affected by metallurgical slags was investigated in order to assess the potential metal release and the soil remediation feasibility. In the landfill horizon, the metal contamination showed a large heterogeneity with respect to: (1) the spatial distribution; (2) the chemical composition of the soil samples; (3) the metal distribution versus the particle-size; (4) the geochemical forms of metals; (5) the morphological aspects of metal-containing particles. Some particles reflected a probable weathering process of geochemical phases containing Cu, Pb, and Zn. This assumption is confirmed by a large metal enrichment factor (metals/Sc, metals/Ti, metals/Al in relation to the typical values in the upper crust) in the organic horizon (peat) located just under the landfill horizon, whereas the metals EFs were low in the lower mineral horizon (marl). The source of metal contamination in the peat horizon may be assessed by the vertical distribution of the Pb isotopic ratios in the soil profile.

In a site remediation perspective, the polluted soil may be excavated and treated by soil washing, especially physical separation techniques. However, the metal fractionation in all the particle size-fractions and the great heterogeneity of the mineralogical forms may cause the failure of soil washing process and may increase the complexity of the treatment train.

Acknowledgements

G. Dermont is thankful to the "Institut National de la Recherche Scientifique Eau Terre et Environnement" (INRS-ETE) for their financial support. We would also like to thank Angus Calderhead and Kathrine Gauvin for their useful comments.

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Tables

List of Tables

Table 1. Mean and ranges of chemical and physical characteristics for the master horizon (soil samples from profiles A, B, G, and D)

Parameters	DL	AS1 Horizon (n= 12)		AS2 Horizon (n= 17)		Peat Horizon (n= 8)		Marl Horizon (n= 3)	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
Major Elements (wt.%)[a]									
Al_2O_3	0.013	8.69	7.18 – 10.20	12.66	6.80 – 19.65	1.23	0.15 – 4.25	0.30	0.28 – 0.30
CaO	0.011	17.35	9.23 – 24.35	4.06	1.82 – 14.13	7.42	4.20 – 9.23	45.50	44.91 – 45.05
Fe_2O_3	0.010	6.43	4.58 – 9.15	15.87	8.44 – 29.31	0.71	0.14 – 2.14	0.31	0.31 – 0.33
K_2O	0.012	1.95	1.58 – 3.20	1.34	0.46 – 2.32	0.22	0.05 – 0.78	0.07	0.07 – 0.08
MgO	0.006	2.27	1.29 – 3.48	0.98	0.48 – 3.40	0.40	0.25 – 0.83	0.63	0.63 – 0.65
MnO	0.002	0.09	0.05 – 0.12	0.10	0.03 – 0.23	0.02	0.01 – 0.05	0.05	0.05 – 0.05
Na_2O	0.011	1.08	0.71 – 1.68	0.92	0.25 – 2.54	0.49	0.35 – 0.85	0.09	0.09 – 0.10
P_2O_5	0.014	0.22	0.16 – 0.29	0.19	0.11 – 0.55	0.11	0.06 – 0.32	<DL	<DL – <DL
SiO_2	0.064	39.79	28.67 – 59.90	35.73	15.83 – 51.34	4.28	0.21 – 13.91	1.21	1.18 – 1.24
TiO_2	0.0002	0.47	0.11 – 0.74	0.41	0.08 – 1.03	0.07	0.01 – 0.26	0.01	0.01 – 0.01
LOI (1025°C)	-	21.3	11.8 – 28.0	26.9	16.2 – 56.6	82.8	62.2 – 89.5	49.3	49.3 – 49.3
Sum oxides+LOI	-	99.6		99.2		97.8		97.5	
C_{Org}	0.10	5.4	2.0 – 12.2	16.5	6.5 – 41.7	37.0	23.3 – 43.7	6.8	6.8 – 6.8
C	0.10	8.4	4.4 – 14.8	19.0	7.9 – 45.6	40.5	27.6 – 46.0	16.6	16.5 – 16.6
N	0.10	0.19	0.10 – 0.42	0.41	0.19 – 1.00	2.09	1.41 – 2.60	0.55	0.55 – 0.56
S	0.10	0.35	0.11 – 0.68	0.74	0.14 – 3.88	3.76	1.37 – 5.82	0.52	0.51 – 0.53
Moisture content	-	1.1	0.7 – 2.5	1.9	0.7 – 5.4	12.3	9.4 – 16.5	1.4	1.4 – 1.4
C/N	-	28	15 – 39	39	21 – 53	18	16 – 20	18	18 – 18
$pH_{(H2O)}$	-	7.7	7.3 – 8.1	7.2	3.9 – 7.9	6.4	5.6 – 7.0	7.6	7.6 – 7.6
Metals (µg/g)									
As	0.63	20.7	6.5 – 77.9	53.2	18.3 – 117.3	5.1	2.9 – 7.0	1.67	1.52 – 1.82
Cd	0.02	4.2	1.5 – 8.3	18.8	3.1 – 100.4	0.71	0.24 – 1.65	0.11	0.10 – 0.12
Co	0.17	16.7	14.4 – 22.6	29.6	14.9 – 47.3	2.9	0.6 – 9.6	0.31	0.26 – 0.37
Cr	0.12	112	49 – 269	185	45 – 1215	17	5 – 38	6.8	6.6 – 7.1
Cu	0.04	357	40 – 1078	850	88 – 4017	44	17 – 109	11	11 – 12
Ni	0.22	49	24 – 72	76	34 – 121	17	10 – 26	5.3	5.3 – 5.4
Pb	0.57	487	38 – 1551	1570	89 – 7603	31	5 – 111	4.7	4.4 – 5.1
Zn	0.10	709	133 – 1366	5780	94 – 29411	125	24 – 361	13	12 – 14
Particle size distribution									
2–10 mm / <2 mm	%	45/55		31/69		1/99		4/96	
<2mm: Sand/ Silt/ Clay	%	69/24/7		64/30/6		ND (Peat)		48/32/20	

[a] Data given in oxide form; DL= detection limit; ND= not determined; LOI= loss on ignition

Table 2. Acceptable metal concentrations in soil for Quebec legislation

Threshold values	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
Criteria A : Background level[a]	6	1.5	15	85	40	50	50	110
Criteria B: Residential and recreational site use[a]	30	5	50	250	100	100	500	500
Criteria C: Commercial or industrial site use[a]	50	20	300	800	500	500	1000	1500
Criteria D: Disposal prohibition[b]	250	100	1500	4000	2500	2500	5000	7500

[a] MDDEP, 1999

[b] MDDEP, 2008b

Table 3. Cross-correlation coefficient from the element concentration of the soil samples (n= 17) of AS2 horizon

	Al	Ca	Fe	S	Si	Corg	As	Cd	Cu	Pb	Zn
Al	1.00										
Ca	-0.10	1.00									
Fe	-0.36	-0.43	1.00								
S	-0.44	-0.11	0.29	1.00							
Si	**0.67**	0.02	**-0.71**	-0.11	1.00						
Corg	-0.37	-0.36	0.36	-0.25	**-0.62**	1.00					
As	-0.48	-0.47	0.24	**0.65**	-0.45	**0.68**	1.00				
Cd	-0.30	-0.04	0.21	**0.95**	0.01	-0.44	-0.06	1.00			
Cu	-0.13	-0.20	-0.11	0.49	0.26	-0.27	-0.26	0.44	1.00		
Pb	-0.41	0.20	-0.02	**0.56**	0.02	-0.31	-0.28	0.47	0.37	1.00	
Zn	-0.18	0.02	0.18	**0.91**	0.05	-0.53	-0.30	**0.96**	0.45	0.45	1.00

Note: the significant coefficients (>0.5) are given in bold and the strong correlation coefficients (>0.9) are given in underlined bold.

Table 4. Geochemical/mineralogical forms of metal-bearing phases

Mineralogical phases	Metal content	Number of identified phases			Metal distribution (%)		
		<63 µm	>63 µm	Total soil	<63 µm	>63 µm	Total soil
Copper-bearing phases	*Cu* (wt.%)						
Cu-Zn Alloy	66–69	0	2	2	0	15	5
Cu Oxide	76–86	4	1	5	15	8	13
Cu Oxide with Zn, Sn	52–70	3	2	5	12	15	13
Fe Oxide with Cu	6–16	4	1	5	15	8	13
Cu Oxide/Carbonate	56–76	3	2	5	12	15	13
Cu-Fe Sulfide (oxidized)	20–25	3	1	4	12	8	10
Cu-Silicate slag	10–30	4	2	6	15	15	15
Sn-Pb Silicate/Oxide with Cu	5–10	2	0	2	8	0	5
Si-C-Fe-O compound with Cu	5–30	3	2	5	12	15	13
Total for Cu		26	13	39	100	100	100
Lead-bearing phases	*Pb* (wt.%)						
Pb Oxide	84–91	3	2	5	7	12	9
Pb-Sn or Pb-Sb Oxide	39–69	2	2	4	5	12	7
Sn Oxide with Pb	5–20	7	1	8	17	6	14
Pb Oxide/Carbonate	70–82	6	2	8	15	12	14
Pb Oxide/Fluoride	66–83	2	1	3	5	6	5
Pb-Sn Oxide/Fluoride	26–30	3	1	4	7	6	7
Pb Sulfide	86–87	2	1	3	5	6	5
Pb Sulfide (oxidized)	68–77	4	1	5	10	6	9
Pb Silicate slag	25–53	6	2	8	15	12	14
Pb with C, O (C>O)	34–58	1	1	2	2	6	3
Pb-Sn with O, F, C	35–45	2	1	3	5	6	5
Si-C-Fe-O compound with Pb	5–20	3	2	5	7	12	9
Total for Pb		41	17	58	100	100	100
Zinc-bearing phases	*Zn* (wt.%)						
Cu-Zn Alloy	27–30	0	2	2	0	10	3
Zn Oxide	72–75	0	1	1	0	5	2
Cu-Sn or Sb Oxide with Zn	5–20	4	0	4	10	0	6
Fe Oxide with Zn	5–25	4	2	6	10	10	10
Zn Sulfide	45–65	27	16	43	66	76	69
Zn Sulfide/Silicate slag	20–30	2	0	2	5	0	3
Si-C-Fe-O compound with Zn	5–10	4	0	4	10	0	6
Total for Zn		41	21	62	100	100	100
Total number of metal-bearing phases		108	51	159			

Table 5. Some examples of elemental composition (in wt.%) of the liberated MBP (i.e., discrete metal-containing particles) by EDX analysis

Ref.	Particle size (µm)	C	O	F	Na	Al	Si	S	P	Cl	K	Ca	Mn	Mg	Fe	Ba	Ti	As	Cu	Pb	Zn	Sn	Sb	SUM	Description of phase (potential mineral species)
Cu-bearing phases																									
P14	20–38	-	12	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	86	-	-	-	-	100	Cu Oxide
P17	20–38	-	10	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-	77	-	-	8	-	100	Cu Oxide with Fe, Sn
P77	20–38	8	36	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	57	-	-	-	-	100	Cu Oxide/Carbonate (malachite)
P98	63–125	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	69	-	27	-	-	100	Cu-Zn alloy (brass)
P96	63–125	-	18	-	-	-	2	-	-	-	-	-	-	-	-	-	-	-	58	-	2	20	-	100	Cu Oxide with Zn, Sn
P28	20–38	2	24	-	-	-	-	2	-	-	-	-	-	-	-	-	-	-	52	-	19	-	-	100	Cu-Zn Oxide
P26	20–38	1	19	-	-	-	1	23	-	-	-	-	-	-	32	-	-	-	24	-	-	-	-	100	Cu-Fe Sulfide/Oxide
Pb-bearing phases																									
P95	63–125	-	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	91	-	-	-	100	Pb Oxide
P86	125–500	-	-	-	-	-	-	14	-	-	-	-	-	-	-	-	-	-	-	86	-	-	-	100	Pb Sulfide (galena)
P30	20–38	5	13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	82	-	-	-	100	Pb Oxide/Carbonate
P1	20–38	1	9	10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	81	-	-	-	100	Pb Oxide/Fluoride
P44	20–38	5	17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	77	-	-	-	100	Pb Carbonate (cerussite)
P92	63–125	-	8	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	77	-	-	-	100	Pb Sulfide oxidized (galena/anglesite)
P58	20–38	1	21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	40	-	38	-	100	Pb-Sn Oxide
P79	125–500	-	39	-	-	-	-	-	-	-	-	-	-	-	8	-	-	1.1	-	39	-	-	13	100	Pb-Sb Oxide with Fe, As
P13	20–38	-	30	-	-	13	15	-	-	-	-	1	-	-	2	-	-	-	-	35	3	-	-	100	Pb-Al Silicate with Zn
P59	20–38	2	29	-	-	16	19	-	-	-	2	-	-	-	-	-	-	-	-	33	-	-	-	100	Pb-Al-K Silicate
Zn-bearing phases																									
P87	125–500	-	28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	72	-	-	100	Zn Oxide
P83	125–500	-	-	-	-	-	-	30	-	-	-	-	-	-	6	-	-	-	-	-	64	-	-	100	Zn Sulfide (sphalerite)
P80	125–500	-	-	-	-	-	-	33	-	-	-	-	1	-	8	-	-	-	-	-	58	-	-	100	Zn Sulfide (sphalerite,), Mn
P109	63–125	-	5	-	-	-	-	30	-	-	-	-	2	-	8	-	-	-	-	-	56	-	-	100	Zn Sulfide (sphalerite), Mn, O
P11	20–38	2	14	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	45	-	37	100	Zn-Sb Oxide
P64	0–20	-	39	-	-	6	13	10	-	-	-	1	-	-	6	-	-	-	-	-	25	-	-	100	Zn Sulfide with Silicate material

Table 6. Summary of distribution of Cu, Pb and Zn according to their mineralogical forms and the different morphological classes

Classes	Cu	Pb	Zn
Distribution (%) of mineralogical forms			
Alloy/Metal	5	0	3
Oxides	38	29	18
Oxides/Carbonates	13	14	0
Oxides/Fluorides	0	12	0
Sulfides	10	14	69
Silicates	15	14	3
Others (unclassified phase)	18	17	6
Distribution (%) of morphological classes			
(1) MBP is liberated (free particle)	59	62	77
(2) One MBP and CP form a simple association	10	10	3
(3) Several MBP and CP form a complex association	24	13	13
(4) MBP is included in volume of CP	3	10	2
(5) MBP is specifically located on surface of CP	4	5	5

MBP= metal-bearing phase (with Cu, Pb and Zn); CP= carrying phase

Table 7. Selected EDX analyzes (element in wt.%) of metal-rich particles

Points of analyzes	C	O	F	Na	Al	Si	S	P	Cl	K	Ca	Mn	Mg	Fe	Ba	Ti	As	Cu	Pb	Zn	Sn	Sb	SUM
Particles of Fig. 7																							
a-1	5	18	-	-	-	-	-	-	-	-	-	-	-	3	-	-	-	-	75	-	-	-	100
a-2	1	28	-	-	-	-	-	-	-	-	-	-	-	64	-	-	-	-	-	4	-	3	100
b-1	1	17	-	-	2	15	-	-	-	-	3	-	-	5	-	-	-	-	56	-	-	-	100
b-2	1	23	-	-	3	13	-	-	-	-	5	-	-	9	-	-	-	-	46	-	-	-	100
b-3	-	21	-	-	2	-	-	-	-	-	-	-	-	77	-	-	-	-	-	-	-	-	100
b-4	2	23	-	-	3	11	-	-	-	1	3	-	-	19	-	-	-	-	38	-	-	-	100
c-1	-	23	-	-	2	16	4	-	-	1	1	-	1	2	15	-	-	-	16	17	-	-	100
c-2	1	22	-	-	1	15	-	-	-	1	4	-	-	2	9	-	-	-	37	7	-	-	100
c-3	-	40	-	1	1	34	-	-	-	-	1	-	19	-	-	-	-	-	-	4	-	-	100
d-1	13	37	-	-	-	5	-	-	-	-	1	-	-	30	-	-	-	-	9	5	-	-	100
d-2	-	-	-	-	-	-	35	-	-	-	-	2	-	8	-	-	-	-	-	56	-	-	100
d-3	1	58	-	-	-	-	15	-	-	-	-	1	-	1	-	-	-	-	-	24	-	-	100
e-1	2	19	-	-	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	78	-	-	100
e-2	1	6	-	-	-	-	-	-	-	-	-	-	-	13	-	-	-	-	-	80	-	-	100
e-3	-	21	-	-	-	-	-	-	-	-	-	-	-	4	-	-	-	-	54	21	-	-	100
e-4	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	78	8	-	-	100
e-5	-	16	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-	36	48	-	-	100
e-6	1	4	-	-	-	-	-	-	-	-	-	-	-	11	-	-	-	-	-	84	-	-	100
e-7	-	20	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	78	-	-	100
f-1	-	33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	67	-	100
f-2	-	33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	67	-	100
f-3	-	30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2	67	-	100
f-4	6	38	-	-	1	2	-	-	-	-	-	-	-	1	-	-	-	2	-	18	31	-	100
f-5	4	38	-	-	3	5	-	-	-	-	-	-	-	1	-	-	-	3	-	15	31	-	100
f-6	-	35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2	63	-	100
Particles of Fig. 8																							
a-1	-	24	-	-	-	-	-	-	-	-	2	-	-	9	-	15	-	3	46	-	-	-	100
a-2	-	24	-	-	-	-	-	-	-	-	3	-	-	10	-	15	-	2	43	3	-	-	100
a-3	-	38	-	-	-	-	-	-	-	-	-	-	-	28	-	34	-	-	-	-	-	-	100
a-4	7	39	-	-	1	12	-	-	-	-	18	-	-	16	-	7	-	-	-	-	-	-	100
a-5	-	23	-	-	1	1	-	-	-	-	2	-	-	16	-	12	-	5	34	6	-	-	100
a-6	-	29	-	-	-	-	-	-	-	-	-	-	-	47	-	19	-	-	-	5	-	-	100
a-7	-	30	-	-	-	-	-	-	-	-	-	1	-	38	-	29	-	-	-	2	-	-	100
b-1	-	45	-	-	-	55	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	100
b-2	2	25	-	-	-	27	-	-	-	-	-	-	-	2	-	-	0.5	4	20	21	-	-	100
b-3	-	27	-	-	2	28	-	-	-	2	2	-	-	2	-	-	-	5	27	7	-	-	100
b-4	1	31	-	-	-	28	-	-	-	1	1	-	-	-	-	-	-	7	17	14	-	-	100
b-5	1	30	-	-	2	25	-	-	-	1	2	-	-	2	-	-	-	6	26	6	-	-	100
c-1	-	42	-	-	22	32	-	-	-	4	-	-	-	-	-	-	-	-	-	-	-	-	100
c-2	13	44	-	-	12	19	-	-	-	2	2	-	1	6	-	1	-	-	-	2	-	-	100
c-3	-	34	-	-	11	20	-	-	-	3	1	-	-	4	-	1	-	-	19	5	-	-	100
c-4	-	34	-	-	16	24	-	-	-	5	-	-	-	2	-	-	-	-	17	2	-	-	100
c-5	16	24	-	-	1	4	-	3	2	-	3	-	1	-	-	-	-	-	33	13	-	-	100
c-6	20	23	-	1	1	2	-	4	3	1	3	-	-	-	-	-	-	-	42	-	-	-	100

Table 8. Concentrations and enrichment factors of metals (As, Cd, Cu, Pb and Zn) for the soil samples of peat and marl horizons (mean values) from the soil profile G

	As	Cd	Cu	Pb	Zn	Sc	Ti	Al
Concentrations (µg/g)								
Peat (n= 5)	4.8	0.371	32	12	113	0.7	127	2210
Marl (n= 2)	1.7	0.108	11	5	13	2.2	80	1557
Upper Crust[a]	2.0	0.102	14.3	17	52	7.0	3117	77440
EF (Sc) Results								
EF (Sc) Peat	26	43	26	8	25			
EF (Sc) Marl	3	3	3	1	1			
EF (Ti) Results								
EF(Ti) Peat	85	149	89	26	74			
EF (Ti) Marl	32	41	31	11	10			
EF (Al) Results								
EF (Al) Peat	115	202	121	36	106			
EF (Al) Marl	42	52	39	14	12			

[a] Wedepohl, 1995

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Fig. 4. Average concentrations of Cu, Pb and Zn according to the anthropogenic soil horizons (AS1 and AS2) and the brownfield sectors (soil profiles G, D, B and A).

Fig. 5. Atomic proportion of the soil samples from AS1 and AS2 horizons on three ternary diagrams (Si-Ca-Fe, Si-Ca-Al, and Corg-Ca-Fe). The sums of Cu, Pb, and Zn concentrations of the soil samples were reported according to four concentration classes.

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Fig. 7. Backscattered electron micrographs of different metal-containing particles (simple or complex mineralogical association of metal-bearing phases and/or carrying phases) from the AS2 horizon. Points (1, 2, 3, etc.) correspond at positions of the chemical analysis by EDX (the results are given in Table 7). For the description, see the text.

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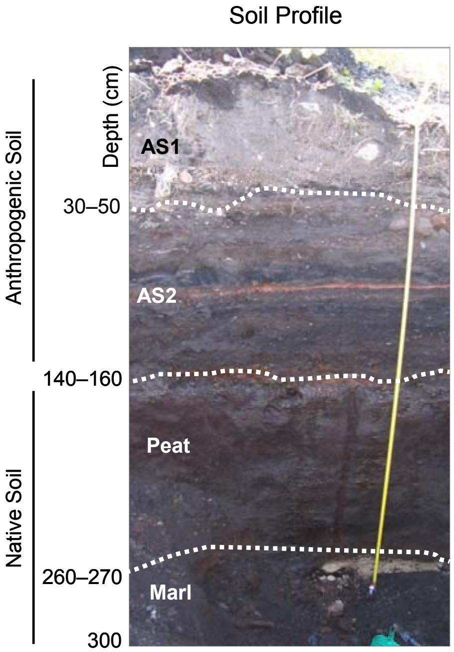


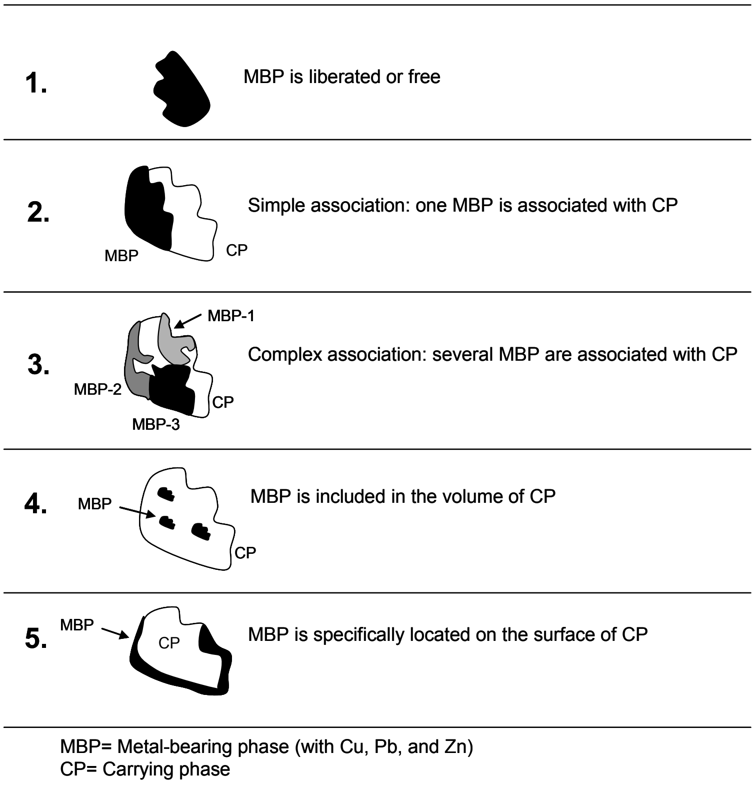
***AS1 (Anthropogenic Soil)*:**
Coarse gravel-sand, minor silt; gravel/cobbles with some (coarse textured) metallurgical waste materials

***AS2 (Anthropogenic Soil)*:**
Fine gravel-sandy loam (texture is very variable); mixture of non-calcareous soil with many (fine or medium textured) metallurgical slag/coal waste materials

***Peat (Bog and Pound Episode)*:**
Organic horizon; material intermediate between muck (sapric) and peat (fibric); no waste materials

Marl (Bog and Pound Episode):
Mineral horizon; calcareous material; some fresh-water shell accumulation with variable amounts of admixed clay and silt; no waste materials

Fig. 1. Soil profile description.



MBP is liberated or free

Simple association: one MBP is associated with CP

Complex association: several MBP are associated with CP

MBP is included in the volume of CP

MBP is specifically located on the surface of CP

MBP= Metal-bearing phase (with Cu, Pb, and Zn)
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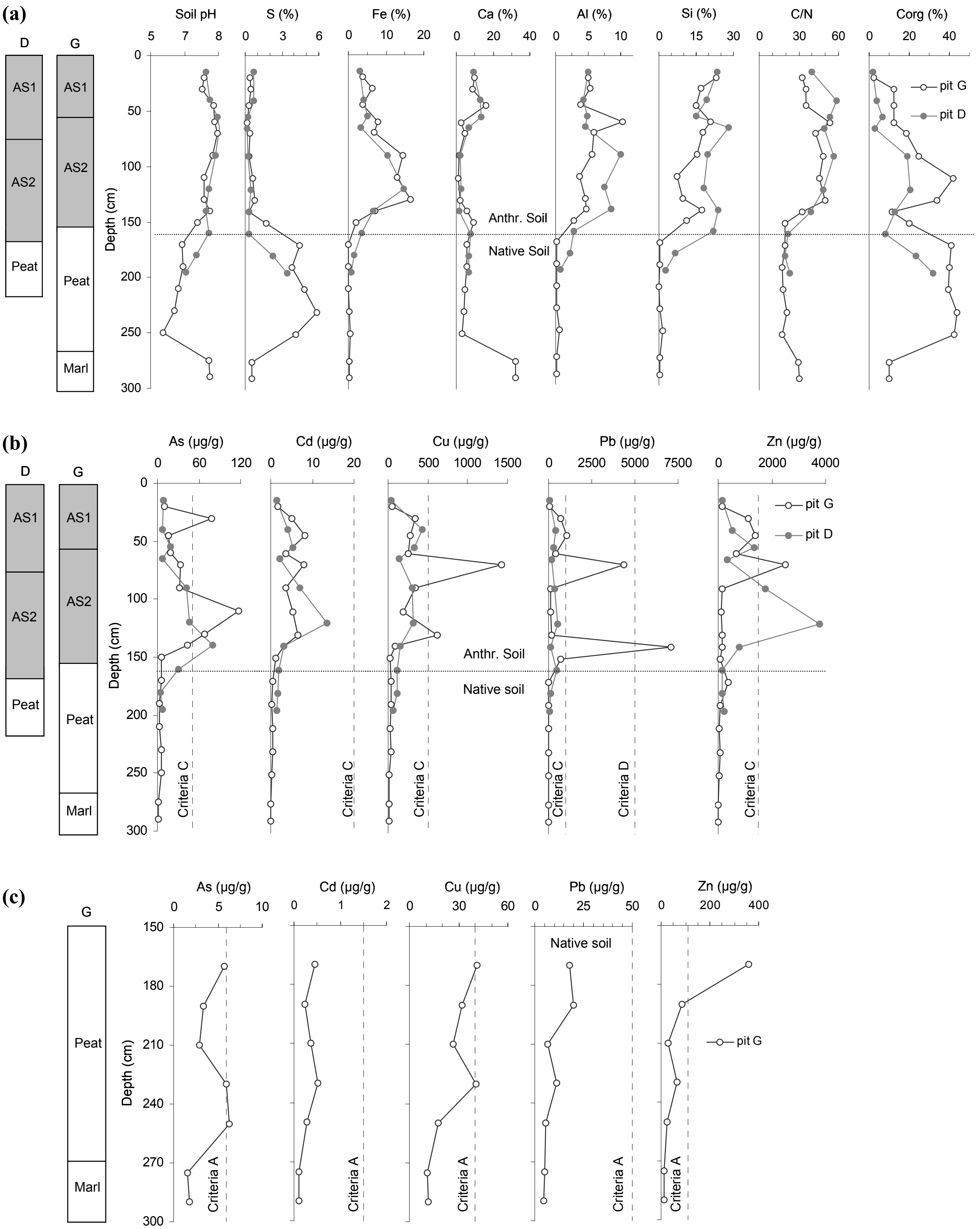

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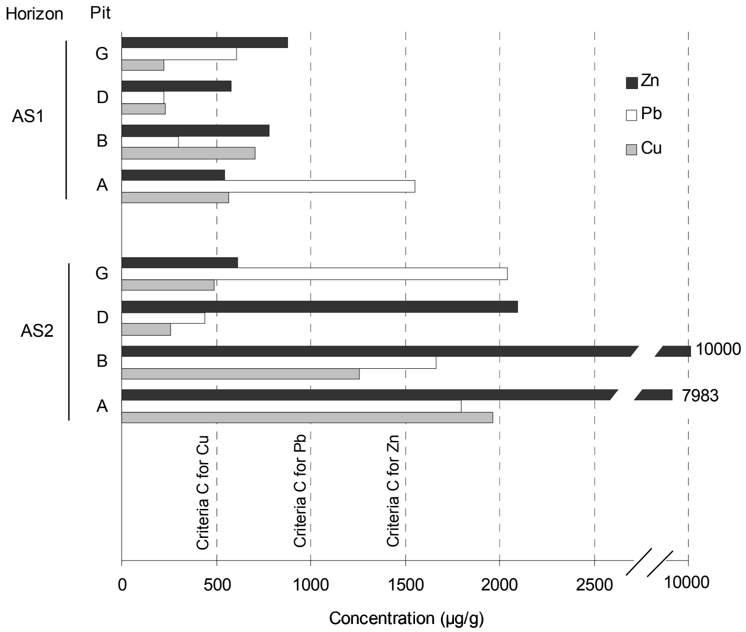

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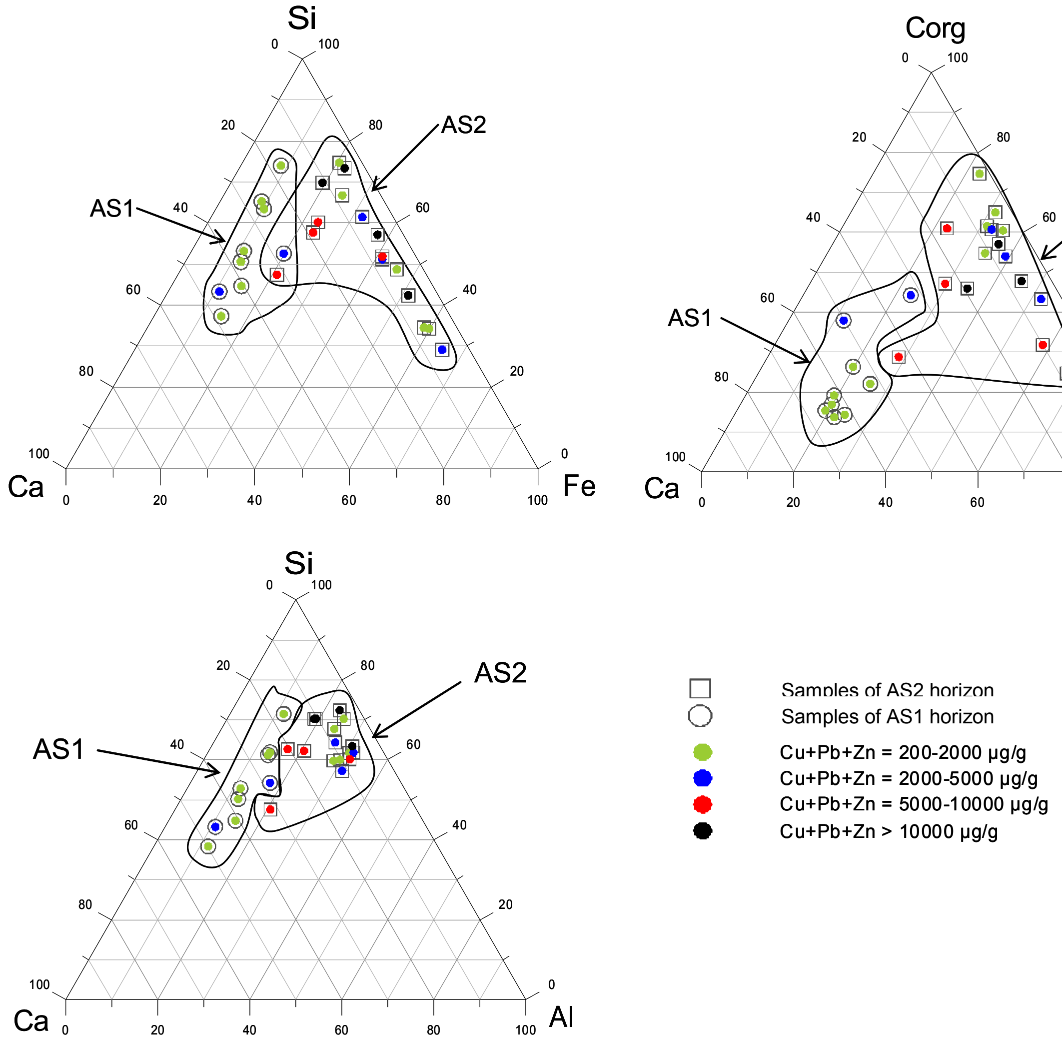

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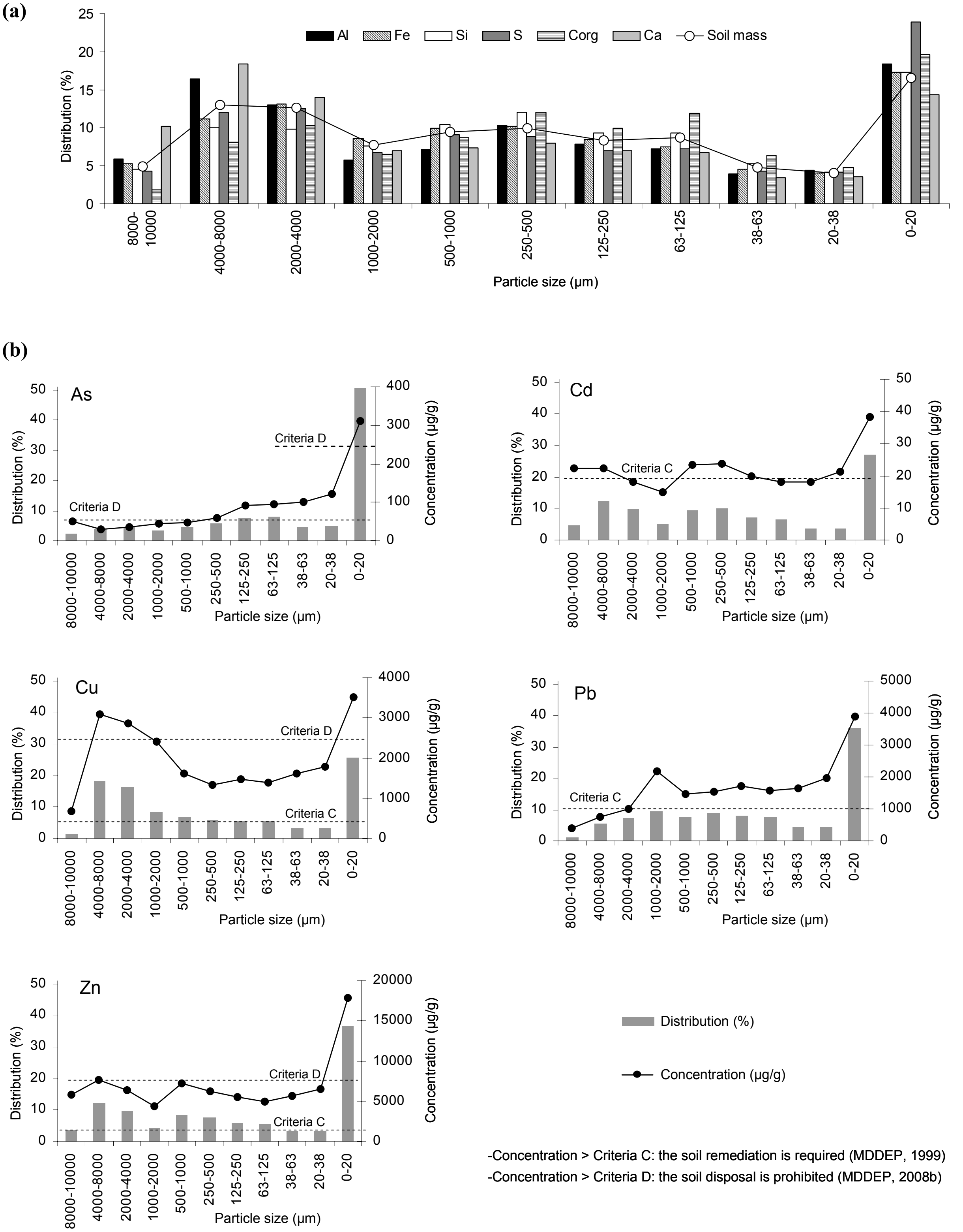
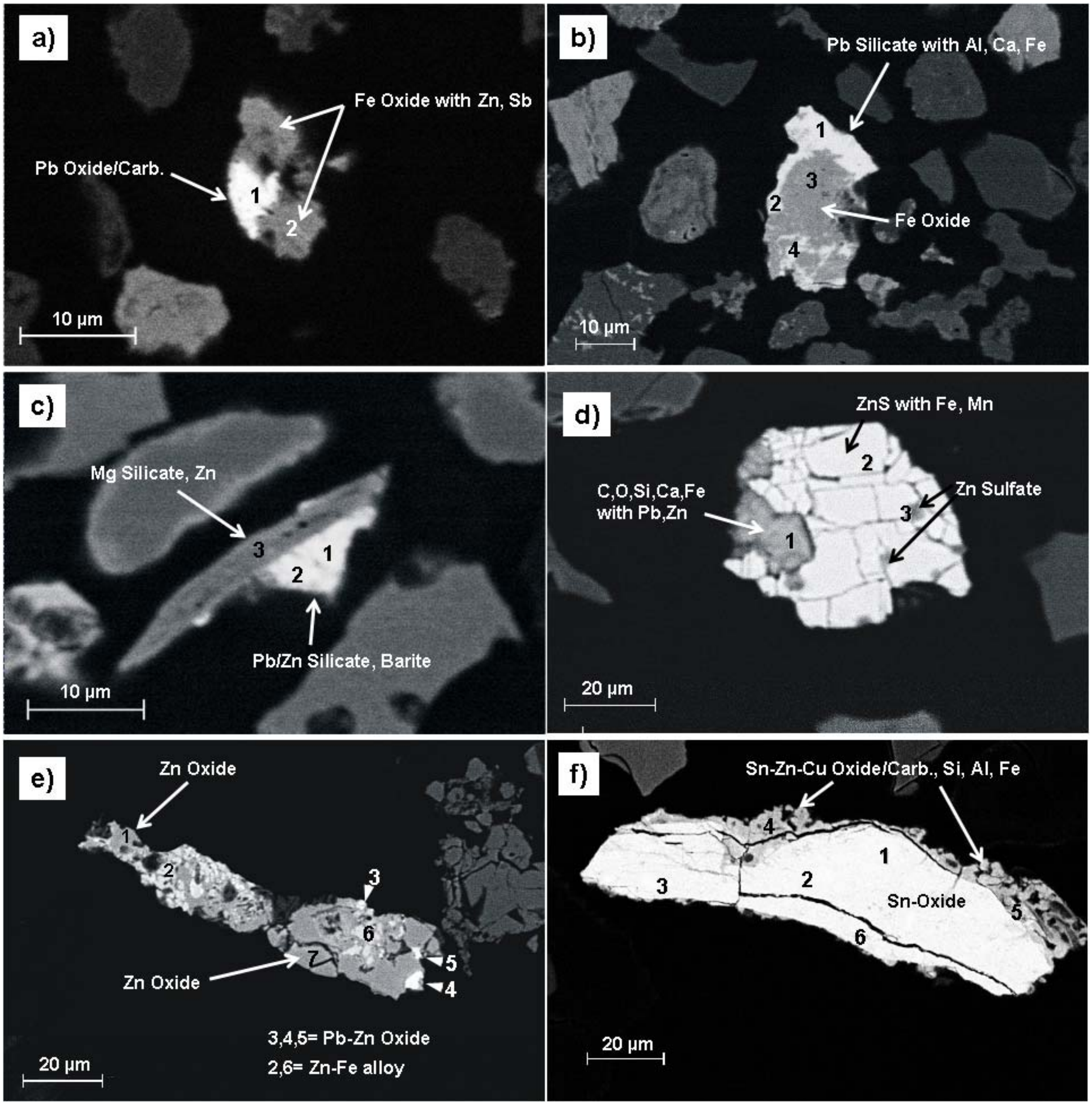


-Concentration > Criteria C: the soil remediation is required (MDDEP, 1999)
-Concentration > Criteria D: the soil disposal is prohibited (MDDEP, 2008b)

Fig. 6. (a) Distribution of Al, Fe, Si, S, Corg, Ca and soil mass versus particle-size fraction; (b) Distribution and concentration of As, Cd, Cu, Pb, and Zn versus particle size fractions.



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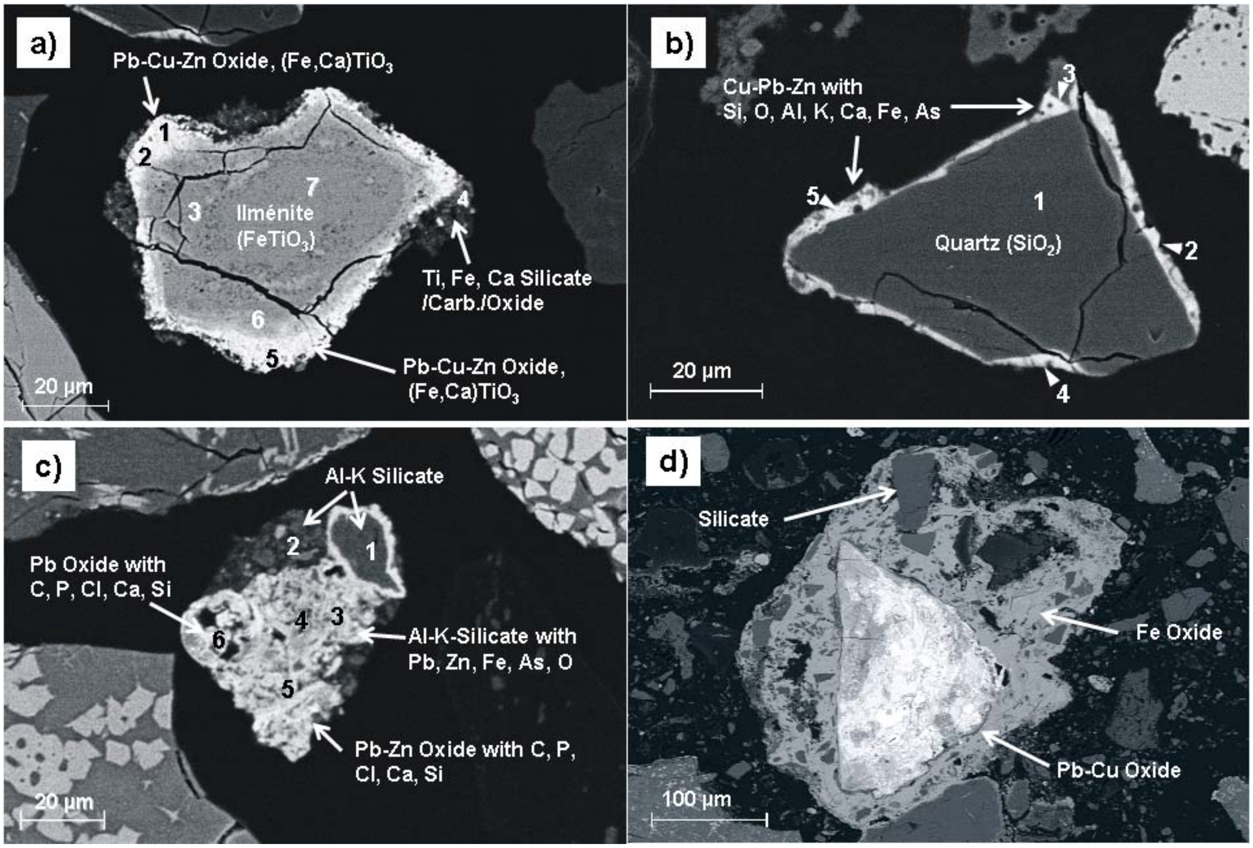

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Chapitre 6: Heavy metals removal from contaminated soils by froth flotation: Part 1. Influence of chemical factors

Résumé

Le lavage de sol par flottation a été étudié pour l'enlèvement de l'arsenic, du cadmium, du cuivre, du plomb et du zinc d'un sol fortement pollué (issu d'une friche industrielle en milieu urbain à Montréal, Canada) après un broyage des fractions granulométriques supérieures à 250 µm. La contamination est de forme particulaire et les métaux sont distribués dans toutes les fractions granulométriques. L'analyse minéralogique des particules riches en métaux par microscopie électronique à balayage couplée à l'analyse par spectrométrie en énergie dispersive (MEB-SEM) révèle que le Zn est répandu dans la matrice du sol sous la forme de sphalérite (ZnS), tandis que le Cu et le Pb sont distribués dans divers composés, principalement des oxydes/hydroxydes et des carbonates. L'influence du type de collecteur de flottation (kérosène et xanthate), de la concentration de collecteur, du pH de la solution et de l'ajout d'une étape chimique d'activation sur l'efficacité d'enlèvement en métal a été évaluée. Des résultats satisfaisants dans l'enlèvement des métaux (42–52%), la sélectivité de la flottation (facteur de concentration >2.5) et la réduction de volume (>80%) ont été obtenus avec le collecteur de type xanthate (amyle xanthate de potassium). Bien que la sélectivité de flottation ait été moins efficace avec le kérosène, ce collecteur se révèle une bonne alternative aux agents de type xanthate puisque son utilisation a permis d'obtenir de meilleurs taux d'enlèvement des métaux (45–60 %). Les mécanismes de transport impliqués dans le procédé de séparation (c'est-à-dire, la flottation vraie et l'entraînement mécanique) sont évalués par les conditions chimiques de la pulpe (pH, type de réactif, implication d'une étape d'activation chimique), la spéciation des métaux, la distribution des métaux dans les fractions granulométriques et les index de sélectivité de séparation de Zn/Ca et de Zn/Fe.

Submission to Science of the Total Environment, April 2008

Heavy metal removal from contaminated soils by froth flotation: Part 1. Influence of chemical factors

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Abstract

A soil washing process by froth flotation was evaluated for the removal of arsenic, cadmium, copper, lead, and zinc from a highly contaminated brownfield soil after crushing of the particle-size fractions >250 µm. The metals were in particulate forms and distributed in all the particle-size fractions. The particle-by-particle study with SEM-EDS showed that Zn was mainly present as sphalerite (ZnS), whereas Cu and Pb were mainly speciated as various oxide/carbonate compounds. The effect of surfactant collector type (kerosene and xanthate), reagent dosage, pulp pH, and a chemical activation step on metal removal efficiency were studied. Satisfactory results in metal recovery (42–52%), flotation selectivity (concentration factor >2.5), and volume reduction (>80%) were obtained with potassium amyl xanthate collector. Although the flotation selectivity was less effective with kerosene, this collector appeared to be a good alternative to sulfide-specific xanthate agents since the use of kerosene gave higher metal recovery (45–60 %). The transportation mechanisms involved in the separation process (i.e., the true flotation and the mechanical entrainment) were evaluated by the pulp chemistry, the metal speciation, the metal distribution in the particle-size fractions, and the separation selectivity indices of Zn/Ca and Zn/Fe.

Keywords: Contaminated soil; Heavy metals; Speciation; Remediation; Froth flotation

1. Introduction

Soil washing is one of the few permanent treatment alternatives to remove metal contaminants from soils. This remediation technology includes a wide array of physical, chemical or biological procedures (Mulligan et al., 2006; Loser et al., 2007; Dermont et al., 2008b; Lestan, et al., 2008; Ortega et al., 2008). Among them, froth flotation is a selective process that exploits difference of surface properties for separating the metal-containing particles from the soil matrix by using surfactants. Froth flotation is widely used in the mineral industry, and metal sulfides are easier to separate than carbonates and oxides (Rao and Leja, 2004; Fuerstenau, 2007). For remediation purposes of metal-contaminated soil, the froth flotation systems aim at concentrating the metals into a smaller volume of soil, and thus considerably reducing the volume of contaminated media. Froth flotation is primarily applicable when metal contaminants are in particulate forms (ideally liberated particles) in a soil particle-size range of 10–300 µm (Fuerstenau, 2007).

Several studies have demonstrated the efficiency of the flotation process for the removal of heavy metals (primarily Cd, Cu, Pb, and Zn) from sediments and soils. Some examples of recent studies are summarized in Table 1 including the media treated (particle-size range is specified), the metal contaminants evaluated (concentrations and fractionation), the flotation mode used (technology, pulp pre-treatment, and collector reagent), and the results obtained in metal removal and volume reduction. Most studies were performed in batch-mode tests using conventional cell flotation machine such as the Denver type cell. Several classes of collector reagents were investigated as to their efficiency in selective separation of heavy metals from soils or sediments (Table 1). The flotation results reported in Table 1 reflect broad range of metal removal efficiency (recovery and concentration factors) depending on soil characteristics, metal distribution in the soil matrix, and flotation parameters used. Froth flotation appears to be a relevant technique for treating fine-grained matrices, especially anoxic dredged sediments (best separation efficiency in the 20–50 µm range) where heavy metals are mostly present in sulfide forms (Table 1; Vanthuyne and Maes, 2007). In addition, some examples of field-scale applications of flotation systems for metal removal have been recently reviewed by Vanthuyne et al. (2003) and Dermont et al. (2008). However, the use of flotation as a remediation technique appears much less studied than other soil washing methods (such as e.g., chemical extraction using chelating/acid agents and particle separation techniques exploiting the difference in size or density of the particles).

The first objective of this study was to evaluate the feasibility of the use of flotation process to remove As, Cd, Cu, Pb, and Zn from the soil after crushing/grinding pre-treatment and to investigate the effects of several experimental parameters on metal removal efficiency. The chemical variables involved were: the collector type, the reagent dosage, the pulp pH, and the addition of a chemical activation step (sulfidization).

The second objective was to compare the flotation response with the soil mineral components, the metal speciation in the particulate phase, and the metal distribution in the particle-size fractions in order to assess the particle transportation mechanisms involved in this soil washing process. The flotation of metal-containing particles may be influenced by the specific characteristics of metal-contaminated soil (soil mineralogy, soil texture, soil composition, metal distribution according to their mineralogical phase, metal distribution according to the particle-size fractions, etc.) as well as by the factors relating to the flotation technology (chemical reagents and hydrodynamic parameters) (Cilek and Yilmazer, 2003; Vanthuyne et al., 2003). The sequential extraction procedures are often used to investigate the chemistry of metals in the contaminated soils for monitoring the soil washing treatment, especially flotation technology (Table 1). In this study, the metal speciation in the particulate phase was “directly” investigated by a micro-spectroscopic technique involving a particle-by-particle examination. Unlike the sequential extraction procedure, direct investigation by the scanning electron microscopy (SEM) and X-ray energy dispersive system (EDS) can evaluate the elemental composition, and the association degree (enclosed, cemented, or liberated nature) of the metal-containing particles. The information relating to the type and mode of the occurrence of the mineralogical forms and the degree of liberation (i.e., mineral association between the metal-bearing phase and the carrying phase) of metal-rich mineral phases are crucial parameters for assessing the froth flotation technology performance since the selective separation process is based on the surface properties of the mineral particles.

It is well known that two main particle transportation mechanisms take part in the flotation process within the mechanically agitated cells: (1) the true flotation mechanism which is a selective process related to the particle-bubble attachment and to detachment processes; (2) the mechanical entrainment mechanism which contributes to the non-selective transportation of fine particles in the froth and which is independent of their hydrophobicity and mineralogy (Cilek and Yilmazer, 2003; Fuerstenau, 2007; Koh and Schwarz, 2007). The true flotation mechanism is related to the pulp chemistry parameters and to the physico-chemical surface properties of the particles (mineralogy, hydrophobicity, chemical reactivity, etc.), whereas the mechanical entrainment mechanism is primarily related to the soil texture, the element distribution within the particle-size fractions, and the hydrodynamic flotation parameters. The hydrodynamic factors of mechanically agitated cells play an important role in the flotation process because these physical factors directly influence the probability of particle-bubble collision, attachment, and detachment (Cilek and Yilmazer, 2003). Due to the high turbulence within the mechanical cell, the hydrophobic and hydrophilic fine particles are mainly entrained in the froth via the inter-bubble water film (i.e., hydraulic or mechanical entrainment mechanism) (Cilek and Yilmazer, 2003; Koh and Schwarz, 2006).

2. Materials and methods

The soil used for the flotation tests was obtained from the anthropogenic soil horizon (depth of 0–150 cm) of a brownfield located at Montreal, Canada. The site is principally affected by illicit landfills containing diverse waste materials rich in metal-contaminants such as metallurgical slags, tailings, and ashes. After drying the primary soil sample, the desired particle-size fraction (<10 mm) was separated by sieving.

2.1. General characteristics of the brownfield soil

The general characteristics (major elements, mean concentrations of heavy metals, chemical parameters and soil texture) of the brownfield soil (0–10 mm) and the used experimental methods are summarized in Table 2 and Table 3. It can be seen in Table 2 that the soil was rich in Si, Fe, Al, and organic carbon. The high content of organic carbon was mainly due to technogenic/anthropogenic carbon associated with combustion coal and ash materials buried in the soil. This assumption was confirmed by the high value of C/N ratio (Table 2). The main mineral species (in proportion >3–5 Wt.%) identified in the 0–2 mm and 2–10 mm fractions by powder X-ray diffraction (XRD) analysis showed the presence of calcite ($CaCO_3$), gypsum ($CaSO_4$, $2H_20$), hematite (αFe_20_3), and silicate minerals: quartz (SiO_2), albite ($NaAlSi_3O_8$), mullite ($Al_6Si_2O_{13}$), and microcline ($KAlSi_3O_8$). The powder X-ray diffraction was conducted with a Siemens D-5000 diffractometer at Laval University, Quebec, Canada (CuKα radiation at 30 mA and 40kV; sample scanning from 4° to to 60° 2θ with a step size of 0.02° 2θ and a scan rate of 1.2s by step). XRD analysis cannot detect the non-crystalline (amorphous) phases such as silicate glassy slags or Fe-silicate slags. No heavy metal-bearing phases were identified by XRD analysis. Optical microscopy observations (with reflected, polarized, and natural light) conducted on a polished thin section from the representative soil samples confirming the occurrence of Fe oxides compounds, calcite, silicate minerals (quartz and feldspars) and indicating the presence of many fragments of metallurgical slags, metallic alloys, charcoal, and coke materials. Microscopy study with SEM-EDX also indicated the significant presence of Fe oxides such as magnetite (Fe_3O_4) and hematite, Fe-Cr alloy, molten Fe-silicate slags, various metallic parts and solder/alloy fragments. The elemental composition of various minerals or glassy slags appeared complex and dominated by silicate compounds (Al-K-Si, Mg-Si, or Fe-Si) and/or Fe oxide materials. The mean concentrations of As, Cd, Cu, Pb, and Zn in the brownfield soil (0–10 mm) were very high compared to threshold values established by Quebec's Soil Protection and Rehabilitation of Contaminated Sites Policy (Table 3). The brownfield soil was not meeting the soil quality level for commercial or industrial use (i.e., the values were exceeding in the criteria C) for the heavy metals (As, Cd, Pb, and Zn). In addition, the Cu and Zn concentrations were exceeding the threshold value related to soil disposal prohibition (criteria D). Preliminary soil characterization study (Dermont et al., 2006) showed that: (1) metal contamination was of particulate nature; (2) metal contamination was abundant in all the particle size fractions (0–10 mm); (3) the mineralogical associations of metal-containing particles were highly variable. In a site remediation perspective, the polluted soil used in this study was to be potentially excavated and relocated in a safe landfill site because no treatment method appeared economically effective compared to conventional disposal approaches.

2.2. Soil preparation procedure

Since metal-contamination level is high in all particle-size fractions of the soil sieved at 10 mm (Dermont et al., 2006), the fractions >250 µm were reduced with a roller crusher in order to obtain a soil with a particle-size range of 0–250 µm. The preparation attempted to provide an appropriate particle-size distribution for the froth flotation technique, to treat all particle-size fractions contaminated, and to increase the degree of liberation of metal mineral phases. The particle size reduction was carefully performed with a procedure combining successive sieving and crushing/grinding steps in order to minimize the production of fine particles. The flotation test samples (100 g) were prepared by quartering step. In addition, a representative sample (2 kg) was used for determining the metal distribution in the soil particle-size fractions and estimating the metal speciation in the solid phase of the ground soil (0–250 µm).

2.3. Specific analytical methods for metal distribution in the soil

2.3.1. Metal distribution in the particle-size fractions

The total concentrations of metal contaminants (As, Cd, Cu, Pb, and Zn) and three major elements (Ca, Fe, S) were determined in five different particle-size fractions (0–20 µm; 20–38 µm; 38–63 µm; 63–125 µm; and 125–250 µm) in order to provide element distribution within the different particle-size fractions of the processed soil. The particle size analysis and division of the various particle-size fractions were conducted with wet vibrating sieving with vibratory sieve shaker “Analysette 3” (Fritsch GmbH). After sieving, the fraction samples were dried, weighted and pulverized for analytical purposes. The total concentration of each element was analyzed by ICP-AES-axial (Varian Vista AX) after a complete sample (200 mg) decomposition by mixed acid digestion (HCl, HNO_3, and HF). High quality trace metal grade acids and Milli-Q® water

(>18 MΩ cm) were used for the digestion procedure. Calculation of results was done on the basis of oven-dry (105 °C) soil mass. The quality control of analytical method was monitored with two NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) certified reference soils: SRM 2710 and SRM 2711. The metal determination accuracy was very satisfactory, since the recovery efficiency was between 94% and 99% for the low and high metal contents in the standard reference soils. The experimental precision was very satisfactory with relative standard deviations (RSD) for trace metals below 5%.

2.3.2. Mineralogy and morphology of metal-containing particles

The particle-by-particle study with a SEM-EDX system provided crucial data relating to the mineralogy and chemistry of metal contaminants in soil solid phase: (1) identification of the mineralogical forms of metal-bearing phases; (2) evaluation of the occurrence of these mineralogical forms in the soil (i.e., estimation of the solid-phase speciation of metals); (3) determination of the range of metal content in the metal-bearing phases; (4) degree of liberation of the metal-bearing phase (i.e., the morphological aspects of the metal-containing particles). The SEM-EDX investigations were conducted on the polished thin sections for the 20–38 μm and 63-125 μm fractions. The polished thin sections were coated with gold for backscattered electron imaging, chemical analyses and morphology observations. Microanalysis was undertaken on back-scattered electron (BSE) images on a Zeiss EVO-50 scanning electron microscope (SEM) interfaced with an Oxford Instruments INCA X-ray energy-dispersive system (EDS). Energy dispersive X-ray (EDX) microanalyses were used to detect the presence of heavy metal contaminants and to give elemental composition in the targeted section of the particles. The spatial resolution with respect to the analysis was limited to about 1 μm by beam spreading (Reed et al., 2005). EDX analyses were treated by the Oxford Instruments INCA software to give wt.%

for the various elements Z ≥6 detected (such as C, O, F, Na, Al, Si, S, P, Cl, K, Ca, Mn, Mg, Fe, Ba, Ti, As, Cu, Cr, Ni, Pb, Zn, Sn, and Sb). Various standard reference materials were used for the EDX calibration in order to provide the elemental composition. In general, the accuracy for the EDX microanalysis was about 1% and the detection sensitivity was 0.1 wt.%. Correction procedures for atomic number Z, absorption and fluorescence effects (ZAF) were applied in the calculation. The hydroxide species could not be identified by EDX analysis because hydrogen (H) was not detected.

2.4. Flotation method

2.4.1. Flotation tests procedure

The experiments were carried out in a Denver D-1 laboratory flotation machine, which was fitted with a mechanically agitated cell and an induced air mixer. This apparatus is widely used as a conventional laboratory flotation machine for research in the mineral industry (Koh and Schwarz, 2007; Cilek and Yilmazer, 2003) and soil remediation (Table 1). The separation principle is based on the affinity of particle's hydrophobic surfaces for air bubbles injected in the slurry of soil. The surface of desired metal minerals is often rendered hydrophobic by the use of a surfactant (collector). Preliminary tests (unpublished data) were performed in order to select certain experimental conditions for the flotation tests (agitation speed, frother type, pulp density, process time, etc.). The used amounts of flotation reagents are reported in mg/g of dry soil. The pulp was prepared for each test by mixing 100 g of soil with distilled water in the flotation cell (volume of 1.25 L) to obtain 10% of solid in pulp. The pulp was then conditioned for 10 min with the collector agent. The frother agent (0.240 mg/g methyl isobutylcarbinol, MIBC) was added in the last minute of the conditioning step. The pulp pH was monitored and adjusted with a NaOH or HCl solution during the conditioning time. After the conditioning, the air valve was opened and flotation test was conducted for 10 min at impeller speed of 1350 rpm. The froth layer was continuously removed during the flotation process. The same froth removing procedure was used for all the tests. During the flotation phase, the impeller shaft and the walls of the cell were periodically washed with process water (similar composition to the initial solution) to return the adhering minerals to the pulp and to maintain a constant pulp level. After completion of the flotation step, the floated fraction (froth) and the residual fraction (tailings) were filtered (for the tailings only), dried, weighed, and crushed (<40 μm) for analytical purposes. The total concentrations of As, Cd, Cu, Pb, Zn, Ca, Fe, and S were determined for each flotation fraction (i.e., feed, froth and tailing) of all flotation tests with the same analytical procedure described in the previous section.

The collectors tested in this study included non-ionic surfactant kerosene (Fisher) and an anionic surfactant potassium amyl xanthate (KAX; chemical formula: $C_6H_{12}OS_2K$). The commercial product used was AERO® 350 xanthate of Cytec Industries Inc. (>90 wt.% of KAX), which is the most powerful of the Cyntec AERO xanthates, since the flotation response was high with long chain xanthates (amyl, octyl, decyl, etc.) (Cytec, 2002; Rao and Finch, 2003). Kerosene collector showed good flotation results in metal removal from sediment and soil (Table 1). These two conventional collectors were used at different concentrations and pulp pH values. The flotation tests were carried out at alkali pH's because of: (1) xanthate collectors are stable at a higher pH's; (2) at low pH (<6), KAX decomposes (Fuerstenau, 2007), therefore, the efficiency of the collector decreases; (3) higher pH's also minimize corrosion of cells and plumbing; (4) acidic conditions may cause the dissolution of the soil components and of the minerals containing the heavy metal contaminants.

The effect of the chemical activation of the pulp by sulfidization was also tested. The additional sulfidization step was done with 10% of solids in the pulp for 20 min at room temperature in ambient air prior to the usual collector conditioning step. Sodium sulfide (Na_2S) is usually used as current sulfidizing agent (Herrera-Urbina et al., 1999; Rashchi et al., 2005). Two concentrations of Na_2S were tested (2 and 5 mg/g). The activation by ions of HS^- altered the surfaces of the particles to make them more disposed to the action of KAX collector. Although the Eh of the pulp may play a key role in optimum sulfidization-flotation, the Eh range was not monitored in the present study. In summary, four different flotation test series were evaluated and compared: (1) collectorless flotation at pH 7.5 and 9; (2) flotation with kerosene collector at different dosages (4, 8, 12, and 16 mg/g) and pulp pH (7.5, 9, 10, 11, and 12); (3) flotation with potassium amyl xanthate (KAX) collector at different dosages (0.25, 0.5, 1, and 2 mg/g) and pulp pH (8, 9, 10, 11, and 12); (4) combination of sulfidization and flotation with 2 mg/g KAX collector at pH 9–9.5. The particular experimental conditions used for the different flotation experiments will be specified later.

2.4.2. Formulas to estimate the flotation efficiency

The flotation process of the contaminated soil (feed soil) provides the metal concentrate (froth) and the residual fractions (tailings). In order to evaluate the flotation performance, the following parameters were evaluated: mass recovery (Eq. 1); element recovery (Eq. 2); and the concentration factor (CF) of the element (Eq. 3).

$$\text{Mass Recovery (\%)} = \frac{\text{Mass}_{\text{Froth}}}{(\text{Mass}_{\text{Froth}} + \text{Mass}_{\text{Tailings}})} \quad \text{(Eq. 1)}$$

$$\text{Element Recovery (\%)} = \frac{[\text{Element}]_{\text{Froth}} \times \text{Mass}_{\text{Froth}}}{([\text{Element}]_{\text{Froth}} \times \text{Mass}_{\text{Froth}} + [\text{Element}]_{\text{Tailings}} \times \text{Mass}_{\text{Tailings}})} \quad \text{(Eq. 2)}$$

$$\text{Element CF} = \frac{\text{Element Recovery (\%)}}{\text{Mass Recovery (\%)}} = \frac{[\text{Element}]_{\text{Froth}}}{[\text{Element}]_{\text{Feed}}} \quad \text{(Eq. 3)}$$

With: $[\text{Element}]_{\text{Froth}}$ = Concentration of element in Froth

$[\text{Element}]_{\text{Tailings}}$ = Concentration of element in Tailings

$[\text{Element}]_{\text{Feed}}$ = Concentration of element in Feed

$\text{Mass}_{\text{Froth}}$ = Mass of Froth

$\text{Mass}_{\text{Tailings}}$ = Mass of Tailings

The elements selected for the recovery calculation include the metal contaminants (As, Cd, Cu, Pb, and Zn) and three major elements (Ca, Fe, and S). Although the metal concentrations in feed soil were measured for each flotation run, the recovery calculations were evaluated with the metal amount of froth and tailings ("calculated feed") in order to respect the mass balance closure. The concentrations of metals (As, Cd, Cu, Pb, and Zn) varied significantly in the feed soil. Therefore, for each test, the total metal mass recovered for all the process streams (i.e., froth and tailings) was taken to be the initial concentration and the recoveries were then calculated with this value. In summary, the mass recovery evaluates the volume reduction of the soil washing process (volume reduction % = 100–Mass recovery), the metal recovery rate evaluates the metal amount removed by flotation process, and the metal CF assesses the flotation selectivity of the metal in relation to the total floated mass. For a selective separation of the metal contaminants, the CF must be larger than 1 and should be as large as possible. The mass recovery should be preferably low to maximize the volume reduction, but concurrently the metal amount recovered should be high enough to obtain a residual soil (tailings) with a metal concentration as low as possible in order to respect the environmental threshold values.

3. Results and discussion

3.1. Metal distribution in soil

3.1.1. Metal distribution in the particle-size fractions

The particle size of the feed material is one of the most significant parameters that may affect the applicability of flotation because the soils usually contain a wide range of particle sizes, and the flotation technology performance is often restricted to a specific particle size range (usually 10–300 µm). The particle-size reduction and grinding stage of the "original soil" (range of 0–10 mm) caused an important redistribution of metal contaminants in the various particle-size fractions of the "processed soil" (range of 0–250 µm) (data not published in this study). Table 4 summarizes the soil particle-size distribution, the concentrations of metals, Ca, Fe, and S and their distribution across five particle-size fractions (0–20 µm; 20–38 µm; 38–63 µm; 63–125 µm; and 125–250 µm) for the processed soil. The crucial points to be considered are: (1) the important amount of the 0–20 µm fraction (29%); (2) the high metal concentration level in this fraction. Consequently, the metal amount in this finest particle-size fraction represented 42–53% of the metal distribution. The selective flotation of metal-containing particles from the particle size fraction <10–20 µm is often ineffective in most mechanical flotation cells because of various phenomena of entrainment and entrapment of the fine hydrophilic undesirable gangue particles (i.e., non-selective process). However, the recovery of fine particles <20 µm in the froth by entrainment mechanism may be profitable in our case since the metal concentrations are particularly high in the finest particle-size fraction (Table 4). Although the 0–20 µm fraction contained the majority of the metal quantities, the contamination was not limited to the fine particles: e.g., the 63–250 µm fractions contain 30–40% of the metal amount (Table 4).

3.1.2. Mineralogy and morphology of metal-containing particles

The chemical composition, mineralogical association and morphological aspects (size, shape, and associated, enclosed, or liberated nature of the metal-bearing phase) of particles containing heavy metals were studied by SEM-EDX. More than 150 EDX analyses were performed to identify Cu/Pb/Zn-bearing phases present in the brownfield soil. The EDX microanalysis was not adapted in our case to determine mineralogical phases containing As and Cd due to their relative low concentrations in the sample. Table 5 summarizes the various mineralogical phases of the Cu, Pb, and Zn observed in the soil. The distribution of metal according to their identified mineralogical phases was estimated on a total of about 100 metal-rich particles containing greater than 10 wt.% Cu, Pb, or/and Zn. The measured contents (in wt.%) of Cu, Pb, and Zn for each class of mineralogical phase are summarized in Table 5. Although the SEM-EDX provides a good overview of the metal partitioning according to their mineralogical phase, the estimation of metal distribution is semi-quantitative in relation to the volume of soil sample considered.

The mineralogical forms of Cu-bearing phases identified in the soil include (in order of occurrence): oxide, oxide/carbonate, sulfides and alloy/metal (Table 5). The groups of Cu oxides and oxides/carbonates represented approximately 50% of the Cu distribution. The Cu-oxide form probably involved tenorite (CuO) and cuprite (Cu_2O), which theoretically contain 79.9 wt.% and 88.8 wt.% of Cu respectively, or a mixture of both ($CuO-Cu_2O$). The Cu carbonate form probably involved malachite $Cu_2(CO_3)(OH)_2$ that theoretically contains 57.5 wt.% of Cu. Copper in variable wt.% is often associated with Zn, Fe and/or Sn in oxidized alloy, solder, or slag particles (Table 5). Although some particles of Cu-Fe sulfide (probably chalcopyrite, $CuFeS_2$) were identified, the sulfide form of Cu was not abundant in the soil sample. The mineralogical forms of Pb-bearing phases are very diverse: oxides, carbonates, oxide/carbonates, oxide/fluorides, sulfides, silicates, and other unclassified phases (Table 5). The groups of Pb oxides and oxides/carbonates represented approximately 40% of the Pb distribution (Table 5). The Pb carbonates, which were also classified in the oxide/carbonate class, probably involved cerussite [$PbCO_3$] and hydrocerussite [$2PbCO_3 \bullet Pb(OH)_2$], which contain 77.5 wt.% and 75.4 wt.% of Pb respectively. Lead in variable wt.% was often chemically associated with Sn oxides, which probably resulted from the weathering of alloy or solder fragments. Zn was mainly occurring as free particles of sphalerite/wurtzite [(Zn,Fe)S] (Table 5). About 20% of the Zn speciation involved oxides and silicates, which contained a relative low content of Zn (Table 5).

The estimation of liberation degree of metal-bearing phase was a crucial parameter in the particle separation by physical process (Dermont et al., 2008). The metal-containing particles were often found as free particles in the ground soil (0–250 μm) in 70% and 80% of the analyzed particles for Cu/Pb and Zn respectively (i.e., the metal-bearing phases are liberated and not associated with a carrying phase). Particularly, all the sphalerite particles observed were free particles. Thus theoretically, the surfaces of metal-containing particles were potentially available for the separation by flotation process. However, a significant proportion of the analyzed particles (20–30%) were composed of several geochemical phases containing Cu, Pb and/or Zn (complex mineralogical association) (Fig. 1 and Table 6). The Cu/Pb/Zn-bearing phases may be associated with another metallic carrying phase (e.g., Sn/Fe oxide) or a non-metallic carrying phase (Al-Si compounds or Fe-Si slag matrix) (Fig. 1c ,e, f, and Table 6). Also, some metal-bearing phases (5–

10% of the features) observed were enclosed within Fe oxides or Fe-Si slag matrix, or in another metallic phase.

3.2. Flotation results

The specific flotation parameters, mass balance (mass recovery and volume reduction), and metal contaminant concentrations (As, Cd, Cu, Pb, and Zn) in feed, froth, and tailings for all the flotation tests are summarized in Table 7. The volume reduction of the highly contaminated soil (>criteria D) ranged from 75 to 90%. The soil washing process by froth flotation has clearly reduced the metal concentrations (especially for Cu and Zn) for environmental acceptation in respect of the criteria D (soil disposal prohibition; MDDEP, 2008). However, metal concentrations in the "clean soil" (tailings fraction) remained greater than the criteria C of the Quebec legislation for soil quality and site use.

3.2.1. Flotation with kerosene: influence of pulp pH and dosage

3.2.1.1. Influence of dosage

The effect of kerosene dosage was tested at natural pH (7.5). An increasing collector dosage from 4 mg/g to 12 mg/g improved the metal recoveries (Fig. 2a). For example, the Zn and Pb recoveries increased from 48% to 55% and from 42% to 51% respectively (Fig. 2a). This was substantially due to mass recovery that also increased (Fig. 2a). The best metal recoveries were obtained at 12 mg/g of kerosene. Generally, the recovery of the metal contaminants are 1.5–2 times higher than those of iron. The recovery of sulfur is usually higher than those of the other elements. The order of metal recovery at various kerosene dosages (4 to 12 mg/g) is: As > Zn > Pb ≈ Cd ≈ Cu. When the kerosene dosage exceeded 12 mg/g, the metal recoveries as well as the mass recovery slightly decreased. It was clearly observed from the flotation experiences that kerosene dosage higher than 12 mg/g has an adverse effect on the froth stability and frothing process. This is probably because the excess amount of kerosene thwarts the effect of frother, which causes a decrease in froth stability and an increase in drainage of particles from froth to pulp. The concentration factor of metals, which evaluates the flotation selectivity, decreased when the kerosene concentration increased (Fig. 2b). The superior metal recoveries observed at higher collector dosage values (12 mg/g) were thus not the result of an increased flotation selectivity, but directly a result from the significant increase of froth mass recovery.

3.2.1.2. Influence of pulp pH

The flotation tests were conducted with 12 mg/g kerosene as collector at natural pH of pulp (7.5) and at elevated pH (9–12). Fig. 2c shows that the best metal recovery was obtained at pH 11, although the variations in metal recovery were not important in the studied range of pH. For instance, the Zn recovery was 57% at pH 9, whereas it was 60% at pH 11. However, Fig. 2d shows that the concentration factor of metals, sulfur and iron varied less than 5% (relative variation). This suggests that the pulp pH (range of 7.5–12) did not have a great influence on the metal removal efficiency. The general order of element recovery has not changed with the pH variation: S > As > Zn > Pb ≈ Cu ≈ Cd >> Fe.

3.2.2. Flotation with xanthate: influence of pulp pH and dosage

3.2.2.1. Influence of dosage

The effect of KAX dosage on metal flotation was tested at pH 9.2. Fig. 3a shows that as xanthate dosage increases, metal removal as well as the mass recovery of floated particles enhances. The best metal recoveries were obtained at 2 mg/g (Fig. 3a). Generally, the recovery of As, Cd, Cu, Pb, and Zn are 2–2.5 times higher than the values for Fe. The flotation efficiency of sulfur was better than all metals, probably due to the flotation of gypsum ($CaSO_4$) and sphalerite (ZnS) particles. The order of metal recovery at optimum dosage is: Zn ≈As > Cu > Pb ≈ Cd, but this order varies according to the dosage values. Moreover, the difference of Cu, Pb, and Zn recoveries were not very significant within the studied dosage range (Fig. 3a). The concentration factor of metals exhibits a divergent tendency to their removal efficiency (Fig. 3b). As in the case of kerosene collector, the improvement of metal removal efficiency with higher xanthate concentrations is not the result of an increased selectivity of metal flotation, but this is due to the augmentation in mass removal of the floated particles.

3.2.2.2. Effect of pulp pH

The effect of pulp pH (8–12) on the xanthates collection process was performed with 0.5 mg/g KAX. Fig. 3c and Fig. 3d show that the metal flotation was influenced by the pulp pH, but this variation remains very limited. Fig. 3c shows that the order of metal recoveries varied according to pH range; however, the As and Zn recoveries were slightly higher than the Cu, Cd, and Pb recoveries at pH 8–11. Fig. 3d shows that increase in pH from 8 to 12 caused a relative change in CF of As, Cd, Cu, Pb, Zn, and S compared to the variations in CF of Fe. In particularly, from pH 11 to 12, the CF of Zn (and Cd) significantly decreased, while the CF of Cu, Pb, and As did not strongly change. These latter experimental observations may be explained with the following remarks: (1) Zn is mainly in sulfide forms, while Cu and Pb are not in sulfide forms (Table 5); (2) sulfide compounds may be oxidized at pH > 11 during conditioning and flotation time (Cauwenberg et al., 1998b). Moreover, the variation in concentration factor of S and those of Zn and Cd showed a good correspondence (Fig. 3d). The similar trend of Cd may be due to a strong correlation between Cd and Zn in the soil matrix (data not published).

3.2.3. Influence of collector type

In order to compare the influence of collector type on metal flotation, the recovery vs. the concentrating factor obtained with the different flotation experiences were plotted in the same x-y diagram for Cu (Fig. 4a), Pb (Fig. 4b), and Zn (Fig. 4c). The metals selected were Cu, Pb, and Zn since their mineralogical forms in the feed soil have been assessed by SEM-EDX study.

The collector is a surfactant agent that attaches on the mineral surface (via physical adsorption or chemisorption) in order to produce an hydrophobic surface or to enhance the hydrophobic character of the mineral phase to be floated. The collectors used in this study were chemically different: kerosene collector is non-specific and non-anionic, while potassium amyl xanthate (KAX) is an anionic surfactant and sulfide-specific collector. Thus theoretically, they strongly differ in their adhesion mechanism onto the particle surface. The adsorption mechanism of kerosene onto the particle surface is primarily related to a physical adsorption (electrostatic interaction), whereas the adsorption mechanism of xanthate onto mineral surface (metal sulfides) is related to chemical bonding and chemisorption (Buckley and Woods, 1997; Fuerstenau, 2007). However, the action of xanthates on metal oxides appears more dependent on an electrostatic mechanism when compared to interaction between xanthate and metal sulfides (Rao and Finch, 2003).

In a general point of view, the Fig. 4 clearly shows that the use of a collector agent has a significant improvement effect on the metal recovery in comparison with collectorless flotation tests. However, Fig. 4 also shows that the concentration factor (i.e., the flotation selectivity) of metals did not improve with the kerosene collector, whereas it mostly increased with xanthate in comparison with collectorless flotation. This suggests that flotation with kerosene is significantly influenced by an entrainment mechanism. Moreover, Fig. 4 clearly shows that the separation of

Cu/Pb/Zn-bearing particles with xanthate as collector was much more selective compared to the flotation tests with kerosene. Nevertheless, the use of sulfide-specific collector (xanthate) had no enhancement effect on metal recovery in comparison with a non-specific collector (kerosene). For instance, the Zn recoveries obtained with kerosene ranged from 50 to 60% depending to the experimental conditions, while the Zn recoveries ranged from 40 to 50% with xanthate (Fig. 4c).

The difference in flotation response between kerosene and xanthate cannot be explained by the mineralogical data of metal-containing particles since the flotation process was systematically less selective with kerosene collector, not only for Zn (which was in sphalerite form), but also for Cu and Pb, which were not in sulfide forms (Fig. 4). The reason for the lack of flotation selectivity in the presence of kerosene collector could be explained by two main points: (1) the non-selective adsorption of the oily reagent on both coal/ashes and hydrophobic mineral particles rich in metals; (2) the non-selective transportation of fine particles in the froth by mechanical entrainment. The non-specific collector gathers the hydrophobic fine particles rich in carbon such as coal, ashes, unburned carbon, and porous slag particles. Owing to natural hydrophobicity, this material type may be easily floated with a conventional oily collector (via physical adsorption) such as kerosene. The difference in flotation selectivity between kerosene and xanthate was probably due to the contribution of the entrainment mechanism of the fine particles in the flotation process because of: (1) the flotation selectivity for all heavy metals decreased when collector quantity used (of xanthate or kerosene) was increased (Fig. 2b and 4b); this suggests that the true flotation was less efficient with a high reagent concentration; (2) kerosene collector concentrations required in the flotation tests are systematically higher than those of xanthate. The entrainment of very fine particles caused overconsumption of collector and a high kerosene dosage was required to obtain satisfactory results in metal recovery.

Fig. 4 also shows that there is more disparity in the metal flotation selectivity with xanthate compared to those of kerosene. This suggests that the variations in pulp chemistry (pH and collector concentration) did not significantly influenced the flotation performance with kerosene collector, while these variations influenced the flotation response with KAX collector (above all for Cu and Zn). This is also observed in the previous sections: (1) Fig. 2 shows that the relative order of metal recovery with kerosene collector did not change with the variations in pulp chemistry (reagent concentration and pH); (2) Fig. 3 shows that the relative order of metal recovery with xanthate collector changed significantly when the pulp pH or the collector dosage have been modified. These results may be related to the specificity of the adsorption mechanism of xanthate onto mineral surfaces which is mainly determined by chemisorption. However, this influence remains limited because certain factors of physical nature (soil particle-size distribution, mechanical entrainment mechanism, hydrodynamic parameters) also play an important role in the flotation.

3.2.4. Influence of metal speciation

SEM-EDX investigations (Table 5) showed that: (1) sphalerite (ZnS) was the predominant mineral form of Zn (~75%); (2) the dominant mineralogical forms of Cu and Pb were oxides and oxides/carbonates (~40–50%); (3) the sulfide compounds of Cu (e.g., chalcopyrite) and Pb (e.g., galena) represented only 10–15% of their distribution. Usually, the metal-sulfide minerals are more easier to concentrate by flotation than the oxide-type minerals (including carbonates) because the surface of sulfide minerals are more hydrophobic (Rao and Leja, 2004). In general, the order of hydrophobicity of metal mineral ores is: native metals > sulfides > sulfates > oxides, carbonate, silicates. Although the flotation of sphalerite (ZnS) is less easy to perform than the flotation of other common metal sulfides (such as e.g., PbS or CuS), the sphalerite particles should have been floating more efficiently than the Cu and Pb oxide/carbonate particles. Thus theoretically, the response in flotation between Zn and those of Cu or Pb should have been markedly dissimilar. Contrasting to this assumption, Fig. 4 shows that the differences in flotation response of Zn vs. Cu and Zn vs. Pb are not especially considerable for the flotation using different chemical conditions (even if there is a small relative distinction of flotation between the metals, especially Zn vs Cu/Pb). This suggests that the mineralogy of metal-containing particle has not a great influence on the flotation of the Cu, Pb, and Zn in this soil washing process.

3.2.5. Influence of sulfidization step

It is generally known that base-oxide minerals or oxidized minerals of lead, zinc and copper are more difficult to float (with conventional xanthate collector) than their sulfide mineral compounds. Unlike the sulfide minerals (of which the surface chemistry is largely determined by electrochemical reactions), the surface chemistry of oxide minerals is largely determined by ion exchange reactions and electrostatic interactions (Fuerstenau, 2007). With oxide minerals, the metal atoms are less apt to form a chemical bond with xanthate ions because of the higher ionic nature of the bond of metal-oxygen than the bond of metal-sulfur (Rao and Leja, 2004). The major problem is that oxidized ore minerals consume large quantities of xanthate collector before the formation of an hydrophobic film of xanthate on the mineral surface because of: (1) the higher solubilities of oxide/carbonate/sulfate minerals compared to sulfide minerals; (2) the metal cations dissolved from mineral lattice (e.g., Pb^{2+} from cerussite $PbCO_3$), may react with xanthate ions and precipitate as an insoluble metal-xanthate compound (undesired reaction) before the formation of hydrophobic film of xanthate on the mineral surface; (3) the extensive hydration of oxide surfaces (Rashchi et al., 2005; Fuerstenau, 2007). Therefore, sulfidizing agents such as

Na_2S frequently used to produce a sulfide surface which could be made hydrophobic by xanthate collectors. The hydrosulfide ion (HS^-) is considered to be the active species in the sulfidisation of base-metal "oxide" minerals and (Herrera-Urbina, 1999; Newell et al., 2007). The sulfidisation mechanism for base-metal "oxide" minerals may be associated with two processes: (1) chemisorption of HS^- onto the mineral surface followed by the formation of a sulfide surface (coating) through anionic exchange; or (2) direct precipitation of base-metal sulfides onto the mineral surface (Rao and Leja, 2004; Newell et al., 2007). Sulfidization is commonly applied in the flotation of the oxidized sulfide ores and oxide/carbonate/sulfate metal minerals such as tenorite (CuO), malachite $Cu_2(CO_3)(OH)_2$, and cerussite ($PbCO_3$). Further, the combination of sulfidization and flotation is frequently used for soil washing applications because of the heterogeneity of mineralogical forms of metal contaminants in the contaminated soil (Table 1). However, the improvement in metal removal efficiency may be low compared to flotation process without chemical activation (Venghaus and Werther, 1998; Vanthuyne and Maes, 2002). The sodium sulfide dosage is a crucial parameter. Unfortunately, only two reagent dosages were tested in this study. At lower dosage of sodium sulfide, the degree of sulfidization was not sufficient and the surface of metal oxide was not "activated" (Shen et al., 2001). At higher concentrations of sodium sulfide, the excess of sulfide ions in the pulp may decrease the flotation recovery because xanthate ions are replaced by sulfide ions at the flotation stage due to sulfide ion adsorption in preference to xanthate adsorption (Rashchi et al., 2005).

In this study, the sulfidization-flotation process was done at pH 9–9.5, a usual pH range condition when the sulfidizing agent are used (Herrera-Urbina et al., 1999; Rashchi et al., 2005). Addition of Na_2S caused a significant increase of pH. Potassium amyl xanthate (KAX) is the preferred xanthate for the recovery of oxide lead and copper minerals after chemical activation by sulfidization (Cytec, 2002). As can be seen from the Fig. 2, the addition of a sulfidization step did not cause a significant change in metal (Cu, Pb, and Zn) recovery and has caused a decrease of the concentration factor of metals. The pre-treatment by sulfidization seems theoretically attractive, but in practice it suffers from several disadvantages: (1) it is difficult to control the dosage of sulfidizing agent; (2) the different oxide minerals respond differently to sulfidization (Shen et al., 2001; Newell et al., 2007). In the case of the treatment of the heterogeneous contaminated soil, the sulfidization may fail to provide an acceptable recovery increase compared to conventional flotation.

3.2.6. Assessment of flotation mechanism via the selectivity index Zn/Fe and Zn/Ca

The concentration factor of metal evaluates the separation selectivity of the metal in relation to the floated mass, however it does not provide direct information on the specific contribution of the true flotation and the mechanical entrainment mechanism in the flotation environment. The authors propose to assess the separation selectivity of metals by comparing their flotation response with Fe and Ca. Iron and calcium are major elements of the mineral soil components; thus they are undesired in the froth concentrates. XRD analysis showed that Fe was mainly present in oxide compounds (hematite), while Ca was present in both carbonate (calcite) and sulfate (gypsum) forms. In addition, the Ca amount (34.7%) was significantly higher than the Fe amount (27.4%) in the 0–20 µm fraction (Table 4). The mineralogy difference between Fe and Ca compounds and their distribution in the finest particle-size fraction may help to compare the flotation selectivity of metal vs. different soil mineral components. Moreover, the study of flotation response between the heavy metal and those of Fe and Ca may be helpful for assessing the contribution of entrainment mechanism and true flotation mechanism through chemical and mineralogical parameters. In order to simplify the discussion, Zn is taken as representative of heavy metals. The Zn concentration factor versus the Fe concentration factor obtained with the different flotation methods were plotted in the same x-y diagram (Fig. 5a). Likewise, the Zn concentration factor versus the Ca concentration factor for the same experiments were plotted in the Fig. 5b. Additionally, the lines corresponding to (y/x = 1), (y/x = 1.5), (y/x = 2), (y/x = 3) were reported in the two x-y diagrams in order to compare the selectivity index of Zn/Fe and Zn/Ca for the different flotation tests.

Fig. 5 clearly shows that the flotation response of Ca and Fe are significantly different. Calcium was more easily recovered than Fe for all flotation experiments. This suggests that calcite and gypsum particles were recovered more in the froth than Fe oxide particles. Consequently, the Zn/Fe selectivity index was higher than the Zn/Ca selectivity index in all the flotation experiments (i.e., independently of the variations of chemical factors in the pulp). These results can be explained in two ways: (1) the difference in the mineralogy of Fe and Ca compounds, which relates to the hydrophobic character of their surface (i.e., hypothesis based on the true flotation mechanism); (2) the difference in the distribution ratio of Zn/Fe (equal to 1.9) and Zn/Ca (equal to 1.5) in the 0–20 μm fraction (Table 4) (i.e., hypothesis based on the entrainment mechanism of the fine particles).

On the one hand, the flotation responses can be related to the difference in the mineralogy between Ca and Fe compounds in the soil. Since the surface of gypsum ($CaSO_4$) is relatively more hydrophobic compared to Fe oxides (such as hematite), the gypsum particles may be floated more easily than the Fe oxide particles via the true flotation mechanism. Thus, the true flotation of gypsum particles may compete with the collection of sphalerite particles and thus affect the flotation selectivity of the metal. On the other hand, the difference in the Zn/Ca and Zn/Fe selectivity indices can be explained by the entrainment mechanism of the fine particles (0–20 μm). Since the Ca amount was significantly higher than the Fe amount in the 0–20 μm fraction

(Table 4), the entrainment mechanism of the fine particles of calcite and gypsum probably contributed to an additional recovery of Ca in the froth. The distribution ratio of Zn/Fe and Zn/Ca in the finest particle-size fractions (0–20 µm and 20–38 µm) are reported on Fig. 5. By comparing this ratio to the selectivity index (of Zn/Ca or Zn/Fe) obtained with the flotation tests, Fig. 5 shows that the flotation responses are simply shifted in relation to the distribution ratio of Zn/Fe and those of Zn/ Ca in the 0–20 µm fractions. This comparison shows that: (1) the entrainment mechanism of fine particles highly influences the transportation mechanism of the particles in the flotation process, especially with kerosene collector; (2) the best concentration factor of Ca (compared to Fe) was probably not the result of the contribution of true flotation mechanism of gypsum particles.

Fig. 5 also shows that the flotation behavior with kerosene and xanthate can be clearly distinguished. The Zn/Fe and Zn/Ca selectivity indices were systematically better with xanthate. On the one hand, the Zn/Fe selectivity index ranged from 1.5 to 2 (< distribution ratio in the 0–20 µm) with kerosene collector, while it ranged from 2 to 3 (> distribution ratio in the 0–20 µm) with KAX collector (Fig. 5a). On the other hand, the Zn/Ca selectivity index ranged from 1.0 to 1.5 (< distribution ratio in the 0–20 µm) with kerosene collector, whereas it ranged from 1.5 to 2.0 (> distribution ratio in the 0–20 µm) with KAX collector (Fig. 5b). Two factors may explain this result: (1) the use of sulfide specific collector (xanthate) contributes to the best separation selectivity of sphalerite particles via the true flotation mechanism; (2) when the kerosene collector is used, the undesired fine particles of hematite, calcite and gypsum more recovered in the froth via the entrainment mechanism. When sulfidization was used prior to flotation procedure (with xanthate), the selective separation between the Zn-bearing particles and the Fe oxides particles became less efficient (Fig. 5a). This may be due to the recovery increase of Fe oxides particles via true flotation mechanism after the sulfidization of their surfaces. A similar trend was observed for Zn/Ca selectivity ratio, but it is difficult to clearly explain this result through specific factors related to the physico-chemical surface properties involved.

3.2.7. Flotation technology vs. the size separation

The response of flotation can be related to the distribution of metal in the 0–20 μm fraction because of: (1) the fine particle-size fraction <20 μm represented approximately 29% of soil mass and contained 42–53% of the metal contamination amount (Table 4); (2) these fine particles <20 μm were easily recovered in the froth by the entrainment mechanism, especially in the flotation cell systems fitted with a mechanical agitation. Table 8 compares some flotation results with a size separation of the 0–20 μm fraction (simulation with 100% efficiency). The flotation experiences selected correspond to the best results in metal recoveries obtained for each collector tested. Table 8 shows that flotation tests provided the best concentration factor of heavy metal when compared to those of size separation of the finest particle-size fraction. This suggests that the true flotation was involved in the metal-containing particle separation process. However, the flotation using kerosene was influenced by the entrainment mechanism of the fine particles, although the concentration factors of metals were substantially higher than those of the size separation. The order of percentages of metal in the 0–20 μm fraction of the feed soil is : As > Zn > Pb > Cd ≈ Cu (Table 8). This order corresponds nearly to the order in metal recovery (As > Zn > Pb ≈ Cd ≈ Cu) when kerosene collector was used (Fig. 2 and Table 8), but it is not the case with xanthate collector (Fig. 3). For instance, recoveries of Zn and As were generally similar, while Cu is generally recovered more than the Pb and Cd with KAX (Fig. 3 and Table 8). When kerosene was used, the entrainment mechanism contributes to an important part of the particle removal process. The flotation with KAX as collector is less affected by the entrainment mechanism, thereby improving the flotation selectivity.

4. Conclusions

The difference in flotation selectivity between the kerosene and xanthate collector cannot be clearly explained by the factors relating to surface chemistry properties (mineralogy of particles, pulp chemistry, flotation reagents, etc.). The recovery of the desired metal-containing particles appeared as the summation of the true flotation process and the mechanical entrainment mechanism. The low flotation selectivity of heavy metals was due to the recovery of the non desired particles into the froth layer: (1) the undesired collection (true flotation) of hydrophobic non-metallic particles such as coal, graphite (highly hydrophobic), and gypsum (fairly hydrophobic), thus competing with flotation of metal-bearing particles; (2) mechanical entrainment of the fine hydrophilic particles (such as hematite) in the froth fraction. The entrainment mechanism significantly influenced the metal recovery in the self-aerated Denver laboratory flotation cell since the metal contamination was high in the finest particle-size fraction. The contribution of the entrainment mechanism was more important when the kerosene was used as collector.

In order to improve this soil washing process by flotation technology, the finest (<20 µm), the coarsest (>125–250 µm) and the intermediate (20–125 µm) particle-size fractions could be treated separately in flotation systems where the experimental parameters are adjusted to treat the particle size. For example, ASH (Air Sparged Hydrocyclone) (Fuerstenau, 2007) and DAF (Dissolved Air Flotation) (Mulleneers et al. 2002; Rodrigues and Rubio, 2007) technologies are well adapted to treat the fine particles. Also, the flotation reagents may be toxic and cause pollution to the environment. Hence, the development of environmentally benign chemical reagents for flotation should be also emphasized.

Acknowledgments

The first author is thankful to the "Institut National de la Recherche Scientifique Eau Terre et Environnement" (INRS-ETE) for financial support. The authors would also like to thank Kathrine Gauvin and Catherine Martineau-Thériault for their useful comments.

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Tables

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Table 1. Flotation laboratory studies in the remediation of metal-contaminated soils/sediments

Case studies	Media (particle size)[a]	Metal (µg/g) [metal fractionation][b]	Technology	Pre-treatment	Collector	Metal recovery (%)	VR (%)	CF
Uhrie et al. (1996)	Artificially contaminated soil (fine grained)	Cu (700)	Wemco Cell	Sulfidization	DTP[c]	78	NA	NA
Cauwenberg et al. (1998a, b)	Sediments (70% <50 µm)	Cd (13), Cu (128), Pb (721), Zn (3200) [50-90% sulfides]	Denver Cell	None	Kerosene[e]	52–60 at pH 8 70–80 at pH 12	82 70	2.9–3.4 2.5–3.0
Stapelfeldt and Huycumu (1998)	Soil from a former steel works (63–250 µm)	Pb (600); Zn (800) [oxidic minerals, Mn/Fe oxides]	Humbolt Wedag cell	Attrition, sulfidization	KAX[c]	75 (Pb), 44 (Zn)	92	>5
Venghaus and Werther (1998)	Soil from industrial site (40–355 µm)	Zn (3200) [52% reducible, 33% carbonates, 13% exchangeable, 1% sulfides/organic, 1% residual]	Cell	Sulfidization/ hydroxylation	DTP[c], KHX[c] OAA[d]	35 at pH 10.5	95	6.6
Abd El-Rahman et al. (1999)	Sediments (70% <50 µm)	Cd (18), Cu (155), Pb (734), Zn (2763)	Denver Cell	None	Diesel[e], or KEX[c]	80–88 (Zn)	61–68	1.5–2.5
Vanthuyne and Maes (2002)	Loamy soil (0–2 mm)	Cd (8), Cu (68), Pb (142), Zn (357) [variable]	Denver Cell	Sulfidization	KEX[c]	40–50	70	1.5–2.5
Vanthuyne et al. (2003)	Sediments (70% <50 µm)	Cd (13), Cu (128), Pb (721), Zn (3200) [50-90% sulfides]	Denver Cell	None	KEX[c] or Kerosene[e]	60–70 at pH 8 80–90 at pH 12	81 67	3.1–3.6 2.4–2.7
Vanthyune and Maes (2007)	Sediments (4 matrix types have been studied)	Cd (5–13), Cu (100–200), Pb (170–340), Zn (870–1515) [variable]	Denver Cell	None	Kerosene[e]	40–90 at pH 8.7	70–80	1.7–3.2

NA: Not Available; VR= Volume reduction (= 100─Mass recovery); CF= Concentrating factor= Metal recovery/(100─VR); SIF: separation in froth; KHX: Potassium Hexyl Xanthate; KEX: Potassium Ethyl Xanthate; KAX= Potassium Amyl Xanthate; NaIPX= Sodium isopropyl Xanthate; DTP: Dithiophosphate; OAA: Oleylamine acetate

[a] Particle size fraction that was treated by flotation

[b] Sequential extraction procedure

[c] Sulfide-specific collector

[d] Oxide-specific collector

[e] Non-specific collector

Table 2. General characteristics of the brownfield soil (0–10 mm)

Parameters	Range
Major mineral elements (%)[a]	
Al	6.84
Ca	3.27
Fe	10.7
K	1.14
Mg	0.48
Mn	0.076
Na	0.619
P	0.103
Si	16.16
Ti	0.408
Other parameters	
Total Carbon (%)[b]	20
Organic Carbon (%)[b]	17.5
Total Nitrogen (%)[b]	0.31
C/N ratio[c]	56
Total Sulfur (µg/g)[d]	8040
LOI at 1025°C (%)	26.2
Moisture (%)	1.2
Soil pH	7.2
Texture (%)[e]	
Clay (0–2 µm)	3
Silt (2–63 µm)	22
Sand (63–2000 µm)	44
Gravel (2000-10000 µm)	31

[a] ICP-AES analysis after soil fusion with $LIBO_2$ and dissolution of fusion product
[b] Leco CHNS-932 autoanalyzer; Organic carbon content was measured after carbonate dissolution
[c] Weight ratio of organic carbon to total nitrogen
[d] ICP-AES analysis after multi-acid digestion (HCl, HNO_3, HF)
[e] Wet sieving and laser diffraction particle size analyzer (for <63 µm)

Table 3. Metal concentrations in the brownfield soil (0–10 mm)

Metal trace elements	Range (µg/g)	Threshold values of Quebec legislation (µg/g)			
	Mean ± SD (n=10)[a]	*Criteria A*	*Criteria B*	*Criteria C*	*Criteria D*
As	101 ± 4	6	30	50	250
Cd	25.2 ± 2.0	1.5	5	20	100
Co	35.0 ± 1.1	15	50	300	1500
Cr	220 ± 18	85	250	800	4000
Cu	2540 ± 153	40	100	500	2500
Ni	86.0 ± 2.6	50	100	500	2500
Pb	2168 ± 108	50	500	1000	5000
Zn	7939 ± 556	110	500	1500	7500

[a] ICP-AES analysis after multi-acid digestion (HCl, HNO_3, HF)
Criteria A: Background level (MDDEP, 1999)
Criteria B: Maximum level allowed to residential and recreational site use (MDDEP, 1999)
Criteria C: Maximum level allowed to commercial or industrial site use (MDDEP, 1999)
Criteria D: Level relating to disposal prohibiting (MDDEP, 2008)

Table 4. Concentration and distribution of metal contaminants (As, Cd, Cu, Pb and Zn) and three major elements (Ca, Fe, S) in five different particle-size fractions of soil

Particle size fractions	Mass	Ca	Fe	S	As	Cd	Cu	Pb	Zn
Concentrations (µg/g)									
125–250 µm		27642	109466	8111	44	16.9	1658	1132	4762
63–125 µm		28348	111523	9662	68	21.6	2179	1786	5950
38–63 µm		26752	115230	8036	74	22.7	2119	1712	6232
20–38 µm		29038	109115	7388	126	28.2	2659	2465	8174
0–20 µm		37026	104566	8209	180	38.6	3644	3596	14768
Bulk soil 0–250 µm		32659	107312	8040	101	25.2	2543	2168	7939
Distributions (%)									
125–250 µm	34.5	31.3	34.7	33.4	15.7	22.9	23.4	18.4	19.9
63–125 µm	19.8	18.4	20.2	22.8	13.9	16.8	17.6	16.6	14.2
38–63 µm	8.7	7.6	9.2	8.3	6.6	7.8	7.5	7.0	6.6
20–38 µm	8.4	8.0	8.4	7.4	10.9	9.3	9.1	9.8	8.3
0–20 µm	28.6	34.7	27.4	28.0	52.9	43.3	42.4	48.3	51.0

Table 5. Geochemical/mineralogical forms of the metal-bearing phases of Cu, Pb, and Zn

Geochemical/mineralogical forms of metal-bearing phases	Metal content	Number of particles identified	Metal distribution in soil (%)
Copper-bearing phases	*Cu (wt.%)*		
Cu-Zn Alloy	65–70	1	6
Cu Oxide (may be associated with Fe, Zn, Sn)	50–85	7	41
Cu Oxide/Carbonate	50–60	2	12
Fe Oxide with Zn	10–20	4	24
Cu-Fe Sulfide/Oxidized sulfide	10–25	2	12
Cu Silicate slag	40–50	1	6
Lead-bearing phases	*Pb (wt.%)*		
Pb Oxide (may be associated with Sn, Sb, Fe, Zn)	40–90	9	21
Pb Oxide/Carbonate	70–85	7	17
Pb Oxide/Fluoride (may be associated with Sn)	25–85	4	10
Pb Sulfide/Oxidized sulfide	45–85	4	10
Pb Silicate (may be associated with C, Fe, K, Ca, Al, …)	10–50	7	17
Pb associated with C, Si, Fe (unidentified phase)	10–60	5	12
Sn Oxide with Pb and Zn	10–15	6	14
Zinc-bearing phases	*Zn (wt.%)*		
Cu-Zn Alloy	30–35	1	2
Zn Sulfide (with 6–8% Fe and 1–2% Mn)	45–65	34	76
Sn, Cu, Pb, or Fe Oxides with Zn	10–25	8	18
Others (mainly silicates)	10–15	2	4

Table 6. Selected EDX analyses (values in wt.%) of metal-containing particles, composing a simple or complex mineralogical association

Sample	C	O	F	Na	Al	Si	S	P	Cl	K	Ca	Mn	Mg	Fe	Ba	Ti	As	Cu	Pb	Zn	Sn	Sb	Sum
a-1	-	19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	80	-	-		-	100
a-2	7	28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	53	-	12	-	-	100
a-3	5	28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	54	-	12	-	-	100
a-4	1	23	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	17	-	33	24	-	100
a-5	-	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	90	-	-	-	-	100
b-1	-	27	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	7	65	-	100
b-2	6	37	-	-	4	11	-	-	-	-	2	-	-	2	-	-	-	-	-	8	30	-	100
b-3	-	25	-	-	-	4	-	-	-	-	-	-	-	-	-	-	0.2	-	18	5	49	-	100
b-4	5	29	-	-	-	7	-	-	-	-	2	-	-	1	-	-	-	-	6	11	38	-	100
c-1	-	31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	69	-	100
c-2	-	46	-	-	7	9	-	-	-	-	-	-	-	3	-	-	-	-	-	9	25	-	100
c-3	-	45	-	-	5	9	-	-	-	-	-	-	-	2	-	-	-	2	-	7	32	-	100
c-4	-	43	-	2	3	5	-	-	-	-	-	-	-	-	-	-	-	-	-	11	35	-	100
d-1	1	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	79	-	3	2	-	100
d-2	5	37	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	57	-	-	-	-	100
e-1	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	85	-	-	-	100
e-2	-	27	-	-	1	2	-	-	-	-	-	-	-	55	-	-	-	-	10	5	-	-	100
f-1	-	26	-	-	2	13	-	-	-	1	2	-	-	6	-	1	-	-	48	-	-	-	100
f-2	-	24	-	-	3	15	-	-	-	1	2	-	-	6	-	1	-	-	48	-	-	-	100
f-3	-	30	-	1	11	21	-	-	-	3	1	-	-	3	12	-	-	-	19	-	-	-	100

Notes: For positions of presented EDX analyses, see Fig. 1

Table 7. Flotation parameters, mass balance, and metal concentrations in the flotation fractions for all tests

Flotation reference	F01	F02	FK1	FK2	FK3	FK4	FK5	FK6	FK7	FK8	FX1	FX2	FX3	FX4	FX5	FX6	FX7	FX8	FSK5	FSK2
Flotation parameters																				
Pre-treatment	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	SU5[a]	SU2[a]
Collector name	–	–	KER	KER	KER	KER	KER	KER	KER	KER	KAX	KAX	KAX	KAX	KAX	KAX	KAX	KAX	KAX	KAX
Collector dosage (mg/g)	0	0	4	8	12	16	12	12	12	12	0.25	0.5	1	2	0.5	0.5	0.5	0.5	2	2
Pulp pH	7.5	9.2	7.5	7.5	7.5	7.5	8.9	10.0	11.0	12.0	9.2	9.2	9.2	9.2	8.2	10.1	10.9	12.0	9.2	9.2
Mass balance (%)																				
Mass Recovery of Froth	10.6	11.5	19.7	24.8	26.8	23.8	25.5	25.1	26.0	24.0	11.2	13.9	14.5	17.0	13.0	13.9	12.1	12.7	19.3	18.5
Volume Reduction[b]	89.4	88.5	80.3	75.2	73.2	76.2	74.5	74.9	74.0	76.0	88.8	86.1	85.5	83.0	87.0	86.1	87.9	87.3	80.7	81.5
Metal concentrations (µg/g)[c]																				
Feed soil																				
As	90	98	109	102	109	110	111	112	112	115	96	101	97	104	96	99	94	97	107	107
Cd	24	24	26	25	26	26	25	27	28	27	24	27	25	26	25	24	28	23	26	27
Cu	2576	2283	2508	2509	2574	2412	2558	2507	2399	2375	2369	2354	2827	2541	2377	2484	2509	2288	2599	2517
Pb	2010	2080	2312	2152	2287	2351	2302	2249	2268	2270	2021	2087	2128	2248	2050	2092	1997	2001	2287	2261
Zn	7447	7567	8348	8153	8690	8249	8567	8430	8228	8682	7739	7894	7773	8554	7714	7587	8566	7542	8052	8282
Froth																				
As	294	328	287	232	237	242	247	260	258	270	348	329	314	313	328	301	317	331	305	302
Cd	55	57	56	45	46	48	43	49	55	51	79	71	66	65	74	65	101	72	60	60
Cu	5251	5372	4957	4419	4510	4381	4695	4517	4536	4580	7512	7091	7629	6987	7348	7549	9660	8410	6182	6019
Pb	5352	5488	4981	4250	4336	4286	4391	4289	4501	4574	6158	5814	5708	5734	6088	5579	5816	5959	5332	5477
Zn	18604	19217	20253	17366	17721	17372	18687	17507	17695	19544	28196	25817	23690	25904	27242	23571	33895	26540	22054	23011
Tailings																				
As	66	68	66	60	63	68	64	63	60	66	65	65	60	61	61	66	63	63	60	63
Cd	21	20	19	18	19	19	18	19	18	19	17	20	18	18	17	18	18	16	18	19
Cu	2260	1881	1833	1771	1864	1797	1827	1833	1650	1680	1720	1590	2010	1630	1637	1667	1523	1401	1742	1722
Pb	1615	1637	1658	1460	1537	1746	1587	1566	1485	1543	1499	1485	1519	1534	1449	1530	1471	1428	1558	1531
Zn	6129	6052	5430	5111	5380	5394	5104	5389	4908	5257	5158	5001	5066	5000	4806	5010	5076	4791	4704	4939

KER= Kerosene; KAX= Potassium Amyl Xanthate.

[a] Sulfidization pre-treatment with 5 mg/g and 2 m/g Na_2S for SU5 and SU2 respectively.

[b] Volume Reduction (%)= 100-Mass recovery of froth.

[c] For the feed soil and the tailings fractions, the underlined values represent the concentrations greater than the level relating to soil disposal prohibiting (MDDEP, 2008).

Table 8. Flotation performance results vs. the size separation of the 0–20 µm fraction

Method	Mass	VR[a]	As	Cd	Cu	Pb	Zn
Recovery (%)							
Flotation with 2 mg/g KAX at pH 9.2 (FX4)	17.0	83.0	51.3	42.2	46.8	43.4	51.5
Flotation with 12 mg/g Kerosene at pH 11 (FK7)	26.0	74.0	60.1	51.6	49.1	51.5	55.8
Size separation of the 0–20 µm fraction	28.6	71.4	52.9	43.3	42.4	48.3	51.0
Concentration Factor (CF= Metal/Mass)							
Flotation with 2 mg/g KAX at pH 9.2 (FX4)			3.0	2.5	2.8	2.6	3.0
Flotation with 12 mg/g Kerosene at pH 11 (FK7)			2.3	2.0	1.9	2.0	2.2
Size separation of the 0–20 µm fraction			1.9	1.5	1.5	1.7	1.8

[a] Volume Reduction (%)= 100–Mass Recovery

Figures

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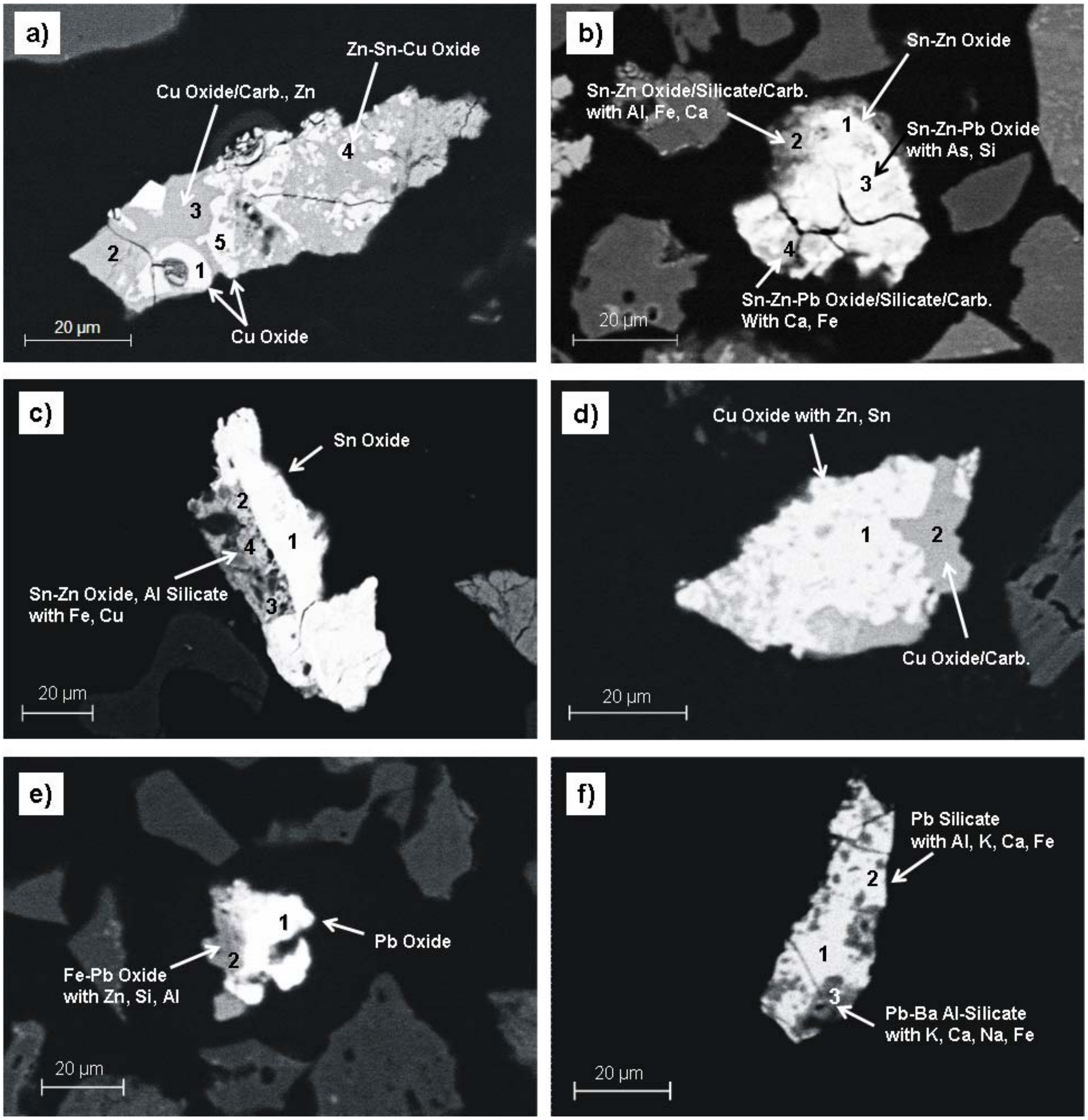
Fig. 1. Backscattered electron micrographs of different metal-containing particles (simple or complex mineralogical association of metal-bearing phases and/or carrying phases) from the brownfield soil processed. Points (1, 2, 3, etc.) correspond at positions of the chemical analysis by EDX (the results are given in Table 6). (a) Particle composed of Cu-Zn oxide/carbonate intermixed with Cu oxide and Zn-Sn-Cu oxide phases. (b) Particle composed of Sn-Zn oxide intermixed with Sn-Zn-Pb oxide, which are fractured and has altered to Sn-Zn-Pb oxide, silicate, carbonate. (c) Particle composed of Sn/Zn oxide, Al-silicate associated with carrying phase of Sn oxide. (d) Cu fragment altered to secondary mineral: Cu oxide (possibly Tenorite CuO) and Cu carbonate (possibly Malachite $[Cu_2(CO_3)(OH)_2]$). (e) Particle composed of Pb oxide portion (probably Plattnerite, PbO_2) associated with Fe oxide (containing Pb and Zn). (f) A partly decomposed Pb silicate and Pb-Ba Al-silicate particle.

Fig. 2. Effect of kerosene collector dosage (0–16 mg/g; at pH 7.5) and pulp pH (7.5–12; with kerosene 12 mg/g) on flotation of heavy metals, Fe, and S: (a) Recovery vs. Collector dosage; (b) Concentration factor vs. Collector dosage; (c) Recovery vs. pulp pH; (d) Concentration factor vs. pulp pH.

Fig. 3. Effect of KAX collector dosage (0–2 mg/g; at pH 9.2) and pulp pH (8–12; with KAX 0.5 mg/g) on flotation of heavy metals, Fe, and S: (a) Recovery vs. Collector dosage; (b) Concentration factor vs. Collector dosage; (c) Recovery vs. pulp pH; (d) Concentration factor vs. pulp pH.

Fig. 4. Recovery versus concentration factor for (a) Cu, (b) Pb, and (c) Zn obtained with different chemical flotation parameters. General flotation parameters: conditioning time of 10 min, flotation time of 10 min, 0.24 mg/g MIBC as frother; 1350 rpm as impeller speed; 10% of pulp density. Specific chemical parameters are reported in Table 7. The error bars correspond to the standard deviations associated with the three flotation tests with 8 mg/g kerosene at pH 7.5.

Fig. 5. (a) Zn concentration factor versus Fe concentration factor and (b) Zn concentration factor versus Ca concentration factor obtained with different chemical flotation parameters. General flotation parameters: conditioning time of 10 min, flotation time of 10 min, 0.24 mg/g MIBC as frother; 1350 rpm as impeller speed; 10% of pulp density. Specific chemical parameters are reported in Table 7. The error bars correspond to the standard deviations associated with the three flotation tests with 8 mg/g kerosene at pH 7.5.



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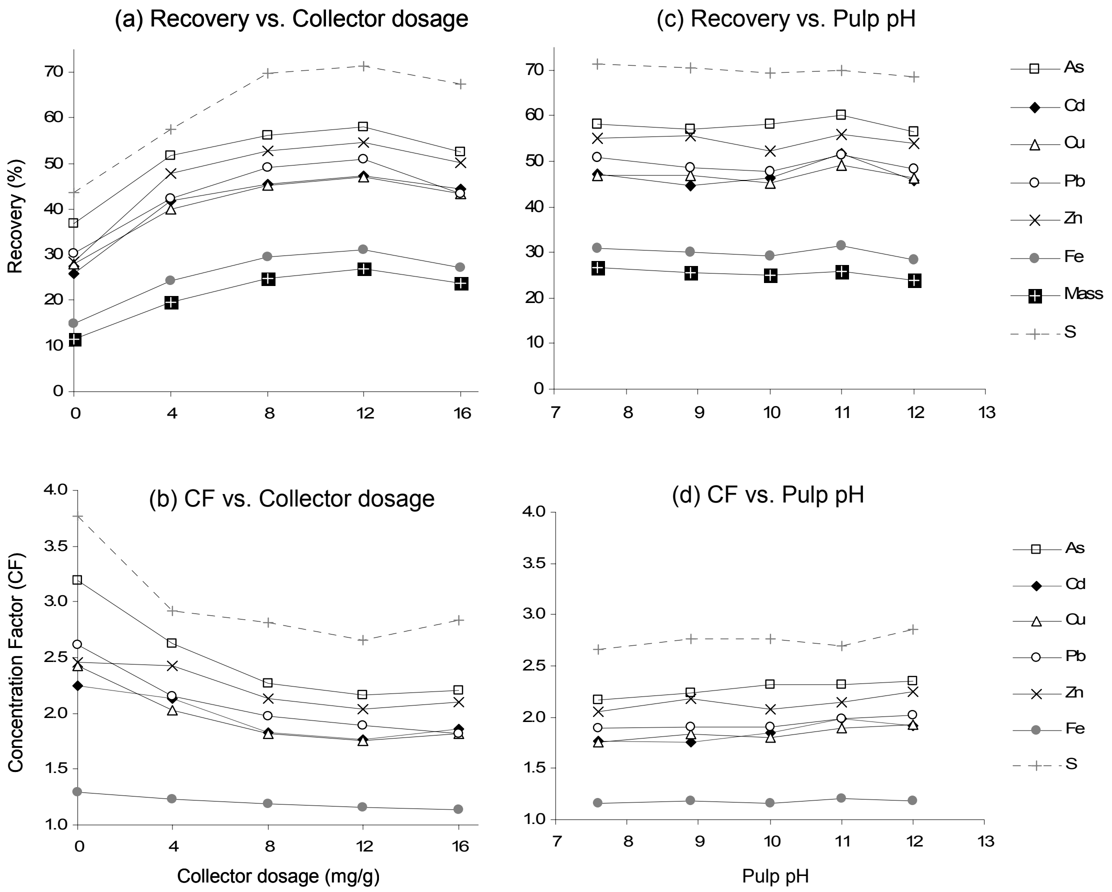

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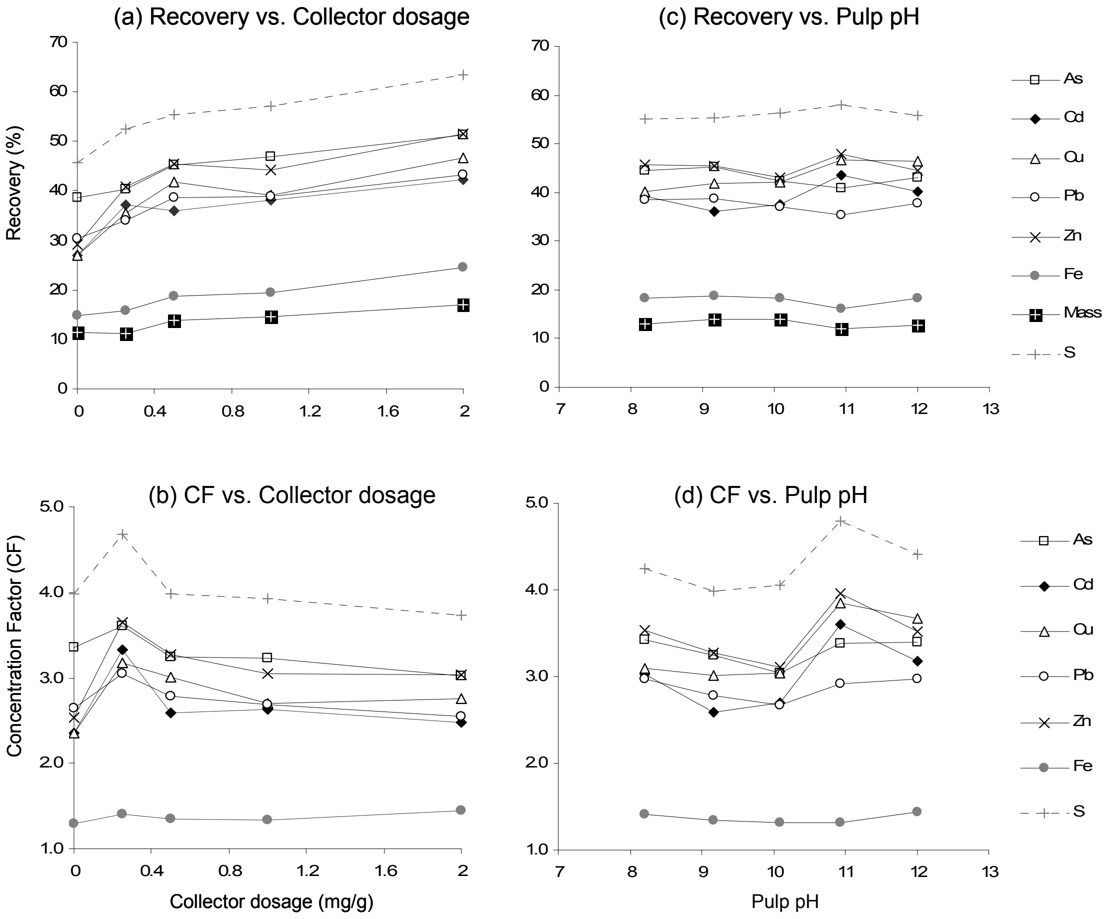

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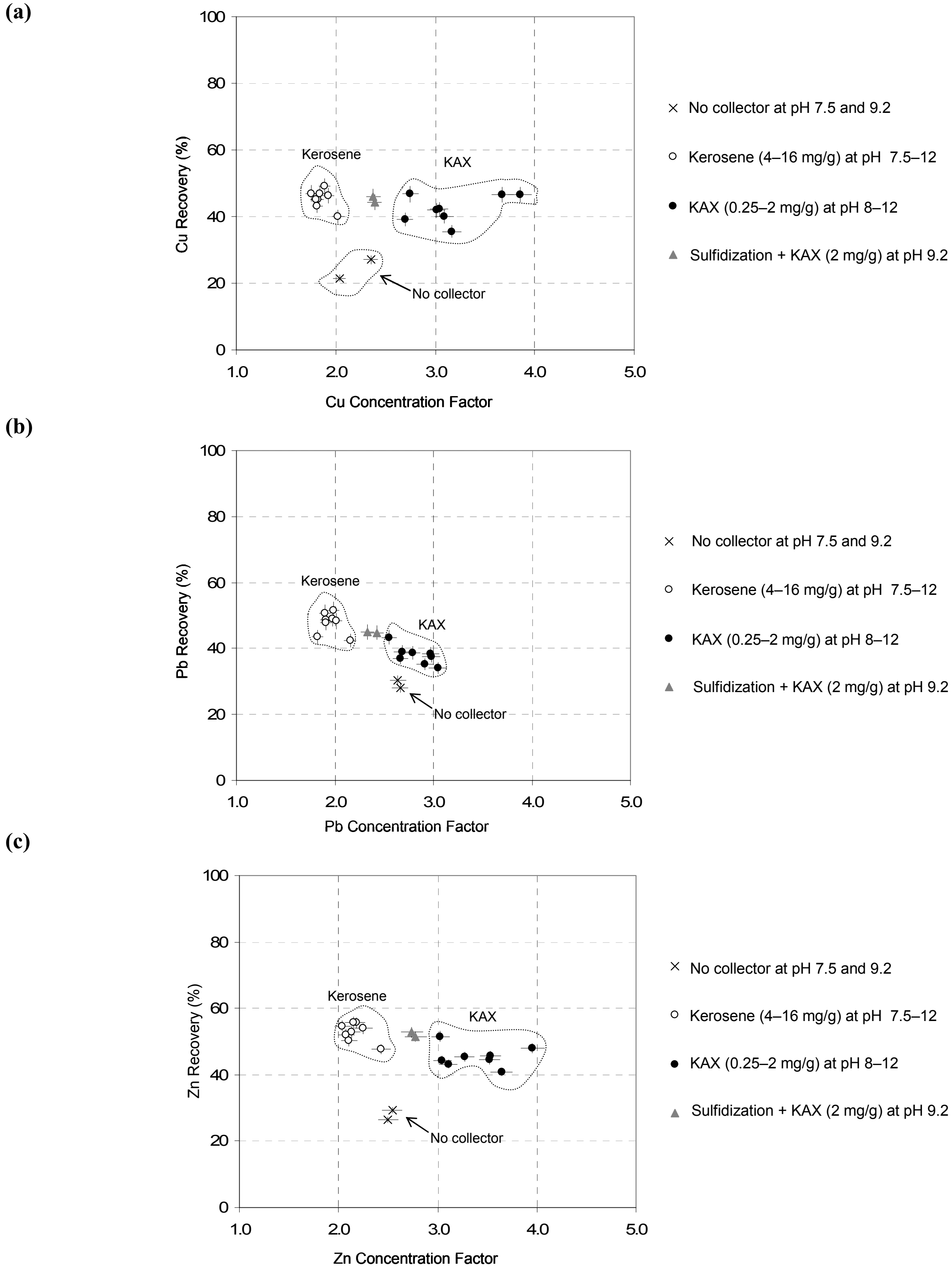

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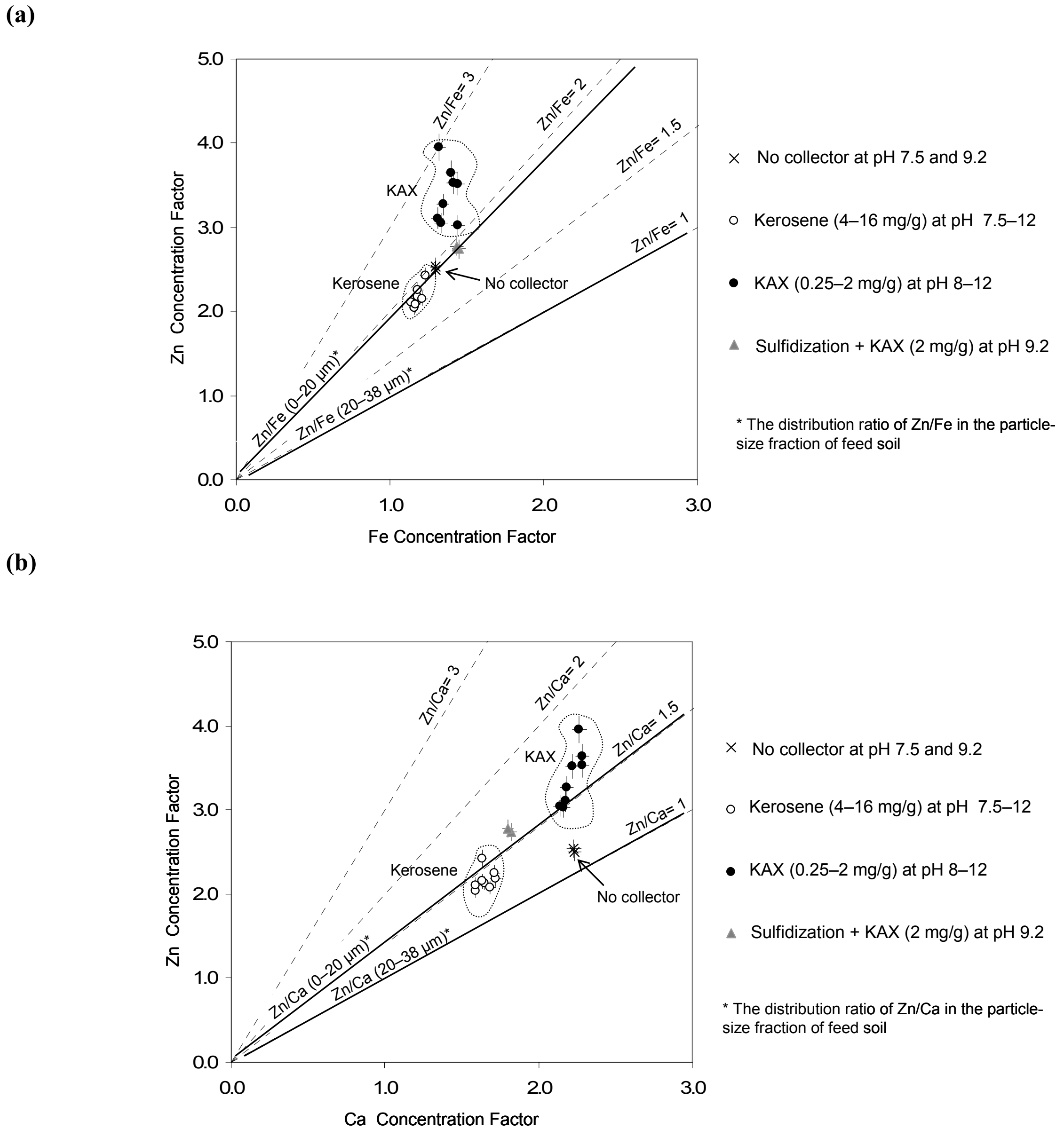

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Chapitre 7: Heavy metals removal from contaminated soils by froth flotation: Part 2. Influence of physical factors and contribution of entrainment mechanism

Résumé

La technologie de flottation (cellules de laboratoire de type Denver) a été étudiée comme technique de décontamination permettant l’enlèvement de l'arsenic, du cadmium, du cuivre, du plomb et du zinc des sols pollués. Les métaux lourds sont distribués sous des formes particulaires résultant de l’enfouissement de déchets solides métallurgiques. La discussion se focalise sur l'influence de différents paramètres physiques (vitesse d’agitation, temps de traitement, dimension des particules, mode d'addition de réactifs, prétraitement par ultrasons) sur la sélectivité de la flottation, et ce, afin d'évaluer la contribution du mécanisme d'entraînement. Une grande proportion de particules riches en métaux a été récupérée dans la fraction de mousse par le mécanisme d'entraînement plutôt que par le véritable processus de flottation. Le mécanisme non sélectif d'entraînement des particules fines (<20 µm) se produit particulièrement lorsque le processus se déroule sur un long laps de temps (> 5 minutes) et lorsqu’une dose élevée de collecteur est ajoutée à la pulpe en une seule étape. La sélectivité de flottation est meilleure pour la fraction granulométrique intermédiaire (20–125 µm). L’utilisation de la méthode de flottation en plusieurs étapes successives permet de diminuer l’effet d’entraînement, ce qui améliore la sélectivité de séparation par flottation. Par cette méthode, 50 à 60% des métaux lourds peuvent être concentrés dans seulement 25% du volume initial du sol.

Submission to Science of the Total Environment, April 2008

Heavy metal removal from contaminated soils by froth flotation: Part 2. Influence of physical factors and contribution of entrainment mechanism

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Abstract

The soil remediation by froth flotation (Denver laboratory cell) was investigated for the removal of arsenic, cadmium, copper, lead, and zinc from highly contaminated soil. The heavy metals were mainly in particulate forms resulting from the disposal of metallurgical wastes at the site. The discussion is focused on the influence of impeller speed, flotation time, soil particle-size, mode of collector addition, and ultrasonic pre-conditioning on the flotation selectivity in order to evaluate the contribution of the entrainment mechanism in the metal removal efficiency. A great proportion of metal-bearing particles were recovered in the froth layer by entrainment mechanism rather than by true flotation process. The non selective entrainment mechanism of the fine particles <20 µm caused a flotation selectivity drop, especially with a long flotation time (>5 min) and when a high collector dose is added to the pulp all at once. The intermediate particle-size fraction (20–125 µm) showed the best flotation selectivity. With multistage flotation, approximately of 50–60% of heavy metal contamination amount may be concentrated in only 25% of the initial soil volume.

Keywords: Contaminated soil; Heavy metals; Soil washing; Froth flotation

1. Introduction

The enormous quantity and the complexity of metal-contaminated soils constitute an important challenge for their remediation. Metal extraction technologies such as soil washing (ex situ treatment), phytoextraction, and electrokinetics provide a cost effective and environmentally proactive alternative to solidification/stabilization and disposal options. Among the soil washing technologies, froth flotation technology aims at reducing the volume of highly contaminated soil by concentrating the metal-containing particles within a small volume of material (the froth fraction) and producing a residual fraction or “clean soil” (the tailings). The separation process is based on selective attachment of the hydrophobic metal-mineral particles to air bubbles. Froth flotation has been relatively little investigated for soil remediation application, although this technology is widely used in the ore processing industry.

The applicability of froth flotation technology for soil washing process is very different from the ore processing practices because: (1) the contaminated soils are often heterogeneous in their composition and their texture; (2) metal contaminants often involve a great variability in their concentration level, their distribution vs. the soil particle-size fraction, and their fractionation/speciation in the soil. Although the surface chemistry obviously plays an important role in flotation environment, the hydrodynamic parameters of the flotation apparatus and the soil particle-size distribution may significantly influence the metal removal efficiency by flotation. The metal-bearing particles can reach the froth fraction by either true flotation or by entrainment mechanism. The preceding study (Dermont et al., in press) showed that the separation of metal-containing particles from contaminated soil by mechanical Denver flotation was little influenced by the factors relating to the surface chemistry such as mineral nature of metal-containing particles, pulp chemistry, collector type, and chemical activation of particle surfaces. This suggest that great proportion of metal-bearing particles were recovered in the froth layer by entrainment mechanism rather than by true flotation process. Entrainment mechanism occurs when fine particles (<20 µm) are suspended in the water layer surrounding the air bubbles and entrained in the froth, especially in the flotation system fitted with a mechanically agitated cell (Fuerstenau, 2007).

In the present paper, the flotation response and the contribution of the entrainment mechanism in the heavy metal removal was investigated according to the following basic parameters : impeller speed, flotation time, particle-size, mode of collector addition (staged flotation), and ultrasonic pre-conditioning of the pulp.

2. Materials and Methods

The soil sample used for the flotation tests was collected from a brownfield site (Montreal, Canada) highly contaminated by heavy metals (As, Cd, Cu, Pb, and Zn) as a result of the disposal of various industrial wastes. The soil preparation procedure for flotation process was previously described in Part 1 of this series, where the general characteristics, the metal distribution vs. particle-size fractions, and the metal speciation in soil solid phase are also specified (Dermont et al., in press). In summary, the mean concentrations of metal contaminants in the processed soil (0–250 µm) were 101, 25, 2540, 2170, and 7940 µg/g for As, Cd, Cu, Pb, and Zn respectively.

2.1. Analytical procedure

The concentrations of heavy metals (As, Cd, Cu, Pb, and Zn) and of Fe were determined for each flotation fraction (i.e., feed, froth, and tailings) of all flotation tests with the same analytical procedure. The total concentration of each element was analyzed by ICP-AES-axial (Varian Vista AX) after a complete sample (200 mg) decomposition by mixed acid digestion

(HCl, HNO_3, and HF). High quality trace metal grade acids and Milli-Q® water (>18 MΩ cm) were used for the sample digestion procedure. Calculation was done on the basis of oven-dry (105 °C) soil mass, and the results were reported as total concentrations. The analytical results were monitored with two standard reference materials (NIST 2710 and 2711). When the study required it, the particle size analysis and the division of the various particle-size fractions (0–20 µm; 20–38 µm; 38–63 µm; 63–125 µm; 125–250 µm) were conducted with wet sieving with vibratory sieve shaker "Analysette 3" (Fritsch GmbH, Germany). After sieving, the fraction samples were dried, weighted, and pulverized for analytical purposes.

2.2. Flotation tests

The flotation tests were carried out at the natural pH of the pulp (7.5 ± 0.2) in a Denver D-1 laboratory-scale flotation machine with a cell volume of 1.25 l and an impeller diameter of 7 cm. The Denver flotation machine produces its own air with induced air mixer, so it was not necessary to have an external air source. The pulp was prepared for each test by mixing 100 g of soil (0–250 µm) with appropriate amount of distilled water in the flotation cell for obtaining 10% of solid in pulp. The pulp was then conditioned for 10 min (except for the study of staged flotation) with the collector agent in the flotation cell with an agitation speed of 1000 rpm. The collector used for all the flotation tests was a non-ionic surfactant kerosene (Fisher Scientific Inc.). The frother agent (methyl isobutylcarbinol, MIBC) was added in the last minute of the conditioning step. The concentrations of flotation reagent used will be specified in each section. No additional chemical agents (activators, depressants, dispersants, or pH regulators) were used in order to keep the same pulp chemistry conditions for all tests. After the conditioning step, the air valve was opened and flotation test was conducted for the given duration. The flotation selectivity during flotation time was studied. The flotation time and impeller speed were adjusted for the optimal metal recovery after a preliminary study. The impeller rotation provides: (1) agitation to maintain solid/liquid suspension and (2) aeration of the pulp by the injection of air bubbles. The suction caused by the impeller rotation provided the aeration required for the formation of foam. The froth layer was manually continuously removed during the flotation process and collected in glass containers where the mineral was decanted. The same froth removing procedure was used for all tests. The pulp level was maintained constant by adding water. After completion of the flotation stage, the various produced fractions (the froth concentrates and the tailings) were filtered (for the tailings), dried, weighted, and pulverized (<40 µm) for analytical purposes. The specific flotation parameters are specifically described in the following sections. The used amounts of flotation reagents were given in mg/g of dry soil.

2.2.1. Effect of impeller speed

Flotation tests were conducted at various values of the impeller speed agitation (1000, 1200, 1350, and 1600 rpm) for 10 min with 0.16 mg/g MIBC as frother, and 4 mg/g kerosene as collector.

2.2.2. Influence of flotation time

The practical flotation time required can be assessed by producing incremental floated fractions. Four separate froth fractions were removed at different time intervals (2.5, 5, 7.5, and 15 min). The specific flotation parameters used were: 10 min conditioning time, 8 mg/g kerosene as collector, 0.240 mg/g MIBC as frother, and 1350 rpm as impeller speed. Several flotation test replicates were performed in order to provide enough mass of each fraction for chemical analysis. The metal concentrations were determined in each froth fraction collected and the residual fraction (the tailings).

2.2.3. Influence of particle-size

The flotation test was performed with bulk soil (0–250 µm) and the particle-size fractions (0–20 µm; 20–38 µm; 38–63 µm; 63–125 µm; 125–250 µm) of the froth and the tailing were analyzed separately to determine metal concentrations. The mass recovery, metal recovery, and flotation selectivity were specifically determined for each particle-size fraction of the processed soil. The specific flotation parameters used were: 10 min conditioning time, 10 min flotation time, 12 mg/g kerosene as collector, 0.240 mg/g MIBC as frother, and 1350 rpm as impeller speed. The flotation test was repeated several times to obtain enough material of each fraction for the analytical purposes.

2.2.4. Effect of staged flotation

A multistage flotation method using four consecutive steps was compared with a one-stage flotation. The collector dosage and total processing time (conditioning and flotation phases) were kept the same as those of one-stage flotation in order to compare the effect of different modes of collector addition on metal removal efficiency. Each step of the multistage flotation method was done with 2.5 min of conditioning time (total of 10 min), 2.5 min of flotation time (total of 10 min) with 2 mg/g kerosene (total of 8 mg/g). After each addition of collector amount, the pulp was conditioned for 2.5 min and the air valve was opened and the flotation was continued for 2.5 min, and the froth layer was removed. This procedure was repeated four times. The one-stage flotation method was done with 10 min of conditioning time and 10 min of flotation time and 8 mg/g of kerosene. The collector was added to the pulp all at once. The flotation test was carried out with the same impeller speed (1350 rpm) and frother amount (0.240 mg/g MIBC). The various froth fractions collected and tailings were prepared for analytical purposes.

2.2.5. Effect of ultrasonic pre-conditioning

The effect on flotation performance of an additional ultrasonic conditioning step was evaluated and compared. The ultrasonic pre-conditioning of the flotation pulp (10% of solid) was conducted for 20 min in a laboratory-scale ultrasonic bath (Bransonic BH-72H), which was capable of a frequency of 20 kHz and a power of 880 W. This treatment was conducted prior to reagents addition and conventional collector conditioning. The flotation parameters used were: 10 min of collector conditioning time, 8 mg/g kerosene as collector, 0.240 mg/g MIBC as frother, 10 min flotation time at 1350 rpm impeller speed. In addition, the soil particle-size distribution and metal distribution within the particle-size fractions were determined on a feed soil sample treated by the same ultrasonic treatment procedure in order to determine the effect of the ultrasonic treatment on the metal distribution.

2.2.6. Flotation performance evaluation

Several factors were determined to evaluate the performance results of flotation process in soil remediation: mass recovery, metal recovery, and concentration factor of metal. The mass recovery (%) is obtained from the ratio of the mass of the floated particles (froth fraction) to the total mass of the feed soil. The metal recovery (%) is calculated from the ratio of the quantity of the metal in the froth fraction to the total quantity of the metal in the froth and tailings. The concentration factor (CF) of metals, which evaluates the flotation selectivity, is defined as the ratio of metal recovery to the mass recovery, which corresponds to the metal concentration ratio of the froth fraction to the feed soil. The calculations were based on dry weight (105°C). Although, the metal concentrations in feed soil was measured for each flotation test, the recoveries and CF calculations were determined with the metal amount of froth and tailings ("calculated feed") in order to respect the mass balance closure. The recoveries and CF of metal contaminants (As, Cd, Cu, Pb, and Zn) will be compared with those of Fe, which was taken as the representative element of soil matrix (Fe oxides). The mass of the floated particles (mass recovery) should be low in order to achieve volume reduction of the initial contaminated soil, but simultaneously the metal recovery must be as high as possible. For a selective separation of the metal contaminant, the CF must be larger than 1 and should be as large as possible. In order to evaluate the uncertainty of the flotation experiments, a conventional flotation test (with 8 mg/g kerosene as collector, 0.240 mg/g MIBC as frother, 10 min flotation time at 1350 rpm as impeller speed) was repeated 3 times. The relative standard deviation obtained in flotation recoveries and CF in this test series will be used to report the error bars of the flotation results in certain diagram.

3. Results and Discussion

3.1. Effect of impeller speed

In the mechanical Denver cell, the dispersion of air-bubbles for flotation is generated by a rotor–stator mechanism which also serves to mix the pulp and air-bubbles. In self-aerating cells, the aeration rate and the impeller speed are not independent and the impeller speed controls the aerating and mixing intensity of the pulp (Koh and Schwarz, 2006). The pulp agitation and the air diffusion are also affected by the frother concentration, the froth thickness, the pulp density (solid/liquid ratio), and the soil particle-size distribution (Cilek and Yilmazer, 2003). The effect of hydrodynamic parameters in the Denver-type cells were investigated and evaluated by several statistical models (Cilek and Yilmazer, 2003; Koh and Schwarz, 2006). These studies showed that hydrodynamics of flotation is related to the suspension of particles in the pulp, the dispersion of air-bubbles in the pulp, and the probability of particle-bubble collision. Among physical parameters, the impeller speed plays an important role in the hydrodynamics of flotation (Koh and Schwarz, 2007). However, it is interesting to note that the agitation speed range selected for this study (1000–1600 rpm) is relatively elevated when compared to other studies involving a similar Denver laboratory flotation cell (volume of 1–2 L) (Cauwenberg et al., 1998a,b; Cilek and Yilmazer, 2003; Vanthuyne et al., 2003). It is clear in Fig. 1a that the metal recovery increased with an increase in the stirring rate until 1350 rpm. This result suggest that the particles were kept in suspension at a higher contact speed and hence the particles could float more easily. Further, the increase of impeller speed to 1350 rpm did not cause a flotation selectivity drop since the concentration factor of heavy metals remains relatively similar in the range from 1000 to 1350 rpm (Fig. 1b). However the increase of the speed above 1350 rpm resulted in a decrease in metal recovery (Fig. 1b). Since the metal recovery is directly related to the mass of solid that floated, it was concluded that a high agitation speed (>1350 rpm) may probably cause a drop in the particle-bubble attachments due to high turbulences occurring in the Denver-type cells. In the subsequent tests, agitator speed was adjusted to 1350 rpm.

3.2. Influence of flotation time

The study of flotation efficiency versus process time may help to understand the transportation mechanism of particles occurring in this flotation process. Table 1 summarizes the element concentrations, the flotation recovery (of metal contaminants and iron), and the selectivity index of metal/Fe for the froth concentrates, tailings, and feed soil. The cumulative recoveries versus the flotation time are plotted in Fig. 2a, whereas the concentration factors versus the flotation time are plotted in Fig. 2b. The froth mass recovery as well as metal recovery increased at the beginning stage of cell flotation (until 5 min), but when the flotation period is prolonged to 15 min, the cumulative of metal removal was not appreciably increased (Fig. 2a). The flotation rate was very important in the first 2.5 min. Fig. 2a shows that approximately 2/3 of the mass and the recovered metal amount were floated within the first 2.5 min, corresponding to 1/6 of experience time. Likewise, about 90% of the recovered metal amount was removed in the first 5 min of flotation time.

However, the separation selectivity for the metals changes during the flotation time. The results in the concentration factor of metals at different flotation times suggest that the flotation selectivity increases for the period 2.5–5 min and decreases for the period 5–15 min (Fig. 2b). For instance, the concentration factor of Zn in the froth fraction increased from 2.0 to 2.3 (i.e., augmentation of 15%) in the first period (2.5–5 min), whereas it decreased from 2.2 to 1.8 (i.e., reduction of 23%) in the last period (5–15 min) (Fig. 2b).

The difference in the flotation selectivity between 2.5 min and 5 min may be related to the recovery of undesired non-metallic hydrophobic particles in the first 2.5 min, thereby causing the low CF in the first 2.5 min. Metal concentration was relatively low in the first fraction floated (collected at 2.5 min) when compared to the metal concentration in the two subsequent froth fractions (collected at 5 and 7.5 min) (Table 1). This is unusual since normally the metal content in the froth concentrate decreased with the treatment time in ore flotation practice. The microscopy observations showed that the processed soil contained a significant part of coal/ashes particles in all the particle-size fractions of the processed soil (Dermont et al., in press). These particles, which have a high hydrophobic character, low density, and a large adsorptive surface area are recovered first and foremost with oily collector such as kerosene. Consequently, there was competition in the kerosene collection between coal/ashes/coke particles and the desired metallic mineral particles in the first 2.5 min. After 2.5 min, the content of coal/ashes particles decreases and the selective flotation of metal-containing particles increases.

Table 1 shows that the floated mass of the different froth fractions decreased with the flotation time. This is usual since normally the content of hydrophobic particles in the pulp decreases with flotation time and the collector concentration also decreases with flotation time. At flotation time >5 min, the CF (i.e., flotation selectivity) of heavy metals (As, Cd, Cu, Pb, and Zn) decreased, whereas the CF of Fe remained practically similar (Fig. 2b). After 5 min, the floated particles were mostly fine particles, which were probably transported via the inter-bubble water film (i.e., hydraulic or mechanical entrainment mechanism) because they have a large reactive surface area (Cilek and Umucu, 2001). Moreover, the selectivity index of metal/Fe decreased after 5 min process time, suggesting that the separation of metal-containing particles is less selective in relation to the Fe oxides particles after 5 min (Table 1). At flotation time >5 min, the mechanical entrainment (independent process of the hydrophobic character of particles) probably became the main particle transportation mechanism, causing separation selectivity drop. This is consistent with the findings of Vanthuyne and Maes (2007), who demonstrated that the recovery of heavy metals from the contaminated sediment by flotation (after 5 min process time) is entirely due to the entrainment mechanism.

3.3. Influence of particle-size

The study of flotation response according to particle-size helps to assess the influence of entrainment mechanism in metal removal. The recovery and the separation selectivity of Zn were specifically evaluated versus five different particle-size fractions. Zinc was taken as representative for the other metal contaminants since these elements showed a relative similar trend in flotation responses. Table 2 summarizes the mass distribution, the Zn distribution, and the Zn concentration factor for each particle-size fraction of the flows involved in the flotation (i.e., froth, tailings and feed). Flotation process is greatly influenced by the particle-size distribution. Table 2 clearly shows that the particle-size distribution (mass distribution) in the froth and tailings was very dissimilar. On the one hand, the froth fraction was markedly enriched in the fine particle-size fractions (<38 µm), especially in the finest fraction (<20 µm). The proportion of the particles 0–20 µm was doubled in the froth fraction (65%) compared to the initial percentage in the feed soil (28%). On the other hand, the tailings were enriched in sand-sized material since the 63–250 µm fractions represented 69% of the tailing texture (54% in the feed soil).

All the particle-size fractions in the froth fraction showed higher Zn concentrations compared to the corresponding particle-size fractions in the feed and tailings (Table 2). However, the metal removal efficiency strongly differed according to the particle-size. Fig. 3 indicates that Zn recovery increased when the particle-size decreased: the rate was ranged from 70% to 80% for the <38 µm fractions, whereas the rate is ranged from 5 to 15% for the >63 µm fractions. However, a similar trend is observed for the recovery of the overall mass; consequently, the flotation selectivity does not increase with the particle-size decrease. Fig. 3 shows that the Zn concentration factor was low for the largest particle-size fraction (125–250 µm) and the finest fraction (0–20 µm), average for the 63–125 µm fraction, and high for the 20–63 µm fractions. This result is consistent with flotation practices (using mechanical flotation cells) since the intermediate particle-size fraction usually shows the best flotation efficiency in the conventional ore processing (Fuerstenau, 2007) and in the sediment remediation investigations (Cauwenberg et al., 1998b). However, the crucial point of the present study is that the metal recovery was relatively high although the flotation selectivity was low for the finest particle-size fraction (0–20 µm).

The low flotation selectivity observed in the 0–20 µm particle-size fraction is not surprising since it is usual that the selective separation of hydrophobic particles from hydrophilic particles is particularly ineffective in the fine particle range (<10–20 µm) with the mechanical agitated flotation cells (Kirjavainen, 1996; Fuerstenau, 2007). In the mechanical agitated flotation cells, the true flotation mechanism (selective separation process) is usually inefficient for the fine particles, which are mainly recovered by entrainment mechanism (a non-selective transportation). The true flotation process is ineffective in the Denver-type cells for the fine particles because the particle/bubble-size ratio and the hydrodynamic conditions (high turbulence) are not favourable for the probability of collision and attachment process between the fine particles and the air-bubbles. The fine particles are mainly recovered via the inter-bubble water film independently of the hydrophobic/hydrophilic properties (i.e., hydraulic entrainment mechanism) (Cilek and Umucu, 2001). In addition, the low selectivity in the fine particle-size range could be related to the froth layer stability which partly depends on the frother type used (Cilek and Yilmazer, 2003). Although flotation selectivity was low, the Zn recovery was relatively high in the finest particle-size fraction (Fig. 3). This result appears contradictory, but it can be easily explained by two experimental parameters specific to the 0–20 μm fraction: (1) the mass recovery was high (62%) due to the mechanical entrainment mechanism (Fig. 3); (2) this particle-size fraction presented a great proportion of the Zn-contamination amount (51%) (Table 2). Consequently, the high rate of metal removal in the 0–20 μm fraction is mainly imputed to the mechanical entrainment mechanism rather than the true flotation process.

Fig. 3 showed that the mass and metal recoveries, and the flotation selectivity in Zn removal were inefficient for the largest particles (125–250 μm). The result is not surprising since the stability of particle-bubble attachment is usually low for the coarser particles even if the particle surface is hydrophobic. The low probability of particle-bubble attachment mechanisms for the coarser particles is mainly due to the limitation of the air-bubble capacity to carry the coarse particle rather than the particle surface chemistry. Unlike the fine particles, the larger particles did not remain entrapped in the inter-bubble water and were not entrained in the froth layer by mechanical (hydraulic) entrainment mechanism, but they drained back into the pulp.

Although the physico-chemical surface properties (hydrophobicity and mineralogy, pulp chemistry, flotation reagent, etc.) obviously play a role in the flotation response, the transportation of the coarsest and the finest particles is primarily limited by physical parameters (hydrodynamic conditions and soil particle-size distribution) which control the probabilities of particle-bubble collision, adhesion, and destabilization (Cilek and Yilmazer, 2003). In this study, the intermediate particle-size fraction (20–125 µm) showed the best flotation selectivity, but the finest particle-size fraction (<20 µm) showed the best metal recovery.

3.4. Effect of staged flotation method

Although the metal recovery improved when the collector amount was tripled (from 4 to 12 mg/g), this increase was not very important: e.g., the Zn recovery ranged from 48% to 55%, i.e., the tripled reagent amount caused only 15% of relative increase in Zn recovery (Dermont et al., in press). Furthermore, the kinetic study showed that the 2/3 of the recovered metal amount was achieved within the first 2.5 min of flotation time. The collector addition can be made in one dose at the beginning of flotation, or by a number of small additions at various time intervals during the flotation. Table 3 summarizes the element concentrations, the flotation recovery and the concentration factors (of metal-contaminants and iron) for the froth fractions, tailings, and feed soil. It can be seen from Table 3 that the metal recovery was significantly enhanced through the staged addition of collector. The metal recovery increased from 45–56% to 50–61%, thus about 5–7% (according to the metal-contaminant type) higher than the rate obtained with the one-stage flotation method (Table 3).

Concurrently, the concentration factor (flotation selectivity) of metal contaminants slightly increased when multiple staged flotation method was used; however, this selectivity improvement was relatively limited because the mass recovery also slightly increased with the multi-step addition mode (Table 3). Small collector increments possibly lead to better overall recoveries and smaller froth volumes. The low efficiency of the one stage process in metal removal may be related to the influence of the entrainment mechanism in flotation response. At high collector doses, the produced froth may become very wet and a large volume of inter-bubble water is recovered. Since the entrainment mechanism is directly related to the water recovery (Neethling and Cilliers, 2002), the non-selective transportation of the particles suspended in the inter-bubble water was then increased. The involvement of the hydraulic entrainment mechanism in flotation environment of the one-stage method possibly caused the flotation selectivity drop. The results clearly showed that successive flotation stages using low concentrations of collector and low practice time were more effective than the one-stage standard flotation method using a high reagent dosage and long soil washing processing time.

3.5. Effect of ultrasonic pre-conditioning

The ultrasonic effects are mainly based on liquid cavitation, which creates extremely strong liquid jets against particle surfaces. The ultrasonic conditioning provides two main effects: (1) the surface cleaning effect which involves the removal of coating or film from individual grains; (2) the breaking effect which involves particle-size reduction by the dispersion of fine particles bonded to sand particles and the disintegration of soil agglomerates. The influence of ultrasounds contributes to the flotation performance through several mechanisms (not fully understood) such as the micro-fragmentation of particles and disturbance of solid/liquid interface by cavitation (Ozkan and Kuyumcu, 2006; Mason, 2007). The effect of ultrasonic conditioning on the flotation performance is shown in Fig. 4. The results suggest that the metal removal may be effectively improved with ultrasonic pre-conditioning. For example, the results obtained in Zn removing with ultrasonic treatment were 58% of recovery with a 2.0 concentrating factor, whereas a 53% of recovery with a 2.1 concentrating factor were obtained without ultrasonic treatment (Fig. 4).

It has long been recognized that the cavitational effect created by ultrasound waves can break down the particle size and expose a fresh surface (Mason et al., 2007). Besides, the cavitation at a solid/liquid interface may change the surface properties of minerals, leading to modify the adsorption of collectors on minerals and the flotation rate (Ozkan and Kuyumcu, 2006). Several studies showed that ultrasonic conditioning may improve the metal removal by soil washing or leaching methods (Meegoda and Perera, 2001; Swamy and Narayana, 2001; Mason, 2007) and froth flotation (Kyllonen et al., 2004). Ultrasonic treatment was also used to enhance the conventional ore and coal flotation (Aldrich and Feng, 1999; Ozkan and Kuyumcu, 2006). In the present study, the ultrasonic preconditioning of the pulp improved the metal recovery, but the flotation selectivity remained practically unchanged (Fig. 4). The increase in metal removal with ultrasonic conditioning was not due to an increase in flotation selectivity, but it was rather the result of a better mass recovery of the overall mass (Fig. 4). Although the physico-chemical particle surface properties obviously contributes to flotation process, the particle size may play a crucial role in the flotation enhancement by ultrasonication.

It can be seen from Fig. 5 that ultrasonic preconditioning of the flotation pulp caused an increase of the relative proportion of the particles <38 μm (from 37% to 41%) in the particle-size distribution of feed soil. Consequently, this involved a change in the metal distribution in the particle-size fractions: e.g., Zn quantity was lowered by the ultrasonic treatment in all fractions except the finest fractions <38 μm (Fig. 5). The other metal distributions showed a similar trend (these data are not reported). This is probably due to the powerful effect of ultrasonic treatment in particle size reduction via breaking and dispersion effects, especially for the particles >38 μm. A similar particle size reduction effect provoked by ultrasonication has been reported, e.g., by Swamy and Narayana (2001) for the 150–300 µm fraction of oxide ores and by Kyllonen et al. (2004) for the <1 mm fraction of Pb-contaminated soil. This particle size reduction may improve the metal removal when the metal contamination is distributed in all the particle-size fractions and when the metal-containing particles resulting from pre-conditioning are primarily free (i.e., high liberation degree of the metal-bearing phase). Alternatively, several studies showed that the effect of ultrasonic treatment in flotation response is mainly due to the cleaning effect of particle surface (Farmer et al., 2000; Newell et al., 2006; Ozkan and Kuyumcu, 2006). Unfortunately, the effect of surface cleaning was not evaluated in the present paper.

The influence of the residence time, solid/liquid ratio, temperature, integration mode of ultrasonic treatment in the flotation stage should be tested further to obtain optimum conditions. In this study, the ultrasound treatment has been used as pre-conditioning and not simultaneously with the flotation stage.

4. Conclusions

This paper shows that the separation process of metal-containing particles from soil by froth flotation process in the mechanically agitated Denver cell is strongly influenced by the entrainment mechanism contribution, the quantity of the fine particles in the soil and the metal distribution in the particle-size fractions. While mechanical entrainment of slime-sized particles is usually considered to be undesirable in mineral processing operations (non-selective flotation), in our case this effect may be profitable since it contributes to the recovery of the fine particles, which contain a great part (40–50%) of the metal contamination. However, the contribution of the mechanical entrainment mechanism causes a flotation selectivity drop of the metal concentration and provokes the overconsumption of the collector. The influence of entrainment mechanism was studied by the evaluation of flotation selectivity versus different parameters of physical nature: impeller speed, flotation time, particle-size fractions, and the effect of ultrasonic pre-conditioning.

The increase in impeller speed from 1000 to 1350 rpm increased the metal recovery without a significant decline of the flotation selectivity. This suggests that the high impeller speed (range of 1000–1350 rpm) is not the major parameter responsible of the entrainment of fine particles in the froth.

The flotation selectivity varied according to the flotation time. At flotation time >5 min, the mechanical entrainment became the main particle transportation mechanism, thus decreasing flotation selectivity for the heavy metals. A long flotation time >5 min may not be practical since the metal removal efficiency was not markedly enhanced and the flotation selectivity decreased.

The study of flotation response versus particle-size showed that flotation selectivity was low for the coarsest (>125 µm) and the finest (<20 µm) particle-size fraction, although metal recovery remained high for the fine particle-size fraction due to the entrainment mechanism of the fine particles and the importance of metal contamination in this fraction. The metal-containing particles were floated with a best selectivity in the particle-size range of 20–125 µm, especially in the 20–63 µm fraction.

The multiple staged procedure using a low reagent dosage and short flotation time is advantageous compared to one-stage flotation method using a high dosage and long time process. The staged flotation was better than the one-stage flotation in metal removal efficiency because the use of a low collector concentration and low flotation time minimized the entrainment mechanism. A metal removal efficiency of 50–60% was achieved for the heavy metals (As, Cd, Cu, Pb, and Zn) and this metal amount is concentrated in 25% of the initial soil volume (i.e., 75% of volume reduction of highly contaminated soil). The use of ultrasonic pre-conditioning improved metal recovery but it did not enhance the flotation selectivity. The enhancement in metal recovery with additional ultrasonication step was mainly due to the particle-size reduction, causing the metal redistribution within the particle-size fractions (from coarse to fine particles). The additional metal contamination in the fine particle-size fraction was probably recovered by the entrainment mechanism (rather than the true flotation process) since the concentration factor of metals did not improved.

The soil washing by flotation process may require crushing, desliming, dewatering, and water treatment. The process water may be used for several cycles of flotation. The generated toxic concentrates (containing metals), which may be recalcitrant to a metal recovery treatment, may require a stabilization/solidification process prior to disposal. In many cases, froth flotation may be used to reduce the metal concentrations to an acceptable level and to considerably reduce the volume of contaminated soil. The flotation reagents may be toxic and may cause pollution to the environment. Particularly, kerosene contains a significant content of polycyclic aromatic hydrocarbons (PAHs), benzene or toluene. Therefore, the development of environmentally benign chemical reagents for flotation should be also emphasized.

Acknowledgments

The first author is thankful to the “Institut National de la Recherche Scientifique Eau Terre et Environnement” (INRS-ETE) for financial support. The authors would also like to thank Kathrine Gauvin and Catherine Martineau-Thériault for their useful comments.

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Tables

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Table 1. Flotation response versus flotation time

Flotation fractions	Mass	As	Cd	Cu	Pb	Zn	Fe
Element concentration (µg/g)							
Froth 1 (0–2.5 min)	-	256	49.9	4513	4503	18548	123473
Froth 2 (2.5–5 min)	-	293	57.4	4995	5018	21450	124672
Froth 3 (5–7.5 min)	-	271	56.2	4636	4502	20672	129870
Froth 4 (7.5–15 min)	-	211	45.1	3804	3657	17699	127241
Total Froth		263	51.8	4600	4585	19266	124275
Tailings	-	72	20.2	1947	1692	5982	105291
Feed	-	121	28.3	2627	2433	9385	110154
Flotation recovery (%)							
Froth 1 (0–2.5 min)	17.0	36.1	30.1	29.3	31.5	33.7	19.1
Froth 2 (2.5–5 min)	6.0	14.6	12.2	11.4	12.4	13.8	6.8
Froth 3 (5–7.5 min)	1.4	3.1	2.7	2.4	2.6	3.0	1.6
Froth 4 (7.5–15 min)	1.2	2.1	1.9	1.7	1.8	2.1	1.4
Total Froth	25.6	55.8	46.9	44.9	48.3	52.6	28.9
Selectivity index Metal/Fe[a]							
Froth 1 (0–2.5 min)	-	1.89	1.57	1.53	1.65	1.76	1.00
Froth 2 (2.5–5 min)	-	2.14	1.79	1.68	1.82	2.02	1.00
Froth 3 (5–7.5 min)	-	1.90	1.69	1.50	1.57	1.87	1.00
Froth 4 (7.5–15 min)	-	1.51	1.38	1.25	1.30	1.56	1.00
Total Froth		1.93	1.62	1.55	1.67	1.82	1.00

Flotation parameters: 10 min conditioning time; 8 mg/g kerosene as collector; 0.240 mg/g MIBC as frother; 1350 as impeller speed; [a] Selectivity index Metal/Fe= Metal recovery/Fe recovery

Table 2. Mass distribution, Zn distribution and Zn concentration in the particle-size fractions of flotation fractions

	Mass distribution (%)					Zn distribution (%)			Zn concentration (µg/g)		
Particle-size fractions	*Feed*[a,c]	*Froth*[a]	*Tail.*[a]	*Froth*[b]	*Tail.*[b]	*Feed*[c]	*Froth*	*Tail.*	*Feed*[c]	*Froth*	*Tail.*
125–250 µm	34.7	1.9	32.8	7.0	45.0	19.2	2.3	38.3	4851	5706	4801
63–125µm	19.2	1.6	17.6	6.0	24.2	13.5	3.1	25.3	6161	8992	5902
38–63 µm	9.1	1.8	7.3	6.6	10.0	6.8	4.2	9.7	6568	10944	5492
20–38 µm	8.9	4.2	4.7	15.6	6.5	9.8	14.3	4.7	9636	15898	4090
0–20 µm	28.0	17.5	10.5	64.8	14.4	50.7	76.0	21.9	15899	20292	8590
Total distribution	100.0	27.0	73.0	100.0	100.0	100.0	100.0	100.0			
Bulk soil (0–250 µm)[c]	100.0	27.0	73.0	-	-	100.0	53.1	46.9	8781	17284	5635

Flotation parameters: 10 min conditioning time; 10 min flotation time; 12 mg/g kerosene as collector; 0.240 mg/g MIBC as frother; 1350 rpm as impeller speed.

[a] Percentages in relation to the total mass of feed soil.

[b] Percentages in relation to the total mass of froth and tailings respectively.

[c] Feed calculated with froth and tailings data.

Table 3. Comparison in flotation efficiency between one-stage method and multi-stage method

Flotation method	Mass	As	Cd	Cu	Pb	Zn	Fe
Element concentration (μg/g)							
Froth of stage 1/4	–	289	57.9	5215	5161	20041	136359
Froth of stage 2/4	–	287	60.6	5123	5023	21932	131234
Froth of stage 3/4	–	266	56.4	4546	4414	20267	131886
Froth of stage 4/4	–	239	55.4	4323	4156	20070	128526
Tailing of multi-stage method	–	65	18.8	1805	1537	5226	103584
Feed of multi-stage method		118	29.1	2659	2441	8990	116996
Froth of one-stage method	–	232	45.2	4419	4250	17366	122532
Tailings of one-stage method	–	60	17.9	1771	1460	5111	96855
Feed of one-stage method	–	102	25.7	2429	2152	8153	103228
Flotation recovery (%)							
Stage 1/4[a]	17.8	41.9	35.2	34.7	34.7	37.4	21.6
Stage 2/4[a]	22.3	52.4	44.5	43.3	46.5	49.2	26.8
Stage 3/4[a]	24.2	56.9	48.5	46.8	50.3	53.7	29.3
Stage 4/4[a]	25.4	60.6	52.1	49.8	53.5	58.0	31.5
One-stage method	24.8	56.3	45.5	45.2	49.0	52.9	29.5
Concentration Factor							
Multi-stage method[b]	-	2.39	2.05	1.96	2.11	2.28	1.24
One-stage method[c]	-	2.27	1.83	1.82	1.97	2.13	1.19

[a] Cumulative data

[b] Each stage involves: 2.5 min conditioning time; 2.5 min flotation time; 2 mg/g kerosene as collector

[c] One-stage method involves: 10 min conditioning time; 10 min flotation time; 8 mg/g kerosene as collector

Figures

List of Figures

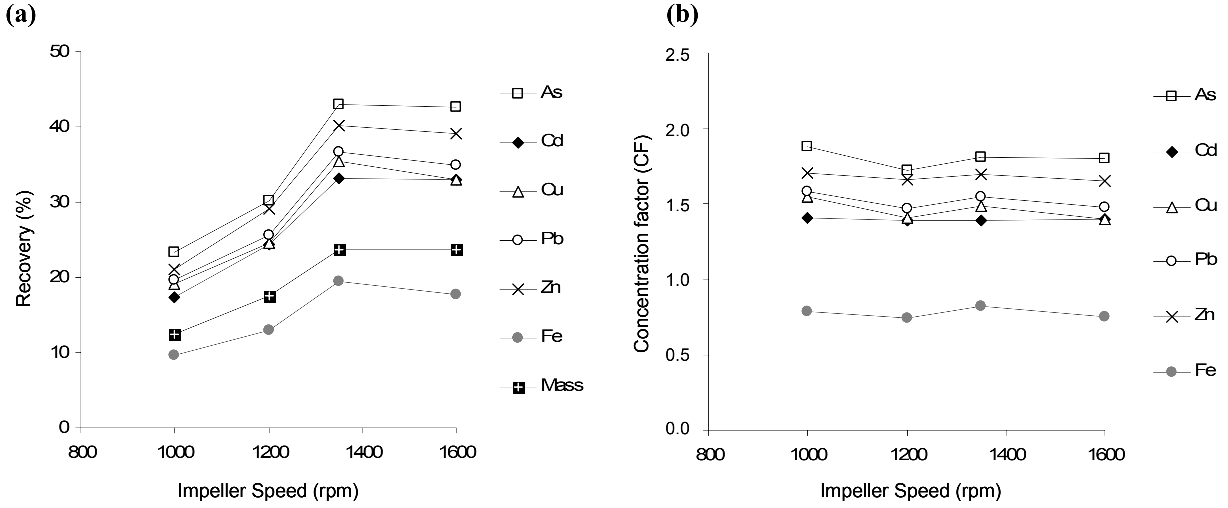


Fig. 1. Influence of impeller speed on (a) recovery and (b) concentration factor of As, Cd, Cu, Pb, Zn, and Fe.

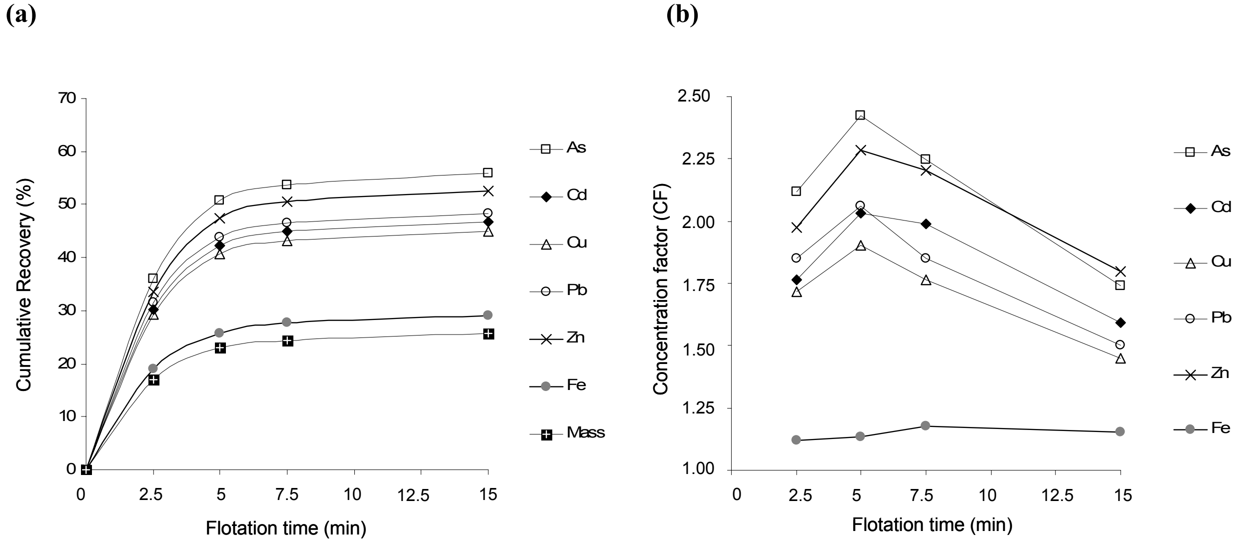


Fig. 2. (a) Cumulative recoveries versus flotation time. (b) Concentration factors of As, Cd, Cu, Pb, Zn, and Fe versus flotation time.

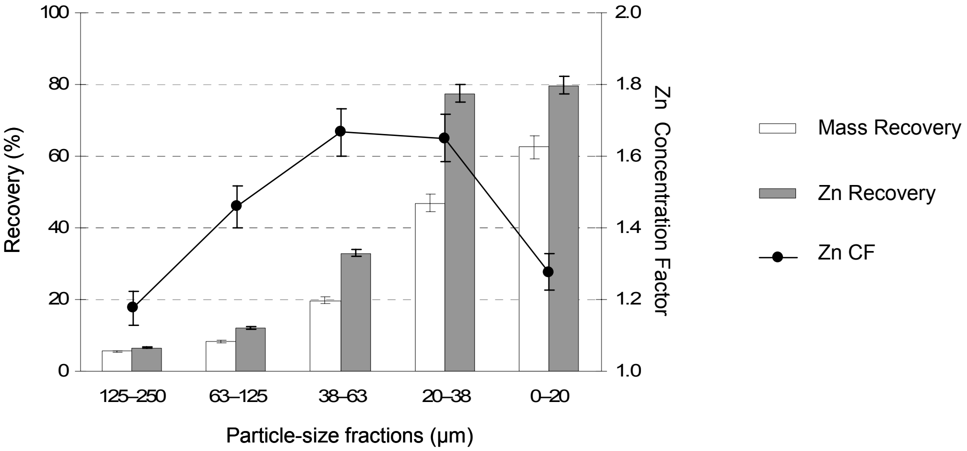


Fig. 3. Mass recovery, Zn recovery and Zn Concentration factor versus the soil particle-size fractions. The error bars correspond to the standard deviations associated to three flotation tests.

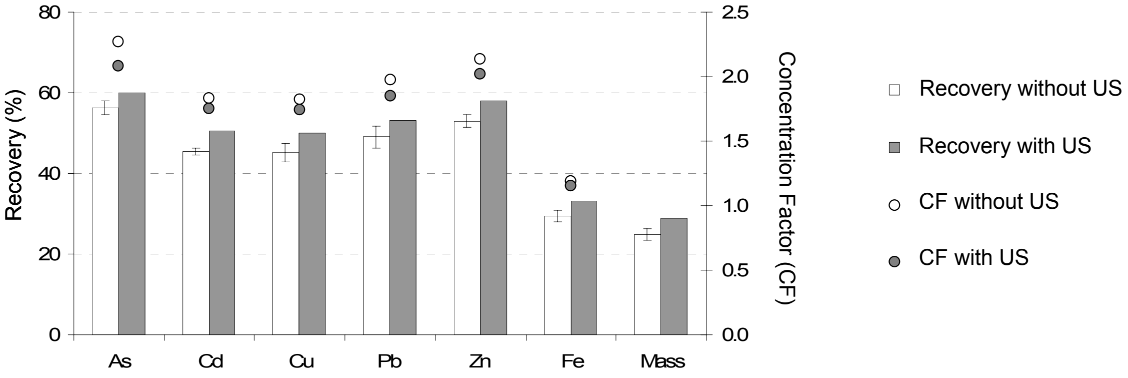


Fig. 4. Influence of ultrasonic pre-conditioning of pulp on recovery and concentration factor of As, Cd, Cu, Pb, Zn, and Fe. The error bars correspond to the standard deviations associated to three flotation tests.

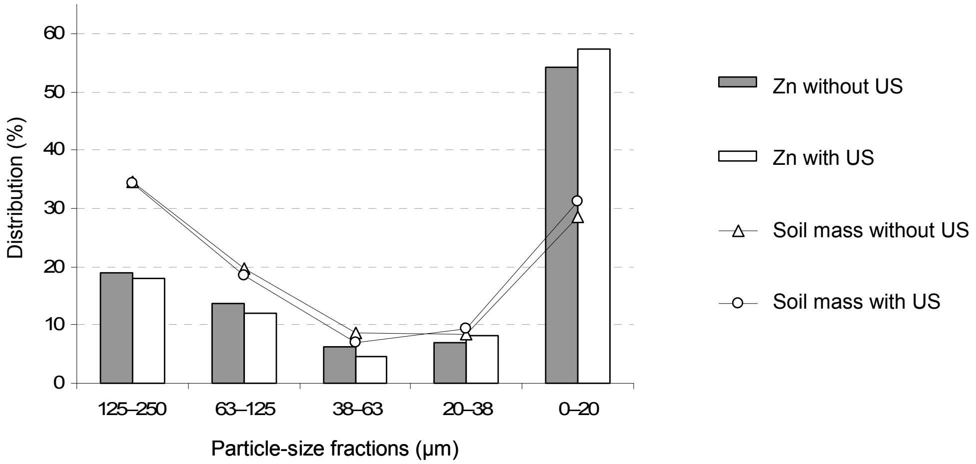


Fig. 5. Influence of ultrasonic treatment of pulp on soil particle-size distribution and Zn distribution in the particle-size fractions.

Annexes

Annexe A

Aspects géotechniques et géophysiques

Annexe A-1 :

Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G., Boussicault, B. (2006). "A multidisciplinary approach to improve characterization and remediation feasibility of urban soils contaminated by heavy metals." *Proc., 59th Canadian Geotechnical Conference, , Canadian Geotechnical Society (CGS),* Vancouver, BC, Canada, Sea to Sky Geotechnique 2006, pp 848-855.

Annexe A-2 :

Compléments et commentaires relatifs aux sections tomographiques reportées dans l'annexe A-1.

Annexe A-3 :

Section tomographique de résistivité électrique de toute la longueur du terrain (Longueur=160 m et Profondeur sondée= 25 m) permettant de visualiser le substrat rocheux et l'ensemble des dépôts meubles.

Notes : Sondages de géophysique réalisés sur le terrain par Bruno Boussicault et Dermont Gérald; Production des sections tomographiques et sélection des paramêtres dans le programmes RS2DINV réalisées par Bruno Boussicault; Interprétations de Dr. Marc Richer-Laflèche et Gérald Dermont.

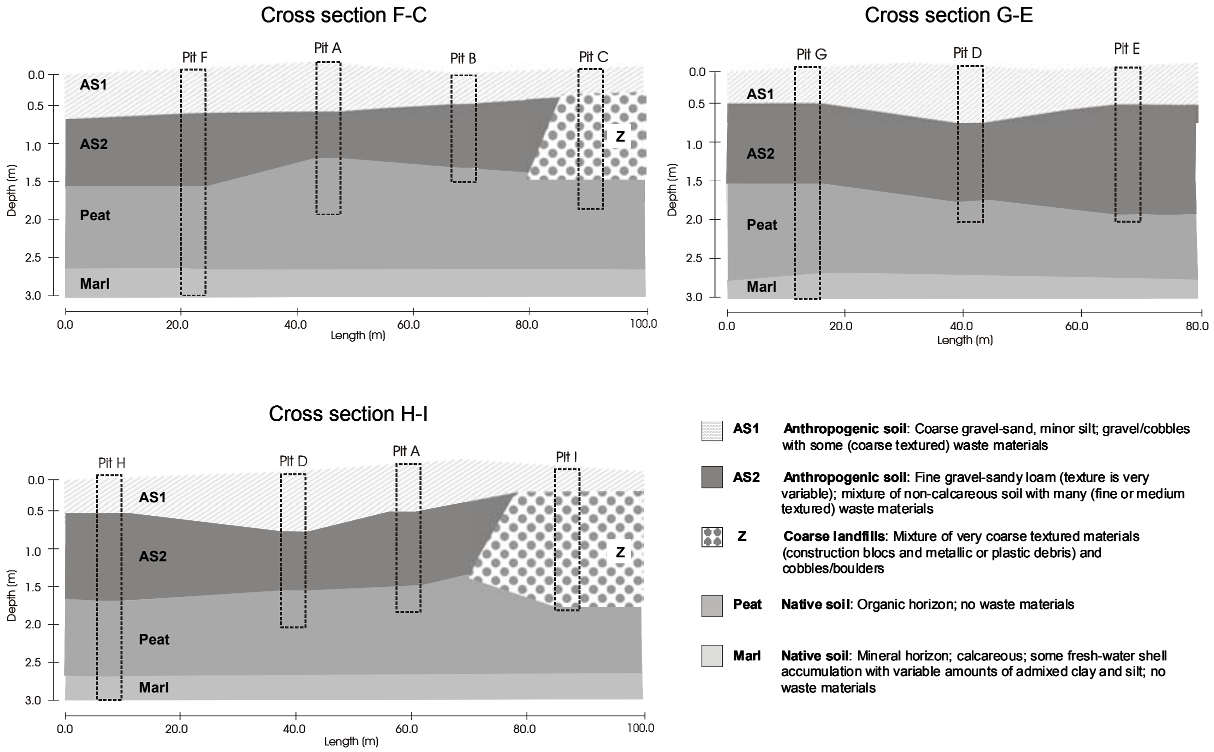
Dermont, G., Bergeron, M., Richer-Laflèche, M., Mercier, G., Boussicault, B. (2006). A multidisciplinary approach to improve characterization and remediation feasibility of urban soils contaminated by heavy metals. *In: 59th Canadian Geotechnical Conference, Canadian Geotechnical Society*, Vancouver, BC, Canada, Sea to sky Geotechnique 2006, 848-855.

Annexe B

Coupes pédologiques du site étudié

Pedological cross-sections of the site

Annexe B : Coupes pédologiques du site étudié (*Pedological cross-sections*).



Note: Localisation des coupes et des fosses pédologiques, voir Figure 5b du Chapitre 1

Annexe C

Limites de détection, précision et le contrôle de la qualité des analyses chimiques à l'aide des matériaux standard de référence (NIST 2710, NIST 2711, AGV-2, BHVO-2)

Detection Limits, Precision and Quality Control of Chemical Analysis with standard reference materials (NIST 2710, NIST 2711, AGV-2, BHVO-2)

Annexe C. Detection Limits, Precision and Quality Control of Chemical Analysis with standard reference materials

Element	Method	Unit[a]	DL[b,c]	RSD[d,e]	Values of SRM 2710			Values of SRM 2711		
Majors					Analyzed[f,g]	Certified	RE (%)	Analyzed[f,g]	Certified	RE (%)
Al	A	Wt %	0.007	< 1%	6.46 ± 0.02	6.44 ± 0.08	100	6.54 ± 0.04	6.53 ± 0.09	100
Ca	A	Wt %	0.008	< 1%	1.26 ± 0.01	1.25 ± 0.03	101	2.90 ± 0.02	2.88 ± 0.08	101
Fe	A	Wt %	0.007	< 1%	3.41 ± 0.01	3.38 ± 0.10	101	2.95 ± 0.02	2.89 ± 0.06	102
K	A	Wt %	0.010	< 1%	2.20 ± 0.01	2.11 ± 0.11	104	2.58 ± 0.02	2.45 ± 0.08	105
Mg	A	Wt %	0.0034	< 1%	0.849 ± 0.002	0.853 ± 0.004	100	1.041 ± 0.007	1.050 ± 0.030	99
Mn	A	Wt %	0.0012	< 1%	1.03 ± 0.01	1.01 ± 0.04	102	0.068 ± 0.007	0.0638 ± 0.0028	106
Na	A	Wt %	0.008	< 1%	1.14 ± 0.01	1.14 ± 0.06	100	1.19 ± 0.01	1.14 ± 0.03	105
P	A	Wt %	0.006	2–4%	0.094 ± 0.002	0.106 ± 0.015	89	0.083 ± 0.004	0.086 ± 0.007	96
Si	A	Wt %	0.03	<1%	28.98 ± 0.11	28.97 ± 0.18	100	30.83 ± 0.19	30.44 ± 0.19	101
S	B	Wt %	ND	2–3 %	0.247 ± 0.007	0.240 ± 0.006	103	0.045 ± 0.001	0.042 ± 0.001	106
Ti	A	Wt %	0.0011	< 1%	0.276 ± 0.001	0.283 ± 0.010	97	0.309 ± 0.002	0.306 ± 0.023	101
Traces										
As	B	µg/g	0.63	1–3%	588 ± 13	626 ± 38	94	99 ± 4	105 ± 8	94
Cd	B	µg/g	0.02	1–2%	21.3 ± 0.5	21.8 ± 0.2	97	41.10 ± 1.20	41.70 ± 0.25	99
Co	B	µg/g	0.17	2–4%	11.4 ± 0.5	(10)[h]		11.5 ± 0.5	(10)[h]	
Cr	B	µg/g	0.12	2–5%	34 ± 1	(39)[h]		45 ± 2	(47)[h]	
Cu	B	µg/g	0.04	1–2%	2759 ± 59	2950 ± 130	94	111 ± 2	114 ± 2	97
Ni	B	µg/g	0.22	1–2%	14.1 ± 0.6	14.3 ± 1.0	99	19.9 ± 0.5	20.6 ± 1.1	97
Pb	B	µg/g	0.57	1–3%	5201 ± 174	5532 ± 80	94	1116 ± 36	1162 ± 31	96
Zn	B	µg/g	0.10	1–3%	6657 ± 190	6952 ± 91	96	344.4 ± 7.1	350.4 ± 4.8	98
Scandium					Values of AGV-2			Values of BHVO-2		
Sc	A	µg/g	0.4	1–2%	12.5 ± 0.2	13 ± 1	96	32.0 ± 0.4	32 ± 1	100

ND: Not determined; Method-A: Fusion/dissolution followed by ICP-AES-radial analysis; Method-B: Multi-acid digestion followed by ICP-AES-axial analysis; DL: Detection Limits; RSD: Relative Standard Deviations; RE: Recovery Efficiency= 100 x (Analyzed value/Certified value); [a]DL and {values ± SD} are given as total element concentration (in Wt % or µg/g) of dry soil sample (105°C); [b]Method-A: DL are evaluated with 3SD of the blank measures (n= 8); [c]Method-B: DL are evaluated with 3SD of the measures (n= 7) of the smaller standard solution diluted by 2; [d]Method-A: RSD range with 3 replicates of the soil sample measures; [e]Method-B: RSD range with 5 measures of 2 selected soil samples; [f]Method-A: {Mean ± SD} values are evaluated with 3 replicates of 1 digestion (n= 3); [g]Method-B: {Mean ± SD} values are evaluated with 3 replicates of 2 digestions (n= 6); [h]Information values

Annexe D

Caractéristiques générales des échantillons de sols (sauf la concentrations des métaux)
des profils A, B, D et G

General characteristics (except metal concentrations) of the soil samples
from the profiles A, B, D, and G

Annexe D. General characteristics of the soil samples for the characterization of the profiles A, B, D, and G

Sample	SH	Depth	Al	Ca	Fe	K	Mg	Mn	Na	P	Si	S	Ti	Sc	pH	Corg	C	N	C/N	$H_2$0	LOI-600	LOI-1025
		(cm)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	(µg/g)	(µg/g)	-	(Wt %)	(Wt %)	(Wt %)	-	(Wt %)	(Wt %)	(Wt %)
DL	-	-	0.007	0.008	0.007	0.010	0.0034	0.0012	0.008	0.006	0.03	NA	11	0.4	-	0.10	0.10	0.10	-	-	-	-
G1	AS1	20	5.07	9.67	3.74	1.60	1.364	0.066	1.24	0.085	23.3	0.42	3539	9.4	7.4	2.2	4.9	0.15	33	1.0	5.7	15.4
G2	AS1	30	5.40	8.91	6.40	1.39	0.977	0.058	0.78	0.104	17.0	0.44	3102	9.9	7.3	12.2	14.8	0.42	35	2.5	19.6	28.0
G3	AS1	45	3.82	16.07	3.80	1.31	0.974	0.048	0.70	0.099	15.1	0.28	3472	6.6	7.8	12.2	14.8	0.42	35	0.9	9.6	26.4
G4	AS1	60	10.43	2.53	7.88	1.31	0.587	0.041	0.66	0.075	20.9	0.14	6146	24.1	7.8	12.6	12.9	0.24	54	0.7	13.5	16.2
G5	AS2	70	5.91	4.88	6.88	1.15	0.635	0.052	0.82	0.135	17.8	0.42	3223	11.4	7.9	18.3	22.1	0.52	43	1.0	24.0	28.9
G6	AS2	90	5.57	1.76	14.48	0.86	0.497	0.084	0.71	0.058	15.4	0.33	2730	9.2	7.7	24.8	25.1	0.52	49	1.1	25.0	30.4
G7	AS2	110	3.64	1.28	12.90	0.38	0.299	0.097	0.18	0.051	7.4	0.65	1776	6.3	7.4	41.7	45.6	1.00	46	2.0	47.3	56.6
G8	AS2	130	4.57	1.93	16.42	0.46	0.314	0.148	0.29	0.052	9.7	0.77	2267	8.7	7.4	34.0	34.3	0.69	50	2.2	35.4	43.6
G9	AS2	140	4.68	5.65	7.06	1.22	0.722	0.068	0.95	0.096	17.3	0.29	2677	7.8	7.6	11.3	12.5	0.39	32	2.2	19.3	24.2
G10	AS2	150	2.81	9.28	2.06	0.898	0.646	0.039	0.65	0.122	11.1	1.72	2079	5.1	7.1	19.8	23.8	1.22	19	6.2	43.7	50.2
G11	Peat	170	0.166	5.62	0.117	0.062	0.166	0.017	0.39	0.034	0.5	4.44	101	0.6	6.4	40.8	43.8	2.26	19	12.1	83.9	87.5
G12	Peat	190	0.195	5.81	0.088	0.059	0.167	0.013	0.39	0.030	0.4	3.81	106	0.7	6.5	40.2	43.7	2.47	18	11.6	83.5	87.6
G13	Peat	210	0.082	4.89	0.058	0.040	0.155	0.009	0.36	0.029	0.1	4.80	44	0.5	6.2	39.7	45.3	2.46	18	11.5	86.1	89.4
G14	Peat	230	0.118	4.22	0.138	0.042	0.156	0.006	0.28	0.027	0.2	5.82	61	0.5	6.1	43.7	46.0	2.20	21	11.3	87.2	89.5
G15	Peat	250	0.544	2.96	0.572	0.158	0.154	0.005	0.26	0.030	1.4	4.12	321	1.3	5.6	42.5	44.9	2.60	17	9.4	87.3	88.1
G16	Marl	275	0.159	32.10	0.227	0.062	0.385	0.039	0.07	DL	0.6	0.51	81	2.4	7.6	6.8	16.6	0.56	30	1.4	13.8	49.3
G17	Marl	290	0.152	32.21	0.221	0.07	0.385	0.039	0.07	DL	0.6	0.53	80	2.0	7.6	6.8	16.5	0.55	30	1.4	13.8	49.3
D1	AS1	15	5.08	9.28	3.16	1.75	1.818	0.065	1.21	0.079	23.3	0.67	3417	9.4	7.4	2.0	4.5	0.11	40	1.0	4.4	14.9
D2	AS1	40	4.23	13.06	4.06	1.39	1.576	0.074	1.05	0.085	19.4	0.68	3170	8.1	7.6	4.0	6.1	0.10	59	1.0	6.1	19.2
D3	AS1	55	4.84	13.60	4.97	1.93	1.213	0.095	0.56	0.128	15.0	0.25	2705	9.4	8.0	6.6	10.6	0.20	53	1.4	12.4	26.5
D4	AS1	65	4.56	6.63	3.24	2.66	0.780	0.035	0.61	0.072	28.0	0.16	4426	7.3	8.0	2.8	4.4	0.10	49	0.7	5.2	11.8
D5	AS2	90	10.05	2.08	10.26	1.68	0.526	0.049	0.50	0.092	19.6	0.20	5381	21.5	7.9	19.0	20.1	0.36	56	0.9	21.9	24.9
D6	AS2	120	7.50	2.63	14.77	1.21	0.530	0.084	0.86	0.064	18.2	0.44	3792	14.1	7.6	20.4	24.0	0.49	49	1.2	26.6	30.8
D7	AS2	140	8.65	1.52	6.61	1.19	0.299	0.023	0.36	0.238	24.0	0.29	4516	15.5	7.4	13.0	13.3	0.34	39	1.2	18.0	19.1
D8	AS2	160	4.87	7.57	3.64	1.52	1.049	0.064	1.28	0.131	22.0	0.35	3256	8.8	7.6	8.2	8.8	0.40	22	2.6	16.6	23.7
D9	Peat	180	2.25	6.60	1.46	0.651	0.499	0.038	0.63	0.138	6.5	2.25	1578	3.8	7.0	23.3	27.6	1.41	20	12.1	58.8	62.2
D10	Peat	195	0.753	6.55	0.641	0.198	0.275	0.018	0.31	0.048	2.7	3.43	496	1.5	6.6	32.1	37.7	1.61	23	16.5	76.6	80.8
B1	AS1	15	4.36	13.16	4.11	1.36	2.097	0.063	0.77	0.082	17.7	0.31	883	ND	7.7	3.5	6.7	0.16	41	1.0	6.1	20.6
B2	AS1	30	4.11	17.37	5.10	1.42	1.352	0.090	0.53	0.126	13.4	0.15	668	ND	8.1	4.1	8.3	0.13	63	1.0	8.3	25.9
B3	AS2	55	8.89	2.30	13.41	1.16	0.463	0.055	0.45	0.082	16.9	0.43	845	ND	7.2	7.3	14.2	0.24	59	1.0	8.4	17.9
B4	AS2	60	8.43	1.66	11.45	1.25	0.481	0.052	0.47	0.094	17.5	0.65	873	ND	7.0	12.0	15.2	0.35	43	2.1	8.9	20.2
B5	AS2	70	3.99	2.17	17.66	0.70	2.051	0.180	0.39	0.048	14.6	3.88	728	ND	3.9	6.5	7.9	0.19	41	3.0	8.5	19.1
B6	AS2	75	7.25	1.32	6.83	1.29	0.498	0.041	0.86	0.056	22.4	0.68	1121	ND	6.3	10.8	13.6	0.24	56	2.0	8.5	19.2
B7	AS2	85	5.68	3.27	5.90	1.35	0.457	0.066	1.23	0.051	21.2	1.48	1058	ND	6.8	7.8	12.0	0.37	32	3.1	10.2	22.9
B8	AS2	100	6.58	10.09	6.70	1.93	0.836	0.125	1.88	0.054	15.1	0.43	756	ND	7.5	6.8	10.1	0.23	43	1.2	9.7	21.9
B9	AS2	115	5.03	1.80	20.50	0.58	0.292	0.107	0.36	0.069	9.2	0.28	458	ND	7.2	17.0	20.2	0.35	57	5.4	15.3	34.5
														ND								
A1	AS1	0-50	4.15	16.08	6.02	1.42	1.575	0.081	0.56	0.103	14.3	0.11	2747	ND	8.1	4.5	8.4	0.14	60	0.7	8.0	24.2
A2	AS2	60-100	6.79	3.06	9.44	1.16	0.534	0.067	0.62	0.091	17.3	1.22	3578	ND	7.2	17.8	19.8	0.44	45	1.8	8.9	26.9
A3	Peat	160-200	1.07	5.93	0.86	0.21	0.352	0.020	0.27	0.054	4.5	1.37	726	ND	6.8	33.5	34.9	1.73	20	13.7	57.5	76.9

ND= Not determined; SH= Soil Horizon; DL= Detection Limit

Annexe E

Concentrations de As, Cd, Co, Cr, Cu, Ni, Pb dans les échantillons de sols des profils A, B, D et G

Concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn for the soil samples from the profiles A, B, D and G

Annexe E. Concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn for the soil samples from the profiles A, B, D and G

Sample	SH	Depth (cm)	As (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Zn (µg/g)
DL	-	-	0.63	0.02	0.17	0.12	0.04	0.22	0.57	0.10
G1	AS1	20	10	1.6	15	54	45	35	72	163
G2	AS1	30	**78**	**5.1**	23	86	**342**	58	**691**	**1116**
G3	AS1	45	16	**8.3**	15	74	**278**	40	**1069**	**1366**
G4	AS1	60	18	3.5	45	104	**252**	98	401	**671**
G5	AS2	70	**33**	**7.9**	24	66	**1425**	51	**4345**	**2512**
G6	AS2	90	**32**	**3.6**	22	45	**344**	47	119	143
G7	AS2	110	**117**	**5.3**	30	58	**187**	63	133	94
G8	AS2	130	**68**	**6.5**	41	78	**622**	79	156	144
G9	AS2	140	**43**	3.1	15	45	88	34	**7104**	146
G10	AS2	150	5.9	1.1	9.0	27	28	17	**692**	73
G11	Peat	170	5.7	0.45	1.5	9.0	41	20	18	361
G12	Peat	190	3.4	0.24	1.0	13	32	21	20	88
G13	Peat	210	2.9	0.37	0.55	7.6	27	13	6.5	28
G14	Peat	230	6.0	0.51	1.5	9.7	41	17	11	65
G15	Peat	250	6.3	0.28	1.2	4.7	17	10	5.4	24
G16	Marl	275	1.5	0.12	0.37	6.6	11	5.4	5.1	12
G17	Marl	290	1.8	0.10	0.26	7.1	12	5.3	4.4	14
D1	AS1	15	8.0	1.5	17	49	40	41	38	133
D2	AS1	40	7.0	4.1	16	87	**430**	51	382	**522**
D3	AS1	55	18	**5.3**	19	79	**325**	45	315	**1328**
D4	AS1	65	6.5	2.2	15	49	**133**	24	159	351
D5	AS2	90	**42**	**6.9**	41	98	**307**	87	326	**1754**
D6	AS2	120	**46**	**13.5**	28	66	**313**	57	**547**	**3792**
D7	AS2	140	**79**	3.1	23	103	**150**	99	458	**796**
D8	AS2	160	15	2.0	16	48	**110**	32	377	146
D9	Peat	180	4.7	1.7	10	33	**109**	23	111	161
D10	Peat	195	7.0	1.5	4.9	19	59	26	48	221
B1	AS1	15	ND	**5.0**	14	**269**	**1078**	65	266	466
B2	AS1	30	ND	**5.0**	16	173	**337**	59	332	**1098**
B3	AS2	55	ND	**14**	47	229	**401**	**121**	354	**6372**
B4	AS2	60	ND	**31**	41	189	**673**	**109**	**1021**	**14347**
B5	AS2	70	ND	**100**	22	123	**2415**	46	**7603**	**29411**
B6	AS2	75	ND	**15**	20	213	**4017**	**113**	**1757**	**5702**
B7	AS2	85	ND	**57**	21	175	**970**	47	342	**13365**
B8	AS2	100	ND	**16**	17	214	**145**	44	89	**8098**
B9	AS2	115	ND	**13**	35	129	**176**	**105**	476	**2922**
A1	AS1	0-50	ND	ND	18	201	**565**	72	**1551**	**542**
A2	AS2	60-100	ND	**18.6**	30	**1215**	**1962**	87	**1799**	**7983**
A4	Peat	160-200	ND	ND	3.0	38	25	11	ND	54
Background and threshold values of Quebec legislation										
Criteria A : Background level[a]			6	1.5	15	85	40	50	50	110
Criteria B: Maximum level to residential and recreational site use[a]			30	5	50	250	100	100	500	500
Criteria C: Maximum level to commercial or industrial site use[a]			50	20	300	800	500	500	1000	1500
Criteria D: Disposal prohibition[b]			250	100	1500	4000	2500	2500	5000	7500

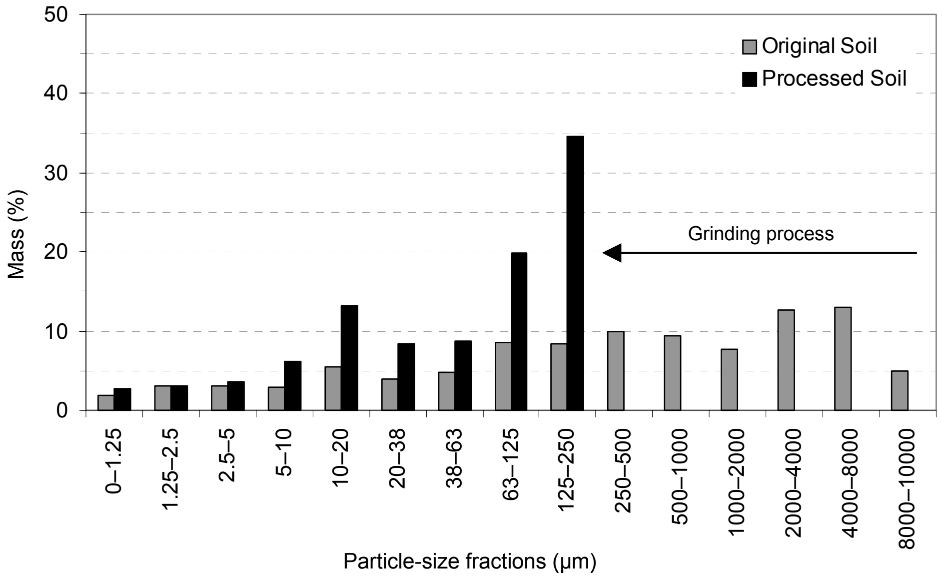
SH= Soil horizon; DL= Detection limit; ND= Not determined; [a]MDDEP, 1999; [b]MDDEP, 2008; The bold values represent the concentrations greater than the residential level; The underlined bold values represent the concentrations greater than the intervention level

Annexe F

Comparaison entre la distribution granulométrique du sol initial (0-10 mm) et celle du sol après le procédé de broyage (0-250 µm)

The particle-size distribution of the original soil (0-10 mm) and the processed soil (0-250 µm) (with crushing/ grinding)

Annexe F:
Particle-size distribution of the original soil (0-10 mm) and the processed soil (0-250 µm) with grinding process (preparation for the flotation process)



Annexe G

Comparaison entre la distribution des métaux (As, Cd, Cu, Pb et Zn) du sol initial (0-10 mm) et celle du sol après le procédé de broyage (0-250 µm)

The particle-size distribution of the original soil (0-10 mm)
and the processed soil (0-250 µm) (with crushing/ grinding process)

Annexe G. The particle-size distribution of the original soil (0-10 mm) and the processed soil (0-250 µm)

	Distributions in the original soil						Distributions in the processed soil*					
Particle size fractions µm	Mass %	As %	Cd %	Cu %	Pb %	Zn %	Mass %	As %	Cd %	Cu %	Pb %	Zn %
2000–10000	30.6	10.6	27.1	35.6	13.6	25.7	–	–	–	–	–	–
250–2000	27.1	13.6	24.6	21.0	25.8	20.3	–	–	–	–	–	–
125–250	8.4	7.5	7.2	5.5	8.1	5.7	34.5	15.7	22.9	23.4	18.4	19.9
63–125	8.6	8.0	6.7	5.4	7.6	5.3	19.8	13.9	16.8	17.6	16.6	14.2
38–63	4.8	4.7	3.7	3.4	4.4	3.3	8.7	6.6	7.8	7.5	7.0	6.6
20–38	4.0	4.9	3.7	3.2	4.4	3.2	8.4	10.9	9.3	9.1	9.8	8.3
0–20	16.5	50.6	27.1	25.8	36.0	36.4	28.6	52.9	43.3	42.4	48.3	51.0

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