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Développement d'un modèle informatique prédictif de traitement par précipitation des effluents métalliques

Par

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RÉSUMÉ

Au début du 21ème siècle, la pollution par les métaux lourds des eaux souterraines et de surfaces, continue de représenter un défi pour les autorités responsables de la protection de l'environnement. Les rejets incontrôlés de métaux et de métalloïdes dans les écosystèmes comme l'Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Tl et Zn, constituent de graves menaces pour la santé humaine et animale. Plusieurs méthodes de traitement des eaux contaminées par les métaux ont été proposées au cours des dernières décennies. Cependant, la technique de précipitation des métaux reste l'option la plus favorable, à l'échelle industrielle, pour des raisons technico-économiques. Dans ce contexte, le présent projet de recherche a été entrepris pour développer un outil informatique qui permet de prédire la spéciation chimique des métaux lors de la précipitation chimique d'un effluent ayant une caractéristique donnée, tout en tenant compte des normes de rejets à atteindre et des coûts totaux de traitement.

Dans un premier temps, les caractéristiques de déshydratation des boues (décantation, filtration et centrifugation), générées à la suite du traitement par précipitation des solutions monométalliques (0.02 mol/L), ont été évaluées. Les tests de précipitation effectués pour 15 différents métaux, ont donné des rendements d'élimination généralement comparables à ceux prédits par le logiciel *MINEQL+*. La précipitation sous forme d'hydroxydes à pH 10.0 était la technique la plus efficace pour l'élimination de huit ions (Al^{3+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}), alors que la précipitation sous forme de phosphates (à pH 6.0 avec l'addition de 0.0133 mol de PO_4^{3-}/L) a donné des taux d'enlèvement les plus élevés pour Ba^{2+}, Ca^{2+}, Cr^{3+}. La précipitation sous formes de sulfures (à pH 7.0 en utilisant 0.02 mol S^{2-}/L) a été la technique de précipitation la plus efficace seulement pour le Cu^{2+} et Sn^{2+}, alors que la précipitation sous formes de carbonates (à pH 8.0 en utilisant 0.02 mol CO_3^{2-}/L) a donné les meilleurs rendements d'élimination pour Pb^{2+}. Les résultats ont montré également que les précipités de phosphates, ont généralement les meilleures caractéristiques de déshydratation (indice de volume des boues (IVB), capacité de filtration (CF), résistance spécifique à la filtration (RSF) et siccité (ST)) par rapport aux carbonates, aux sulfures et aux hydroxydes. La précipitation par formation de carbonates est particulièrement intéressante pour les solutions contenants Mn^{2+} et Pb^{2+}.

Dans un deuxième temps, cette étude a exploré les caractéristiques de déshydratation des boues générées à l'issue du traitement par précipitation de solutions multimétalliques équimolaires et

de solutions synthétiques représentatives de drainages miniers acides (DMA). Les résultats ont révélé que les propriétés de déshydratation des boues métalliques varient, en fonction de la matrice utilisée (Cl^- ou SO_4^{2-}), de l'agent précipitant et des métaux présents dans l'effluent à traiter. Des analyses aux rayons X (DRX) ont montré que les hydroxydes métalliques (pH 10.0) et les phosphates métalliques (pH 7.0) sont de nature amorphe, donc difficile à déshydrater. Pour ces deux méthodes de traitement, la substitution de la matrice chlorure par la matrice sulfate améliore considérablement les propriétés de déshydratation (RSF = 6.60×10^{13} et 2.35×10^{13} m/kg, respectivement pour les matrices chlorures et sulfates). Dans les cas des traitements par les sulfures et les carbonates (à pH 8.0), les précipités obtenus sont respectivement de nature semi-cristalline et cristalline et aucune influence significative sur les caractéristiques de déshydratation n'a été détectée.

La troisième partie du projet a porté sur l'effet de trois matrices réelles sur les caractéristiques de séparation solide-liquide des boues générées par les différentes techniques de précipitation, soit un lixiviat de sol contaminé, un lixiviat de cendres d'incinération et un lixiviat de boues de station d'épuration. Les valeurs de RSF obtenues suite à la filtration sous pression des précipités de traitement du lixiviat de sol suivent l'ordre croissant suivant: sulfures (4.3×10^{12} m/kg) < phosphates (6.4×10^{12} m/kg) < hydroxydes [$Ca(OH)_2$] (14.2×10^{12} m/kg) < hydroxydes [NaOH] (19.7×10^{12} m/kg) < carbonates (26.5×10^{12} m/kg). Pour le traitement du lixiviat de cendres, les résultats obtenus sont similaires et ce, quelque soit le mode de traitement utilisé; les valeurs de RSF varient entre 5 et 7×10^{12} m/kg, alors que IVB est compris entre 39 et 50 mL/g. Les meilleures caractéristiques de déshydratation des précipités issus du traitement du lixiviat de boues d'épuration ont été obtenues par précipitation avec les phosphates (IVB = 180 mL/g et SRF = 7.6×10^{12} m/kg). Dans tous les cas, la méthode de filtration sous pression [ST = 11 à 73% (p/p)] s'est avérée plus efficace que la centrifugation [ST = 5 à 11% (p/p)] pour la déshydratation des précipités métalliques.

Dans la dernière partie du projet un nouveau progiciel portant l'acronyme *PITEM* (Programme Informatique de Traitement des Effluents Métalliques) a été développé pour la prédiction du traitement des effluents métalliques par les techniques de précipitation. *PITEM* intègre, dans un premier temps, un modèle de spéciation chimique se basant sur la *méthode de constante d'équilibre*, afin de calculer les concentrations en métaux résiduelles et les types de précipités métalliques formés. *PITEM* utilise les données thermodynamiques fournies par la base de données du logiciel *MINEQL+* couplé avec le code informatique nommé *EST* (*Equilibrium system tool*). *PITEM* inclut également un modèle mathématique pour la prédiction des caractéristiques de déshydratation et de production de boues développé à partir des résultats expérimentaux de cette thèse, et un module économique pour l'évaluation du coût total de traitement par précipitation. *PITEM* est écrit en langage Visual Basic sous la plate-forme de *Microsoft EXCEL* et il est conçu sous forme d'outil informatique facile à utiliser à des fins industrielles et/ou académiques.

Les résultats de simulation montrent que les valeurs de ST sont généralement en accord avec celles obtenues expérimentalement. Le coût unitaire de traitement estimé par le programme pour les quatre scénarios de traitement par précipitation, suit l'ordre ascendant suivant : carbonates (Na_2CO_3) < sulfures (Na_2S) < phosphates (Na_3PO_4) < hydroxydes (NaOH). Dans les cas étudiés, la neutralisation par les carbonates est apparue la technique la plus économique et ce, en raison des bonnes caractéristiques de déshydratation des boues générées.

Cette étude doctorale a permis, pour la première fois, de mettre au point un modèle informatisé permettant à la fois de prédire l'équilibre des espèces chimiques en solution et des précipités formés lors du traitement d'effluents métalliques, ainsi que de prédire le comportement de déshydratation des boues métalliques. De plus, ce modèle permet d'estimer les coûts de traitement de ces effluents et de gestion des boues métalliques, ce qui permet d'établir la technique de précipitation à privilégier, selon la situation rencontrée (concentrations et types de métaux en solution, normes en vigueur, coûts des produits chimiques et de disposition des boues métalliques). Ce modèle simple d'utilisation facilite la prise de décision en ce qui à trait au choix technologique en matière de traitement des effluents pollués par les métaux toxiques.

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μ	viscosité du filtrat
A	surface
b	pente de la droite (V vs. t/V)
BDETH2	benzene-1,3-diamidoethanethiol
c	masse de solide/unite de volume de filtrat
CF	capacité de filtration
C_f	taux d’humidité final (%)
C_i	taux d’humidité initial (%)
CTT	coût total de traitement
DDP	dipropyl dithiophosphate de potassium
DDTC	diéthyldithiocarbamate
DMA	drainage minier acide
DMTC	diméthyldithiocarbamate
DRX	diffraction aux rayons X
DTC	dithiocarbamate
EST	equilibria speciation tool
I	force ionique
IVB	indice de volume de boue
M	metal divalent
Na_2BDP	disodium *N,N*’-bis-(dithiocarboxy)piperazine
P	pression
PB	production de boue
PITEM	programme informatisé de traitement des effluents métalliques
PyDETH2	pyridine-2-6-diamineethanethiol
rpm	rotations par minute
RSF	résistance spécifique à la filtration
S	échangeur d’ions
S/L	solide-liquide
ST	solides totaux
t	temps
tbs	tonne de boue sèche
TCS	thiocarbonate de sodium
TMT	2,4,6-trimercapto-1,3,5-triazine
TRH	temps de rétention hydraulique
V	volume

CHAPITRE I

SYNTHÈSE

1. SYNTHÈSE

1.1 Introduction et problématique

La contamination de l'environnement par les métaux lourds est une conséquence directe du progrès technologique et industriel (Davydova 2005; Nriagu 1996; Nriagu et Pacyna 1988; Wong *et al.* 2006). Le principal problème associé à cette contamination d'origine anthropique est la toxicité qui atteint tous les organismes vivants, en particulier, l'être humain (Baath 1989; Chapman *et al.* 2003; Florea et Büsselberg 2006; Galvin 1996; Sharma et Agrawal 2005). Il est donc essentiel d'éliminer ou de réduire la présence de ces contaminants inorganiques dans les eaux de surfaces et souterraines, en vue de réduire la possibilité d'absorption par les plantes, les animaux et les humains, et l'accumulation éventuelle dans la chaîne alimentaire (Kabata-Pendias 2001; McLaughlin *et al.* 2000).

Pour ces raisons, la recherche scientifique sur les métaux lourds a pris une ampleur croissante et beaucoup de travaux ont été menés au cours de ces dernières décennies pour développer des méthodes efficaces et peu coûteuses pour le traitement des effluents ayant une contamination inorganique (Blais *et al.* 1999; Kurniawan *et al.* 2006). Parmi les différentes technologies développées, la précipitation chimique est de loin la méthode la plus commune pour l'enlèvement des métaux contenus dans les effluents industriels (Patterson et Minear, 1975; Patterson *et al.* 1977; Cherry, 1982; Levasseur *et al.* 2005). Il s'agit en effet d'une méthode simple et relativement économique pour traiter les effluents contaminés. D'une façon générale, le traitement des effluents industriels chargés en métaux par les techniques de précipitation génèrent habituellement des quantités considérables de résidus, ou boues métalliques, lesquels sont souvent considérés comme étant des déchets dangereux. Les coûts de traitement de ces effluents ainsi que la gestion des boues métalliques générées peuvent être importants.

La prise de décision en ce qui a trait à la mise en œuvre de projets de traitement par précipitation des effluents contaminés par des métaux nécessite une connaissance détaillée de la faisabilité technico-économique des activités de traitement des effluents et de gestion des boues métalliques. Avant d'en arriver à une décision définitive concernant le traitement d'effluents par précipitation chimique, des études de préfaisabilité et de faisabilité technico-économique doivent être effectuées. Or, à l'heure actuelle, il n'existe pas d'outils informatiques de prédiction de traitement d'effluents par précipitation tenant compte des normes à atteindre, des coûts en produits chimiques et des frais de gestion et de disposition des boues métalliques.

Dans ce contexte, le présent projet de recherche a été entrepris pour développer un outil informatique écrit en langage Visual Basic sous *Microsoft EXCEL*. Le logiciel permet de prédire la spéciation chimique des métaux lors de la précipitation chimique d'un effluent donné, tout en tenant compte des normes à atteindre et des coûts totaux de traitement dans un procédé classique de décontamination (produits chimiques, coûts de traitement et de disposition des boues métalliques générées lors de la précipitation, etc.).

Cette thèse de doctorat a été divisée en six chapitres. Le premier chapitre « Synthèse » présente une revue bibliographique sur les diverses connaissances scientifiques associées à la précipitation chimique des métaux, ainsi que les différents logiciels d'équilibres chimiques disponibles. Ce premier chapitre comporte également une discussion générale sur les résultats les plus importants de ce projet de doctorat.

Le deuxième chapitre est constitué de l'article : Blais J.F., Z. Djedidi., R. Ben Cheikh., R.D. Tyagi et G. Mercier (2008) *Metals precipitation from effluents- A review*. Practice Periodical Toxic Hazardous Radioactive Waste Management. 12(3), 135-149.

Ce premier article traite de manière détaillée les caractéristiques spécifiques des contaminants métalliques, de leur comportement et de leur élimination des effluents par les techniques de précipitation. Une revue de l'effet des principaux métaux toxiques sur la santé humaine a été également établie. Le troisième chapitre est constitué de l'article : Djedidi Z., J. Ben Khaled., R. Ben Cheikh., J.F. Blais., G. Mercier et R.D. Tyagi (2009) *Comparative study of dewatering chracteristics of metal precipitates generated during treatment of monometallic solutions*. Hydrometallurgy. 95, 61-69.

Dans cet article les caractéristiques de déshydratation des boues (décantation, filtration et centrifugation), générées à la suite du traitement par précipitation des solutions monométalliques ont été évaluées et ces informations ont, par la suite, été intégrées au programme *PITEM* pour la prédiction de la production de boues métalliques

Le quatrième chapitre regroupe l'article : Djedidi Z., M. Bouda., M.A. Souissi, R. Ben Cheikh., G. Mercier., R.D. Tyagi et J.F Blais (2009) *Comparative study of dewatering characteristics of metal precipitates generated during treatment of synthetic polymetallic and AMD solutions*. Hydrometallurgy. 98(3-4), 247-256.

Dans cette partie du projet, les caractéristiques de déshydratation, exprimées en termes de décantation, filtration et centrifugation, des boues générées à l'issue du traitement par précipitation des solutions multimétalliques et des drainages miniers acides synthétiques, ont été évaluées dans cette étude. Ces résultats expérimentaux ont permis de valider les prédictions obtenues par le progiciel *PITEM* pour le traitement d'effluents multimétalliques synthétiques.Le cinquième chapitre est constitué de l’article : Djedidi Z., M. Bouda., M.A. Souissi., R. Ben Cheikh., G. Mercier., R.D. Tyagi et J.F Blais (2009) *Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge*. J. Hazard. Mater. 172 (2-3), 1372-1382.

Cette étude concerne le traitement par précipitation de trois lixiviats acides (lixiviat de sol, lixiviat de cendre d’incinérateur et lixiviat de boues de station d’épuration) contaminés par les métaux lourds et ce, en utilisant une variété d’agents précipitants. Les caractéristiques de déshydratation des boues générées ont été également étudiées dans cette partie du projet et les résultats obtenus ont, ensuite, été utilisés pour valider les prédictions du modèle dans le cas du traitement de lixiviat de sol

Le sixième chapitre comprend l’article : Djedidi Z., M. Bouda, R. Ben Cheikh, J.F. Blais, G. Mercier et R.D. Tyagi (2009) *Development of a new chemical equilibrium and techno-economic model for the treatment of metal-polluted effluents by precipitation.* Hydrometallurgy. (soumis le 23 juin 2009).

Ce dernier article décrit le nouveau progiciel informatique portant l’acronyme *PITEM* (Programme Informatisé de Traitement des Effluents Métalliques) qui a été développé pour la prédiction du traitement des effluents métalliques par les techniques de précipitation.

1.2 Revue de littérature

De nombreux travaux de recherche ont été réalisés aux cours des dernières décennies afin de développer des procédés efficaces et peu coûteux pour traiter les effluents chargés en métaux (Blais *et al.* 1999; Kurniawan *et al.* 2006). Le Tableau 1.1 regroupe les principales technologies utilisées ou proposées pour l'enlèvement des métaux toxiques de ces effluents.

Les métaux peuvent être éliminés par précipitation sous formes d'oxydes/hydroxydes, sulfures, carbonates et phosphates. Des agents de précipitation sélectifs ont également été développés au cours de ces dernières années pour le traitement de certains types d'effluents (Andrus 2000). Dans certain cas, les réactions d'oxydo-réduction peuvent également intervenir pour la précipitation de certains métaux, comme le chrome et l'arsenic. Des procédés de décontamination des effluents industriels utilisent également des microorganismes pour récuperer les métaux sous formes de précipités. D'autres techniques comme la coagulation et/ou la floculation peuvent être associées à la précipitation chimique pour améliorer les caractéristiques de déshydratation des flocs métalliques générés. La déshydratation mécanique des boues est la séparation entre les phases solide et liquide (S/L) et elle est qualifiée généralement en termes de capacité de décantation, de filtration (filtre-presse) et de centrifugation.

Parmi les technologies de traitement développées jusqu'à nos jours, la précipitation reste de loin la méthode la plus utilisée pour l'enlèvement des métaux des eaux souterraines, des eaux de surface et des effluents industriels (FRTR 2005; Levasseur *et al.* 2005; Mirbagheri et Hosseini 2004).

Tableau 1.1 Technologies de traitement des effluents pollués par les métaux

Technologies	Exemples	Références
Précipitation chimique	Précipitation par formation d'hydroxydes, carbonates, sulfures ou phosphates, réactions d'oxydo-réduction	Baltpurvins *et al.* (1996a,b, 1997); Couillard et Mercier (1992); USEPA (2000) Robinson et Sum (1980)
Bioprécipitation	Marais artificielles, bioréacteurs (bactéries sulfato-réductrices)	Kaksonen *et al.* (2003); Mack *et al.* (2004); Maine *et al.* (2006); VanRoy *et al.* (2006)
Échange d'ion	Résines synthétiques (comportant des groupements sulfonique, carboxylique, thiocarbamate, thiols, hydroxyle, amine), résines échangeuses de chélates (comportant des groupements phosphoniques, aminophosphonique, iminodiacétique ou oxime), résine imprégnée de solvant (DEHPA, PEIMPA), matériaux naturels (zéolite, argile)	Dabrowski *et al.* (2004); Juang *et al.* (2003) Lin *et al.* (2000); Mondal et Das (2004)
Adsorption	Charbon actif granulé (GAC), alumine activée, lignine, chitosane, alginate, zéolite, argile, cendres volantes, tourbe, laine, cotton, oxydes naturels	Bailey *et al.* (1999); Babel et Kurniawan (2003); Wang *et al.* (2003); Wingenfelder *et al.* (2005)
Biosorption	Déchets agro-industriels (fruits, coque de céréales, écorces), biomasses de foresterie (écorce et sciure de bois), algue, bactérie, champignon, plantes terrestres et aquatiques (phytofiltration ou phytoaccumulation), boues de station d'épuration, levure	Al-Asheh et Duvnjak (1999); Gardea-Torresdey *et al.* (2004); Kamal *et al.* (2004); Kapoor et Viraraghavan (1995); Kurniawan *et al.* (2006); Romera *et al.* (2006)
Séparation physique	Microfiltration, ultrafiltration, nanofiltration, osmose inverse, pervaporation membranaire, distillation	Ben Frarès *et al.* (2005); Brooks (1986); DiPalma *et al.* (2003); Lin *et al.* (2004)
Séparation électrochimique	Électrocoagulation, électrodéposition, électrodialyse, peroxydation électrochimique	Arienzo *et al.* (2001); Djedidi *et al.* (2005); Juang et Wang (2000); Lai et Lin (2006); Meunier *et al.* (2004, 2006)
Extraction par solvant	Bis-(2-ethyl-hexul)phosphoric acid (D2EHPA), acide bis-(2,4,4-trimethylpentyl)-phosphonique, hydroxyoximes, tri-n-octylmethylammonium	Belkhouche *et al.* (2005); Lin *et al.* (2002); Silva *et al.* (2005)
Flotation	Flottation à air dissout (DAF)	Aldrich et Feng (2000); Doyle (2003); Lazaridis *et al.* (2001); Zamboulis *et al.* (2004)
Cémentation	Fer, aluminium	Brooks (1991); Hayes (1985); Nelson *et al.* (2000) USEPA (1992)

1.2.1 Hydroxydes de métaux

La méthode de précipitation qui demeure la plus courante pour éliminer les métaux des eaux usées consiste à les précipiter sous forme d'hydroxydes. La procédure habituelle est l'ajout de produits chimiques, tels que la chaux (CaO ou $Ca(OH)_2$), $Mg(OH)_2$, $NaHCO_3$, Na_2CO_3, $(NH_4)_2CO_3$, $NaOH$ et NH_4OH. La Figure 1.1 montre un schéma simplifié d'un procédé type de précipitation, incluant la formation et la séparation S/L par décantation. L'hydroxyde de sodium ($NaOH$) étant l'agent de précipitation utilisé et les contre-ions choisis sont les chlorures.

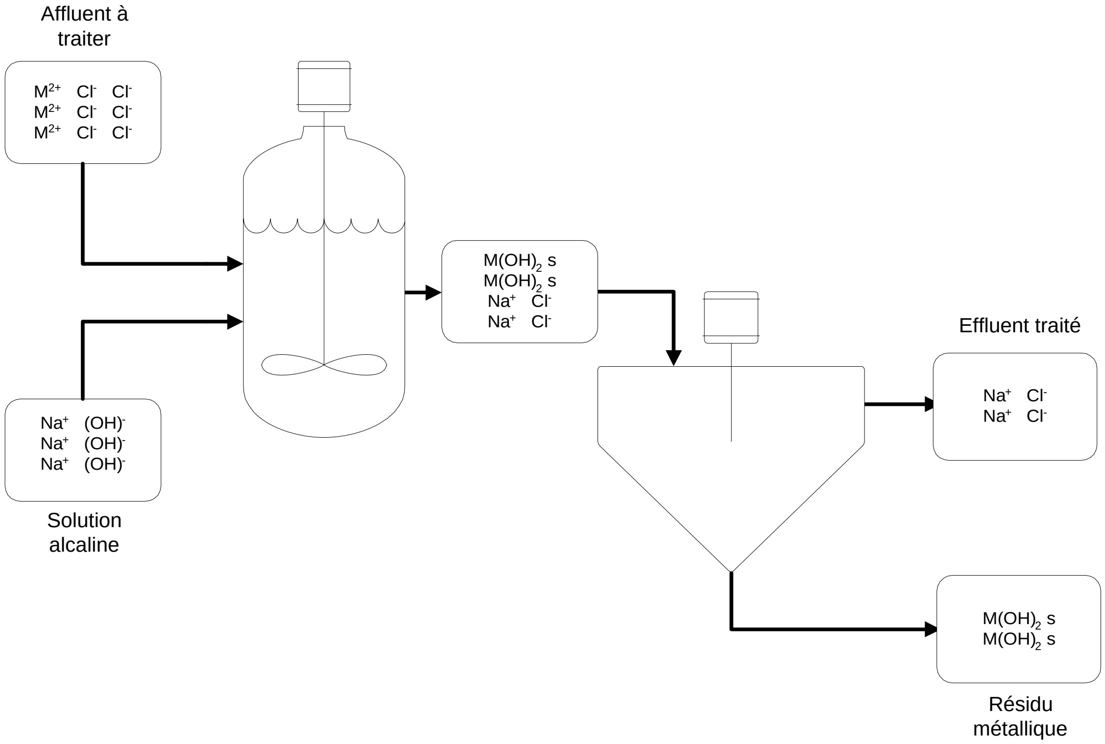

Figure 1.1 **Schéma simplifié du principe de l'enlèvement des métaux par précipitation sous forme d'hydroxydes**

D'un point de vue chimique, la précipitation est un phénomène complexe résultant de l'induction des conditions de sursaturation. Plus simplement, elle peut être décrite selon trois étapes : 1) la nucléation ou germination, 2) la croissance cristalline et 3) la floculation (Patterson 1988).

La nucléation a été étudiée par plusieurs auteurs et ce, essentiellement dans le cas de l'élimination du fer et du zinc contenus dans les drainages miniers acides (DMA) (Zinck et Aubé 1998). La nucléation ou germination correspond à l'apparition du premier germe par condensation des sels métalliques, puis à la croissance de ce dernier jusqu'à l'atteinte des conditions de sursaturation et la formation de phase solide (Duan et Gregory 2003).

Les métaux solubles peuvent être récupérés sous formes d'hydroxydes selon l'Équation 1.1 par l'intermédiaire de plusieurs réactifs alcalins, comme (CaO ou $Ca(OH)_2$), $Mg(OH)_2$, NaOH et NH_4OH (Kurniawan 2006; Meunier *et al.* 2002, 2006; Mirbagheri et Hosseini 2004; Viadero *et al.* 2006).

Équation 1.1 $$M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2\downarrow$$

La précipitation des métaux sous forme d'hydroxydes peut être également obtenue par utilisation de sous-produits alcalins, tels que les cendres volantes provenant des incinérateurs (Gitari *et al.* 2006).

Le minimum de solubilité de la majorité des hydroxydes métalliques est atteint à des pH compris entre 9.5 et 10.0 (Charerntanyarak 1999; Dyer *et al.* 1998). Généralement, les métaux tels que Cd, Co, Cu, Mn, Ni, Pb et le Zn précipitent sous forme d'hydroxydes à des pH supérieurs à cinq, fournissant des possibilités de séparation des ions ferriques (Fe^{3+}), qui précipitent à leur tour à des pH inférieur à quatre (Brooks 1986; Hayes 1985).

Le Tableau 1.2 présente les valeurs de constantes de produits de solubilité (pKs) de quelques hydroxydes métalliques. Généralement, la formation de ces hydroxydes métalliques est accompagnée par des phénomènes d'adsorption et/ou de coprécipitation contribuant à l'amélioration du taux d'élimination des métaux (Blais *et al.* 1999; Chu 1999; Couillard et Mercier 1992; Marchioretto *et al.* 2005). Au cours d'une précipitation, les cyanures peuvent causer des interférences, tandis que les agents de chélation comme l'EDTA ou la NTA, inhibent l'élimination des métaux (Lin *et al.* 1998).

L'utilisation de la chaux lors du traitement des effluents acides et très chargés en sulfates comme les DMA, impliquent la formation d'une boue secondaire constituée essentiellement de gypse ($CaSO_4.2H_2O$). Cette boue secondaire peut augmenter considérablement les coûts de transport et de gestion des déchets solides générés (Baltpurvins *et al.* 1997; Jüttner *et al.* 2000), et peut également influencer d'une façon significative les paramètres de déshydratation ou de séparation S/L (Blais *et al.* 1999; Viadero *et al.* 2006). Pour ces raisons, le traitement de ce type d'effluent est conseillé en utilisant des agents alcalins de précipitation comme NaOH ou NH_4OH qui forment des sous produits solubles (complexes).

Tableau 1.2 Constantes des produits de solubilité des hydroxydes métalliques

Métaux	État d'oxydation	Réactions	pK_s
Aluminium	(3+)	$Al(OH)_3$ (alpha) $\leftrightarrow 3\ OH^{(-)} + Al^{(3+)}$	33.5
Antinoine	(3+)	$Sb(OH)_3 \leftrightarrow 3\ OH^{(-)} + Sb^{(3+)}$	49.1
Baryum	(2+)	$Ba(OH)_2 \leftrightarrow 2\ OH^{(-)} + Ba^{(2+)}$	2.3
Béryllium	(2+)	$Be(OH)_2$ (alpha) $\leftrightarrow 2\ OH^{(-)} + Be^{(2+)}$	21.1
Cadmium	(2+)	$Cd(OH)_2 \leftrightarrow 2\ OH^{(-)} + Cd^{(2+)}$	13.6
Calcium	(2+)	$Ca(OH)_2$ (portlandite) $\leftrightarrow 2\ OH^{(-)} + Ca^{(2+)}$	5.3
Chrome	(2+)	$Cr(OH)_2 \leftrightarrow 2\ OH^{(-)} + Cr^{(2+)}$	17.2
	(3+)	$Cr(OH)_3 \leftrightarrow 3\ OH^{(-)} + Cr^{(3+)}$	30.2
Cobalt	(2+)	$Co(OH)_2 \leftrightarrow 2\ OH^{(-)} + Co^{(2+)}$	14.8
	(3+)	$Co(OH)_3 \leftrightarrow 3\ OH^{(-)} + Co^{(3+)}$	44.3
Cuivre	(1+)	$Cu(OH) \leftrightarrow OH^{(-)} + Cu^{(+)}$	14.7
	(2+)	$Cu(OH)_2 \leftrightarrow 2\ OH^{(-)} + Cu^{(2+)}$	18.6
Fer	(2+)	$Fe(OH)_2 \leftrightarrow 2\ OH^{(-)} + Fe^{(2+)}$	15.1
	(3+)	$Fe(OH)_3 \leftrightarrow 3\ OH^{(-)} + Fe^{(3+)}$	37.4
Mercure	(1+)	$Hg_2(OH)_2 \leftrightarrow 2\ OH^{(-)} + Hg_2^{(2+)}$	23.7
	(2+)	$Hg(OH)_2 \leftrightarrow 2\ OH^{(-)} + Hg^{(2+)}$	25.4
Plomb	(2+)	$Pb(OH)_2 \leftrightarrow 2\ OH^{(-)} + Pb^{(2+)}$	16.1
Magnésium	(2+)	$Mg(OH)_2 \leftrightarrow 2\ OH^{(-)} + Mg^{(2+)}$	10.8
Manganèse	(2+)	$Mn(OH)_2 \leftrightarrow 2\ OH^{(-)} + Mn^{(2+)}$	12.7
Nickel	(2+)	$Ni(OH)_2 \leftrightarrow 2\ OH^{(-)} + Ni^{(2+)}$	14.7
Argent	(1+)	$Ag(OH) \leftrightarrow OH^{(-)} + Ag^{(+)}$	7.7
Thallium	(1+)	$TlOH \leftrightarrow OH^{(-)} + Tl^{(+)}$	1.1
	(3+)	$Tl(OH)_3 \leftrightarrow 3\ OH^{(-)} + Tl^{(3+)}$	45.2
Étain	(2+)	$Sn(OH)_2 \leftrightarrow 2\ OH^{(-)} + Sn^{(2+)}$	28.1
	(4+)	$Sn(OH)_4 \leftrightarrow 4\ OH^{(-)} + Sn^{(4+)}$	56.0
Zinc	(2+)	$Zn(OH)_2 \leftrightarrow 2\ OH^{(-)} + Zn^{(2+)}$	15.7

1.2.2 Sulfures de métaux

La précipitation des métaux sous formes de sulfures (Équation 1.2) est obtenue en utilisant Na_2S, NaHS, H_2S ou FeS comme agents de précipitation (Al-Tarazi *et al.* 2004; Marchioretto *et al.* 2005; Robinson et Sum 1980;Veeken et Rulkens 2003).

Équation 1.2 $M^{2+} + S^{2-} \leftrightarrow MS\downarrow$

Il est cependant nécessaire, dans le cas de traitement des effluents acides, de procéder à une première neutralisation par une base (NaOH) avant l'ajout des sels de sulfures (Charerntanyarak 1999). Cette étape étant nécessaire pour éviter le dégagement de gaz toxiques (H_2S), dans la gamme des pH acides. Dans le cas où le fer ferrique (Fe III) et l'aluminium (Al III) sont présents dans l'effluent, la coprécipitation et l'adsorption des métaux (comme le Cr, Pb et le Zn) peuvent avoir lieu sur $Fe(OH)_3$ et $Al(OH)_3$ qui possèdent généralement des structures amorphes (Marchioretto *et al.* 2005).

Le Tableau 1.3 donne les différentes valeurs de pKs de quelques sulfures métalliques. D'une façon générale, les sulfures métalliques montrent des solubilités inférieures à celles des hydroxydes. Les sulfures métalliques sont généralement stables et ce, dans une large gamme de pH (Islamoglu *et al.* 2006).

Il est à noter que la précipitation des métaux sous forme de sulfures présente des avantages par rapport à celle des hydroxydes : 1) la concentration résiduelle des métaux dans les effluents est de l'ordre de µg/ L (mg/L pour les hydroxydes); 2) l'interférence des agents de chélation (EDTA, NTA, etc) dans les eaux usées est moins significative; 3) la précipitation donne une meilleure sélectivité; 4) des taux d'élimination des métaux élevés obtenus pour des temps de rétention hydrauliques (TRH) assez bas; 5) dans la majorité des cas, les boues générées montrent des propriétés d'épaississement et de déshydratation meilleures que celles des boues d'hydroxydes; 6) les sulfures métalliques peuvent être traités dans les fonderies pour la récupération des métaux de base (Kim et Amodeo 1983; Kim *et al.* 2002).

Tableau 1.3 Constantes des produits de solubilité des sulfures métalliques

Métaux	État d'oxydation	Reactions	pK_s
Baryum	(2+)	$BaS \leftrightarrow Ba^{(2+)} + S^{(2-)}$	-3.3
Béryllium	(2+)	$BeS \leftrightarrow Be^{(2+)} + S^{(2-)}$	- 6.5
Cadmium	(2+)	CdS (greenockite) $\leftrightarrow Cd^{(2+)} + S^{(2-)}$	26.1
Cobalt	(2+)	CoS (alpha) $\leftrightarrow Co^{(2+)} + S^{(2-)}$	20.4
Cuivre	(1+)	$Cu_2S \leftrightarrow 2\ Cu^{(+)} + S^{(2-)}$	47.6
	(2+)	CuS (covellite) $\leftrightarrow Cu^{(2+)} + S^{(2-)}$	35.2
Fer	(2+)	$FeS \leftrightarrow Fe^{(2+)} + S^{(2-)}$	17.2
	(3+)	$Fe_2S_3 \leftrightarrow 2\ Fe^{(3+)} + 3\ S^{(2-)}$	85.0
Mercure	(1+)	$Hg_2S \leftrightarrow Hg_2^{(2+)} + S^{(2-)}$	47.0
	(2+)	HgS (cinnabar) $\leftrightarrow Hg^{(2+)} + S^{(2-)}$	52.4
Plomb	(2+)	PbS (galène) $\leftrightarrow Pb^{(2+)} + S^{(2-)}$	27.0
Manganèse	(2+)	MnS (rose) $\leftrightarrow Mn^{(2+)} + S^{(2-)}$	9.6
	(2+)	MnS (vert) $\leftrightarrow Mn^{(2+)} + S^{(2-)}$	12.6
Nickel	(2+)	NiS (alpha) $\leftrightarrow Ni^{(2+)} + S^{(2-)}$	18.5
	(2+)	NiS (gamma) $\leftrightarrow Ni^{(2+)} + S^{(2-)}$	25.7
Argent	(1+)	Ag_2S (acanthite) $\leftrightarrow 2\ Ag^{(+)} + S^{(2-)}$	49.2
Thallium	(1+)	$Tl_2S \leftrightarrow 2\ Tl^{(+)} + S^{(2-)}$	20.1
Étain	(2+)	$SnS \leftrightarrow Sn^{(2+)} + S^{(2-)}$	25.0
	(4+)	$SnS_2 \leftrightarrow Sn^{(4+)} + 2\ S^{(2-)}$	70.0
Zinc	(2+)	ZnS (sphalérite) $\leftrightarrow Zn^{(2+)} + S^{(2-)}$	23.0
	(2+)	ZnS (wurtzite) $\leftrightarrow Zn^{(2+)} + S^{(2-)}$	24.3

1.2.3 Carbonates de métaux

Les carbonates, comme Na_2CO_3 et $CaCO_3$, peuvent être également utilisés pour la neutralisation et la précipitation des métaux (Guillard et Lewis 2002; McAnally *et al.* 1984; Preis et Gamsjager 2001; Sun et Huang 2002). La réaction des ions carbonates avec les ions métalliques divalents est donnée par l'Équation 1.3.

Équation 1.3 $$M^{2+} + (CO_3)^{2-} \leftrightarrow M(CO_3)\downarrow$$

Le Tableau 1.4 présente les valeurs de pKs de quelques carbonates métalliques. La majorité des carbonates ont une plus grande solubilité que les hydroxydes métalliques.

Tableau 1.4 Constantes des produits de solubilité des carbonates métalliques

Métaux	État d'oxydation	Réactions	pK_s
Baryum	(2+)	$BaCO_3$ (witherite) ↔ $Ba^{(2+)} + CO_3^{(2-)}$	8.6
Cadmium	(2+)	$CdCO_3$ (otavite) ↔ $Cd^{(2+)} + CO_3^{(2-)}$	12.0
Calcium	(2+)	$CaCO_3$ (calcite) ↔ $Ca^{(2+)} + CO_3^{(2-)}$	8.5
	(2+)	$CaCO_3$ (aragonite) ↔ $Ca^{(2+)} + CO_3^{(2-)}$	8.3
Cobalt	(2+)	$CoCO_3 \leftrightarrow Co^{(2+)} + CO_3^{(2-)}$	10.0
Cuivre	(2+)	$CuCO_3 \leftrightarrow Cu^{(2+)} + CO_3^{(2-)}$	11.5
Fer	(2+)	$FeCO_3$ (sidérite) ↔ $Fe^{(2+)} + CO_3^{(2-)}$	10.2
Mercure	(1+)	$Hg_2CO_3 \leftrightarrow Hg_2^{(2+)} + CO_3^{(2-)}$	16.1
Plomb	(2+)	$PbCO_3$ (cerrusite) ↔ $Pb^{(2+)} + CO_3^{(2-)}$	13.1
Magnésium	(2+)	$MgCO_3$ (magnésite) ↔ $Mg^{(2+)} + CO_3^{(2-)}$	7.5
	(2+)	$MgCO_3.3H_2O \leftrightarrow 3\ H_2O + Mg^{(2+)} + CO_3^{(2-)}$	4.7
Manganèse	(2+)	$MnCO_3$ (rhodochrosite) ↔ $Mn^{(2+)} + CO_3^{(2-)}$	10.6
Nickel	(2+)	$NiCO_3 \leftrightarrow Ni^{(2+)} + CO_3^{(2-)}$	6.9
Argent	(1+)	$Ag_2CO_3 \leftrightarrow 2\ Ag^{(+)} + CO_3^{(2-)}$	11.1
Thallium	(1+)	$Tl_2CO_3 \leftrightarrow 2\ Tl^{(+)} + CO_3^{(2-)}$	3.8
Zinc	(2+)	$ZnCO_3$ (smithsonite) ↔ $Zn^{(2+)} + CO_3^{(2-)}$	10.0
	(2+)	$ZnCO_3.H_2O \leftrightarrow H_2O + Zn^{(2+)} + CO_3^{(2-)}$	10.3

1.2.4 Phosphates de métaux

Bien que rarement pratiqué, il est possible d'enlever les métaux divalents en solution par le biais de la formation de phosphates métalliques insolubles tel que le décrit à l'Équation 1.4 (Mavropoulos *et al.* 2002; Naeem *et al.* 2003; Pigaga *et al.* 2002).

Équation 1.4 $$3\ M^{2+} + 2\ (PO_4)^{3-} \leftrightarrow M_3(PO_4)_2\downarrow$$

L'addition de sels ou de minéraux de phosphates (apatite et hydroxyapatite) est une technique qui a été prouvée fiable pour l'immobilisation des métaux dans les sols et les déchets (Bolan *et al.* 2003; McGowen *et al.* 2001; Porter *et al.* 2004).

Le Tableau 1.5 présente les valeurs de pKs de quelques phosphates métalliques. Généralement, les phosphates métalliques présentent des solubilités inférieures à celles des hydroxydes.

Tableau 1.5 Constantes des produits de solubilité des phosphates métalliques

Métaux	État d'oxydation	Réactions	pK_s
Aluminium	(3+)	$AlPO_4 \leftrightarrow Al^{(3+)} + PO_4^{(3-)}$	22.5
Baryum	(2+)	$Ba_3(PO_4)_2 \leftrightarrow 3\ Ba^{(2+)} + 2\ PO_4^{(3-)}$	29.3
Béryllium	(2+)	$Be_3(PO_4)_2 \leftrightarrow 3\ Be^{(2+)} + 2\ PO_4^{(3-)}$	38.6
Cadmium	(2+)	$Cd_3(PO_4)_2 \leftrightarrow 3\ Cd^{(2+)} + 2\ PO_4^{(3-)}$	32.6
Calcium	(2+)	$Ca_3(PO_4)_2$ (beta) $\leftrightarrow 3\ Ca^{(2+)} + 2\ PO_4^{(3-)}$	28.9
	(2+)	$CaHPO_4 \leftrightarrow H^{(+)} + Ca^{(2+)} + PO_4^{(3-)}$	19.3
	(2+)	$CaHPO_4.2H_2O \leftrightarrow 2\ H_2O + H^{(+)} + Ca^{(2+)} + PO_4^{(3-)}$	19.0
Cobalt	(2+)	$Co_3(PO_4)_2 \leftrightarrow 3\ Co^{(2+)} + 2\ PO_4^{(3-)}$	34.7
	(2+)	$CoHPO_4 \leftrightarrow H^{(+)} + Co^{(2+)} + PO_4^{(3-)}$	19.1
Cuivre	(2+)	$Cu_3(PO_4)_2 \leftrightarrow 3\ Cu^{(2+)} + 2\ PO_4^{(3-)}$	36.9
	(2+)	$Cu_3(PO_4)_2.3H_2O \leftrightarrow 3\ H_2O + 3\ Cu^{(2+)} + 2\ PO_4^{(3-)}$	35.1
Fer	(2+)	$Fe_3(PO_4)_2 \leftrightarrow 3\ Fe^{(2+)} + 2\ PO_4^{(3-)}$	36.0
	(2+)	$Fe_3(PO_4)_2.8H_2O \leftrightarrow 8\ H_2O + 3\ Fe^{(2+)} + 2\ PO_4^{(3-)}$	36.0
	(3+)	$FePO_4 \leftrightarrow Fe^{(3+)} + PO_4^{(3-)}$	25.8
	(3+)	$FePO_4.2H_2O \leftrightarrow 2\ H_2O + Fe^{(3+)} + PO_4^{(3-)}$	26.4
Mercure	(1+)	$Hg_2HPO_4 \leftrightarrow H^{(+)} + Hg_2^{(2+)} + PO_4^{(3-)}$	24.8
Plomb	(2+)	$Pb_3(PO_4)_2 \leftrightarrow 3\ Pb^{(2+)} + 2\ PO_4^{(3-)}$	43.5
	(2+)	$PbHPO_4 \leftrightarrow H^{(+)} + Pb^{(2+)} + PO_4^{(3-)}$	23.8
Magnésium	(2+)	$Mg_3(PO_4)_2 \leftrightarrow 3\ Mg^{(2+)} + 2\ PO_4^{(3-)}$	23.3
	(2+)	$MgHPO_4.3H_2O \leftrightarrow 3\ H_2O + H^{(+)} + Mg^{(2+)} + PO_4^{(3-)}$	18.2
Manganèse	(2+)	$Mg_3(PO_4)_2 \leftrightarrow 3\ Mg^{(2+)} + 2\ PO_4^{(3-)}$	23.8
	(2+)	$MnHPO_4 \leftrightarrow H^{(+)} + Mn^{(2+)} + PO_4^{(3-)}$	25.4
Nickel	(2+)	$Ni_3(PO_4)_2 \leftrightarrow 3\ Ni^{(2+)} + 2\ PO_4^{(3-)}$	31.3
Argent	(1+)	$Ag_3PO_4 \leftrightarrow 3\ Ag^{(+)} + PO_4^{(3-)}$	17.6
Zinc	(2+)	$Zn_3(PO_4)_2 \leftrightarrow 3\ Zn^{(2+)} + 2\ PO_4^{(3-)}$	35.4
	(2+)	$Zn_3(PO_4)_2.4H_2O \leftrightarrow 4\ H_2O + 2\ PO_4^{(3-)} + 3\ Zn^{(2+)}$	35.4

1.2.5 Agents sélectifs de précipitation

Plusieurs agents sélectifs de précipitation ont été développés au cours de ces dernières années pour la récupération des métaux divalents et monovalents contenus dans les effluents. Les agents de chélation les plus étudiés actuellement sont les dithiocarbamates (DTC) et leurs dérivées, lesquels ont été bien décrits par plusieurs auteurs (Andrus 2000; Fu *et al.* 2006; Matlock *et al.* 2002). Les agents de chélation se divisent en deux catégories : les macromolécules et les petites molécules.

La première catégorie inclut les xanthates (Chang *et al.* 2002), dichloro-éthylène dithiocarbamate d'ammonium polymérisé ou polydialkylaminedithiocarbamates.

Les petits agents moléculaires sont commercialisés sous deux formes, le diéthyldithiocarbamate (DDTC, $(C_2H_5)_2NCS_2Na.3H_2O$) (Andrus 2000) et le diméthyldithiocarbamate (DMTC, $(CH_3)_2NCS_2Na.2H_2O$) (Andrus 2000; Fu *et al.* 2006). Un des plus connus est le 2,4,6-trimercapto-1,3,5-triazine (TMT) ($Na_3S_3C_3N_3.9H_2O$) fabriqué par Degussa (Matlock *et al.* 2001). Cet agent précipitant réagit avec les ions divalents selon l'Équation 1.5 :

Équation 1.5 $$2\ (S_3C_3N_3)^{3-} + 3\ M^{2+} \rightarrow M_3(S_3C_3N_3)_2\downarrow$$

Cet agent de chélation peut être utilisé pour précipiter les ions comme Ag(+), Cd(2+), Hg(+), Hg(2+), Tl(+), Pb(2+) et Zn(2+) contenus dans les effluents industriels et les eaux naturelles contaminées (Henke *et al.* 2001).

Un autre agent spécifique de précipitation des métaux divalents est le Thio-Red®, qui est synthétisé par ETUS Inc. Cet agent de précipitation contient du thiocarbamate de potassium ou de sodium (TCS) ($[Na,K]_2CS_3.nH_2O$) (Henke 1998; Matlock *et al.* 2002).

Les précipités de thiocarbamates métalliques (MCS_3, où M = Cd(2+), Cu(2+), Ni(2+), Pb(2+), Zn(2+) et autres ions métalliques divalents), se forment conformément à l'Équation 1.6:

Équation 1.6 $CS_3^{2-} + M^{2+} \rightarrow MCS_3\downarrow$

Récemment, un procédé de précipitation par polymérisation a été proposé par Fu *et al.* (2006, 2007). Cette approche consiste à l'utilisation de deux groupements dithiocarboxyliques ayant des caractéristiques de chélation. Il s'agit du disodium N,N'-bis-(dithiocarboxy)piperazine (Na_2BDP) ($(CH_2)_4(NCS_2Na)_2.6H_2O$), qui sert essentiellement à précipiter le cuivre et le nickel en solution.

Le dipropyl dithiophosphate a été proposé par Ying et Fang (2006) comme un autre agent potentiel de précipitation des métaux. L'équation de la réaction de cette molécule (ex. dipropyl dithiophosphate de potassium (DDP)) avec les métaux lourds comme le plomb, le cadmium, le mercure et le cuivre est la suivante :

Équation 1.7 $2\ C_6H_{14}O_2PS_2K + M^{2+} \rightarrow C_{12}H_{28}O_4P_2S_4M\downarrow + 2\ K^+$

Les principaux avantages de l'utilisation de ces agents sélectifs de précipitation sont : 1) la formation d'un précipité métallique ayant une très faible valeur de solubilité. 2) une production de résidu métallique inférieure à celle produite lors de l'utilisation des agents de précipitation usuels comme l'hydroxyde de sodium ou la chaux. Cependant, le coût élevé de ces réactifs empêche leur utilisation fréquente pour des applications industrielles (Meunier *et al.* 2002).

1.2.6 Oxydation et réduction des métaux

Les techniques d'oxydation et de réduction peuvent également être utilisées pour la décontamination et la diminution de la mobilité des métaux contenus dans les eaux souterraines (Evanko et Dzombak 1997). Le permanganate de potassium, le peroxyde d'hydrogène, l'hypochlorite ou le chlore gazeux peuvent être utilisés pour déclencher des réactions d'oxydation, alors que les réactions de réduction sont induites suite à l'ajout de métaux alcalins comme le sodium, le dioxyde de soufre, les sulfites et le sulfate ferreux (Vanbroekhoven *et al.* 2005). L'oxydation est une approche utilisée notamment pour l'élimination de l'arsenic, puisque la forme oxydée (As^{5+}) est moins soluble et mobile que la forme réduite et trivalente (As^{3+}) (Jiang 2001; Liest *et al.* 2000). La forme pentavalente (As^{5+}) peut notamment être précipitée par formation d'arséniate ferrique (Williams et Silver 1984). Inversement, le chrome hexavalent (Cr^{6+}) doit souvent être réduit dans sa forme trivalente (Cr^{3+}) pour être aisément précipité sous formes d'hydroxydes ou d'autres phases solides (Avudainayagam *et al.* 2003; Sulzbacher *et al.* 1997).

1.2.7 Bioprécipitation

Les effluents possédant une contamination inorganique peuvent être traités par voie biologique, où les métaux sont précipités sous l'action des microorganismes (Moller *et al.* 2004). Cette voie de dépollution inclut les systèmes passifs de marécages artificiels (Maine *et al.* 2006; VanRoy *et al.* 2006), ou les réacteurs biologiques contenant des microorganismes réducteurs de sulfates

(Barnes *et al.* 1994; Kaksonen *et al.* 2003; Mack *et al.* 2004; White *et al.* 1998; Wildeman *et al.* 1995).

La technologie des marécages artificiels a été très utilisée fréquemment au cours de ces dernières décennies pour le traitement des DMA (Sheoran et Sheoran 2006; USEPA 1993).

1.2.8 Procédés hybrides

Des agents de coagulation comme les sels d'aluminium et de fer ferrique sont souvent ajoutés pour favoriser la séparation S/L (Duan et Gregory 2003; Licskó 1997). Pour augmenter la taille des flocs, la coagulation est suivie d'une floculation des particules instables (Semerjian et Ayoub 2003). Des polymères organiques qui sont synthétisés à partir du polyacrylamide modifié sont souvent utilisés pour cette étape de floculation (Chang 1995; Charerntanyarak 1999; Viadero *et al.* 2006). Des polymères cationiques à base de fer et d'aluminium sont également utilisés et sont disponibles sur le marché (Andrus 2000). Les polymères cationiques comme le polyethyleneimine (PEI) et des polymères anioniques comme son dérivé phosphonomethylé (PPEI), peuvent être employés pour la précipitation et la récupération des métaux lourds (Navarro *et al.* 2005). Le PEI est également utilisé comme un complexant pour les métaux pour améliorer l'étape de l'ultrafiltration (Geckeler et Volchek 1996).

Finalement, les techniques de précipitation peuvent être couplées à des procédés d'adsorption (Naeem *et al.* 2003; Nielsen *et al.* 1997), membranaires (DiPalma *et al.* 2003) et échangeurs d'ions (Papadopoulos *et al.* 2004), pour améliorer l'efficacité du procédé dans l'élimination des métaux des effluents contaminés.

1.3 Modélisation informatique des équilibres chimiques

De nombreux programmes informatiques ont été développés pour prédire la spéciation des métaux dans les eaux naturelles, les lixiviats de sol, les solutions synthétiques et les effluents industriels (Baltpurvins 1996b; Chaston *et al.* 1996; Del Piero *et al.* 2006; Suarez et Goldberg 1994). Une liste des différents programmes informatiques de spéciation des métaux est donnée au Tableau 1.6. Ces modèles peuvent être utilisés pour obtenir de bonnes approximations de la concentration résiduelle des ions libres, des formes complexes ainsi que les masses de solides formés lors de différents scénarios de précipitation ou de lixiviation (Accornero *et al.* 2005; Apul *et al.* 2005; Gomez del Rio *et al.* 2006; Ettler *et al.* 2006; Halim *et al.* 2005). La majorité de ces modèles thermodynamiques d'équilibre chimique sont malheureusement conçus à des fins spécifiques (Mattigod 1995). Les connaissances sur les caractéristiques de déshydratation des précipités métalliques issues de l'expérimentation doivent être couplées aux modèles de spéciation chimique pour espèrer avoir une bonne évaluation de la performance technico-économique lors du traitement des effluents métalliques par les divers techniques de précipitation (Djedidi *et al.* 2009 a,b).

Tableau 1.6 Programmes informatisés de spéciation des métaux

Programmes	Références	Sites Web
AQUACHEM	Korfali et Davies (2004)	http://www.flowpath.com/software/aquachem/aquachem_ov.htm
CHEAQS/GECHEQ	Romero et Joensson (2005)	http://home.tiscali.nl/cheaqs/
CHEMEQL	Müller (1996)	http://www.eawag.ch/research/surf/forschung/chemeql.html
JCHESS/CHESS	Van der Lee et De Windt (2000)	http://chess.ensmp.fr/
CSMC	Tauler et Casassas (1988)	
EQ3/6	Wolery (1992); Wolery et Daveler (1992)	http://www.llnl.gov/IPandC/technology/software/softwaretitles/eq36.php
ESTA	May *et al.* (1985)	
FITEQL	Westall (1982)	http://www.lwr.kth.se/forskningsprojekt/MoW/fiteql.htm
GEOCHEM	Sposito et Matigod (1977, 1980)	
HYDRAQL	Papelis *et al.* (1988)	
HYPHEN	Gans *et al.* (1996)	
HYSS	Alderighi *et al.* (1999)	http://www.chim1.unifi.it/group/vacsab/hyss.htm
IONPAIR	Tharilkill (1970)	
JESS	May et Murray (1991a,b)	http://jess.murdoch.edu.au/jess/jess_home.htm
MICROQL	Westall (1979)	http://www.polyql.ethz.ch/
MINEQL+	Westall *et al.* (1976)	http://www.mineql.com/
MINTEQ/ MINTEQA2/ PRODEFA2	Allison *et al.* (1991); Felmy *et al.* (1984); HydroGeoLogic (1998a,b)	http://epa.gov/ceampubl/mmedia/minteq/index.htm
VISUAL MINTEQ	Romero et Joensson (2005)	http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm
NETPATH	Plummer *et al.* (1991, 1994)	http://water.usgs.gov/software/netpath.html
PHREEQC	Parkhurst et Appelo (1999)	http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
PHREEQE	Parkhurst *et al.* (1980)	http://www.nea.fr/abs/html/nesc9674.html
PHRQPITZ	Plummer *et al.* (1988)	http://water.usgs.gov/software/phrqpitz.html
RAMASES	Leung et Darvell (1990)	
REDEQL2	McDuff et Morel (1973)	
SOILCHEM	Sposito et Coves (1988)	http://www.cnr.berkeley.edu/~ayang/soilchem.html
SOLMNEQ.88/ SOLMNEQ	Kharaka et Barnes (1973); Kharaka *et al.* (1988); Savage (1986)	
SPECIES	Barak (1990)	http://www.soils.wisc.edu/~barak/species.htm
TRANSPEC	Bhavsar *et al.* (2004)	
WHAM/MODEL VI	Meers *et al.* (2006); Tipping (1998)	http://windermere.ceh.ac.uk/aquatic_processes/wham/index.html
WATEQ4F/WATEQ	Ball (1987, 2002); Truesdell et Jones (1974)	http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/software.htm
WINHUMIC V	Romero et Joensson (2005)	http://www.lwr.kth.se/english/OurSoftware/WinHumicV/index.htm

1.4 Hypothèses de travail et objectifs de recherche

1.4.1 Hypothèses et objectif principal

Les hypothèses de recherche ont été établies à partir de l'analyse de la documentation scientifique spécifique au projet de recherche. Le traitement des effluents industriels acides chargés en métaux par les techniques de précipitation génèrent habituellement des quantités considérables de résidus, ou boues métalliques, lesquels sont souvent considérés comme étant des déchets dangereux. Les coûts de traitement de ces effluents et de disposition des boues métalliques peuvent être importants. Or, à l'heure actuelle, il n'existe pas d'outils permettant de prédire quel serait le réactif de précipitation le plus performant sur le plan technico-économique, tenant compte des caractéristiques des effluents, des normes à atteindre, des coûts de disposition des boues métalliques, etc. L'hypothèse sous jacente à ce projet et, par conséquent, l'objectif central de celui-ci réside dans la possibilité de *développer un modèle prédictif permettant de définir les conditions optimales de précipitation des métaux, pour minimiser les coûts de traitement des effluents et de disposition des boues métalliques, tout en respectant les normes à satisfaire en ce qui concerne la qualité des effluents*.

1.4.2 Objectifs spécifiques de recherche

Les objectifs spécifiques ciblés pour l'atteinte de l'objectif principal peuvent être définis de la manière suivante :

1. Mettre au point, à partir d'expérimentations au laboratoire, une base de données concernant la production de boues métalliques suite au traitement de diverses solutions monométalliques acides et ce, par précipitation pour former des hydroxydes, des phosphates, des sulfures ou des carbonates métalliques;

2. Étudier les caractéristiques de déshydratation des précipités monométalliques et ce, par décantation (IVB, ST), filtration sous pression (RSF, CF, ST) et par centrifugation (ST);
3. Étudier l'effet de la matrice (Cl^- versus SO_4^{-2}) en terme de concentrations résiduelles en métaux suite au traitement de solutions multimétalliques par les diverses méthodes de précipitation (hydroxydes, phosphates, sulfures ou carbonates) et comparaison par rapport aux résultats de simulations du logiciel de spéciation *MINEQL+*;
4. Étudier l'effet de la matrice (Cl^- versus SO_4^{-2}) sur les propriétés de déshydratation mécaniques des boues métalliques générées à la suite du traitement des solutions multimétalliques par les différentes techniques de précipitation;
5. Évaluer les caractéristiques de déshydratation des boues issues du traitement par les méthodes de précipitation de deux compositions synthétiques de DMA;
6. Évaluer les taux d'élimination des métaux par les méthodes de précipitation et ce, pour trois types d'effluents réels : lixiviat de sol, lixiviat de cendres volantes et lixiviat des boues de stations d'épuration;
7. Étudier les caractéristiques de déshydratation des boues métalliques issues du traitement par précipitation de ces trois effluents réels;
8. Développer un modèle informatique sur *Microsoft EXCEL* permettant de prédire lors du traitement des effluents par précipitation :
    i. La spéciation des métaux et des éléments en solution;
    ii. Les concentrations résiduelles en cations et anions après traitement et comparaison par rapport aux normes de rejets fixés par une législation donnée;
    iii. Le volume généré des boues humides et ce, après une séparation S/L mécanique;

   iv. Les coûts totaux de traitement suivant un schéma de procédé conventionnel de traitement des effluents métalliques par précipitation.

9 Intégrer les connaissances sur les caractéristiques des boues métalliques issues à partir des expérimentations dans la base de données du progiciel *PITEM*;

10 Valider le modèle à l'aide des connaissances sur les caractéristiques de déshydratation des boues issues de solutions multimétalliques synthétiques et du lixiviat de sol.

1.5 Démarche méthodologique

La réalisation de ce projet de recherche a exigé la réalisation de travaux expérimentaux, ainsi que des travaux de modélisation et de simulation informatique. La présente section décrit succinctement la nature des travaux associés à l'atteinte de chacun des objectifs spécifiques du projet.

Plusieurs séries d'essais de précipitation de métaux ont été effectuées au laboratoire. Ces tests ont été d'abord effectués sur des solutions synthétiques acides préparées à l'aide d'acide inorganique (ajustement du pH à 2.0) et contenant un métal (Fe^{II}, Fe^{III}, Al^{III}, Cu^{II}, Ni^{II}, Zn^{II}, Cr^{III}, Cd^{II}, Mn^{II}, ect). Lors des tests de précipitation, des volumes de 1.5 L de solution ont été traités par addition d'agents précipitants (NaOH, KH_2PO_4/NaOH, NaOH/Na_2S ou NaOH/$NaHCO_3$) et l'atteinte de différents pH finaux déterminés par les simulations faites à l'aide du logiciel *MINEQL+* (version 4.5) qui sont 10.0, 6.0, 8.0 et 7.0, respectivement pour les hydroxydes, les phosphates, les carbonates et les sulfures.

Deux séries d'essais de précipitation en solutions multimétalliques ont été réalisés, la première en utilisant une matrice de sulfate (utilisation d'acide sulfurique et de sels de sulfate) et la seconde en employant une matrice de chlorure (utilisation d'acide chlorhydrique et de sels de chlorure). De même, lors de ces essais, les tests ont été effectués en utilisant la chaux ou l'hydroxyde de sodium comme base pour former des hydroxydes et Na_2HPO_4, Na_2S ou $NaHCO_3$ pour former respectivement des phosphates, des sulfures ou des carbonates.

Une fois ces essais complétés, des expériences ont été conduites dans des conditions semblables avec deux compositions typiques de DMA (DMA1 et DMA2), ainsi qu'avec des effluents réels issus de la décontamination d’un sol pollué par les métaux, de cendres volantes et de boues d’épuration municipales.

1.5.1 Caractérisation des boues métalliques

Cette partie du projet a consisté à caractériser les boues métalliques produites suite au traitement de plusieurs types d’effluents dans différentes conditions opératoires. La caractérisation des boues implique l’étude de la décantation des flocs générés évaluée par le paramètre IVB (Indice du Volume de Boue), le comportement vis-à-vis d’une filtration sous pression exprimé en termes de %ST (Pourcentage de solides totaux) de la boue filtrée, de RSF (Résistance Spécifique à la Filtration) et CF (Capacité de Filtration). Le comportement des boues vis-à-vis de la centrifugation a été également étudié en considérant le paramètre %ST (p/p) du gâteau de la centrifugation.

1.5.2 Conception du modèle informatisé et intégration des connaissances sur les boues

Cette étape a consisté à développer un modèle informatique portant l’acronyme *PITEM* (Programme Informatisé de Traitement d’Effluents Métalliques). Il s’agit d’un progiciel fonctionnant sous le logiciel *Microsoft EXCEL* et permettant de prédire l’efficacité et l’économique d’un procédé de traitement par précipitation d’effluents métalliques. Il est composé essentiellement de deux modules de calcul connexes qui sont :

1. le module de spéciation chimique;
2. et le module de l’estimation de la production de boues et de calcul économique.

Les connaissances issues des travaux sur la caractérisation des boues monométalliques ont été intégrées dans le modèle informatisé. *PITEM* est amené à pouvoir prédire le comportement des procédés de traitement des effluents par précipitation en termes de production de boues métalliques, de consommation de réactifs chimiques et de qualité des effluents et ce, en fonction de la composition initiale des effluents, du réactif de précipitation utilisé, ainsi que des pH initial et final.

1.5.3 Validation expérimentale du modèle

Une fois les travaux de modélisation complétés, des essais de validation du modèle ont été exécutés par une série d'essais de traitement de solutions multimétalliques synthétiques et d'effluents industriels et de décontamination de matrices polluées par les métaux à savoir des lixiviats de sol contaminé, de cendres d'incinérateur et de boue de station d'épuration. Les résultats de ces essais ont été comparés aux résultats de simulation effectués en parallèle aux travaux expérimentaux de laboratoire.

1.6 Discussion et intégration des résultats

1.6.1 Étude comparative des caractéristiques de déshydratation des boues générées au cours du traitement par précipitation des solutions monométalliques

L'objectif de la première partie du projet est de développer les connaissances de base sur les propriétés de déshydratation des boues (décantation, filtration sous pression et centrifugation) issues de traitement de solutions monométalliques par précipitation sous formes d'hydroxydes, de phosphates, de sulfures ou de carbonates.

Dans le but de définir les pH de précipitation, des simulations avec le logiciel *MINEQL+* (version 4.5) ont été effectuées pour les quatre systèmes suivants : les hydroxydes (Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Al^{3+}, Pb^{2+} et Sn^{2+}), les sulfures (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+} et Zn^{2+}), les phosphates (Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Al^{3+}, Pb^{2+} et Sn^{2+}) et les carbonates (Ba^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} et Zn^{2+}). Toutes ces simulations ont été établies pour une matrice de chlorures, excepté pour le plomb où l'anion utilisé est le nitrate et ce, pour des considérations de solubilité.

Les tests de précipitation ont été effectués à température ambiante ($22 \pm 2^{o}C$) avec des volumes de 1.5 L pour chaque solution monométallique ayant une concentration de 2.0×10^{-3} mol/L et soumise à une agitation de 160 rpm. Un temps de 15 min a été jugé suffisant pour chaque essai de précipitation afin que le système atteigne l'équilibre (Hove *et al.* 2008).

Les essais de précipitation ont été effectués avec les quatre agents de précipitation suivants :

- L'hydroxyde de sodium NaOH (solution mère);
- Le sulfure de sodium (Na_2S) à des quantités stœchiométriques;

- Le monopotassium de phosphate (KH_2PO_4) à des quantités stœchiométriques;
- Le bicarbonate de sodium ($NaHCO_3$) à des quantités stœchiométriques.

Les essais de précipitation sous forme d'hydroxydes ont été réalisés en ajustant le pH de travail à 10.0 pour tous les métaux par ajout de l'hydroxyde de sodium. Cependant, pour l'aluminium, le magnésium et le calcium, les pH de précipitation ont été ajustés respectivement à 7.5, 12.0 et 12.5.

Pendant les autres essais de traitement, les agents de précipitation ont été tout d'abord ajoutés aux solutions monométalliques suivis d'un ajustement de pH à 6.0, 8.0 et 7.0 à l'aide de NaOH respectivement pour les phosphates, les carbonates et les sulfures. Il est à noter que dans le cas des carbonates et les sulfures, un premier ajustement de pH a été fait à 5.5 dans le but d'éviter le dégagement respectif de CO_2 et de H_2S (Baltpurvins *et al.* 1996a,b; Charerntanyarak 1999; Feng *et al.* 2000).

Les valeurs de pH 10.0, 6.0, 8.0 et 7.0 de précipitation des métaux sous forme d'hydroxydes, de phosphates, de carbonates et de sulfures ont été déduites des résultats des simulations avec *MINEQL+* (version 4.5).

Une fois le temps de précipitation écoulé, la suspension formée a été décantée dans un cylindre de 2 L de capacité. Le volume de la suspension décantée a été noté après 30 min pour le paramètre IVB, qui est le volume en millilitres occupé par gramme de suspension après 30 min de décantation.

Par comparaison entre les valeurs de IVB pour six métaux (Cd^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+} et Zn^{2+}), l'ordre ascendant suivant a été obtenu pour les différents types de flocs formés : Sulfures < Phosphates < Hydroxydes < Carbonates. Cette même tendance a été confirmée dans les travaux de Lewis et Swartbooi (2006) quand ils ont constaté que les suspensions de sulfures décantent plus rapidement que celles des hydroxydes et des carbonates.

De la même manière, un ordre ascendant a été défini en comparant les valeurs d'IVB pour les différents métaux : $Pb^{2+} < Ca^{2+} = Cu^{2+} \leq Ba^{2+} < Zn^{2+} = Fe^{3+} < Cr^{3+} = Sn^{2+} = Mn^{2+} < Ni^{2+} \leq Co^{2+} < Al^{3+} < Fe^{2+} < Cd^{2+} < Mg^{2+}$.

La résistance spécifique à la filtration (RSF), la capacité de filtration (CF), ainsi que la concentration finale en solides du gâteau (%ST) ont été utilisées pour évaluer les caractéristiques de déshydratation des boues (séparation S/L) issues des divers types de traitement.

L'expression mathématique de RSF est donnée par la formule suivante (Viadero *et al.* 2006):

Équation 1.8 $$RSF = \frac{2bPA^2}{\mu.c}$$

Où « b » est la pente de la droite V = f (t/V), « V » est le volume du filtrat à l'instant « t », « P » est la pression, « A » est la surface du filtre, « µ » est la viscosité cinématique du filtrat, « c » est le poids du solide par unité de volume du filtrat.

Équation 1.9 $$c = \frac{1}{C_i/(100 - C_i) - C_f/(100 - C_f)}$$

Avec "C_i" est le contenu initial en eau, "C_f" est le contenu final en eau.

La viscosité cinématique a été mesurée par un viscosimètre programmable type Brookfield DV-II+Pro avec une vitesse du pendule égale à 60 tours/min.

Quelques propriétés de déshydratation des boues monométalliques sont données dans les Tableaux 1.7 à 1.10. Les flocs d'hydroxydes de métaux ont généralement de faibles capacités de filtration (CF), excepté pour le plomb avec une valeur de 22.8 kg/(m^2.h) (Tableau 1.7). De même pour les sulfures (Tableau 1.8), seules le cuivre et le cobalt montrent de bonnes capacités de filtration avec respectivement des CF de 5.3 et 5.6 kg/(m^2.h). Les suspensions de carbonates ont des capacités de filtration élevées pour le plomb, le cadmium, le baryum et le manganèse avec des valeurs respectives de 26.0, 11.7, 10.2 et 8.1 kg/(m^2.h) (Tableau 1.9). Les phosphates ont montré des capacités de filtration les plus élevées pour cinq des métaux étudiés qui sont Ba^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+} et Zn^{2+} et possédant des capacités variant entre 34 et 65 kg/(m^2.h) (Tableau 1.10).

Par comparaison des différentes valeurs des capacités de filtration pour Cd^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+} et Zn^{2+}, un ordre descendant a été établi pour ces métaux : Phosphates > Carbonates > Hydroxydes = Sulphides.

En termes de RSF, une relation directe a été constatée entre ce paramètre et la CF. En effet, lorsque les boues possèdent des capacités de filtration élevées, elles ne présentent pratiquement aucune résistance à la filtration, ou elles ont de très faibles RSF. Les valeurs de RSF mesurées pour les hydroxydes de nickel, de chrome et de cuivre, respectivement de 7.36×10^{13}, 9.9×10^{12} m/kg et 15.2×10^{11} m/kg sont dans le même ordre de grandeur des RSF déterminés dans les travaux de Knocke *et al.* (1980), variant de 8 à 200×10^{11} m/kg, 5 à 50×10^{11} m/kg et 5 à 30×10^{11} m/kg, respectivement pour les hydroxydes de cuivre, de chrome et de nickel.

En termes de ST des boues après filtration, il a été constaté que les valeurs les plus élevées correspondent aux hydroxydes de calcium, de cuivre, de fer (II), de magnésium et d'étain, aux phosphates d'aluminium, de barium, de chrome(III), de fer(III), de nickel et de zinc, et aux carbonates de cadmium, de manganèse et de plomb. Les valeurs de ST les plus faibles (4 et 8% p/p) ont été obtenues avec les précipités $Al(OH)_3$ et $Fe(OH)_3$. D'une façon générale (indépendamment du type de précipité formé), un ordre descendant pour les ST des boues a été établi pour les différents métaux étudiés : $Ba^{2+} > Pb^{2+} > Mg^{2+} > Cd^{2+} > Sn^{2+} = Cr^{3+} = Mn^{2+} > Zn^{2+} = Cu^{2+} > Ca^{2+} > Fe^{2+} = Ni^{2+} > Co^{2+} > Fe^{3+} = Al^{3+}$.

Les valeurs de ST des précipités métalliques obtenues à la suite d'une centrifugation à 3000 × g pendant 15 min à l'aide d'une centrifugeuse du type Beckman Coulter Allegra^{TM} 6 Centrifuge, sont données dans les Tableaux 1.7 à 1.10. Les résultats expérimentaux montrent que la centrifugation est beaucoup moins efficace que la filtration sous pression à éliminer l'eau des flocs métalliques.

De manière similaire à la filtration, les valeurs de ST mesurées après centrifugation pour chaque précipité varient dans une large plage (de 0.1 à 45.1% (p/p)). Par exemples, des valeurs de ST de 9.0 et 4.0% (p/p) ont été mesurées respectivement pour $Cd(OH)_2$ et $MnHPO_4$, contre 41.0 et 31.0% (p/p) atteints respectivement pour $CdCO_3$ et $MnCO_3$. L'ordre suivant peut être proposé par comparaison des valeurs de ST mesurées pour les différents métaux : $Al^{3+} \leq Fe^{3+} \leq Zn^{2+} \leq Co^{2+} \leq Mg^{2+} \leq Ni^{2+} \leq Ca^{2+} \leq Fe^{2+} < Cu^{2+} \leq Cr^{3+} \leq Mn^{2+} < Sn^{2+} < Cd^{2+} < Ba^{2+} < Pb^{2+}$.

Tableau 1.7 **Caractéristiques de déshydratation des boues métalliques associées au traitement des solutions monométalliques utilisant NaOH comme agent précipitant**

Métaux	Décantation	Filtration					Centrifugation
	IVB (mL/g)	Temps (min)	ST (% p/p)	Boues (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Chlorures							
Al^{3+}	25.1	377	4.2	37.6	0.15	87.7	2.4
Ca^{2+}	19.0	10.3	34.5	2.19	14.67	-	12.3
Cd^{2+}	55.1	56.0	22.7	16.0	2.58	4.31	9.0
Co^{2+}	69.7	260	24.0	7.74	0.27	34.4	8.9
Cr^{3+}	48.3	44.0	24.7	8.34	2.15	9.90	10.7
Cu^{2+}	33.7	67.0	23.4	7.92	1.28	3.01	19.9
Fe^{2+}	92.8	177	25.6	6.44	0.37	34.6	14.1
Fe^{3+}	10.7	126	8.0	24.6	0.60	25.6	4.8
Mg^{2+}	1100	40.0	64.6	0.76	1.41	27.8	9.4
Mn^{2+}	32.6	40.0	30.4	4.84	1.57	5.16	12.6
Ni^{2+}	48.1	413	12.3	15.3	0.18	73.6	5.4
Pb^{2+}	6.0	3.4	51.4	8.88	74.66	-	34.0
Sn^{2+}	39.7	162	37.6	6.96	0.69	19.1	28.0
Zn^{2+}	13.4	21.0	8.7	20.6	3.27	3.46	0.1
Sulfates							
Al^{3+}	29.8	111	6.8	30.3	0.72	22.1	2.9
Co^{2+}	65.9	150	14.9	13.6	0.55	27.2	5.7
Cu^{2+}	30.3	51	26.2	8.88	1.63	8.86	10.7
Fe^{3+}	34.7	338	11.5	25.0	0.36	42.0	5.9
Ni^{2+}	46.2	374	9.5	20.1	0.20	69.6	4.0
Zn^{2+}	42.2	42	10.7	21.5	2.20	5.99	2.8

Tableau 1.8 Caractéristiques de déshydratation des boues métalliques associées au traitement des solutions monométalliques (dans une matrice chlorures) utilisant Na_2S comme agent de précipitation

Métaux	Décantation	Filtration					Centrifugation
	IVB (mL/g)	Temps (min)	ST (% p/p)	Boues (kg/m^3)	CF (kg/(m^2.h))	RSF (m/kg × 10^{12})	ST (% p/p)
Cd^{2+}	8.9	63	14.1	22.5	1.82	7.87	9.2
Co^{2+}	5.3	5.0	8.8	27.5	16.43	0.28	6.3
Cu^{2+}	8.0	5.5	16.6	13.4	15.64	0.18	13.9
Fe^{2+}	38.0	168	13.7	12.6	0.41	27.1	6.6
Fe^{3+}	33.5	552	15.0	17.9	0.11	67.5	7.3
Mn^{2+}	30.5	15	30.9	5.9	3.66	2.73	11.2
Ni^{2+}	11.3	24	17.1	13.0	3.38	4.06	9.5
Pb^{2+}	6.9	20	26.5	18.4	8.36	1.40	20.8
Sn^{2+}	17.2	74	30.0	11.3	1.58	9.41	12.9
Zn^{2+}	23.4	159	18.6	11.3	0.55	24.6	7.5

Tableau 1.9 **Caractéristiques de déshydratation des boues métalliques associées au traitement des solutions monométalliques (dans une matrice chlorures) utilisant KH_2PO_4 comme agent de précipitation**

Métaux	Décantation	Filtration					Centrifugation
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Al^{3+}	62.6	69	15.1	15.6	2.25	8.81	6.1
Ba^{2+}	4.1	0.9	88.6	4.84	238.19	-	31.7
Ca^{2+}	12.1	54	8.9	27.6	2.66	-	4.0
Cd^{2+}	62.0	1.5	51.2	9.07	156.45	-	34.4
Co^{2+}	32.1	23	14.3	19.0	6.86	2.57	7.3
Cr^{3+}	7.6	1.5	42.5	8.23	121.6	-	17.1
Cu^{2+}	7.8	11	9.0	40.8	15.04	0.52	5.0
Fe^{2+}	15.9	29	21.2	14.6	5.60	2.67	8.3
Fe^{3+}	30.7	214	12.3	31.2	0.70	21.5	5.8
Mg^{2+}	86.8	88	19.5	10.2	1.52	10.6	4.3
Mn^{2+}	51.7	48	15.0	17.5	3.06	4.57	3.6
Ni^{2+}	42.5	42	24.8	7.51	3.09	6.42	7.3
Pb^{2+}	7.2	2.0	43.9	13.8	131.18	-	16.2
Zn^{2+}	33.9	1.3	58.4	4.71	127.24	-	10.5

Tableau 1.10 Caractéristiques de déshydratation des boues métalliques associées au traitement des solutions monométalliques (dans une matrice chlorures) utilisant $NaHCO_3$ comme agent de précipitation

Métaux	Décantation	Filtration					Centrifugation
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Ba^{2+}	34.4	4.1	62.2	5.99	31.59	-	20.2
Cd^{2+}	176	3.5	70.6	5.61	36.90	0.05	40.9
Co^{2+}	44.3	229	11.1	19.0	0.35	52.0	4.4
Fe^{2+}	52.1	136	13.0	13.6	0.48	29.5	5.7
Mn^{2+}	3.6	3.3	57.9	3.71	23.81	-	30.7
Ni^{2+}	44.2	40	19.0	11.9	3.01	4.16	6.7
Pb^{2+}	7.6	2.3	76.4	6.89	93.27	-	45.1
Zn^{2+}	21.6	139	17.6	12.0	0.59	23.0	5.3

1.6.2 Étude comparative des caractéristiques de déshydratation des boues générées au cours du traitement par précipitation des solutions multimétalliques et des DMA

Le but de cette partie du projet est d'illustrer l'effet de la matrice (Cl^- versus SO_4^{2-}) sur les concentrations métalliques résiduelles et les caractéristiques de déshydratation des boues générées et ce, à la suite du traitement de solutions multimétalliques synthétiques par précipitation en formant des hydroxydes, des sulfures, des phosphates et des carbonates métalliques. Ces mêmes paramètres ont été également étudiés dans le cas des boues issues de deux compositions types de DMA.

Quatre solutions multimétalliques à pH acides égale à 2.0 (acidification par H_2SO_4 ou HCl) ont été préparées ayant des concentrations égales $[M^{n+}]$ de 4.0×10^{-3} mol/L en chaque métal :

- **Sln A**: contient Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} et Ni^{2+} dans une matrice chlorure ;
- **Sln B**: contient Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} et Ni^{2+} dans une matrice sulfate ;
- **Sln C**: contient Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} et Cd^{2+} dans une matrice chlorure ;
- **Sln D**: contient Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} et Cd^{2+} dans une matrice sulfate.

Deux compositions types de DMA (DMA1 et DMA2) ont été également étudiées.

Les domaines de solubilité ont été calculés à l'aide du logiciel *MINEQL+* (version 4.5) pour les quatre systèmes suivants : hydroxydes et phosphates pour la solution **Sln B (**Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} et Ni^{2+}), sulfures et carbonates pour la solution **Sln D (**Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} et Cd^{2+}). L'anion choisi pour respecter l'électroneutralité de tous les systèmes était les sulfates (SO_4^{2-}), la température a été fixée à 298 °K et le nombre d'itérations était limité à 100. Les domaines de solubilité ont été calculés dans une gamme de pH variant de 2.0 à 14.0 pour les deux systèmes hydroxydes et phosphates et de 5 à 14 pour les carbonates et les sulfures.

Les essais de précipitation ont été réalisés avec les cinq agents de précipitations suivants : 1) Hydroxyde de sodium (2.5 mol NaOH/L); 2) Chaux (20 g $Ca(OH)_2$/L); 3) Sulfure de sodium (Na_2S); 4) Hydrogénophosphate de sodium (Na_2HPO_4); et 5) Hydrogénocarbonate de sodium ($NaHCO_3$).

Une fois l'étape de décantation terminée, une partie de la suspension a été soumise à une filtration sous pression et l'autre partie à une centrifugation, de la même manière que décrit précédemment.

Une bonne corrélation a été observée entre les valeurs expérimentales et celles prédites par *MINEQL+* à pH 10.0 pour tous les métaux contenus dans les différentes solutions synthétiques étudiées. Il est important de noter que les concentrations résiduelles du zinc (3.21×10^{-6} mol/L) et du nickel (3.40×10^{-7} mol/L) sont inférieures à celles prédites par la théorie (4.59×10^{-6} et 1.02×10^{-6} mol/L, respectivement pour le zinc et le nickel). Ceci peut être expliqué par la présence des hydroxydes d'aluminium et de fer. En effet, l'adsorption et/ou la coprécipitation des métaux pourrait se produire sur $Al(OH)_3$ et $Fe(OH)_3$ (Marchioretto *et al.* 2005; Slavek et Pickering 1988).

Le traitement de **Sln A**, **Sln B** ainsi que les deux compositions de DMA (DMA1 et DMA2) par ajout de phosphates à pH 7.0 donne généralement des taux d'élimination des métaux de transition (Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} et Cd^{2+}) supérieures à ceux calculés par le logiciel *MINEQL+*. Aux faibles valeurs de pH (2.5 à 4.0), l'aluminium et le fer (III) précipitent sous forme de phosphate amorphe : $AlPO_4.\times H_2O$ avec $\times$ = 2-3 et $FePO_4.\times H_2O$ avec $\times$ = 1-2 (Mustafa *et al.*

1999) qui sont de bons échangeurs d'ions et peuvent agir comme des matériaux fiables d'adsorption pour les cations métalliques bivalents selon l'Équation 1.10.

Équation 1.10 $\mathbf{nS\text{-}OH + M^{2+}\,(aq) = (S\text{-}O)_nM^{2-n} + nH^{+}\,(aq)}$

avec "S" correspondant à l'échangeur ionique et "M" le métal bivalent.

Les résultats expérimentaux de l'élimination des métaux des solutions **Sln C** et **Sln D** sous forme de carbonates (MCO_3) sont satisfaisants, mais sont légèrement inférieurs à ceux prédits par *MINEQL+*. Ceci peut être expliqué par des considérations cinétiques.

Comme dans le cas des carbonates, le traitement par les sulfures est une précipitation combinée consistant à un ajustement de pH de 2.0 à 5.0 suivie d'un ajout stœchiométrique de Na_2S. Les résultats expérimentaux sont en accord avec les résultats de simulation du logiciel *MINEQL+* dans les mêmes conditions opératoires.

Dans chaque cas d'essai de précipitation, les boues générées sont essentiellement constituées de précipités métalliques hydratés et de sels dissous interstitiels. Cependant, pour les mêmes conditions, l'agent de précipitation utilisé pour l'élimination des ions métalliques des milieux aqueux, a une influence significative sur la séparation S/L des boues produites.

Le traitement de la solution **Sln A** par NaOH à pH 10.0, produit des flocs qui décantent lentement avec un IVB = 428 mL/g (Tableau 1.11). Le traitement de la même solution par ajout de Na_2HPO_4 à pH 7.0 produit des boues qui décantent plus rapidement avec un IVB = 235 mL/g (Tableau 1.12). Dans ces deux modes de traitement, la substitution de la matrice chlorure (**Sln A**) par une matrice sulfate (**Sln B**), améliore la décantation des boues métalliques. Cette amélioration est due d'une part à la nature amorphe des précipités obtenus et à l'augmentation de la force ionique ΔI. Ceci est en accord avec les travaux antérieurs de Dustan *et al.* (2005) et Moghadam *et al.* (2005).

Le traitement de la solution **Sln C** par ajout de Na_2S ou de Na_2CO_3 à pH près de 8.0, génère des boues ayant une bonne décantation avec des IVB = 121 et 37 mL/g respectivement, pour les sulfures et les carbonates (Tableaux 1.13 et 1.14). Dans ces deux cas de traitement, la substitution de la matrice chlorure (**Sln C**) par la matrice sulfate (**Sln D**) n'a pas d'effet significatif sur les caractéristiques de décantation.

Le comportement des boues, dans le cas du traitement des DMA par NaOH ou $Ca(OH)_2$ à pH 10.0 a été également étudié. Les résultats expérimentaux présentés dans le Tableau 1.11 montrent que la substitution de NaOH par $Ca(OH)_2$ fait diminuer la valeur de IVB. Cette diminution est due essentiellement à la formation d'une boue secondaire, le gypse ($CaSO_4.2H_2O$) (Balpurvins *et al.* 1996a,b).

Les résultats expérimentaux (Tableaux 1.11 à 1.14) montrent que les boues générées à partir des matrices sulfates se déshydratent mieux que celles formées dans les matrices chlorures et ce, en termes des valeurs de solides totaux (% ST) des gâteaux obtenues à la suite de la filtration sous pression (Dustan *et al.* 2005).

Le traitement de DMA1 et DMA2 par NaOH a généré des boues avec des valeurs de ST respectives de 19.0 et 21.1% (p/p), correspondant à une production de boues de 12.5 et 15.0 kg/m^3. Dans les mêmes conditions opératoires, la substitution de l'agent précipitant NaOH par $Ca(OH)_2$ pour le traitement des DMA, a généré des boues qui se filtrent mieux; ayant des valeurs de ST plus élevées (près de 30% (p/p), mais correspondant à une plus importante production de boues causée par la formation du gypse) (Tableau 1.11).

En termes de RSF, les boues générées à partir de la matrice sulfate présentent une meilleure filtrabilité par rapport à celles formées à dans la matrice chlorure. Deux tendances ont été établies en termes de RSF pour les deux compositions de DMA:

- DMA 1: phosphates < hydroxydes ($Ca(OH)_2$) < hydroxydes (NaOH) < carbonates < sulfures.
- DMA 2: phosphates < hydroxydes ($Ca(OH)_2$) < carbonates < hydroxydes (NaOH) < sulfures.

Tableau 1.11 Caractéristiques de déshydratation des boues issues du traitement de la solution multimétalliques par NaOH ou $Ca(OH)_2$ à pH 10.0

	Décantation	**Filtration**					**Centrifugation**
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Matrice chlorure (**Sln A**)	428	303	7.4	26.2	0.23	66.0	3.7
Matrice sulfate (**Sln B**)	377	152	11.2	21.6	0.57	23.5	4.4
DMA 1							
NaOH	216	113	19.0	12.5	0.76	6.0	6.5
$Ca(OH)_2$	49	96	30.2	29.5	3.33	3.4	18.9
DMA 2							
NaOH	292	229	21.1	15.0	0.50	14.9	8.2
$Ca(OH)_2$	65	71	31.0	40.8	6.43	2.2	18.7

Tableau 1.12 Caractéristiques de déshydratation des boues issues du traitement de la solution multimétalliques par Na_2HPO_4 à pH 7.0

	Décantation	**Filtration**					**Centrifugation**
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Matrice chlorure (**Sln A**)	235	140	18.5	19.2	0.91	11.0	5.7
Matrice sulfate (**Sln B**)	208	55	16.7	24.5	2.65	2.9	6.9
DMA 1	137	31	21.9	22.7	5.70	1.2	9.3
DMA 2	134	54	16.0	45.0	4.77	2.0	10.6

Tableau 1.13 Caractéristiques de déshydratation des boues issues du traitement de la solution multimétalliques par Na_2CO_3 à pH 8.0

	Décantation	**Filtration**					**Centrifugation**
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Matrice chlorure (**Sln C**)	37	17	19.1	13.0	5.16	1.6	9.8
Matrice sulfate (**Sln D**)	56	13	41.9	5.9	6.73	1.1	17.5
DMA 1	358	128	20.8	11.9	0.70	7.6	7.4
DMA 2	275	64	15.0	23.3	1.95	3.9	6.9

Tableau 1.14 Caractéristiques de déshydratation des boues issues du traitement de la solution multimétalliques par Na_2S à pH 8.0

	Décantation	**Filtration**					**Centrifugation**
	IVB (mL/g)	Temps (min)	ST (% p/p)	PB (kg/m^3)	CF ($kg/(m^2.h)$)	RSF ($m/kg \times 10^{12}$)	ST (% p/p)
Matrice chlorure (**Sln C**)	121	120	16.6	13.9	0.69	10.8	7.1
Matrice sulfate (**Sln D**)	122	115	17.4	13.2	0.72	9.7	7.4
DMA 1	214	260	18.9	16.5	0.43	16.8	7.5
DMA 2	241	308	13.7	29.0	0.47	19.4	6.3

1.6.3 Enlèvement des métaux contenus dans les lixiviats de sol, de cendres volantes d'incinération et de boues de station d'épuration et caractéristiques de déshydratation des boues

Le but de cette partie du projet est d'évaluer l'efficacité de diverses techniques de précipitation des métaux contenus dans trois types de matrices polluées, tels qu'un lixiviat de sol, un lixiviat de cendres volantes et un lixiviat de boues de stations d'épuration. Les caractéristiques de déshydratation des boues générées vis-à-vis des séparations mécaniques S/L, ont été également étudiées.

Des essais de lixiviation en mode batch (cuvée) ont été conduits dans le but de produire des lixiviats de sol, de cendres volantes et de boues de station d'épuration, nécessaires pour les tests de précipitation. La lixiviation des boues de stations d'épuration a été menée selon les conditions optimales définies par Beauchesne *et al.* (2007) qui consistent en l'ajout de 56 kg de Fe^{3+} et 8 kg de H_2O_2 par tonne de boue sèche (tbs), l'acidification étant effectuée par H_2SO_4 pour amener le pH du mélange entre 2.0 et 2.5. Les lixiviats de sol et des cendres volantes ont été obtenus avec des densités de pulpe égale à 10% (p/p) à pH 2.0 (acidification avec HCl).

Deux modes de précipitation ont été étudiés pour les trois lixiviats obtenus à savoir, une précipitation simple [NaOH ou $Ca(OH)_2$ à pH 10.0] et une précipitation combinée [($NaOH+Na_2S$) à pH 7.5, ($NaOH+Na_2CO_3$) à pH 7.5 et (Na_2HPO_4+NaOH) à pH 8.0].

Les résultats expérimentaux ont montré que l'élimination des métaux par simple précipitation à pH 10.0 donne des rendements meilleurs lors de l'ajout de $Ca(OH)_2$ et ce, pour les lixiviats de sol et les cendres d'incinérateur. Dans le cas des précipitations combinées, les taux d'élimination des ions métalliques concordent bien avec ceux prédits par le logiciel *MINEQL+*.

Le traitement par précipitation des trois effluents étudiés par NaOH ou $Ca(OH)_2$, ainsi que la combinaison de NaOH avec Na_2S ou Na_2CO_3 ou Na_2HPO_4, a généré des boues ayant des caractéristiques spécifiques vis-à-vis de la décantation, de la filtration sous pression et de la centrifugation. Le Tableau 1.15 présente quelques caractéristiques de déshydratation des boues produites à partir des trois effluents étudiés.

La déshydratation (filtration sous pression) des boues générées à la suite du traitement du lixiviat de sol a été établie comme suit, en se basant sur les valeurs de RSF : Sulfures (4.3×10^{12} m/kg) < Phosphates (6.4×10^{12} m/kg) < Hydroxydes [$Ca(OH)_2$] (14.2×10^{12} m/kg) < Hydroxydes [NaOH] (19.7×10^{12} m/ kg) < Carbonates (26.5×10^{12} m/kg).

Tableau 1.15 Caractéristiques de déshydratation des boues issues du traitement des trois lixiviats

Lixiviat	Réactifs	Décantation	Filtration				Centrifugation
		IVB (mL/g)	ST (% p/p)	PB (kg/m^3)	CF (kg/m^2.h)	RSF (m/kg ×10^{12})	ST (%p/p)
Sol	NaOH	117 ± 0	18.8 ± 1.0	6.7 ± 0.2	1.6 ± 0.1	19.7 ± 1.3	8.0 ± 0.4
	$Ca(OH)_2$	98 ± 0	25.2 ± 1.4	3.9 ± 0.2	1.1 ± 0.2	14.2 ± 2.5	7.7 ± 0.3
	$NaOH + Na_2S$	72 ± 7	18.4 ± 1.1	5.3 ± 0.1	2.9 ± 0.2	4.3 ± 0.3	8.1 ± 0.4
	$NaOH + Na_2CO_3$	113 ± 4	72.7 ± 3.3	1.8 ± 0.1	0.6 ± 0.0	26.5 ± 4.0	7.6 ± 0.7
	$NaOH + Na_2HPO_4$	132 ± 0	36.7 ± 0.8	3.3 ± 0.2	2.2 ± 0.2	6.4 ± 2.0	6.8 ± 0.3
Cendre	NaOH	39 ± 0	16.3 ± 3.2	56.4 ± 2.2	1.9 ± 0.3	6.2 ± 0.3	10.0 ± 0.0
	$Ca(OH)_2$	50 ± 0	16.4 ± 1.2	46.3 ± 5.4	2.5 ± 0.3	5.0 ± 0.8	9.7 ± 0.3
	$NaOH + Na_2S$	46 ± 0	16.0 ± 0.1	58.6 ± 0.6	1.6 ± 0.2	7.3 ± 0.2	10.4 ± 0.5
	$NaOH + Na_2CO_3$	48 ± 0	17.3 ± 0.1	61.3 ± 1.5	2.0 ± 0.6	5.3 ± 0.2	11.3 ± 1.1
Boue de station d'épuration	NaOH	221 ± 3	15.1 ± 0.5	8.0 ± 0.0	0.6 ± 0.0	23.5 ± 0.4	5.1 ± 0.1
	$Ca(OH)_2$	177 ± 2	16.1 ± 1.4	7.9 ± 0.1	0.7 ± 0.0	19.8 ± 0.5	6.0 ± 0.1
	$NaOH + Na_2S$	391 ± 2	14.3 ± 0.3	6.5 ± 0.1	0.4 ± 0.2	31.7 ± 1.2	7.1 ± 1.8
	$NaOH + Na_2CO_3$	277 ± 2	10.6 ± 0.5	7.2 ± 0.0	0.4 ± 0.1	23.9 ± 0.2	5.1 ± 0.7
	$Na_2HPO_4 + NaOH$	180 ± 2	20.4 ± 2.1	7.6 ± 0.1	1.5 ± 0.2	07.6 ± 0.2	7.7 ± 0.1

Les boues obtenues à la suite du traitement du lixiviat de cendres ont des caractéristiques de déshydratation comparables et ce, quelque soit la technique de précipitation employée. En effet, les valeurs de RSF et IVB sont comprises respectivement entre 5.0 et 7.3 $\times 10^{12}$ m/kg et entre 39 et 50 mL/g (Tableau 1.15).

Les boues obtenues à la suite du traitement du lixiviat des boues de station d'épuration ont montré les meilleures caractéristiques de déshydratation (décantation et filtration sous pression) à la suite de la précipitation combinée aux phosphates ($NaOH+Na_2HPO_4$) avec des valeurs de RSF de 7.6 $\times 10^{12}$ m/kg et IVB de 180 mL/g (Tableau 1.15).

1.6.4 Développement d'un nouveau logiciel de prédiction de traitement des effluents métalliques par précipitation

Le but de cette partie de projet est de développer un modèle informatique qui permet de prédire dans un contexte technico-économique, le traitement des effluents métalliques et ce, par diverses techniques de précipitation. Ce programme informatisé nommé *PITEM* (Programme Informatisé de Traitement des Effluents Métalliques) est écrit en langage Visual Basic sous *Microsoft EXCEL*, intégrant un module de spéciation chimique qui prédit les phases solides susceptibles de se former dans un scénario de précipitation donné, et un module économique permettant d'estimer le coût unitaire de traitement et de gestion des boues métalliques.

Pour simuler les systèmes d'équilibres chimiques, *PITEM* utilise les données thermodynamiques fournies par la base de données du logiciel *MINEQL+* couplé avec le code informatique nommé EST (Equilibrium system tool) développé par Del piero *et al.* (2006). La base de données de *MINEQL+* a été utilisé et actualisé étant donné son accessibilité, son nombre important d’équations chimiques, de même que sa bonne réputation dans le domaine de la chimie aquatique.

L’innovation introduite par *PITEM*, est qu’il prend en considération les caractéristiques de déshydratation des boues métalliques et l’aspect économique du procédé de traitement par les techniques de précipitation. Le coût unitaire de traitement, exprimé en Dollars Américain par mètre cube d’effluent traité, est estimé selon une conception simplifiée d’un procédé industriel de décontamination représenté à la Figure 1.2.

Les coûts des équipements pour la déshydratation des boues, des réservoirs de stockage, des pompes, etc., ont été tirés de www.matche.com et ont été actualisés (Juin 2009) en utilisant l’indice du coût des équipements Marshall & Swift pour le quatrième trimestre de l’année 2008, publié périodiquement dans la revue Chemical Engineering (Chemical Engineering 2009).

Pour un même effluent, la production de boues humides exprimée en kg par mètre cube d’effluent traité, diffère d’un agent de précipitation à un autre en raison des différences entre leurs caractéristiques de déshydratation mécanique (Djedidi *et al.* 2009a,b). Pour cette raison, le logiciel *PITEM* doit fournir une bonne estimation du paramètre ST (p/p) et, par la suite, de la production de boues (kg/m^3) et ce, après une filtration mécanique sous pression. Pour cette raison, les caractéristiques de déshydratation des boues établies dans les études précédentes ont été incorporées dans la base de données du modèle. Il est à noter que la base de données pourrait être mise à jour dans le cadre de futurs travaux de recherche pour donner au logiciel *PITEM* plus de précision et un plus grand champ d’utilisation.

Le coût total de traitement (CTT) est calculé en se basant sur les données d'entrées économiques illustrées au Tableau 1.16. Il faut noter que des données d'entrées sont fixées par défaut et peuvent être ajustées au besoin.

Les résultats de simulation du logiciel *PITEM* ont montré que la différence entre les coûts totaux de traitement (CTT) par les différentes techniques de précipitation (hydroxydes, sulfures, phosphates et carbonates), est essentiellement attribuable à trois paramètres qui sont : les coûts en produits chimiques, les coûts de transport et les coûts de disposition des boues métalliques (Tableau 1.17). En effet, les paramètres du coût d'opération (excepté pour ces derniers paramètres), sont directement ou indirectement liés aux coûts en capitaux (CC). Ce dernier est étroitement lié aux dimensions des équipements et, par la suite, au débit de l'effluent fixé dans notre cas, soit 1000 m^3/jr (Tableau 1.16). On peut donc conclure que pour un débit constant, les seuls paramètres qui varient et ce, quelque soit le mode de précipitation choisi, sont : les coûts en produits chimiques, les coûts de transport et les coûts de disposition des boues métalliques.

Les résultats de simulation pour le traitement d'un lixiviat de sol par les différentes techniques de précipitation sont donnés au Tableau 1.17. Le CTT varie entre 4.62 et 5.18 $/$m^3$. De toute évidence, le coût le plus bas est attribué au traitement par ajout de carbonates (Na_2CO_3). Ceci est dû au bas prix de Na_2CO_3 (0.15 $/kg) et également aux caractéristiques de déshydratation intéressantes des boues générées après une filtration sous pression (production de boue prédite = 1.7 kg/m^3 et expérimentale = 1.8 kg/m^3).

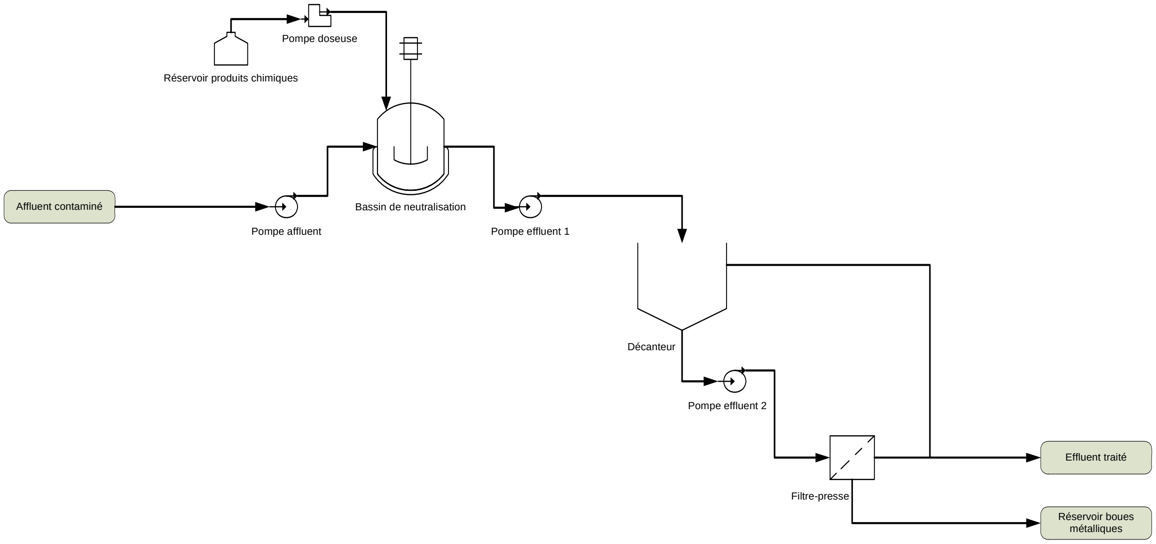

Figure 1.2 Schéma simplifié du procédé industriel de traitement des effluents

Tableau 1.16 **Données d’entrées économiques et d’opération utilisées pour l’estimation du coût total de traitement des effluents**

Paramètres	Unités	Valeurs	Paramètres	Unités	Valeurs
Paramètres de base			**Coûts d’opération**		
Débit d’effluent	m^3/jour	1000	**Coûts directs**		
Période d’opération annuelle	jours/an	350	NaOH	$/kg	0.50
Période d’opération journalière	heures/jour	24	$Ca(OH)_2$	$/kg	0.10
Facteur d’efficacité d’opération	%	90	Na_2S	$/kg	0.30
			Na_2CO_3	$/kg	0.15
Coûts en capitaux			Na_3PO_4	$/kg	0.70
Taux d’intérêt annuel	%	8	Main-d’ œuvre	$/h	25
Période d’amortissement	Années	10	Coût d’électricité	$/kWh	0.07
Durée de vie des équipements	Années	20	Supervision et main d’œuvre de bureau	% MOO	15
Frais de gestion de construction	% CC	52	Entretien et réparation	% CC	3
Frais contingents	% CC	10	Matériaux courants	% ER	15
Marshall & Swift Cost Index	-	1487.2	Frais de laboratoire	% MOO	1
			Transport des boues	$/tonne humide	20
Installation/isolation des équipements	% CC	39	Disposition des boues	$/tonne humide	60
Instrumentation et contrôle	% CE	13			
Conduits et tuyauterie	% CE	31	**Coûts indirects**		
Systèmes électriques	% CE	10	Taxes	% CC	2
Bâtiments de procédés et de services	% CE	29	Assurances	% CC	0.5
Aménagement du terrain	% CE	10	Dépenses générales	% MO	60
Facilités et services	% CE	55			
Acquisition du terrain	% CE	6	**Coûts généraux**		
Ingénierie et supervision	% CE	32	Administration	% MO	15
Dépenses de construction	% CE	34	Recherche et développement	% CDI	3

Coûts en capitaux: CC, coûts des équipements: CE, entretien et réparation: ER, main d’œuvre d’opération: MOO, main d’œuvre : MO, coûts directes et indirectes : CDI

Tableau 1.17 Coûts totaux (US$/m^3) pour les quatre scénarios de traitement de lixiviat de sol

Paramètres	**Techniques de précipitation**			
	Hydroxydes	Carbonates	Phosphates	Sulfures
Coûts d'opération				
Coûts directes				
Produits chimiques	0.314	0.111	0.265	0.136
Main d'œuvre	0.297	0.297	0.297	0.297
Énergie	0.014	0.014	0.014	0.014
Supervision	0.241	0.241	0.241	0.241
Maintenance	0.555	0.555	0.555	0.555
Matériaux courants	0.083	0.083	0.083	0.083
Frais de laboratoire	0.016	0.016	0.016	0.016
Transport des boues	0.110	0.033	0.066	0.086
Disposition des boues	0.331	0.099	0.198	0.258
Total des coûts directs	***1.951***	***1.450***	***1.735***	***1.638***
Coûts indirects	1.575	1.573	1.575	1.574
Coûts généraux	0.414	0.406	0.424	0.413
Coûts en capitaux				
Dépréciation	0.928	0.925	0.929	0.927
Intérêts	0.315	0.315	0.315	0.315
Coûts totaux de traitement	**5.183**	**4.619**	**4.978**	**4.868**

1.7 Conclusions et recommandations

Le traitement des effluents industriels acides chargés en métaux par les techniques de précipitation génèrent habituellement des quantités considérables de résidus, ou boues métalliques, lesquels sont souvent considérés comme des déchets dangereux. Les coûts de traitement de ces effluents et de disposition des boues métalliques peuvent être importants. Cette problématique a incité à développer un modèle informatique portant l'acronyme *PITEM* (Programme Informatisé de Traitement d'Effluents Métalliques), conçu pour la prédiction du traitement des effluents métalliques par les techniques de précipitation et ce, dans un contexte technico-économique. Ce programme est écrit en langage Visual Basic sous *Microsoft EXCEL*, intégrant un module de spéciation chimique qui permet de prédire les phases solides susceptibles de se former dans un scénario de précipitation donné, et un module économique permettant d'estimer le coût unitaire de traitement et de gestion des boues métalliques humides.

La production de boue humide (après séparation solide-liquide), représente un paramètre critique dans la prédiction du coût de traitement des effluents métalliques. En effet, le transport et la disposition des boues générées, constituent une proportion élevée des coûts dans un scénario donné de traitement d'effluents chargés en métaux.

Par conséquent, la réalisation de ce projet de recherche a nécessité la réalisation de travaux expérimentaux afin étudier le comportement des suspensions métalliques vis-à-vis des séparations mécaniques solide-liquide (filtration sous pression et centrifugation), qui demeurent les méthodes les plus employées à l'échelle industrielle. Les connaissances issues de ces travaux sur la caractérisation des boues ont par la suite été intégrées dans le progiciel *PITEM*.

Les tailles et les densités des flocs sont deux paramètres déterminants dans les caractéristiques de déshydratation des boues métalliques. Une bonne maîtrise des connaissances des flocs métalliques est donc indispensable pour donner au modèle plus de précision dans la prédiction de la production de boues. En effet, la force ionique « I », la valeur du pH de précipitation, la concentration initiale du métal à éliminer et la concentration en carbone organique dissous COD sont étroitement liés au contenu final en eau de la boue générée et ce, après séparation solide-liquide. Ces paramètres doivent être étudiés davantage dans le cadre de futurs travaux de recherche.

Les phases solides susceptibles de se former lors du traitement par précipitation des effluents contaminés par les métaux sont diverses. Des essais supplémentaires de traitement d'effluents monométalliques devraient donc être conduits pour alimenter la base de données du modèle de nouvelles caractéristiques de déshydratation des boues. Ceci permettra d'élargir les champs d'application de *PITEM*.

Une autre partie de recherche pourrait être intégrée au progiciel *PITEM*, laquelle consiste à l'étude de l'influence de l'application du procédé de densification des boues, appelé en anglais *High Density Sludge (HDS)* sur l'équilibre des métaux et éléments en solution, ainsi que sur la production de boues métalliques et la consommation de réactifs de précipitation. Des essais de traitement de divers types d'effluents (monométalliques, multimétalliques et effluents réels) devraient être menés avec recirculation des boues métalliques pour au moins une dizaine de cycles. Une fois ces essais terminés, les caractéristiques de déshydratation des boues métalliques seraient introduits dans la base de données de *PITEM*.

Finalement, la présente thèse de doctorat a permis de développer, pour la toute première fois, un modèle informatisé permettant à la fois de prédire : 1) l'équilibre des espèces chimiques en solution et des précipités formés lors du traitement d'effluents métalliques; 2) le comportement de déshydratation des boues métalliques; et 3) les coûts de traitement de ces effluents et de gestion des boues métalliques. Cet outil informatisé permet aux décideurs de définir, selon la situation rencontrée (concentrations et types de métaux en solution, normes en vigueur, coûts des produits chimiques et de disposition des boues métalliques), la meilleure option d'un point de vue technico-économique, pour le traitement par précipitation d'effluents chargés en métaux toxiques.

1.8 Bibliographie

Accornero, M., Marini, L., Ottonello, G., et Zuccolini, M.V. (2005) “The fate of major constituents and chromium and other trace elements when acid waters from the derelict Libiola mine (Italy) are mixed with stream waters”. *Appl. Geochem.*, 20, 1368-1390.

Al-Asheh, S., et Duvnjak, Z. (1999) “Sorption of heavy metals from synthetic metal solutions and industrial wastewater using plant materials”. *Water Qual. Res. J. Can.*, 34(3), 481-503.

Alderighi, L., Gans, P., Ienco, A., Peters, D., Sabatini, A., et Vacca, A. (1999) “Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species”. Coordination Chem. Rev., 184, 311-318.

Aldrich, C., et Feng, D. (2000) “Removal of heavy metals from wastewater effluents by biosorptive flotation”. *Min. Eng.*, 13(10-11), 1129-1138.

Allison, J.D., Brown, D.S., et Novo-Gradac, K.J. (1991) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0. User’s manual.* Report EPA/600/3-91/021, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgie, États-Unis.

Al-Tarazi, M., Heesink, A.B.M., et Versteeg, G.F. (2004) “Precipitation of metal sulphides using gaseous hydrogen sulphide: mathematical modelling”. *Chem. Eng. Sci.*, 59(3), 567-579.

Andrus, M.E. (2000) “A review of metal precipitation chemicals for metal-finishing applications”. *Met. Finish.,* 11, 20-23.

Apul, D.S., Gardner, K.H., Eighmy, T.T., Fallman, A.M., et Comans, R.N.J. (2005) “Simultaneous application of dissolution/precipitation and surface complexation/surface precipitation modeling to contaminant leaching”. *Environ. Sci. Technol.*, 39(15), 5736-5741.

Arienzo, M., Chiarenzelli, J., et Scrudato, R. (2001) “Remediation of metal-contaminated aqueous systems by electrochemical peroxidation: an experimental investigation”. *J. Hazard. Mater.*, 87(1-3), 187-198.

Avudainayagam, S., Meghraj, M., Owens, G., Kookana, R.S., Chittleborough, D., et Naidu, R. (2003) “Chemistry of chromium in soils with emphasis on tannery waste sites”. *Rev. Environ. Contam. Toxicol.*, 178, 53-91.

Baath, E. (1989) “Effects of heavy metals in soil on microbial processes and populations (a review)”. *Water Air Soil Pollut.*, 47, 335-379.

Babel, S., et Kurniawan, T.A. (2003) “Low-cost adsorbents for heavy metals uptake from contaminated water: a review”. *J. Hazard. Mater.*, 97(1-3), 219-243.

Bailey, S.E., Olin, T.J., Bricka, R.M., et Arian, D. (1999) “A review of potentially low-cost sorbents for heavy metals”. *Water Res.,* 33(11), 2469-2479.

Ball, J. (2002) *User’s manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters (program version 2.46).* Report 91-183, United States Geological Survey, Reston, VA, États-Unis.

Ball, J., Nordstrom, D.K., et Zachmann, D.W. (1987) *WATEQ4F-A personal computer fortran translation of the geochemical model WATEQ2 with revised data base*. Report 87-50, United States Geological Survey, Menlo Park, CA, États-Unis.

Baltpurvins, K.A., Burns, R.C., et Lawrance, G.A. (1996a) "Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation". *Waste Manag*., 16(8), 717-725.

Baltpurvins, K.A., Burns, R.C., et Lawrance, G.A. (1996b) "Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater". *Environ. Sci. Technol*., 30, 1493-1499.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., et Stuart, A.D. (1997) "Effect of electrolyte composition on zinc hydroxide precipitation by lime". *Water Res*., 31, 973-980.

Barak, P. (1990) "SPECIES: a spreadsheet program for modeling speciation of soil solution". *J. Agron. Educ*., 19, 44-46.

Barnes, L.J., Scheeren, P.J.M., et Buisman, C.J.N. (1994) *Emerging technology for bioremediation of metals*. Means, J.L., et Hinchee, R.E. (Éditeurs), Lewis Publishers, Boca Raton, Floride, États-Unis, pp. 38-49.

Beauchesne, I., Ben Cheikh, R., Mercier, G., Blais, J.F et Ouarda, T (2007) "Chemical treatment of sludge: In-depth study on toxic metal removal efficiency, dewatering ability and fertilizing property preservation". *Water Res*., 41, 2028-2038.

Belkhouche, N.E., Didi, M.A., et Villemin, D. (2005) "Separation of nickel and copper by solvent extraction using Di-2 ethylhexylphosphoric acide-based synergistic mixture". *Solvent Extraction Ion Exchange*, 23(5), 677-693.

Ben Frarès, N., Taha, S., et Dorange, G. (2005) "Influence of the operating conditions on the elimination of zinc ions by nanofiltration". *Desalination,* 185, 245-253.

Bhavsar, S.P., Diamond, M.L., Gandhi, N., et Nilsen, J. (2004) "Dynamic coupled metal transport-speciation model: application to assess a zinc-contaminated lake". *Environ. Toxicol. Chem.*, 23(10), 2410-2420.

Blais, J.F., Dufresne, S., et Mercier, G. (1999) "State of the art of the technological development from metal removal from industrial effluents". *J. Water Sci*., 12(4), 689-713.

Bolan, N.S., Adriano, D.C., Duraisamy, P., Mani, A., et Arulmozhiselvan, K. (2003) "Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition". *Plant Soil*, 250(1), 83-94.

Brooks, C.S. (1986) "Metal recovery from industrial wastes". *J. Metals*, 38, 50-57.

Brooks, C.S. (1991) *Metal recovery from industrial wastes*. Lewis Publishers Inc., Chelsea, Michigan, États-Unis.

Chang, L.Y. (1995). "A waste minimization study of chelated copper complex in wastewater-Treatability and and process analysis". *Waste Manag*., 15(3), 209-220.

Chang, Y.K., Chang, J.E., Lin, T.T., et Hsu, Y.M. (2002) "Integrated copper-containing wastewater treatment using xanthate process". *J. Hazard. Mater*., B94, 89-99.

Chapman, P.M., Wang, F., Janssen, C.R., Goulet, R.R., et Kamunde, C.N. (2003) "Conducting ecological risk assessments of inorganic metals and metalloids: current status". *Hum. Ecol. Assess*., 9, 641-697.

Charerntanyarak, L. (1999) “Heavy metals removal by chemical coagulation and precipitation”. *Water Sci. Technol.,* 39(10-11), 135-138.

Chaston, S., Grassia, G.S., et Sheehy, A.J. (1996) “The next iteration factor (NIF) method for calculating equilibrium conditions in subsurface wasters, for the isolation of microorganisms from petroleum reservoirs”. *Aust. J. Chem*., 49, 943-949.

Chemical Engineering (2009) Site Web : http://www.che.com/. Consulté le 1 mars 2009.

Cherry, K.F. (1982) *Plating waste treatment*. Ann Arbor science, Ann Arbor, Michigan, États-Unis, 324 p.

Chu, W. (1999) “Lead metal removal by recycled alun sludge”. *Water Res*., 33(13), 3019-3025.

Couillard, D., et Mercier, G. (1992) “Précipitations sélectives des métaux solubilisés biologiquement de boues aérobies d’épuration”. *Can. J. Chem. Eng*., 70, 1021-1029.

Dabrowski, A., Hubicki, Z., Podkoscielny, P., et Robens, E. (2004) “Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method”. *Chemosphere*, 56, 91-106.

Davydova, S. (2005) “Heavy metals as toxicants in big cities”. *Microchem. J*., 79, 133-136.

Del Piero, S., Melchior, A., Polese, P., Portanova, R., et Tolazzi, M. (2006) “A novel multipurpose Excel tool for equilibrium speciation based on Newton-Raphson method and on a hybrid genetic algorithm”. *Annali di Chimica*, 96, 1-21.

DiPalma, L., Ferrantelli, P., Merli, C., et Petrucci, E. (2003) “Treatment of the solution extracted from metal contaminated soils by reverse osmosis and chemical precipitation”. *Annali Di Chimica*, 93(12), 1005-1011.

Djedidi, Z., Bouda, M., Cheikh, R.B., Blais, J.F., Mercier, G., et Tyagi, R.D. (2009a) "Comparative study of dewatering characteristics of metal precipitates generated during treatment synthetic polymetallic and AMD solutions". *Hydrometallurgy*, 98(3-4), 247-256.

Djedidi, Z., Drogui, P., Ben Cheikh, R., Mercier, G., et Blais, J.F. (2005) "Laboratory study of successive soil saline leaching and electrochemical lead recovery". *J. Environ. Eng. Div. ASCE*, 131(2), 305-314.

Djedidi, Z., Khaled, J.B., Cheikh, R.B., Blais, J.F., Mercier, G., et Tyagi, R.D. (2009b) "Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions". *Hydrometallurgy*, 95(1-2), 61-69.

Doyle, F.M. (2003) "Ion flotation - its potential for hydrometallurgical operations". *Int. J. Min. Proc.*, 72(1-4), 387-399.

Duan, J., et Gregory, J. (2003) "Coagulation by hydrolysing metal salts". *Adv. Colloid Interface Sci.*, 100-102, 475-502.

Dustan, A.C., Cohen, B., et Petrie, J.G., (2005) "Modelling dewatering behaviour through an understanding of solids formation processes. Part II – Solids separation considerations". *Adv. Colloid Interface Sci.*, 113(2-3), 85-97.

Dyer, J.A., Scrivner, N.C., et Dentel, S.K. (1998) "A practical guide for determining the solubility of metal hydroxides and oxides in water". *Environ. Prog.*, 17(1), 1-8.

Ettler, V., Matura, M., Mihaljevic, M., et Bezdicka, P. (2006) "Metal speciation and attenuation in stream waters and sediments contaminated by landfill leachate". *Environ. Geol.*, 49(4), 610-619.

Evenko, C.R., et Dzomback, D.A. (1997) *Remediation of metals-contamined soils and groundwater*. Technology evaluation report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvanie, États-Unis, 53 p.

Felmy, A.R., Girvin, D.C., et Jenne, E.A. (1984) *MINTEQ: a computer program for calculating aquous geochemical equilibria*. Report EPA/600/3-84/032, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgie, États-Unis.

Feng, D., Aldrich, C., et Tan, H. (2000) "Treatment of acid mine drainage by use of heavy metal precipitation and ion exchange". *Min. Eng.*, 13(6), 623-642.

Florea, A.M., et Büsselberg, D. (2006) "Occurence, use and potential toxic effects of metals and metal compounds". *BioMetals*, 19, 419-427.

FRTR (2005) *Federal remediation technologies roundtable*. Site Web : http://www.frtr.gov. Consulté le 1 décembre 2005.

Fu, F., Chen, R., et Xiong, Y. (2006) "Application of a novel strategy - coordination polymerization precipitation to the treatment of Cu^{2+}-containing wastewaters". *Sep. Purif. Technol.*, 52(2), 388-393.

Fu, F., Chen, R., et Xiong, Y. (2007) "Comparative investigation of N,N'-bis-(dithiocarboxy)piperazine and diethyldithiocarbamate as precipitants for Ni(II) in simulated wastewater". *J. Hazard. Mater.*, 147(1-2), 437-442.

Galvin, R.M. (1996) "Occurrence of metals in waters: an overview". *Water SA*, 22(1), 7-18.

Gans, P., Sabatini, A., et Vacca, A. (1996) “Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs”. *Talanta*, 43(10), 1739-1753.

GardeaTorresdey, J.L., delaRosa, G., et PeraltaVidea, J.R. (2004) “Use of phytofiltration technologies in the removal of heavy metals: A review”. *Pure Appl. Chem*., 76(4), 801-813.

Geckler, K., et Volchek, K. (1996) “Removal of hazardous substances from water using ultrafiltration in conjunction with soluble polymer”. *Environ. Sci. Technol*., 30(3), 725-733.

Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., et Okujeni, C. (2006) “Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements”. *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng*., 41(8), 1729-1747.

Gomez del Rio, J., Sanchez, P., Morando, P.J., et Cicerone, D.S. (2006) “Retention of Cd, Zn and Co on hydroxyapatite filters”. *Chemosphere*, 64, 1015-1020.

Guillard, D., et Lewis, A.E. (2002) “Optimisation of nickel hydroxycarbonate precipitation using a laboratory pellet reactor”. *Ind. Eng. Chem*., 41, 3110-3114.

Halim, C.E., Short, S.A., Scott, J.A., Amal, R., et Low, G. (2005) “Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC”. *J. Hazard. Mater*., 125(1-3), 46-61.

Hayes, P.C. (1985) *Process selection in extractive metallurgy*. Hayes Publishing Co., Brisbane, Australie.

Henke, K.R. (1998) “Chemistry of heavy metal precipitates resulting from reactions with Thio-Red”. *Water Environment Res.*, 70(6), 1178-1185.

Henke, K.R., Hutchinson, A.R., Krepps, M.K., et Atwood, D.A. (2001) “The chemistry of 2,4,6-trimercapto-1,3,5-triazine (TMT): acid dissolution constants and group 2 complexes”. *Inorg. Chem.*, 40(17), 4443-4447.

Hove, M., van Hill, R.P., et Lewis, A.E., 2008. “Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH”. *Chem. Eng. Sci.*, 63, 1626-1635.

HydroGeoLogic (1998a) *Diffuse-layer sorption reactions for use in MINTEQA2 for HWIR metals and metalloids.* United States Environmental Protection Agency, National Exposure Research Laboratory, Ecosystem Research Division, Athens, Georgie, États-Unis.

HydroGeoLogic (1998b) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: user manual supplement for version 4.0.* United States Environmental Protection Agency, National Exposure Research Laboratory, Ecosystem Research Division, Athens, Georgia, États-Unis.

Islamoglu, S., Yilmaz, L., et Ozbelge, H.O. (2006) “Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents”. *Sep. Sci. Technol.*, 41(15), 3367-3385.

Jiang, J.Q. (2001) “Removing arsenic from groundwater for the developing world - a review”. *Water Sci. Technol.*, 44(6), 89-98.

Juang, R.S., et Wang, S.W. (2000) “Electrolytic recovery of binary metals and EDTA from strong complexed solutions”. *Water Res.*, 34(12), 3179-3185.

Juang, R.S., Lin, S.H., et Wang, T.Y. (2003) "Removal of metal ions from the complexed solutions in fixed bed using a strong acid ion exchange resin". *Chemosphere.*, 53(10), 1221-1228.

Jüttner, K., Galla, U., et Schmieder, H. (2000) "Electrochemical approaches to environmental problems in the process industry". *Electrochim. Acta*, 45, 2575-2594.

Kabata-Pendias, A. (2001) *Trace elements in soils and plants. 3rd Edition*. Kabata-Pendias, A., et Pendias, H. (Éditeurs), CRC Press LLC, Boca Raton, Floride, États-Unis, 413 p.

Kaksonen, A.H., Riekkola-Vanhanen, M.L., et Puhakka, J.A. (2003) "Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater". *Water Res.*, 37(2), 255-266.

Kamal, M., Ghaly, A.E., Mahmoud, N., et Côté, R. (2004) "Phytoaccumulation of heavy metals by aquatic plants". *Environ. Int.*, 29(8), 1029-1039.

Kapoor, A., et Viraraghavan, T. (1995) "Fungal biosorption - an alternative treatment option for heavy metal bearing wastewaters : a review". *Bioresource Technol.*, 53, 195-206.

Kharaka, Y.K., et Barnes, L.J. (1973) *SOLMNEQ: solution-mineral equilibrium computations*. Report PB-215899, United States Geological Survey, Computer Contributions, National Technical Information Service, United States Gov. Print. Office, Washington, DC, États-Unis.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., et DeBraal, J.D. (1988) *SOLMNEQ.88: a computer program for geochemical modeling of water-rock interactions*. Report 88-4227, United States Geological Survey, Water Resources Investigations, Reston, VA, États-Unis.

Kim, B.M., et Amodeo, P.A. (1983) “Calcium sulphide process for treatment of metal-containing wastes”. *Environ. Progress*, 2, 175-180.

Kim, B.R., Gaines, W.A., Szafranski, M.J., Bernath, E.F., et Miles, A.M. (2002) “Removal of heavy metals from automotive wastewater by sulphide precipitation”. *J. Environ. Eng. Div. ASCE*, 128(7), 612-623.

Knocke, W.R., Ghosh, M.M., et Novak, J.T. (1980) “Vaccum filtration of metal hydroxide sludges”. *J. Environ. Eng. Div. ASCE*, 106(2), 363-376.

Korfali, S.I., et Davies, B.E. (2004) “Speciation of metals in sediment and water in a river underlain by linestone: role of carbonate species for purification capacity of rivers”. *Adv. Environ. Res.*, 8, 599-612.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., et Babel, S. (2006) “Comparison of low-cost adsorbents for treating wastewaters laden with heavy metals”. *Sci. Total Environ.*, 366(2-3), 409-426.

Lai, C.L., et Lin, K.S. (2006) “Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation”. *J. Hazard. Mater.*, 136(2), 183-187.

Lazaridis, N.K., Matis, K.A., et Webb, M. (2001) “Flotation of metal-loaded clay anion exchangers. Part I: the case of chromate”. *Chemosphere*, 42, 373-378.

Leist, M., Casey, R.J., et Caridi, D. (2000) “The management of arsenic wastes: problems and prospects”. *J. Hazard. Mater.,* B76, 125-138.

Leung, V.W.H., et Darvell, B.W. (1990) "The ramases algorithm for multiple equilibria – III acceleration and standardized formation constants (RAMASES II)". *Talanta*, 37(4), 425-429.

Levasseur, B., Blais, J.F., et Mercier, G. (2005) "Study of the metal precipitation from decontamination leachates of municipal wastes fly ash incinerators". *Environ. Technol.*, 26(4), 421-431.

Lewis, A., et Swartbooi, A. (2006) "Factors affecting metal removal in mixed sulphide precipitation". *Chem. Eng. Technol.*, 29(2), 277-280.

Licskó, I. (1997) "Realistic coagulation mechanisms in the use of aluminium and iron(III) salts". *Water Sci. Technol.*, 36(4), 103-110.

Lin, S.H., Kao, H.C., Huang, S.H., et Juang, R.S. (2002) "Equilibrium and kinetic studies of the extraction of chelated copper(II) anions with Aliquat 336". *J. Chem. Technol. Biotechnol.*, 77(2), 168-174.

Lin, S.H., Lai, S.L., et Leu, H.G. (2000) "Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process". *J. Hazard. Mater.*, 76, 139-153.

Lin, S.H., Wang, T.Y., et Juang, R.S. (2004) "Metal rejection by nanofiltration from diluted solutions in the presence of complexing agents". *Sep. Sci. Technol.*, 39(2), 363-376.

Lin, X., Burns, R.C., et Lawrance, G.A. (1998) "Effect of electrolyte composition, and of added iron(III) in the presence of selected organic complexing agents, on nickel(II) precipitation by lime". *Water Res.*, 32(12), 3637-3645.

Mack, C., Burgess, J.E., et Duncan, J.R. (2004) "Membrane bioreactors for metal recovery from wastewater : A review". *Water SA*, 30(4), 521-532.

Maine, M.A., Sune, N., Hadad, H., Sanchez, G., et Bonetto, C. (2006) “Nutrient and metal removal in a constructed wetland for wastewater treatment from a metallurgic industry”. *Ecol. Eng*., 26(4), 341-347.

Marchioretto, M.M., Bruning, H., et Rulkens, W. (2005) “Heavy metals precipitation in sewage sludge”. *Sep. Sci. Technol*., 40(16), 3393-3405.

Matlock, M.M., Henke, K.R., Atwood, D.A., et Robertson, D. (2001) “Aqueous leaching properties and environmental implications of cadmium, lead and zinc trimercaptotriazine (TMT) compounds”. *Water Res*., 35(15), 3649-3655.

Matlock, M.M., Henke, K.R., et Atwood, D.A. (2002) “Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs”. *J. Hazard. Mater.*, B92, 129-142.

Mattigod, S.V. (1995) *Chemical equilibrium and reaction models: applications and future trends. Chemical equilibrium and reaction models*. SSSA Special Publication Number 42, Soil Science Society of America, American Society of Agronomy, Madison, Wisconsin, États-Unis, pp. l-5.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., et Saldanha, M. (2002) “Studies on the mechanisms of lead immobilization by hydroxyapatite”. *Environ. Sci. Technol*., 36(7), 1625-1629.

May P.M., et Murray, K. (1991a) “JESS, a joint expert speciation system – I. Raison d’être”. *Talanta*, 38(12), 1409-1417.

May P.M., et Murray, K. (1991b) “JESS, a joint expert speciation system – II. The thermodynamic database”. *Talanta*, 38(12), 1419-1426.

May P.M., Murray, K., et Williams, D.R. (1985) "The use of glass electrodes for the determination of formation constants—II simulation of titration data". *Talanta*, 32(6), 483-489.

McAnally, S., Benefield, L., et Reed, R.B. (1984). "Nickel removal from a synthetic nickel-plating waste water using sulphide and carbonate for precipitation and coprecipitation". *Sep. Sci. Technol*., 19, 191-217.

McDuff, R.E., et Morel, E.M. (1973) *Description and use of the chemical equilibrium program REDEQL2*. Technical Report EQ-73-02, California Institute of Technology, Pasadena, CA, États-Unis.

McGowen, S.L., Basta, N.T., et Brown, G.O. (2001) "Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil". *J. Environ. Qual*., 30, 493-500.

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., et Cook, N. (2000) "Soil testing for heavy metals". *Commun. Soil Sci. Plant Anal*., 31, 1661-1700.

Meers, E., Unamuno, V.R., Du Laing, G., Vangronsveld, J., Vangroekhoven, K., Samson, R., Diels, L., Geebelen, W., Ruttens, A., Vandegehuchte, M., et Tack, F.M.G. (2006) "Zn in the soil solution of unpolluted soils as affected by soil characteristics". *Geoderma*, 136, 107-119.

Meunier, N., Blais, J.F., Lounes, M., Tyagi, R.D., et Sasseville, J.L. (2002) "Different options for metal recovery after sludge decontamination at the Montreal Urban Community wastewater treatment plant". *Water Sci. Technol*., 46(10), 33-41.

Meunier, N., Drogui, P., Gourvenec, C., Mercier, G., Hausler, R., et Blais, J.F. (2004) "Removal of metals in leachate from sewage sludge using electrochemical technology". *Environ. Technol.*, 25(2), 235-245.

Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., et Blais, J.F. (2006) "Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate". *J. Hazard. Mater.*, 137(1), 581-590.

Mirbagheri, S.A., et Hosseini, S.N. (2004) "Pilot plant investigation on petrochemical wastewater treatmentfor the removal of copper and chromium with the objective of reuse". *Desalination*, 171(1), 85-93.

Moghadam, M.A., Soheili, M., et Esfahani, M.M. (2005) "Effect of ionic strength on settling of activated sludge". *Iranian J. Environ. Health Sci. Eng.*, 2(1), 1-5.

Moller, A., Grahn, A., et Welander, U. (2004) "Precipitation of heavy metals from landfill leachates by microbially-produced sulphide". *Environ. Technol.*, 25(1), 69-77.

Mondal, B.C., et Das, A.K. (2004) "Functionalized chelating resins for selective sorption of metal ions: an overview". *J. Indian Chem. Soc.*, 81(2), 95-110.

Müller, B. (1996) *CHEMEQL, version 2.0. User's guide to application.* Swiss Federal Institute of Environmental Sciences and Technology (EAWAG), Dübendorf, Suisse.

Mustafa, S., Naeem, A., Murtaza, S., Rehana, N., et Samad, H.Y. (1999) "Comparative sorption properties of metal (III) phosphates". *J. Colloid Interface Sci.*, 220(1), 63-74.

Naeem, A., Mustafa, S., Dilara, B., Rehana, N., et Murtaza, S. (2003) "Effect of precipitation on the sorption of metal cations by $AlPO_4$". *J. Chem. Soc. Pakistan*, 25(2), 98-103.

Navarro, R.R., Wada, S et Tatsumi, K. (2005) "Heavy metal precipitation by polycation-polyanion complex of PEI and its phosphonomethylated derivative". *J. Hazard. Mater.*, 123, 203-209.

Nelson, A., Wang, W., Demopoulos, G.P., et Houlachi, G. (2000) "The removal of cobalt from zinc electrolyte by cementation: a critical review". *Min. Proc. Ext. Met. Rev.,* 20, 325-356.

Nriagu, J. (1996) "A history of global metal pollution". *Science*, 272, 22-24.

Nriagu, J.O., et Pacyna, J.M. (1988) "Quantitative assessment of world-wide contamination of air, water, and soils by trace metals". *Nature*, 333, 134-139.

Papadopoulos, A., Fatta, D., Parperis, K., Mentzis, A., Haralambous, K.J., et Loizidou, M. (2004) "Nickel uptake from a wastewater stream produced in a metal finishing industry combination of ion-exhange and precipitation methods". *Sep. Purif. Technol.*, 39(3), 181-188.

Papelis, C., Hayes, K.F., et Leckie, J.O. (1988) *HYDRAQL: a program for the computation of chemical equilibrium composition of aqueous batcvh systems including surface-complexation modeling of ion adsorption at the oxide/solution interface*. Technical report 306, Department of Civil Engineering, Stanford University, Stanford, CA, États-Unis.

Parkhurst, D., et Appelo, C. (1999) *User's guide to PHREEQC (ver. 2.4.2). A computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations*. Report 99-4259, United States Geological Survey, Water Resources Investigations, Reston, VA, États-Unis.

Parkhurst, D.L., Thorstenson, D.C., et Plummer, L.N. (1980) *PHREEQE. A computer program for geochemical calculations*. Report 80-96, United States Geological Survey, Water Resources Investigations, Reston, VA, États-Unis.

Patterson, J.W. (1988) Metal treatment and recovery. Dans: *Metal speciation: theory, analysis and application*. Kramer, J.R., et Allen, H.E. (Éditeurs), Lewis Publishers, Inc., Chelsea, Michigan, États-Unis, pp.333-345.

Patterson, J.W., Allen, H.E., et Scala, J.J. (1977) "Carbonate precipitation for heavy metals pollutants". *J. Water Pollut. Control Fed.,* 49, 2397-2410.

Patterson, J.W., et Minear, R.A. (1975) Physical-chemical methods of heavy metals removal. Dans : *Heavy metals in the aquatic environment*. Krenkel, P.A. (Éditeur), Pergamon Press, Oxford, Angleterre, pp. 261-276.

Pigaga, A., Juskenas, R., et Selkis, A. (2002) "Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation". *Sep. Sci. Technol.,* 37(13), 3155-3168.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., et Dunkle, S.A. (1988) *A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brine*. Report 88-4153, United States Geological Survey, Water-Resources Investigations, Reston, VA, États-Unis, 310 p.

Plummer, L.N., Prestemon, E.C., et Parkhurst, D.L. (1991) *An interactive code (NETPATH) for modeling net geochemical reactions along a flow path*. Report 91-4-78, United States Geological Survey, Water-Resources Investigations, Reston, VA, États-Unis.

Plummer, L.N., Prestemon, E.C., et Parkhurst, D.L. (1994) *An interactive code (NETPATH) for modeling net geochemical reactions along a flow path version 2.0*. Report 94-4169, United States Geological Survey, Water-Resources Investigations, Reston, VA, États-Unis.

Porter, S.K., Scheckel, K.G., Impellitteri, C.A., et Ryan, J.A. (2004) "Toxic metals in the environment: Thermodynamic considerations for possible immobilization strategies for Pb, Cd, As, and Hg". *Crit. Rev. Environ. Sci. Technol.*, 34(6), 495-604.

Preis, W., et Gamsjager, H. (2001) "Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems". *Chem. Monthly*, 132, 1327-1346.

Robinson, A.K., et Sum, J.C. (1980) *Sulphide precipitation of heavy metals*. EPA/600/2-80/139, United States Environmental Protection Agency, Washington, DC, États-Unis.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M.L., et Munoz, J.A. (2006) "Biosorption with algae: A statistical review". *Crit. Rev. Biotechnol.*, 26(4), 223-235.

Romero, R., et Joensson, J.A. (2005) "Determination of free copper concentrations in natural waters by using supported liquid membrane extraction under equilibrium conditions". *Anal. Bioanal. Chem.*, 381(7), 1452-1459.

Savage, D. (1986) "The geochemical interactions of simulated borosilicate waste glass, granite and water at 100^{o}-350^{o}C and 50 Mpa". *Nuclear Chem. Waste Manag.*, 6(1), 15-39.

Semerjian, L., et Ayoub, G.M. (2003) "High-pH-magnesium coagulation-flocculation in wastewater treatment". *Adv. Environ. Res.*, 7, 389-403.

Sharma, R.K., et Agrawal, M. (2005) "Biological effects of heavy metals: an overview". *J. Environ. Biol.*, 26(2), 301-313.

Sheoran, A.S., et Sheoran, V. (2006) “Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review”. *Min. Eng.*, 19(2), 105-116.

Silva, J.E., Paiva, A.P., Soares, D., Labrincha, A., et Castro, F. (2005) “Solvent extraction applied to the recovery of heavy metals from galvanic sludge”. *J. Hazard. Mater.*, 120(1-3), 113-118.

Slavek, J., et Pickering, W.F. (1988) “Metal ion interaction with the hydrous oxides of aluminium”. *Water Air Soil Pollut.*, 39(1-2), 201-216.

Sposito, G., et Coves, J. (1988) *SOILCHEM: a computer program for the calculation of chemical speciation in soils*. Kearney Foundation of Soil Science, Department of Soil & Environmental Sciences, University of California, Riverside, CA, États-Unis.

Sposito, G., et Matigod, S. (1977) *GEOCHEM: a computer program for the calculation of chemical equilibria in soil solutions and other natural water systems*. Department of Soil & Environmental Sciences, University of California, Riverside, CA, États-Unis.

Sposito, G., et Matigod, S. (1980) *GEOCHEM: computer program for the calculation of chemical equilibria in soil solutions and other natural water systems*. Department of Soil & Environmental Sciences, University of California, Riverside, CA, États-Unis.

Suarez, D.L., et Goldberg, S. (1994) Modeling soil solution, mineral formation and weathering. Dans: *Quantitative modeling of soil forming processes*. Soil Science Society of America (Éditeur), SSSA Special Publication, Madison, WI, États-Unis, Chap. 3, pp. 37-60.

Sulzbacher, K., Ecke, H., Lagerkvist, A., et Calmano, W. (1997) “Anaerobic reduction of hexavalent chromium in filter sludge of an electrochemical process”. *Environ. Technol.*, 18, 301-307.

Sun, J., et Huang, J.C. (2002) “Co-removal of hexavalent chromium during copper precipitation”. *Water Sci. Technol.*, 46(4-5), 413-419.

Tauler, R., et Casassas, E. (1988) “A simplex search for conditions giving maximal and/or minimal concentrations of species in distribution plots”. *Anal. Chim. Acta*, 206, 189-202.

Thrailkill, J. (1970) *Solution geochemistry of the water of limestone terrains*. Report 19, Water Resources Institute of Research, University of Kentucky, Lexington, Kentucky, États-Unis.

Tipping, E. (1998) “Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances”. *Aqueous Geochem.*, 4, 3-48.

Truesdell, A.H., et Jones, B.F. (1974) “WATEQ, a computer program for calculating chemical equilibria of natural waters”. *J. Res. U.S. Geol. Surv.*, 2, 233-248.

USEPA (1992) *Mercury and arsenic wastes. Removal, recovery, treatment, and disposal*. Pollution Technology Review No. 214, Noyes Data Corporation, Park Ridge, New Jersey, États-Unis, 127 p.

USEPA (1993) *Constructed wetlands-based treatment*. EPA/540/R-93/523, United States Environmental Protection Agency, Washington, DC, États-Unis.

USEPA (2000) *Chemical precipitation*. EPA/832/F-00/018, United States Environmental Protection Agency, Washington, DC, États-Unis.

Van der Lee, J., et De Windt, L. (2000) *CHESS tutorial and cookbook. User’s guide*. Report LHM/RD/99/05, CIG-École des Mines de Paris, Fontainebleau, France.

Vanbroekhoven, K., Dejonghe, W., et Diels, L. (2005) Treatment of contaminated soil and groundwater: in situ immobilization of metals. Dans: *Soil and sediment remediation. Mechanisms, technologies and applications*. Lens, P., Grotenhuis, T., Malina, G. et Tabak, H. (Éditeurs), IWA Publishing, Londres, Angleterre, Chap. 13, pp. 248-263.

VanRoy, S., Vanbroekhoven, K., Dejonghe, W., et Diels, L. (2006) “Immobilization of heavy metals in the saturated zone by sorption and *in situ* bioprecipitation processes”. *Hydrometallurgy*, 83(1-4), 195-203.

Veeken, A.H.M., et Rulkens, W.H. (2003) “Innovative developments in the selective removal and reuse of heavy metals from wastewaters”. *Water Sci. Technol*., 47(10), 9-16.

Viadero, R.C., Wei, X.C., et Buzby, K.M. (2006) “Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization”. *Environ. Eng. Sci*., 23(4), 734-743.

Wang, Y.H., Lin, S.H., et Juang, R.S. (2003) “Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents”. *J. Hazard. Mater*., 102(2-3), 291-302.

Westall, J.C. (1979) *MICROQL. 1. a chemical equilibrium program in BASIC. II. Computation of adsorption equilibria in BASIC*. Technical report, Swiss Federal Institute of Environmental Sciences and Technology (EAWAG), Dübendorf, Suisse.

Westall, J.C. (1982) *FITEQL. a computer program for determination of equilibrium constants from experimental data*. Report 82-01, Department of Chemistry, Oregon State University, Corvallis, OR, États-Unis.

Westall, J.C., Zachary, J.L., et Morel, F.M.N. (1976) *MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems*. Technical note 18, Massachusetts Institute of Technology, Cambridge, MA, États-Unis.

White, C., Sharman, A.K., et Gadd, G.M. (1998) "An integrated microbial process for the bioremediation of soil contaminated with toxic metals". *Nature Biotechnol.*, 16, 572-575.

Wildeman, T., Gusek, J., Cevaal, J., Whiting, K., et Scheuering, J. (1995) *Bioremediation of inorganics*. Hinchee, R.E., Means, J.L., et Burris, D.R. (Éditeurs), Battelle Press, Columbus, Ohio, États-Unis, pp. 141-148.

Williams, J.W., et Silver, S. (1984) "Bacterial resistance and detoxification of heavy metals". *Enz. Microb. Technol.*, 6, 530-537.

Wingenfelder, Hansen, C., Furrer, G., et Schulin, R. (2005) "Removal of heavy metals from mine water by natural zeolites". *Environ. Sci. Technol.*, 39, 4606-4613.

Wolery, T. (1992) *EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, user's guide and related documentation (version 7.0).* Report UCRL-MA-110662 PT III, Lawrence Livermore National Laboratory, Livermore, CA, États-Unis.

Wolery, T., et Daveler, S.A. (1992) *EQ6, a computer program for reaction path modeling of aqueous geochemical systems: theoretical manual, user's guide and related documentation (version 7.0).* Report UCRL-MA-110662 PT IV, Lawrence Livermore National Laboratory, Livermore, CA, États-Unis.

Wong, C.S.C., Li, X.D., et Thornton, I. (2006) "Urban environmental geochemistry of trace metals". *Environ. Pollut.*, 142(1), 1-16.

Ying, X., et Fang, Z. (2006) “Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate”. *J. Hazard. Mater.*, 137(3), 1636-1642.

Zamboulis, D., Pataroudi, S.I., Zouboulis, A.I., et Matis, K.A. (2004) “The application of sorptive flotation for the removal of metal ions”. *Desalination*, 162, 159-168.

Zinck, J.M., et Aubé, B.C. (2000) “Optimisation of lime treatment processes”. *CIM Bulletin*, 93(1043), 98-105.

CHAPITRE II

METALS PRECIPITATION FROM EFFLUENTS-A REVIEW

Le Chapitre 2 est constitué de l'article suivant:

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Résumé

Au début du 21ème siècle, la pollution par les métaux lourds des eaux souterraines et de surfaces, continue de représenter un défi pour les autorités responsables de la protection de l'environnement. Les rejets incontrôlés des métaux dans les écosystèmes comme l'Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Tl et Zn, constituent de graves menaces pour la santé humaine et animale. Plusieurs méthodes de traitement des eaux contaminées par les métaux ont été proposées au cours des dernières décennies. Cependant, la technique de précipitation des métaux reste l'option la plus favorable à l'échelle industrielle pour des raisons technico-économiques et de simplicité. La revue suivante présente les connaissances actuelles sur les différentes techniques alternatives de précipitation des métaux. La discussion porte sur les caractéristiques spécifiques des contaminants métalliques, ainsi que de leurs comportements vis-à-vis des différentes techniques de précipitation.

Metals precipitation from effluents – A review

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2. METALS PRECIPITATION FROM EFFLUENTS – A REVIEW

2.1 Abstract

At the onset of 21st century, the pollution of surface and groundwater by toxic metals continues to represent a challenge for the authorities responsible for environmental protection. The uncontrolled rejection of metals in aquatic ecosystems such as Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Tl and Zn, constitute a serious threat to human and animal health. Several methods of treatment of waters polluted by metals have been proposed during the last several decades. However, the technique of precipitation of metals remains the most favorable option on an industrial scale due to reasons of cost-effectiveness, performance and simplicity. The present review presents current knowledge on various technical alternatives for precipitation of metals. The discussion relates to the individual characteristics of the metal contaminants, as well as their behavior compared to various techniques of precipitation.

2.2 Keywords

Precipitation; Metal; Removal; Water; Hydroxide; Sulphide; Carbonate; Phosphate.

2.3 Nomenclature

AMD	acid mine drainage
BDETH2	benzene-1,3-diamidoethanethiol
DDTC	diethyldithiocarbamate
DMTC	dimethyldithiocarbamate
DTC	dithiocarbamate
Na_2BDP	disodium *N*,*N*'-bis-(dithiocarboxy)piperazine
PDD	potassium dipropyl dithiophosphate
PyDETH2	pyridine-2-6-diamineethanethiol
STC	sodium thiocarbonate
TMT	2,4,6-trimercapto-1,3,5-triazine

2.4 Introduction

Environmental contamination with heavy metals is a consequence of technological and industrial advances (Davydova 2005; Nriagu 1996; Nriagu and Pacyna 1988; Wong *et al.* 2006). The principal problem associated with this anthropogenic contamination is toxicity against all living organisms, in particular, humans (Baath 1989; Chapman *et al.* 2003; Florea and Büsselberg 2006; Galvin 1996; Sharma and Agrawal 2005). The risks associated with the presence of potentially toxic metals in soils and waters are rather well known and well documented (Allen 2002; Kabata-Pendias 2001; Lippmann 2000). It is, therefore, essential to remove or reduce the presence of these inorganic contaminants in order to diminish the possibility of uptake by plants, animals and humans and eventual accumulation in the food chain and also to prevent them from contaminating surface and groundwater by dissolution or dispersion (Kabata-Pendias 2001; McLaughlin *et al.* 2000).

For these reasons, lot of research has been carried out in the last decades to develop efficient and cheap methods for the treatment of metal–polluted effluents (Blais *et al.* 1999; Kurniawan *et al.* 2006). Table 2.1 illustrates the principal technologies used and proposed for the removal of potentially toxic metals from effluents. Among these technologies, precipitation is the most widely used approach for the removal of metals from groundwater, surface water and industrial effluents (FRTR 2005; Levasseur *et al.* 2005; Mirbagheri and Hosseini 2004). This review discusses different precipitation techniques used for the removal and recovery of toxic metals from effluents.

2.5 Chemical precipitation

Metals can be removed by precipitation as metal oxides/hydroxides, sulphides, carbonates and phosphates. Selective metal precipitants have also been developed in the last few years for the removal of toxic metals from effluents. Oxidation/reduction reactions can also be used for the precipitation of specific metal contaminants, like As and Cr. Most cheaper and efficient technological options often involve biological activities for the precipitation of metals from industrial effluents. Coagulation-flocculation techniques can also be used in combination with precipitation methods to treat metal-contaminated solutions. These methods are discussed in the following sections.

2.5.1 Metal hydroxides

From a chemical point of view, precipitation is a complex phenomenon resulting from the formation of conditions of supersaturation. Simply speaking, it can be described according to the three steps: 1) nucleation or germination, 2) crystalline growth, and 3) flocculation (Patterson 1988).

Nucleation was studied by various authors, in particular, with regard to the removal of zinc and iron originating from the acid mining drainage (Zinck and Aubé 1998). Nucleation or germination corresponds to the appearance of the first germ by condensation of metal salts, followed by the growth of this germ until the stage of supersaturation of the solution and the formation of the solid (Duan and Gregory 2003).

The behavior of a metal in an aqueous solution is controlled by its chemical speciation, i.e. ionic and molecular species which it forms. If there are no other complexing ligands other than the hydroxide (OH^-) ions in solution, the metal cation (M^{z+}) will be often hydrolyzed and the complex obtained is generally a function of the pH. The complexes formed can be cations (e.g., $M(OH)_{z-1}{}^{+}$), neutral molecules (e.g., $M(OH)_{Z}\,(aq)$), or anions (e.g., $M(OH)_{z+1}{}^{-}$), where, Z is the oxidation state of the metal. In addition to these mononuclear complexes, polynuclear species containing more than one metal atom (e.g., $M_X\,(OH)_{xz-2}{}^{2+}$) can be formed. All these reactions of hydrolysis play a significant role in the chemistry of water and, consequently, the solubility of metals in water (Dyer *et al.* 1998).

From a practical point of view, soluble metals can be recovered in insoluble forms as hydroxides according to Equation 1 by using several alkaline reagents, like lime (CaO or $Ca(OH)_2$), $Mg(OH)_2$, NaOH and NH_4OH (Meunier *et al.* 2002, 2006; Mirbagheri and Hosseini 2004; Viadero *et al.* 2006).

Équation 2.1 $\mathbf{M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2\downarrow}$

The precipitation of metals in the form of metal hydroxides can also be achieved by use of by-products, such as fly-ashes from incinerators (Gitari *et al.* 2006).

Majority of metals, namely, Cd, Co, Cu, Mn, Ni and Zn precipitate at a pH greater than six or seven, providing possibilities of separation of the ferric ions (Fe(3+)), which precipitate at a pH lower than five (Brooks 1986; Hayes 1985). The minimal solubility of the hydroxides of the majority of metals is reached at an approximate pH of 9.5- 10.0 (Charerntanyarak 1999; Dyer *et al.* 1998).

The formation of the hydroxides at different pH (according to solubility curves) does not however allow, in the majority of the cases, obtaining a precipitate of good quality (mixed precipitate) due to the potential of coprecipitation coupled with capacity of ionic exchange and adsorption of these hydroxides (Blais *et al.* 1999; Brooks 1986; Couillard and Mercier 1992).

Table 2.2 presents the values of pK_s ($-\operatorname{Log} K_{sp}$) of various metal hydroxides. The descending order of the solubility of hydroxides is noted as follows : Tl(+) > Ba(2+) > Ca(2+) > Ag(+) > Mg(2+) > Mn(2+) > Cd(2+) > Cu(+) ≥ Ni(2+) ≥ Co(2+) > Fe(2+) > Zn(2+) > Pb(2+) > Cr(2+) > Cu(2+) > Be(2+) > Hg(+) > Hg(2+) > Sn(2+) > Cr(3+) > Al(3+) > Fe(3+) > Co(3+) > Tl(3+) > Sb(3+) > Sn(4+).

During precipitation, cyanides cause interference, whereas sequestering agents, like EDTA or NTA, inhibit elimination of metals (Lin *et al.* 1998).

Moreover, presence of highly acidic effluents containing sulphates involves formation of large quantities of secondary precipitates ($CaSO_4.2H_2O$) when alkaline agents such as calcium hydroxide (hydrated lime) are used. This considerably increases quantity of metallic sludges and raises costs of handling and disposal (Baltpurvins *et al.* 1997; Jüttner *et al.* 2000). They can also destabilize primary metal precipitate by inducing formation of colloids and hence solid/liquid separation stage becomes more difficult (Blais *et al.* 1999; Viadero *et al.* 2006). For the given reason, it is often preferable to use alkaline agents such as NaOH and NH_4OH, which form soluble by-products, when recovery of metals is necessary.

2.5.2 Metal sulphides

Metal precipitation as sulphide, which is described in Equation 2, is carried out using reagents like Na_2S, NaHS, H_2S or FeS (Al-Tarazi *et al.* 2004; Marchioretto *et al.* 2005; Robinson and Sum 1980).

Équation 2.2 $M^{2+} + S^{2-} \leftrightarrow MS\downarrow$

In the case of acidic effluents, it is however necessary to carry out initial partial neutralization with a base, such as NaOH, prior to the addition of sulphides (Charerntanyarak 1999). This step is necessary to avoid the formation of pollutant gas, H_2S.

Table 2.3 shows the pK_s values of different metal sulphides. In general, metal sulphides exhibit lower solubility than their hydroxide counterparts, achieving a more complete precipitation, and providing a better stability over a broader pH range (Islamoglu *et al.* 2006). The comparison of Tables 2.2 and 3 shows that the sulphides of following metals are more insoluble than the corresponding hydroxides: Cd(2+), Co(2+), Cu(+), Cu(2+), Fe(2+), Fe(3+), Hg(+), Hg(2+), Pb(2+), Ni(2+), Ag(+), Tl(+), Sn(4+) et Zn(2+).

Precipitation by sulphides also has other advantages when compared with precipitation by hydroxides: 1) the residual metal concentrations in the effluents are lower; 2) the interference of the chelation agents in wastewater is less problematic; 3) precipitation gives better selectivity; 4) high reaction rates result from low hydraulic retention time; 5) sulphide sludges show properties of thickening and drying better than hydroxide sludges, and 6) certain metal sulphides can be treated in the foundries for the recovery of metals (Kim and Amodeo 1983; Kim *et al.* 2002).

However, sulphide precipitation is generally more expensive than hydroxide precipitation. Moreover, there are also safety concerns associated with the possibility of H_2S formation in acidic conditions or when the molar concentrations of sulphide ions exceed the molar concentrations of metals in solution (Veeken and Rulkens 2003).

2.5.3 Metal carbonates

The carbonates, such as $Na_2 CO_3$ and $CaCO_3$, can also be used for the neutralization of solutions and the precipitation of metals (Guillard and Lewis 2002; McAnally *et al.* 1984; Preis and Gamsjager 2001; Sun and Huang 2002). The reaction of carbonate ions and divalent metal ions is illustrated in Equation 3.

Équation 2.3 $\mathbf{M^{2+} + (CO_3)^{2-} \leftrightarrow M(CO_3)\downarrow}$

Table 2.4 presents the values of pK_s of various metal carbonates. The majority of carbonates have solubility greater than the metal hydroxides. In fact, higher values of pK_s are noted only for carbonates of Ba(2+), Ca(2+), Ag(+) et Tl(+) when compared to the corresponding hydroxides.

2.5.4 Metal phosphates

Although seldom practised, it is possible to remove metals in solution through insoluble metal phosphate formation as described in Equation 4 (Mavropoulos *et al.* 2002; Naeem *et al.* 2003; Pigaga *et al.* 2002).

Équation 2.4 $\mathbf{3\ M^{2+} + 2\ (PO_4)^{3-} \leftrightarrow M_3(PO_4)_2\downarrow}$

The addition of soluble salts of phosphate or minerals (e.g. apatite and hydroxyapatite) is a technique which has been proven reliable for the immobilization of metals in the soils and wastes (Bolan *et al.* 2003; McGowen *et al.* 2001; Porter *et al.* 2004).

Table 2.5 presents the values of pK_s of various metal phosphates. The majority of phosphates have lower solubility than the metal hydroxides. In fact, higher values of pKs are noted for following phosphates in comparison with the corresponding hydroxides : Ba(2+), Be(2+), Cd(2+), Ca(2+), Co(2+), Cu(2+), Fe(2+), Hg(+), Pb(2+), Mg(2+), Mn(2+), Ni(2+), Ag(+) et Zn(2+).

2.5.5 Selective precipitating agents

Several precipitating agents have been developed in the last years for chemically precipitating divalent and univalent heavy metals from water and effluents. The most heavy metal chelators being studied currently are dithiocarbamate (DTC) and their ramifications have been well reported (Andrus 2000; Fu *et al.* 2006; Matlock *et al.* 2002). This type of precipitants can be divided into two categories: macromolecular trapping agents and small molecular precipitants.

The first category includes xanthate (Chang *et al.* 2002), polymerized ethylenedichloride-ammonia dithiocarbamates or polydialkylaminedithiocarbamates. Small molecular precipitants are commonly marketed in two forms, diethyldithiocarbamate (DDTC, $(C_2H_5)_2NCS_2Na.3H_2O$) (Andrus 2000) and dimethyldithiocarbamate (DMTC, $(CH_3)_2NCS_2Na.2H_2O$) (Andrus 2000; Fu *et al.* 2006).

One of the most well known is the 2,4,6-trimercapto-1,3,5-triazine, trisodium salt nonahydrate (TMT) ($Na_3S_3C_3N_3.9H_2O$) manufactured by Degussa (Matlock *et al.* 2001). This reagent reacts with divalent ions according to the Equation 5:

Équation 2.5 $$2\,(S_3C_3N_3)^{3-} + 3\,M^{2+} \rightarrow M_3(S_3C_3N_3)_2\downarrow$$

This reagent can be used to precipitate metal ions such as Ag(+), Cd(2+), Hg(+), Hg(2+), Tl(+), Pb(2+) and Zn(2+) from industrial wastewaters and polluted natural waters (Henke *et al.* 2001).

Another chemical reagent for precipitating divalent heavy metals from water is Thio-Red®, which is manufactured by ETUS Inc. This reagent contains potassium/sodium thiocarbonate (STC) ($[Na, K]_2CS_3.nH_2O$) (Henke 1998; Matlock *et al.* 2002). Thio-Red® precipitates metal thiocarbonates (MCS_3, where M = Cd(2+), Cu(2+), Ni(2+), Pb(2+), Zn(2+) and other divalent metal ions), which may be produced through the following generation reaction:

Équation 2.6 $\mathbf{CS_3^{2-} + M^{2+} \rightarrow MCS_3\downarrow}$

Recently, a process of coordination polymerization precipitation has been proposed by Fu *et al.* (2006, 2007). This includes the use of a two dithiocarboxy-group potential bridging ligand, disodium *N,N'*-bis-(dithiocarboxy)piperazine (Na_2BDP) ($(CH_2)_4(NCS_2Na)_2.6H_2O$) for Cu and Ni precipitation from solution.

Dipropyl dithiophosphate has also been proposed by Ying and Fang (2006) as another potential metal precipitating agent. The reaction equation of that molecule (take potassium dipropyl dithiophosphate (PDD) as an example) and heavy metal, such as lead, cadmium, mercury and copper, is as follows:

Équation 2.7 $\mathbf{2\ C_6H_{14}O_2PS_2K + M^{2+} \rightarrow C_{12}H_{28}O_4P_2S_4M\downarrow + 2\ K^+}$

The principal advantages of using metal precipitant agents are: 1) the formation of metal compounds which have a very low solubility and, 2) the lesser production of metallic residue in comparison to the production of metallic sludge using common chemicals, like sodium hydroxyde or lime. However, the high cost of these reagents inhibits their use for different industrial applications (Meunier *et al.* 2002).

2.5.6 Metal oxidation and reduction

Reductive and oxidative techniques may also be used to detoxify or decrease the mobility of metal pollutants in groundwater. This appoach is commonly used in pump and treat operations, but can also be performed *in situ* by injection of the chemical into the groundwater (Evanko and Dzombak 1997). Potassium permanganate, hydrogen peroxide, hypochlorite or chlorine gas can be used for oxidization reactions, whereas reduction reactions are induced by the addition of alkali metals such as sodium, sulphur dioxide, sulphite salts and ferrous sulphate (Vanbroekhoven *et al.* 2005).

2.5.7 Bioprecipitation

The effluents containing metals can also be treated in biological systems in which metals are precipitated by the action of microorganisms (Moller *et al.* 2004). These systems also include passive systems of constructed wetlands (Maine 2006; VanRoy *et al.* 2006), or, of the biological reactors comprising specifically sulphate reducing microorganisms (Kaksonen *et al.* 2003; Mack *et al.* 2004; White *et al.* 1998).

When the groundwater or contaminated surface water are treated in a wetland ecosystem, metals are removed by different processes, including ion exchange, adsorption, absorption, and precipitation followed by different oxidation and reduction reactions of geochemical and biological origin. Principally, in wetland systems, the ion exchange reactions are attributed to contact of metals with humic acids and the organic substances. In addition, oxidation and reduction reactions catalyzed by bacteria present in the aerobic and anaerobic zones of the wetlands play a major role in the precipitation of metals in the forms of hydroxides and sulphides. Precipitated and adsorbed metals elute in the stagnant water basins or are filtered by passage through the plants. The wetlands technology has been very much used during the last decades in the treatment of the acid mine drainage (AMD) (Sheoran and Sheoran 2006; USEPA 1993).

Several types of reactors have been devised for the removal of metals by means of the sulphide generated by sulphate-reducing bacteria (Wildeman *et al.* 1995). The responsible microorganisms are notably species of *Desulphovibrio*. The sulphide formed by these anaerobes has also been used to treat metal-contaminated groundwater pumped through a biological treatment system (Barnes *et al.* 1994).

2.5.8 Coagulation-flocculation

Coagulating agents such as aluminium and iron salts are often added after metal precipitation to favorize the precipitates separation (Duan and Gregory 2003; Licskó 1997). This coagulation process destabilizes colloidal particles and improves their sedimentation. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky particles (Semerjian and Ayoub 2003). Organic polymers which are made of modified polyacrylamide are usually used for this flocculation step (Charerntanyarak 1999; Viadero *et al.* 2006). Iron/cationic polymer blends and aluminium/cationic polymer blends are also available in the market (Andrus 2000). The metal precipitates separation is carried out in a settling tank (Alves *et al.* 2005). The resulting metallic sludge can be dewatered by filtration (Viadero *et al.* 2006).

2.6 Metallic pollutants

Majority of the metal elements in the periodic table of the elements can be toxic when they are adsorbed in higher concentration by the living organisms (Kabata-Pendias 2001; Lippmann 2000). However, certain toxic metals are normally present in the environment at elevated concentrations, are the subject of investigation for public health and animal protection authorities. As an example, USEPA indexes a dozen priority metal contaminants. These metals include : Antinomy (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Tl), and Zinc (Zn). Table 2.6 summarizes the principal problems of human toxicity associated with these pollutants. The following sections describe some significant characteristics of these contaminants, as well as their behavior compared to various techniques of precipitation.

2.6.1 Antimony

In antimony compounds, the most common oxidation states are 5+, 3+, and 3-. Antimony exists mainly as Sb(3+) and Sb(5+) in environmental, biological, and geochemical samples (Filella *et al.* 2002). Under oxic conditions, antimony is usually present as Sb(5+) in solution, whereas Sb(3+) is dominant in anoxic systems. SbO_2^+ is the species of Sb(5+) existing in solution under very acidic conditions and the anion $[Sb(OH)_6]^-$ is the main species present under mildly acidic, neutral, and alkaline conditions.

The trivalent form of Sb is usually more toxic than the pentavalent form (Flynn *et al.* 2003). The relatively low solubility ($pK_s = 49.1$) of antimony hydroxide ($Sb(OH)_3$) in water limits the ionic species formed by Sb(3+) in solution. Sb(3+) is present as $Sb(OH)_2^+$ in acidic media and as $Sb(OH)_4^-$ under basic conditions. The free Sb^{3+} ion is stable in solution only in highly acidic media. In anoxic conditions, and in the presence of sulphur, antimony forms insoluble stibnite, $Sb_2S_{3(s)}$, and soluble SbS_2^{2-}, depending on pH.

2.6.2 Arsenic

Arsenic, a metalloid, exists in the soil environment as arsenite (As 3+) or as arsenate (As 5+) (Terlecka 2005). Both forms of this element are highly toxic. However, arsenate is less water soluble than arsenite and is relatively immobile in soil (Magalhaes 2002). Arsenite compounds (e.g. AsO_3^{3-}) can be formed in anaerobic conditions by reduction of arsenate (e.g. AsO_4^{3-}). The most common method of removing arsenic from aqueous process streams is to precipitate the sulphide As_2S_3, or metal arsenates (Leist *et al.* 2000; Magalhaes 2002; USEPA 1992). Arsenic(5+) can be precipitated from process solutions below about pH = 2 with Fe(3+) to form ferric arsenate ($FeAsO_4.2H_2O$, $pK_s = 20.3$). Other metal arsenate precipitates (e.g. calcium/magnesium arsenates) can also be formed as it shown in Table 2.7. Arsenite present in water can be biologically-oxidized in arsenate, which is precipitated out more readily by treatment with ferric ions (Williams and Silver 1984). Arsenic chemistry and removal technologies have been reviewed by Jiang (2001) and Leist *et al.* (2000).

2.6.3 Beryllium

Beryllium occurs most often as the divalent cation. The principal ions are BeO_2^{2-}, $Be_2O_3^{2-}$, BeO^{6-} and Be_2O^{2+}. In the alkaline environment, Be forms complex anions such as $Be(OH)CO_3^-$ and $Be(CO_3)_2^{2-}$. Be is uncommon in natural waters but is sometimes found as the chloride, nitrate and sulphate salts. These compounds are relatively soluble in water in the following the sequence: $Cl^- > NO_3^- > SO_4^{2-}$. Be also forms soluble complexes with anions such as citrate, fluoride, oxalate, and phosphates. Be containing effluent can notably be treated by formation of insoluble $Be(OH)_2$

($pK_s = 21.1$) using caustic soda (Sankhesara and Kamath 1980). Be can also be efficiently removed from solution as Be phosphate ($Be_3(PO_4)_2$, $pK_s = 38.6$). The environmental chemistry of Be has been discused in details by Taylor *et al.* (2003) and Vesely *et al.* (2002).

2.6.4 Cadmium

Cadmium (Cd) is almost always found in the 2+ valence state. In solution, Cd occurs in different forms (Cd^{2+}, $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdCl_3^-$, $CdCl_4^{2-}$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ and organic chelates). Cd forms several complexes with anions: halides, nitrate, sulphate, thiosulphate, ammonia and cyanide, generally not very stable. A large number of salts and basic salts of Cd are sparingly soluble or very sparingly soluble, i.e., hydroxide ($pK_s = 13.6$), carbonate ($pK_s = 12.0$), phosphate ($pK_s = 32.6$) and sulphide ($pK_s = 26.1$).

2.6.5 Chromium

Cr shows highly variable oxidation states (2+, 3+ and 6+) and it is also known to form complex cationic and anionic ions (e.g., $Cr(OH)_2^+$, CrO_4^{2-}). Naturally occuring Cr compounds have principal valences of 3+ (chromic) and 6+ (chromate). The hexavalent form ($HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$) is toxic and highly soluble in water, whereas trivalent form is considerably less toxic, less water soluble, and hence less mobile in soil.

The Cr(3+) ions form complexes with chlorides, fluorides, sulphates, ammonium salts, cyanides, sulphocyanides, oxalates and citrates. In most cases, the trivalent chromium can be efficiently removed from solution by precipitation as chromium hydroxyde ($Cr(OH)_3$, $pK_s = 30.2$).

Although most heavy metals can be precipitated readily by pH adjustment, Cr(6+) is highly soluble and does not precipitate out of solution at any pH adjustment. Consequently, treatment for Cr(6+) usually consists of a two-stage process (Avudainayagam *et al.* 2003). First, the reduction of Cr(6+) to Cr(3+) and, second, the precipitation of Cr(3+) as $Cr(OH)_3$. Reducing agents commonly used are sulphur dioxide or a solution of sodium bisulphate. Other suitable reducing agents include sodium sulphite, sodium hydrosulphite, and ferrous sulphite. Cr(6+) present in soils and the groundwater can also be reduced biologically to Cr(3+) following addition of an organic substrate (e.g. manure, benzoate, molasses) (Chirwa and Wang 1997; Losi *et al.* 1994). The reduction of hexavalent chromium could equally be done by generation of H_2S in anaerobic medium in the presence of sulphates (Sulzbacher *et al.* 1997).

The chromates of the alkali metals, and also ferric, cupric, manganous and magnesium chromates are soluble, but the majority of the chromates of the other metals (e.g. Ba, Pb, Ag and Tl) are rather insoluble (Table 2.8).

2.6.6 Copper

Cu ions can exist in both an oxidized, cupric (Cu^{2+}), or reduced, cuprous (Cu^{+}), state. Monovalent Cu forms complexes with chloride, nitrate, ammonia and thiosulphate, and salts which are sparingly soluble such as cyanide, chloride, bromide, iodide, and sulphocyanide. The precipitation of Cu(+) as sulphide (Cu_2S, $pK_s = 47.6$) is a more efficient option than as a copper hydroxyde ($Cu(OH)$, $pK_s = 14.7$).

Divalent Cu forms complexes with chloride, amine, sulphocyanide, bromide, iodide, nitrate, oxalate, and pyrophosphate, and soluble salts with the exception of ferrocyanide, sulphide and carbonate. The solubility of copper hydroxide ($Cu(OH)_2$, $pK_s = 18.6$) and carbonate ($CuCO_3$, $pK_s = 11.5$) is much greater than the solubility of copper phosphate ($Cu_3(PO_4)_2$, $pK_s = 36.9$) and sulphide (CuS, $pK_s = 35.2$). Cu precipitation in wastewater has been reviewed in details by Baltpurvins *et al.* (1996a).

2.6.7 Mercury

Mercury (Hg) exists in three oxidation states: Hg(0), Hg(1+), and Hg(2+). Anthropogenic sources of mercury are numerous and occur worldwide (Lippmann 2000). Mercury and its derivatives constitute toxins that accumulate slowly and are dangerous to life forms (Boszke *et al.* 2002). Mercuryl ions (Hg^{2+}) generally form weaker complexes than do mercury ions (Hg_2^{2+}). Hg^0 and $(CH_3)_2Hg$ are easily volatile fractions, whereas $HgCl_2$, Hg(OH)Cl and $Hg(OH)_2$ are easily soluble compounds.

The following compounds of monovalent mercury are sparingly soluble: the halide, the chromate (Hg_2CrO_4, $pK_s = 8.7$) and the sulphide (Hg_2S, $pK_s = 47.0$). Divalent mercury forms the following weakly soluble compounds: iodide, thiocyanic and sulphide (HgS, $pK_s = 52.4$). Moreover, Hg(2+) forms a large number of complexes which are often quite stable: chloride, hydrobromic, hydroiodic, thiocyanic, amine, sulphurous and thiosulphuric complexes.

Methods and technologies use to remove mercury from then environment have been recently reviewed by Atwood and Zaman (2006). Removal of mercury by precipitating out using a sulphur-containing ligand is an economical and efficient option. Sodium or potassium dimethyldithiocarbamate (SDTC) and sodium thiocarbonate (STC) are the most used reagents for Hg removal from effluent. Trisodium salt of 2,4,6-trimercaptotriazine (TMT) is also a chemical reagent largely used for precipitating divalent and univalent heavy metals. However, this ligand is even less effective than those mentionned earlier. TMT forms unstable complexes with mercury. New efficient thiol-based ligands have been developed for Hg removal from effluent. This includes pyridine-2-6-diamineethanethiol ($PyDETH_2$) and benzene-1,3-diamidoethanethiol ($BDETH_2$) (Atwood and Zaman 2006).

2.6.8 Nickel

The Ni(2+) form is most commonly found in aquatic and soil environments (Denkhaus and Salnikow 2002; Watts 1998). The most prevalent Ni species in solution are Ni^{2+}, $NiOH^+$, $HNiO_2^-$ and $Ni(OH)_3^-$. Nickel salts are reasonably soluble in water, except the ferri- and ferrocyanides, sulphide (NiS, $pK_s = 18.5$ to 25.7) and phosphate ($Ni_3(PO_4)_2$, $pK_s = 31.3$). Likewise, the existence of the following complexes of Ni is known: hydrochloric and sulphuric (very stable), amine (fairly stable), oxalic, thiocyanide, metaphosphoric, pyrophosphoric and cyanide complexes.

2.6.9 Lead

Lead exists in two oxidation states: Pb(2+) and Pb(4+). Lead is one of the heavy metals with relatively lower mobility and a tendency to adsorb to organic matter, clays and oxide/hydroxide complexes by forming precipitates (Khan and Frankland 1983) such as Pb carbonates ($PbCO_3$, $2PbCO_3Pb(OH)_2$, $4PbCO_3.2Pb(OH)_2$) (Mercier *et al.* 2002; Zimdahl and Skogerboe 1977), orthophosphates of Pb, primary pyromorphites and plumbogummites (last three formed in anaerobic environment) (Nriagu 1974). The Pb(2+) forms complexes which are slightly stable with nitrate, chloride, and cyanide, and other fairly stable complexes with acetic, organic hydroxyl and thiosulphuric acids. Moreover, sparingly soluble salts of divalent Pb are the chloride, bromide, iodide, fluoride, sulphate ($PbSO_4$, $pK_s = 31.3$) and carbonate ($PbCO_3$, $pK_s = 13.1$). Lead sulphide (PbS, $pK_s = 27.0$) and phosphate ($Pb_3(PO_4)_2$, $pK_s = 43.5$) are much less soluble than lead hydroxide ($Pb(OH)_2$, $pK_s = 16.1$).

2.6.10 Selenium

Selenium, like sulphur, has four different oxidation states: selenide (Se(2-)), elemental Se (Se(0)), selenite (Se(4+) and selenate (Se(6+)). Under strongly reducing conditions, Se(2-) is stable and exists as insoluble metal selenides (Table 2.9). In the moderate redox potential condition Se(4+) is the major species, whereas Se(6+) is predominant at high redox potentials (Séby *et al.* 2001). The biological reduction of the selenate and selenite can be used for formation of elementary Se which is less toxic and insoluble. The dominant hydrolysis complexes for the 2-, 4+ and 6+ oxidation states of Se are HSe^-, $HSeO_3^-$, and SeO_4^{2-}, respectively, in the pH range of 3 to 9. Se(4+) can be notably removed from solution by precipitation using ferric salts (Sasidhar *et al.* 1991).

2.6.11 Silver

Silver is found in the environment in four oxidation states: 0, 1+, 2+, and 3+, with 0 and 1+ being the most common, while 2+ and 3+ are seldom seen naturally in the environment. Ag can form several ionic species, such as simple cations (Ag^+, Ag^{2+}, AgO^+) and complexed anions, mainly with Cl and S : $AgCl_2^-$, $AgCl_3^{2-}$, $AgCl_4^{3-}$, $Ag(HS)_2^-$, $Ag_2S_3H_2^{2-}$, $Ag(S_2O_3)_2^{3-}$, and $Ag(SO_4)_2^{3-}$. Silver forms a large number of complexes, some of which are very stable, e.g. the thiosulphuric and cyanide complexes. Almost all silver salts are sparingly soluble; the nitrate, perchlorate, fluoride, acetate and chlorate are soluble. Humic substances are also known to absorb and complex Ag. Soluble Ag can be notably removed from effluent by precipitation as $AgCl_{(s)}$ ($pK_s = 9.8$) using a chloride salt (e.g. NaCl) (Hendrickson *et al.* 1984).

2.6.12 Thallium

In geochemical environments, Tl is known to occur in three oxidation states, 1+, 2+, and 3+ (Glaser 1995). Tl(3+) concentration in solution is normally very low when the pH > 3.0 (Lin and Nriagu 1998). By contrast, Tl(1+) is very soluble. Thallium can be removed from solution by precipitation using lime or caustic at pH 8 to 10 (Twidwell and Williams-Beam 2002). If thallous ions are present sodium hypochlorite can be added as a preliminary step to oxidize the thallous specie to the thallic form. Thallic hydroxide precipitates along with other metal hydroxides. The slurry is then treated by conventional coagulation.

2.6.13 Zinc

Zinc is almost always found in the Zn(2+) valence state. Zinc is highly mobile metal present in groundwater in soluble forms at neutral and acidic pH (Smith *et al.* 1995). Zinc forms complexes with amine, cyanide, thiocyanide, oxalic and hydrochloric complexes, and others with ethylene diamine, pyridine, aniline and hydrazine. There is a large number of sparingly soluble Zn compounds, including the following: cobalticyanide, ammonia-zinc phosphate, the iodate and $ZnCO_3$ ($pK_s = 10.0$). Zinc sulphide ($pK_s = 23.0\text{-}24.3$) and phosphate ($pK_s = 35.4$) are much less soluble than zinc hydroxide ($pK_s = 15.7$).

2.7 Computer modelling for metals precipitation

Many computer programs have been developed to predict metal speciation in natural waters, soil solutions, synthetic solutions and industrial effluents (Chaston *et al.* 1996; Del Piero *et al.* 2006; Suarez and Goldberg 1994). A list of different computer programs for metal speciation is given in Table 2.10. These models can be used to get good approximations of the residual metal concentrations in solution for different metal precipitation and leaching scenarios (Accornero *et al.* 2005; Apul *et al.* 2005; Gomez del Rio *et al.* 2006; Ettler *et al.* 2006; Halim *et al.* 2005). However, there is a lack of computer software or mathematical model allowing to compare, from a techno-economic point-of-view (chemicals consumption and cost, sludge management (dewatering, transportion, disposal) cost, e.g.), different methods of metal precipitation. There is a need to develop such tools which could be largely used in different industries like metallurgy, mining, metal finishing, and petrochemistry.

2.8 Aknowledgments

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2.9 References

Accornero, M., Marini, L., Ottonello, G., and Zuccolini, M.V. (2005) “The fate of major constituents and chromium and other trace elements when acid waters from the derelict Libiola mine (Italy) are mixed with stream waters. *Appl. Geochem.*, 20, 1368-1390.

Al-Asheh, S., and Duvnjak, Z. (1999) “Sorption of heavy metals from synthetic metal solutions and industrial wastewater using plant materials”. *Water Qual. Res. J. Can.*, 34(3), 481-503.

Alderighi, L., Gans, P., Ienco, A., Peters, D., Sabatini, A., and Vacca, A. (1999) “Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species”. Coordination Chem. Rev., 184, 311-318.

Aldrich, C., and Feng, D. (2000) “Removal of heavy metals from wastewater effluents by biosorptive flotation”. *Min. Eng.*, 13(10-11), 1129-1138.

Allen, H.E. (2002) *Bioavailability of metals in terrestrial ecosystems : importance of partitioning for bioavailability to invertebrates, microbes, and plants*. Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida, USA, 176 p.

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. (1991) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0. User’s manual*. Report EPA/600/3-91/021, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgia, USA.

Al-Tarazi, M., Heesink, A.B.M., and Versteeg, G.F. (2004) “Precipitation of metal sulphides using gaseous hydrogen sulphide: mathematical modelling”. *Chem. Eng. Sci.*, 59(3), 567-579.

Alves, L.C., Henrique, H.M., Xavier, A.M.F., and Cammarota, M.C. (2005) "Potential treatment alternative for laboratory effluents". *Bioresource Technol.*, 96, 1650-1657.

Andrus, M.E. (2000) "A review of metal precipitation chemicals for metal-finishing applications". *Met. Finish.,* 11, 20-23.

Apul, D.S., Gardner, K.H., Eighmy, T.T., Fallman, A.M., and Comans, R.N.J. (2005) "Simultaneous application of dissolution/precipitation and surface complexation/surface precipitation modeling to contaminant leaching". *Environ. Sci. Technol.*, 39(15), 5736-5741.

Arienzo, M., Chiarenzelli, J., and Scrudato, R. (2001) "Remediation of metal-contaminated aqueous systems by electrochemical peroxidation: an experimental investigation". *J. Hazard. Mater.*, 87(1-3), 187-198.

Atwood, D.A., and Zaman, M.K. (2006) "Mercury removal from water". *Struct. Bond.,* 120, 163-182.

Avudainayagam, S., Meghraj, M., Owens, G., Kookana, R.S., Chittleborough, D., and Naidu, R. (2003) "Chemistry of chromium in soils with emphasis on tannery waste sites". *Rev. Environ. Contam. Toxicol.*, 178, 53-91.

Baath, E. (1989) "Effects of heavy metals in soil on microbial processes and populations (a review)". *Water Air Soil Pollut.*, 47, 335-379.

Babel, S., and Kurniawan, T.A. (2003) "Low-cost adsorbents for heavy metals uptake from contaminated water: a review". *J. Hazard. Mater.*, 97(1-3), 219-243.

Bailey, S.E., Olin, T.J., Bricka, R.M., and Arian, D. (1999) "A review of potentially low-cost sorbents for heavy metals". *Water Res.,* 33(11), 2469-2479.

Ball, J. (2002) *User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters (program version 2.46)*. Report 91-183, United States Geological Survey, Reston, VA, USA.

Ball, J., Nordstrom, D.K., Zachmann, D.W. (1987) *WATEQ4F-A personal computer fortran translation of the geochemical model WATEQ2 with revised data base*. Report 87-50, United States Geological Survey, Menlo Park, CA, USA.

Baltpurvins, K.A., Burns, R.C., and Lawrance, G.A. (1996a) "Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation". *Waste Manag*., 16(8), 717-725.

Baltpurvins, K.A., Burns, R.C., and Lawrance, G.A. (1996b) "Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater". *Environ. Sci. Technol*., 30, 1493-1499.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., and Stuart, A.D. (1997) "Effect of electrolyte composition on zinc hydroxide precipitation by lime". *Water Res*., 31, 973-980.

Barak, P. (1990) "SPECIES: a spreadsheet program for modeling speciation of soil solution". *J. Agron. Educ*., 19, 44-46.

Barnes, L.J., Scheeren, P.J.M., and Buisman, C.J.N. (1994) *Emerging technology for bioremediation of metals*. Means, J.L., and Hinchee, R.E. (Eds.), Lewis Publishers, Boca Raton, Florida, USA, pp. 38-49.

Beauchesne, I., Ben Cheikh, R., Mercier, G., Blais, J.F and T. Ouarda, Chemical treatment of sludge: In-depth study on toxic metal removal efficiency, dewatering ability and fertilizing property preservation, Water Res. 41 (2007) 2028-2038.

Belkhouche, N.E., Didi, M.A., and Villemin, D. (2005) "Separation of nickel and copper by solvent extraction using Di-2 ethylhexylphosphoric acide-based synergistic mixture". *Solvent Extraction Ion Exchange*, 23(5), 677-693.

Ben Frarès, N., Taha, S., and Dorange, G. (2005) "Influence of the operating conditions on the elimination of zinc ions by nanofiltration. *Desalination,* 185, 245-253.

Bhavsar, S.P., Diamond, M.L., Gandhi, N., and Nilsen, J. (2004) "Dynamic coupled metal transport-speciation model: application to assess a zinc-contaminated lake". *Environ. Toxicol. Chem.*, 23(10), 2410-2420.

Blais, J.F., Dufresne, S., and Mercier, G. (1999) "State of the art of the technological development from metal removal from industrial effluents". *J. Water Sci*., 12(4), 689-713 (in French).

Bolan, N.S., Adriano, D.C., Duraisamy, P., Mani, A., and Arulmozhiselvan, K. (2003) "Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition". *Plant Soil*, 250(1), 83-94.

Boszke, L., Glosinska, G., and Siepak, J. (2002) "Some aspects of speciation of mercury in a water environment". *Polish J. Environ. Studies*, 11(4), 285-298.

Brenneisen, P., Steinbrenner, H., and Sies, H. (2005) "Selenium, oxidative stress, and health aspects". *Mol. Aspects Med*., 26, 256-267.

Brooks, C.S. (1986) "Metal recovery from industrial wastes". *J. Metals*, 38, 50-57.

Brooks, C.S. (1991) *Metal recovery from industrial wastes*. Lewis Publishers, Inc., Chelsea, Michigan, USA.

Caussy, D., Gochfeld, M., Gurzau, E., Neagu, C., and Ruedel, H. (2003) “Lessons from case studies of metals: investigating exposure, bioavailability, and risk”. *Ecotoxicol. Environ. Safety*, 56, 45-51.

Chang, Y.K., Chang, J.E., Lin, T.T., and Hsu Y.M. (2002) “Integrated copper-containing wastewater treatment using xanthate process”. *J. Hazard. Mater*., B94, 89-99.

Chapman, P.M., Wang, F., Janssen, C.R., Goulet, R.R., and Kamunde, C.N. (2003) “Conducting ecological risk assessments of inorganic metals and metalloids: current status”. *Hum. Ecol. Assess*., 9, 641-697.

Charerntanyarak, L. (1999) “Heavy metals removal by chemical coagulation and precipitation”. *Water Sci. Technol.,* 39(10-11), 135-138.

Chaston, S., Grassia, G.S., and Sheehy, A.J. (1996) “The next iteration factor (NIF) method for calculating equilibrium conditions in subsurface wasters, for the isolation of microorganisms from petroleum reservoirs”. *Aust. J. Chem*., 49, 943-949.

Chirwa, E.M.N., and Wang, Y.T. (1997) “Hexavalent chromium reduction by *Bacillus* sp. in a packed-bed bioreactor”. *Environ. Sci. Technol*., 31, 1446-1451.

Clarkson, T.W. (1998) “Human toxicology of mercury”. *J. Trace Elements Exp. Med*., 11, 303-317.

Couillard, D., and Mercier, G. (1992) Précipitations sélectives des métaux solubilisés biologiquement de boues aérobies d’épuration. *Can. J. Chem. Eng*., 70, 1021-1029 (in French).

Dabrowski, A., Hubicki, Z., Podkoscielny, P., and Robens, E. (2004) "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method". *Chemosphere*, 56, 91-106.

Davydova, S. (2005) "Heavy metals as toxicants in big cities". *Microchem. J.*, 79, 133-136.

Del Piero, S., Melchior, A., Polese, P., Portanova, R., and Tolazzi, M. (2006) "A novel multipurpose Excel tool for equilibrium speciation based on Newton-Raphson method and on a hybrid genetic algorithm". *Annali di Chimica*, 96, 1-21.

Denkhaus, E., and Salnikow, K. (2002) "Nickel essentiality, toxicity and carcinogenicity". *Crit. Rev. Onc./Hemat.*, 42, 35-56.

DiPalma, L., Ferrantelli, P., Merli, C., and Petrucci, E. (2003) "Treatment of the solution extracted from metal contaminated soils by reverse osmosis and chemical precipitation". *Annali Di Chimica*, 93(12), 1005-1011.

Djedidi, Z., Drogui, P., Ben Cheikh, R., Mercier, G., and Blais, J.F. (2005) "Laboratory study of successive soil saline leaching and electrochemical lead recovery". *J. Environ. Eng. Div. ASCE*, 131(2), 305-314.

Doyle, F.M. (2003) "Ion flotation - its potential for hydrometallurgical operations". *Int. J. Min. Proc.*, 72(1-4), 387-399.

Drake, P.L., and Hazelwood, K.J. (2005) "Exposure-related health effects of silver and silver compounds: a review". *Ann. Occup. Hyg.*, 49(7), 575-585.

Duan, J., and Gregory, J. (2003) "Coagulation by hydrolysing metal salts". *Adv. Colloid Interface Sci.*, 100-102, 475-502.

Dustan, A.C., Cohen, B., Petrie, J.G., 2005. Modelling dewatering behaviour through an understanding of solids formation processes. Part II – Solids separation considerations. Adv. Colloid Interface Sci. 113 (2-3), 85-97.

Dyer, J.A., Scrivner, N.C., and Dentel, S.K. (1998) "A practical guide for determining the solubility of metal hydroxides and oxides in water". *Environ. Prog*., 17(1), 1-8.

Efline, G.S. (1986) *Method of removing heavy metal from wastewater streams*. U.S. Patent, no. 4,612,125.

Efline, G.S. (1987) *Method of removing heavy metal from wastewater streams*. U.S. Patent, no. 4,678,584.

Ettler, V., Matura, M., Mihaljevic, M., and Bezdicka, P. (2006) "Metal speciation and attenuation in stream waters and sediments contaminated by landfill leachate". *Environ. Geol*., 49(4), 610-619.

Evenko, C.R., and Dzomback, D.A. (1997) *Remediation of metals-contamined soils and groundwater*. Technology evaluation report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvania, USA, 53 p.

Felmy, A.R., Girvin, D.C., and Jenne, E.A. (1984) *MINTEQ: a computer program for calculating aquous geochemical equilibria*. Report EPA/600/3-84/032, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgia, USA.

Feng, D., Aldrich, C., Tan, H., 2000. Treatment of acid mine drainage by use of heavy metal precipitation and ion exchange. Min. Eng. 13 (6), 623-642.

Filella, M., Belzile, N., and Chen, Y.W. (2002) “Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry”. *Earth-Sci. Rev.*, 59, 265-285.

Florea, A.M., and Büsselberg, D. (2006) “Occurence, use and potential toxic effects of metals and metal compounds”. *BioMetals*, 19, 419-427.

Flynn, H.C., Meharg, A.A., Bowyer, P.K., and Paton, G.I. (2003) “Antimony bioavailability in mine soils”. *Environ. Pollut.,* 124(1), 93-100.

Fraga, C.G. (2005) “Relevance, essentiality and toxicity of trace elements in human health”. *Mol. Aspects Med.*, 26, 235-244.

FRTR (2005) *Federal remediation technologies roundtable*. Website "http://www.frtr.gov", [cited December, 1, 2005].

Fu, F., Chen, R., and Xiong, Y. (2006) “Application of a novel strategy - coordination polymerization precipitation to the treatment of Cu^{2+}-containing wastewaters”. *Sep. Purif. Technol.*, 52(2), 388-393.

Fu, F., Chen, R., and Xiong, Y. (2007) “Comparative investigation of N,N'-bis-(dithiocarboxy)piperazine and diethyldithiocarbamate as precipitants for Ni(II) in simulated wastewater”. *J. Hazard. Mater.*, (in press).

Galvin, R.M. (1996) “Occurrence of metals in waters: an overview”. *Water SA*, 22(1), 7-18.

Gans, P., Sabatini, A., and Vacca, A. (1996) “Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs”. *Talanta*, 43(10), 1739-1753.

Gaetke, L.M., and Chow, C.K. (2003) "Copper toxicity, oxidative stress, and antioxidant nutrients". *Toxicol.*, 189, 147-163.

Galvan-Arzete, S., and Santamaria, A. (1998) "Thallium toxicity". *Toxicol. Lett.*, 99, 1-13.

GardeaTorresdey, J.L., delaRosa, G., and PeraltaVidea, J.R. (2004) "Use of phytofiltration technologies in the removal of heavy metals: A review". *Pure Appl. Chem.*, 76(4), 801-813.

Gebel, T. (1997) "Arsenic and antimony: comparative approach on mechanistic toxicology". *Chemico-Biological Interactions*, 107, 131-144.

Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., and Okujeni, C. (2006) "Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements". *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng.*, 41(8), 1729-1747.

Glaser, J. (1995) "Advances in thallium aqueous solution chemistry". *Adv. Inorg. Chem.*, 43, 1-78.

Goldhaber, S.B. (2003) "Trace element risk assessment: essentiality vs. toxicity". *Regulatory Toxicol. Pharmacol.*, 38, 232-242.

Gomez del Rio, J., Sanchez, P., Morando, P.J., and Cicerone, D.S. (2006) "Retention of Cd, Zn and Co on hydroxyapatite filters". *Chemosphere*, 64, 1015-1020.

Guillard, D., and Lewis, A.E. (2002) "Optimisation of nickel hydroxycarbonate precipitation using a laboratory pellet reactor". *Ind. Eng. Chem.*, 41, 3110-3114.

Halim, C.E., Short, S.A., Scott, J.A., Amal, R., and Low, G. (2005) "Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC". *J. Hazard. Mater.*, 125(1-3), 46-61.

Hayes, P.C. (1985) *Process selection in extractive metallurgy*. Hayes Publishing Co., Brisbane, Australia.

Hendrickson, J.J., Benjamin, M.M., Ferguson, J.F., and Goebel, L. (1984) "Removal of silver and mercury from spent COD test solutions". *J. Water Pollut. Control Fed.,* 56(5), 468-473.

Henke, K.R. (1998) "Chemistry of heavy metal precipitates resulting from reactions with Thio-Red". *Water Environment Res.*, 70(6), 1178-1185.

Henke, K.R., Hutchinson, A.R., Krepps, M.K., and Atwood, D.A. (2001) "The chemistry of 2,4,6-trimercapto-1,3,5-triazine (TMT): acid dissolution constants and group 2 complexes". *Inorg. Chem.*, 40(17), 4443-4447.

Hove, M., van Hill, R.P., Lewis, A.E., 2008. Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. Chem. Eng. Sci. 63, 1626-1635.

HydroGeoLogic (1998a) *Diffuse-layer sorption reactions for use in MINTEQA2 for HWIR metals and metalloids*. United States Environmental Protection Agency, National Exposure Research Laboratory, Ecosystem Research Division, Athens, Georgia, USA.

HydroGeoLogic (1998b) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: user manual supplement for version 4.0*. Report for United States Environmental Protection Agency, National Exposure Research Laboratory, Ecosystem Research Division, Athens, Georgia, USA.

Islamoglu, S., Yilmaz, L., and Ozbelge, H.O. (2006) “Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents”. *Sep. Sci. Technol.*, 41(15), 3367-3385.

Jain, C.K., and Ali, I. (2000) “Arsenic: occurence, toxicity and speciation techniques”. *Water Res.*, 34(17), 4304-4312.

Jiang, J.Q. (2001) “Removing arsenic from groundwater for the developing world - a review”. *Water Sci. Technol.*, 44(6), 89-98.

Juang, R.S., and Wang, S.W. (2000) “Electrolytic recovery of binary metals and EDTA from strong complexed solutions”. *Water Res.*, 34(12), 3179-3185.

Juang, R.S., Lin, S.H., and Wang, T.Y. (2003) “Removal of metal ions from the complexed solutions in fixed bed using a strong acid ion exchange resin”. *Chemosphere.*, 53(10), 1221-1228.

Jüttner, K., Galla, U., and Schmieder, H. (2000) “Electrochemical approaches to environmental problems in the process industry”. *Electrochim. Acta*, 45, 2575-2594.

Kabata-Pendias, A. (2001) *Trace elements in soils and plants. 3rd Edition*. In: Kabata-Pendias, A., and H. Pendias (Eds.), CRC Press LLC, Boca Raton, Florida, USA, 413 p.

Kaksonen, A.H., Riekkola-Vanhanen, M.L., and Puhakka, J.A. (2003) “Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater”. *Water Res.*, 37(2), 255-266.

Kamal, M., Ghaly, A.E., Mahmoud, N., and Côté, R. (2004) “Phytoaccumulation of heavy metals by aquatic plants”. *Environ. Int.*, 29(8), 1029-1039.

Kapoor, A., and Viraraghavan, T. (1995) “Fungal biosorption - an alternative treatment option for heavy metal bearing wastewaters : a review”. *Bioresource Technol*., 53, 195-206.

Kazantzis, G. (2000) “Thallium in the environment and health effects”. *Environ. Geochem. Health*, 22, 275-280.

Khan, D.H., and Frankland, B. (1983) “Chemical forms of Cd and lead in some contaminated soils”. *Environ. Pollut. Ser. B*, 6, 15-31.

Kharaka, Y.K., and Barnes, L.J. (1973) *SOLMNEQ: solution-mineral equilibrium computations*. Report PB-215899, United States Geological Survey, Computer Contributions, National Technical Information Service, United States Gov. Print. Office, Washington, DC, USA.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., and DeBraal, J.D. (1988) *SOLMNEQ.88: a computer program for geochemical modeling of water-rock interactions*. Report 88-4227, United States Geological Survey, Water Resources Investigations, Reston, VA, USA.

Kim, B.M., and Amodeo, P.A. (1983) “Calcium sulphide process for treatment of metal-containing wastes”. *Environ. Progress*, 2, 175-180.

Kim, B.R., Gaines, W.A., Szafranski, M.J., Bernath, E.F., and Miles, A.M. (2002) “Removal of heavy metals from automotive wastewater by sulphide precipitation”. *J. Environ. Eng. Div. ASCE*, 128(7), 612-623.

Kobayashi, J. (1978) *Pollution by cadmium and the itai-itai disease in Japan*. In: Oehme, F.W. (Ed.), Toxicity of heavy metals in the environment, Marcel Dekker, New York, NY, USA, pp. 199-260.

Korfali, S.I., and Davies, B.E. (2004) “Speciation of metals in sediment and water in a river underlain by linestone: role of carbonate species for purification capacity of rivers”. *Adv. Environ. Res.*, 8, 599-612.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., and Babel, S. (2006) “Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals”. *Sci. Total Environ.*, 366(2-3), 409-426.

Lai, C.L., and Lin, K.S. (2006) “Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation”. *J. Hazard. Mater.*, 136(2), 183-187.

Lazaridis, N.K., Matis, K.A., and Webb, M. (2001) “Flotation of metal-loaded clay anion exchangers. Part I: the case of chromate”. *Chemosphere*, 42, 373-378.

Leist, M., Casey, R.J., and Caridi, D. (2000) “The management of arsenic wastes: problems and prospects”. *J. Hazard. Mater.,* B76, 125-138.

Leung, V.W.H., and Darvell, B.W. (1990) “The ramases algorithm for multiple equilibria – III acceleration and standardized formation constants (RAMASES II)”. *Talanta*, 37(4), 425-429.

Levasseur, B., Blais, J.F., and Mercier, G. (2005) “Study of the metal precipitation from decontamination leachates of municipal wastes fly ash incinerators”. *Environ. Technol.*, 26(4), 421-431.

Licskó, I. (1997) “Realistic coagulation mechanisms in the use of aluminium and iron(III) salts”. *Water Sci. Technol.*, 364, 103-110.

Lin, S.H., Kao, H.C., Huang, S.H., and Juang, R.S. (2002) "Equilibrium and kinetic studies of the extraction of chelated copper(II) anions with Aliquat 336". *J. Chem. Technol. Biotechnol.*, 77(2), 168-174.

Lin, S.H., Kao, H.C., Huang, S.H., and Juang, R.S. (2002) "Equilibrium and kinetic studies of the extraction of chelated copper(II) anions with Aliquat 336". *J. Chem. Technol. Biotechnol.*, 77(2), 168-174.

Lin, S.H., Lai, S.L., and Leu, H.G. (2000) "Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process". *J. Hazard. Mater.*, 76, 139-153.

Lin, S.H., Wang, T.Y., and Juang, R.S. (2004) "Metal rejection by nanofiltration from diluted solutions in the presence of complexing agents". *Sep. Sci. Technol.*, 39(2), 363-376.

Lin, T.S., and Nriagu, J.O. (1998) *Speciation of thallium in natural waters*. In: Nriagu, J.O. (Ed.), Thallium in the Environment., John Wiley & Sons, Inc., New York, NY, USA, Chap. 3, pp. 31-43.

Lin, X., Burns, R.C., and Lawrance, G.A. (1998) "Effect of electrolyte composition, and of added iron(III) in the presence of selected organic complexing agents, on nickel(II) precipitation by lime". *Water Res.*, 32(12), 3637-3645.

Lippmann, M. (2000) *Environmental toxicants. Human exposures and their health effects*. John Wiley & Sons, Inc., New York, NY, USA, 987 p.

Losi, M.E., Amrhein, C., and Frankenberger, W.T.Jr. (1994) "Bioremediation of chromate-containated groundwater by reduction and precipitation in srface soils". *J. Environ. Qual.*, 23, 1141-1150.

Mack, C., Burgess, J.E., and Duncan, J.R. (2004) "Membrane bioreactors for metal recovery from wastewater : A review". *Water SA*, 30(4), 521-532.

Magalhaes, M.C.F. (2002) "Arsenic. An environmental problem limited by solubility". *Pure Appl. Chem.*, 74(10), 1843-1850.

Maine, M.A., Sune, N., Hadad, H., Sanchez, G., and Bonetto, C. (2006) "Nutrient and metal removal in a constructed wetland for wastewater treatment from a metallurgic industry". *Ecol. Eng.*, 26(4), 341-347.

Marchioretto, M.M., Bruning, H., and Rulkens, W. (2005) "Heavy metals precipitation in sewage sludge". *Sep. Sci. Technol.*, 40(16), 3393-3405.

Matlock, M.M., Henke, K.R., and Atwood, D.A. (2002) "Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs". *J. Hazard. Mater.*, B92, 129-142.

Matlock, M.M., Henke, K.R., Atwood, D.A., and Robertson, D. (2001) "Aqueous leaching properties and environmental implications of cadmium, lead and zinc trimercaptotriazine (TMT) compounds". *Water Res.*, 35(15), 3649-3655.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., and Saldanha, M. (2002) "Studies on the mechanisms of lead immobilization by hydroxyapatite". *Environ. Sci. Technol.*, 36(7), 1625-1629.

May P.M., and Murray, K. (1991a) "JESS, a joint expert speciation system – I. Raison d'être". *Talanta*, 38(12), 1409-1417.

May P.M., and Murray, K. (1991b) "JESS, a joint expert speciation system – II. The thermodynamic database". *Talanta*, 38(12), 1419-1426.

May P.M., Murray, K., and Williams, D.R. (1985) “The use of glass electrodes for the determination of formation constants—II simulation of titration data”. *Talanta*, 32(6), 483-489.

McAnally, S., Benefield, L., and Reed, R.B. (1984). “Nickel removal from a synthetic nickel-plating waste water using sulphide and carbonate for precipitation and coprecipitation”. *Sep. Sci. Technol*., 19, 191-217.

McDuff, R.E., and Morel, E.M. (1973) *Description and use of the chemical equilibrium program REDEQL2*. Technical Report EQ-73-02, California Inst. Technol., Pasadena, CA, USA.

McGowen, S.L., Basta, N.T., and Brown, G.O. (2001) “Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil”. *J. Environ. Qual*., 30, 493-500.

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., and Cook, N. (2000) “Soil testing for heavy metals”. *Commun. Soil Sci. Plant Anal*., 31, 1661-1700.

Meers, E., Unamuno, V.R., Du Laing, G., Vangronsveld, J., Vangroekhoven, K., Samson, R., Diels, L., Geebelen, W., Ruttens, A., Vandegehuchte, M., and Tack, F.M.G. (2006) “Zn in the soil solution of unpolluted soils as affected by soil characteristics”. *Geoderma*, 136, 107-119.

Mercier, G., Duchesne, J., and Carles-Gibergues, A. (2002) “A simple and fast screening test to detect soils polluted by lead”. *Environ. Pollut*., 118, 285-296.

Meunier, N., Blais, J.F., Lounes, M., Tyagi, R.D., and Sasseville, J.L. (2002) “Different options for metal recovery after sludge decontamination at the Montreal Urban Community wastewater treatment plant”. *Water Sci. Technol*., 46(10), 33-41.

Meunier, N., Drogui, P., Gourvenec, C., Mercier, G., Hausler, R., and Blais, J.F. (2004) “Removal of metals in leachate from sewage sludge using electrochemical technology”. *Environ. Technol.*, 25(2), 235-245.

Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., and Blais, J.F. (2006) “Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate”. *J. Hazard. Mater.*, 137(1), 581-590.

Mirbagheri, S.A., and Hosseini, S.N. (2004) “Pilot plant investigation on petrochemical wastewater treatmentfor the removal of copper and chromium with the objective of reuse”. *Desalination*, 171(1), 85-93.

Moghadam, M.A., Soheili, M., Esfahani, M.M., 2005. Effect of ionic strength on settling of activated sludge. Iranian J. Environ. Health Sci. Eng. 2 (1), 1-5.

Moller, A., Grahn, A., and Welander, U. (2004) “Precipitation of heavy metals from landfill leachates by microbially-produced sulphide”. *Environ. Technol.*, 25(1), 69-77.

Mondal, B.C., and Das, A.K. (2004) “Functionalized chelating resins for selective sorption of metal ions: an overview”. *J. Indian Chem. Soc.*, 81(2), 95-110.

Mustafa, S., Naeem, A., Murtaza, S., Rehana, N., Samad, H.Y., 1999. Comparative sorption properties of metal (III) phosphates. J. Colloid Interface Sci. 220 (1), 63-74.

Müller, B. (1996) *CHEMEQL, version 2.0. User’s guide to application.* Swiss Federal Institute of Environmental Sciences and Technology (EAWAG), Dübendorf, Switzerland.

Naeem, A., Mustafa, S., Dilara, B., Rehana, N., and Murtaza, S. (2003) “Effect of precipitation on the sorption of metal cations by $AlPO_4$”. *J. Chem. Soc. Pakistan*, 25(2), 98-103.

Nelson, A., Wang, W., Demopoulos, G.P., and Houlachi, G. (2000) "The removal of cobalt from zinc electrolyte by cementation: a critical review". *Min. Pro. Ext. Met. Rev.*, 20, 325-356.

Nriagu, J. (1974) "Lead orthophosphates – IV, Formation and stability in the environnement". *Geochim. Cosmochim. Acta*, 38, 887-898.

Nriagu, J. (1996) "A history of global metal pollution". *Science*, 272, 22-24.

Nriagu, J.O., and Pacyna, J.M. (1988) "Quantitative assessment of world-wide contamination of air, water, and soils by trace metals". *Nature*, 333, 134-139.

Papelis, C., Hayes, K.F., and Leckie, J.O. (1988) *HYDRAQL: a program for the computation of chemical equilibrium composition of aqueous batcvh systems including surface-complexation modeling of ion adsorption at the oxide/solution interface*. Technical report 306, Department of Civil Engineering, Stanford University, Stanford, CA, USA.

Parkhurst, D., and Appelo, C. (1999) *User's guide to PHREEQC (ver. 2.4.2). A computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations*. Report 99-4259, United States Geological Survey, Water Resources Investigations, Reston, VA, USA.

Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N. (1980) *PHREEQE. A computer program for geochemical calculations*. Report 80-96, United States Geological Survey, Water Resources Investigations, Reston, VA, USA.

Patterson, J.W. (1988) *Metal treatment and recovery*. In: Kramer, J.R., and Allen, H.E. (Eds.), Metal speciation: theory, analysis and application, Lewis Publishers, Inc., Chelsea, Michigan, USA, pp.333-345.

Pigaga, A., Juskenas, R., and Selkis, A. (2002) "Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation". *Sep. Sci. Technol.,* 37(13), 3155-3168.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A. (1988) *A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brine*. Report 88-4153, United States Geological Survey, Water-Resources Investigations, Reston, VA, USA, 310 p.

Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L. (1991) *An interactive code (NETPATH) for modeling net geochemical reactions along a flow path.* Report 91-4-78, United States Geological Survey, Water-Resources Investigations, Reston, VA, USA.

Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L. (1994) *An interactive code (NETPATH) for modeling net geochemical reactions along a flow path version 2.0*. Report 94-4169, United States Geological Survey, Water-Resources Investigations, Reston, VA, USA.

Porter, S.K., Scheckel, K.G., Impellitteri, C.A., and Ryan, J.A. (2004) "Toxic metals in the environment: Thermodynamic considerations for possible immobilization strategies for Pb, Cd, As, and Hg". *Crit. Rev. Environ. Sci. Technol.*, 34(6), 495-604.

Preis, W., and Gamsjager, H. (2001) "Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems". *Chem. Monthly*, 132, 1327-1346.

Purcell, T.W., and Peters, J.J. (1998) "Sources of silver in the environment". *Environ. Toxicol. Chem.*, 17(4), 539-546.

Ratte, H.T. (1999) "Bioaccumulation and toxicity of silver compounds: a review". *Environ. Toxicol. Chem.*, 18(1), 89-108.

Robinson, A.K., and Sum, J.C. (1980) *Sulphide precipitation of heavy metals*. EPA/600/2-80/139, United States Environmental Protection Agency, Washington, DC, USA.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M.L., and Munoz, J.A. (2006) "Biosorption with algae: A statistical review". *Crit. Rev. Biotechnol*., 26(4), 223-235.

Romero, R., and Joensson, J.A. (2005) "Determination of free copper concentrations in natural waters by using supported liquid membrane extraction under equilibrium conditions. *Anal. Bioanal. Chem*., 381(7), 1452-1459.

Sankhesara, B.M., and Kamath, P.R. (1980) "Effluent treatment for pollutants management - processing of beryl". *Chem. Eng. World*, 15(7), 29-34.

Sasidhar, P., Ayengar, B., Anand Babu, C., Siriah, H.N., Lal, K.B., and Amalraj, R.V. (1991) "Coprecipitation of selenites from acidic effluents". *Indian J. Environ. Health*, 33(4), 440-444.

Savage, D. (1986) "The geochemical interactions of simulated borosilicate waste glass, granite and water at 100^o -350^o C and 50 Mpa". *Nuclear Chem. Waste Manag*., 6(1), 15-39.

Semerjian, L., and Ayoub, G.M. (2003) "High-pH-magnesium coagulation-flocculation in wastewater treatment". *Adv. Environ. Res*., 7, 389-403.

Sharma, R.K., and Agrawal, M. (2005) "Biological effects of heavy metals: an overview". *J. Environ. Biol*., 26(2), 301-313.

Sheoran, A.S., and Sheoran, V. (2006) "Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review". *Min. Eng*., 19(2), 105-116.

Silva, J.E., Paiva, A.P., Soares, D., Labrincha, A., and Castro, F. (2005) "Solvent extraction applied to the recovery of heavy metals from galvanic sludge". *J. Hazard. Mater.*, 120(1-3), 113-118.

Slavek, J., Pickering, W.F., 1988. Metal ion interaction with the hydrous oxides of aluminium. Water Air Soil Pollut. 39 (1-2), 201-216.

Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C., Tixier, J.S., Brauning, S.E., Gavaskar, A.R., and Royer, M.D. (1995) *Remedial options for metals-contaminated sites*. Lewis Publishers, Boca Raton, Florida, USA.

Sposito, G., and Coves, J. (1988) *SOILCHEM: a computer program for the calculation of chemical speciation in soils*. Kearney Foundation of Soil Science, Department of Soil & Environmental Sciences, University of California, Riverside, CA, USA.

Sposito, G., and Matigod, S. (1977) *GEOCHEM: a computer program for the calculation of chemical equilibria in soil solutions and other natural water systems*. Department of Soil & Environmental Sciences, University of California, Riverside, CA, USA.

Sposito, G., and Matigod, S. (1980) *GEOCHEM: computer program for the calculation of chemical equilibria in soil solutions and other natural water systems*. Department of Soil & Environmental Sciences, University of California, Riverside, CA, USA.

Suarez, D.L., and Goldberg, S. (1994) *Modeling soil solution, mineral formation and weathering*. In: Soil Science Society of America (Ed.), Quantitative modeling of soil forming processes, SSSA Special Publication, Madison, WI, USA, Chap. 3, pp. 37-60.

Sulzbacher, K., Ecke, H., Lagerkvist, A., and Calmano, W. (1997) "Anaerobic reduction of hexavalent chromium in filter sludge of an electrochemical process". *Environ. Technol.*, 18, 301-307.

Sun, J., and Huang, J.C. (2002) "Co-removal of hexavalent chromium during copper precipitation". *Water Sci. Technol.*, 46(4-5), 413-419.

Tauler, R., and Casassas, E. (1988) "A simplex search for conditions giving maximal and/or minimal concentrations of species in distribution plots". *Anal. Chim. Acta*, 206, 189-202.

Taylor, T.P., Ding, M., Ehler, D.S., Foreman, T.M., Kaszuba, J.P., and Sauer, N.N. (2003) "Beryllium in the environment: A review". *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng.*, 38(2), 439-469.

Terlecka, E. (2005) "Arsenic speciation analysis in water samples: a review of the hyphenated techniques". *Environ. Monitoring Assessment*, 107, 259-284.

Thrailkill, J. (1970) *Solution geochemistry of the water of limestone terrains*. Report 19, Water Resources Institute of Research, University of Kentucky, Lexington, Kentucky, USA.

Tinggi, U. (2003) "Essentiality and toxicity of selenium and its status in Australia: a review". *Toxicol. Lett.*, 137, 103-110.

Tipping, E. (1998) "Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aqueous Geochem.*, 4, 3-48.

Truesdell, A.H., and Jones, B.F. (1974) "WATEQ, a computer program for calculating chemical equilibria of natural waters". *J. Res. U.S. Geol. Surv.*, 2, 233-248.

Twidwell, L.G., and Williams-Beam, C. (2002) “Potential technologies for removing thallium from mine and process wastewater: an abbreviated annotation of the literature”. *Eur. J. Min. Proc. Environ. Protection*, 2(1), 1-10.

USEPA (1992) *Mercury and arsenic wastes. Removal, recovery, treatment, and disposal*. Pollution Technology Review No. 214, Noyes Data Corporation, Park Ridge, New Jersey, USA, 127 p.

USEPA (1993) *Constructed wetlands-based treatment*. EPA/540/R-93/523, United States Environmental Protection Agency, Washington, DC, USA.

USEPA (2000) *Chemical precipitation*. EPA/832/F-00/018, United States Environmental Protection Agency, Washington, DC, USA.

Van der Lee J., and De Windt L. (2000) *CHESS tutorial and cookbook. User’s guide*. Report LHM/RD/99/05, CIG-École des Mines de Paris, Fontainebleau, France.

Vanbroekhoven, K., Dejonghe, W., and Diels, L. (2005) *Treatment of contaminated soil and groundwater: in situ immobilization of metals*. In: Lens, P., Grotenhuis, T., Malina, G., and Tabak, H. (Eds.), Soil and sediment remediation. Mechanisms, technologies and applications”, IWA Publishing, London, England, Chap. 13, pp. 248-263.

VanRoy, S., Vanbroekhoven, K., Dejonghe, W., and Diels, L. (2006) “Immobilization of heavy metals in the saturated zone by sorption and *in situ* bioprecipitation processes”. *Hydrometallurgy*, 83(1-4), 195-203.

Veeken, A.H.M., and Rulkens, W.H. (2003) “Innovative developments in the selective removal and reuse of heavy metals from wastewaters”. *Water Sci. Technol.*, 47(10), 9-16.

Vesely, J., Norton, S.A., Skrivan, P., Majer, V., Kram, P., Navratil, T., and Kaste, J.M. (2002) “Environmental chemistry of beryllium”. *Rev. Min. Geochem.,* 50, 291-317.

Viadero, R.C., Wei, X.C., and Buzby, K.M. (2006) “Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization”. *Environ. Eng. Sci*., 23(4), 734-743.

Vig, K., Megharaj, M., Sethunathan, N., and Naidu, R. (2003) “Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review”. *Adv. Environ. Res*., 8(1), 121-135.

Wang, S., and Shi, X. (2001) “Molecular mechanisms of metal toxicity and carcinogenesis”. *Molec. Cell. Biochem*., 222, 3-9.

Wang, Y.H., Lin, S.H., and Juang, R.S. (2003) “Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents”. *J. Hazard. Mater*., 102(2-3), 291-302.

Watts, R.J. (1998) *Hazardous wastes. Sources, pathways, receptors*. Watts, R.J. (Ed.), John Wiley & Sons, Inc., New York, NY, USA, 764 p.

Wegert, H., and Stutzel, K. (1984) “New products used for waters treatment: POC and TMT 15”. *Eau Ind. Nuis.,* 86, 52-54.

Westall, J.C. (1979) *MICROQL. 1. a chemical equilibrium program in BASIC. II. Computation of adsorption equilibria in BASIC*. Technical report, Swiss Federal Institute of Environmental Sciences and Technology (EAWAG), Dübendorf, Switzerland.

Westall, J.C. (1982) *FITEQL. a computer program for determination of equilibrium constants from experimental data*. Report 82-01, Department of Chemistry, Oregon State University, Corvallis, OR, USA.

Westall, J.C., Zachary, J.L., and Morel, F.M.N. (1976) *MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems*. Technical note 18, Massachusetts Institute of Technology, Cambridge, MA, USA.

White, C., Sharman, A.K., and Gadd, G.M. (1998) "An integrated microbial process for the bioremediation of soil contaminated with toxic metals". *Nature Biotechnol.*, 16, 572-575.

Wildeman, T., Gusek, J., Cevaal, J., Whiting, K., and Scheuering, J. (1995) *Bioremediation of inorganics*. Hinchee, R.E., Means, J.L., and Burris, D.R. (Eds.), Battelle Press, Columbus, Ohio, USA, pp. 141-148.

Williams, J.W., and Silver, S. (1984) "Bacterial resistance and detoxification of heavy metals". *Enz. Microb. Technol.*, 6, 530-537.

Windholz, M., Budavari, S., Blumetti, R.F., and Otterbein, E.S. (1983) *The Merck index. An encyclopedia of chemicals, drugs, and biologicals*. Tenth Edition. Merck & Co., Inc., Rahway, New Jersey, USA.

Winge, D.R., and Mehra, R.K. (1990) "Host defenses against copper toxicity. Int. Rev. Exp. Pathol., 31, 47-83.

Wingenfelder, Hansen, C., Furrer, G., and Schulin, R. (2005) "Removal of heavy metals from mine water by natural zeolites". *Environ. Sci. Technol.*, 39, 4606-4613.

Wolery, T. (1992) *EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, user's guide and related documentation (version 7.0).* Report UCRL-MA-110662 PT III, Lawrence Livermore National Laboratory, Livermore, CA, USA.

Wolery, T., and Daveler, S.A. (1992) *EQ6, a computer program for reaction path modeling of aqueous geochemical systems: theoretical manual, user's guide and related documentation (version 7.0).* Report UCRL-MA-110662 PT IV, Lawrence Livermore National Laboratory, Livermore, CA, USA.

Wong, C.S.C., Li, X.D., and Thornton, I. (2006) "Urban environmental geochemistry of trace metals". *Environ. Pollut*., 142(1), 1-16.

Ying, X., and Fang, Z. (2006) "Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate". *J. Hazard. Mater*., 137(3), 1636-1642.

Zahir, F., Rizwi, S.J., Haq, S.K., and Khan, R.H. (2005) "Low dose mercury toxicity and human health". *Environ. Toxicol. Pharmacol*., 20, 351-360.

Zamboulis, D., Pataroudi, S.I., Zouboulis, A.I., and Matis, K.A. (2004) "The application of sorptive flotation for the removal of metal ions". *Desalination*, 162, 159-168.

Zimdahl, R.L., and Skogerboe, R.K. (1977) "Behavior of lead in soils". *Environ. Sci. Technol*., 11, 1202-1207.

Zinck, J.M., and Aubé, B.C. (2000) "Optimisation of lime treatment processes". *CIM Bulletin*, 93(1043), 98-105.

Tableau 2.1 Technologies for treatment of effluents polluted with heavy metals

Types of technology	Examples of technology	References
Chemical precipitation	Precipitation as metal hydroxide, sulphide, carbonate or phosphate, oxidation/reduction reaction	Baltpurvins *et al.* (1996a,b, 1997); Couillard and Mercier (1992); USEPA (2000) Robinson and Sum (1980)
Bioprecipitation	Constructed wetland, bioreactor (sulphate-reducing bacteria)	Kaksonen *et al.* (2003); Mack *et al.* (2004); Maine *et al.* (2006); VanRoy *et al.* (2006)
Ion exchange	Synthetic resin (sulphonic, carboxylic, thiocarbamate, thiols, hydroxyl, amide groups), chelating exchange resin (phosphonic, aminophosphonic, iminodiacetate, oxime groups), solvent impregnated resin (DEHPA, PEIMPA), natural material (zeolite, clay)	Dabrowski *et al.* (2004); Juang *et al.* (2003) Lin *et al.* (2000); Mondal and Das (2004)
Adsorption	Granulated activated carbon (GAC), activated alumina, lignin, chitosan, alginate, zeolite, clay, fly-ash, peat, wool, cotton, natural oxide	Bailey *et al.* (1999); Babel and Kurniawan (2003); Wang *et al.* (2003); Wingenfelder *et al.* (2005)
Biosorption	Agro-industrial (fruit/cereal shell, peel or husk) biomass, forestry (bark, leave, sawdust) biomass, algae, bacteria, fungi, terrestrial and aquatic plant (phytofiltration or phytoaccumulation), sewage sludge, yeast	Al-Asheh and Duvnjak (1999); Gardea-Torresdey *et al.* (2004); Kamal *et al.* (2004); Kapoor and Viraraghavan (1995); Kurniawan *et al.* (2006); Romera *et al.* (2006)
Physical separation	Microfiltration, ultrafiltration, nanofiltration, reverse osmosis, membrane pervaporation, freeze crystallization, distillation	Ben Frarès *et al.* (2005); Brooks (1986); DiPalma *et al.* (2003); Lin *et al.* (2004)
Electrochemical separation	Electrocoagulation, electrodeposition, electrodialysis, electrochemical peroxidation	Arienzo *et al.* (2001); Djedidi *et al.* (2005); Juang and Wang (2000); Lai and Lin (2006); Meunier *et al.* (2004, 2006)
Solvent extraction	Bis-(2-ethyl-hexul)phosphoric acid (D2EHPA), bis-(2,4,4-trimethylpentyl)-phosphonic acid, hydroxyoximes, tri-n-octylmethylammonium	Belkhouche *et al.* (2005); Lin *et al.* (2002); Silva *et al.* (2005)
Flotation	Dissolved-air flotation (DAF), sorptive flotation	Aldrich and Feng (2000); Doyle (2003); Lazaridis *et al.* (2001); Zamboulis *et al.* (2004)
Cementation	Iron, aluminium	Brooks (1991); Hayes (1985); Nelson *et al.* (2000) USEPA (1992)

Tableau 2.2 Constants of solubility products of metal hydroxides

Metals	State oxidation	Reactions	pK_s
Aluminium	(3+)	$Al(OH)_3$ (alpha) ↔ 3 $OH^{(-)}$ + $Al^{(3+)}$	33.5
Antinomy	(3+)	$Sb(OH)_3$ ↔ 3 $OH^{(-)}$ + $Sb^{(3+)}$	49.1
Barium	(2+)	$Ba(OH)_2$ ↔ 2 $OH^{(-)}$ + $Ba^{(2+)}$	2.3
Beryllium	(2+)	$Be(OH)_2$ (alpha) ↔ 2 $OH^{(-)}$ + $Be^{(2+)}$	21.1
Cadmium	(2+)	$Cd(OH)_2$ ↔ 2 $OH^{(-)}$ + $Cd^{(2+)}$	13.6
Calcium	(2+)	$Ca(OH)_2$ (portlandite) ↔ 2 $OH^{(-)}$ + $Ca^{(2+)}$	5.3
Chromium	(2+)	$Cr(OH)_2$ ↔ 2 $OH^{(-)}$ + $Cr^{(2+)}$	17.2
	(3+)	$Cr(OH)_3$ ↔ 3 $OH^{(-)}$ + $Cr^{(3+)}$	30.2
Cobalt	(2+)	$Co(OH)_2$ ↔ 2 $OH^{(-)}$ + $Co^{(2+)}$	14.8
	(3+)	$Co(OH)_3$ ↔ 3 $OH^{(-)}$ + $Co^{(3+)}$	44.3
Copper	(1+)	$Cu(OH)$ ↔ $OH^{(-)}$ + $Cu^{(+)}$	14.7
	(2+)	$Cu(OH)_2$ ↔ 2 $OH^{(-)}$ + $Cu^{(2+)}$	18.6
Iron	(2+)	$Fe(OH)_2$ ↔ 2 $OH^{(-)}$ + $Fe^{(2+)}$	15.1
	(3+)	$Fe(OH)_3$ ↔ 3 $OH^{(-)}$ + $Fe^{(3+)}$	37.4
Mercury	(1+)	$Hg_2(OH)_2$ ↔ 2 $OH^{(-)}$ + $Hg_2^{(2+)}$	23.7
	(2+)	$Hg(OH)_2$ ↔ 2 $OH^{(-)}$ + $Hg^{(2+)}$	25.4
Lead	(2+)	$Pb(OH)_2$ ↔ 2 $OH^{(-)}$ + $Pb^{(2+)}$	16.1
Magnesium	(2+)	$Mg(OH)_2$ ↔ 2 $OH^{(-)}$ + $Mg^{(2+)}$	10.8
Manganese	(2+)	$Mn(OH)_2$ ↔ 2 $OH^{(-)}$ + $Mn^{(2+)}$	12.7
Nickel	(2+)	$Ni(OH)_2$ ↔ 2 $OH^{(-)}$ + $Ni^{(2+)}$	14.7
Silver	(1+)	$Ag(OH)$ ↔ $OH^{(-)}$ + $Ag^{(+)}$	7.7
Thallium	(1+)	$TlOH$ ↔ $OH^{(-)}$ + $Tl^{(+)}$	1.1
	(3+)	$Tl(OH)_3$ ↔ 3 $OH^{(-)}$ + $Tl^{(3+)}$	45.2
Tin	(2+)	$Sn(OH)_2$ ↔ 2 $OH^{(-)}$ + $Sn^{(2+)}$	28.1
	(4+)	$Sn(OH)_4$ ↔ 4 $OH^{(-)}$ + $Sn^{(4+)}$	56.0
Zinc	(2+)	$Zn(OH)_2$ ↔ 2 $OH^{(-)}$ + $Zn^{(2+)}$	15.7

Tableau 2.3 Constants of solubility products of metal sulphides

Metals	State oxidation	Reactions	pK_s
Barium	(2+)	$BaS \leftrightarrow Ba^{(2+)} + S^{(2-)}$	-3.3
Beryllium	(2+)	$BeS \leftrightarrow Be^{(2+)} + S^{(2-)}$	- 6.5
Cadmium	(2+)	CdS (greenockite) $\leftrightarrow Cd^{(2+)} + S^{(2-)}$	26.1
Cobalt	(2+)	CoS (alpha) $\leftrightarrow Co^{(2+)} + S^{(2-)}$	20.4
Copper	(1+)	$Cu_2S \leftrightarrow 2\ Cu^{(+)} + S^{(2-)}$	47.6
	(2+)	CuS (covellite) $\leftrightarrow Cu^{(2+)} + S^{(2-)}$	35.2
Iron	(2+)	$FeS \leftrightarrow Fe^{(2+)} + S^{(2-)}$	17.2
	(3+)	$Fe_2S_3 \leftrightarrow 2\ Fe^{(3+)} + 3\ S^{(2-)}$	85.0
Mercury	(1+)	$Hg_2S \leftrightarrow Hg_2^{(2+)} + S^{(2-)}$	47.0
	(2+)	HgS (cinnabar) $\leftrightarrow Hg^{(2+)} + S^{(2-)}$	52.4
Lead	(2+)	PbS (galene) $\leftrightarrow Pb^{(2+)} + S^{(2-)}$	27.0
Manganese	(2+)	MnS (pink) $\leftrightarrow Mn^{(2+)} + S^{(2-)}$	9.6
	(2+)	MnS (green) $\leftrightarrow Mn^{(2+)} + S^{(2-)}$	12.6
Nickel	(2+)	NiS (alpha) $\leftrightarrow Ni^{(2+)} + S^{(2-)}$	18.5
	(2+)	NiS (gamma) $\leftrightarrow Ni^{(2+)} + S^{(2-)}$	25.7
Silver	(1+)	Ag_2S (acanthite) $\leftrightarrow 2\ Ag^{(+)} + S^{(2-)}$	49.2
Thallium	(1+)	$Tl_2S \leftrightarrow 2\ Tl^{(+)} + S^{(2-)}$	20.1
Tin	(2+)	$SnS \leftrightarrow Sn^{(2+)} + S^{(2-)}$	25.0
	(4+)	$SnS_2 \leftrightarrow Sn^{(4+)} + 2\ S^{(2-)}$	70.0
Zinc	(2+)	ZnS (sphalerite) $\leftrightarrow Zn^{(2+)} + S^{(2-)}$	23.0
	(2+)	ZnS (wurtzite) $\leftrightarrow Zn^{(2+)} + S^{(2-)}$	24.3

Tableau 2.4 Constants of solubility products of metal carbonates

Metals	Oxidation State	Reactions	pK_s
Barium	(2+)	$BaCO_3$ (witherite) ↔ $Ba^{(2+)} + CO_3^{(2-)}$	8.6
Cadmium	(2+)	$CdCO_3$ (otavite) ↔ $Cd^{(2+)} + CO_3^{(2-)}$	12.0
Calcium	(2+)	$CaCO_3$ (calcite) ↔ $Ca^{(2+)} + CO_3^{(2-)}$	8.5
	(2+)	$CaCO_3$ (aragonite) ↔ $Ca^{(2+)} + CO_3^{(2-)}$	8.3
Cobalt	(2+)	$CoCO_3 \leftrightarrow Co^{(2+)} + CO_3^{(2-)}$	10.0
Copper	(2+)	$CuCO_3 \leftrightarrow Cu^{(2+)} + CO_3^{(2-)}$	11.5
Iron	(2+)	$FeCO_3$ (siderite) ↔ $Fe^{(2+)} + CO_3^{(2-)}$	10.2
Mercury	(1+)	$Hg_2CO_3 \leftrightarrow Hg_2^{(2+)} + CO_3^{(2-)}$	16.1
Lead	(2+)	$PbCO_3$ (cerrusite) ↔ $Pb^{(2+)} + CO_3^{(2-)}$	13.1
Magnesium	(2+)	$MgCO_3$ (magnesite) ↔ $Mg^{(2+)} + CO_3^{(2-)}$	7.5
	(2+)	$MgCO_3.3H_2O \leftrightarrow 3\ H_2O + Mg^{(2+)} + CO_3^{(2-)}$	4.7
Manganese	(2+)	$MnCO_3$ (rhodochrosite) ↔ $Mn^{(2+)} + CO_3^{(2-)}$	10.6
Nickel	(2+)	$NiCO_3 \leftrightarrow Ni^{(2+)} + CO_3^{(2-)}$	6.9
Silver	(1+)	$Ag_2CO_3 \leftrightarrow 2\ Ag^{(+)} + CO_3^{(2-)}$	11.1
Thallium	(1+)	$Tl_2CO_3 \leftrightarrow 2\ Tl^{(+)} + CO_3^{(2-)}$	3.8
Zinc	(2+)	$ZnCO_3$ (smithsonite) ↔ $Zn^{(2+)} + CO_3^{(2-)}$	10.0
	(2+)	$ZnCO_3.H_2O \leftrightarrow H_2O + Zn^{(2+)} + CO_3^{(2-)}$	10.3

Tableau 2.5 Constants of solubility products of metal phosphates

Metals	Oxidation State	Reactions	pK_s
Aluminium	(3+)	$AlPO_4 \leftrightarrow Al^{(3+)} + PO_4^{(3-)}$	22.5
Barium	(2+)	$Ba_3(PO_4)_2 \leftrightarrow 3\ Ba^{(2+)} + 2\ PO_4^{(3-)}$	29.3
Beryllium	(2+)	$Be_3(PO_4)_2 \leftrightarrow 3\ Be^{(2+)} + 2\ PO_4^{(3-)}$	38.6
Cadmium	(2+)	$Cd_3(PO_4)_2 \leftrightarrow 3\ Cd^{(2+)} + 2\ PO_4^{(3-)}$	32.6
Calcium	(2+)	$Ca_3(PO_4)_2$ (beta) $\leftrightarrow 3\ Ca^{(2+)} + 2\ PO_4^{(3-)}$	28.9
	(2+)	$CaHPO_4 \leftrightarrow H^{(+)} + Ca^{(2+)} + PO_4^{(3-)}$	19.3
	(2+)	$CaHPO_4.2H_2O \leftrightarrow 2\ H_2O + H^{(+)} + Ca^{(2+)} + PO_4^{(3-)}$	19.0
Cobalt	(2+)	$Co_3(PO_4)_2 \leftrightarrow 3\ Co^{(2+)} + 2\ PO_4^{(3-)}$	34.7
	(2+)	$CoHPO_4 \leftrightarrow H^{(+)} + Co^{(2+)} + PO_4^{(3-)}$	19.1
Copper	(2+)	$Cu_3(PO_4)_2 \leftrightarrow 3\ Cu^{(2+)} + 2\ PO_4^{(3-)}$	36.9
	(2+)	$Cu_3(PO_4)_2.3H_2O \leftrightarrow 3\ H_2O + 3\ Cu^{(2+)} + 2\ PO_4^{(3-)}$	35.1
Iron	(2+)	$Fe_3(PO_4)_2 \leftrightarrow 3\ Fe^{(2+)} + 2\ PO_4^{(3-)}$	36.0
	(2+)	$Fe_3(PO_4)_2.8H_2O \leftrightarrow 8\ H_2O + 3\ Fe^{(2+)} + 2\ PO_4^{(3-)}$	36.0
	(3+)	$FePO_4 \leftrightarrow Fe^{(3+)} + PO_4^{(3-)}$	25.8
	(3+)	$FePO_4.2H_2O \leftrightarrow 2\ H_2O + Fe^{(3+)} + PO_4^{(3-)}$	26.4
Mercury	(1+)	$Hg_2HPO_4 \leftrightarrow H^{(+)} + Hg_2^{(2+)} + PO_4^{(3-)}$	24.8
Lead	(2+)	$Pb_3(PO_4)_2 \leftrightarrow 3\ Pb^{(2+)} + 2\ PO_4^{(3-)}$	43.5
	(2+)	$PbHPO_4 \leftrightarrow H^{(+)} + Pb^{(2+)} + PO_4^{(3-)}$	23.8
Magnesium	(2+)	$Mg_3(PO_4)_2 \leftrightarrow 3\ Mg^{(2+)} + 2\ PO_4^{(3-)}$	23.3
	(2+)	$MgHPO_4.3H_2O \leftrightarrow 3\ H_2O + H^{(+)} + Mg^{(2+)} + PO_4^{(3-)}$	18.2
Manganese	(2+)	$Mg_3(PO_4)_2 \leftrightarrow 3\ Mg^{(2+)} + 2\ PO_4^{(3-)}$	23.8
	(2+)	$MnHPO_4 \leftrightarrow H^{(+)} + Mn^{(2+)} + PO_4^{(3-)}$	25.4
Nickel	(2+)	$Ni_3(PO_4)_2 \leftrightarrow 3\ Ni^{(2+)} + 2\ PO_4^{(3-)}$	31.3
Silver	(1+)	$Ag_3PO_4 \leftrightarrow 3\ Ag^{(+)} + PO_4^{(3-)}$	17.6
Zinc	(2+)	$Zn_3(PO_4)_2 \leftrightarrow 3\ Zn^{(2+)} + 2\ PO_4^{(3-)}$	35.4
	(2+)	$Zn_3(PO_4)_2.4H_2O \leftrightarrow 4\ H_2O + 2\ PO_4^{(3-)} + 3\ Zn^{(2+)}$	35.4

Tableau 2.6 Most important toxic effects related to metals on humans

Metals	Toxicities	References
Antinomy	Dermatisis, keratinis, conjunctivitis and nasal ulteration, possible human carcinogen	Gebel (1997); Windholz *et al.* (1983)
Arsenic	Burning and dryness of the mouth and throat, dysphasia, vomiting, dermatosis, muscular cramps, facial edema and cardiac abnormalities, cancers of the lung, skin, bladder, kidneys, and liver, damage to respiratory, cardio-vascular, nervous and haematopoietic systems, death	Florea and Büsselberg (2006); Gaussy *et al.* (2003); Jain and Ali (2000); Jiang (2001); Wang and Shi (2001)
Beryllium	Lung disease, berylliosis, carcinogen, cytotoxicity (impact enzyme function, DNA synthesis, protein phosphorylation, and cell division)	Kabata-Pendias (2001); Taylor *et al.* (2003)
Cadmium	Kidney damage, renal necrosis and dysfunction, pulmonary edema and pneumonitis, Itai-Itai disease, prostate and lung cancers	Gaussy *et al.* (2003); Lippmann (2000); Vig *et al.* (2003); Wang and Shi (2001)
Chromium	Skin irritation, headache, nausea, diarrhea, vomiting, liver and kidney problems, renal failure, irritation of the respiratory tract, emphysema, chronic bronchitis, bronchopneumonia, lung cancer	Goldhaber (2003); Lippmann (2000); Wang and Shi (2001)
Copper	Weakness, lethargy, and anorexia, abdominal pain, cramps, nausea, diarrhea, vomiting, liver cirrhosis, Wilson's disease, damage to renal tubules, hepatic necrosis, vascular collapse	Fraga (2005); Gaetke and Chow (2003); Goldhaber (2003); Kabata-Pendias (2001); Winge and Mehra (1990)
Mercury	Memory loss, dementia, deficit in attention, ataxia, dysphasia, dizziness, irritability, blindness and deafness, disruption of fine motor function, gingivitis, gastrointestinal irritation, kidney dysfunction, alters normal cardiovascular homoeostasis, decreases overall immunity of the body, multiple schlerosis, pulmonary edema, decrease rate of fertility	Clarkson (1998); Gaussy *et al.* (2003); Lippmann (2000); Zahir *et al.* (2005)
Lead	Memory and learning deficits, high blood pressure, insomnia and anorexia, muscle irritability, encephalopathy, tremors and ataxia, damage to neurologic, hematologic and renals systems, fertility damage, chronic nephropathy	Davydova (2005); Florea and Büsselberg (2006); Gaussy *et al.* (2003); Kabata-Pendias (2001); Lippmann (2000)
Nickel	Dermatisis, headache, nausea, allergic dermatitis, chronic asthma, coughing, lung fibrosis, cardio-vascular and kidney diseases, lung and nasal cancer	Davydova (2005); Denkhaus and Salnikow (2002); Wang and Shi (2001)
Selenium	Selenosis (hair and nail loss and brittleness), gastrointestinal problems, skin rash, garlic odor, hypochromic anaemia, leucopenia, weakness, convulsions, nervous system abnormalities	Brenneisen *et al.* (2005); Goldhaber (2003); Tinggi (2003)
Silver	Irreversible pigmentation of the skin (argyria) and eyes (argyrosis), upper (nose and throat) and lower (chest) respiratory tract irritation, bronchitis, emphysema and reduction in pulmonary volume	Drake and Hazelwood (2005); Kabata-Pendias (2001); Purcell and Peters (1998); Ratte (1999)
Thallium	Fatigue, headache, insomnia, nausea, vomiting, hair fall, gastro-enteritis, alopecia, burning feet syndrome, ataxia, convulsions, delirium, hallucinations, tachycardia, hypotension, coma	Galvan-Arzate and Santamaria (1998); Kazantzis (2000)
Zinc	Depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst, gastrointestinal irritation and vomiting	Goldhaber (2003); Kabata-Pendias (2001)

Tableau 2.7 Constants of solubility products of metal arsenates

Metals	Oxidation State	Reactions	pK_s
Aluminium	(3+)	$AlAsO_4.2H_2O \leftrightarrow 2\ H_2O + AsO_4^{(3-)} + Al^{(3+)}$	15.9
Barium	(2+)	$Ba_3(AsO_4)_2 \leftrightarrow 2\ AsO_4^{(3-)} + 3\ Ba^{(2+)}$	50.3
Calcium	(2+)	$Ca_3(AsO_4)_2.4H_2O \leftrightarrow 4\ H_2O + 2\ AsO_4^{(3-)} + 3\ Ca^{(2+)}$	19.1
Cobalt	(2+)	$Co_3(AsO_4)_2 \leftrightarrow 2\ AsO_4^{(3-)} + 3\ Co^{(2+)}$	28.4
Copper	(2+)	$Cu_3(AsO_4)_2.2H_2O \leftrightarrow 2\ H_2O + 2\ AsO_4^{(3-)} + 3\ Cu^{(2+)}$	35.3
Iron	(3+)	$FeAsO_4.2H_2O \leftrightarrow 2\ H_2O + AsO_4^{(3-)} + Fe^{(3+)}$	20.3
Lead	(2+)	$Pb_3(AsO_4)_2 \leftrightarrow 2\ AsO_4^{(3-)} + 3\ Pb^{(2+)}$	35.6
Manganese	(2+)	$Mn_3(AsO_4)_2.8H_2O \leftrightarrow 8\ H_2O + 2\ AsO_4^{(3-)} + 3\ Mn^{(2+)}$	28.9
Nickel	(2+)	$Ni_3(AsO_4)_2.8H_2O \leftrightarrow 8\ H_2O + 2\ AsO_4^{(3-)} + 3\ Ni^{(2+)}$	25.7
Silver	(1+)	$Ag_3AsO_4 \leftrightarrow AsO_4^{(3-)} + 3\ Ag^{(+)}$	23.5
Zinc	(2+)	$Zn_3(AsO_4)_2.2.5H_2O \leftrightarrow 2.5\ H_2O + 2\ AsO_4^{(3-)} + 3\ Zn^{(2+)}$	27.5

Tableau 2.8 **Constants of solubility products of some metal chromates**

Metals	Oxidation State	Reactions	pK_s
Barium	(2+)	$BaCrO_4 \leftrightarrow CrO_4^{(2-)} + Ba^{(2+)}$	9.7
Calcium	(2+)	$CaCrO_4 \leftrightarrow CrO_4^{(2-)} + Ca^{(2+)}$	2.3
Copper	(2+)	$CuCrO_4 \leftrightarrow CrO_4^{(2-)} + Cu^{(2+)}$	5.4
Lead	(2+)	$PbCrO_4 \leftrightarrow CrO_4^{(2-)} + Pb^{(2+)}$	12.6
Magnesium	(2+)	$MgCrO_4 \leftrightarrow CrO_4^{(2-)} + Mg^{(2+)}$	-5.4
Mercury	(1+)	$Hg_2CrO_4 \leftrightarrow CrO_4^{(2-)} + Hg_2^{(2+)}$	8.7
Silver	(1+)	$Ag_2CrO_4 \leftrightarrow CrO_4^{(2-)} + 2\ Ag^{(+)}$	11.6
Thallium	(1+)	$Tl_2CrO_4 \leftrightarrow CrO_4^{(2-)} + 2\ Tl^{(+)}$	12.0

Tableau 2.9 Constants of solubility products of selenides, selenites and selenates

Metals	Se Oxidation State	Reactions	pK_s
Aluminium	(4+)	$Al_2(SeO_3)_3 \leftrightarrow 2\ Al^{(3+)} + 3\ SeO_3^{(2-)}$	32.5
	(6+)	$Al_2(SeO_3)_3 \leftrightarrow 2\ Al^{(3+)} + 3\ SeO_4^{(2-)}$	21.5
Barium	(2-)	$BaSe \leftrightarrow Ba^{(2+)} + Se^{(2-)}$	-21.9
	(4+)	$BaSeO_3 \leftrightarrow Ba^{(2+)} + SeO_3^{(2-)}$	6.6
	(6+)	$BaSeO_4 \leftrightarrow Ba^{(2+)} + SeO_4^{(2-)}$	7.5
Beryllium	(4+)	$BeSeO_3 \leftrightarrow Be^{(2+)} + SeO_3^{(2-)}$	8.0
	(6+)	$BeSeO_4 \leftrightarrow Be^{(2+)} + SeO_4^{(2-)}$	7.2
Cadmium	(2-)	$CdSe \leftrightarrow Cd^{(2+)} + Se^{(2-)}$	35.2
	(4+)	$CdSeO_3 \leftrightarrow Cd^{(2+)} + SeO_3^{(2-)}$	8.9
Calcium	(2-)	$CaSe \leftrightarrow Ca^{(2+)} + Se^{(2-)}$	-10.9
	(4+)	$CaSeO_3 \leftrightarrow Ca^{(2+)} + SeO_3^{(2-)}$	5.5
	(6+)	$CaSeO_4 \leftrightarrow Ca^{(2+)} + SeO_4^{(2-)}$	4.8
Cobalt	(2-)	$CoSe \leftrightarrow Co^{(2+)} + Se^{(2-)}$	31.2
	(4+)	$CoSeO_3 \leftrightarrow Co^{(2+)} + SeO_3^{(2-)}$	6.8
	(6+)	$CoSeO_4 \leftrightarrow Co^{(2+)} + SeO_4^{(2-)}$	6.5
Copper	(2-)	$CuSe \leftrightarrow Cu^{(2+)} + Se^{(2-)}$	48.1
	(4+)	$CuSeO_3 \leftrightarrow Cu^{(2+)} + SeO_3^{(2-)}$	7.7
	(6+)	$CuSeO_4 \leftrightarrow Cu^{(2+)} + SeO_4^{(2-)}$	7.1
Iron	(2-)	$FeSe \leftrightarrow Fe^{(2+)} + Se^{(2-)}$	26.0
	(4+)	$FeSeO_3 \leftrightarrow Fe^{(2+)} + SeO_3^{(2-)}$	10.0
	(6+)	$FeSeO_4 \leftrightarrow Fe^{(2+)} + SeO_4^{(2-)}$	6.5
Lead	(2-)	$PbSe \leftrightarrow Pb^{(2+)} + Se^{(2-)}$	42.1
	(4+)	$PbSeO_3 \leftrightarrow Pb^{(2+)} + SeO_3^{(2-)}$	11.5
	(6+)	$PbSeO_4 \leftrightarrow Pb^{(2+)} + SeO_4^{(2-)}$	6.8
Magnesium	(4+)	$MgSeO_3 \leftrightarrow Mg^{(2+)} + SeO_3^{(2-)}$	4.9
	(6+)	$MgSeO_4 \leftrightarrow Mg^{(2+)} + SeO_4^{(2-)}$	5.8
Manganese	(2-)	$MnSe \leftrightarrow Mn^{(2+)} + Se^{(2-)}$	12.1
	(4+)	$MnSeO_3 \leftrightarrow Mn^{(2+)} + SeO_3^{(2-)}$	6.9
	(6+)	$MnSeO_4 \leftrightarrow Mn^{(2+)} + SeO_4^{(2-)}$	6.1
Mercury	(2-)	$HgSe \leftrightarrow Hg^{(2+)} + Se^{(2-)}$	56.6
	(4+)	$HgSeO_3 \leftrightarrow Hg^{(2+)} + SeO_3^{(2-)}$	18.4
Nickel	(2-)	$NiSe \leftrightarrow Ni^{(2+)} + Se^{(2-)}$	32.7
	(4+)	$NiSeO_3 \leftrightarrow Ni^{(2+)} + SeO_3^{(2-)}$	5.0
	(6+)	$NiSeO_4 \leftrightarrow Ni^{(2+)} + SeO_4^{(2-)}$	6.6
Silver	(2-)	$Ag_2Se \leftrightarrow 2\ Ag^{(+)} + Se^{(2-)}$	53.8
	(4+)	$Ag_2SeO_3 \leftrightarrow 2\ Ag^{(+)} + SeO_3^{(2-)}$	14.7
	(6+)	$Ag_2SeO_4 \leftrightarrow 2\ Ag^{(+)} + SeO_4^{(2-)}$	7.3
Thallium	(2-)	$Tl_2Se \leftrightarrow 2\ Tl^{(+)} + Se^{(2-)}$	33.1
	(4+)	$Tl_2(SeO_3)_3 \leftrightarrow 2\ Tl^{(3+)} + 3\ SeO_3^{(2-)}$	38.7
	(6+)	$Tl_2SeO_4 \leftrightarrow 2\ Tl^{(+)} + SeO_4^{(2-)}$	4.0
Tin	(2-)	$SnSe \leftrightarrow Sn^{(2+)} + Se^{(2-)}$	38.4
Zinc	(2-)	$ZnSe \leftrightarrow Zn^{(2+)} + Se^{(2-)}$	29.4
	(4+)	$ZnSeO_3 \leftrightarrow Zn^{(2+)} + SeO_3^{(2-)}$	7.7
	(6+)	$ZnSeO_4 \leftrightarrow Zn^{(2+)} + SeO_4^{(2-)}$	6.7

Tableau 2.10 Computer programs of metal speciation

Programs	References	Websites
AQUACHEM	Korfali and Davies (2004)	http://www.flowpath.com/software/aquachem/aquachem_ov.htm
CHEAQS/GECHEQ	Romero and Joensson (2005)	http://home.tiscali.nl/cheaqs/
CHEMEQL	Müller (1996)	http://www.eawag.ch/research/surf/forschung/chemeql.html
JCHESS/CHESS	van der Lee and De Windt (2000)	http://chess.ensmp.fr/
CSMC	Tauler and Casassas (1988)	
EQ3/6	Wolery (1992); Wolery and Daveler (1992)	http://www.llnl.gov/IPandC/technology/software/softwaretitles/eq36.php
ESTA	May *et al.* (1985)	
FITEQL	Westall (1982)	http://www.lwr.kth.se/forskningsprojekt/MoW/fiteql.htm
GEOCHEM	Sposito and Matigod (1977, 1980)	
HYDRAQL	Papelis *et al.* (1988)	
HYPHEN	Gans *et al.* (1996)	
HYSS	Alderighi *et al.* (1999)	http://www.chim1.unifi.it/group/vacsab/hyss.htm
IONPAIR	Tharilkill (1970)	
JESS	May and Murray (1991a,b)	http://jess.murdoch.edu.au/jess/jess_home.htm
MICROQL	Westall (1979)	http://www.polyql.ethz.ch/
MINEQL+	Westall *et al.* (1976)	http://www.mineql.com/
MINTEQ/MINTEQA2/PRODEFA2	Allison *et al.* (1991); Felmy *et al.* (1984); HydroGeoLogic (1998a,b)	http://epa.gov/ceampubl/mmedia/minteq/index.htm
VISUAL MINTEQ	Romero and Joensson (2005)	http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm
NETPATH	Plummer *et al.* (1991, 1994)	http://water.usgs.gov/software/netpath.html
PHREEQC	Parkhurst and Appelo (1999)	http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
PHREEQE	Parkhurst *et al.* (1980)	http://www.nea.fr/abs/html/nesc9674.html
PHRQPITZ	Plummer *et al.* (1988)	http://water.usgs.gov/software/phrqpitz.html
RAMASES	Leung and Darvell (1990)	
REDEQL2	McDuff and Morel (1973)	
SOILCHEM	Sposito and Coves (1988)	http://www.cnr.berkeley.edu/~ayang/soilchem.html
SOLMNEQ.88/SOLMNEQ	Kharaka and Barnes (1973); Kharaka *et al.* (1988); Savage (1986)	
SPECIES	Barak (1990)	http://www.soils.wisc.edu/~barak/species.htm
TRANSPEC	Bhavsar *et al.* (2004)	
WHAM/MODEL VI	Meers *et al.* (2006); Tipping (1998)	http://windermere.ceh.ac.uk/aquatic_processes/wham/index.html
WATEQ4F/WATEQ	Ball (1987, 2002); Truesdell and Jones (1974)	http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/software.htm
WINHUMIC V	Romero and Joensson (2005)	http://www.lwr.kth.se/english/OurSoftware/WinHumicV/index.htm

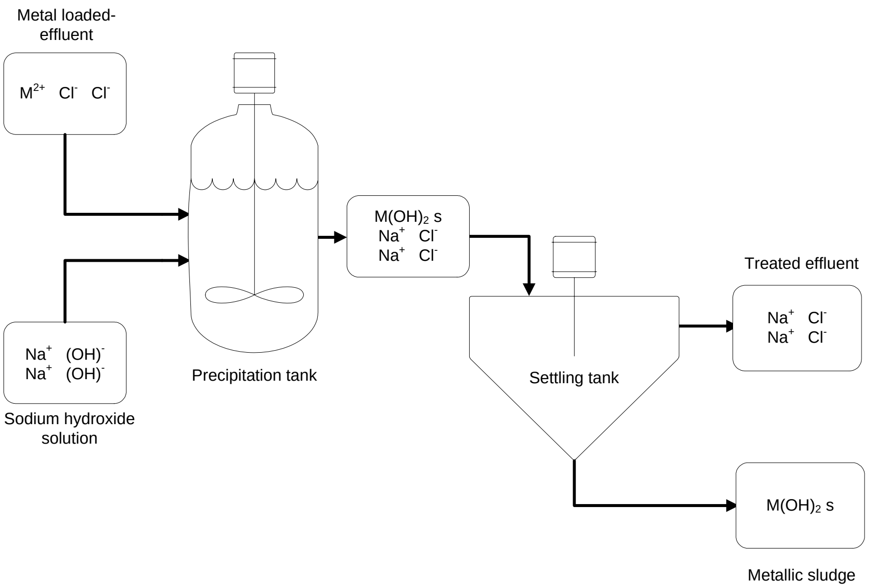

Figure 2.1 **Scheme of a conventional metal-loaded effluent treatment process using sodium hydroxide as precipitating agent**

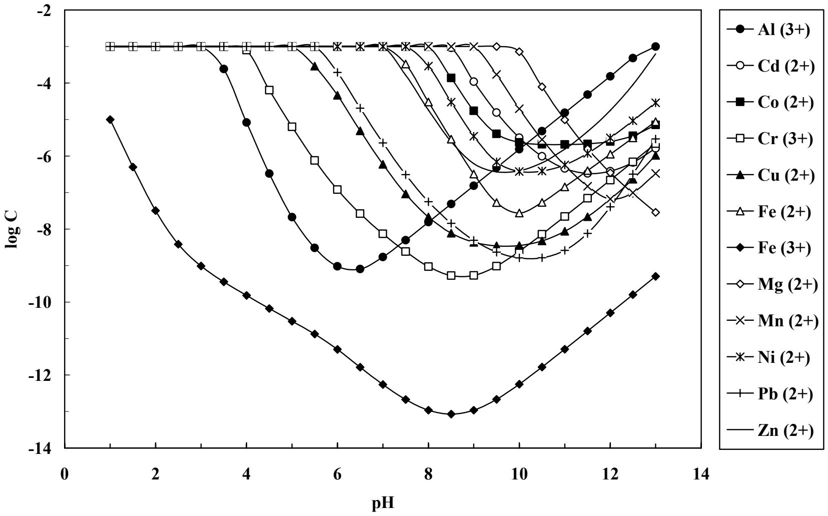

Figure 2.2 **Solubility of different metal hydroxides based on chemical equilibrium calculations using the *MINEQL+* software. Simulation conditions: T = 25^{o}C, [Cl$^-$]$_i$ = 10^{-2} M and [metal]$_i$ = 10^{-3} M**

CHAPITRE III

COMPARATIVE STUDY OF DEWATERING CHARACTERISTICS OF PRECIPITATES GENERATED DURING TREATMENT OF MONOMETALLIC SOLUTIONS

Le Chapitre 3 est constitué de l'article suivant:

Zied Djedidi, Jihène Ben Khaled, Ridha Ben Cheikh, Jean François Blais, Guy Mercier et Rajeshwar Dayal Tyagi (2009) Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions. *Hydrometallurgy*. 95, 61-69.

Résumé

Les caractéristiques de déshydratation des boues (décantation, filtration et centrifugation), générées à la suite du traitement par précipitation des solutions monométalliques (0.02 mol/L), ont été évaluées dans cette étude. Les tests de précipitation effectués pour 15 différents métaux, ont donné des rendements d'élimination généralement comparables à ceux prédits par le logiciel *MINEQL+*, à l'exception des cas de précipitations sous formes de sulfures ou de phosphates où l'effet de la cinétique peut être considéré. La précipitation sous forme d'hydroxydes à pH 10.0 était la technique la plus efficace pour l'élimination de huit ions (Al^{3+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}), alors que la précipitation sous forme de phosphates (à pH 6.0 avec l'addition de 0.0133 mol PO_4^{3-}/L) a donné des taux d'enlèvement les plus élevés pour Ba^{2+}, Ca^{2+}, Cr^{3+}. La précipitation sous formes de sulfures (à pH 7.0 en utilisant 0.02 mol S^{2-}/L) a été la technique de précipitation la plus efficace seulement pour le Cu^{2+} et Sn^{2+}, alors que la précipitation sous formes de carbonates (à pH 8.0 en utilisant 0.02 mol CO_3^{2-}/L) a donné les meilleurs taux d'élimination pour Pb^{2+} seulement). Les résultats ont également montré que les précipités de phosphates, ont généralement les meilleures caractéristiques de déshydratation (IVB, CF, RSF et ST) par rapport aux carbonates, aux sulfures et aux hydroxydes. En effet, en considérant seulement les caractéristiques de déshydratation des boues, la précipitation aux phosphates semble être la technique la plus appropriée pour la précipitation de plusieurs cations (Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+} , Ni^{2+} et Zn^{2+}). La formation des hydroxydes métalliques constitue la meilleure option pour l'élimination de Ca^{2+}, Cu^{2+}, Mg^{2+} et Sn^{2+}, alors que la précipitation sous forme de carbonates est particulièrement intéressante pour les solutions contenants Mn^{2+} et Pb^{2+}.

Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions

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3. COMPARATIVE STUDY OF DEWATERING CHARACTERISTICS OF PRECIPITATES GENERATED DURING TREATMENT OF MONOMETALLIC SOLUTIONS

3.1 Abstract

The sludge dewatering properties (settling, filtration and centrifugation) of metal precipitates generated during treatment of monometallic solutions (0.020 mol/L) have been evaluated in this research. The precipitation tests carried out on 15 different metals gave metal removal yields generally similar to those predicted by *MINEQL+* software, with the exception that kinetic aspects should be considered during precipitation of metal sulphides and phosphates. Hydroxides precipitation at pH 10.0 was the most efficient technique for the removal of eight metallic ions (Al^{3+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}), whereas phosphates precipitation (at pH 6.0 with an addition of 0.0133 mol PO_4^{3-}/L) gave highest removal yields for Ba^{2+}, Ca^{2+}, Cr^{3+}. Sulphides precipitation (at pH 7.0 and using, 0.020 mol S^{2-}/L) has been found the most efficient technique only for Cu^{2+} and Sn^{2+} precipitation, whereas carbonates precipitation (at pH 8.0 and using 0.020 mol CO_3^{2-}/L) gave better removal yield only for Pb^{2+}. Results have also shown that metal phosphates have generally better dewatering characteristics (SVI, filtration capacity, SRF, sludge solids content) than metal carbonates, sulphides and hydroxides. In fact, considering only the sludge dewatering characteristics, phosphates precipitation appears the most appropriate technique for the precipitation of many metals (Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+} , Ni^{2+} and Zn^{2+}). Metal hydroxides formation constitutes the best option for Ca^{2+}, Cu^{2+}, Mg^{2+} and Sn^{2+} removal, whereas precipitation of metal carbonates is particularly interesting for treatment of Mn^{2+} and Pb^{2+} containing solutions.

3.2 Keywords

Metal; Precipitation; Sludge; Dewatering; Hydroxide, Sulphide; Phosphate, Carbonate.

3.3 Nomenclature

μ	viscosity of the filtrate
A	surface area
b	slope of the plot (V vs. t/V)
c	weight of solids/unit volume of filtrate
FC	filtration capacity
ORP	oxidoreduction potential
P	pressure
rpm	rotations per minute
SRF	specific resistance to filtration
SVI	sludge volume index
t	time
V	volume

3.4 Introduction

The risks associated with the presence of potentially toxic metals in the waters and soils resulting from human activities have been largely studied (Nriagu and Pacyna, 1988; Nriagu, 1996; Wong *et al.* 2006). These contaminants are potentially toxic for microorganisms, plants, animals and humans (Lippmann, 2000; Allen, 2002; Sharma and Agrawal, 2005).

In the last decades, a lot of research works have been accomplished to develop efficient and cheap technologies for the treatment of metal–polluted effluents (Kurniawan *et al.* 2006). The technologies proposed notably include chemical precipitation (Blais *et al.* 2007) or bioprecipitation (Kaksonen *et al.* 2003), ion exchange (Mondal and Das, 2004), adsorption (Babel and Kurniawan, 2003) or biosorption (Romera *et al.* 2006), physical separation (Ben Frarès *et al.* 2005), electrochemical separation (Meunier *et al.* 2006), solvent extraction (Belkhouche *et al.* 2005), flotation (Zamboulis *et al.* 2004) and cementation (Nelson *et al.* 2000).

Among these technologies, precipitation is still the most widely used approach for metals removal from groundwater, surface water, leachates and industrial effluents (Mirbagheri and Hosseini 2004; FRTR 2005; Lacour *et al.* 2005). Metal separation from solutions by formation of metal hydroxides is the most common precipitation method in reason of the relative low costs of hydroxide salts (Baltpurvins *et al.* 1996; Meunier *et al.* 2002). Soluble metals can be precipitated as hydroxides according to Equation 1 by using different alkaline reagents, like CaO, $Ca(OH)_2$, $Mg(OH)_2$, NaOH and NH_4OH (Mirbagheri and Hosseini, 2004; Kurniawan *et al.* 2006).

Équation 3.1 $\mathbf{M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2\downarrow}$

Some others precipitating agents can be used to reach lower residual soluble metal concentrations (Islamoglu *et al.* 2006) and/or to produce metallic sludge having better thickening and dewatering properties (Kim *et al.* 2002; Viadero *et al.* 2006). Other precipitation techniques notably include the formation of insoluble metal sulphides (Veeken and Rulkens, 2003; Al-Tarazi *et al.* 2004), metal carbonates (McAnally *et al.* 1984; Guillard and Lewis, 2002), and metal phosphates (Ayati and Madsen, 2000; Mavropoulos *et al.* 2002; Pigaga *et al.* 2002).

Metal precipitation as sulphides (Equation 2), is usually carried out using chemicals like Na_2S, NaHS, H_2S or FeS (Al-Tarazi *et al.* 2004; Marchioretto *et al.* 2005).

Équation 3.2 $M^{2+} + S^{2-} \leftrightarrow MS\downarrow$

The carbonates, such as Na_2CO_3, $NaHCO_3$ and $CaCO_3$, can be used for the neutralization of effluents and metals precipitation according to the equation 3 (McAnally *et al.* 1984; Guillard and Lewis, 2002).

Équation 3.3 $M^{2+} + (CO_3)^{2-} \leftrightarrow M(CO_3)\downarrow$

It is possible to remove metals from effluents through insoluble metal phosphate formation as described in equation 4 (Mavropoulos *et al.* 2002; Pigaga *et al.* 2002).

Équation 3.4 $3\ M^{2+} + 2\ (PO_4)^{3-} \leftrightarrow M_3(PO_4)_2\downarrow$

The metal precipitation is usually carried out in a settling tank (Alves *et al.* 2005), and the metallic sludge produced is usually dewatered by filtration or centrifugation (Meunier *et al.* 2002; Viadero *et al.* 2006).

Different selective precipitating agents, like dithiocarbamate derivates (DTC, DDTC, DMTC), thiocarbonate salts (STC), and 2,4,6-trimercapto-1,3,5-triazine (TMT), have also been developed in the last years for the treatment of metal-polluted effluents (Matlock *et al.* 2001, 2002). However, their relative high cost is an obstacle to their use for many industrial applications (Meunier *et al.* 2002).

Oxidation/reduction reactions can also be used for the precipitation of specific metal pollutants, like arsenic and chromium (Evanko and Dzombak, 1997; Vanbroekhoven *et al.* 2005). Finally, coagulation-flocculation methods can be used in combination with precipitation techniques to treat metal-polluted effluents (Licskó, 1997; Charerntanyarak, 1999; Duan and Gregory, 2003).

In the past, the choice of a precipitating technique for the treatment of metal-polluted effluents was principally based on the cost of the chemicals used. However, it is evident that the decision should also consider the quantities and the dewatering characteristics of metallic sludge produced.

The aim of the present work was to develop basic technological knowledge on the dewatering (settling, filtration and centrifugation) properties of sludge produced by metals precipitation as metal hydroxides, sulphides, carbonates and phosphates. The performance of chemical equilibrium software (*MINEQL+*) was evaluated to predict residual soluble metal concentrations and generated solids in normal operational conditions used for treatment of metal-polluted effluents.

3.5 Material and methods

3.5.1 Solubility domain prediction

Solubility domains were calculated using the chemical equilibrium modelling system *MINEQL+* (version 4.5). This program may be used to compute equilibrium among dissolved, solid and adsorbed phases suitable for aqueous solutions based on the appropriate thermodynamic stability constants. In the present study, models were constrained to include only those solid phases that were found to govern solubility (example: oxides are not considered due to kinetic considerations). Ionic strength was considered "off" within the program. All calculations were performed at a constant temperature of 298K with the number of iteration cycles constrained to 100. Solubility domains were generated for four systems: hydroxides (Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Al^{3+}, Pb^{2+} and Sn^{2+}), sulphides (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+} and Zn^{2+}), phosphates (Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Al^{3+}, Sn^{2+} and Pb^{2+}) and carbonates (Ba^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}). The counter ion is chloride (Cl^{1-}) for all metals, except nitrate (NO_3^{1-}) for lead. The concentration of all metals was always initially set at 0.020 mol/L. Calculations were made for all systems over the pH range 2-14, with the exception of carbonate systems, for which the pH range 5-11.

3.5.2 Preparation of the monometallic solutions

Monometallic synthetic solutions having a concentration $[M^{n+}]$ of 0.020 mol/L were prepared starting from metal sulphate or chloride salts : Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Ba^{2+} (Mat Lab), Al^{3+} (Baker), Mg^{2+} (ACP), Ca^{2+} and Co^{2+} (Fisher Scientific Ltd.), Sn^{2+} (Caledon Lab), except for Pb^{2+}, where the nitrate salt (BDH ACS 453) was employed because of the limit of the lead solubility. Distilled water was used for all the experiments. In the case of hydroxide precipitation assays, the pH of the monometallic solutions was firstly adjusted to 2.0 with HCl 6.0 mol/L (Fisher Scientific Ltd., ACS reagent).

3.5.3 Metal precipitation assays

Metal precipitation tests were realized at ambient temperature (22 ± 2^oC) and with volumes of 1.5 L of each monometallic solution with a concentration of 0.020 mol/L in 2.0 L beakers (diameter 125 mm). Mixing of the solution was conducted using magnetic stir bar (length: 37 mm, diameter: 8 mm) with a speed mixing of 160 rpm. Speed mixing was determined with a Digital Photo Tachometer Model 461893 Extech instruments.

For each selected pH, a reaction time of 15 min was allowed for the system to reach equilibrium (Hove *et al.* 2008). Speed mixing was selected for a well mixture to obtain flocs with good dewaterability and filterability (Yudin *et al.* 1974; Sun *et al.* 2006; Wang *et al.* 2007) : generally high mixing speed generate small flocs sludge difficult to dewater and filtrate.

Metal precipitation tests were realized with the following four precipitating agents:

- Sodium hydroxide (mother solution at 2.5 mol/L);
- Sodium sulphide (Na_2S) at stoichiometric quantities;
- Monopotassium phosphate (KH_2PO_4) at stoichiometric quantities;
- Sodium bicarbonate ($NaHCO_3$) at stoichiometric quantities.

Hydroxide precipitation tests were done by adjusting the pH of the monometallic solutions (volume of 1.5 L) to 10.0 with the sodium hydroxide solution. However, for the Al^{3+}, Mg^{2+} and Ca^{2+} solutions, the precipitation pH values were respectively adjusted to 7.5, 12.0 and 12.5.

During the other precipitation tests, precipitant agents were firstly added to monometallic solutions. A pH adjustment was done by adding sodium hydroxide to 6.0, 8.0 and 7.0 respectively for phosphate, carbonate and sulphide. To note that in the case of sulphides and carbonates, an adjustment of the pH in values close to 5.50 was made to avoid the emission of hydrogen sulphide and dioxide carbon gases (Baltpurvins *et al.* 1996; Charerntanyarak, 1999; Feng *et al.* 2000). pH 10.0, 6.0, 8.0 and 7.0 values for metal precipitation tests for hydroxide, phosphate, carbonate and sulphide systems have been selected from *MINEQL+* software (version 4.5) simulations. Phosphate salt has been added at concentrations of 0.020 mol/L (for Al^{3+}, Fe^{3+} and Cr^{3+} precipitation assays) and 0.0133 mol/L (for the other metals). In the same way, carbonate and sulphide salts have been added at a final concentration of 0.020 mol/L. In exception, a concentration of 0.10 mol/L of carbonate salt was added for the treatment of the Ni^{2+} solution and a concentration of 0.030 mol/L of sulphide salt was added for the treatment of the Fe^{3+} solution. After addition of the precipitating agents, a pH adjustment was made, and the monometallic solutions were agitated during a 15 min period to reach equilibrium under a speed mixing of 160 rpm.

3.5.4 Sludge settling

After the agitation period, the suspensions were settled for 30 min in 2 L capacity cylinders and the resulting volumes of the settled sludge were measured to evaluate the sludge volume index (SVI) values. Volumes of 400 mL of the settled sludge were then sampled after the supernatants were removed by pumping.

3.5.5 Sludge filtration

Specific resistance to filtration (*SRF*) and filtration capacity (*FC*) were used to characterize the dewaterability of the sludge resulting from metals precipitation with the different precipitating agents (Degrémont, 1989). The mathematical expression of *SRF* is given by the following formula (Viadero *et al.* 2006):

Équation 3.5 $$SRF = \frac{2bPA^2}{\mu . c}$$

Where "b" is the slope of the plot (V vs. t/V), "P" is the vacuum, "A" is the filter area, "µ" is the viscosity of filtrate and "c" is the weight of solids/unit volume of filtrate.

Équation 3.6 $$c = \frac{1}{C_i/(100 - C_i) - C_f/(100 - C_f)}$$

Where "C_i" is the initial moisture content and "C_f" is the final moisture content.

Whatman No. 2 (8.0 µm pore size) membranes having an effective area of 12.50 cm^2 were used during the pressure filtration tests. A pressure of 31.7 kPa was applied on 200 mL volumes of the settled sludge samples inside a Fisherbrand stainless-steel pressure vessel (model 09-753-25A, Fisher Scientific Ltd.). The pressure was applied until no liquid was extracted. Filtrate and sludge viscosities were measured using a Brookfield DV-II+Pro programmable rheometer at a module speed of 60 rpm.

3.5.6 Sludge filtration

Volumes of 100 mL of the settled sludge samples were centrifuged at 3000 x *g* (3760 rpm) for 15 min using a Beckman Coulter Allegra^{TM} 6 Centrifuge, in order to evaluate this technique for the metallic sludge dewatering.

3.5.7 Analytical methods

The pH and ORP were determined before and after each experiment by using a pH-meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Nepean, Canada) equipped with a double junction Cole-Parmer electrode with Ag/AgCl reference cell for pH (daily calibration between 2 and 10). Total solids were measured according to the APHA method 1603 (APHA *et al.* 1999). Metals in solution were measured by plasma emission spectroscopy with a simultaneous ICP-AES (inductively coupled plasma - atomic emission spectroscopy, Vista Ax CCO simultaneous ICP-AES from Varian, Mississauga, Canada). Before analysis, liquid samples were first filtered on a Whatman 934-AH membrane (1.5 µm pore size) and were then acidified to give a 5% HCl solution. Analytical quality controls were performed with a certified standard solution (PlasmaCal Multielement Standard 900-Q30-100, SCP Science, Baie d'Urfé, Canada).

3.6 Results and discussion

3.6.1 Prediction of residual metal concentration

In order to fix the working pH, which allows the precipitation of the metals in the desired forms (metal hydroxides, carbonates, sulfides and phosphates), computer simulations have been carried out using the *MINEQL+* software. These predictions have concerned the 15 metals examined and, for each one, in the case of the four tested precipitating agents. Figures 3.1 to 3.3 illustrate some obtained results from computer simulations.

Tables 3.1 to 3.4 present the initial and final concentrations of soluble metals during the precipitation tests and the corresponding metal removal yields. Computer simulation results using the *MINEQL+* software are also presented, as well as the quantities of NaOH added to adjust the pH of the solutions. With the exception of hydroxide precipitation, each precipitation method involves a combined precipitation system, since precipitates are generally performed at a particular pH. For example, when employing sulphide precipitation at pH greater than 6.0, hydroxide precipitation can also occur (Anderson, 1994).

The analysis of the results while using of the chloride matrix (Table 3.1), hydroxides precipitate almost totally all the studied metals, except the Ca^{2+} where the yield was 56% and the Ba^{2+} which does not precipitate at all (results not shown). The substitution of the chloride matrix by the sulfate one in the case of six metals among those studied has led to no noticeable change in the results.

For hydroxides precipitation, the residual metal soluble concentrations and removal yields predicted by the *MINEQL+* software correspond very well with the experimental results, with the exception of $Mg(OH)_2$ and $Sn(OH)_2$ precipitation. In theses cases, low removal yields of 48%

and 30%, respectively, have been measured in the short term precipitation period, whereas a 24 h reaction period has allowed reaching precipitation yields similar to those predict by *MINEQL+*. It is important to take into consideration that the *MINEQL+* software, and the others comparable models, consider the chemical reactions at their equilibrium (infinite time). Consequently, they do not integrate kinetic aspects, which can be significant in metal precipitation techniques operate using short (in term of minutes) reaction periods.

In the case of sulphides (Table 3.2), they precipitate nine of the 15 studied metals with yields greater than 90% (at pH 7-8), the remaining five (Al^{3+}, Cr^{3+}, Ca^{2+}, Ba^{2+} and Mg^{2+}) do not precipitate at all (results not shown). Residual soluble metal concentrations and removal yields experimentally measured are in good accordance to those predicted by simulation in the cases of Cu^{2+}, Fe^{2+}, Sn^{2+} and Zn^{2+}. However, *MINEQL+* software overestimates the precipitation of Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+} as metal sulphides. A longer reaction time could probably enhance the removal yields for these metals. However, it is evident that kinetic aspects should be considered when computer modeling is use to predict the efficiency of metal precipitation techniques based on sulphide precipitation.

In the cases of Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}, there is probably formation of aqueous polysulphide species, which consumed sulphides during solubilization of Na_2S, creating concentrated areas in solution of S^{2-}. A similar phenomenon is encountered when working with large excess of sulphides for the treatment of metals contaminated effluents (Luther *et al.* 1996; van Hill *et al.* 2005; Lewis and Swartbooi, 2006). It should be noted that Fe^{3+} removal as sulphide can not be predicted by *MINEQL+*.

Carbonates were efficient to precipitate eight studied metals (removal yields ≥ 94%) at pH 7-8, and without any effect on the six others (Fe^{3+}, Al^{3+}, Cr^{3+}, Ca^{2+}, Sn^{2+} and Mg^{2+}) (Table 3.3). In this case, *MINEQL+* overestimated the carbonates precipitation for Ba^{2+}, Cd^{2+}, Co^{2+}, but underestimated the precipitation of Ni^{2+}.

Phosphates were also a good precipitating agent (removal yields ≥ 94%) at pH 3-7 for almost all studied metals (Table 3.4), except for Mg^{2+} (84% at pH 9), Ni^{2+} (78.5% after 24 h), and Sn^{2+} which does not precipitate at all. The comparison of experimental results with MINEQL+ predictions shows that the latter significantly overestimated the precipitation of Ba^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and underestimated the formation of lead phosphates. It should be noted that aluminum and chromium removal as phosphate precipitates can not be predicted by *MINEQL+*.

3.6.2 Settling characteristics

The obtained sludge in the different tests is essentially constituted of hydrated metallic precipitates and interstitial salted water. However, the precipitating agent used for removing metallic ions from solutions has a significant influence on the solid/liquid separation of the resulting metallic sludge. Tables 3.5 to 3.8 give some important technical data on the dewatering properties of the different types of metallic precipitates.

Firstly, SVI value indicates the behaviour of the sludge during a 30 min gravity settling period. Very large ranges (from 3.6 to 1100 mL/g) have been determined in SVI values between the different metals and types of precipitates. By comparing the average SVI values for six metals (Cd^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}), the following general ascending order has been obtained for the different types of precipitates: metal sulphides < phosphates < hydroxides < carbonates. This trend is confirmed in the work of Lewis and Swartbooi (2006) where they found that sulphide precipitates settle faster than hydroxide and carbonates precipitates. In the same way, the following general order of SVI values can be defined by comparing the average SVI values measured for the different metals: $Pb^{2+} < Ca^{2+} = Cu^{2+} \leq Ba^{2+} < Zn^{2+} = Fe^{3+} < Cr^{3+} = Sn^{2+} = Mn^{2+} < Ni^{2+} \leq Co^{2+} < Al^{3+} < Fe^{2+} < Cd^{2+} < Mg^{2+}$. Best settling properties have then been measured for lead precipitates (heavy and large size flocs), whereas Mg forms microscopic precipitates (small size flocs) that are difficult to separate by settling.

Systems obtained after hydroxide precipitation differ by their ionic strength. For divalent metals, this strength value is 0.040 and 0.060 M respectively for chloride and sulphate matrix. Therefore counter-anions (Cl^{-1} and SO_4^{-2}) activities have values of 4.86×10^{-2} and 5.04×10^{-2}. Also, for trivalent metals, the counter-anions activities have values of 7.56×10^{-2} and 8.87×10^{-2} respectively for chloride and sulphate matrix. In fact, this variation is more pronounced compared to divalent metals. Experimental results (Table 3.5) show a definite variation in SVI, QF and SRF values, and this can probably be explained by the change in ionic strength in the studied systems (chloride and sulphate).

3.6.3 Filtration characteristics

Some important filtration properties of the different metal precipitates are given in Tables 3.5 to 3.8. The precipitates of metal hydroxides for the two matrixes (chloride and sulphate), have low filtration capacities, except for the Pb^{2+} with a value of 22.8 kg/(m^2.h) (Table 3.5). Similarly, for the sulphides (Table 3.6), only Cu^{2+} and Co^{2+} show good filtration capacities with 5.3 and 5.6 kg/(m^2.h), respectively. Metal carbonates have high filtration capacities for Pb^{2+}, Cd^{2+}, Ba^{2+} and Mn^{2+} with values of 26.0, 11.7, 10.2 and 8.1 kg/(m^2.h), respectively (Table 3.7). The metal phosphates precipitates showed the best filtration capacity for five of the studied metals, which are namely Ba^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+} and Zn^{2+} and possess capacities ranging from 34 to 65 kg/(m^2.h) (Table 3.8).

By comparing the average filtration capacity values for Cd^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}, the following general descending order has been obtained for the different precipitates: metal phosphates > carbonates > hydroxides = sulphides. In general way, the following order of filtration capacity can also be defined for the different metals: $Ba^{2+} > Pb^{2+} > Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} \geq Mn^{2+} = Ca^{2+} \geq Co^{2+} > Ni^{2+} \geq Fe^{2+} = Mg^{2+} = Al^{3+} = Fe^{3+}$. Lead and barium form dense and compact precipitates which are easily separated by filtration or centrifugation. The high molecular weight of these two atoms could explain the high values of solids content measured by filtration and centrifugation. In contrast, Al^{3+} and Fe^{3+} produce (smaller size flocs) hydrated and gelatinous precipitates that are very difficult to separate. Sludge with higher floc density and larger floc size is much easier to dewater and settle (Wen *et al.* 1997). This hydrophilic character could be explained by the A character or hard acid aspect which is slightly more pronounced for these metals in accordance with the others (Stumm and Morgan, 1996).

In terms of SRF, a parallelism between this parameter and the filtration capacity has been observed. In fact, a sludge having high filtration capacity has practically no resistance to filtration or a very low SRF value. During hydroxides precipitation (in chloride matrix), it is also been noticed that seven of the studied metallic sludge (Al^{3+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+},$Ni^{2+}$and Sn^{2+}) have high SRF, with values exceeding 1×10^{13} m/kg (Table 3.5). The measured SRF values of nickel, chromium and cupric hydroxides (7.36×10^{13}, 9.9×10^{12} m/kg and 15.2×10^{11} m/kg respectively), have the same order of magnitude to SRF values determined by Knocke *et al.* (1980), ranged from 8 to 200×10^{11} m/kg, 5 to 50×10^{11} m/kg and 5 to 30×10^{11} m/kg for cupric, chromium and nickel hydroxides, respectively.

It has equally been noticed that among 15 studied metals, precipitation using sulphides and phosphates (Tables 3.6 and 3.8) gives generally the lowest SRF values, with the exception of Mn^{2+} with a lowest SRF value during precipitation using carbonates (Table 7).

In terms of sludge total solids, it has been noticed that the highest solids values have been measured for the hydroxides of Ca^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+} and Sn^{2+}, for the phosphates of Al^{3+}, Ba^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Zn^{2+}, and for the carbonates of Cd^{2+}, Mn^{2+} and Pb^{2+}. Lowest sludge solids (4 and 8% w/w) have been obtained after filtration of $Al(OH)_3$ and $Fe(OH)_3$ precipitates. In general way (independently of the types of precipitates), the following order of sludge solids has been established for the different metals: $Ba^{2+} > Pb^{2+} > Mg^{2+} > Cd^{2+} > Sn^{2+} = Cr^{3+} = Mn^{2+} > Zn^{2+} = Cu^{2+} > Ca^{2+} > Fe^{2+} = Ni^{2+} > Co^{2+} > Fe^{3+} = Al^{3+}$. The percentage of total solids obtained of nickel, chromium and cupric hydroxides (12.3, 24.7 and 23.4% w/w respectively) are consistent with those obtained by Knocke *et al.* (1980) ranged from 9.0 to 15.2% w/w, 19.5 to 28.5% w/w and 11.0 to 20.0% w/w for these same metals.

Therefore, considering the different dewatering properties, it appears that phosphates are the best adapted agents for water elimination during vacuum filtration of many metal precipitates (Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+} , Ni^{2+} and Zn^{2+}), whereas hydroxides are preferable for dewatering of Ca^{2+}, Cu^{2+}, Mg^{2+} and Sn^{2+} precipitates. Finally, carbonates seem particularly appropriate for solid/liquid separation of Mn^{2+} and Pb^{2+} precipitates.

3.6.4 Centrifugation characteristics

Solids contents of the metallic precipitates separated by centrifugation are given Tables 3.5 to 3.8. The results show clearly that centrifugation (at $3000 \times g$) is far less efficient that vacuum filtration (31.7 kPa) to eliminate water from metallic precipitates.

In similar way to filtration, very large ranges of solids contents (from 0.1 to 45.1% w/w) have been measured between the different metal and types of precipitates. As examples, 9 and 4% w/w solids were respectively measured for the $Cd(OH)_2$ and $MnHPO_4$ precipitates after centrifugation, whereas 41 and 31% w/w of solids has been reached for the $CdCO_3$ and $MnCO_3$ precipitates respectively. The following general order can be proposed by comparing the average solids contents values measured for the different metals: $Al^{3+} \leq Fe^{3+} \leq Zn^{2+} \leq Co^{2+} \leq Mg^{2+} \leq Ni^{2+} \leq Ca^{2+} \leq Fe^{2+} < Cu^{2+} \leq Cr^{3+} \leq Mn^{2+} < Sn^{2+} < Cd^{2+} < Ba^{2+} < Pb^{2+}$.

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3.8 References

Allen, H.E., 2002. Bioavailability of metals in terrestrial ecosystems : importance of partitioning for bioavailability to invertebrates, microbes, and plants. Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida, 176 p.

Al-Tarazi, M., Heesink, A.B.M., Versteeg, G.F., 2004. Precipitation of metal sulphides using gaseous hydrogen sulphide: mathematical modelling. Chem. Eng. Sci. 59 (3), 567-579.

Alves, L.C., Henrique, H.M., Xavier, A.M.F., Cammarota, M.C., 2005. Potential treatment alternative for laboratory effluents. Bioresource Technol. 96, 1650-1657.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), 1999. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1015 Fifteenth Street, NW, Washington, DC.

Anderson, W.C. Innovative Site Remediation Technology-Chemical Treatment. American

Academy of Environmental Engineers.

Ayati, M., Madsen, H.E.L., 2000. Crystallization of some heavy-metals phosphates alone and in the presence of calcium ion. J. Crystal. Growth. 208, 579-591.

Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater. 97 (1-3), 219-243.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., 1996. Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation. Waste Manag. 16(8), 717-725.

Belkhouche, N.E., Didi, M.A., Villemin, D., 2005. Separation of nickel and copper by solvent extraction using Di-2 ethylhexylphosphoric acide-based synergistic mixture. Solvent Extraction Ion Exchange 23 (5), 677-693.

Ben Frarès, N., Taha, S., Dorange, G., 2005. Influence of the operating conditions on the elimination of zinc ions by nanofiltration. Desalination 185, 245-253.

Blais, J.F., Djedidi, Z., Ben Cheikh, R., Tyagi, R.D., Mercier, G., 2008. Metals precipitation from effluents – A review. Practice Periodical Toxic Hazardous Radioactive Waste Management 12(3), 135-149.

Charerntanyarak, L., 1999. Heavy metals removal by chemical coagulation and precipitation. Water Sci. Technol. 39(10-11), 135-138.

Degrémont, 1989. Mémento technique de l'eau. 9th Edition, Paris, France.

Duan, J., Gregory, J., 2003. Coagulation by hydrolysing metal salts. Adv. Colloid Interface Sci. 100-102, 475-502.

Evenko, C.R., Dzomback, D.A., 1997. Remediation of metals-contamined soils and groundwater. Technology evaluation report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvania, 53 p.

Feng, D., Aldrich, C., Tan, H., 2000. Treatment of acid mine drainage by use of heavy metal precipitation and ion exchange. Min. Eng. 13(6), 623-642.

FRTR, 2005. Federal remediation technologies roundtable. Website "http://www.frtr.gov", [cited December, 1, 2005].

Guillard, D., Lewis, A.E., 2002. Optimisation of nickel hydroxycarbonate precipitation using a laboratory pellet reactor. Ind. Eng. Chem. 41, 3110-3114.

Hove, M., van Hill, R.P., Lewis, A.E., 2008. Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. Chem. Eng. Sci. 63, 1626-1635.

Islamoglu, S., Yilmaz, L., Ozbelge, H.O., 2006. Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents. Sep. Sci. Technol. 41 (15), 3367-3385.

Kaksonen, A.H., Riekkola-Vanhanen, M.L., Puhakka, J.A., 2003. Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater. Water Res. 37 (2), 255-266.

Kim, B.R., Gaines, W.A., Szafranski, M.J., Bernath, E.F., Miles, A.M., 2002. Removal of heavy metals from automotive wastewater by sulphide precipitation. J. Environ. Eng. Div. ASCE 128 (7), 612-623.

Knocke, W.R., Ghosh, M.M., Novak, J.T., 1980.Vaccum filtration of metal hydroxide sludges. J. Environ. Eng. Div. ASCE 106 (2), 363-376.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S., 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci. Total Environ. 366 (2-3), 409-426.

Lacour, S., Van Hille, R.P., Peterson, K., Lewis, A.E., 2005. Comparison of simulators for process and aqueous chemistry modeling. AIChE J. 51 (8), 2358-2368.

Lewis, A., Swartbooi, A., 2006. Factors affecting metal removal in mixed sulphide precipitation. Chem. Eng. Technol. 29 (2), 277-280.

Licskó, I., 1997. Realistic coagulation mechanisms in the use of aluminium and iron(III) salts. Water Sci. Technol. 364, 103-110.

Lippmann, M., 2000. Environmental toxicants. Human exposures and their health effects. John Wiley & Sons, Inc., New York, NY, 987 p.

Luther, G.W., Rikard, D.T., Theberge, S., Olroyd, A., 1996. Determination of metal (bi)sulphide stability constants of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Ni^{2+} by voltammetric methods. Environ. Sci. Technol. 30, 671-679.

Marchioretto, M.M., Bruning, H., Rulkens, W., 2005. Heavy metals precipitation in sewage sludge. Sep. Sci. Technol. 40 (16), 3393-3405.

Matlock, M.M., Henke, K.R., Atwood, D.A., 2002. Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs. J. Hazard. Mater. B92, 129-142.

Matlock, M.M., Henke, K.R., Atwood, D.A., Robertson, D., 2001. Aqueous leaching properties and environmental implications of cadmium, lead and zinc trimercaptotriazine (TMT) compounds. Water Res. 35 (15), 3649-3655.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., Saldanha, M., 2002. Studies on the mechanisms of lead immobilization by hydroxyapatite. Environ. Sci. Technol. 36 (7), 1625-1629.

McAnally, S., Benefield, L., Reed, R.B., 1984. Nickel removal from a synthetic nickel-plating waste water using sulphide and carbonate for precipitation and coprecipitation. Sep. Sci. Technol. 19, 191-217.

Meunier, N., Blais, J.F., Lounes, M., Tyagi, R.D., Sasseville, J.L., 2002. Different options for metal recovery after sludge decontamination at the Montreal Urban Community wastewater treatment plant. Water Sci. Technol. 46 (10), 33-41.

Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., Blais, J.F., 2006. Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. J. Hazard. Mater. 137 (1), 581-590.

Mirbagheri, S.A., Hosseini, S.N., 2004. Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. Desalination 171 (1), 85-93.

Mondal, B.C., Das, A.K., 2004. Functionalized chelating resins for selective sorption of metal ions: an overview. J. Indian Chem. Soc. 81 (2), 95-110.

Nelson, A., Wang, W., Demopoulos, G.P., Houlachi, G., 2000. The removal of cobalt from zinc electrolyte by cementation: a critical review. Min. Proc. Ext. Met. Rev. 20, 325-356.

Nriagu, J., 1996. A history of global metal pollution. Science 272, 22-24.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of world-wide contamination of air, water, and soils by trace metals. Nature 333, 134-139.

Pigaga, A., Juskenas, R., Selkis, A., 2002. Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation. Sep. Sci. Technol. 37 (13), 3155-3168.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M.L., Munoz, J.A., 2006. Biosorption with algae: A statistical review. Crit. Rev. Biotechnol. 26 (4), 223-235.

Sharma, R.K., Agrawal, M., 2005. Biological effects of heavy metals: an overview. J. Environ. Biol. 26 (2), 301-313.

Stumm, W., Morgan, J.J., 1996. Aquatic chemistry, Third Edition, John Wiley and Sons, New-York, NY, 1022 p.

Sun, J.M., Li, F., Huang, J.C., 2006. Optimum pH for the Cr^{6+} co-removal with mixed Cu^{2+}, Zn^{2+}, and Ni^{2+} precipitation. Ind. Eng. Chem. Res. 45, 1557-1562.

Van Hill, R.P., Peterson, K.A., Lewis, A.E., 2005. Copper sulphide precipitation in a fluidised bed reactor. Chem. Eng. Sci. 60, 2571-2578.

Vanbroekhoven, K., Dejonghe, W., Diels, L., 2005. Treatment of contaminated soil and groundwater: in situ immobilization of metals. In: Soil and sediment remediation. Mechanisms, technologies and applications. Lens, P., Grotenhuis, T., Malina, G., Tabak, H. (Eds), IWA Publishing, London, England, Chap. 13, pp. 248-263.

Veeken, A.H.M., Rulkens, W.H., 2003. Innovative developments in the selective removal and reuse of heavy metals from wastewaters. Water Sci. Technol. 47 (10), 9-16.

Viadero, R.C., Wei, X.C., Buzby, K.M., 2006. Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization. Environ. Eng. Sci. 23(4), 734-743.

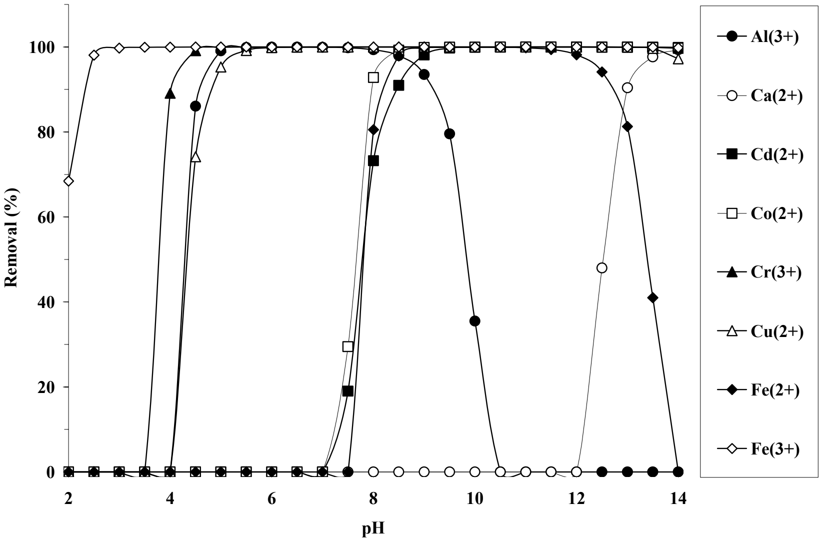
Wang, Z., Zhang, Q., Yang, C., Mao, Z., Shen, X., 2007. Simulation of barium sulphate precipitation using CFD and FM-PDF modeling in a continuous stirred tank. Chem. Eng. Technol. 30(12), 1642-1649.

Wen, H.J., Liu, C.I., Lee, D.J., 1997. Effects of polymer dosage on alum sludge dewatering characteristics and physical properties. Colloids Surf. A. Physicochem. Eng. Aspects. 122 (1-3), 89-96.

Wong, C.S.C., Li, X.D., Thornton, I., 2006. Urban environmental geochemistry of trace metals. Environ. Pollut. 142 (1), 1-16.

Yudin, B.A., Kolesnikov, V.N., Kornienko, V.P., 1974. Effects of precipitation conditions on the crystal size of silver oxalate–nickel oxalate salt mixtures. Part 1. Metallurgiya 7(139), 11-14.

Zamboulis, D., Pataroudi, S.I., Zouboulis, A.I., Matis, K.A., 2004. The application of sorptive flotation for the removal of metal ions. Desalination 162, 159-168.



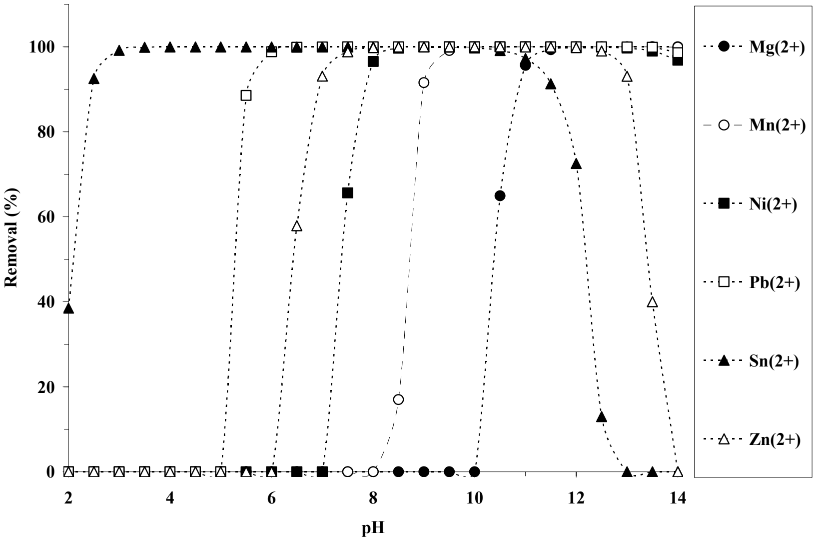


Figure 3.1 **Solubility of different metal hydroxides based on chemical equilibrium calculations using the *MINEQL+* software. Simulation conditions: T = 25°C, $[Cl^-]_i$ = 0.040 mol/L for divalent ions, 0.060 mol/L for trivalent ions and $[metal]_i$ = 0.020 mol/L. I = 0**

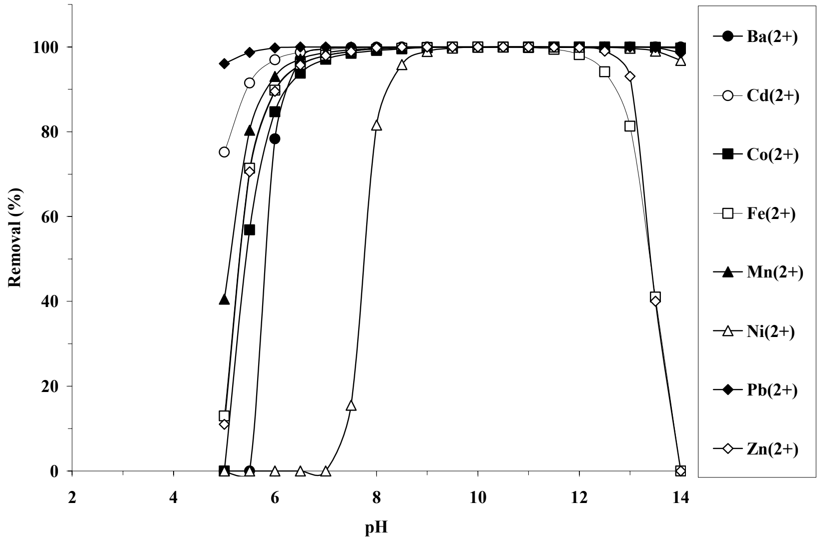


Figure 3.2 **Solubility of different metal carbonates based on chemical equilibrium calculations using the *MINEQL+* software. Simulation conditions: T = 25°C, $[Cl^-]_i$ = 0.040 mol/L and $[metal]_i$ = 0.020 mol/L, $[CO_3^{2-}]_i$ = 0.020 mol/L. I = 0**

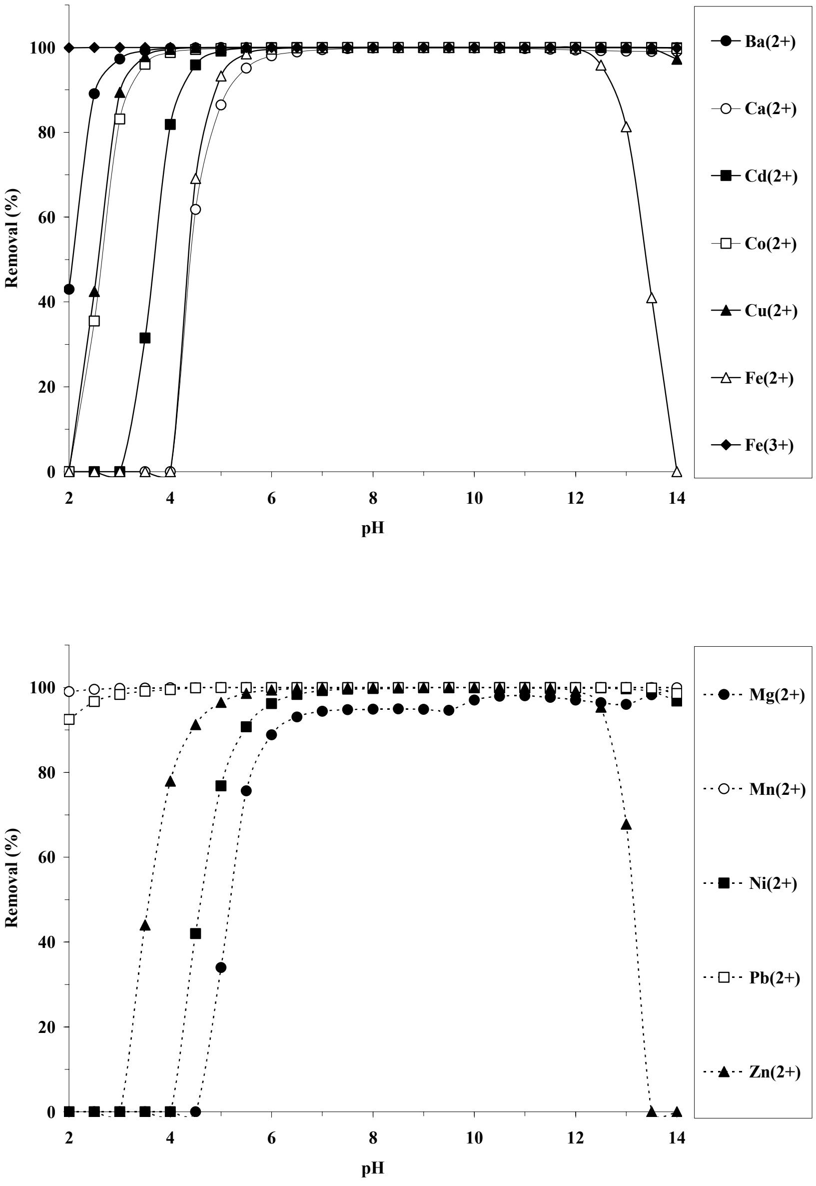


Figure 3.3 **Solubility of different metal phosphates based on chemical equilibrium calculations using the *MINEQL+* software. Simulation conditions: T = 25°C, $[Cl^-]_i$ = 0.040 mol/L for divalent ions, 0.060 mol/L for trivalent ions, and $[metal]_i$ = 0.020 mol/L, $[PO_4^{3-}]_i$ =0.0133 mol/L and 0.020 mol/L for Fe^{3+}, Al^{3+} and Cr^{3+}. I = 0**

Tableau 3.1 **Metals precipitation, sludge production and economic data associated to the treatment of the synthetic mono-metallic solutions using NaOH as precipitating agent**

Metals	Precipitation tests					*MINEQL*+ prediction		
	Final pH	NaOH (kg/m^3)	[M]$_i$ (mg/L)	[M]$_f$ (mg/L)	*Removal (%)*	[M]$_f$ (mg/L)	*Removal (%)*	Precipitates
Chloride matrix								
Al^{3+}	7.5	2.64	550	6.78	*98.8*	1.21	*99.8*	$Al(OH)_3$
Ca^{2+}	12.4	13.4	583	258	*55.6*	252	*56.7*	$Ca(OH)_2$
Cd^{2+}	10.0	1.68	3000	2.05	*99.9*	2.10	*99.9*	$Cd(OH)_2$
Co^{2+}	10.2	1.88	1220	2.63	*99.8*	0.24	*99.9*	$Co(OH)_2$
Cr^{3+}	10.0	3.02	1050	0.58	*99.9*	0.11	*99.9*	$Cr(OH)_3$
Cu^{2+}	10.6	1.74	1260	0.07	*99.9*	0.13	*99.9*	$Cu(OH)_2$
Fe^{2+}	10.0	2.17	1190	0.66	*99.9*	0.36	*99.9*	$Fe(OH)_2$
Fe^{3+}	10.0	2.55	1210	0.26	*99.9*	0.12	*99.9*	$Fe(OH)_3$
Mg^{2+}	12.0	2.64	491	258 (2.11)*	*47.6 (99.6)**	0.79	*99.8*	$Mg(OH)_2$
Mn^{2+}	10.0	1.89	1120	4.49	*99.6*	1.23	*99.9*	$Mn(OH)_2$
Ni^{2+}	10.3	2.01	1220	0.43	*99.9*	0.12	*99.9*	$Ni(OH)_2$
Pb^{2+}	10.1	1.77	4340	2.44	*99.9*	0.43	*99.9*	$Pb(OH)_2$
Sn^{2+}	10.0	1.99	2040	1420 (20.8)*	*30.3 (98.9)**	6.13	*99.7*	$Sn(OH)_2$
Zn^{2+}	10.0	1.95	1370	0.36	*99.9*	0.14	*99.9*	$Zn(OH)_2$
Sulfate matrix								
Al^{3+}	8.1	3.29	540	2.00	*99.6*	0.23	*99.9*	$Al(OH)_3$
Co^{2+}	10.0	2.13	1130	0.54	*99.9*	0.12	*99.9*	$Co(OH)_2$
Cu^{2+}	10.0	1.95	1220	1.09	*99.9*	0.11	*99.9*	$Cu(OH)_2$
Fe^{3+}	10.0	4.24	1120	0.62	*99.9*	0.11	*99.9*	$Fe(OH)_3$
Ni^{2+}	10.0	2.13	1120	0.67	*99.9*	0.40	*99.9*	$Ni(OH)_2$
Zn^{2+}	10.0	2.12	1330	0.60	*99.9*	0.23	*99.9*	$Zn(OH)_2$

* Sn^{2+} and Mg^{2+} removal yields measured after a 24-h reaction period.

Tableau 3.2 Metals precipitation, sludge production and economic data associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using Na_2S as precipitating agent

Metals	Precipitation tests					*MINEQL+* prediction		
	Final pH	NaOH (kg/m^3)	$[M]_i$ (mg/L)	$[M]_f$ (mg/L)	*Removal (%)*	$[M]_f$ (mg/L)	*Removal (%)*	Precipitates
Cd^{2+}	7.1	0.11	2250	190 (0.08)*	*91.5 (99.9)**	2.25	*99.9*	CdS
Co^{2+}	7.9	0.00	1180	28.6 (0.09)*	*97.5 (99.9)**	0.00	*100*	CoS
Cu^{2+}	7.2	0.13	1270	0.49	*99.9*	0.25	*99.9*	CuS
Fe^{2+}	7.1	0.00	1120	152	*86.4*	128	*88.5*	FeS
Fe^{3+}	7.3		1120	4.08	*99.6*	-	-	Fe_2S_3
Mn^{2+}	7.1	0.00	1100	90.0 (1.05)*	*91.8 (99.9)**	0.22	*99.9*	MnS
Ni^{2+}	7.8	0.00	1170	6.72 (0.52)*	*99.4 (99.9)**	0.23	*99.9*	NiS
Pb^{2+}	7.1	0.11	4140	0.04	*99.9*	0.41	*99.9*	PbS
Sn^{2+}	7.0	0.20	2370	1.53	*99.9*	0.47	*99.9*	SnS
Zn^{2+}	7.2	0.16	1310	0.21	*99.9*	2.75	*99.8*	ZnS

* Cd^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} removal yields with molar ratio $R_{Me\text{-}S} = 1.3$ (Me =Cd^{2+}, Co^{2+} or Mn^{2+} or Ni^{2+}).

Tableau 3.3 **Metals precipitation, sludge production and economic data associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using $NaHCO_3$ as precipitating agent**

Metals	Precipitation tests					*MINEQL+* prediction		
	Final pH	NaOH (kg/m^3)	$[M]_i$ (mg/L)	$[M]_f$ (mg/L)	*Removal (%)*	$[M]_f$ (mg/L)	*Removal (%)*	Precipitates
Ba^{2+}	8.1	0.73	2670	144	*94.6*	1.07	*99.9*	$BaCO_3$
Cd^{2+}	8.0	0.93	2250	268	*88.1*	7.19	*99.7*	$CdCO_3$
Co^{2+}	8.0	1.16	1180	43.9	*96.3*	10.0	*99.2*	$CoCO_3$
Fe^{2+}	8.0	1.20	1120	2.02	*99.8*	6.58	*99.4*	$FeCO_3$
Mn^{2+}	8.0	0.84	1100	10.7	*99.0*	7.91	*99.3*	$MnCO_3$
Ni^{2+}	7.9	0.92	1170	67.7	*94.2*	217	*81.6*	$NiCO_3$, $Ni(OH)_2$
Pb^{2+}	7.9	0.79	4140	0.03	*99.9*	0.41	*99.9*	$PbCO_3$, $Pb_3(OH)_2(CO_3)_2$
Zn^{2+}	7.1	1.07	1310	25.1	*98.1*	26.9	*97.9*	$ZnCO_3.1H_2O$

Tableau 3.4 Metals precipitation, sludge production and economic data associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using KH_2PO_4 as precipitating agent

Metals	Precipitation tests					*MINEQL+* prediction		
	Final pH	NaOH (kg/m^3)	$[M]_i$ (mg/L)	$[M]_f$ (mg/L)	*Removal (%)*	$[M]_f$ (mg/L)	*Removal (%)*	Precipitates
Al^{3+}	3.0	1.36	550	31.7	*94.2*	-	-	$AlPO_4$
Ba^{2+}	6.0	0.89	2940	35.1	*98.8*	0.29	*99.9*	$Ba_3(PO4)_2$
Ca^{2+}	8.0	2.00	802	8.93	*98.9*	1.28	*99.8*	$Ca_3(PO4)_2$
Cd^{2+}	6.0	1.40	3040	53.6	*98.2*	1.52	*99.9*	$Cd_3(PO4)_2$
Co^{2+}	6.0	1.11	1290	99.6	*92.3*	1.54	*99.9*	$Co_3(PO4)_2$
Cr^{3+}	6.0	1.88	1050	17.5	*98.3*	-	-	$CrPO_4$
Cu^{2+}	6.0	1.40	1220	5.55	*99.5*	0.12	*99.9*	$Cu_3(PO4)_2$
Fe^{2+}	6.0	1.24	1120	8.09	*99.3*	4.46	*99.6*	$Fe_3(PO4)_2$
Fe^{3+}	3.0	1.57	1120	2.68	*99.8*	0.89	*99.9*	$FePO_4.2H_2O$
Mg^{2+}	9.0	1.99	480	76.8	*84.0*	53.5	*88.9*	$Mg_3(PO4)_2$
Mn^{2+}	6.0	1.19	1200	17.1	*98.6*	0.12	*99.9*	$MnHPO_4$
Ni^{2+}	6.0	0.85	1150	580 (247)*	*49.6 (78.5)**	43.9	*96.2*	$Ni_3(PO4)_2$
Pb^{2+}	7.0	1.35	4140	0.47	*99.9*	20.7	*99.5*	$Pb_3(PO4)_2$
Zn^{2+}	6.0	1.28	1440	11.7	*99.2*	8.48	*99.4*	$Zn_3(PO4)_2$

* Ni^{2+} removal yield measured after a 24-h reaction period.

Tableau 3.5 **Metallic sludge dewatering properties associated to the treatment of the synthetic mono-metallic solutions using NaOH as precipitating agent**

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	Solids (% w/w)	Sludge production (kg/m^3)	Capacity (kg/(m^2.h))	SRF (m/kg x 10^{12})	Solids (% w/w)
Chloride matrix							
Al^{3+}	25.1	377	4.2	37.6	0.15	87.7	2.4
Ca^{2+}	19.0	10.3	34.5	2.19	14.67	-	12.3
Cd^{2+}	55.1	56.0	22.7	16.0	2.58	4.31	9.0
Co^{2+}	69.7	260	24.0	7.74	0.27	34.4	8.9
Cr^{3+}	48.3	44.0	24.7	8.34	2.15	9.90	10.7
Cu^{2+}	33.7	67.0	23.4	7.92	1.28	3.01	19.9
Fe^{2+}	92.8	177	25.6	6.44	0.37	34.6	14.1
Fe^{3+}	10.7	126	8.0	24.6	0.60	25.6	4.8
Mg^{2+}	1100	40.0	64.6	0.76	1.41	27.8	9.4
Mn^{2+}	32.6	40.0	30.4	4.84	1.57	5.16	12.6
Ni^{2+}	48.1	413	12.3	15.3	0.18	73.6	5.4
Pb^{2+}	6.0	3.4	51.4	8.88	74.66	-	34.0
Sn^{2+}	39.7	162	37.6	6.96	0.69	19.1	28.0
Zn^{2+}	13.4	21.0	8.7	20.6	3.27	3.46	0.1
Sulfate matrix							
Al^{3+}	29.8	111	6.8	30.3	0.72	22.1	2.9
Co^{2+}	65.9	150	14.9	13.6	0.55	27.2	5.7
Cu^{2+}	30.3	51	26.2	8.88	1.63	8.86	10.7
Fe^{3+}	34.7	338	11.5	25.0	0.36	42.0	5.9
Ni^{2+}	46.2	374	9.5	20.1	0.20	69.6	4.0
Zn^{2+}	42.2	42	10.7	21.5	2.20	5.99	2.8

Tableau 3.6 **Metallic sludge dewatering properties associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using Na_2S as precipitating agent**

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	Solids (% w/w)	Sludge production (kg/m^3)	Capacity (kg/(m^2.h))	SRF (m/kg x 10^{12})	Solids (% w/w)
Cd^{2+}	8.9	63	14.1	22.5	1.82	7.87	9.2
Co^{2+}	5.3	5.0	8.8	27.5	16.43	0.28	6.3
Cu^{2+}	8.0	5.5	16.6	13.4	15.64	0.18	13.9
Fe^{2+}	38.0	168	13.7	12.6	0.41	27.1	6.6
Fe^{3+}	33.5	552	15.0	17.9	0.11	67.5	7.3
Mn^{2+}	30.5	15	30.9	5.9	3.66	2.73	11.2
Ni^{2+}	11.3	24	17.1	13.0	3.38	4.06	9.5
Pb^{2+}	6.9	20	26.5	18.4	8.36	1.40	20.8
Sn^{2+}	17.2	74	30.0	11.3	1.58	9.41	12.9
Zn^{2+}	23.4	159	18.6	11.3	0.55	24.6	7.5

Tableau 3.7 Metallic sludge dewatering properties associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using $NaHCO_3$ as precipitating agent

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	Solids (% w/w)	Sludge production (kg/m^3)	Capacity (kg/(m^2.h))	SRF (m/kg x 10^{12})	Solids (% w/w)
Ba^{2+}	34.4	4.1	62.2	5.99	31.59	-	20.2
Cd^{2+}	176	3.5	70.6	5.61	36.90	0.05	40.9
Co^{2+}	44.3	229	11.1	19.0	0.35	52.0	4.4
Fe^{2+}	52.1	136	13.0	13.6	0.48	29.5	5.7
Mn^{2+}	3.6	3.3	57.9	3.71	23.81	-	30.7
Ni^{2+}	44.2	40	19.0	11.9	3.01	4.16	6.7
Pb^{2+}	7.6	2.3	76.4	6.89	93.27	-	45.1
Zn^{2+}	21.6	139	17.6	12.0	0.59	23.0	5.3

Tableau 3.8 **Metallic sludge dewatering properties associated to the treatment of the synthetic mono-metallic solutions (in chloride matrix) using KH_2PO_4 as precipitating agent**

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	Solids (% w/w)	Sludge production (kg/m^3)	Capacity ($kg/(m^2.h)$)	SRF ($m/kg \times 10^{12}$)	Solids (% w/w)
Al^{3+}	62.6	69	15.1	15.6	2.25	8.81	6.1
Ba^{2+}	4.1	0.9	88.6	4.84	238.19	-	31.7
Ca^{2+}	12.1	54	8.9	27.6	2.66	-	4.0
Cd^{2+}	62.0	1.5	51.2	9.07	156.45	-	34.4
Co^{2+}	32.1	23	14.3	19.0	6.86	2.57	7.3
Cr^{3+}	7.6	1.5	42.5	8.23	121.6	-	17.1
Cu^{2+}	7.8	11	9.0	40.8	15.04	0.52	5.0
Fe^{2+}	15.9	29	21.2	14.6	5.60	2.67	8.3
Fe^{3+}	30.7	214	12.3	31.2	0.70	21.5	5.8
Mg^{2+}	86.8	88	19.5	10.2	1.52	10.6	4.3
Mn^{2+}	51.7	48	15.0	17.5	3.06	4.57	3.6
Ni^{2+}	42.5	42	24.8	7.51	3.09	6.42	7.3
Pb^{2+}	7.2	2.0	43.9	13.8	131.18	-	16.2
Zn^{2+}	33.9	1.3	58.4	4.71	127.24	-	10.5

CHAPITRE IV

COMPARATIVE STUDY OF DEWATERING CHARACTERISTICS OF METAL PRECIPITATES DURING TREATMENT OF SYNTHETIC POLYMETALLIC AND AMD SOLUTIONS

Le Chapitre 4 est constitué de l'article suivant:

Zied Djedidi, Bouda Médard, Ridha Ben Cheikh, Guy Mercier, Rajeshwar Dayal Tyagi et Jean François Blais (2009) Comparative study of dewatering characteristics of metal precipitates during treatment synthetic polymetallic and AMD solutions. *Hydrometallurgy*. 98, 247-256.

Résumé

Les caractéristiques de déshydratation, exprimées en termes de décantation, filtration et centrifugation, des boues générées à l'issue du traitement par précipitation des solutions multimétalliques et des drainages miniers acides synthétiques, ont été évaluées dans cette étude. Les résultats ont montré que les propriétés de déshydratation des boues métalliques varient, en fonction de la matrice utilisée (Cl^- ou SO_4^{2-}), de l'agent précipitant et des métaux présents dans l'effluent. Les hydroxydes métalliques (pH 10.0) et les phosphates métalliques (pH 7.0) sont de natures amorphes, donc ils sont difficiles à déshydrater. Pour ces deux méthodes de traitement, la substitution de la matrice chlorure par la matrice sulfate, améliore considérablement les caractéristiques de déshydratation (résistance spécifique à la filtration = 6.60×10^{13} et 2.35×10^{13} m/kg, respectivement pour les matrices chlorures et sulfates). Dans les cas des traitements par les sulfures et les carbonates (à pH 8.0), les précipités obtenus sont respectivement de nature semi-cristalline et cristalline et aucune influence significative sur les caractéristiques de déshydratations n'a été détectée, lors de la substitution de la matrice chlorure par la matrice sulfate.

Comparative study of dewatering characteristics of metal precipitates generated during treatment of synthetic polymetallic and AMD solutions

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4. COMPARATIVE STUDY OF DEWATERING CHARACTERISTICS OF METAL PRECIPITATES DURING TREATMENT OF SYNTHETIC POLYMETALLIC AND AMD SOLUTIONS

4.1 Abstract

The sludge dewatering characteristics expressed in terms of settling, filtration and centrifugation of metal precipitates generated during treatment of polymetallic solutions and synthetic acid mine drainage have been evaluated in this research. Results show that dewatering properties of metallic sludge vary depending on the type of matrix (Cl^-; SO_4^{2-}), precipitating agent, and metals present in effluent. Metal hydroxides (at pH 10.0) and metal phosphates precipitates (at pH 7.0) are amorphous in nature, thus difficult to dewater. In these treatment methods, the substitution of chloride matrix by sulphate one improves considerably dewatering properties (specific resistance to filtration = 6.60×10^{13} and 2.35×10^{13} m/kg for the chloride and sulphate matrix, respectively). In the case of sulphide and carbonate treatments (pH 8.0), precipitates obtained are semi crystalline, and crystalline form, respectively, and no influence of the matrix was detected on dewatering characteristics.

4.2 Keywords

Metal; Precipitation; Sludge; Dewatering; Hydroxide, Sulphide; Phosphate, Carbonate.

4.3 Nomenclature

μ	viscosity of the filtrate (Pa.s)
A	surface area (m^2)
AMD	acid mine drainage
b	slope of the plot (V vs. t/V)
c	weight of solids/unit volume of filtrate (kg.m^{-3})
C_f	final concentration (mol.L^{-1})
C_i	initial concentration (mol.L^{-1})
FC	filtration capacity (kg.m^{-2}.s^{-1})
I	ionic strength (mol.L^{-1})
M	bivalent metal
P	pressure (Pa)
rpm	rotations per minute
S	exchanger
SRF	specific resistance to filtration (m.kg^{-1})
SVI	sludge volume index (mL.g^{-1})
t	time (s)
TS	total solids (w.w^{-1})
V	volume (m^3)
XRD	X-ray diffraction

4.4 Introduction

Precipitation is the most commonly used process for the removal of metals from industrial wastewaters because it offers a most cost-effective solution applicable to large operating units (Patterson, 1988, Baltpurvins *et al.* 1996a, Mishra, 1999, Blais *et al.* 2008). Many studies have demonstrated efficiency of the precipitation in removing various metals (for example, nickel, copper, zinc, cadmium and lead) as sulphide, carbonate and phosphate instead of hydroxide (McAnally *et al.* 1984, Preis and Gamsjager, 2001; Guillard and Lewis, 2002; Mavropoulos *et al.* 2002; Pigaga *et al.* 2002; Naeem *et al.* 2003; Veeken and Rulkens, 2003, Al-Tarazi *et al.* 2004).

From a chemical point of view, precipitation is a complex phenomenon resulting from the formation of conditions of supersaturation. It can be described by three steps: 1) nucleation or germination; 2) crystalline growth; and 3) flocculation (Patterson, 1988). In many precipitation systems, the characteristic reaction and nucleation times are very short, of the order of milliseconds or less (Sohnel and Garside, 1992), and thus, kinetic considerations are of minor concern compared to thermodynamics.

One method that appears to be potentially useful for the prediction of effluent composition effects employs the use of solubility curves concept (Baltpurvins *et al.* 1996b). This involves the calculations of the treatment efficiency in terms of residual metal ion concentration versus pH. The construction of a solubility domain is a complex process and involves the simultaneous solution of all the relevant mass action expressions for the overall system, in reference to their mass balances.

Computer simulation tools (*HYDRAQL, MINEQL+, MINTEQA2, PHREEQC*) incorporating extensive databases have also been developed to simulate aqueous-based chemical systems involving a variety of species over a broad range of temperature, pH and composition (Westall *et al.* 1976; Papelis *et al.* 1988; Allison *et al.* 1991; Parkhurst and Appelo, 1999). These models can be used to get good approximations of the residual metal concentrations in solution for different metal precipitation scenarios (Apul *et al.* 2005; Halim *et al.* 2005).

Besides yield and selectivity, a good knowledge of settling (SVI), filterability (SRF, FC) and dewatering characteristics (TS) of the metal precipitates produced is also necessary to evaluate the techno-economic performance of different metal precipitation methods.

The purpose of this study is to illustrate the matrix effect (Cl^- versus SO_4^{2-}) in terms of residual metal concentration and dewatering characteristics of sludge generated after hydroxide, phosphate, carbonate, and sulphide precipitation of polymetallic solutions. These parameters are also studied in the case of sludge generated from two typical compositions of synthetic AMD. All residual metal concentrations have been compared to those calculated with *MINEQL+* software.

4.5 Material and methods

4.5.1 Solubility domain predictions

Solubility domains were calculated using the chemical equilibrium modelling system *MINEQL+* (version 4.5). This program may be used to compute equilibrium among dissolved, solid and adsorbed phases suitable for aqueous solutions based on the appropriate thermodynamic stability constants. In the present study, models were constrained to include only those solid phases that were found to govern solubility (example: oxides are not considered due to kinetic considerations). Ionic strength was considered "off" within the program. All calculations were performed at a constant temperature of 298K with the number of iteration cycles constrained to 100. Solubility domains were generated for four systems: hydroxides and phosphates for the first polymetallic solution (Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+}), sulphides and carbonates for the second polymetallic solution (Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+}). The counter ion is sulphate (SO_4^{2-}) for all systems. The concentration of all metals was always initially set at 4.00×10^{-3} mol/L. Calculations were made over the pH range 2-14, for hydroxide and phosphate, and 5-14 for sulphide and carbonate systems.

4.5.2 Adsorption prediction

Adsorption prediction of Ni and Zn ions onto to ferrihydrite in the case of neutralized AMD1 was modeled using the Two-Layer FeOH adsorption model from *MINEQL+* (version 4.5). A surface complexation database for sorption of inorganic species on $Fe(OH)_3$ (s) is included in the *MINEQL+* thermodynamic database. These surface complexation reactions and constants were taken from Dzombak and Morel (1990) and were readily incorporated in geochemical speciation codes, and have been gainfully employed in understanding metal speciation in such diverse aquatic environments as acid mine drainage (Ball *et al.* 2001).

The system is defined as follow: total ferric iron of 1.29×10^{-2} M; total zinc of 4.59×10^{-6} M; total nickel of 1.02×10^{-6} M; ionic strength I of 0.46 M; and pH of 10.0.

4.5.3 Preparation of the polymetallic solutions

Polymetallic synthetic solutions having a concentration $[M^{n+}]$ of 0.004 mol/L for each metal were prepared starting from metal sulphate or chloride salts : Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} (Lab Mat), Al^{3+} (Baker). Distilled water was used for all the experiments. In the case of hydroxide precipitation assays, the pH of polymetallic solutions was firstly adjusted to 2.0 with HCl 6.0 mol/L or H_2SO_4 3.0 mol/L (Fisher Scientific Ltd., ACS reagent) for the chloride and sulphate matrix, respectively.

Four polymetallic solutions were prepared:

- **Sln A**: contains Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} in chloride matrix ;
- **Sln B**: contains Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} in sulphate matrix ;
- **Sln C**: contains Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in chloride matrix ;
- **Sln D**: contains Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in sulphate matrix.

4.5.4 Preparation of the AMD solutions

Two typical compositions of acid mine drainage (AMD1 and AMD2) were studied in this work. Composition of the AMD1 was selected on the basis of the median concentrations of 10 AMDs of mining sites reported in the literature (MEND, 1994). AMD2 composition was also determined using median from metal concentration values of 11 AMDs reported in Gilbert *et al.*

(2003), Demopoulos *et al.* (1997), Hammarstrom *et al.* (2003), Yabe and Oliveira (2001), Feng *et al.* (2004), Wurzburger and Overton (2004), Tabak *et al.* (2003), Cocos *et al.* (2002), Chartrand and Bunce (2003) and MEND (1996).

AMD solutions were prepared starting from metal sulphate salts to 1.5 L of distilled water. In addition H_2SO_4 3.0 mol/L and Na_2SO_4 (Fisher Scientific Ltd., ACS reagent) were added to achieve pH = 2.73, $[SO_4^{2-}] = 8.43\times10^{-2}$ mol/L for AMD1 and pH = 2.48, $[SO_4^{2-}] = 5.38\times10^{-2}$ mol/L for AMD2.

4.5.5 Precipitation assays

Precipitation tests were realized at ambient temperature (22 ± 2°C) and with volumes of 1.5 L of each solution in 2.0 L beakers (diameter 125 mm). Mixing of solution was conducted using magnetic stir bar (length: 37 mm, diameter: 8 mm) with a speed mixing of 160 rpm. Speed mixing was determined with a Digital Photo Tachometer Model 461893 Extech instruments. For each working pH, a reaction time of 20 min was allowed for the system to reach equilibrium (Hove *et al.* 2008).

Precipitation tests were realized with the following five precipitating agents: 1) Sodium hydroxide (2.5 mol NaOH/L); 2) Lime (20 g $Ca(OH)_2$/L); 3) Sodium sulphide (Na_2S); 4) Disodium hydrogen phosphate (Na_2HPO_4); and 5) Sodium bicarbonate ($NaHCO_3$).

Hydroxide precipitation tests were done by adjusting pH solutions (volume of 1.5 L) to 10.0 with the sodium hydroxide or lime solution. Precipitating agents were added in stoichiometric proportion (with a slight excess) with the soluble metal concentrations present in solution.

During the other precipitation tests, precipitating agents were firstly added to solutions. A pH adjustment was done by adding sodium hydroxide to 7.0 for phosphate and 8.0 for carbonate and sulphide systems. To note that in the case of sulphides and carbonates, an initial adjustment of the pH in values close to 5.50 was made to avoid the emission of hydrogen sulphide and dioxide carbon gases (Baltpurvins *et al.* 1996a; Charerntanyarak, 1999; Feng *et al.* 2000).

4.5.6 Sludge settling

After mixing, suspensions were settled for 30 min in 2 L capacity cylinders and the resulting volumes of the settled sludge were measured to evaluate the SVI values. Volumes of 400 mL of the settled sludge were then sampled after the supernatants were removed by pumping.

4.5.7 Sludge filtration

SRF (specific resistance to filtration) and FC (filtration capacity) were used to characterize the dewaterability of the sludge resulting from metals precipitation with the different precipitating agents (Degrémont, 1989). SRF is given by the following formula (Viadero *et al.* 2006):

Équation 4.1

$$SRF = \frac{2bPA^2}{\mu . c}$$

Équation 4.2

$$FC = \frac{D}{A.T_f}$$

Where “b” is the slope of the plot (V vs. t/V), “V” is the volume of filtrate, m^3; at the moment “t”, s; “P” is the vacuum of filtration, Pa (N/m^2); “A” is the filtration area, m^2; “μ” is the viscosity of filtrate, Pa.s ($N.s/m^2$); “D” is the weight of dry sludge after filtration, Kg; “T_f” is the final time of the filtration, s; and “c” is the weight of solids/unit volume of filtrate, kg/m^3.

Équation 4.3 $$c = \frac{1}{C_i/(100 - C_i) - C_f/(100 - C_f)}$$

Where "C_i" is the initial moisture content,%; "C_f" is the final moisture content,%.

Whatman No. 2 (8.0 µm pore size) membranes having an effective area of 12.50 cm^2 were used during the pressure filtration tests. A pressure of 31.7 kPa was applied on 200 mL volumes of the settled sludge samples inside a Fisherbrand stainless-steel pressure vessel (model 09-753-25A, Fisher Scientific Ltd.).Volume of the filtrate collected at different times was recorded until no additional water flowed out of the sludge (T_f) (USEPA, 1987). Filtrate and sludge viscosities were measured using a Brookfield DV-II+Pro programmable rheometer at a module speed of 60 rpm. Moreover, the weights of the dewatered sludge have been measured to evaluate the sludge production in term of kg of sludge per cubic meter of treated effluent.

4.5.8 Sludge centrifugation

Volumes close to 100 mL of the settled sludge samples were centrifuged at 3000 × *g* (3760 rpm) for 15 min using a Beckman Coulter Allegra^{TM} 6 Centrifuge, in order to evaluate this technique for the metallic sludge dewatering by estimating the final solids content of the sludge.

4.5.9 Analytical methods

The pH was determined before and after each experiment by using a pH-meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Nepean, Canada) equipped with a double junction Cole-Parmer electrode with Ag/AgCl reference cell for pH (daily calibration between 2 and 10). Total solids were measured according to the APHA method 1603 (APHA *et al.* 1999). Metals in solution were measured by plasma emission spectroscopy with a simultaneous ICP-AES (inductively coupled plasma - atomic emission spectroscopy, Vista Ax CCO simultaneous ICP-AES from Varian, Mississauga, Canada). Before analysis, liquid samples were first filtered on a Whatman 934-AH membrane (1.5 µm pore size) and were then acidified to give a 5% HCl solution. Analytical quality controls were performed with a certified standard solution (PlasmaCal Multielement Standard 900-Q30-100, SCP Science, Baie d'Urfé, Canada).

XRD patterns of the samples were obtained with a Simens D5000 diffractometer equipped with a rotative anode and copper target ($K_{\alpha1}$ copper with K_{α} = 1.5406 Å). Synthesized precipitate samples from Sln A and Sln C were characterized by X-ray diffraction (XRD) in order to determine nature of formed precipitates.

4.6 Results and discussion

4.6.1 Prediction of residual metal concentrations

In order to fix the working pH, which allows the precipitation of the metals in the desired forms) (metal hydroxides, carbonates, sulphides and phosphates), computer simulations have been carried out using the *MINEQL+* software. These predictions have concerned polymetallic solutions: first solution (Sln B) is treated by adding NaOH or Na_2HPO_4, whereas the second solution (Sln D) is treated by adding Na_2S or Na_2CO_3.

Figs. 1 and 2 illustrate results from MINEQL+ simulations. pH values of 10.0, 7.0, 8.0 and 8.0 were selected respectively for hydroxide, phosphate, sulphide and carbonate precipitation tests in laboratory.

Tables 1 to 4 compare the results of the computer simulations and experimental metal removal yields. Very good correlations have been observed between the experimental values at pH 10.0 by adding caustic soda and those predicted with *MINEQL+* at the same pH for all metals contained in the different synthetic solutions studied (Table 4.1).

The metal precipitates observed by XRD analyses (Figs. 4.3 and 4.4) and predicted by *MINEQL+* simulations are indicated in Tables 4.1 to 4.4.

It is noticed that after synthetic AMD1 treatment with NaOH, residual concentrations of zinc (3.21×10^{-6} M) and nickel (3.40×10^{-7} M) are lower than predicted by precipitation theory (4.59×10^{-6} and 1.02×10^{-6} M, for the Zn and Ni ions, respectively). This gap could be explained by the presence of aluminum and iron hydroxides. In fact, adsorption and/or coprecipitation of metals might occur with $Fe(OH)_3$ and $Al(OH)_3$ (Slavek *et al.* 1988; Marchioretto *et al.* 2005).

In order to model the Ni and Zn ions adsorption onto the ferrihydrite ($Fe(OH)_3$ majority against $Al(OH)_3$), *MINEQL+* simulation was done by considering the adsorption model. AMD1 neutralized contains ferrihydrite whose chemistry is modeled with the Two-Layer FeOH model compiled by Dzombak and Morel (1990); *Fe(st)OH* and *Fe(wk)OH*, as the strong and weak binding surface hydroxyl species. Simulation results show that residual concentrations for Zn and Ni ions at pH 10.0 are lower than measured experimentally (1.61×10^{-11} M and 1.36×10^{-12} M, respectively). This is due to kinetic considerations (short reaction time). Simulation results show also that strong binding surface hydroxyl species (*Fe(st)OH*) adsorb about 95% of studied metals.

These same phenomena could also explain the difference between the experimental and theoretical residual concentrations of zinc and cadmium in AMD2 (Table 4.1).

The substitution of the chloride matrix (Sln A) by the sulphate one (Sln B) has led no noticeable change in the results concerning final metal concentrations (Djedidi *et al.* 2009).

Treatment by adding a stoichiometric quantity of Na_2HPO_4 (with a slight excess) at pH 7.0 (caustic soda adjustment) to polymetallic solutions A and B as well as synthetic AMD (AMD1 and AMD2) give generally bivalent metal transition precipitation (Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+}) greater than those calculated with *MINEQL+* software (Table 4.2). At low pH values (2.5 to 4.0), aluminum and iron(III) precipitate under amorphous phosphate forms: $AlPO_4.xH_2O$, x = 2-3 and $FePO_4.xH_2O$, x=1-2 (Mustafa *et al.* 1999), which are reliable exchange materials and can act as an efficient sorbent for metal(II) cations. In fact, ion exchange between protons from the surface and metal(II) cations from solutions was found to be responsible for metal sorption by metal(III) phosphates (Mustafa *et al.* 1999), according to the reaction:

Équation 4.4 $nS\text{-}OH + M^{2+}(aq) = (S\text{-}O)_nM^{2-n} + nH^+(aq)$

Where “S” stands for the exchanger, and “M” for bivalent metal.

Same authors have reported that a reaction time of 1 h was sufficient for the system to reach equilibrium (Naeem *et al.* 2002). This is essentially confirmed for Ni in AMD1 and Cd in AMD2 which are removed to 90 and 99%, respectively against theoretical values of 0 and 9% calculated by *MINEQL+* software.

The experimental metals removal from Sln C and Sln D through insoluble metal carbonate (MCO_3) gave satisfactory results close to 99% but generally slightly below the *MINEQL+* software prediction (Table 4.3). This is can be explained by kinetic considerations. In fact, it is important to take into consideration that *MINEQL+* software and the other comparable models, consider the chemical reactions at their equilibrium (infinite times). Consequently, they do not integrate kinetic aspects, which can be significant in metal precipitation techniques operate using short reaction periods (Djedidi *et al.* 2009).

During the first stage of AMDs treatment with carbonates (adjustment of pH until 5.0), metal(III) have been precipitated in hydroxides form ($Al(OH)_3$ and $Fe(OH)_3$). These two precipitates are efficient sorbent for metal(II) cations and will contribute to improving their uptake in the process (Marchioretto *et al.* 2005). This may explain the discrepancy between theoretical (3.48×10^{-5}, 2.51×10^{-4} M) and experimental (1.70×10^{-7}, 2.29×10^{-6} M) residual concentration values for the nickel and zinc, respectively in the case of AMD 1 neutralization with carbonates (Table 3).

As in the case of carbonate, treatment by Na_2S is a combined precipitation which consists of adding NaOH (pH 5.0) followed by addition of Na_2S in stoichiometric proportions (pH 8.0). The obtained experimental results are in agreement with results of *MINEQL+* simulations in the same conditions and are given in Table 4.4. Substitution of the chloride matrix (Sln C) by the sulphate one (Sln D) has led no noticeable change in the results concerning final metal concentrations except for Mn^{2+}. Its theoretical rate of uptake varies from 97% in Sln C to 91% in Sln D, whereas experimental results follow this trend (from 97% to 89% in Sln C and Sln D, respectively). In the case of AMD treatment, experimental metal(II) removal is almost total and this is confirmed by *MINEQL+* simulations, except for the nickel and zinc.

4.6.2 Settling characteristics

In each studied precipitation test, sludge generated is essentially constituted of hydrated metallic precipitates and interstitial dissolved salts. However, for the same operating conditions, precipitating agent used for removing metallic ions from aqueous solutions has significant influence on the solid/liquid separation of the resulting sludge. Tables 4.5 to 4.8 gave some important technical data on the hydrated precipitates dewatering properties.

XRD patterns of the solids isolated from Sln A and Sln C treatment are presented in Figs 4.3 and 4.4. X-ray patterns examination showed that sludge generated from hydroxide and phosphate precipitation are amorphous in nature, unlike sulphides and carbonates are in semi crystalline, and crystalline forms, respectively.

Sln A treatment with caustic soda (NaOH) at pH 10.0, produces sludges which settle slowly with SVI = 428 mL/g (Table 4.5). Treatment of the same solution by adding Na_2HPO_4 at pH 7.0 generates flocs which settle better with SVI = 235 mL/g (Table 4.6). In both treatment modes mentioned above, the substitution of the chloride matrix (Sln A) by the sulphate one (Sln B) improves flocs settling; SVI are 377 and 208 mL/g for hydroxides and phosphates sludges, respectively. Improving on flocs settling is mainly due to the fine amorphous nature of the precipitates (Fig. 4.3) and to the increase of the ionic strength ΔI (from chloride to sulphate matrix) which is estimated at 3.0×10^{-2} M. I is calculated from the formula $I = \frac{1}{2} \Sigma C_i Z_i^2$; where C_i and Z_i are the concentration and the charge of the i^{th} specie, respectively. This is in agreement with previous works of Dustan *et al.* (2005), Moghadam *et al.* (2005) and Djedidi *et al.* (2009).

Sln C treatment by adding Na_2S at pH close to 8.0 generates sludges with good settling (SVI = 121 mL/g) (Table 4.8). Limestone neutralization (carbonate) of the same solution at pH 8.0 produces flocs which settle rapidly (SVI = 37 mL/g) (Table 4.7). In the case of sulphide and carbonate precipitation, the substitution of the chloride matrix (Sln C) by the sulphate one (Sln D) has no significant effect on settling characteristics and this is due to the semi crystalline, and crystalline form of sulphide and carbonate sludges, respectively (Fig. 4.4).

The behavior towards floc settling generated from the neutralization of AMDs by adding caustic soda or lime at pH 10.0 has been studied. Experimental results in Table 4.5 show that the substitution of caustic soda by lime for hydroxide precipitation of AMD, decrease SVI values. This decrease does not mean that settling is better but it can be explained by the formation of gypsum ($CaSO_4.2H_2O$) as secondary sludge due to the high concentration of ion sulphate (SO_4^{2-}) in AMD (MEND, 1994; Balpurvins *et al.* 1996).

Sludges generated from simple precipitation of AMD (hydroxide or phosphate precipitation) are essentially constituted of metal hydroxides ($M(OH)_n$ n= 2 and 3) or metal phosphates (MPO_4 and $M_3(PO_4)_2$). It appears that for both compositions AMD1 and AMD2, phosphates settle better than hydroxides with NaOH (Tables 4.5 and 4.6). Regarding combined precipitation of AMD (carbonate or sulphide precipitation), sludges generated are mixtures of hydroxides ($Al(OH)_3$ and $Fe(OH)_3$), carbonates or sulphides. Results in Tables 4.7 and 4.8, show that settling is faster in the case of sulphides than carbonates, for both AMD effluents.

4.6.3 Filtration characteristics

Some important filtration properties of the different effluents metals precipitates are given in Tables 4.5 to 4.8. Experimental results show the matrix effect on vacuum filtration characteristics; such as TS and SRF.

TS of sludge generated after neutralization of Sln A and Sln B by adding caustic soda (pH 10.0) varies from 7.4 to 11.2% (w/w). TS vary also from 18.5% (Sln A) to 16.7% (Sln B) in the case of phosphate precipitation (Table 4.6). Sln C and Sln D neutralization by limestone (Na_2CO_3) generate sludge which their measured total solids are 19.1 and 41.9% (w/w) (Table 4.7), respectively. TS for sludges generated after sulphide precipitation are 16.6% for Sln C, and 17.4% for Sln D (Table 4.8).

It concludes that sludges generated in sulphate matrix compact generally better than those generated in chloride matrix, this is due to chemical rearrangement, in which water and sulphates are rejected and the solid densifies (Dustan *et al.* 2005).

Treatment of AMD1 and AMD2, by adding NaOH pH 10.0, has generated sludges with TS of 19.0 and 21.1%, respectively, corresponding to wet sludge production of 12.5 and 15.0 kg/m^3 (Table 4.5). In the same operating conditions, the substitution of caustic soda by lime ($Ca(OH)_2$), has led to production of sludge with higher TS (close to 30%, with a important wet sludge production (29.5 and 40.8 kg/m^3), due to the secondary sludge formation (gypsum). Concerning, wet sludge production after AMD treatment, two quite similar trends have been set:

- AMD1: hydroxides ($Ca(OH)_2$) > phosphates > sulphides > hydroxides (NaOH) > carbonates;

- AMD2: phosphates > hydroxides ($Ca(OH)_2$) > sulphides > carbonates > hydroxides (NaOH).

In terms of SRF, a parallelism between this parameter and the FC has been observed. In fact, a sludge having low FC has generally a high SRF values. Whatever the treatment mode used in this work, sludges produced from sulphate matrix have best filterability than those produced from chloride matrix. It is noticed that, aggregates from chloride and sulphate solutions show different structural characteristics (Dustan, 2001). Aggregates formed in chloride matrix are larger but have a tendency towards decreasing size under vacuum filtration. It is proposed that in the chloride case, under the stress of compression, the structural rearrangement within aggregate and/or sediment proceed more easily than in the corresponding sulphate case (Dustan *et al.* 2005). This rearrangement decrease floc size and make filtration slower. In fact SRF values calculated in the case of the Sln A and Sln B treatment by adding caustic soda (pH 10) are respectively 66.0×10^{12} and 23.5×10^{12} m/kg. For these same solutions, SRF values are 11.0×10^{12} and 2.8×10^{12} m/kg, respectively in the case of phosphate precipitation (pH 7.0).

Regarding to Sln C and Sln D, SRF values are 1.6×10^{12} and 1.1×10^{12} m/kg for the carbonate precipitation (Table 4.7), whereas values of 10.8×10^{12} and 9.7×10^{12} m/kg have been measured for the sulphide precipitation (Table 4.8).

The gap between SRF values is more important in the case of precipitates generated in Sln A and Sln B. This is due to their amorphous nature (Fig. 4.3). Unlike, precipitates produced in Sln C and Sln D have an intermediate state of crystallinity (Fig. 4.4) and this could explain the low gap between SRF values.

In general way, the following ascending orders in terms of SRF can be defined for the different AMD treatment:

- AMD1: phosphates < hydroxides ($Ca(OH)_2$) < hydroxides (NaOH) < carbonates < sulphides;
- AMD2: phosphates < hydroxides ($Ca(OH)_2$) < carbonates < hydroxides (NaOH) < sulphides

4.6.4 Centrifugation

TS of the polymetallic and AMDs precipitates separated by centrifugation are given in Tables 4.5 to 4.8. The results show clearly that centrifugation (at $3000 \times g$) is far less efficient that vacuum filtration (31.7 kPa) to eliminate water from metallic precipitates. In all treatment mode studied, final TS of sludge obtained after centrifugation and pressure filtration follow the same trend.

4.7 Conclusion

This paper has presented dewatering behaviour of sludges generated from simple precipitation (hydroxide, phosphate), and combined precipitation (sulphide, carbonate) from equimolar polymetallic and synthetic AMD solutions.

In term of residual metal concentration, experimental results correlate well with those predicted by *MINEQL+* simulations. However, adsorption and/or coprecipitation mechanisms can improve metals removal yields predicted by computer simulations.

In the case of polymetallic solutions, hydroxide and phosphate precipitates are amorphous in nature and water which is chemically bonded to sludge particles and is thus resistant to dewatering and compaction. Limestone (carbonate) neutralization produces a dense, granular sludge which settles rapidly and compacts well.

Dewatering characteristics of sludge produced from AMD depend on metals concentrations and ionic strength (I), however two descending trends have been established in terms of FC. AMD1: hydroxides ($Ca(OH)_2$) > phosphates > sulphides > hydroxides (NaOH) > carbonates. AMD2: phosphates > hydroxides ($Ca(OH)_2$) > sulphides > carbonates > hydroxides (NaOH).

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4.9 References

Al-Tarazi, M., Heesink, A.B.M., Versteeg, G.F., 2004. Precipitation of metal sulphides using gaseous hydrogen sulphide: Mathematical modeling. Chem. Eng. Sci. 59 (3), 567–579.

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0. User's manual. Report EPA/600/3-91/021, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgia.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), 1999. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1015 Fifteenth Street, NW, Washington, DC.

Apul, D.S., Gardner, K.H., Eighmy, T.T., Fallman, A.M., Comans, R.N.J., 2005. Simultaneous application of dissolution/precipitation and surface complexation/surface precipitation modeling to contaminant leaching. Environ. Sci. Technol. 39 (15), 5736-5741.

Ball. J.W., Runkel, R.L., Nordstrom, D.K., 2001. Reactive transport modeling at high flow-Wightman Fork/Alamosa River USA. In:Cidu, R.(ED.), Porc. 10th Internat. Symp. Water Rock Interaction .Swets and Zeitlinger, Lisse.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., 1996a. Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation. Waste Manag. 16 (8), 717-725.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., 1996b. Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater. Environ. Sci. Technol. 30, 1493-1499.

Blais, J.F., Djedidi, Z., Ben Cheikh, R., Tyagi, R.D., Mercier, G., 2008. Metals precipitation from effluents – A review. Practice Periodical Toxic Hazard. Radioactive Waste Manag. 12 (3), 135-149.

Charerntanyarak, L., 1999. Heavy metals removal by chemical coagulation and precipitation. Water Sci. Technol. 39 (10-11), 135-138.

Chartrand, M.M.G., Bunce, N.J., 2003. Electrochemical remediation of acid mine drainage. J. Appl. Electrochem. 33, 259-264.

Cocos, I.A., Zagury, G.J., Clément, B., Samson, R., 2002. Multiple factor design for reactive mixture selection for use in reactive walls in mine drainage treatment. Water Res. 32, 167-177.

Degrémont, 1989. Mémento technique de l'eau. 9th Edition, Paris, France.

Demopoulos, G.P, Zinck, J.M., Kondos, P.D., 1995. Multiple stage precipitation of heavy metals from acidic aqueous solution. US patent No. 5,672,280.

Djedidi, Z., Khaled, J.B., Cheikh, R.B., Blais, J.F., Mercier, G., Tyagi, R.D., 2009. Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions. Hydrometallurgy 95, 61-69.

Dustan, A.C., 2001. The effect of precipitation conditions on product character and dewatering: an integrated study for based-metal hydroxides. Ph.D. thesis, University of Cape Town, South Africa.

Dustan, A.C., Cohen, B., Petrie, J.G., 2005. Modelling dewatering behaviour through an understanding of solids formation processes. Part II – Solids separation considerations. Adv. Colloid Interface Sci. 113 (2-3), 85-97.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. Jhon Wiley and Sons, New York.

Feng, D., Aldrich, C., Tan, H., 2000. Treatment of acid mine drainage by use of heavy metal precipitation and ion exchange. Min. Eng. 13 (6), 623-642.

Feng, D., van Deventer, J.S.J., Aldrich, C., 2004. Removal of pollutants from acid mine wastewater using metallurgical by-product slags. Sep. Purif. Technol. 40, 61-67.

Gilbert, O., De Pablo, J., Cortima, J.L., Ayora, C., 2003. Evaluation of municipal compost/limestone/iron mixtures as filing material for permeable reactive barriers for in-situ acide mine drainage treatment. J. Chem. Technol. Biotechnol. 78, 489-496.

Guillard, D., Lewis, A.E., 2002. Optimization of nickel hydroxycarbonate precipitation using a laboratory pellet reactor. Ind. Eng. Chem. Res. 41, 3110-3114.

Halim, C.E., Short, S.A., Scott, J.A., Amal, R., Low, G., 2005. Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC. J. Hazard. Mater. 125 (1-3), 46-61.

Hammarstrom, J.M., Sibrell, P.L., Belkin, H.E., 2003. Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the FriendshipHill National Historical Site, Pennsylvania, USA. Appl. Geochem. 18, 1705-1721.

Hove, M., van Hill, R.P., Lewis, A.E., 2008. Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. Chem. Eng. Sci. 63, 1626-1635.

Marchioretto, M.M., Bruning, H., Rulkens, W., 2005. Heavy metals precipitation in sewage sludge. Sep. Sci. Technol. 40 (16), 3393-3405.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., Saldanha, M., 2002. Studies on the mechanisms of lead immobilization by hydroxyapatite. Environ. Sci. Technol. 36 (7), 1625-1629.

McAnally, S., Benefield, L., Reed, R.B., 1984. Nickel removal from synthetic and actual nickel plating wastewater using sulphide and carbonate for precipitation and coprecipitation. 39th Purdue Industrial Waste Conference, pp. 81-98.

MEND, 1996. Metals removal from acidic drainage - Chemical methods. Report 3.21.2a, Mine Environment Neutral Drainage (MEND) Program, Ottawa, Ontario, Canada.

MEND, 1994. Acid mine drainage – Status of chemical treatment and sludge management practices. Report 3.32.1., Mine Environment Neutral Drainage (MEND) Program, Ottawa, Ontario, Canada.

Mishra, S.K., 1999. Resource recovery in waste treatment increasingly used. Min. Eng. 51 (4), 29-34.

Moghadam, M.A., Soheili, M., Esfahani, M.M., 2005. Effect of ionic strength on settling of activated sludge. Iranian J. Environ. Health Sci. Eng. 2 (1), 1-5.

Mustafa, S., Naeem, A., Murtaza, S., Rehana, N., Samad, H.Y., 1999. Comparative sorption properties of metal (III) phosphates. J. Colloid Interface Sci. 220 (1), 63-74.

Naeem, A., Mustafa, S., Rehana, N., Dilara, B., Murtaza, S., 2002. The sorption of divalent metal ions on AlPO4. J. Colloid Interface Sci. 252 (1), 6-14.

Papelis, C., Hayes, K.F., Leckie, J.O., 1988. HYDRAQL: a program for the computation of chemical equilibrium composition of aqueous batcvh systems including surface-complexation modeling of ion adsorption at the oxide/solution interface. Technical report 306, Department of Civil Engineering, Stanford University, Stanford, CA.

Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N., 1980. PHREEQE. A computer program for geochemical calculations. Report 80-96, United States Geological Survey, Water Resources Investigations, Reston, VA.

Patterson, J.W., 1988. Metal treatment and recovery. In : Kramer, J.R., Allen, H.E. (Eds.), Metal speciation: Theory and application. Lewis Publishers, Inc., Chelsea, Michigan.

Pigaga, A., Juskenas, R., Selkis, A., 2002. Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation. Sep. Purif. Technol. 37 (13) 3155-3168.

Preis, W., Gamsjager, H., 2001. Thermodynamic investigation of phase equilibria in metal carbonate-water-carbon dioxide systems. Chem. Monthly 132, 1327-1346.

Slavek, J., Pickering, W.F., 1988. Metal ion interaction with the hydrous oxides of aluminium. Water Air Soil Pollut. 39 (1-2), 201-216.

Sohnel, O., Garside, J., 1992. Precipitation, basic principles and industrial applications. Butterworth Heinemann, Oxford, England.

Tabak, H.H., Scharp, R., Burckle, J., Kawahara, F.K., Govin, R., 2003. Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. Biodegradation 14, 423–436.

U.S. Environmental Protection Agency, Office of Research and Development, 1987. Design Manual-Dewatering Municipal Waste-water Sludges.

Veeken, A.H.M., Rulkens, W.H., 2003. Innovative developments in the selective removal and reuse of heavy metals from wastewaters. Water Sci. Technol. 47 (10), 9-16.

Viadero, R.C., Wei, X.C., Buzby, K.M., 2006. Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization. Environ. Eng. Sci. 23 (4), 734-743.

Westall, J.C., Zachary, J.L., Morel, F.M.N., 1976. MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems. Technical note 18, Massachusetts Institute of Technology, Cambridge, MA.

Wurzburger, S.R., Overton, J.M., 2004. Process for treating acid mine with moderate sulphate content. US patent No. 6,790,352.

Yabe, M.J.S., Oliveira, E.D., 2001. Heavy metals removal in industrial effluents by sequential adsorbent treatment. Adv. Environ. Res. 7, 263-272.

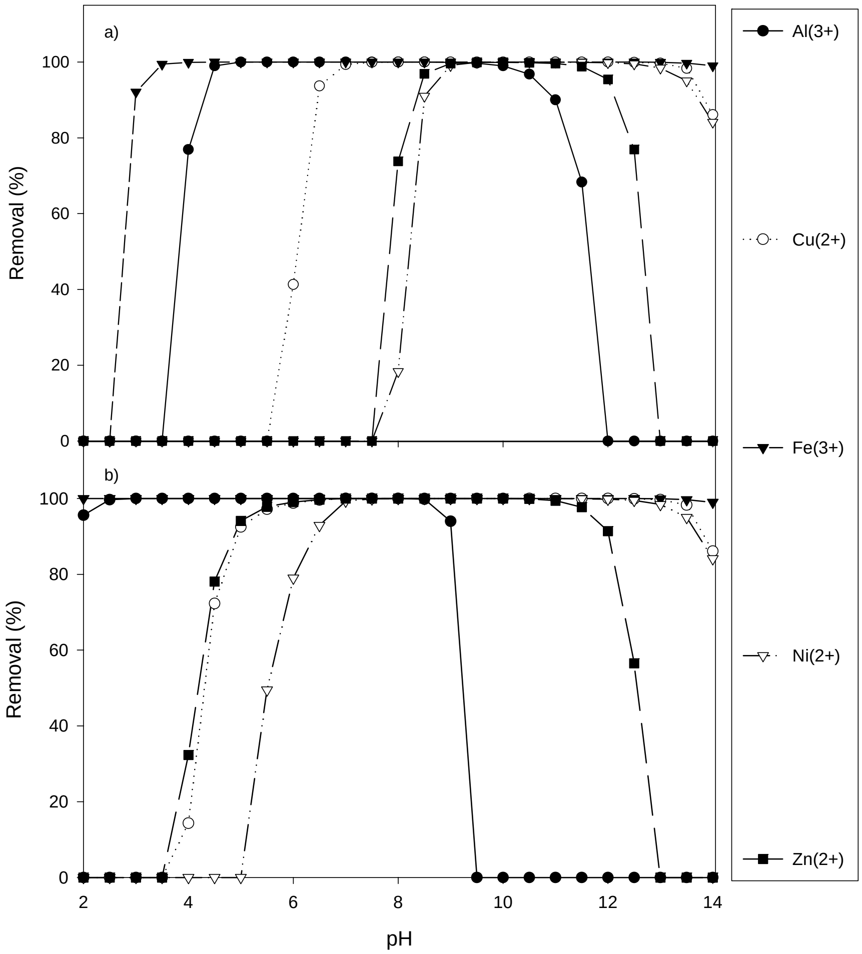

Figure 4.1 Solubility of metal hydroxide (a) and phosphate (b) in polymetallic solution, based on chemical equilibrium calculation using ***MINEQL+*** software. Solids formed: (a) – $Al(OH)_3$; $Cu(OH)_2$; $Fe(OH)_3$; $Ni(OH)_2$; $Zn(OH)_2$. (b) – $AlPO_4$; $Cu_3(PO_4)_2$; $FePO_4$; $Ni_3(PO_4)_2$; $Zn_3(PO_4)_2$

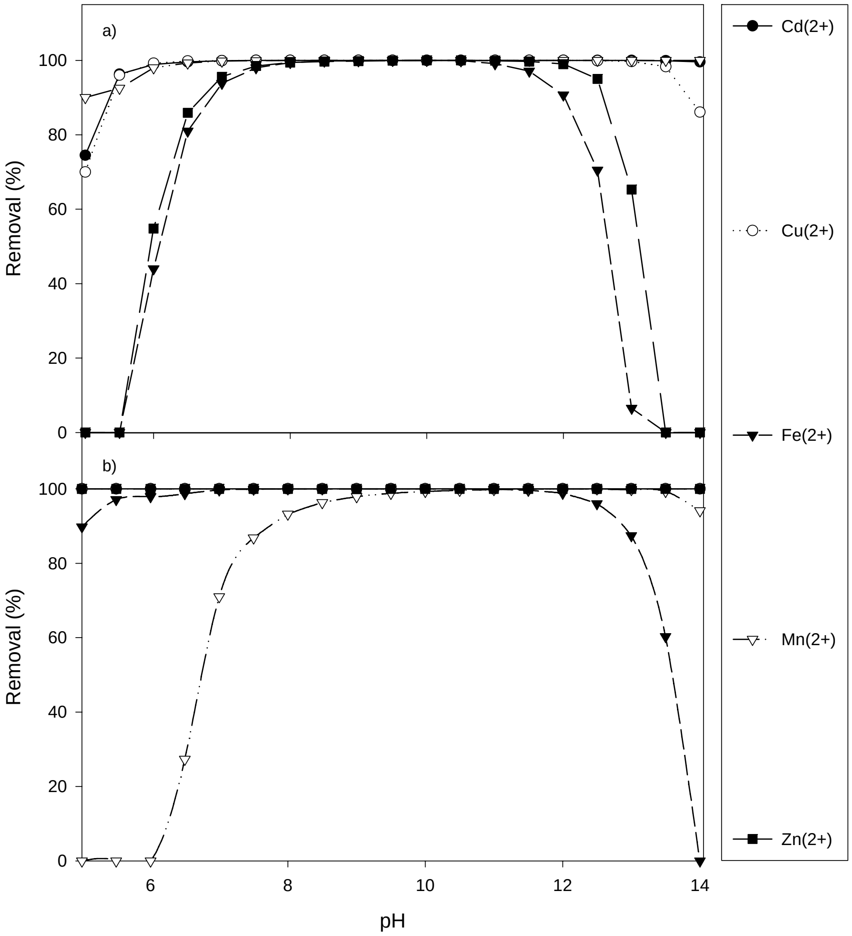

Figure 4.2 **Solubility of metal carbonate (a) and sulphide (b) in polymetallic solution, based on chemical equilibrium calculation using *MINEQL+* software. Solids formed: (a) – $CdCO_3$; $CuCO_3$; $FeCO_3$; $MnCO_3$; $ZnCO_3$. (b) – CdS; CuS; FeS; MnS; ZnS**

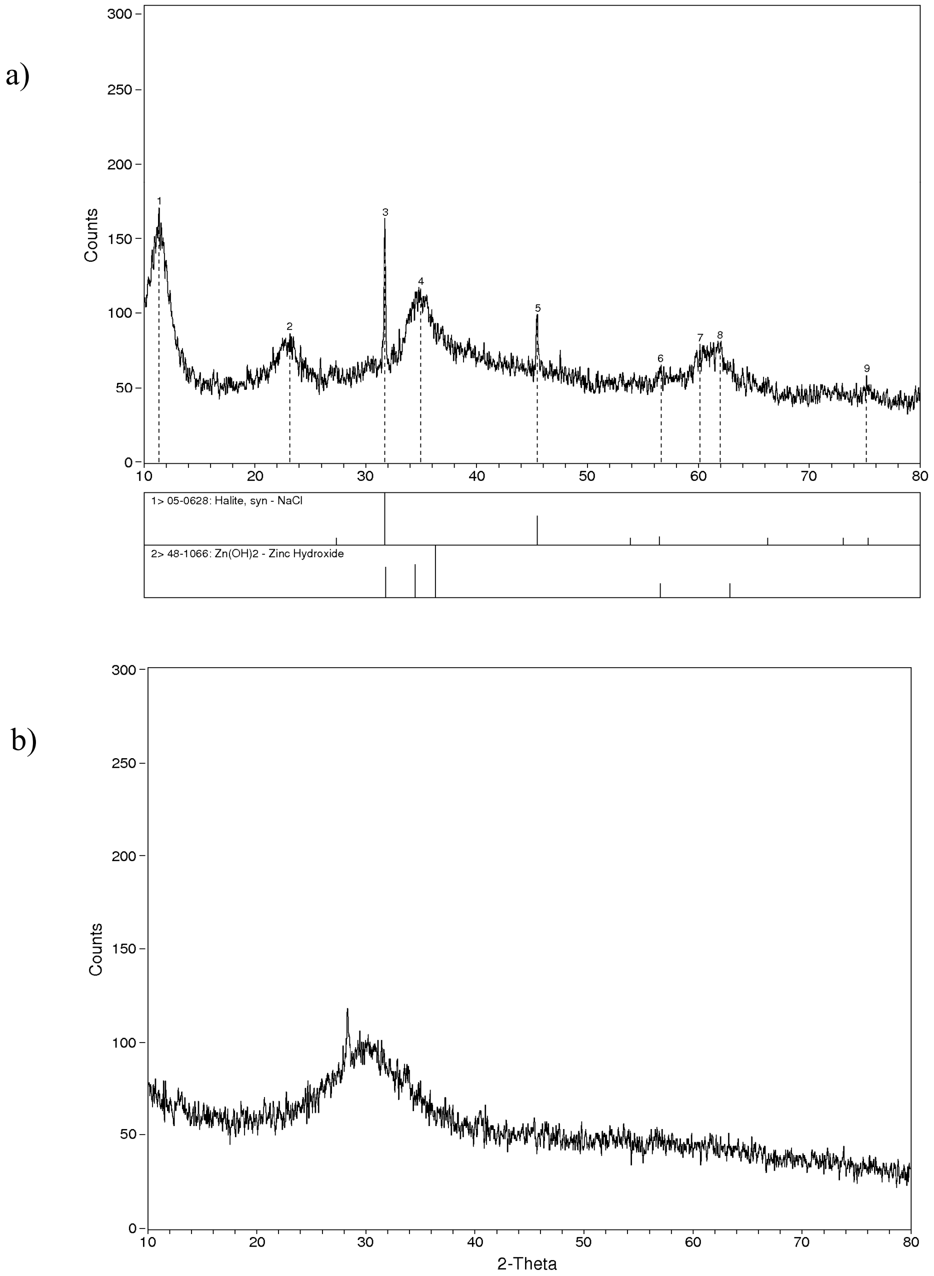

Figure 4.3 XRD patterns of metal hydroxide (a) and phosphate (b) in polymetallic solution (A)

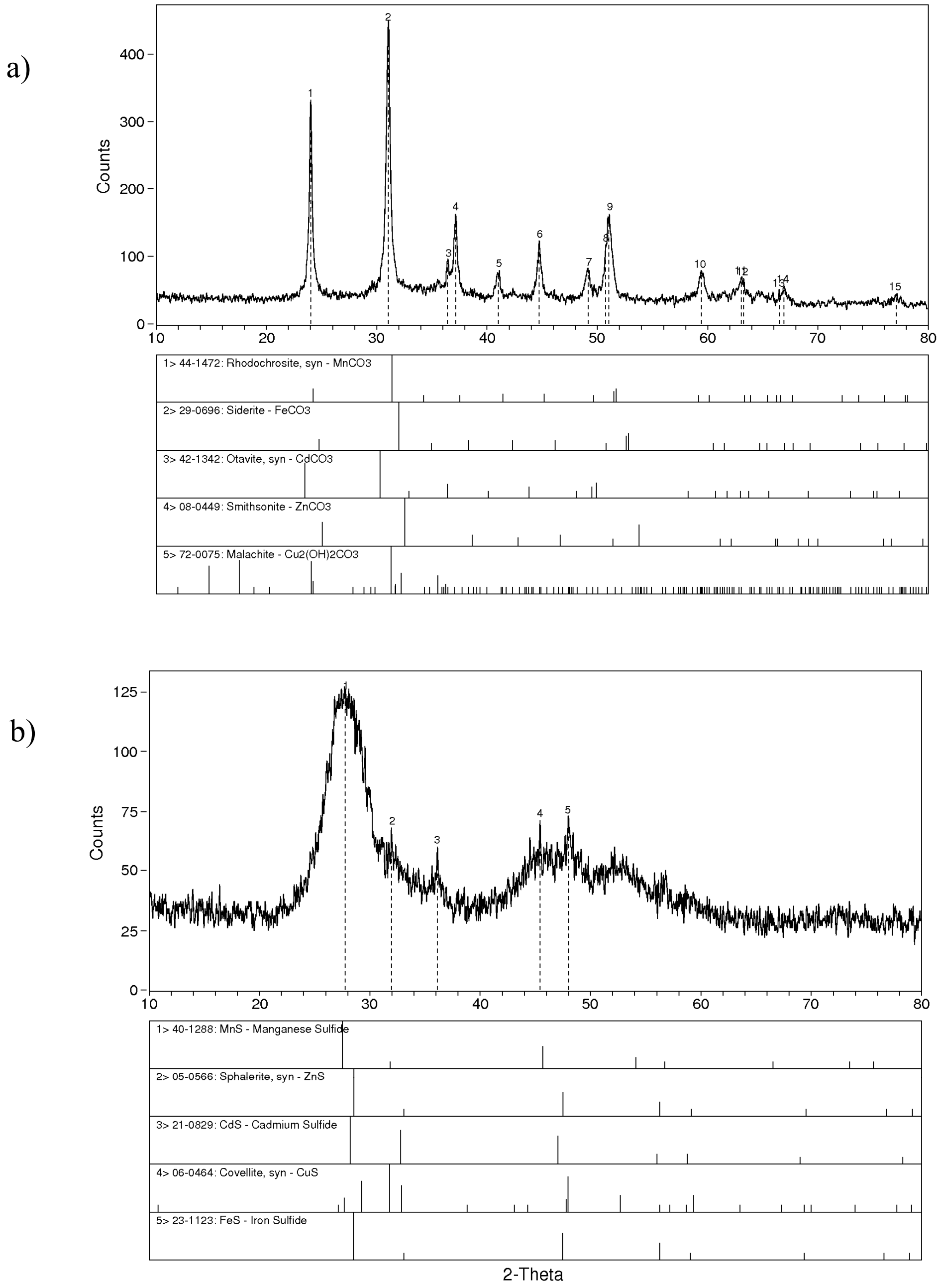

Figure 4.4 XRD patterns of metal carbonate (a) and sulphide (b) in polymetallic solution (C)

Tableau 4.1 Metals precipitation of the synthetic poly-metallic solutions using NaOH as precipitating agent at pH 10.0

Metals	Precipitation tests					*MINEQL+* prediction		
	Final pH	NaOH (mol/L)	$[M]_i$ (mol/L)	$[M]_f$ (mol/L)	*Removal (%)*	$[M]_f$ (mol/L)	*Removal (%)*	Precipitates
Chloride matrix (Sln A)								
Fe^{3+}	10.0	4.25×10^{-2}	4.03×10^{-3}	1.25×10^{-6}	*99.9*	4.50×10^{-9}	*100*	$Fe(OH)_3$
Cu^{2+}			3.77×10^{-3}	9.44×10^{-7}	*99.9*	3.80×10^{-8}	*99.9*	$Cu(OH)_2$
Al^{3+}			3.87×10^{-3}	1.58×10^{-4}	*95.9*	4.01×10^{-5}	*95.3*	$Al(OH)_3$,*Gibbsite*
Zn^{2+}			4.00×10^{-3}	1.07×10^{-6}	*99.9*	4.50×10^{-6}	*99.9*	$Zn(OH)_2$
Ni^{2+}			3.88×10^{-3}	6.82×10^{-7}	*99.9*	9.20×10^{-7}	*99.9*	$Ni(OH)_2$
Sulphate matrix (Sln B)								
Fe^{3+}	10.0	5.30×10^{-2}	4.00×10^{-3}	2.51×10^{-6}	*99.9*	4.45×10^{-9}	*100*	$Fe(OH)_3$
Cu^{2+}			4.08×10^{-3}	2.05×10^{-6}	*99.9*	3.78×10^{-8}	*99.9*	$Cu(OH)_2$
Al^{3+}			4.00×10^{-3}	1.42×10^{-4}	*96.5*	4.59×10^{-4}	*95.9*	$Al(OH)_3$,*Gibbsite*
Zn^{2+}			4.00×10^{-3}	1.53×10^{-6}	*99.9*	4.01×10^{-6}	*99.9*	$Zn(OH)_2$
Ni^{2+}			4.00×10^{-3}	1.19×10^{-6}	*99.9*	1.14×10^{-6}	*99.9*	$Ni(OH)_2$
AMD 1								
Fe^{3+}	10.0	7.35×10^{-2}	1.29×10^{-2}	1.88×10^{-5}	*99.9*	5.30×10^{-9}	*100*	$Fe(OH)_3$
Al^{3+}			2.63×10^{-3}	2.15×10^{-4}	*91.8*	4.97×10^{-5}	*98.1*	$Al(OH)_3$,*Gibbsite*
Cu^{2+}			6.69×10^{-4}	3.93×10^{-6}	*99.4*	3.99×10^{-8}	*99.9*	$Cu(OH)_2$
Zn^{2+}			1.83×10^{-3}	3.21×10^{-6}	*99.8*	4.59×10^{-6}	*99.9*	$Zn(OH)_2$
Pb^{2+}			1.72×10^{-5}	2.41×10^{-7}	*99.7*	1.64×10^{-9}	*99.9*	$Pb(OH)_2$
Ni^{2+}			3.48×10^{-5}	3.40×10^{-7}	*99.3*	1.02×10^{-6}	*97.0*	$Ni(OH)_2$
AMD 2								
Fe^{3+}	10.0	9.64×10^{-2}	1.40×10^{-2}	9.13×10^{-6}	*99.9*	5.40×10^{-9}	*100*	$Fe(OH)_3$
Al^{3+}			1.20×10^{-2}	2.37×10^{-4}	*98.0*	4.98×10^{-5}	*99.6*	$Al(OH)_3$,*Gibbsite*
Cu^{2+}			4.58×10^{-4}	5.67×10^{-6}	*98.7*	3.98×10^{-8}	*99.9*	$Cu(OH)_2$
Zn^{2+}			6.13×10^{-4}	2.29×10^{-6}	*99.6*	4.43×10^{-6}	*99.3*	$Zn(OH)_2$
Pb^{2+}			6.47×10^{-6}	4.34×10^{-7}	*93.3*	1.70×10^{-10}	*99.9*	$Pb(OH)_2$
Cd^{2+}			4.43×10^{-5}	8.90×10^{-8}	*99.9*	8.17×10^{-6}	*98.6*	$Cd(OH)_2$

Ksp values used to predict metal solubilities: $Fe(OH)_3$ ($10^{-38.8}$),$Cu(OH)_2$ ($10^{-19.32}$),$Al(OH)_3$ ($10^{-33.7}$), $Zn(OH)_2$ ($10^{-16.76}$), $Ni(OH)_2$ ($10^{-17.2}$), $Pb(OH)_2$ ($10^{-19.84}$), $Cd(OH)_2$ ($10^{-14.35}$).

Tableau 4.2 Metals precipitation of the synthetic poly-metallic solutions using Na_2HPO_4 as precipitating agent

Metals		Precipitation tests					*MINEQL+* prediction		
	Final pH	PO_4 added (mol/L)	NaOH added (mol/L)	$[M]_i$ (mol/L)	$[M]_f$ (mol/L)	*Removal (%)*	$[M]_f$ (mol/L)	*Removal (%)*	Precipitates
Chloride matrix (Sln A)									
Fe^{3+}	7.0	1.75×10^{-2}	2.99×10^{-2}	4.00×10^{-3}	2.29×10^{-5}	*99.4*	1.30×10^{-9}	*100*	$FePO_4.2H_2O$
Cu^{2+}				4.00×10^{-3}	7.08×10^{-5}	*99.8*	8.60×10^{-7}	*99.8*	$Cu_3(PO_4)_2.3H_2O$
Al^{3+}				4.00×10^{-3}	6.30×10^{-6}	*99.8*	1.71×10^{-9}	*100*	$AlPO_4$
Zn^{2+}				4.00×10^{-3}	1.83×10^{-6}	*99.5*	2.86×10^{-5}	*99.3*	$Zn_3(PO_4)_2.4H_2O$
Ni^{2+}				4.00×10^{-3}	1.14×10^{-5}	*99.7*	3.77×10^{-5}	*99.4*	$Ni_3(PO_4)_2$
Sulphate matrix (Sln B)									
Fe^{3+}	7.0	1.75×10^{-2}	3.38×10^{-2}	4.00×10^{-3}	2.13×10^{-5}	*99.5*	2.63×10^{-9}	*100*	$FePO_4.2H_2O$
Cu^{2+}				4.07×10^{-3}	6.61×10^{-6}	*99.8*	9.65×10^{-6}	*99.8*	$Cu_3(PO_4)_2.3H_2O$
Al^{3+}				4.00×10^{-3}	1.70×10^{-3}	*99.6*	1.63×10^{-9}	*100*	$AlPO_4$
Zn^{2+}				4.00×10^{-3}	2.60×10^{-6}	*99.9*	8.85×10^{-6}	*99.8*	$Zn_3(PO_4)_2.4H_2O$
Ni^{2+}				4.00×10^{-3}	1.34×10^{-4}	*96.7*	1.54×10^{-4}	*96.1*	$Ni_3(PO_4)_2$
AMD 1									
Fe^{3+}	7.0	1.80×10^{-2}	5.24×10^{-2}	1.29×10^{-2}	1.97×10^{-5}	*99.9*	4.39×10^{-9}	*100*	$FePO_4.2H_2O$
Al^{3+}				2.63×10^{-3}	2.37×10^{-5}	*99.1*	2.86×10^{-9}	*100*	$AlPO_4$
Cu^{2+}				6.72×10^{-4}	5.67×10^{-6}	*99.1*	5.60×10^{-6}	*99.2*	$Cu_3(PO_4)_2.3H_2O$
Zn^{2+}				1.83×10^{-3}	1.99×10^{-6}	*99.9*	4.43×10^{-6}	*99.8*	$Zn_3(PO_4)_2.4H_2O$
Pb^{2+}				2.15×10^{-5}	4.83×10^{-8}	*99.8*	1.38×10^{-7}	*99.9*	$Pb_3(PO_4)_2$
Ni^{2+}				3.71×10^{-5}	3.58×10^{-9}	*90.4*	3.71×10^{-5}	*0.00*	-
AMD 2									
Fe^{3+}	7.0	2.90×10^{-2}	7.17×10^{-2}	1.40×10^{-2}	2.01×10^{-5}	*99.9*	3.72×10^{-9}	*100*	$FePO_4.2H_2O$
Al^{3+}				1.20×10^{-2}	3.82×10^{-5}	*99.7*	3.80×10^{-9}	*100*	$AlPO_4$
Cu^{2+}				4.60×10^{-4}	1.42×10^{-6}	*99.7*	3.16×10^{-6}	*99.3*	$Cu_3(PO_4)_2.3H_2O$
Zn^{2+}				6.11×10^{-4}	2.29×10^{-6}	*99.6*	4.28×10^{-6}	*99.3*	$Zn_3(PO_4)_2.4H_2O$
Pb^{2+}				8.59×10^{-5}	3.86×10^{-7}	*95.7*	1.16×10^{-8}	*99.9*	$Pb_3(PO_4)_2$
Cd^{2+}				4.11×10^{-5}	8.90×10^{-8}	*99.7*	3.74×10^{-5}	*9.00*	$Cd_3(PO_4)_2$

Ksp values used to predict metal solubilities: $FePO_4.2H_2O$ ($10^{-26.4}$), $Cu_3(PO_4)_2.3H_2O$ ($10^{-36.85}$), $AlPO_4$ ($10^{-22.5}$), $Zn_3(PO_4)_2.4H_2O$ ($10^{-35.42}$), $Ni_3(PO_4)_2$ ($10^{-31.3}$), $Pb_3(PO_4)_2$ ($10^{-43.53}$), $Cd_3(PO_4)_2$ ($10^{-32.6}$)

Tableau 4.3 Metals precipitation of the synthetic poly-metallic solutions using Na_2CO_3 as precipitating agent

Metals	Precipitation tests						*MINEQL+* prediction		
	Final pH	CO_3 added (mol/L)	NaOH added (mol/L)	$[M]_i$ (mol/L)	$[M]_f$ (mol/L)	*Removal (%)*	$[M]_f$ (mol/L)	*Removal (%)*	Precipitates
Chloride matrix (Sln C)									
Fe^{2+}	8.0	2.1×10^{-2}	2.32×10^{-2}	4.00×10^{-3}	1.47×10^{-5}	*99.6*	6.95×10^{-6}	*99.9*	$FeCO_3$
Cu^{2+}				4.00×10^{-3}	5.35×10^{-6}	*99.9*	4.38×10^{-7}	*99.9*	$Cu_2(OH)_2CO_3$
Cd^{2+}				4.00×10^{-3}	3.75×10^{-5}	*99.1*	6.64×10^{-7}	*99.9*	$CdCO_3$
Zn^{2+}				4.00×10^{-3}	2.23×10^{-5}	*99.4*	1.30×10^{-5}	*99.7*	$ZnCO_3.1H_2O$
Mn^{2+}				4.00×10^{-3}	5.97×10^{-5}	*99.3*	3.20×10^{-6}	*99.9*	$MnCO_3$
Sulphate matrix (Sln D)									
Fe^{2+}	8.0	2.1×10^{-2}	2.29×10^{-2}	4.00×10^{-3}	3.92×10^{-5}	*99.0*	3.09×10^{-5}	*99.2*	$FeCO_3$
Cu^{2+}				4.07×10^{-3}	3.62×10^{-6}	*99.9*	4.66×10^{-7}	*99.9*	$Cu_2(OH)_2CO_3$
Cd^{2+}				4.00×10^{-3}	4.06×10^{-5}	*98.7*	6.30×10^{-7}	*99.9*	$CdCO_3$
Zn^{2+}				4.00×10^{-3}	4.83×10^{-5}	*98.8*	3.49×10^{-5}	*99.1*	$ZnCO_3.1H_2O$
Mn^{2+}				4.00×10^{-3}	4.30×10^{-5}	*98.9*	1.10×10^{-5}	*99.9*	$MnCO_3$
AMD 1									
Fe^{3+}	8.1	2.7×10^{-2}	5.60×10^{-2}	1.29×10^{-2}	1.02×10^{-5}	*99.9*	8.17×10^{-10}	*100*	$Fe(OH)_3$
Al^{3+}				2.63×10^{-3}	1.89×10^{-5}	*99.3*	4.04×10^{-7}	*99.9*	$Al(OH)_3$
Cu^{2+}				6.67×10^{-4}	3.93×10^{-6}	*99.4*	5.26×10^{-7}	*99.9*	$Cu_2(OH)_2CO_3$
Zn^{2+}				1.83×10^{-3}	2.29×10^{-6}	*99.9*	2.51×10^{-4}	*86.3*	$ZnCO_3.1H_2O$
Pb^{2+}				1.72×10^{-5}	2.90×10^{-7}	*99.4*	6.84×10^{-7}	*96.0*	$Pb_3(OH)_2(CO_3)_2$
Ni^{2+}				3.48×10^{-5}	1.70×10^{-7}	*99.5*	3.48×10^{-5}	*0.00*	-
AMD 2									
Fe^{3+}	8.0	1.2×10^{-2}	7.81×10^{-2}	1.40×10^{-2}	9.31×10^{-6}	*99.9*	8.17×10^{-10}	*100*	$Fe(OH)_3$
Al^{3+}				1.20×10^{-2}	6.45×10^{-5}	*99.5*	4.04×10^{-7}	*99.9*	$Al(OH)_3$
Cu^{2+}				4.57×10^{-4}	7.24×10^{-6}	*98.4*	3.86×10^{-7}	*99.9*	$Cu_2(OH)_2CO_3$
Zn^{2+}				6.08×10^{-4}	3.67×10^{-6}	*99.4*	1.64×10^{-4}	*73.0*	$ZnCO_3.1H_2O$
Pb^{2+}				6.47×10^{-6}	4.34×10^{-7}	*93.1*	5.06×10^{-7}	*92.2*	$Pb_3(OH)_2(CO_3)_2$
Cd^{2+}				4.43×10^{-5}	8.90×10^{-8}	*99.8*	5.58×10^{-6}	*87.4*	$CdCO_3$

Ksp values used to predict metal solubilities: $FeCO_3$ ($10^{-10.24}$), $Cu_2(OH)_2CO_3$ ($10^{-33.3}$), $CdCO_3$ ($10^{-12.0}$), $MnCO_3$ ($10^{-10.58}$), $ZnCO_3.1H_2O$ ($10^{-10.26}$),$Fe(OH)_3$ ($10^{-38.8}$), $Al(OH)_3$ ($10^{-33.70}$), $Pb_3(OH)_2(CO_3)_2$ ($10^{-18.77}$).

Tableau 4.4 Metals precipitation of the synthetic poly-metallic solutions using Na_2S as precipitating agent

Metals	Precipitation tests						Mineql prediction		
	Final pH	S added (mol/L)	NaOH added (mol/L)	$[M]_i$ (mg/L)	$[M]_f$ (mg/L)	*Removal (%)*	$[M]_f$ (mg/L)	*Removal (%)*	Precipitates
Chloride matrix (Sln C)									
Fe^{2+}	8.0	2.1×10^{-2}	0	4.00×10^{-3}	8.95×10^{-7}	*99.9*	1.41×10^{-7}	*100*	FeS
Cu^{2+}				4.00×10^{-3}	9.44×10^{-7}	*99.9*	5.68×10^{-13}	*100*	CuS *(covellite)*
Cd^{2+}				3.98×10^{-3}	2.67×10^{-7}	*99.9*	8.58×10^{-12}	*100*	CdS
Zn^{2+}				4.01×10^{-3}	1.52×10^{-7}	*99.9*	2.77×10^{-9}	*100*	ZnS *(sphalerite)*
Mn^{2+}				4.01×10^{-3}	1.31×10^{-4}	*96.7*	1.20×10^{-4}	*97.0*	MnS
Sulphate matrix (Sln D)									
Fe^{2+}	8.1	2.1×10^{-2}	0	4.00×10^{-3}	1.68×10^{-5}	*99.6*	3.86×10^{-6}	*99.9*	FeS
Cu^{2+}				4.08×10^{-3}	6.29×10^{-7}	*99.9*	8.46×10^{-12}	*100*	CuS *(covellite)*
Cd^{2+}				4.00×10^{-3}	2.66×10^{-7}	*99.9*	3.40×10^{-11}	*100*	CdS
Zn^{2+}				4.00×10^{-3}	6.16×10^{-7}	*99.9*	1.08×10^{-8}	*100*	ZnS *(sphalerite)*
Mn^{2+}				4.00×10^{-3}	4.44×10^{-4}	*88.9*	3.75×10^{-4}	*90.6*	MnS
AMD 1									
Fe^{3+}	8.1	2.7×10^{-3}	2.78×10^{-2}	1.29×10^{-2}	2.42×10^{-5}	*99.8*	8.17×10^{-10}	*100*	$Fe(OH)_3$
Al^{3+}				2.63×10^{-3}	2.19×10^{-5}	*99.2*	4.04×10^{-7}	*99.9*	$Al(OH)_3$
Cu^{2+}				6.67×10^{-4}	4.72×10^{-7}	*99.9*	7.85×10^{-13}	*100*	CuS *(covellite)*
Zn^{2+}				1.83×10^{-3}	2.75×10^{-6}	*99.9*	3.36×10^{-9}	*100*	ZnS *(sphalerite)*
Pb^{2+}				1.29×10^{-5}	1.93×10^{-7}	*98.5*	2.80×10^{-11}	*100*	PbS
Ni^{2+}				3.48×10^{-5}	1.70×10^{-8}	*100*	1.15×10^{-17}	*100*	NiS
AMD 2									
Fe^{3+}	8.1	1.3×10^{-3}	4.45×10^{-2}	1.40×10^{-2}	1.68×10^{-5}	*99.9*	8.17×10^{-10}	*100*	$Fe(OH)_3$
Al^{3+}				1.20×10^{-2}	3.08×10^{-5}	*99.7*	4.04×10^{-7}	*99.9*	$Al(OH)_3$
Cu^{2+}				4.57×10^{-4}	4.72×10^{-7}	*99.9*	1.59×10^{-14}	*100*	CuS *(covellite)*
Zn^{2+}				6.08×10^{-4}	3.06×10^{-7}	*99.9*	4.88×10^{-12}	*100*	ZnS *(sphalerite)*
Pb^{2+}				8.59×10^{-6}	4.83×10^{-9}	*100*	3.99×10^{-12}	*100*	PbS
Cd^{2+}				4.43×10^{-5}	8.90×10^{-9}	*100*	1.42×10^{-12}	*100*	CdS

Ksp values used to predict metal solubilities: FeS ($10^{-20.9}$), CuS ($10^{-139.6}$), ZnS ($10^{-28.75}$), MnS ($10^{-17.13}$), $Fe(OH)_3$ ($10^{-38.8}$), $Al(OH)_3$ ($10^{-33.7}$), PbS ($10^{-31.27}$), NiS ($10^{-30.1}$)

Tableau 4.5 Metallic sludge dewatering properties associated to the treatment of the synthetic poly-metallic solutions using NaOH or $Ca(OH)_2$ as precipitating agent at pH 10.0

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	TS (% w/w)	Production (kg/m^3)	FC ($kg/(m^2.h)$)	SRF ($m/kg \times 10^{12}$)	TS (% w/w)
Chloride matrix (Sln A)	428	303	7.4	26.2	0.23	66.0	3.7
Sulphate matrix (Sln B)	377	152	11.2	21.6	0.57	23.5	4.4
AMD 1							
NaOH	216	113	19.0	12.5	0.76	6.0	6.5
$Ca(OH)_2$	49	96	30.2	29.5	3.33	3.4	18.9
AMD 2							
NaOH	292	229	21.1	15.0	0.50	14.9	8.2
$Ca(OH)_2$	65	71	31.0	40.8	6.43	2.2	18.7

Tableau 4.6 **Metallic sludge dewatering properties associated to the treatment of the synthetic poly-metallic solutions using Na_2HPO_4 as precipitating agent**

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	TS (% w/w)	Production (kg/m^3)	FC ($kg/(m^2.h)$)	SRF ($m/kg \times 10^{12}$)	TS (% w/w)
Chloride matrix (Sln A)	235	140	18.5	19.2	0.91	11.0	5.7
Sulphate matrix (Sln B)	208	55	16.7	24.5	2.65	2.9	6.9
AMD 1	137	31	21.9	22.7	5.70	1.2	9.3
AMD 2	134	54	16.0	45.0	4.77	2.0	10.6

Tableau 4.7 Metallic sludge dewatering properties associated to the treatment of the synthetic poly-metallic solutions using Na_2CO_3 as precipitating agent at pH

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	TS (% w/w)	Production (kg/m^3)	FC (kg/(m^2.h))	SRF (m/kg × 10^{12})	TS (% w/w)
Chloride matrix (Sln C)	37	17	19.1	13.0	5.16	1.6	9.8
Sulphate matrix (Sln D)	56	13	41.9	5.9	6.73	1.1	17.5
AMD 1	358	128	20.8	11.9	0.70	7.6	7.4
AMD 2	275	64	15.0	23.3	1.95	3.9	6.9

Tableau 4.8 Metallic sludge dewatering properties associated to the treatment of the synthetic poly-metallic solutions using Na_2S as precipitating agent

Metals	Settling	Filtration					Centrifugation
	SVI (mL/g)	Time (min)	TS (% w/w)	Production (kg/m^3)	FC (kg/(m^2.h))	SRF (m/kg × 10^{12})	TS (% w/w)
Chloride matrix (Sln C)	121	120	16.6	13.9	0.69	10.8	7.1
Sulphate matrix (Sln D)	122	115	17.4	13.2	0.72	9.7	7.4
AMD 1	214	260	18.9	16.5	0.43	16.8	7.5
AMD 2	241	308	13.7	29.0	0.47	19.4	6.3

CHAPITRE V

METALS REMOVAL FROM SOIL, FLY ASH AND SEWAGE SLUDGE LEACHATES BY PRECIPITATION AND DEWATERING PROPRETIES OF THE GENERATED SLUDGE

Le Chapitre 5 est constitué de l'article suivant:

Zied Djedidi, Med Ali Souissi, Médard Bouda, ridha Ben Cheikh, Guy Mercier, Rajeshwar Dayal Tyagi et Jean-François Blais (2009) Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge. *Journal of Hazardous Materials.* (article accepté le 30 juillet 2009).

Résumé

Cette étude concerne le traitement par précipitation de trois lixiviats acides contaminés par les métaux lourds et ce, en utilisant une variété d'agents précipitants. Deux modes de traitement (précipitation simple ou combinée) ont été réalisés pour évaluer les différents rendements d'élimination des métaux, ainsi que les capacités de déshydratation des boues générées. Il a été constaté que pour les trois lixiviats étudiés, l'ajout de $Ca(OH)_2$ donne des meilleurs taux d'enlèvement que lors de l'ajout de NaOH au même pH 10.0. En outre, la combinaison de NaOH et Na_2S permet une meilleure élimination pour les cations Pb^{2+}, Zn^{2+}, Cu^{2+} et Mn^{2+} qu'avec $NaOH/Na_2CO_3$ ou $NaOH/Na_2HPO_4$. La déshydratation des précipités formés pendant le traitement du lixiviat de sol, à la suite d'une filtration sous pression, a été établie en se basant sur les valeurs de la résistance spécifique à la filtration (RSF) : sulfures (4.3×10^{12} m/kg) < phosphates (6.4×10^{12} m/kg) < hydroxydes [$Ca(OH)_2$] (14.2×10^{12} m/kg) < hydroxydes [NaOH] (19.7×10^{12} m/kg) < carbonates (26.5×10^{12} m/kg). Pour le traitement du lixiviat de cendres, les résultats obtenus sont similaires et ce, quelque soit le mode de traitement utilisé, les valeurs de RSF varient entre 5 et 7×10^{12} m/kg, quand à l'indice de volume des boues (IVB), il est compris entre 39 et 50 mL/g. Les précipités générés à la suite du traitement du lixiviat des boues de station d'épuration par ajout de phosphates, ont donné les meilleurs résultats en termes des paramètres IVB et RSF (180 mL/g et 7.6×10^{12} m/kg, respectivement). Les résultats expérimentaux ont également montré que quelque soit l'agent précipitant utilisé, la méthode de filtration sous pression est plus efficace pour l'élimination de l'eau [ST: 11 à 73% (p/p)] que la méthode de centrifugation [5 à 11% (p/p)].

Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge

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5. METALS REMOVAL FROM SOIL, FLY ASH AND SEWAGE SLUDGE LEACHATES BY PRECIPITATION AND DEWATERING PROPERTIES OF THE GENERATED SLUDGE

5.1 Abstract

This study concerns the treatment by precipitation of three acidic and metal-rich leachates by using various reagents. Two treatment modes (simple and combined precipitation) have been performed to evaluate the metals removal efficiency and the dewatering ability of the generated sludge. It appears that for the three leachates used, the $Ca(OH)_2$ addition gave better metals removal at pH 10.0 than the use of NaOH at the same pH. Moreover, the combination of NaOH and Na_2S allows better removal for Pb^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} ions than with $NaOH/Na_2CO_3$ or $NaOH/Na_2HPO_4$. The dewaterability (vacuum filtration) of precipitates produced during the treatment of soil leachate was established as follows on the basis of the specific resistance to filtration values (SRF): sulphides (4.3×10^{12} m kg^{-1}) < phosphates (6.4×10^{12} m kg^{-1}) < hydroxides [$Ca(OH)_2$] (14.2×10^{12} m kg^{-1}) < hydroxides [NaOH] (19.7×10^{12} m kg^{-1}) < carbonates (26.5×10^{12} m kg^{-1}). For the fly ash leachate treatment, the obtained results were quite similar no matter the treatment mode used; the SRF values were in a range of 5 to 7×10^{12} m kg^{-1}, while sludge volume index (SVI) ranged from 39 to 50 mL g^{-1}. The sludge generated during the treatment of sewage sludge filtrate using phosphate salt gave the best results regarding to SVI and SRF parameters (180 mL g^{-1} and 7.6×10^{12} m kg^{-1}, respectively). Experimental results shown that whatever precipitating agent used, vacuum filtration is more efficient in water elimination [total solids: 11 to 73% (w w^{-1})] than centrifugation [5 to 11% (w w^{-1})] from sludge.

5.2 Keywords

Heavy metals; Precipitation; Sludge dewatering; Hydroxide; Sulphide.

5.3 Nomenclature

μ	viscosity of the filtrate (Pa.s)
A	surface area (m^2)
b	slope of the plot (V vs. t/V)
c	weight of solids/unit volume of filtrate ($kg.m^{-3}$)
C_f	final moisture content (%)
C_i	initial moisture content (%)
FC	filtration capacity ($kg.m^{-2}.s^{-1}$)
I	ionic strength ($mol.L^{-1}$)
P	pressure (Pa)
rpm	rotations per minute
SRF	specific resistance to filtration ($m.kg^{-1}$)
SP	sludge production ($kg.m^{-3}$)
SVI	sludge volume index ($mL.g^{-1}$)
t	time (s)
tds	ton of dry sludge
TS	total solids ($w.w^{-1}$)
V	volume (m^3)
WTP	wastewater treatment plant

5.4 Introduction

Environmental contamination with toxic metals is mainly due to industrial activities [1-3]. Coupled with the anthropogenic pollution, it constitutes a major risk to all living organisms, in particular, humans [4-8]. It is, therefore, essential to remove or reduce the presence of these inorganic contaminants in order to diminish the possibility of uptake by plants, animals and humans and their accumulation in the food chain and also to prevent them from contaminating surface and groundwater by dissolution or dispersion [9-10]. A lot of researches have been accomplished in last decade to develop efficient and economic process to remove heavy metals from polluted effluents [11-12]. In a complete integrated chain of treatment steps necessary for removal of heavy metals, leachate treatment is a key process step not only regarding to metals removal performance, but also with respect to costs and final amount of residual metallic sludge.

Among these technologies, chemical precipitation is still the most widely used approach for metals removal from groundwater, surface water, leachates and industrial effluents [13-16]. Metal separation from solutions by formation of metal hydroxides is the most common precipitation method due to the relative low costs of hydroxide salts [17-19]. Soluble metals can be precipitated as hydroxides by using different alkaline reagents, like CaO, $Ca(OH)_2$, $Mg(OH)_2$, NaOH and NH_4OH [12-13,20]. Heavy metals, like Cr, Cu, Pb, Mn, and Zn do not precipitate at pH below 7.0, allowing their separation from ferric ion [21-23] and aluminium ion [22-23], which precipitate at pH below 6.5.

Some other precipitating agents can be used to reach lower residual soluble metal concentrations [24] and/or to produce metallic sludge having better thickening and dewatering properties [25-26]. These others precipitation techniques notably include the formation of insoluble metal phosphates [27-28], metal sulphides [29-30] and metal carbonates [31-32]. Common reagents used for those techniques are Na_2HPO_4, Na_2S, NaHS, FeS, $NaHCO_3$ and Na_2CO_3, respectively. The lower solubility of metal sulphides, carbonates and phosphates in the acid region below pH 7.0 permits reduction of metal solubility to values that are orders of magnitude lower than reachable by hydroxide precipitation [21].

Nowadays, a combination of hydroxide and sulphide precipitation on the one hand and hydroxide carbonate precipitation on the other hand is being considered [33-34]. A common configuration is a two-stage process in which hydroxide precipitation is followed by sulphide or carbonate precipitation. This process has the advantage to reduce the reagents consumption.

In the metals precipitation process, sludge dewatering is a paramount process. It reduces the volume of sludge and, consequently, the costs for transporting and dispose the sludge to its ultimate disposal site. Drying bed, lagoon, belt filter press, vacuum filter, and centrifuge are some common sludge dewatering methods. However, the mechanical dewatering devices such as the belt filter press, vacuum filter, and centrifuge are commonly employed for sludge dewatering [35-36]. The efficiency of mechanical dewatering depends mainly on the dewaterability of sludge. It has been established that the cellulose content, pH, particle charge, organic content, solid concentration, grease content, compressibility coefficient, mechanical strength of particles, floc density and floc size of the sludge can effect the sludge dewaterability in one way or another [37-40].

The aims of the present work were to study the efficiency of various precipitation reagents used in the metals precipitation process. Sludge dewatering has also been studied through mainly parameters like total solids (TS), specific resistance to filtration (SRF), filtration capacity (FC), sludge production, and settling properties (sludge volume index - SVI). The performance of the chemical equilibrium software *MINEQL+* was evaluated to predict residual soluble metal concentrations, dissolved solids and major species present in sludge at work pH, in normal operational conditions used for treatment of metal-polluted effluents.

5.5 Material and methods

5.5.1 Soil

The soil used in this work comes from the Pointe-aux-Lièvres site (Québec, QC, Canada) and it contained 73% (w w^{-1}) of sand, 21% (w w^{-1}) of silt and 6% (w w^{-1}) of clay. Some physical pre-treatments (Grizzly, Tyler Sweco sieves, Reichert spiral and hydrocyclone) have been applied to this soil to obtain particle size fractions having different levels of metal contamination. The more metal-contaminated fraction consisting in 86 kg of soil inferior to 20 μm and having 45% (w w^{-1}) of water content has been used for this work. The metal concentrations in the soil leachate used in this research are presented in Table 1, Pb and Zn concentrations are above the criteria C (commercial and industrial use) set by the Ministry of Environment and Fauna of Quebec [41], which are respectively 1000 and 1500 mg kg^{-1}.

5.5.2 Fly ash

The mixture of boiler and electrofilter ashes used in this study comes from Québec City municipal waste incinerator. The sampling has been carried out in a collector to meet the real proportions of production for these two types of ash, namely 39% (w w^{-1}) (boiler) and 61% (w w-$^{-1}$) (electrofilter). Ashes were sampled on the spot and then placed in 20 L polyethylene containers. The particle size distribution of boiler and electrofilter ashes measured by Microtrac S3500 is ranging between 0.30 and 270 μm.

5.5.3 Sewage sludge

The mix sludge (primary and secondary sewage sludge) used in this work was obtained from the Québec City wastewater treatment plant (WTP). This WTP treats about 231000 m^3 per day and services around 270000 inhabitants. Samples were collected in polypropylene bottles and stored at 4°C until further use.

5.5.4 Batch reactor leaching experiments

Batch reactor leaching tests were performed in order to produce an amount of soil, fly ash and sewage sludge leachates needed for precipitation treatment.

Experiments were conducted in 10 L acrylic tank reactors containing 1000 g (dry weight) of soil or fly ash in which, a volume of tap water was added to reach a pulp density of 10% (w w^{-1}). The suspension was then acidified to a pH 2.0 ± 0.2 with HCl (12 M).

Sewage sludge leaching was conducted according to optimal conditions defined by Beauchesne *et al.* [42] which are the addition of 56 kg Fe^{3+} tds^{-1}, 8 kg H_2O_2 tds^{-1}, and enough H_2SO_4 to reach a pH between 2.0 and 2.5.

In all matrices (soil, fly ash and sewage sludge), mixing was achieved by a variable speed mixer (Caframo RZR50 rotor) operated at 300 rpm and using a three blade axial impeller (Stainless steel SS-316L) with a 7.62 cm diameter. After 6 h of leaching, the mixture was centrifuged at 3000 × *g* (3625 rpm) for 10 min using a Beckman Coulter Allegra^{TM} 6 centrifuge, in order to separate solids and liquid. Supernatant was then filtered using Whatman no. 4 membrane under a vacuum.

5.5.5 *MINEQL+* simulations

Chemical composition systems were calculated using the chemical equilibrium computer program *MINEQL+* (version 4.5). This program may be used to compute equilibrium among dissolved, solid and adsorbed phases suitable for aqueous solutions based on the appropriate thermodynamic stability constants. In the present study, models were constrained to include only those solid phases that were found to govern solubility (example: oxides are not considered due to kinetic considerations). During model setup, the Debye-Huckel method for the ionic strength correction was selected because of its frequent use in the research literature, and oversaturated solids were allowed to precipitate. All calculations were performed at a constant temperature of 298K with the number of iteration cycles constrained to 100. In order to have a realistic values for the model input, samples of soil, sewage sludge, and fly ash leachates were analyzed and the resulting constituent concentrations were used as input data. The counter ion is chloride (Cl^-) for all systems to balance electrical charges. Calculations were made over the pH range 2-12 for all systems (Figures 1, 2, and 3). Quantities of precipitant agents (1.2 × stoichiometry of metals in solution) were added to the input data to simulate the carbonate, phosphate, and sulphide precipitations at a fixed pH of 7.5, 8.0, and 7.5, respectively (Tables 2, 4, and 6). It should be noted that hydroxide simulation (NaOH) at pH 10.0 was conducted without adding precipitant agent.

5.5.6 Metal precipitation assays

Metal precipitation tests were realized at ambient temperature ($22 \pm 2^{o}C$) and with volume of 1 L of each leachate in 2 L beakers (diameter 125 mm). Mixing of the solution was conducted using magnetic stir bar (length: 37 mm, diameter: 8 mm) with a speed mixing of 160 rpm. Speed mixing was determined with a Digital Photo Tachometer (Extech Instruments, Model 461893).

For each selected pH, a reaction time of 20 min was allowed for the system to reach equilibrium. Speed mixing was selected to obtain flocs with good dewaterability and filterability [43-45]. Generally, high mixing speed generates small flocs sludge difficult to dewater and filtrate.

Two treatment modes have been studied for the three leachates namely, simple precipitation [NaOH, $Ca(OH)_2$] and combined precipitation [$NaOH+Na_2S$, $NaOH+Na_2CO_3$ and Na_2HPO_4+NaOH].

Simple precipitation tests by adding caustic soda (NaOH at 2.5 M (97% ACS reagent)) or lime ($Ca(OH)_2$ at 0.28 M) were done by adjusting pH's leachates (volume of 1 L) to 10.0 ± 0.2.

During the combined precipitation tests, in the case of sulphides and carbonates, an adjustment of the pH close to 5.0 was made to avoid the emission of hydrogen sulphide and dioxide carbon gases [46-47]. Thereafter, precipitant agents ($Na_2CO_3.H_2O$ (99.5%, ACS reagent) or $Na_2S.9H_2O$ (98%, ACS reagent)) were added to leachates at 1.2 × stoichiometry of metals remaining in solution. Finally, a pH adjustment was done by adding sodium hydroxide to 7.5 for these two systems. For phosphates systems $Na_2HPO_4.7H_2O$ (98%, ACS reagent) was firstly added to leachates (pH 2.0) at 1.2 × stoichiometry of metals in solution, then a pH adjustment to 8.0 was made. In all cases leachates were agitated during a 20 min period to reach equilibrium under a speed mixing of 160 rpm.

Precipitation tests were also carried out by adding caustic soda (NaOH) over the pH range 2.0-12.0 for the three leachates. The pH of each system was then increased in the unit pH intervals (pH 2.0 to 12.0). An equilibrium period of 20 min between pH adjustments was allowed, after which time the reaction vessel was sampled. Residual metal concentration was thereafter determined by ICP-AES (figures 1, 2 and 3).

5.5.7 Sludge settling

After the agitation period, the suspensions were settled for 30 min in 2 L capacity cylinders and the resulting volumes of the settled sludge were measured to evaluate the SVI values. Volumes of 400 mL of the settled sludge (soil and sewage sludge leachates) and 800 mL (fly ash leachate) were then sampled after the supernatants were removed by pumping. These experiments were conducted in triplicates.

5.5.8 Sludge filtration

SRF and FC were used to characterize the dewaterability of the sludge resulting from metals precipitation with the different precipitating agents [48]. The mathematical expression of SRF is given by the following formula [26]:

Équation 5.1 $$SRF = \frac{2bPA^2}{\mu . c}$$

Where "b" is the slope of the plot (V vs. t/V), "V" is the volume of filtrate, m^3; "P" is the vacuum of filtration, Pa (N/m^2); "A" is the filter area, m^2; "μ" is the viscosity of filtrate, Pa.s ($N.s/m^2$) and "c" is the weight of solids/unit volume of filtrate, Kg/m^3.

Équation 5.2 $$c = \frac{1}{C_i/(100 - C_i) - C_f/(100 - C_f)}$$

Where "C_i" is the initial moisture content,% and "C_f" is the final moisture content,%.

Whatman No. 2 (8.0 μm pore size) membranes having an effective area of 12.50 cm^2 were used during the pressure filtration tests. A pressure of 31.7 kPa was applied on 200 mL volumes of the settled sludge samples inside a Fisherbrand stainless-steel pressure vessel (model 09-753-25A, Fisher Scientific Ltd.). The pressure was applied until no liquid was extracted. Filtrate and sludge viscosities were measured using a Brookfield DV-II+Pro programmable rheometer at a module speed of 60 rpm. These experiments were conducted in triplicates.

5.5.9 Sludge centrifugation

100 mL of the settled sludge samples were centrifuged at 3000 × *g* (3760 rpm) for 15 min using a Beckman Coulter Allegra^{TM} 6 Centrifuge, in order to evaluate this technique for the metallic sludge dewatering. 3000 × *g* (3760 rpm) and 15 min were selected because of its frequent use in the research literature [61-62] .These experiments were conducted in triplicates.

5.5.10 Analytical methods

The pH was determined before and after each experiment by using a pH-meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Nepean, Canada) equipped with a double junction Cole-Parmer electrode with Ag/AgCl reference cell (daily calibration between 2 and 10). TS were measured according to the APHA method 1603 [49]. Metals in solution were measured by plasma emission spectroscopy with a simultaneous ICP-AES (inductively coupled plasma - atomic emission spectroscopy, Vista Ax CCO simultaneous ICP-AES from Varian, Mississauga, Canada). Before analysis, liquid samples were first filtered on a Whatman 934-AH membrane (1.5 µm pore size) and were then acidified to give a 5% (w w^{-1}) HCl solution. Analytical quality controls were performed with a certified standard solution (PlasmaCal Multielement Standard 900-Q30-100, SCP Science, Baie d'Urfé, Canada). Determination of metal concentration was done with one measure.

5.6 Results and discussion

5.6.1 Soil leachate

5.6.1.1 Simple precipitation

The treatment of soil leachate, at pH 10.0 with lime, generally gives higher removal for all metals studied than those with caustic soda at the same pH (Table 5.1). This trend can be explained by the fact that, the soil leachate contains soluble humic substances [50-52] which are likely to form a metal-humic acid complexes through the carboxyl (COO^-) and hydroxyl (OH^-) groups. The competition on the complexation sites between Ca^{2+} and the transition metal is given by the following equation [53]:

Équation 5.3 $\textbf{Me-Hum} + \textbf{Ca}^{2+} = \textbf{Ca-Hum} + \textbf{Me}^{2+}$

In this fact, the contribution of Ca^{2+} ions through the $Ca(OH)_2$ solution, will allow the release of Me^{2+} metal ions while leading their precipitation. The residual concentration of Pb, fairly high after the sodium hydroxide treatment (12.8 ± 1.3 mg L^{-1}), is essentially dues to the Pb-Hum complex which is stable in comparison to the other divalent metals. Moreover, the Ca-Hum complexes are more stable than Na-Hum. Consequently, Na^+ ions, cannot release metals from Me-Hum complex as Ca^{2+} ions.

During the treatment with lime, the equilibrium of above equation is therefore moved to the release of Pb^{2+} ions, promoting their precipitation mainly in hydroxide form, $Pb(OH)_2$, with a residual concentration of 0.05 ± 0.03 mg L^{-1}.

Regarding to the aluminium, the residual concentrations after NaOH and $Ca(OH)_2$ treatments are respectively 3.8 ± 0.5 and 1.7 ± 0.1 mg L^{-1}. This is due to the amphoteric character of this metal. Indeed, $Al(OH)_3$ is formed at low pH, but begins to solubilise at pH 9.5. Fig. 5.1 shows clearly this result. The results demonstrate the good correlation between the *MINEQL+* predictions and precipitation assays of the soil leachate performed using NaOH and followed step by step by ICP at different pH (from 2.0 to 12.0). The humic substances and adsorption phenomena should explain the gaps at low pH.

5.6.1.2 NaOH with Na_2S

When Na_2S is added at pH 5.0 (1.2×the stoichiometry of the metals in solution) there has been an elimination of almost all metals in the form of sulphides (MeS) at pH 7.5. The removal yields around 100% were obtained for Pb, Cu, Zn, Ni and Mn (Table 5.1). These results are in agreement with those obtained by Marchioretto *et al.* [34].

5.6.1.3 NaOH with Na_2CO_3

The precipitation of metals from soil leachate, when combining the NaOH with Na_2CO_3, gave removal of 98%, except for Mg^{2+} and Mn^{2+} ions. This treatment process, combining the precipitation of Pb in the form of hydroxides $Pb(OH)_2$, and carbonates $PbCO_3$ has allowed reaching the standards releases with a residual concentration of 0.35 ± 0.13 mg L^{-1}. Some difficulties occurred during the removal of Mn and Mg in carbonate forms. Their removals are respectively estimated to 50% and 33%. This is in agreement with the results of *MINEQL+* software simulation at pH 7.5 (Table 5.2).

5.6.1.4 Na_2HPO_4 with NaOH

The use of Na_2HPO_4 in combination with NaOH has allowed a very good removal of heavy metals. Indeed, metals such as Pb and Cu have been almost completely removed (< 0.1 mg L^{-1}). According to the simulation with the *MINEQL+* software (Table 5.2), the Pb is removed in form of $Pb_3(PO_4)_2$ and the Ca is precipitated in form of $Ca_4H(PO_4)_3.3H_2O$, this confirms the experimental results (Table 5.1).

5.6.2 Fly ash leachate

5.6.2.1 Simple precipitation

Experimental results show that the treatment of fly ash leachate, by precipitation at pH 10.0, with $Ca(OH)_2$ gives better results than with NaOH. The Zn and Pb, which are the main contaminants of this effluent, are efficiently removed (Table 5.3).

At the beginning of the precipitation (pH 2.0 to 5.0), the Al^{3+} and Fe^{3+} ions are removed in form of phosphates $AlPO_4$ and $FePO_4$ and hydroxides $Al(OH)_3$ and $Fe(OH)_3$ (Table 5.4). These solid species are adsorbent materials, which contribute to the effectiveness of the process [34, 54-55]. At pH 5.0, phases governing the phosphate concentration in the solution are $AlPO_4$, $Zn_3(PO_4)_2.4H_2O$ and $Pb_3(PO_4)_2$ (Table 5.4). Starting from pH 6-7, the phosphate concentration is controlled by one phase, badly crystallized, of calcium phosphates which can evolve towards the octa-calcium phosphate amorphous of formula $Ca_8(PO_4)_4(HPO_4)_2.5H_2O$ with Ca/P = 1.33 [56-57]. It is noteworthy that the presence of Mg prevents the transition of the octa-calcium phosphate amorphous phase toward hydroxyapatite of formula $Ca_{10}(PO_4)_6(OH)_2$ which is more thermodynamically stable [57-59].

Furthermore, the high diminution of sulphate concentration in the case of precipitation with lime shows that more $CaSO_4.2H_2O$ (gypsum) can be formed, which contribute probably at metals removal effectiveness. The Fig. 5.2 shows the *MINEQL+* software prediction and experimental points for the simple treatment of fly ash leachate by NaOH. During metal hydroxides precipitation at neutral or alkaline pH, there is a good correlation between theory and experimental values. However, at low pH (below 5.5), the gap between the two curves is significant and can be explained by other phenomena, like adsorption, that were not taken into account by *MINEQL+*.

5.6.2.2 NaOH with Na_2S

The results show that, the metals precipitation using NaOH (pH 5.0) and Na_2S (to adjust the pH at 7.5) gives metal removal of 99% from fly ash leachate. Starting from pH 5.0, the Zn^{2+} and Pb^{2+} ions are removed essentially in the form of ZnS and PbS with residual concentrations of 0.08 ± 0.06 mg L^{-1} and 0.24 ± 0.04 mg L^{-1}, respectively. Marchioretto *et al.* [34] have already obtained the same results using the same conditions. In our study conditions, at pH 5.0 during the NaOH adding, the Zn and Pb are recovered in the form of phosphates (Table 5.4)

5.6.2.3 NaOH with Na_2CO_3

After Na_2CO_3 being added to the fly ash leachate at pH 5.0 (to adjust pH at 7.0), the precipitation of certain metals, in the form of carbonates is inhibited by the $CaCO_3$ formation. At this pH, the results obtained with the *MINEQL+* software confirm this fact (Table 5.4). It appears therefore inappropriate to treat leachates loaded in Ca, by carbonates addition.

5.6.3 Sewage sludge

5.6.3.1 Simple precipitation

Table 5.5 shows the results of hydroxides precipitation at pH 10.0 during the sludge leachate treatment by NaOH or $Ca(OH)_2$. Both reagents have given the similar metals removal. At this pH, sludge generated are essentially constituted by the metal hydroxides except, the Ca^{2+} ions which have crystallized in the form of calcium phosphate, starting from pH 6-7 (Table 5.6). Mg and Al have been eliminated at an average rate of 75 and 90%, respectively. Others metals have been almost completely removed.

The results of the precipitation assay of the sewage sludge performed using NaOH are shown in Fig. 5.3 in comparison to *MINEQL+* software predictions. As the precedent cases, there is a correlation from pH 6.0 and up, but below this value, the two curves present a significant gap.

5.6.3.2 NaOH with Na_2S

When Na_2S is added from pH 5.0 to sewage sludge leachate, all metals have been precipitated in the form of sulphides at pH 7.5; only Mg has been weakly eliminated (Table 5.5). However, it is to notice that the phosphates removal is realised with a part of Ca in the form of amorphous octa-calcium phosphate, starting from pH 6-7 [57,59].

5.6.3.3 NaOH with Na_2CO_3

Satisfactory results were obtained for almost all metals during the treatment of sewage sludge leachate, with Na_2CO_3 addition at pH 5.0. In this case, Mg^{2+} ions were weakly removed. It's noticed that low residual concentration of PO_4^{3-} ions (0.55 ± 0.01 mg L^{-1}) is due to the presence of CO_3^{2-} ions, which improve the conversion rate of the crystalline phase of calcium phosphate toward amorphous octa-calcium phosphate [57].

5.6.3.4 Na_2HPO_4 with NaOH

Experimental results confirm that the effluent treatment by phosphate addition at pH 8.0, generally gives best metal removal, except the Mg^{2+} ions which usually precipitate above pH 10.0. The high diminution of the concentration of Ca^{2+} ions (64.1 ± 2.1 mg L^{-1}) is due to the excess of Na_2HPO_4 added, which has allowed to form more calcium phosphates.

5.6.4 Sludge dewatering properties

Treatment by precipitation of the three effluents (soil, fly ash and sewage sludge leachates) with NaOH or $Ca(OH)_2$ as well as the combination of NaOH with Na_2S or Na_2CO_3 or Na_2HPO_4 has generated sludge with specific characteristics regarding the settling, filtration and centrifugation. These sludge are essentially constituted of metallic hydrated precipitates and interstitial dissolved salts [20]. The size and density of the flocs as well as the salinity have a major influence on solid/liquid separation [60]. Table 5.7 shows the different dewatering properties of the sludge produced by the treatment of the three effluents studied.

5.6.4.1 Sludge from the soil leachate precipitation

Treatment of soil leachate, that has been essentially polluted by Pb (about 700 mg L^{-1}), has generated the sludge formed over 80% of lead salts: $Pb(OH)_2$, PbS, $PbCO_3$ or $Pb_3(PO_4)_2$.

SVI is a parameter that indicates the behaviour of the sludge during a 30 min gravity settling period. These values determined during the sludge settling from the soil leachate are in a range of 36 to 117 mL g^{-1}. It is to notice that, during the simple precipitation (hydroxide precipitation), the sludge generated by use of $Ca(OH)_2$, settle better than those formed by addition of NaOH (Table 5.7). In fact, the substitution of Na^+ by Ca^{2+}, increase solution ionic strength (I) which improve settling properties [20,38-39]. According to the precipitation mode used, the SVI values follow this order: sulphides < hydroxides ($Ca(OH)_2$) < carbonates < hydroxides (NaOH) < phosphates.

It was noticed that during the assays, the parameters of the vacuum filtration (TS, sludge production, FC and SRF) were essentially influenced by the reagent used. Parallelisms, between TS and sludge production (SP) on one side, and SRF with FC on another side, have been observed. Thus, for one given treatment mode, more the TS values are higher less wet sludge is produced. Lower FC values correspond to the highest SRF values (sludge difficult to filtrate). Sludge generated from the most widely precipitation technique (hydroxide, NaOH) has SRF value of 19.7×10^{12} m kg^{-1}, ($\mu = 1.05 \times 10^{-3}$ Pa.s, c = 7.8 Kg m^{-3}, and b = $1.61 \times 10^{11}/R^2 = 0.98$), whilst, sludge obtained by the combined treatment with NaOH and Na_2S are the easiest to filter (SRF= 4.3×10^{12} m Kg^{-1}) (table 5.7). In general, the order of solid/liquid separation, under vacuum filtration, is given by the following trends: sulphides < phosphates < hydroxides < carbonates.

On the other hand, concerning the TS, the order is given by: carbonates > phosphates > hydroxides > sulphides. It is important to note that TS of 72.0% (w/w) was obtained after limestone treatment (Na_2CO_3). This was expected since 80% (w/w) of sludge is constituted of PbCO3 precipitate and the latter behaves towards to the dewatering operation through a pressure filtration (in the same conditions) by generating a sludge cake having TS of 76.4% (w/w) [20].

TS of the sludge separated by centrifugation are given in Table 5.7. The results show clearly that centrifugation (at 3000 × *g*) is far less efficient than vacuum filtration (31.7 kPa) to eliminate water from metallic precipitates.

5.6.4.2 *Sludge from the fly ash leachate precipitation*

Metallic ions at high concentrations in the fly ash leachate (Al^{3+},Ca^{2+}, Fe_t, Mg^{2+}, Pb^{2+}, and Zn^{2+}) generate some precipitates which control the dewatering characteristics.

Generally, the pH increase from 2.0 to 5.0 of fly ash leachate has carried precipitation of the totality of Al^{3+}, Fe^{3+} ions in the form of hydroxides and more than 80% of Zn^{2+}, Pb^{2+}, Fe^{2+} and Cu^{2+} in the form of phosphates $M_3(PO_4)_2$, this is confirmed during the precipitation assay performed per NaOH over the pH range 2-12 (Fig. 5.2). It is noticed that from pH 5.0 all metals precipitate almost quantitatively and all precipitates have in majority the same nature which will control the settling (SVI between 39 and 50 mL g^{-1}), vacuum filtration and centrifugation properties, whatever the reagent used. In fact, experimental results confirmed it, and all TS and SRF values are closed (between 16 to 17% (w/w) and 5 to 7 × 10^{12} m kg^{-1} for TS and SRF, respectively). It should be noted that sludge generated by caustic soda (NaOH) treatment at pH 10.0 has an intermediate behaviour on dewatering characteristics by vacuum filtration (SRF= 6.2×10^{12} m kg^{-1}, where $\mu = 1.10 \times 10^{-3}$ Pa.s, c = 140 Kg m^{-3}, and b = $9.75 \times 10^{11}/R^2 = 0.99$).

5.6.4.3 *Sludge from the sewage sludge leachate precipitation*

SVI values obtained during the characterisation of the sludge in the assays of metal precipitation, contained in the sewage sludge leachate are in a range of 177 to 391 mL g^{-1} according to the reagents used. It appears that simple treatment with $Ca(OH)_2$ and combined treatment ($NaHPO_4$ and NaOH) generate sludge with best settling properties.

As for the SRF values, they are in the range of 8 to 32 × 10^{12} m kg^{-1}, depending on the reagent used. It appears that the combined treatment (NaOH with Na_2HPO_4) generates sludge easier to filter than for the others cases studied (SRF = 7.6 × 10^{12} m Kg^{-1} with μ = 1.17×10^{-3} Pa.s, c = 22.4 Kg m^{-3}, and b = 1.98 $\times10^{11}$/R^2 = 0.99). On the other hand, the combined treatment of sewage sludge leachate by NaOH and Na_2S produces sludge having bad filtration properties (SRF= 31.7 × 10^{12} m kg^{-1}). The TS percentages of the sludge produced were quite comparable for the treatment by NaOH, $Ca(OH)_2$ and NaOH/Na_2S (14 to 16%), low in the case of the NaOH with Na_2CO_3 combination (10-11%) and quite high for NaOH with Na_2HPO_4 combination (20%).

5.7 Conclusion

Various precipitant agents were used in this work to evaluate the efficiency of metals removal from three acidic leachates: soil, incinerator fly ash and sewage sludge leachates. Dewatering properties of the formed precipitates were also studied.

Two modes of treatment have been used, a simple treatment by addition of hydroxide salts and a combined treatment by a mixture of hydroxide salt and others precipitant agents. The results obtained are specific to the type of leachate used. However, it appears that for each leachate, the simple treatment by adding $Ca(OH)_2$ gives better metals removal at pH 10.0 than NaOH at same pH. For all leachates used, treatment with combination of NaOH and Na_2S leads to better removal for Pb^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} ions than in the two other cases (NaOH with Na_2CO_3 or Na_2HPO_4.).

The dewaterability (vacuum filtration) of precipitates produced during the treatment of soil leachate was established as follows on the basis of the specific resistance to filtration values (SRF): sulphides (4.3×10^{12} m kg^{-1}) < phosphates (6.4×10^{12} m kg^{-1}) < hydroxides [$Ca(OH)_2$] (14.2×10^{12} m kg^{-1}) < hydroxides [NaOH] (19.7×10^{12} m kg^{-1}) < carbonates (26.5×10^{12} m kg^{-1}).

The behavior towards dewatering characteristics from the neutralization of the studied leachates by adding caustic soda (NaOH) or lime ($Ca(OH)_2$) at pH 10.0 has been studied. Experimental results in table 5.7 show that the substitution of caustic soda (Na^+) by lime (Ca^{2+}), decrease SRF values (better filterability). This decrease is due essentially to the increase of the ionic strength I. this can be easily verified by the following formula: $I = ½ \Sigma C_i Z_i^2$; where C_i and Z_i are the concentration and the charge of the ith specie, respectively. This is in agreement with previous works of Dustan *et al.* [39], Moghadam *et al.* [38], and Djedidi *et al.* [20].-

For fly ash treatment, the obtained results are quite similar whatever the treatment mode is used. The SRF values are in a range of 5.0 to 7.3 $\times 10^{12}$ m kg^{-1} and those of SVI are in a range of 39 to 50 mL g^{-1}.

The precipitates formed in the case of sewage sludge by the combined treatment (NaOH with Na_2HPO_4) at pH 8.0 gave best results for the settling and vacuum filtration (180 mL g^{-1} and 7.6 $\times 10^{12}$ m kg^{-1}, respectively).

5.8 Acknowledgements

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5.9 References

[1] J. Nriagu, A history of global metal pollution, Science 272 (1996) 22-24.

[2] S. Davydova, Heavy metals as toxicants in big cities, Microchem. J. 79 (2005) 133-136.

[3] C.S.C. Wong, X.D. Li, I. Thornton, Urban environmental geochemistry of trace metals, Environ. Pollut. 142 (1) (2006) 1-16.

[4] M. Limg/Lann, Environmental toxicants. Human exposures and their health effects, John Wiley & Sons Inc., New York, NY, 2000, 987 p.

[5] H.E. Allen, Bioavailability of metals in terrestrial ecosystems : importance of partitioning for bioavailability to invertebrates, microbes, and plants, Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida, 2002, 176 p.

[6] P.M. Chapman, F. Wang, C.R. Janssen, R.R. Goulet, C.N. Kamunde, Conducting ecological risk assessments of inorganic metals and metalloids: current status, Hum. Ecol. Assess. 9 (2003) 641-697.

[7] R.K. Sharma, M. Agrawal, Biological effects of heavy metals: an overview, J. Environ. Biol. 26 (2) (2005) 301-313.

[8] A.M. Florea, D. Büsselberg, Occurence, use and potential toxic effects of metals and metal compounds, BioMetals 19 (2006) 419-427.

[9] M.J. McLaughlin, B.A. Zarcinas, D.P.Stevens, N. Cook, Soil testing for heavy metals, Commun. Soil Sci. Plant Anal. 31 (2000) 1661-1700.

[10] A. Kabata-Pendias, Trace elements in soils and plants. 3rd Edition, A. Kabata-Pendias, H. Pendias (Eds.), CRC Press LLC, Boca Raton, Florida, 2001, 413 p.

[11] J.F. Blais, S. Dufresne, G. Mercier, State of the art of the technological development from metal removal from industrial effluents, J. Water Sci. 12 (4) (1999) 689-713 (in French).

[12] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366 (2-3) (2006) 409-426.

[13] S.A. Mirbagheri, S.N. Hosseini, Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse, Desalination 171 (1) (2004) 85-93.

[14] FRTR, Federal remediation technologies roundtable, Website: http://www.frtr.gov, 2005.

[15] S. Lacour, R.P. Van Hille, K. Peterson, A.E. Lewis, Comparison of simulators for process and aqueous chemistry modelling, AIChE J. 51 (8) (2005) 2358-2368.

[16] J.F. Blais, Z. Djedidi, R.B. Cheikh, R.D. Tyagi, G. Mercier, Metals precipitation from effluents – A review, Practice Periodical Toxic Hazard. Radioactive Waste Manag. 12 (3) (2008) 135-149.

[17] K.A. Baltpurvins, R.C. Burns, G.A. Lawrance, Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation, Waste Manag. 16 (8) (1996) 717-725.

[18] K.A. Baltpurvins, R.C. Burns, G.A. Lawrance, Use of the solubility domain approach for the modeling of the hydroxide precipitation of heavy metals from wastewater, Environ. Sci. Technol. 30 (1996) 1493-1499.

[19] N. Meunier, J.F. Blais, M. Lounes, R.D. Tyagi, J.L. Sasseville, Different options for metal recovery after sludge decontamination at the Montreal Urban Community wastewater treatment plant, Water Sci. Technol. 46 (10) (2002) 33-41.

[20] Z. Djedidi, J.B. Khaled, R.B. Cheikh, J.F. Blais, G. Mercier, R.D. Tyagi, Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions, Hydrometallurgy (In Press. DOI: 10.1016/j.hydromet.2008.04.014).

[21] C.S. Brooks, Metal recovery from industrial waste, Lewis Publishers Inc., Chelsea, Michigan, 1991.

[22] C.E. Martínez, M.B. McBride, Aging of coprecipitated Cu in alumina: Changes in structural location, chemical form, and solubility, Geochimica Cosmochimica Acta 64 (10) (2000) 1729-1736.

[23] G. Lee, J.M. Bigham, G. Faure, Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee, Appl. Geochem. 17 (5) (2002) 569-581.

[24] S. Islamoglu, L. Yilmaz, H.O. Ozbelge, Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents, Sep. Sci. Technol. 41 (15) (2006) 3367-3385.

[25] B.R. Kim, W.A. Gaines, M.J. Szafranski, E.F. Bernath, A.M. Miles, Removal of heavy metals from automotive wastewater by sulphide precipitation, J. Environ. Eng. Div. ASCE 128 (7) (2002) 612-623.

[26] R.C. Viadero, X.C. Wei, K.M. Buzby, Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization, Environ. Eng. Sci. 23 (4) (2006) 734-743.

[27] E. Mavropoulos, A.M. Rossi, A.M. Costa, C.A.C. Perez, J.C. Moreira, M. Saldanha, Studies on the mechanisms of lead immobilization by hydroxyapatite, Environ. Sci. Technol. 36 (7) (2002) 1625-1629.

[28] A. Pigaga, R. Juskenas, A. Selkis, Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation, Sep. Sci. Technol. 37 (13) (2002) 3155-3168.

[29] A.H.M. Veeken, W.H. Rulkens, Innovative developments in the selective removal and reuse of heavy metals from wastewaters, Water Sci. Technol. 47 (10) (2003) 9-16.

[30] M. Al-Tarazi, A.B.M. Heesink, G.F. Versteeg, Precipitation of metal sulphides using gaseous hydrogen sulphide: mathematical modelling, Chem. Eng. Sci. 59 (3) (2004) 567-579.

[31] S. McAnally, L. Benefield, R.B. Reed, Nickel removal from a synthetic nickel-plating waste water using sulphide and carbonate for precipitation and coprecipitation, Sep. Sci. Technol. 19 (1984) 191-217.

[32] D. Guillard, A.E. Lewis, Optimisation of nickel hydroxycarbonate precipitation using a laboratory pellet reactor, Ind. Eng. Chem. 41 (2002) 3110-3114.

[33] USEPA, Wastewater Treatment Technologies. Development Document for the CWT Point Source Category, U.S. Environmental Protection Agency, Washington, DC, 1998.

[34] M.M. Marchioretto, H. Bruning, W. Rulkens, Heavy metals precipitation in sewage sludge, Sep. Sci. Technol. 40 (16) (2005) 3393-3405.

[35] G. Tchobanoglous, F.L. Burton, Wastewater engineering treatment, disposal and reuse. 3rd Edition, McGraw-Hill, New-York, NY, 1991.

[36] Y.G. Choi, T.H. Chung, Effects of humus soil on the settling and dewatering characteristics of activated sludge, Water Science Technol. 42 (9) (2000) 127-134.

[37] D.B. Mitchell, M.E. Schweers, Hazardous waste reduction using organic polymers, Pollut. Eng. 21 (3) (1989) 84-96.

[38] M.A. Moghadam, M. Soheili, M.M. Esfahani, Effect of ionic strength of activated sludge, Iranian J. Environ. Health Sci. Eng. 2 (1) (2005) 1-5.

[39] A.C. Dustan, B. Cohen, J.G. Petrie, Modelling dewatering behaviour through and understanding of solids formation process. Part II-solids separation considerations. Adv. Colloid Interface Sci. 113 (2005) 85-97.

[40] T.P. Nguyen, N. Hilal, N.P. Hankins, J.T. Novak, Determination of the effect of cations and cationic polyelectrolytes on the characteristics and final properties of synthetic and activated sludge, Desalination 222 (2008) 307-317.

[41] MEFQ, Politique de protection des sols et de réhabilitation des terrains contaminés, Ministère de l'Environnement et de la Faune, Gouvernement du Québec, Québec, QC, Canada, 1999, 132 p. (in French).

[42] I. Beauchesne, R. Ben Cheikh, G. Mercier, J.F. Blais, T. Ouarda, Chemical treatment of sludge: In-depth study on toxic metal removal efficiency, dewatering ability and fertilizing property preservation, Water Res. 41 (2007) 2028-2038.

[43] B.A. Yudin, V.N. Kolesnikov, V.P. Kornienko, Effects of precipitation conditions on the crystal size of silver oxalate–nickel oxalate salt mixtures. Part 1, Metallurgiya 139 (7) (1974) 11-14.

[44] J.M. Sun, F. Li, J.C. Huang, Optimum pH for the Cr^{6+} co-removal with mixed Cu^{2+}, Zn^{2+}, and Ni^{2+} precipitation, Ind. Eng. Chem. Res. 45 (2006) 1557-1562.

[45] Z. Wang, Q. Zhang, C. Yang, Z. Mao, X. Shen, Simulation of barium sulphate precipitation using CFD and FM-PDF modeling in a continuous stirred tank, Chem. Eng. Technol. 30 (12) (2007) 1642-1649.

[46] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol. 39 (10-11) (1999) 135-138.

[47] D. Feng, C. Aldrich, H. Tan, Treatment of acid mine drainage by use of heavy metal precipitation and ion exchange, Min. Eng. 13 (6) (2000) 623-642.

[48] Degrémont, Mémento technique de l'eau, 9th Edition, Paris, France, 1989 (in French).

[49] APHA, AWWA, WPCF, Standards Methods for Examination of Water and Wastewaters, 20th ed., American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, DC, 1999.

[50] D. McKnight, G. Aiken, Sources and age of aquatic humus, In: Aquatic Humic Substances. Ecology and Biogeochemistry, D. Hessen, L. Tranvik (Eds.), Springer-Verlag, New York, NY, 1998.

[51] A.K. Pandey, S.D. Pandey, V. Misra, Stability constants of metal-humic acid complexes and its role in environmental detoxification, Ecotoxicol. Environ. Safety 47 (2000) 195-200.

[52] L.K. Koopal, W.H. van Riemsdijk, D.G. Kinniburgh, Humic matter and contaminants. General aspects and modeling metal ion binding, Pure Appl. Chem. 73 (12) (2001) 2005-2016.

[53] W. Stumm, J.J. Morgan, Aquatic Chemistry, Third Edition, John Wiley and Sons, New-York, NY, 1996, 1022 p.

[54] A. Naeem, S. Mustafa, N. Rehana, B. Dilara, S. Murtaza, The sorption of divalent metal ions on $AlPO_4$, J. Colloid Interface Sci. 252 (1) (2002) 6-14.

[55] S. Mustafa, A. Naeem, S. Murtaza, N. Rehana, H.Y. Samad, Comparative sorption properties of metal (III) phosphates, J. Colloid Interface Sci. 220 (1999) 63-74.

[56] F. Cabanes, Déphosphatation des effluents : Précipitation et valorisation du phosphore, Ph.D. thesis, INPL, Toulouse, France, 2006 (in French).

[57] H.E.L. Madsen, Influence of foreign metal ions on crystal growth and morphology of brushite ($CaHPO_4$, $2H_2O$) and its transformation to octacalcium phosphate and apatite, J. Crystal Growth 310 (2008) 2602-2612.

[58] F. Abbona, A. Baronnet, A XRD and TEM study on the transformation of amorphous calcium phosphate in the presence of magnesium, J. Crystal Growth 165 (1996) 98-105.

[59] A. Gunnars, S. Blomqvist, G. Martinsson, Inorganic formation of apatite in brackish seawater from the Baltic Sea: an experimental approach, Marine Chem. 91 (2004) 15-26.

[60] H.J. Wen, C.I. Liu, D.J. Lee, Effects of polymer dosage on alum sludge dewatering characteristics and physical properties, Colloids Surf. A. Physicochem. Eng. Aspects. 122 (1-3) (1997) 89-96.

[61] A. Salmquillo, H. Bosh, G. Rauret and H. Mentau, Certified reference materials for extractable trace metals in soils: effect of the particle size. Fresenius Journal of Analytical Chemistry. 360 (3-4) (1998).

[62] A. El-Assar, D. Kitcher, and C.F. Forster, The release of heavy metals from digested sludge by centrifugation. Environmental Technology, 1479-487X. 19 (5) (1998) 537-542.

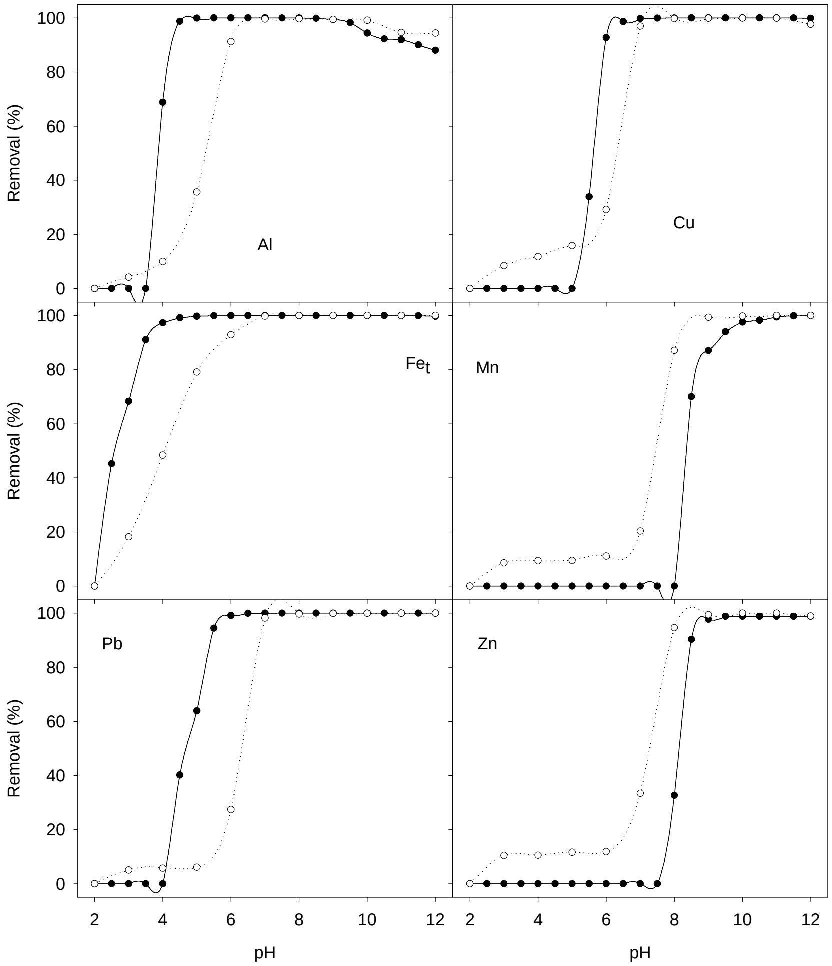

Figure 5.1 **Metal removal efficiency in the soil leachate (simple precipitation with NaOH) vs pH. Symbols: (●) *MINEQL+* predictions; (○) Experimental points**

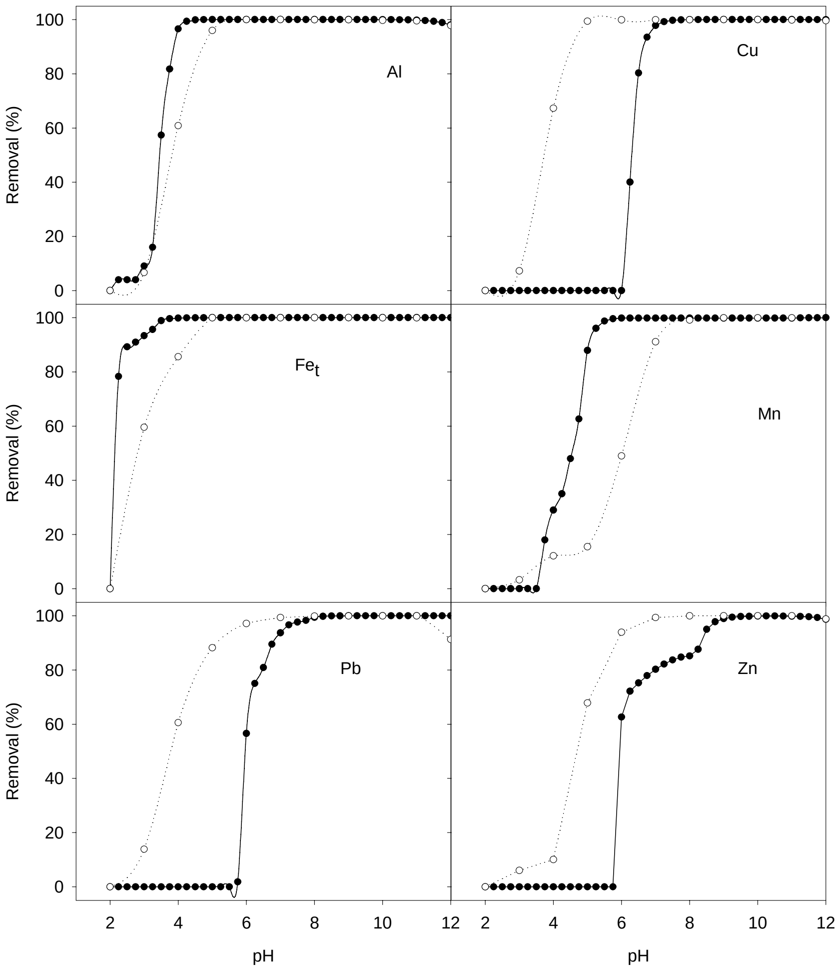

Figure 5.2 **Metal removal efficiency in the fly ash leachate (simple precipitation with NaOH) vs pH. Symbols: (●) *MINEQL+* predictions; (○) Experimental points**

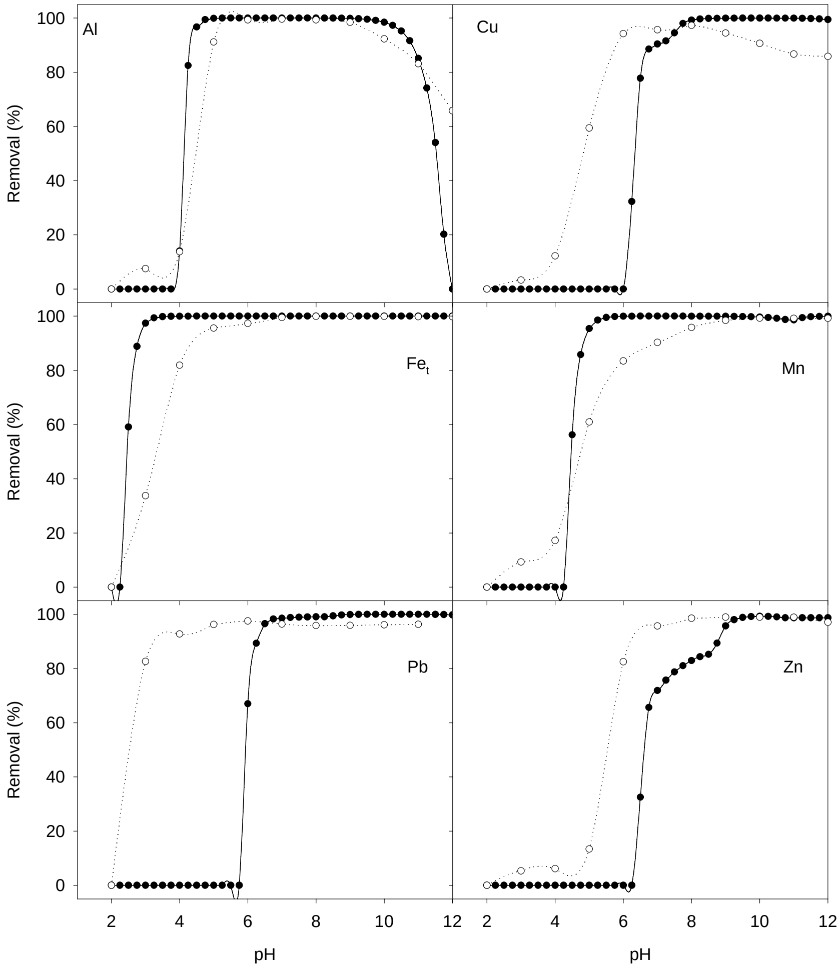

Figure 5.3 **Metal removal efficiency in the sewage sludge leachate (simple precipitation with NaOH) vs pH. Symbols: (●) *MINEQL+* predictions; (○) Experimental points**

Tableau 5.1 Composition (mg L^{-1}) and removal yields (%) of the soil leachates before and after precipitation treatment

Elements		Before precipitation		After precipitation treatment				
		(1)	(2)	NaOH$^{(1)}$	$Ca(OH)_2$$^{(1)}$	NaOH+$Na_2S$$^{(1)}$	NaOH+$Na_2CO_3$$^{(1)}$	NaOH+$Na_2HPO_4$$^{(2)}$
Al^{3+}	mg/L	23.3	19.3	3.79 ± 0.50	1.74 ± 0.10	0.62 ± 0.58	0.41 ± 0.21	0.35 ± 0.06
	%	-	-	*83.7*	*92.5*	*97.3*	*98.2*	*98.2*
Ba^{2+}	mg/L	1.28	1.28	1.28 ± 0.00	1.01 ± 0.03	0.93 ± 0.08	0.94 ± 0.07	0.06 ± 0.01
	%	-	-	*00.0*	*21.1*	*27.3*	*26.6*	*95.3*
Ca^{2+}	mg/L	253	273	276 ± 6	629 ± 33	243 ± 3	231 ± 18	169 ± 1
	%	-	-	-	-	*03.9*	*8.7*	*38.1*
Cd^{2+}	mg/L	0.08	0.01	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	%	-	-	*100*	*100*	*100*	*100*	*100*
Co^{2+}	mg/L	0.06	0.06	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
	%	-	-	*83.3*	*83.3*	*83.3*	*83.3*	*83.3*
Cr^{3+}	mg/L	0.25	0.13	0.03 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
	%	-	-	*88.0*	*96.0*	*96.0*	*96.0*	*100*
Cu^{2+}	mg/L	26.9	28.5	1.22 ± 0.65	0.06 ± 0.00	0.02 ± 0.01	0.33 ± 0.07	0.06 ± 0.01
	%	-	-	*95.5*	*99.8*	*99.9*	*98.8*	*99.8*
Fe_t	mg/L	39.7	32.2	0.92 ± 0.24	0.03 ± 0.01	0.27 ± 0.08	0.12 ± 0.08	0.20 ± 0.01
	%	-	-	*97.7*	*99.9*	*99.3*	*99.7*	*99.4*
Mg^{2+}	mg/L	32.4	24.0	10.0 ± 4.7	8.74 ± 4.40	18.4 ± 5.9	21.6 ± 0.7	21.3 ± 0.1
	%	-	-	*69.1*	*73.0*	*43.2*	*33.3*	*11.3*
Mn_t	mg/L	6.05	5.71	0.11 ± 0.01	0.02 ± 0.00	0.05 ± 0.01	3.22 ± 0.40	0.73 ± 0.04
	%	-	-	*98.2*	*99.7*	*99.2*	*46.8*	*87.2*
Ni^{2+}	mg/L	0.27	0.13	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.08 ± 0.01	0.09 ± 0.01
	%	-	-	*96.3*	*100*	*100*	*70.4*	*66.6*
Pb^{2+}	mg/L	696	719	12.8 ± 1.3	0.05 ± 0.03	0.19 ± 0.17	0.35 ± 0.13	0.08 ± 0.01
	%	-	-	*98.2*	*100*	*99.9*	*99.9*	*100*
Zn^{2+}	mg/L	4.25	4.19	0.13 ± 0.04	0.02 ±0.01	0.04 ± 0.04	0.23 ± 0.20	0.10 ± 0.02
	%	-	-	*96.9*	*99.5*	*99.1*	*94.6*	*97.6*
P	mg/L	3.37	1.28	0.16 ± 0.00	0.00 ± 0.00	0.13 ± 0.08	0.10 ± 0.05	15.3 ± 0.1
	%	-	-	*95.3*	*100*	*96.1*	*97.0*	-
S	mg/L	1.81	1.34	1.81 ± 0.00	1.28 ± 0.10	-	1.63 ± 0.20	0.98 ± 0.02
	%	-	-	*0.0*	*29.3*	-	*9.9*	*26.9*

(1) Refers to the 1st leachate.

(2) Refers to the 2nd leachate.

Tableau 5.2 ***MINEQL+* software predictions of the most abundant solid species and complexes (%) obtained by treatment of soil leachate**

Elements	NaOH (pH 10.0)	NaOH (pH 5.0)	$NaOH+Na_2S$ (pH 7.5)	$NaOH+Na_2CO_3$ (pH 7.5)	$NaOH+Na_2HPO_4$ (pH 8.0)
Al^{3+}	(89.1) $Al(OH)_3$, (10.9) $Al(OH)_4^-$	(100) $Al(OH)_3$	(100) $Al(OH)_3$	(100) $Al(OH)_3$	100 ($AlPO_4$)
Ca^{2+}	(99.9) Ca^{2+} (0.01) $CaOH^+$	(100) Ca^{2+}	(100) Ca^{2+}	(100) Ca^{2+}	(75.1) Ca^{2+}, (24.9) $Ca_4H(PO_4)_3.3H_2O$
Cu^{2+}	(100) $Cu(OH)_2$	(100) Cu^{2+}	(100) CuS	(100) $CuCO_3$	(100) $Cu_3(PO_4)_2$
Fe_t	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(100)$FePO_4$
Mg^{2+}	(70.7) Mg^{2+}, (2.8) $MgOH^+$, (26.5) $Mg(OH)_2$	(100) Mg^{2+}	(100) Mg^2	(99.0) Mg^{2+}, (1.0) $MgHCO_3^+$	(100) Mg^{2+}
Mn_t	(14.9) Mn^{2+}, (3.8) $MnOH^+$, (80.8) $Mn(OH)_2$	(100) Mn^{2+}	(78.4) MnS, (21.6) Mn^{2+}	(72.9) Mn^{2+}, (27.1) $MnCO_3$	(100) $MnHPO_4$
Pb^{2+}	(100) $Pb(OH)_2$	(100) Pb^{2+}	(100) PbS	(89.0) $PbCO_3$, (11.0) $Pb(OH)_2$	(79.5) $Pb_3(PO_4)_2$, (20.5) $Pb(OH)_2$
Zn^{2+}	(6.6) $Zn(OH)_3^-$, (7.5) $Zn(OH)_{2(aq)}$, (88.3) $Zn(OH)_2$	(100) Zn^{2+}	(100) ZnS	(17.0) Zn^{2+}, (1.7) $ZnOH^+$, (4.9) $ZnCO_{3(aq)}$, (75.5) $ZnCO_3.H_2O$	(86.1) $Zn_3(PO_4)_2.2H_2O$, (11.1) Zn^{2+}, (2.8) $ZnOH^+$

Tableau 5.3 Composition (mg L^{-1}) and removal yields (%) of the fly ash leachates before and after precipitation treatment

Elements		Before precipitation		After precipitation treatment			
		(1)	(2)	NaOH(1)	$Ca(OH)_2$(1)	$NaOH+Na_2S$(1)	$NaOH+Na_2CO_3$(2)
Al^{3+}	mg/L	2060	1710	8.56 ± 2.77	19.5 ± 1.7	0.68 ± 0.05	0.33 ± 0.01
	%	-	-	*99.6*	*99.1*	*100*	*100*
Ba^{2+}	mg/L	3.95	2.88	0.52 ± 0.02	0.35 ± 0.03	0.21 ± 0.01	0.20 ± 0.01
	%	-	-				
Ca^{2+}	mg/L	11000	11100	9650 ± 10	-	9590 ± 40	9750 ± 60
	%	-	-	*12.3*	-	*12.8*	*12.2*
Cd^{2+}	mg/L	22.9	27.7	0.14 ± 0.08	0.00 ± 0.00	0.00 ± 0.00	19.4 ± 0.5
	%	-	-	*99.4*	*100*	*100*	*30.0*
Co^{2+}	mg/L	1.38	1.38	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.26 ± 0.06
	%	-	-	*100*	*100*	*99.3*	*81.2*
Cr^{3+}	mg/L	7.16	8.52	0.04 ± 0.02	0.01 ± 0.00	0.01 ± 0.01	0.03 ± 0.02
	%	-	-	*99.4*	*99.9*	*99.9*	*99.6*
Cu^{2+}	mg/L	41.6	63.8	2.43 ± 1.88	0.03 ± 0.01	0.03 ± 0.01	0.75 ± 0.09
	%	-	-	*94.2*	*99.9*	*99.9*	*98.8*
Fe_t	mg/L	321	243	0.82 ± 0.42	0.19 ± 0.06	0.05 ± 0.02	0.00 ± 0.00
	%	-	-	*99.7*	*99.9*	*100*	*100*
Mg^{2+}	mg/L	766	850	4.31 ± 1.85	1.60 ± 0.39	633 ± 11	743 ± 13
	%	-	-	*99.4*	*99.8*	*17.4*	*12.6*
Mn_t	mg/L	42.6	48.2	0.03 ± 0.02	0.02 ± 0.00	0.51 ± 0.04	15.1 ± 0.5
	%	-	-	*99.9*	*100*	*82.5*	*68.6*
Ni^{2+}	mg/L	6.34	8.83	0.01 ± 0.01	0.00 ± 0.00	0.03 ± 0.02	0.64 ± 0.14
	%	-	-	*99.8*	*100*	*99.5*	*92.8*
Pb^{2+}	mg/L	147	159	0.29 ± 0.21	0.04 ± 0.03	0.24 ± 0.04	0.42 ± 0.34
	%	-	-	*99.8*	*100*	*99.8*	*99.7*
Zn^{2+}	mg/L	928	1030	0.16 ± 0.17	0.02 ± 0.00	0.08 ± 0.06	22.5 ± 0.7
	%	-	-	*100*	*100*	*100*	*97.8*
P	mg/L	587	578	0.46 ± 0.01	0.13 ± 0.08	0.12 ± 0.11	0.10 ± 0.07
	%	-	-	*99.9*	*100*	*100*	*100*
S	mg/L	419	419	137 ± 17	30.8 ± 2.1	328 ± 1	319 ± 6
	%	-	-	*67.3*	*92.6*	-	*23.9*

(1) Refers to the 1st leachate.

(2) Refers to the 2nd leachate.

Tableau 5.4 *MINEQL+* software predictions of the most abundant solid species and complexes (%) obtained by treatment of fly ash leachate

Elements	NaOH (pH 10.0)	NaOH (pH 5.0)	NaOH+Na_2S (pH 7.5)	NaOH+Na_2CO_3 (pH 7.5)
Al^{3+}	(99.9) $Al(OH)_3$, (0.1) $Al(OH)_4^-$	(85.6) $Al(OH)_3$, (14.4) $AlPO_4$	(100) $Al(OH)_3$	
Ca^{2+}	(86.3) Ca^{2+}, (6.8) $Ca_4H(PO_4)_3.3H_2O$, (2.6) $CaSO_4.2H_2O$, (2.0) $CaSO_4$(aq)	(100) Ca^{2+}	(88.4) Ca^{2+}, (6.5) $Ca_4H(PO_4)_3.3H_2O$, (1.0) $CaSO_4.2H_2O$, (2.0) $CaSO_4$(aq)	(88.4) Ca^{2+}, (6.5) $Ca_4H(PO_4)_3.3H_2O$, (1.0) $CaSO_4.2H_2O$, (2.0) $CaSO_4$(aq)
Cu^{2+}	(100) $Cu(OH)_2$	(74.3) Cu^{2+}, (22.4) $CuCl^+$, (1.5) $CuCl_2$(aq), (1.5) $CuSO_4$(aq)	(100) CuS	(100) $CuCO_3$
Fe_t	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$
Mg^{2+}	(98.0) $Mg(OH)_2$, (2.0) Mg^{2+}	(98.3) Mg^{2+}, (1.7) $MgSO_4$(aq)	(98.3) Mg^{2+}, (1.7) $MgSO_4$(aq)	(98.3) Mg^{2+}, (1.7) $MgSO_4$(aq)
Mn_t	(98.2) $Mn(OH)_2$, (1.8) Mn^{2+}	(92.8) $MnHPO_4$, (5.4) Mn^{2+}, (1.3) $MnCl^+$	(90.4) $MnHPO_4$, (9.6) MnS	(88.9) $MnHPO_4$, (11.1) $MnCO_3$
Pb^{2+}	(100) $Pb(OH)_2$	(96.7) $Pb_3(PO_4)_2$, (1.3) $PbCl_2$(aq), (1.5) $PbCl^+$	(100) PbS	(100) $Pb_3(PO4)_2$
Zn^{2+}	(100) $Zn(OH)_2$	(60.3) $Zn_3(PO_4)_2.4H_2O$, (23.5) Zn^{2+}, (11.6) $ZnCl^+$, (3.6) $ZnCl_2$(aq)	(62.7) $Zn_3(PO_4)_2.4H_2O$, (37.3) ZnS	(85.5) $Zn_3(PO_4)_2.4H_2O$, (11.2) $ZnCO_3.1H_2O$, (3.3) Zn^{2+}

Tableau 5.5 Composition (mg L^{-1}) and removal yields (%) of the sewage sludge leachates before and after precipitation treatment

Elements		Before precipitation		After precipitation treatment				
		(1)	(2)	NaOH$^{(1)}$	$Ca(OH)_2$$^{(1)}$	$NaOH+Na_2S$$^{(1)}$	$NaOH+Na_2CO_3$$^{(2)}$	$NaOH+Na_2HPO_4$$^{(2)}$
Al^{3+}	mg/L	46.3	47.9	4.77 ± 1.44	5.20 ±0.47	0.47 ± 0.01	0.20 ± 0.04	0.13 ± 0.03
	%	-	-	*89.7*	*88.8*	*99.0*	*99.6*	*99.7*
Ba^{2+}	mg/L	0.82	0.71	0.16 ± 0.01	0.34 ± 0.05	0.07 ± 0.00	0.08 ± 0.01	0.02 ± 0.01
	%	-	-	*80.5*	*58.5*	*91.5*	*90.2*	*97.2*
Ca^{2+}	mg/L	439	406	242 ± 39	-	236 ± 4	246 ± 14	64.1 ± 2.1
	%	-	-	*44.9*	-	*46.2*	*39.4*	*84.2*
Cd^{2+}	mg/L	0.56	0.53	0.00 ± 0.00	0.00 ± 0.00	0.05 ± 0.01	0.01 ± 0.00	0.04 ± 0.03
	%	-	-	*100*	*100*	*91.1*	*98.1*	*92.5*
Co^{2+}	mg/L	0.27	0.23	0.03 ± 0.00	0.02 ± 0.00	0.04 ± 0.01	0.03 ± 0.01	0.06 ± 0.02
	%	-	-	*88.9*	*92.6*	*85.2*	*87.0*	*73.9*
Cr^{3+}	mg/L	0.58	0.55	0.01 ± 0.01	0.01 ±0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	%	-	-	*98.3*	*98.3*	*100*	*100*	*100*
Cu^{2+}	mg/L	4.41	4.85	0.52 ± 0.09	0.48 ± 0.03	0.19 ± 0.02	0.34 ± 0.06	0.47 ± 0.04
	%	-	-	*88.2*	*89.1*	*95.7*	*93.0*	*90.3*
Fe_t	mg/L	867	783	2.50 ± 0.24	2.72 ± 0.12	0.88 ± 0.10	1.00 ± 0.06	0.53 ± 0.08
	%	-	-	*99.7*	*99.7*	*99.9*	*99.9*	*99.9*
Mg^{2+}	mg/L	36.1	35.2	9.44 ± 1.11	15.7 ± 3.4	34.1 ± 0.5	32.9 ± 0.8	31.7 ± 0.5
	%	-	-	*73.9*	*56.5*	*05.5*	*06.5*	*09.9*
Mn_t	mg/L	8.21	7.78	0.12 ± 0.03	0.12 ±0.02	0.39 ± 0.04	1.26 ± 0.35	0.13 ± 0.03
	%	-	-	*98.5*	*98.5*	*95.2*	*83.8*	*98.3*
Ni^{2+}	mg/L	0.79	0.69	0.11 ± 0.01	0.12 ± 0.01	0.04 ± 0.01	0.12 ± 0.03	0.10 ± 0.01
	%	-	-	*86.1*	*84.8*	*94.9*	*82.6*	*85.5*
Pb^{2+}	mg/L	2.15	1.62	0.22 ± 0.01	0.20 ± 0.01	0.02 ± 0.02	0.00 ± 0.00	0.01 ± 0.01
	%	-	-	*89.8*	*90.7*	*99.1*	*100*	*99.4*
Zn^{2+}	mg/L	5.62	5.14	0.37 ± 0.02	0.32 ± 0.01	0.03 ± 0.01	0.07 ± 0.03	0.05 ± 0.01
	%	-	-	*93.4*	*94.3*	*99.5*	*98.6*	*99.0*
P	mg/L	80.8	80.3	4.08 ± 0.04	3.84 ± 0.07	2.64 ± 0.08	0.55 ± 0.01	26.4 ± 2.8
	%	-	-	*95.0*	*95.2*	*96.7*	*99.3*	-
S	mg/L	780	704	677 ± 18	681 ± 20	687 ± 4	679 ± 17	664 ± 25
	%	-	-	*13.2*	*12.7*	-	*03.5*	*05.7*

(1) Refers to the 1st leachate.

(2) Refers to the 2nd leachate.

Tableau 5.6 MINEQL + software prediction of the most abundant solid species and complexes (%) obtained by treatment of sewage sludge leachate

Elements	NaOH (pH 10.0)	NaOH (pH 5.0)	NaOH+Na_2S (pH 7.5)	NaOH+Na_2CO_3 (pH 7.5)	NaOH+Na_2HPO_4 (pH 8.0)
Al^{3+}	(98.3) $Al(OH)_3$, (1.5) $Al(OH)_4^-$	(100) $AlPO_4$	(100) $Al(OH)_3$	(100) $Al(OH)_3$	(79.2) $AlPO_4$, (20.8) $Al(OH)_3$
Ca^{2+}	(15.4) Ca^{2+}, (52.5) $CaSO_{4(aq)}$, (31.9) $Ca_4H(PO_4)_3.3H_2O$	(20) Ca^{2+}, (55.4) $CaSO_{4(aq)}$, (24.6) $CaSO_4.2H_2O$	(30.4) $Ca_4H(PO_4)_3.3H_2O$, (52.2) $CaSO_{4(aq)}$, (17.4) Ca^{2+}	(30.4) $Ca_4H(PO_4)_3.3H_2O$, (52.2) $CaSO_{4(aq)}$, (17.4) Ca^{2+}	(83.7) $Ca_4H(PO_4)_3.3H_2O$, (16.3) $CaSO_{4(aq)}$
Cu^{2+}	(100) $Cu(OH)_2$	(25.8) Cu^{2+}, (74.2) $CuSO_{4(aq)}$	(100) CuS	(100) $CuCO_3$	(100) $Cu_3(PO4)_2$
Fe_t	(100) $Fe(OH)_3$	(94.9) $Fe(OH)_3$, (5.1) $FePO_4$	(100) $Fe(OH)_3$	(100) $Fe(OH)_3$	(42.7) $Fe(OH)_3$, (57.5) $FePO_4$
Mg^{2+}	(58.8) $Mg(OH)_2$, (29.6) $MgSO_{4(aq)}$, (10.5) Mg^{2+}	(68.8) $MgSO_{4(aq)}$, (31.2) Mg^{2+}	(68.9) $MgSO_{4(aq)}$, (31.1) Mg^{2+}	(68.9) $MgSO_{4(aq)}$, (31.1) Mg^{2+}	(18.2) Mg^{2+}, (17.8) $MgHPO_{4(aq)}$, (64.0) $MgSO_{4(aq)}$
Mn_t	(100) $MnHPO_4$	(95.4) $MnHPO_4$, (3.1) $MnSO_{4(aq)}$, (1.4) Mn^{2+}	(100) $MnHPO_4$	(100) $MnHPO_4$	(100) $MnHPO_4$
Pb^{2+}	(100) $Pb(OH)_2$	(87.5) $PbSO_{4(aq)}$, (9.4) Pb^{2+}, (4.1) $Pb(SO_4)_2^{-2}$	(100) PbS	(100) $Pb_3(PO_4)_2$	(100) $Pb_3(PO_4)_2$
Zn^{2+}	(99.1) $Zn(OH)_2$	(24.2) Zn^{2+}, (68.4) $ZnSO_{4(aq)}$, (7.4) $Zn(SO_4)_2^{-2}$	(100) ZnS	(79) $Zn_3(PO_4)_2.4H_2O$, (21) $ZnCO_3.H_2O$	(100) $Zn_3(PO_4)_2.4H_2O$

Tableau 5.7 Dewatering characteristics of the sludge produced during treatment of the leachates

Leachates	Reagents	Settling	Filtration				Centrifugation
		SVI ($mL\ g^{-1}$)	TS ($\%w\ w^{-1}$)	SP ($kg\ m^{-3}$)	FC ($kg\ m^{-2}\ h^{-1}$)	SRF ($m\ kg^{-1} \times 10^{12}$)	TS ($\%w\ w^{-1}$)
Soil	NaOH	117 ± 0	18.8 ± 1.0	6.7 ± 0.2	1.6 ± 0.1	19.7 ± 1.3	8.0 ± 0.4
	$Ca(OH)_2$	098 ± 0	25.2 ± 1.4	3.9 ± 0.2	1.1 ± 0.2	14.2 ± 2.5	7.7 ± 0.3
	NaOH + Na_2S	072 ± 7	18.4 ± 1.1	5.30 ± 0.1	2.9 ± 0.2	4.3 ± 0.3	8.1 ± 0.4
	NaOH + Na_2CO_3	113 ± 4	72.7 ± 3.3	1.8 ± 0.1	0.6 ± 0.0	26.5 ± 4.0	7.6 ± 0.7
	NaOH + Na_2HPO_4	132 ± 0	36.7 ± 0.8	3.3 ± 0.2	2.2 ± 0.2	6.4 ± 2.0	6.8 ± 0.3
Fly ash	NaOH	39 ± 0	16.3 ± 3.2	56.4 ± 2.2	1.9 ± 0.3	6.2 ± 0.3	10.0 ± 0.0
	$Ca(OH)_2$	50 ± 0	16.4 ± 1.2	46.3 ± 5.4	2.5 ± 0.3	5.0 ± 0.8	9.7 ± 0.3
	NaOH + Na_2S	46 ± 0	16.0 ± 0.1	58.6 ± 0.6	1.6 ± 0.2	7.3 ± 0.2	10.4 ± 0.5
	NaOH + Na_2CO_3	48 ± 0	17.3 ± 0.1	61.3 ± 1.5	2.0 ± 0.6	5.3 ± 0.2	11.3 ± 1.1
Sewage sludge	NaOH	221 ± 3	15.1 ± 0.5	8.0 ± 0.0	0.6 ± 0.0	23.5 ± 0.4	5.1 ± 0.1
	$Ca(OH)_2$	177 ± 2	16.1 ± 1.4	7.9 ± 0.1	0.7 ± 0.0	19.8 ± 0.5	6.0 ± 0.1
	NaOH + Na_2S	391 ± 2	14.3 ± 0.3	6.5 ± 0.1	0.4 ± 0.2	31.7 ± 1.2	7.1 ± 1.8
	NaOH + Na_2CO_3	277 ± 2	10.6 ± 0.5	7.2 ± 0.0	0.4 ± 0.1	23.9 ± 0.2	5.1 ± 0.7
	Na_2HPO_4 + NaOH	180 ± 2	20.4 ± 2.1	7.6 ± 0.1	1.5 ± 0.2	07.6 ± 0.2	7.7 ± 0.1

CHAPITRE VI

DEVELOPMENT OF A NEW CHEMICAL AND TECHNO-ECONOMIC MODEL FOR THE TREATMENT OF METAL-POLLUTED EFFLUENTS BY PRECIPITATION TECHNIQUES

Le Chapitre 6 est constitué de l'article suivant :

Zied Djedidi, Médard Bouda, Ridha Ben Cheikh, Jean François Blais, Guy Mercier et Rajeshwar Dayal Tyagi (2009) Development of a new chemical equilibrium and techno-economic model for the treatment of metal-polluted effluents by precipitation. *Hydrometallurgy*. (soumis le 23 juin 2009).

Résumé

Un nouveau progiciel informatique portant l'acronyme *PITEM* (Programme Informatisé de Traitement des Effluents Métalliques) a été développé pour la prédiction du traitement des effluents métalliques par les techniques de précipitation. *PITEM* intègre un modèle de spéciation chimique permettant de calculer les concentrations résiduelles en métaux, un modèle mathématique pour la prédiction des caractéristiques de déhydratation et de production de boues et un module économique pour l'évaluation du coût total de traitement et ce, par les techniques de précipitation étudiées. *PITEM* est écrit en langage Visual Basic sous la plate-forme de *Microsoft EXCEL* et il est conçu comme un progiciel facile à utiliser à des fins industrielles et/ou académiques. Des essais de précipitation ont été réalisés avec des solutions multimétalliques et avec un lixiviat de sol dans le but de comparer la production de boue humide expérimentale à celle prédite par le programme après une séparation solide-liquide (S/L) par l'intermédiaire d'une filtration sous pression. Les résultats de simulation montrent que les valeurs de ST sont en accord avec celles calculées expérimentalement, excepté dans le cas de la précipitation du lixiviat de sol par les sulfures à pH 7.5, où la valeur de ST prédite [23.1% (p/p)] est légèrement supérieure à la valeur expérimentale [18.4% (p/p)]. Cette divergence est attribuable à la formation de colloïdes de soufre. Le coût unitaire de traitement estimé par le programme pour les quatre scénarios de traitement par précipitation, suit l'ordre ascendant suivant : carbonates (Na_2CO_3) < sulfures (Na_2S) < phosphates (Na_3PO_4) < hydroxydes (NaOH). La neutralisation par les carbonates est la plus économique, en raison des bonnes caractéristiques de déshydratation des boues générées.

Development of a new chemical equilibrium and techno-economic model for the treatment of metal-polluted effluents by precipitation techniques

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6. DEVELOPMENT OF A NEW CHEMICAL AND TECHNO-ECONOMIC MODEL FOR THE TREATMENT OF METAL-POLLUTED EFFLUENTS BY PRECIPITATION TECHNIQUES

6.1 Abstract

A new computer program (*PITEM*) for the prediction of metal-finishing effluent treatment by precipitation techniques has been developed. *PITEM* integrates a mathematical model for the prediction of the sludge dewaterability and the volume of metallic sludge produced, and an economic module for the evaluation of the treatment costs of metal-rich effluent by precipitation techniques. It integrates also a chemical equilibrium model to predict the nature of the potential solid phase expected. *PITEM* is written with Visual Basic Language under the *Microsoft EXCEL* platform and is designed as easy-to-use software for industrial and/or academic purposes. Nevertheless, *PITEM* database must be updated as in the context of future research to give it more accurate output data and a wider field use. Precipitation assays have been conducted in laboratory with multi-metallic solutions and polluted-soil leachate in order to compare wet sludge production with those predicted by the program after a mechanical S/L separation by a pressure filtration. Simulation results show that predicted total solids (TS) are in agreement with those calculated experimentally, except in the case of soil leachate precipitation with sulfide at pH 7.5 where TS predicted (23.1% w/w) is slightly higher (less water content) than the experimental value (18.4%) due to the formation of colloidal sulfur. Unitary treatment costs ($\$/m^3$) estimated by the program for the four scenarios of soil leachate treatment by precipitation follow the ascending order: carbonates (Na_2CO_3) < sulfides (Na_2S) < phosphates (Na_3PO_4) < hydroxides (NaOH). Limestone (carbonate) neutralization is the most cost-effective soil leachate treatment due to the good dewatering characteristics of the generated sludge (TS = 72.7%).

6.2 Keywords

Metal; Precipitation; Sludge; Chemical equilibrium software; Hydroxide; Sulfide; Phosphate; Carbonate.

6.3 Nomenclature

A	filter area (m^2)
C_i	initial concentration of metal “i”
C_s	solid concentration in the suspension (kg/m^3)
EST	equilibria speciation tool
f	number of filtration cycles
GA	genetic algorithm
M_i	molecular weight of metal “i” precipitate
PES	process engineering system
PITEM	programme informatisé de traitement des effluents métalliques
Pr_i	proportion of metal precipitate “i” in the mixture
PSp	predicted Sludge production (kg/m^3)
S/L	solid-liquid
SP	sludge production (kg/m^3)
T_c	cycle time (sec)
TS	total solids (% w/w)
TSp	predicted mixture total solids (% w/w)
TTC	total treatment cost
V	filtrate volume (m^3)
XRD	X-ray diffraction
y_i	theoretical yield of precipitation reaction of metal “i”
α	specific resistance of the cake (m/kg)
μ	viscosity of the filtrate (Pa.s)

6.4 Introduction

It is essential to remove or reduce the presence of inorganic contaminants in order to diminish the possibility of uptake by plants, animals and humans and their accumulation in the food chain and also to prevent them from contaminating surface and groundwater by dissolution or dispersion (McLaughlin *et al.* 2000; Kabata-Pendias, 2001). A lot of researches have been accomplished in last decades to develop efficient and economic process to remove heavy metals from polluted effluents (Blais *et al.*1999; Kurniawan *et al.* 2006).

Among these technologies, precipitation still the most commonly used process for the removal of metals from industrial effluents because it offers a most cost-effective solution applicable to large operating units (Patterson, 1988; Baltpurvins *et al.* 1996a; Mishra, 1999; Blais *et al.* 2008). Soluble metals can be precipitated as hydroxides by using different alkaline reagents, like CaO, $Ca(OH)_2$, $Mg(OH)_2$, NaOH and NH_4OH (Mirbagheri and Hosseini, 2004; Djedidi *et al.* 2009a,b). Some other precipitating agents can be used to reach lower residual soluble metal concentrations (Islamoglu *et al.* 2006) and/or to produce metallic sludge having better thickening and dewatering properties (Kim *et al.* 2002; Viadero *et al.* 2006). These others precipitation techniques notably include the formation of insoluble metal phosphates (Mavropoulos *et al.* 2002; Pigaga *et al.* 2002), metal sulfides (Veeken and Rulkens, 2003; Al-Tarazi *et al.* 2004) and metal carbonates (McAnally *et al.* 1984; Guillard and Lewis, 2002).

In some cases, the handling costs of generated sludge are an important part of the total wastewater costs, and its disposal is a relevant environmental concern (Metcalf and Eddy, 1991; USEPA, 1996). In metal precipitation techniques, sludge dewatering is an important process. It reduces the volume of sludge and, consequently, the costs for transporting the sludge to its ultimate disposal site. Moreover, dewatered sludge is generally much easier to handle and transport. Drying bed, belt filter press, plate and frame filter press, vacuum filter, and centrifuge are some common sludge dewatering methods. The efficiency of mechanical dewatering depends mainly on the dewaterability of the sludge. The floc size and density are found to be the major factors affecting dewaterability. Sludge with higher floc density and larger floc size is generally much easier to dewater (Mitchell and Schweers, 1989; Nguyen *et al.* 2008).

Computer simulation tools (*HYDRAQL, MINEQL+, MINTEQA2, PHREEQC*) incorporating extensive databases have also been developed to simulate aqueous-based chemical systems involving a variety of species over a broad range of temperature, pH and composition (Westall *et al.* 1976; Parkhurst *et al.* 1980; Papelis *et al.* 1988; Allison *et al.* 1991). Many computer-assisted thermodynamic chemical equilibrium models have been written over the years but many of these are designed for a narrow purpose (Mattigod *et al.* 1995). A good knowledge of dewatering characteristics of the metal precipitates produced is also necessary to evaluate the techno-economic performance of different metal precipitation methods (Djedidi *et al.* 2009a,b).

Decision-making, regarding to the implementation of metal-contaminated effluent treatment projects, requires detailed knowledge of techno-economic feasibility of metal removal and metallic sludge management. Before reaching a final decision on the treatment of effluents by precipitation process, techno-economic pre-feasibility and feasibility should be made. It is important to note, that PES often integrate many disciplines and solutions approaches within a certain process optimization project and contribute significantly to the feasibility and economics of the plant design (Klatt and Marquardt, 2009).

Thus, the aim of the present work is to develop a PES for the prediction of metal-rich effluent treatment by precipitation techniques. This computer tool integrates a mathematical model that provides a new validated, and generalizable predictor for the sludge volume generated, an economic module for the evaluation of the total cost of effluent treatment and disposal, and also a chemical equilibrium model to predict the solid phase to be precipitate. Laboratory precipitation assays were also conducted to verify the validity of the software predictions.

6.5 Description of the program

6.5.1 Structure in *Microsoft EXCEL* software

PITEM is a computerized model written with Visual Basic Language under *Microsoft EXCEL*. This program includes two main modules; a thermodynamic chemical equilibrium model couples with a techno-economic module. *PITEM* provides the most cost-effective solution among precipitation techniques for the treatment of metal-rich effluents. Fig. 6.1 shows the basic steps of *PITEM* operating organigram.

The model user must supply chemical and economic data specific to the studied case (input data). In total, the model includes 22 dialog boxes for the input of operating conditions. Fig. 6.2 shows a flowsheet of the dialog boxes interfaces used in *PITEM*, whereas Fig. 6.3 shows two examples of interfaces. In practice, opening up some dialog boxes is associated with the choice of treatment mode, so that several dialog boxes are not opened during this same simulation. This program is available on the INRS web site under the following link: http://www.inrs-ete.uquebec.ca/index.php?page=5_3.

6.5.2 Chemical equilibrium module

To simulate chemical equilibrium systems, *PITEM* uses thermodynamic data extracted from *MINEQL+* database coupled with the computer code of EST developed by Del Piero *et al.* (2006). The EST approach is based on classical stoichiometric mass balance equations. First, thermodynamic activities and mass-action equations are described for aqueous species. Then, a set of functions are defined that must be solved simultaneously to determine equilibrium for a given set of conditions. Many of these functions are derived from mole-balance equations for element valence state or from mass-action equations for pure phases and solid solutions.

Additional functions are derived for alkalinity, activity water, and aqueous charge balance. Each function is reduced to contain a minimum of number of variables, such that the number of functions equals the number of variables. To solve the resulting nonlinear system of equation EST use Newton-Raphson method. This method ensures a rapid quadratic convergence but requires initial estimates close enough to the true solution and can also diverge in particular chemical systems. To circumvent this problem more robust numerical methods like GA is used in EST, which, on the other hand, presents the disadvantage to be slower. It should be noted that GA are a group of mathematical techniques which were initially designed to simulate the behaviour of biologically based adaptive systems. Despite GA were not initially developed as an optimisation technique in itself, it can be modified to produce a powerful optimiser based on parallel search technique (Del Piero *et al.* 2006).

PITEM computes interactions between 19 metallic ions abundant in industrial inorganic effluents. Thermodynamic database is extensive and adequate for solving a broad range of problems without need for additional user-supplied constants. However, the standard database can easily be modified if it is found to be incomplete or inadequate for a specific problem.

It is noticed that the ionic strength “I” has not been considered by the software to correct ionic equilibrium concentrations. Indeed, calculations using this parameter showed that its use doesn’t have quite any influence on the final results, essentially on an industrial scale.

6.5.3 Techno-economic module

6.5.3.1 Economic considerations

The innovation introduced for *PITEM*, is that it takes into account the economic aspect in the treatment project by precipitation techniques. Effluent treatment cost is estimated according to a simplified plant design of industrial process for metal-effluent decontamination and is given by Figure 6.4. Metal rich-effluent and chemical reagents (from chemical reagent tank) are routed to the neutralization tank through influent and dosing pumps, respectively. Once the precipitation operation is completed, effluent is pumped (effluent pump 1) to the settler. To complete dewatering operation, the obtained low-solids slurries are sent (effluent pump 2) to a pressure filtration (filter press). Sludge cake (high-solids) is deposited in storage vessel before waste handling and disposal operations. Finally, effluent generated after dewatering operations (settling and filtration) can be discharged to the sewer.

It should be noted that equipment cost is an important element in process economics (Ulrich, 1984). Equipment costs for sludge dewatering, storage tanks, pumps, etc., were derived from www.matche.com. Equipment cost data were updated (June 2009) using the Marshall & Swift Equipment cost index for the fourth quarter of 2008 published periodically in Chemical Engineering (Chemical Engineering, 2009).

Labor, equipment, contractor hauling, chemical treatment, and off-site metallic sludge landfill disposal have been combined within the *PITEM* program to provide an accurate economic forecast of the studied wastewater treatment operations. Economic *PITEM* module was designed based on the calculation techniques used in chemical engineering (Ulrich, 1984). The TTC expressed in terms of US$/unit volume of effluent (m^3) or in terms of US$/year, represents one of the several output data provided by the model. TTC is calculated by summation of the direct, indirect, general and the capital costs.

6.5.3.1 Sludge production

Wet SP (after S/L separation process), is one of the most important parameters in the cost prediction for the treatment of metal-contaminated effluent. In fact, the sludge handling and disposal are the most significant challenges in wastewater management (Fytili and Zabaniotou, 2008). For the same effluent, SP differs from one precipitant agent to another due to differences between their dewatering characteristics (Djedidi *et al.* 2009a,b). For this reason, *PITEM* must provide a good estimate for the final total solids of the metallic sludge (w/w) and, subsequently, the metallic sludge production per unit of treated effluent (kg/m^3), and this after a mechanical dewatering through a pressure filtration. To achieve this step, several laboratory precipitation tests were conducted for synthetic and real metallic solutions (Djedidi *et al.* 2009a,b).

Sludge dewatering characteristics are inserted in *PITEM* program database. It should be noted that database model must be updated as in the context of future research to give *PITEM* more accurate output data and a wider field use.

6.5.3.3 Other examples of PITEM output data

In addition of its easy-use, *PITEM* provides to user a suitable forecast to better analyze simulations results. In fact, besides SP and TTC, output data could be presented as a curve (Fig. 6.4) (metal speciation over the desired pH range), or as a summary sheet including specific characteristics to each studied metal (Fig. 6.5).

6.6 Material and methods

6.6.1 *MINEQL+* and *PITEM* simulations

To check the validity of *PITEM* in chemical equilibrium calculation, simulations were carried out to predict in term of residual metal concentration, the efficiency of the treatment of a soil leachate by hydroxide, phosphate, carbonate, and sulfide precipitations. *MINEQL+* software (version 4.5) was chosen as a reference tool. This program may be used to compute equilibrium among dissolved, solid and adsorbed phases suitable for aqueous solutions based on the appropriate thermodynamic stability constants. In the present study, models were constrained to include only those solid phases that were found to govern solubility (example: oxides are not considered due to kinetic considerations). Ionic strength was considered "off" within the program. All calculations were performed at a constant temperature of 298K with the number of iteration cycles constrained to 100. *PITEM* and *MINEQL+* simulations were carried out for soil leachate contaminated with Al^{3+} (8.64×10^{-4} mol/L), Cu^{2+} (4.23×10^{-4} mol/L), Fe^{3+} (7.10×10^{-4} mol/L), Pb^{2+} (3.36×10^{-3} mol/L), and Zn^{2+} (6.58×10^{-5} mol/L), at pHs 10.0, 7.5, 7.5 and 8.0 for metal hydroxide, sulfide, carbonate, and phosphate precipitations, respectively. The counter ion is chloride (Cl^{-1}), for all systems.

6.6.2 Composition and preparation of the effluents

6.6.2.1. Soil leachate

Soil used in this work comes from the Pointe-aux-Lièvres site (Québec, QC, Canada) and it contained 73% (w/w) of sand, 21% (w/w) of silt and 6% (w/w) of clay. Some physical pre-treatments (Grizzly, Tyler Sweco sieves, Reichert spiral and hydrocyclone) have been applied to this soil to obtain granulometric fractions having different levels of metal contamination. The more metal-contaminated fraction (with particle size inferior to 20 μm and having 45% w/w of water content) has been used for this work. The Pb and Zn concentrations in the soil fraction used in this research were above the criteria C (commercial and industrial use) set by the Ministry of Environment and Fauna of Quebec (MDDEPQ, 1999), which are respectively 1000 and 1500 mg/kg.

Batch reactor leaching tests were performed in order to produce an amount of soil leachate needed for precipitation treatment. Experiments were conducted in a 10.0 L acrylic tank reactor containing 1000 g (dry weight) of soil in which, a volume of tap water was added to reach a pulp density of 10% (w/w). The suspension was then acidified to a pH 2.0 ± 0.2 with HCl (12 mol/L).

Mixing was achieved by a variable speed mixer (Caframo RZR50 rotor) operated at 300 rpm and using a three blade axial impeller (Stainless steel SS-316L) with a 7.62 cm diameter. After 6 h of leaching, the mixture was centrifuged at 3000 × *g* (3625 rpm) for 10 min using a Beckman Coulter Allegra^{TM} 6 centrifuge, in order to separate solids and liquid. Supernatant was then filtered using Whatman no. 4 membrane under a vacuum.

6.6.2.2 Multi-metallic synthetic solutions

Multi-metallic synthetic solutions having a concentration $[M^{n+}]$ of 4.00×10^{-3} mol/L for each metal were prepared starting from metal sulfate or chloride salts : Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} (Lab Mat), Al^{3+} (Baker). Distilled water was used for all the experiments.

Two multi-metallic solutions were prepared:

Sln A: contains Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in chloride matrix;

Sln B: contains Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} in sulfate matrix.

6.6.3 Precipitation assays

Precipitation tests were realized at ambient temperature ($22 \pm 2^{o}C$). For each working pH, a reaction time of 20 min was allowed for the system to reach equilibrium (Hove *et al.* 2008). Hydroxide precipitation tests were done by adjusting pH solutions to 10.0 with the sodium hydroxide solution. During the other precipitation tests, precipitating agents were firstly added to solutions. A pH adjustment was done subsequently by adding sodium hydroxide to 7.0 for phosphate and 8.0 for sulfide system in the case of synthetic solutions. A pH adjustment to 8.0 for the phosphate and 7.5 for the sulfide and carbonate systems was also made in the case of soil leachate. All precipitation essays were done in triplicate.

6.6.4 Sludge filtration

Whatman No. 2 (8.0 µm pore size) membranes having an effective area of 12.50 cm^2 were used during the pressure filtration tests. A pressure of 31.7 kPa was applied on 200 mL volumes of the settled sludge samples inside a Fisherbrand stainless-steel pressure vessel (model 09-753-25A, Fisher Scientific Ltd.). Filtration was stopped when no additional water flowed out of the sludge. Weights of the dewatered sludge have been measured to evaluate the sludge production in term of kg of sludge per cubic meter of treated effluent.

To extrapolate the laboratory conditions to the industrial full-scale ones, the following relationship between the filter pressure and area has been used (Leclerc, 1997):

Équation 6.1 $$\mathbf{V/A \times t_c = [2\,(-\Delta P) \times \boldsymbol{f} / \mu \times \alpha \times C_s \times t_c]^{1/2}}$$

Where “V” is the filtrate volume (m^3), “A” the filter area (m^2), “μ” the viscosity (Pa.s), “α” the specific resistance of the cake (m/kg), “C_s” the solid concentration in the suspension (kg/m^3), “f” the number of filtration cycles, and “T_c” the cycle time (sec).

The application of this formula to our laboratory conditions ($A = 12.5\ cm^2$, $P = 31.7$ kPa) gives for instance for an industrial full-scale case using a 4.0 m^2 filter press and a 2.5 m^3 sludge volume, a required pressure of 5×10^2 kPa (5.0 bars). This value corresponds well to pressure ranges used in the industrial full-scale filter-press.

6.6.5 Analytical methods

The pH was determined before and after each experiment by using a pH-meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Nepean, Canada) equipped with a double junction Cole-Parmer electrode with Ag/AgCl reference cell for pH (daily calibration between 2 and 10). TS were measured according to the APHA method 1603 (APHA *et al.* 1999). Metals in solution were measured by plasma emission spectroscopy with a simultaneous ICP-AES (inductively coupled plasma - atomic emission spectroscopy, Vista Ax CCO simultaneous ICP-AES from Varian, Mississauga, Canada). Before analysis, liquid samples were first filtered on a Whatman 934-AH membrane (1.5 µm pore size) and were then acidified to give a 5% HCl solution. Analytical quality controls were performed with a certified standard solution (PlasmaCal Multielement Standard 900-Q30-100, SCP Science, Baie d’Urfé, Canada).

6.7 Results and discussion

6.7.1 Prediction of residual metal concentrations

Residual metal concentrations were calculated by *PITEM* in the case of soil leachate treatment by hydroxide, sulfide, phosphate, and carbonate precipitations. Simulation results were compared with those calculated in the same conditions with *MINEQL+*. Tables 6.1 and 6.2 show that residual metal concentrations, calculated with these two models, are almost identical. This confirms the validity of *PITEM*'s chemical model to simulate equilibrium among dissolved and solid phases suitable for aqueous solutions. It should be noted that experimental residual metal concentrations are greater than those calculated theoretically (*PITEM* and *MINEQL+*) (Tables 6.1 and 6.2) except for Zn for the two cases. This difference could be explained by the presence of aluminum and iron hydroxides (adsorption and/or coprecipitation of metals might occur with $Fe(OH)_3$ and $Al(OH)_3$) (Slavek *et al.* 1988; Marchioretto *et al.* 2005; Djedidi *et al.* 2009a).

This can be explained by kinetic considerations. In fact, it is important to take into considerations that *MINEQL+* and *PITEM*s and other comparable models, consider the chemical reactions at their equilibrium (infinite times). Consequently, they do not integrate kinetic aspects, which can be significant in metal precipitation techniques using short reaction periods (Çelen *et al.* 2007; Djedidi *et al.* 2009a,b).

6.7.2 Prediction of metal precipitates and sludge production

6.7.2.1 Multi-metallic synthetic solutions

Sln A treatment at pH 7.5 by adding soda ash (Na_2CO_3) generates metallic sludge having the following predicted composition: 18% $FeCO_3$, 17% $Cu_2(OH)_2CO_3$, 27% $CdCO_3$, 20% $ZnCO_3$ and 18% $MnCO_3$ (Table 6.3). These proportions of metal precipitate in the mixture (Pr_i) are calculated using the formula:

Équation 6.2 $$\mathbf{Pr_i = C_i \times M_i \times y_i / \sum C_i \times M_i \times y_i}$$

Where "C_i" is the initial concentration of the considered metal, "M_i" the precipitate molecular weight, and "y_i" the theoretical yield of the precipitation reaction extracted from *PITEM* chemical equilibrium calculations data. Total solids of the mono-metallic precipitates, after filtration (TS_i), are directly extracted from the experimental data presented in the reference (Djedidi *et al.* 2009b). The predicted mixture total solids (TSp) have been calculated using the formula:

Équation 6.3 $\mathbf{TSp = \sum Pr_i \times TS_i}$

The predicted sludge production values (PSp) were deduced directly from the total solids values (TSp, kg/m^3) using the relation:

Équation 6.4 $\mathbf{PSp = M_d / TSp}$

Where "M_d" is the produced dry sludge weight, equal to $\sum C_i \times M_i \times y_i$.

The obtained metal precipitates have been identified by XRD and confirmed by *MINEQL+* simulations in a subsequent study (Djedidi *et al.* 2009a,b). Sludge obtained after mechanical dewatering operation (pressure filtration), has a TS equal to 40.6% (w/w), corresponding to sludge production of 6.3 kg/m^3 (Table 6.3). TS value (43.4%), corresponding to sludge production of 5.9 kg/m^3, is predicted by *PITEM* and calculated by combining linearly the proportions of each precipitate in the sludge and their specific TS set in an earlier study (Djedidi *et al.* 2009a,b). It should be noted, that Sln A treatment by limestone neutralization (carbonates) generates flocs having good dewatering characteristics (TS equal to 40.6%). This was confirmed by previous works (MEND, 1994).

TS (18.2% and 13.2%) and SP (11.2 and 14.4 kg/m^3) predicted by *PITEM* in the case of Sln A and Sln B treatment by sodium sulfide (Na_2S) and caustic soda (NaOH), respectively are in agreement with experimental values (TS: 16.6 and 11.2%; SP: 12.3 and 16.3 kg/m^3) (Table 6.3).

6.7.2.2 Soil leachate

ICP analyses show that soil leachate is contaminated with metals: Al^{3+} (8.64×10^{-4} mol/L), Fe^{3+} (7.10×10^{-4} mol/L), Pb^{2+} (3.36×10^{-3} mol/L), Cu^{2+} (4.23×10^{-4} mol/L), and Zn^{2+} (6.58×10^{-5} mol/L).

Soil leachate treatment with limestone (Na_2CO_3) generate sludge composed of 7% $Fe(OH)_3$, 4% $Cu_2(OH)_2CO_3$, 6% $Al(OH)_3$, 8% $Pb(OH)_2$, and 74% $PbCO_3$ (Table 6.4). These metal precipitates are predicted by *PITEM* and confirmed by *MINEQL+* simulations in a subsequent study (Djedidi *et al.* 2009a,b).

Sludge obtained after mechanical dewatering operation (pressure filtration), has a TS equal to 72.7% corresponding to a sludge production of 1.7 kg/m^3 (Table 6.4). TS value of 63.6%, corresponding to sludge production of 1.8 kg/m^3, are predicted by *PITEM*, and were calculated by combining linearly the proportions of each precipitate in the sludge and their specific TS set in an earlier study (Djedidi *et al.* 2009a,b).

In the case of soil leachate treatment by adding phosphates (Na_3PO_4) or sulfides (Na_2S), sludge obtained after dewatering process (pressure filtration) have TS equal to 36.7 and 18.4%, corresponding to SP of 3.3 and 5.3 kg/m^3, respectively (Table 6.4). Experimental values are consistent with those predicted by *PITEM* in the case of phosphate precipitation: TS (37.2%) and PS (3.3 kg/m^3). It should be noted, that predicted TS value in the case of soil leachate treatment by sulfide (TS: 23.1%) is slightly higher to experimental value, corresponding to a lower sludge production PS (4.3 kg/m^3). Difficulty encountered during the S/L separation is essentially due to the production of colloidal sulfur formed by the oxidation of sulfide (S^{2-}) by ferric ions (Fe^{3+}) (MEND, 1996).

6.7.3 Prediction of the soil leachate treatment cost

PITEM cost estimation is based on input data presented in Table 6.5 and a simplified scheme of an industrial process for effluent decontamination presented in Fig. 6.6. Table 6.6 shows the total costs estimation based on US$ per unit volume processed for the four scenarios of soil leachate treatment.

PITEM's simulation results show that difference between TTC among the studied precipitation techniques (hydroxides, sulfides, carbonates and phosphates) is mainly due to three parameters: chemicals, sludge handling and sludge disposal (Table 6.6). In fact, operating cost parameters (except, for these three last parameters) are linked directly or indirectly to the capital cost. The latter is closely related to the equipment design and thereafter to the maximum effluent flow rate allowed in such industrial project. It can therefore be concluded that for a constant effluent flow rate (1000 m^3/day in this case), the only variable parameters whatever treatment scenario, are: chemicals, sludge handling and sludge disposal.

PITEM simulation results revealed that, the TTC for soil leachate treatment varied from 4.62 to 5.18 \$/m^3 (Table 6.6). Obviously, the lower unit cost was detected for the limestone (Na_2CO_3) treatment. This was expected and is due to limestone relative cheap price (0.15 \$/kg), and to the interesting dewatering characteristics of the generated sludge towards pressure filtration (predicted TS = 63.6%). Highest TTC is assigned to the most widely used precipitation technique (hydroxide). This is essentially due to the high cost of NaOH (0.50 $/kg) (Table 6.5) and to the relatively low TS obtained after mechanical S/L separation 18.8% (result not shown).

6.8 Conclusion

A new computer program (*PITEM*) for the prediction of treatment of metal polluted-effluents by precipitation techniques has been developed. *PITEM* is written with Visual Basic Language under the *Microsoft EXCEL* platform and is designed as easy-to-use software. *PITEM*'s outputs regarding to the total solids of the generated sludge are in agreement with those obtained experimentally in the studied cases, except during soil leachate treatment with sulfides where TS predicted (23.1% w/w) is slightly higher (less water content) than the experimental value (18.4%) due to the formation of colloidal sulfur. Unitary treatment costs ($\$/m^3$) estimated by the program for the four scenarios of soil leachate treatment by precipitation follow the ascending order: carbonates (Na_2CO_3) < sulfides (Na_2S) < phosphates (Na_3PO_4) < hydroxides (NaOH). *PITEM*'s database (dewatering characteristics) must be updated as in the context of future research to give *PITEM* more accurate output data and a wider field use.

6.9 Acknowledgements

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6.10 References

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0. User's manual. Report EPA/600/3-91/021, United States Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgia, USA.

Al-Tarazi, M., Heesink, A.B.M., Versteeg, G.F., 2004. Precipitation of metal sulfides using gaseous hydrogen sulfide: mathematical modelling. Chem. Eng. Sci. 59 (3), 567-579.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), 1999. Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA, AWWA and WEF, Washington, DC.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., 1996. Heavy metals in wastewater: modelling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitation. Waste Manag. 16 (8), 717-725.

Blais, J.F., Djedidi, Z., Ben Cheikh, R., Tyagi, R.D., Mercier, G., 2008. Metals precipitation from effluents – A review. Practice Periodical Toxic Hazard. Radioactive Waste Manag. 12 (3), 135-149.

Blais, J.F., Dufresne, S., Mercier, G., 1999. State of the art of the technological development from metal removal from industrial effluents. J. Water Sci. 12 (4), 689-713 (in French).

Çelen, I., Buchanan, J.R., Burns, R.T., Robinson, R.B., Raman, D.R., 2007. Using a chemical equilibrium model to predict amendments requires to precipitate phosphorus as struvite in liquid swine manure. Water Res. 41 (8), 1689-1696.

Chemical Engineering www.che.com., March 2009.

Del Piero, S., Melchior, A., Polese, P., Portanova, R., Tolazzi, M., 2006. A novel multipurpose EXCEL tool for equilibrium speciation based on Newton-Raphson method and on a hybrid genetic algorithm. Annali di chimica 96 (1-2), 29-49.

Djedidi, Z., Bouda, M., Cheikh, R.B., Blais, J.F., Mercier, G., Tyagi, R.D., 2009. Comparative study of dewatering characteristics of metal precipitates generated during treatment synthetic polymetallic and AMD solutions. Hydrometallurgy 98 (3-4), 247-256.

Djedidi, Z., Khaled, J.B., Cheikh, R.B., Blais, J.F., Mercier, G., Tyagi, R.D., 2009. Comparative study of dewatering characteristics of metal precipitates generated during treatment of monometallic solutions, Hydrometallurgy 95 (1-2), 61-69.

Fytili, D., Zabaniotou, A., 2008. Utilization of sewage sludge in EU application of old and new methods- A review. Renewable Sustainable Energy Rev. 12, 116-140.

Guillard, D., Lewis, A.E., 2002. Optimisation of nickel hydroxycarbonate precipitation using a laboratory pellet reactor. Ind. Eng. Chem. 41, 3110-3114.

Hove, M., van Hill, R.P., Lewis, A.E., 2008. Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. Chem. Eng. Sci. 63, 1626-1635.

Islamoglu, S., Yilmaz, L., Ozbelge, H.O., 2006. Development of a precipitation based separation scheme for selective removal and recovery of heavy metals from cadmium rich electroplating industry effluents. Sep. Sci. Technol. 41 (15), 3367-3385.

Kabata-Pendias, A., 2001. Trace elements in soils and plants. 3rd Edition. Kabata-Pendias, A., Pendias, H. (Eds.), CRC Press LLC, Boca Raton, Florida, USA, 413 p.

Kim, B.R., Gaines, W.A., Szafranski, M.J., Bernath, E.F., Miles, A.M., 2002. Removal of heavy metals from automotive wastewater by sulfide precipitation, J. Environ. Eng. Div. ASCE 128 (7), 612-623.

Klatt, K.U and Marquardt, W., 2009. Perspectives for process systems engineering-Personal views from academia and industry. Comput. Chem. Eng. 33, 536-550.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S., 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci. Total Environ. 366 (2-3), 409-426.

Leclerc, D., 1997. Filtration sur support, aspects théoriques. Techniques de l'ingénieur. Cahier J. 3501, 1-15.

Marchioretto, M.M., Bruning, H., Rulkens, W., 2005. Heavy metals precipitation in sewage sludge. Sep. Sci. Technol. 40 (16), 3393-3405.

Mattigod, S.V., 1995. Chemical equilibrium and reaction models: applications and future trends. Chemical equilibrium and reaction models. SSSA Special Publication Number 42, Soil Science Society of America, American Society of Agronomy, Madison, Wisconsin, USA, pp. l-5.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., Saldanha, M., 2002. Studies on the mechanisms of lead immobilization by hydroxyapatite. Environ. Sci. Technol. 36 (7), 1625-1629.

McAnally, S., Benefield, L., Reed, R.B., 1984. Nickel removal from a synthetic nickel-plating waste water using sulfide and carbonate for precipitation and coprecipitation. Sep. Sci. Technol. 19, 191-217.

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., Cook, N., 2000. Soil testing for heavy metals. Commun. Soil Sci. Plant Anal. 31, 1661-1700.

MDDEPQ, 1999. Politique de protection des sols et de réhabilitation des terrains contaminés. Ministère du développement durable de l'environnement et des parcs du Québec, Gouvernement du Québec, Québec, Canada, 132 p. (in French).

MEND, 1994. Acid mine drainage – Status of chemical treatment and sludge management practices. Report 3.32.1., Mine Environment Neutral Drainage (MEND) Program, Ottawa, Ontario, Canada.

MEND, 1996. Metals removal from acidic drainage - Chemical methods. Report 3.21.2a, Mine Environment Neutral Drainage (MEND) Program, Ottawa, Ontario, Canada.

Metcalf & Eddy Inc., 1991. Wastewater engineering: treatment, disposal and reuse. 3rd ed. McGraw-Hill, New-York, NY, USA.

Mirbagheri, S.A., Hosseini, S.N., 2004. Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. Desalination 171 (1), 85-93.

Mishra, S.K., 1999. Resource recovery in waste treatment increasingly used. Min. Eng. 51 (4), 29-34.

Mitchell, D.B., Schweers, M.E., 1989. Hazardous waste reduction using organic polymers. Pollut. Eng. 21 (3), 84-96.

Nguyen, T.P., Hilal, N., Hankins, N.P., Novak, J.T., 2008. Determination of the effect of cations and cationic polyelectrolytes on the characteristics and final properties of synthetic and activated sludge. Desalination 222 (1-3), 307-317.

Papelis, C., Hayes, K.F., Leckie, J.O., 1988. HYDRAQL: a program for the computation of chemical equilibrium composition of aqueous batch systems including surface-complexation modeling of ion adsorption at the oxide/solution interface. Technical report 306, Department of Civil Engineering, Stanford University, Stanford, CA, USA.

Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N., 1980. PHREEQE. A computer program for geochemical calculations. Report 80-96, United States Geological Survey, Water Resources Investigations, Reston, VA, USA.

Patterson, J.W., 1988. Metal treatment and recovery. In : Kramer, J.R., Allen, H.E. (Eds.), Metal speciation: Theory and application. Lewis Publishers Inc., Chelsea, Michigan, USA.

Pigaga, A., Juskenas, R., Selkis, A., 2002. Waste treatment of two electroplating solutions of Cu and Zn by mixing and precipitation. Sep. Sci. Technol. 37 (13), 3155-3168.

Slavek, J., Pickering, W.F., 1988. Metal ion interaction with the hydrous oxides of aluminium. Water Air Soil Pollut. 39 (1-2), 201-216.

Ulrich, G.D., 1984. A guide to chemical engineering process design and economics. John Wiley & Sons Inc., New York, NY, USA, 472 p.

USEPA, 1996. Management of water treatment plant residuals. Technology transfer handbook. EPA 625-R-95-008, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, OH, USA.

Veeken, A.H.M., Rulkens, W.H., 2003. Innovative developments in the selective removal and reuse of heavy metals from wastewaters. Water Sci. Technol. 47 (10), 9-16.

Viadero, R.C., Wei, X.C., Buzby, K.M., 2006. Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization. Environ. Eng. Sci. 23 (4), 734-743.

Westall, J.C., Zachary, J.L., Morel, F.M.N., 1976. MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems. Technical note 18, Massachusetts Institute of Technology, Boston, MA, USA.

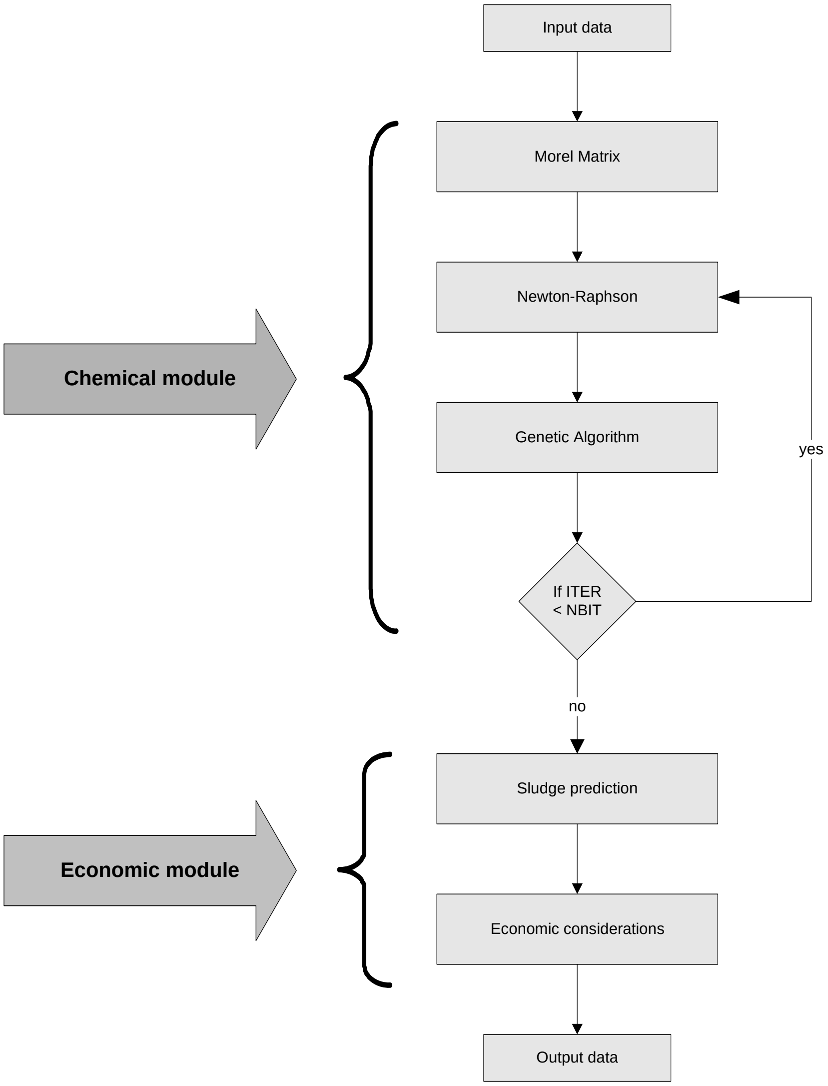


Figure 6.1 **Simplified organigram of the computer program (*PITEM*)**

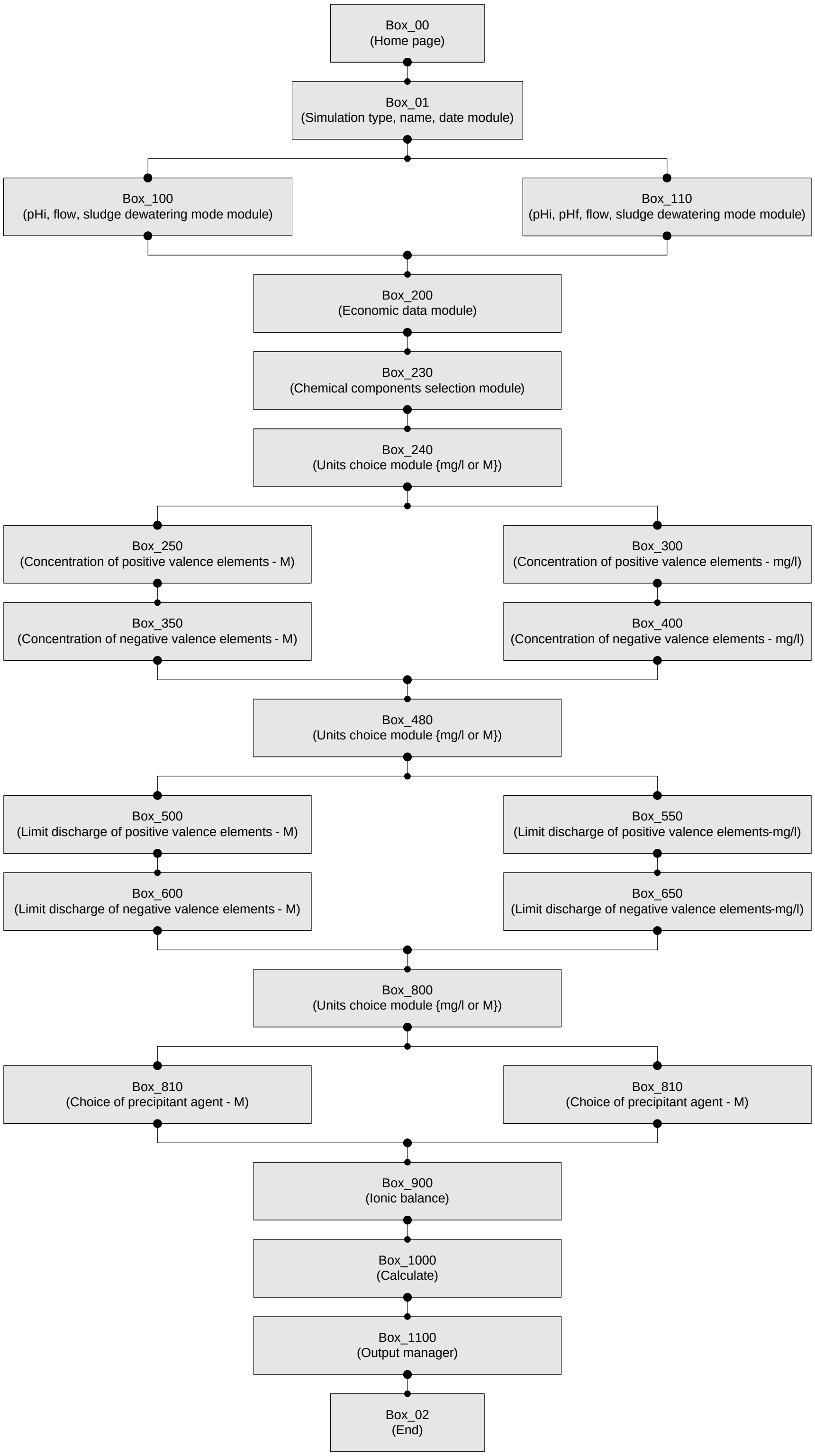
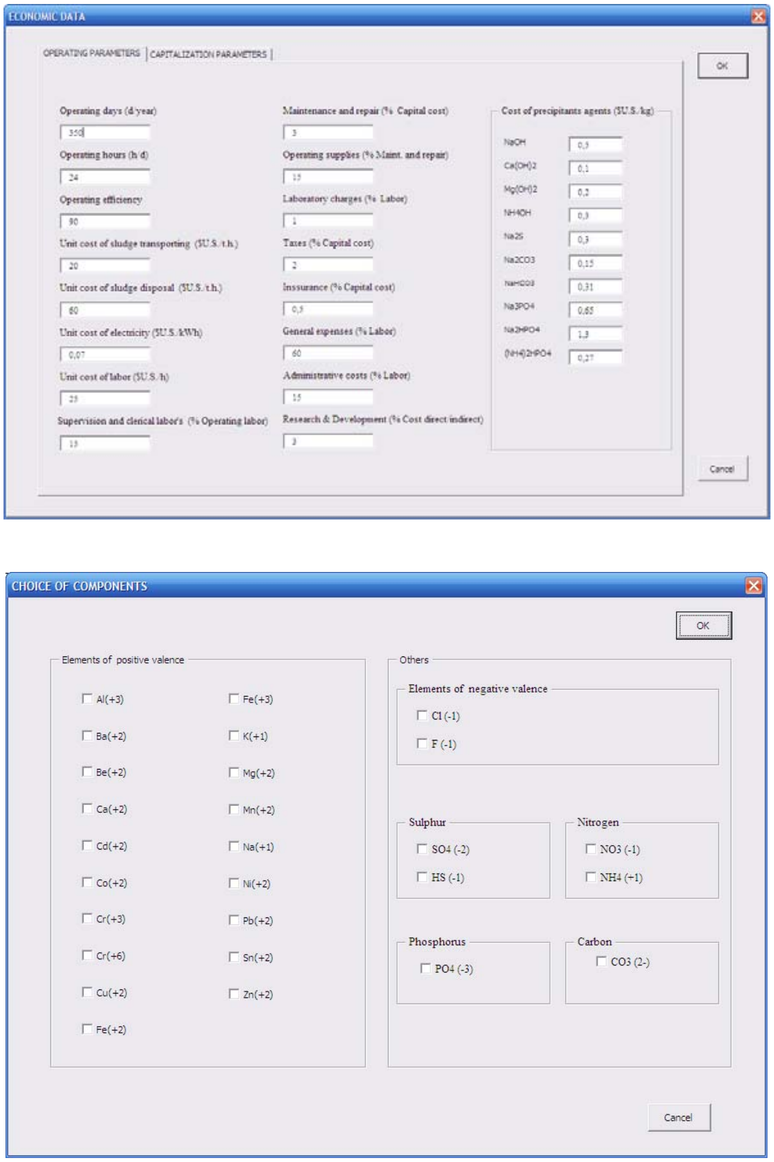


Figure 6.2 **Organigram of *PITEM* user interfaces**



ECONOMIC DATA

Operating days (d/year)
350

Operating hours (h/d)
24

Operating efficiency
90

Unit cost of sludge transporting ($U.S./t.h.)
20

Unit cost of sludge disposal ($U.S./t.h.)
60

Unit cost of electricity ($U.S./kWh)
0,07

Unit cost of labor ($U.S./h)
25

Supervision and clerical labor's (% Operating labor)
15

Maintenance and repair (% Capital cost)
3

Operating supplies (% Maint. and repair)
15

Laboratory charges (% Labor)
1

Taxes (% Capital cost)
2

Inssurance (% Capital cost)
0,5

General expenses (% Labor)
60

Administrative costs (% Labor)
15

Research & Development (% Cost direct/indirect)
3

Cost of precipitants agents ($U.S./kg)

NaOH	0,5
Ca(OH)2	0,1
Mg(OH)2	0,2
NH4OH	0,3
Na2S	0,3
Na2CO3	0,15
NaHCO3	0,31
Na3PO4	0,65
Na2HPO4	1,3
(NH4)2HPO4	0,27

CHOICE OF COMPONENTS

Elements of positive valence

- ☐ Al(+3)
- ☐ Ba(+2)
- ☐ Be(+2)
- ☐ Ca(+2)
- ☐ Cd(+2)
- ☐ Co(+2)
- ☐ Cr(+3)
- ☐ Cr(+6)
- ☐ Cu(+2)
- ☐ Fe(+2)
- ☐ Fe(+3)
- ☐ K(+1)
- ☐ Mg(+2)
- ☐ Mn(+2)
- ☐ Na(+1)
- ☐ Ni(+2)
- ☐ Pb(+2)
- ☐ Sn(+2)
- ☐ Zn(+2)

Others

Elements of negative valence

- ☐ Cl (-1)
- ☐ F (-1)

Sulphur

- ☐ SO4 (-2)
- ☐ HS (-1)

Nitrogen

- ☐ NO3 (-1)
- ☐ NH4 (+1)

Phosphorus

- ☐ PO4 (-3)

Carbon

- ☐ CO3 (2-)

Figure 6.3 **Examples of *PITEM* user interfaces**

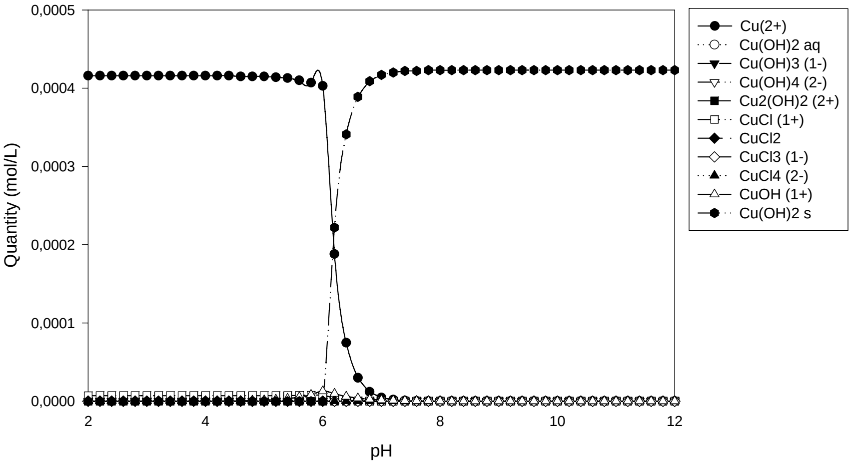
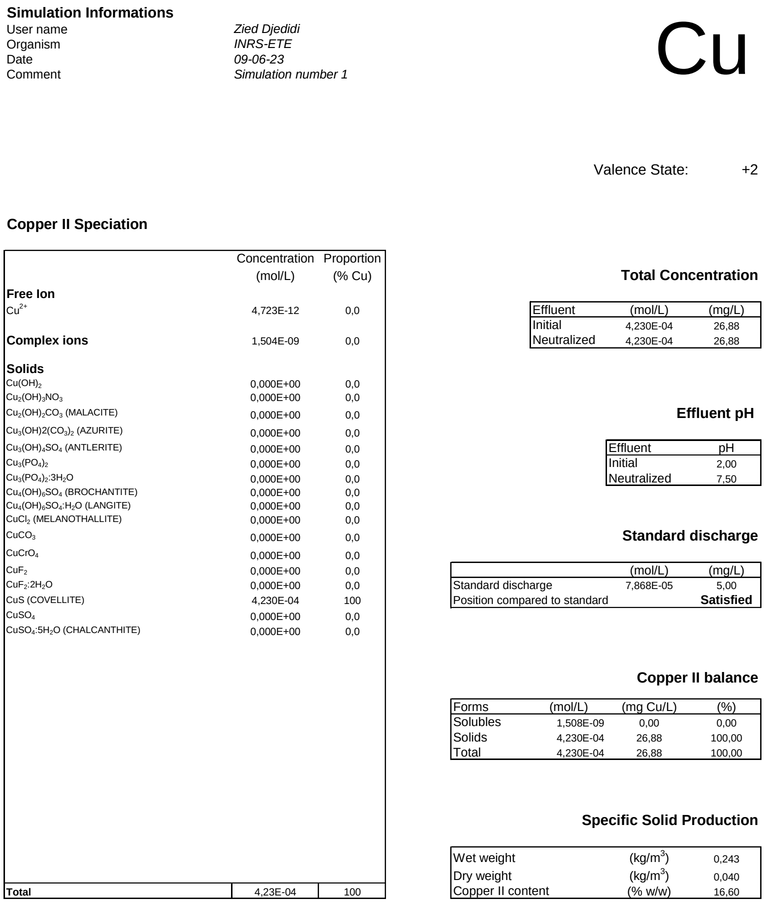


Figure 6.4 **Effect of soil leachate pH on the quantity (mol/L) of the different copper species based on chemical equilibrium calculations using the *PITEM* software. $[Cu]_i = 4.23\times10^{-4}$ mol/L, $[Cl]_i = 2.85\times10^{-2}$ mol/L**



Simulation Informations

User name	*Zied Djedidi*
Organism	*INRS-ETE*
Date	*09-06-23*
Comment	*Simulation number 1*

Cu

Valence State: +2

Copper II Speciation

	Concentration (mol/L)	Proportion (% Cu)
Free Ion		
Cu^{2+}	4,723E-12	0,0
Complex ions	1,504E-09	0,0
Solids		
$Cu(OH)_2$	0,000E+00	0,0
$Cu_2(OH)_3NO_3$	0,000E+00	0,0
$Cu_2(OH)_2CO_3$ (MALACITE)	0,000E+00	0,0
$Cu_3(OH)2(CO_3)_2$ (AZURITE)	0,000E+00	0,0
$Cu_3(OH)_4SO_4$ (ANTLERITE)	0,000E+00	0,0
$Cu_3(PO_4)_2$	0,000E+00	0,0
$Cu_3(PO_4)_2:3H_2O$	0,000E+00	0,0
$Cu_4(OH)_6SO_4$ (BROCHANTITE)	0,000E+00	0,0
$Cu_4(OH)_6SO_4:H_2O$ (LANGITE)	0,000E+00	0,0
$CuCl_2$ (MELANOTHALLITE)	0,000E+00	0,0
$CuCO_3$	0,000E+00	0,0
$CuCrO_4$	0,000E+00	0,0
CuF_2	0,000E+00	0,0
$CuF_2:2H_2O$	0,000E+00	0,0
CuS (COVELLITE)	4,230E-04	100
$CuSO_4$	0,000E+00	0,0
$CuSO_4:5H_2O$ (CHALCANTHITE)	0,000E+00	0,0
Total	4,23E-04	100

Total Concentration

Effluent	(mol/L)	(mg/L)
Initial	4,230E-04	26,88
Neutralized	4,230E-04	26,88

Effluent pH

Effluent	pH
Initial	2,00
Neutralized	7,50

Standard discharge

	(mol/L)	(mg/L)
Standard discharge	7,868E-05	5,00
Position compared to standard		**Satisfied**

Copper II balance

Forms	(mol/L)	(mg Cu/L)	(%)
Solubles	1,508E-09	0,00	0,00
Solids	4,230E-04	26,88	100,00
Total	4,230E-04	26,88	100,00

Specific Solid Production

Wet weight	(kg/m^3)	0,243
Dry weight	(kg/m^3)	0,040
Copper II content	(% w/w)	16,60

Figure 6.5 **Example of output data for copper balance, sludge production and other characteristics generated by the *PITEM* software during the simulation of the treatment of soil leachate using sodium sulfide (Na_2S)**

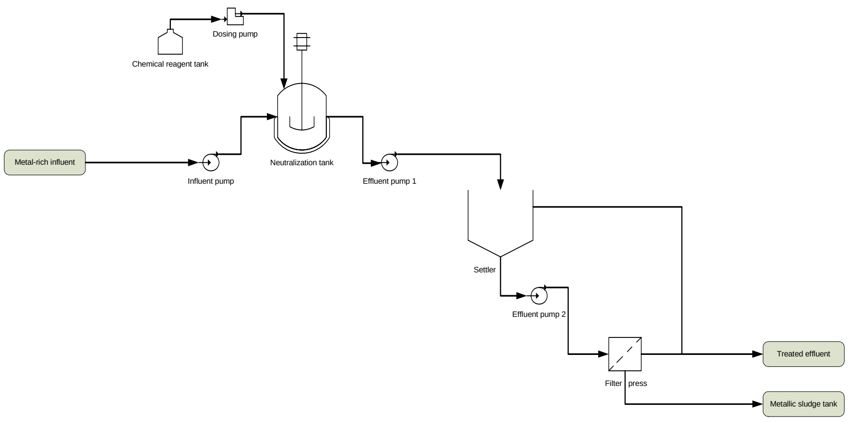


Figure 6.6 **Flowsheet of the effluent treatment process**

Tableau 6.1 Experimental and predicted residual metal concentrations using *MINEQL+* and *PITEM* softwares for soil leachate treatment using hydrated lime and sodium sulfide

Metals		**Hydroxides (pH 10.0)**			**Sulfides (pH 7.5)**		
	$[M]_i$ (mol/L)	$[M]_f$ Exp (mol/L)	$[M]_f$ *PITEM* (mol/L)	$[M]_f$ *MINEQL+* (mol/L)	$[M]_f$ Exp (mol/L)	$[M]_f$ *PITEM* (mol/L)	$[M]_f$ *MINEQL+* (mol/L)
Al^{3+}	**8.64×10^{-4}**	6.45×10^{-5}	4.00×10^{-5}	4.00×10^{-5}	2.30×10^{-5}	1.31×10^{-7}	1.31×10^{-7}
Cu^{2+}	**4.23×10^{-4}**	9.44×10^{-7}	1.51×10^{-9}	1.51×10^{-9}	3.15×10^{-7}	8.85×10^{-15}	8.89×10^{-15}
Fe^{3+}	**7.10×10^{-4}**	5.37×10^{-7}	4.42×10^{-8}	4.42×10^{-8}	4.83×10^{-6}	1.69×10^{-9}	1.69×10^{-9}
Pb^{2+}	**3.36×10^{-3}**	2.45×10^{-7}	1.61×10^{-9}	1.61×10^{-9}	9.17×10^{-7}	5.30×10^{-12}	5.35×10^{-12}
Zn^{2+}	**6.58×10^{-5}**	3.06×10^{-7}	7.65×10^{-6}	7.65×10^{-6}	6.12×10^{-7}	1.99×10^{-10}	1.99×10^{-10}

Tableau 6.2 Experimental and predicted residual metal concentrations by *MINEQL+* and *PITEM* softwares for soil leachate treatment using Na_2CO_3 and Na_2HPO_4

Metals		**Carbonates (pH 7.5)**			**Phosphates (pH 8.0)**		
	$[M]_i$ (mol/L)	$[M]_f$ Exp (mol/L)	$[M]_f$ *PITEM* (mol/L)	$[M]_f$ *MINEQL+* (mol/L)	$[M]_f$ Exp (mol/L)	$[M]_f$ *PITEM* (mol/L)	$[M]_f$ *MINEQL+* (mol/L)
Al^{3+}	**8.64×10^{-4}**	1.52×10^{-5}	1.31×10^{-7}	1.31×10^{-7}	1.30×10^{-5}	4.05×10^{-7}	4.05×10^{-7}
Cu^{2+}	**4.23×10^{-4}**	5.19×10^{-6}	5.05×10^{-7}	5.07×10^{-7}	9.44×10^{-7}	1.01×10^{-7}	1.26×10^{-7}
Fe^{3+}	**7.10×10^{-4}**	2.15×10^{-6}	1.69×10^{-9}	1.69×10^{-9}	3.58×10^{-6}	8.63×10^{-10}	8.63×10^{-10}
Pb^{2+}	**3.36×10^{-3}**	1.69×10^{-6}	6.74×10^{-7}	6.72×10^{-7}	3.86×10^{-7}	6.60×10^{-10}	6.76×10^{-10}
Zn^{2+}	**6.58×10^{-5}**	3.52×10^{-6}	6.58×10^{-5}	6.58×10^{-5}	1.53×10^{-6}	9.88×10^{-8}	8.58×10^{-8}

Tableau 6.3 *PITEM* predictions of total solids and sludge production after pressure filtration generated by treatment of synthetic multi-metallic solution based on the characteristics of mono-metallic sludge

	Metals	*PITEM* prediction		Mixture total solids (% w/w)		Sludge production (kg/m^3)	
		Proportion of metal precipitate in the mixture (% w/w)	TS of each monometallic precipitate after filtration (% w/w)	Predicted	Experimental	Predicted	Experimental
Carbonates (solution A)	Fe $^{(+2)}$	(18) $FeCO_3$	13.0	43.4	40.6	5.9	6.3
	Cu $^{(+2)}$	(17) $Cu_2(OH)_2CO_3$	46.0				
	Cd $^{(+2)}$	(27) $CdCO_3$	70.6				
	Zn $^{(+2)}$	(20) $ZnCO_3$	17.6				
	Mn $^{(+2)}$	(18) $MnCO_3$	57.9				
Sulfides (solution A)	Fe $^{(+2)}$	(17) FeS	13.7	18.2	16.6	11.2	12.3
	Cu $^{(+2)}$	(19) CuS	16.6				
	Cd $^{(+2)}$	(28) CdS	14.4				
	Zn $^{(+2)}$	(19) ZnS	18.6				
	Mn $^{(+2)}$	(17) MnS	30.9				
Hydroxides (solution B)	Fe $^{(+3)}$	(23) $Fe(OH)_3$	11.5	13.2	11.2	14.4	16.3
	Cu $^{(+2)}$	(20) $Cu(OH)_2$	26.2				
	Al $^{(+3)}$	(16) $Al(OH)_3$	6.8				
	Zn $^{(+2)}$	(21) $Zn(OH)_2$	10.7				
	Ni $^{(+2)}$	(20) $Ni(OH)_2$	9.5				

Tableau 6.4 ***PITEM* predictions of total solids and sludge production after pressure filtration generated by treatment of soil leachate based on the characteristics of mono-metallic sludge**

	Metals	*PITEM* prediction		Mixture total solids (% w/w)		Sludge production (kg/m^3)	
		Proportion of metal precipitate in the mixture (% w/w)	TS of each monometallic precipitate after filtration (% w/w)	Predicted	Experimental	Predicted	Experimental
Carbonates	Fe $^{(+3)}$	(7) $Fe(OH)_3$	8.0	63.6	72.7	1.7	1.8
	Cu $^{(+2)}$	(4) $Cu_2(OH)_2CO_3$	52.8				
	Al $^{(+3)}$	(6) $Al(OH)_3$	4.2				
	Pb $^{(+2)}$	(8) $Pb(OH)_2$	51.4				
	Pb $^{(+2)}$	(74) $PbCO_3$	76.4				
Phosphates	Fe $^{(+3)}$	(11) $FePO_4.2H_2O$	12.3	37.2	36.7	3.3	3.3
	Cu $^{(+2)}$	(4) $Cu_3(PO_4)_2$	9.0				
	Al $^{(+3)}$	(10) $AlPO_4.1H_2O$	15.1				
	Pb $^{(+2)}$	(14) $Pb(OH)_2$	51.4				
	Pb $^{(+2)}$	(60) $Pb_3(PO_4)_2$	43.9				
Sulfides	Fe $^{(+3)}$	(8) $Fe(OH)_3$	8.0	23.1	18.4	4.3	5.3
	Cu $^{(+2)}$	(4) CuS	16.6				
	Al $^{(+3)}$	(7) $Al(OH)_3$	4.2				
	Pb $^{(+2)}$	(81) PbS	23.8				

Tableau 6.5 Operating and economic parameters used for the estimation of the effluent treatment costs

Parameters	Units	Values	Parameters	Units	Values
Basic parameters			Operating costs		
Effluent flow	m^3/day	1000	Direct costs		
Operating days	day/year	350	NaOH	$/kg	0.50
Operating hours	h/day	24	$Ca(OH)_2$	$/kg	0.10
Operating efficiency	%	90	Na_2S	$/kg	0.30
			Na_2CO_3	$/kg	0.15
Capital costs			Na_3PO_4	$/kg	0.70
Annual interest rate	%	8	Labor unit cost	$/h	25
Depreciation period	Years	10	Electricity cost	$/kWh	0.07
Equipment lifetime	Years	20	Supervisory and clerical labor	% Operating labor	15
Construction management fees	% Capital cost	52	Maintenance and repair	% Capital cost	3
Contingencies fees	% Capital cost	10	Operating supplies	% Maintenance and repair	15
Marshall & Swift Cost Index	-	1487.2	Laboratory charges	% Operating labor	1
			Waste handling	$/w.t.	20
Equip. installation & insulation	% Equipments costs	39	Waste disposal	$/w.t	60
Instrumentation and control	% Equipments costs	13			
Piping	% Equipments costs	31	Indirect costs		
Electrical materials	% Equipments costs	10	Taxes	% Capital cost	2
Building process and services	% Equipments costs	29	Insurances	% Capital cost	0.5
Site preparation	% Equipments costs	10	General expenses	% Labor	60
Facilities and services	% Equipments costs	55			
Land acquisition	% Equipments costs	6	General costs		
Engineering and supervision	% Equipments costs	32	Administrative costs	% Labor	15
Construction costs	% Equipments costs	34	Research & Development	% Direct and indirect costs	3

Tableau 6.6 **Total costs (US$/m^3) for the four scenarios of soil leachate treatment**

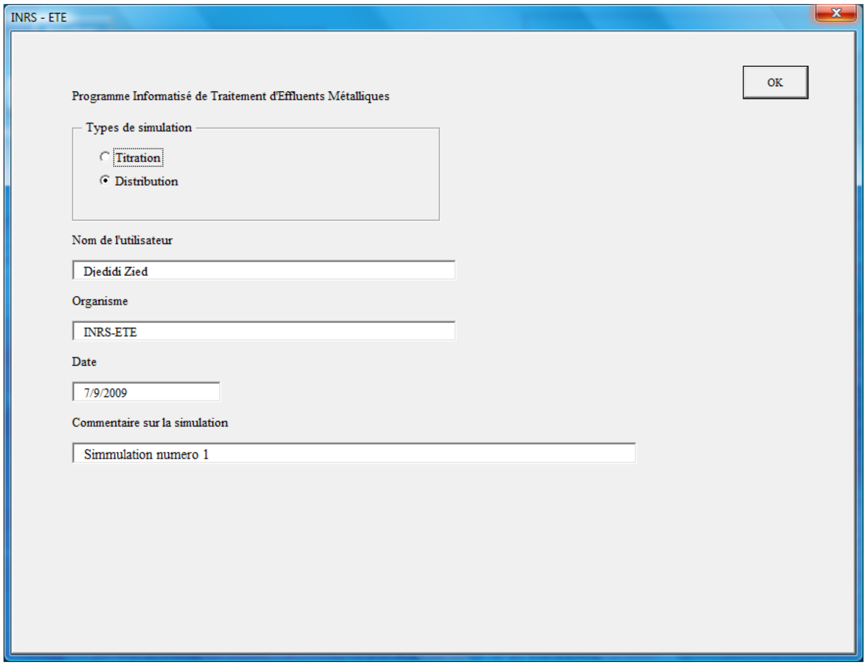
Items	Precipitation techniques			
	Hydroxides	Carbonates	Phosphates	Sulfides
Operating costs				
Direct costs				
Chemicals	0.314	0.111	0.265	0.136
Labor	0.297	0.297	0.297	0.297
Energy	0.014	0.014	0.014	0.014
Supervision	0.241	0.241	0.241	0.241
Maintenance	0.555	0.555	0.555	0.555
Supplies	0.083	0.083	0.083	0.083
Laboratory	0.016	0.016	0.016	0.016
Sludge handling	0.110	0.033	0.066	0.086
Sludge disposal	0.331	0.099	0.198	0.258
Total direct costs	*1.951*	*1.450*	*1.735*	*1.638*
Indirect costs	1.575	1.573	1.575	1.574
General costs	0.414	0.406	0.424	0.413
Capitalization costs				
Depreciation	0.928	0.925	0.929	0.927
Interests	0.315	0.315	0.315	0.315
Total costs	5.183	4.619	4.978	4.868

ANNEXE

BOÎTES DE DIALOGUE DU PROGICIEL *PITEM*

Fenêtre 1

Fenêtre 2



Programme Informatisé de Traitement d'Effluents Métalliques

Types de simulation

○ Titration
● Distribution

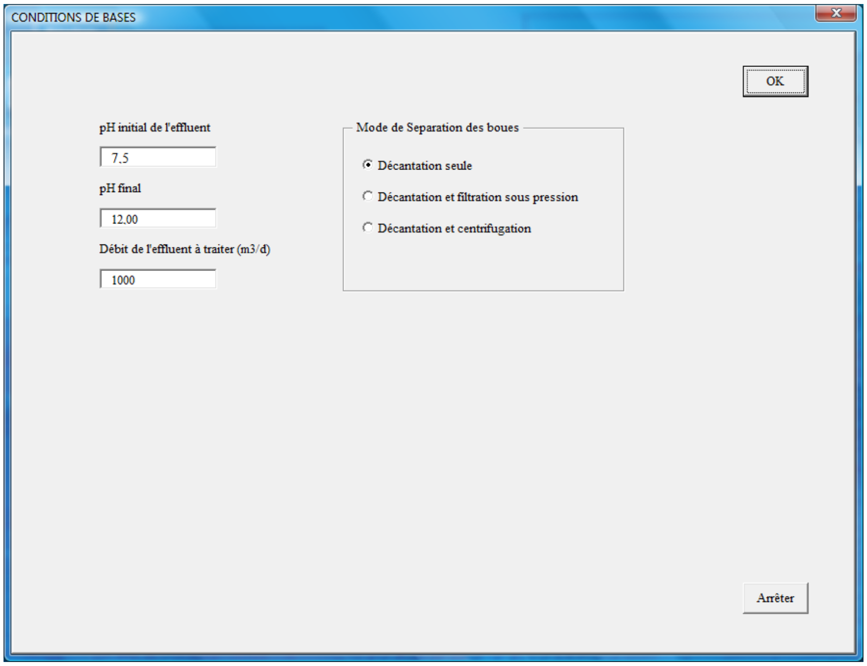
Nom de l'utilisateur: Diedidi Zied

Organisme: INRS-ETE

Date: 7/9/2009

Commentaire sur la simulation: Simmulation numero 1

Fenêtre 3

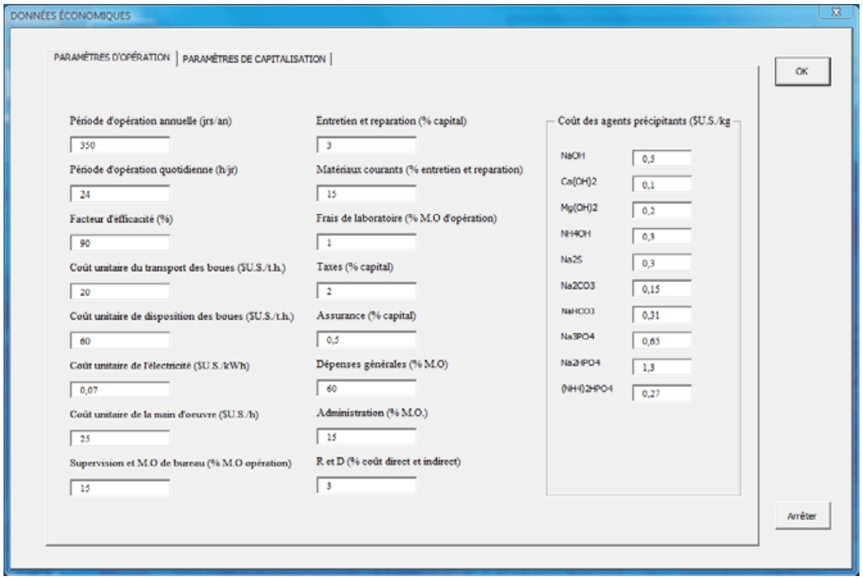


pH initial de l'effluent	7.5
pH final	12.00
Débit de l'effluent à traiter (m3/d)	1000

Mode de Separation des boues

- ● Décantation seule
- ○ Décantation et filtration sous pression
- ○ Décantation et centrifugation

Fenêtre 4



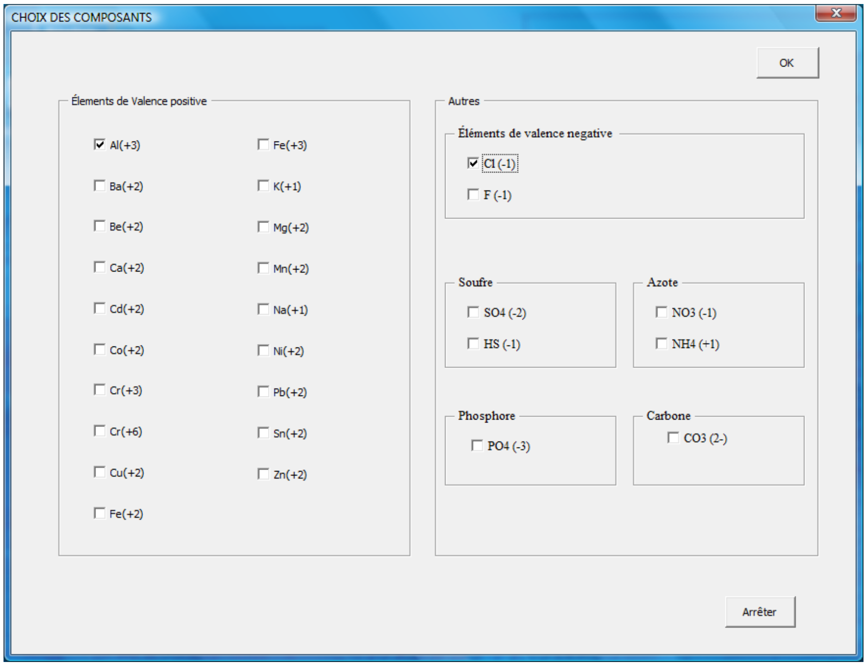
Période d'opération annuelle (jrs/an)	350
Période d'opération quotidienne (h/jr)	24
Facteur d'efficacité (%)	90
Coût unitaire du transport des boues ($U.S./t.h.)	20
Coût unitaire de disposition des boues ($U.S./t.h.)	60
Coût unitaire de l'électricité ($U.S./kWh)	0,07
Coût unitaire de la main d'oeuvre ($U.S./h)	25
Supervision et M.O de bureau (% M.O opération)	15

Entretien et reparation (% capital)	3
Matériaux courants (% entretien et reparation)	15
Frais de laboratoire (% M.O d'opération)	1
Taxes (% capital)	2
Assurance (% capital)	0,5
Dépenses générales (% M.O)	60
Administration (% M.O.)	15
R et D (% coût direct et indirect)	3

Coût des agents précipitants ($U.S./kg

$NaOH$	0,5
$Ca(OH)_2$	0,1
$Mg(OH)_2$	0,2
NH_4OH	0,3
Na_2S	0,3
Na_2CO_3	0,15
$NaHCO_3$	0,31
Na_3PO_4	0,65
Na_2HPO_4	1,3
$(NH_4)_2HPO_4$	0,27

Fenêtre 5


CHOIX DES COMPOSANTS

Élements de Valence positive

☑ Al(+3)
☐ Ba(+2)
☐ Be(+2)
☐ Ca(+2)
☐ Cd(+2)
☐ Co(+2)
☐ Cr(+3)
☐ Cr(+6)
☐ Cu(+2)
☐ Fe(+2)
☐ Fe(+3)
☐ K(+1)
☐ Mg(+2)
☐ Mn(+2)
☐ Na(+1)
☐ Ni(+2)
☐ Pb(+2)
☐ Sn(+2)
☐ Zn(+2)

Autres

Éléments de valence negative

☑ Cl (-1)
☐ F (-1)

Soufre

☐ SO4 (-2)
☐ HS (-1)

Azote

☐ NO3 (-1)
☐ NH4 (+1)

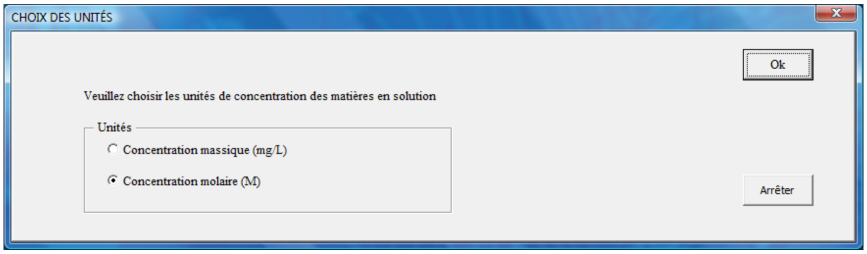
Phosphore

☐ PO4 (-3)

Carbone

☐ CO3 (2-)

Fenêtre 6

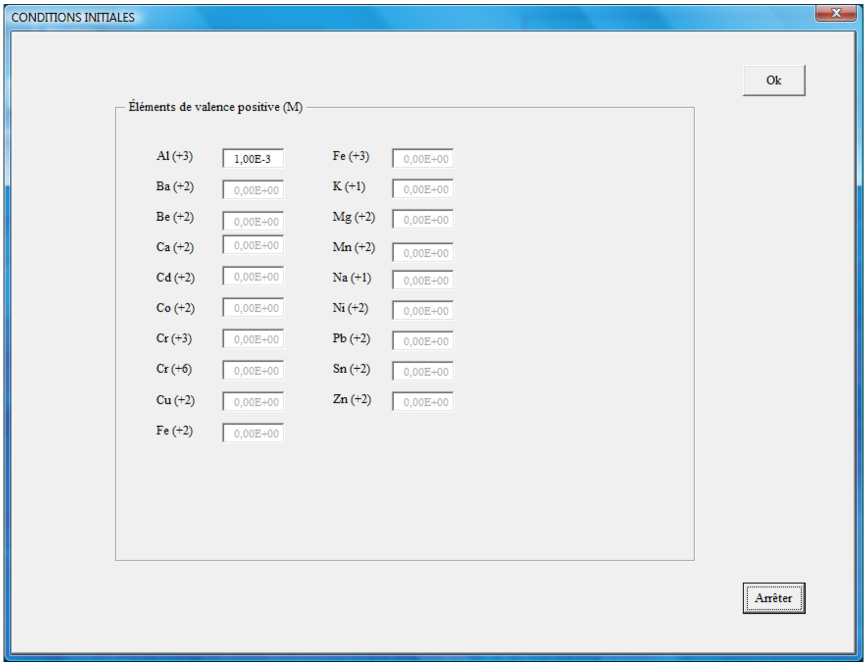

CHOIX DES UNITÉS

Veuillez choisir les unités de concentration des matières en solution

Unités

○ Concentration massique (mg/L)
● Concentration molaire (M)

Fenêtre 7

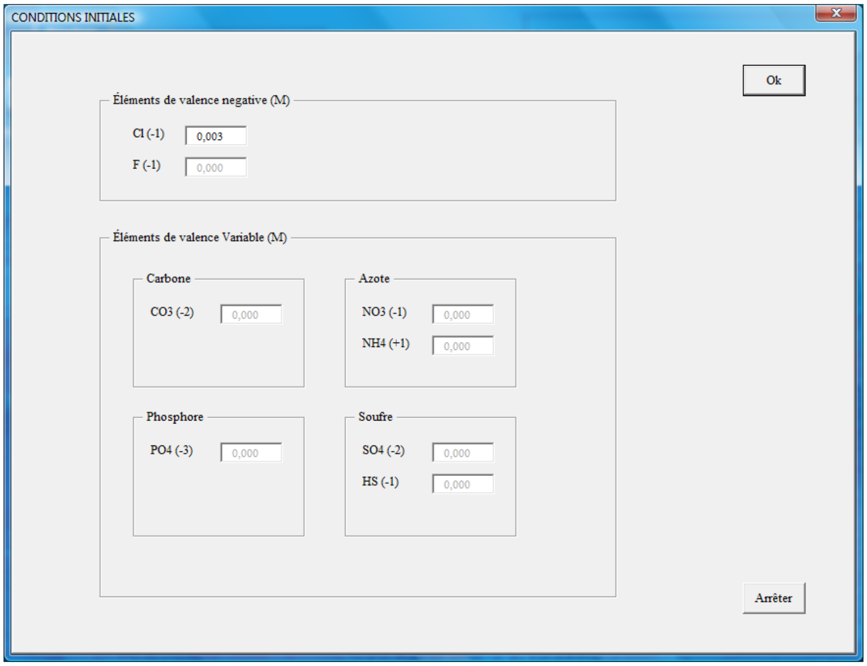


Éléments de valence positive (M)

Al (+3) 1,00E-3
Ba (+2) 0,00E+00
Be (+2) 0,00E+00
Ca (+2) 0,00E+00
Cd (+2) 0,00E+00
Co (+2) 0,00E+00
Cr (+3) 0,00E+00
Cr (+6) 0,00E+00
Cu (+2) 0,00E+00
Fe (+2) 0,00E+00

Fe (+3) 0,00E+00
K (+1) 0,00E+00
Mg (+2) 0,00E+00
Mn (+2) 0,00E+00
Na (+1) 0,00E+00
Ni (+2) 0,00E+00
Pb (+2) 0,00E+00
Sn (+2) 0,00E+00
Zn (+2) 0,00E+00

Fenêtre 8



Éléments de valence negative (M)

Cl (-1) 0,003
F (-1) 0,000

Éléments de valence Variable (M)

Carbone

CO3 (-2) 0,000

Azote

NO3 (-1) 0,000
NH4 (+1) 0,000

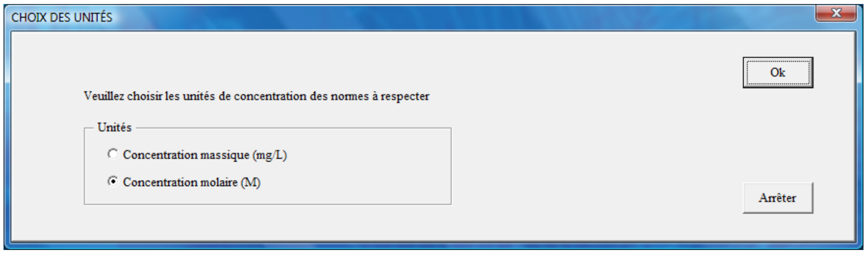
Phosphore

PO4 (-3) 0,000

Soufre

SO4 (-2) 0,000
HS (-1) 0,000

Fenêtre 9



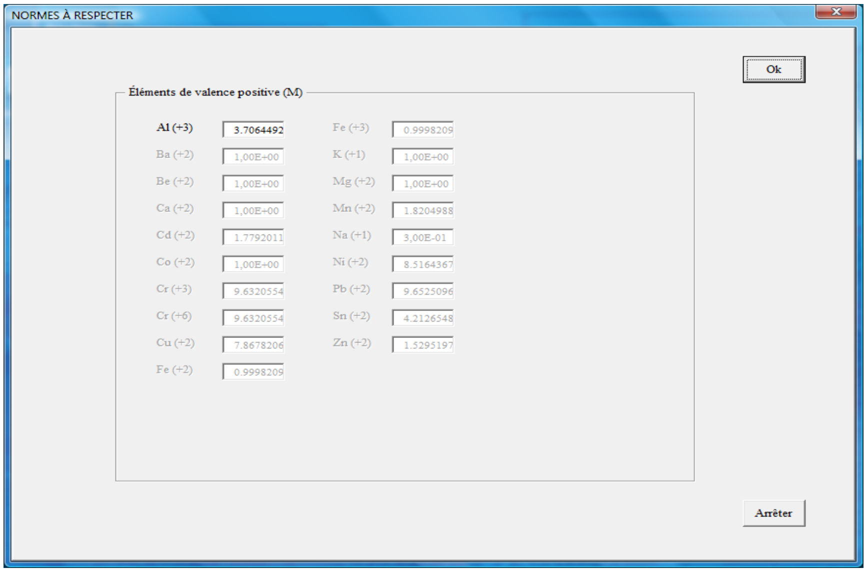
Veuillez choisir les unités de concentration des normes à respecter

Unités

○ Concentration massique (mg/L)

● Concentration molaire (M)

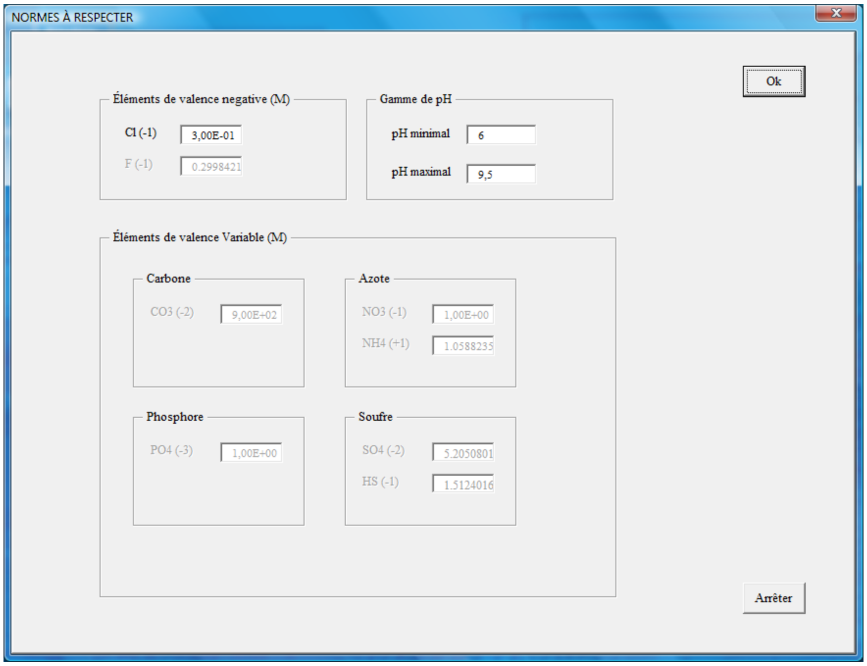
Fenêtre 10



Éléments de valence positive (M)

Al (+3)	3.7064492	Fe (+3)	0.9998209
Ba (+2)	1,00E+00	K (+1)	1,00E+00
Be (+2)	1,00E+00	Mg (+2)	1,00E+00
Ca (+2)	1,00E+00	Mn (+2)	1.8204988
Cd (+2)	1.7792011	Na (+1)	3,00E-01
Co (+2)	1,00E+00	Ni (+2)	8.5164367
Cr (+3)	9.6320554	Pb (+2)	9.6525096
Cr (+6)	9.6320554	Sn (+2)	4.2126548
Cu (+2)	7.8678206	Zn (+2)	1.5295197
Fe (+2)	0.9998209		

Fenêtre 11



Éléments de valence negative (M)

Cl (-1) 3,00E-01

F (-1) 0.2998421

Gamme de pH

pH minimal 6

pH maximal 9,5

Éléments de valence Variable (M)

Carbone

CO3 (-2) 9,00E+02

Azote

NO3 (-1) 1,00E+00

NH4 (+1) 1.0588235

Phosphore

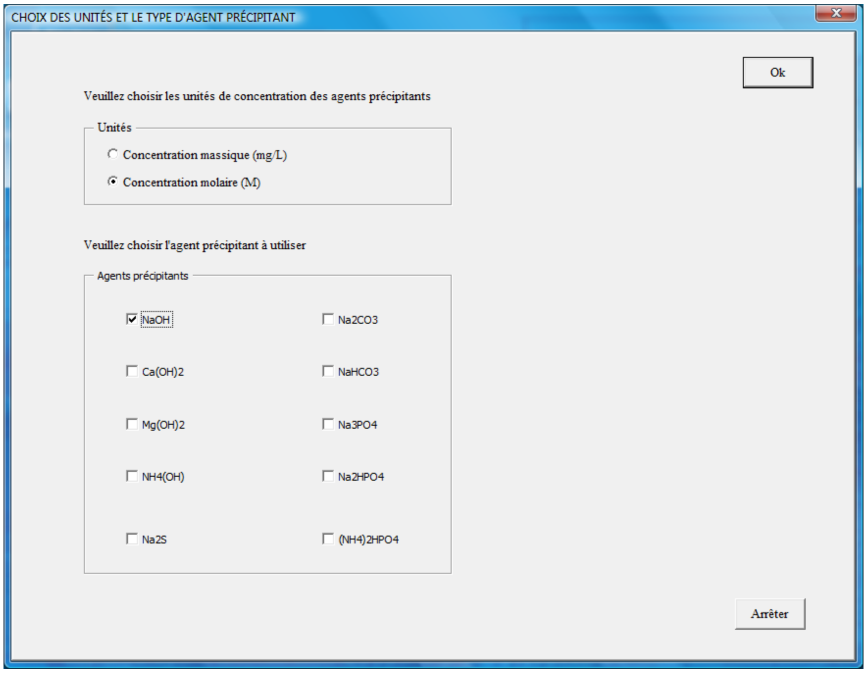
PO4 (-3) 1,00E+00

Soufre

SO4 (-2) 5.2050801

HS (-1) 1.5124016

Fenêtre 12



Veuillez choisir les unités de concentration des agents précipitants

Unités

○ Concentration massique (mg/L)

● Concentration molaire (M)

Veuillez choisir l'agent précipitant à utiliser

Agents précipitants

☑ NaOH

☐ Ca(OH)2

☐ Mg(OH)2

☐ NH4(OH)

☐ Na2S

☐ Na2CO3

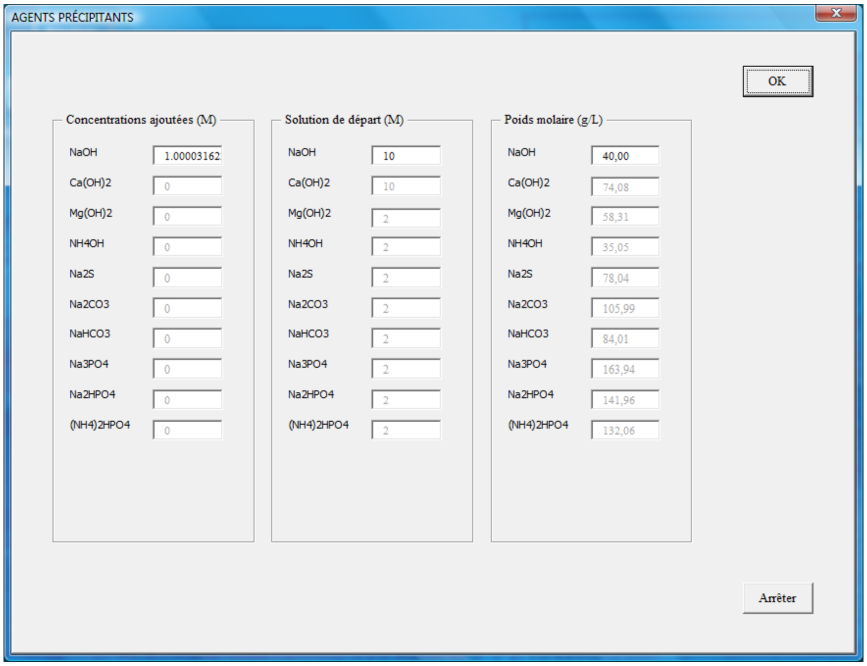
☐ NaHCO3

☐ Na3PO4

☐ Na2HPO4

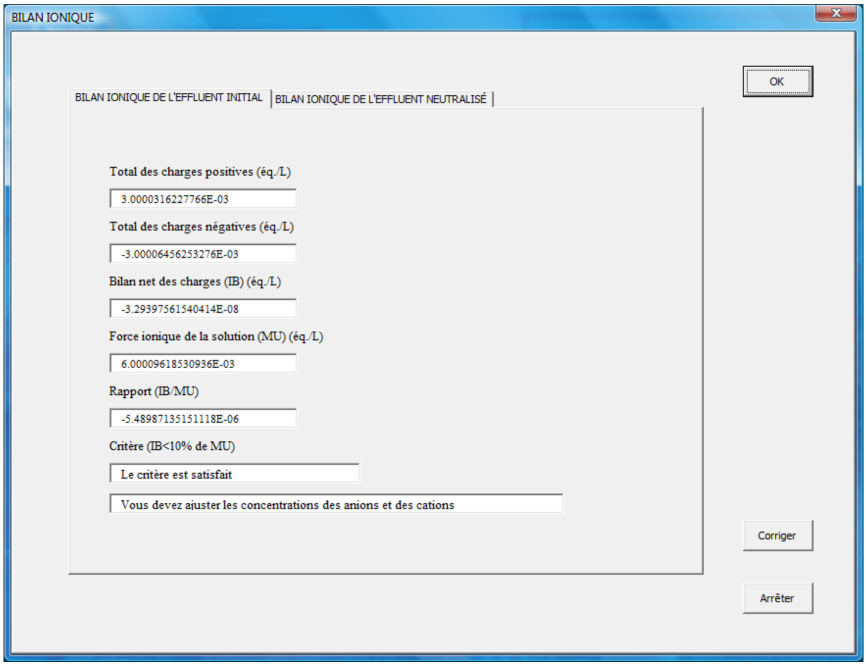
☐ (NH4)2HPO4

Fenêtre 13



	Concentrations ajoutées (M)	Solution de départ (M)	Poids molaire (g/L)
NaOH	1.00003162	10	40,00
Ca(OH)2	0	10	74,08
Mg(OH)2	0	2	58,31
NH4OH	0	2	35,05
Na2S	0	2	78,04
Na2CO3	0	2	105,99
NaHCO3	0	2	84,01
Na3PO4	0	2	163,94
Na2HPO4	0	2	141,96
(NH4)2HPO4	0	2	132,06

Fenêtre 14



Total des charges positives (éq./L)
3.0000316227766E-03

Total des charges négatives (éq./L)
-3.00006456253276E-03

Bilan net des charges (IB) (éq./L)
-3.29397561540414E-08

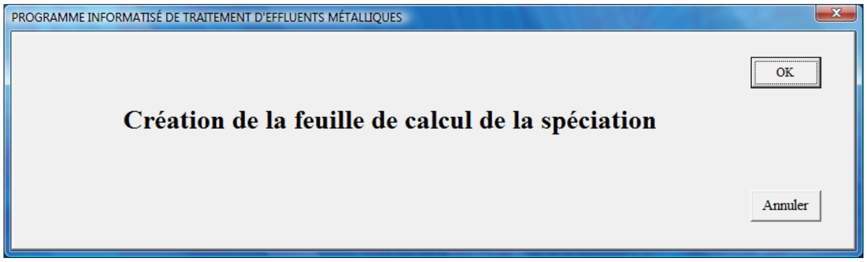
Force ionique de la solution (MU) (éq./L)
6.00009618530936E-03

Rapport (IB/MU)
-5.48987135151118E-06

Critère (IB<10% de MU)
Le critère est satisfait

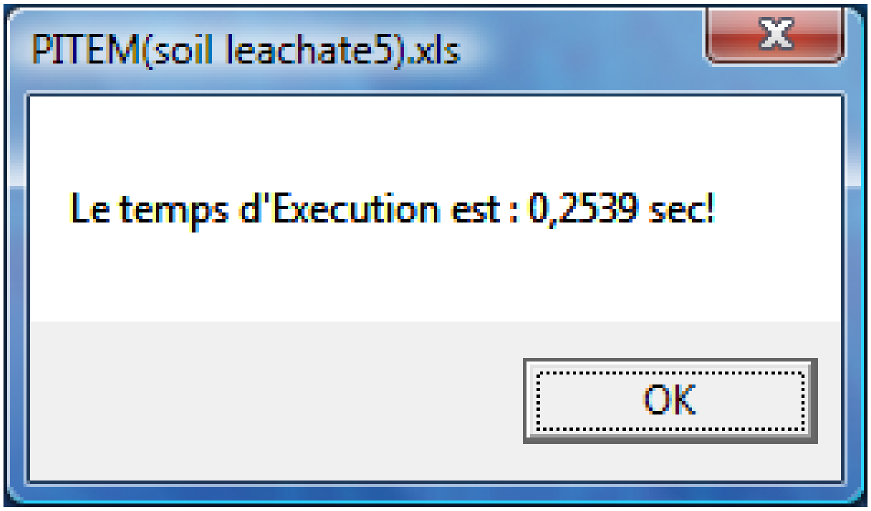
Vous devez ajuster les concentrations des anions et des cations

Fenêtre 15



Création de la feuille de calcul de la spéciation

Fenêtre 16



Le temps d'Execution est : 0,2539 sec!