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ENLÈVEMENT ET RÉCUPÉRATION DU CHROME (III) DES BOUES DE TANNERIE

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1. Shen S., R.D. Tyagi et J.F. Blais (2001) Extraction of Cr(III) and other metals from tannery sludge by mineral acids. *Environ. Technol.* **22**, 1007-1014.

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RÉSUMÉ

Malgré les teneurs élevées en Cr(III) dans les boues de tannerie, la plupart de celles-ci sont encore disposées par enfouissement partout dans le monde par manque de méthodes appropriées de traitement. Depuis le début des années 90, la récupération du Cr(III) des boues de tannerie a été étudiée par différents chercheurs. Les concentrations élevées en Al, Fe, Ca, Mg et Zn dans l'agent tannant sont nuisibles aux propriétés du cuir tanné. Pour faciliter l'enlèvement du chrome des boues de tannerie et recycler le chrome comme agent tannant, ces cinq métaux doivent d'abord être enlevés autant que possible de l'extrait acide des boues de tannerie.

Cette étude a permis, dans un premier temps, d'établir les conditions optimales d'extraction du Cr(III) à partir des boues de tannerie en utilisant l'acide sulfurique. Ainsi, l'effet de divers paramètres (le temps d'extraction, le type d'acides minéraux, la consommation de l'acide, le pH, la concentration en solides des boues, la température et le type des boues) sur les rendements de lixiviation des métaux a été étudié. Les résultats ont montré que l'efficacité maximum d'extraction du Cr(III) des boues de tannerie se situe aux environs de 90 %. Les résultats ont aussi indiqué qu'une période de 2 h est suffisante pour l'extraction de la plupart des métaux à partir des boues de tannerie. De plus, cette étude a révélé que l'acide sulfurique constitue l'acide inorganique le plus intéressant, sur le plan coût/efficacité, pour l'extraction du chrome à partir de ce type de boues. Les différents tests effectués ont montré que la gamme optimale de pH pour l'extraction du chrome se situe entre 2.0 et 3.0. De même, selon les tests réalisés la concentration optimale en solides des boues pour l'extraction du Cr(III) se situe aux environs de 75-80 g/L. Également, les essais de lixiviation conduits à différentes températures ont démontré que le rendement d'extraction du chrome diminue avec la hausse de la température des boues. Finalement, le type des boues traitées (humides ou séchées) n'a aucun effet sur le rendement de lixiviation du Cr(III).

Pour expliquer les observations expérimentales et fournir la base théorique des conditions optimales d'extraction du chrome, des calculs thermodynamiques ont été effectués afin de définir les précipités pouvant être formés lors du procédé d'extraction en milieu acide. L'énergie libre de Gibbs ($\Delta G = RT\ln(Qc/Kc)$) de précipitation a été employée pour examiner la formation des précipités pendant le procédé de lixiviation. Les constantes d'équilibre d'activité (Ka) de diverses précipitations ont été tirées de la littérature. Les valeurs de Ka ont été corrigées pour obtenir les valeurs correspondantes du produit de concentration (Qc) et de la constante d'équilibre de concentration (Kc) en utilisant les coefficients d'activité (γ) d'ions. Ces calculs ont proposé que les composés suivants peuvent être formés : (am)$Cr(OH)_3$, (am)$CrPO_4$, (am)$Fe(OH)_3$, α-FeOOH (goethite), $FePO_4 \cdot 2H_2O$, (am)$AlPO_4 \cdot 2H_2O$ et $CaSO_4 \cdot 2H_2O$ (gypse). Les solubilités de ces précipités diminuent avec la hausse de la force ionique (ou la concentration en solides des boues). Les résultats des calculs ont été appuyés par les observations expérimentales.

Par la suite, l'isolement du Cr(III) à partir du lixiviat acide (extrait acide) contenant également d'autres métaux (Al, Fe(III), Ca, Mg et Zn) a été étudié et a conduit au développement d'un nouveau procédé. Cette technologie inclut la dilution du lixiviat, l'enlèvement de l'Al et du Fe par précipitation d'hydroxydes à pH 4.0-5.0, l'enlèvement de l'Al et du Fe résiduels, ainsi que du Zn par leur précipitation avec un agent organique (cupferron), la séparation du Cr(III) du Ca et du Mg par une précipitation à pH 6.0-8.0. Enfin, le Cr(III) isolé est obtenu sous forme d'un précipité d'hydroxyde ($Cr(OH)_3$). Ce procédé simple est fort intéressant puisqu'il ne nécessite pas l'oxydation du Cr(III) en Cr(VI) et l'utilisation de résines échangeuses d'ions. De plus, le cupferron utilisé peut être récupéré et réutilisé.

Un essai pilote sur l'isolement du Cr(III) a également été exécuté. Environ 450 g de boues séchées de tannerie (équivalent à 1490 g de boues humides) a été utilisé dans l'essai. Le volume utile du réacteur était de 30 L. Un rendement global de récupération du Cr(III) de 44 % (25.7 g) a été mesuré dans le précipité final contenant le $Cr(OH)_3$. Le taux molaire relatif d'Al, du Ca, du Cr, du Fe, du Mg et du Zn dans le précipité était 3.8, 1.8, 100.0, 0.8, 3.3 et 0.2, respectivement. La concentration en Cr dans ce produit est de 32.5 % et le rapport des concentrations des métaux nuisibles par rapport au Cr ((Al + Fe + Ca + Mg + Zn)/5Cr) est inférieur ou égal à 0.02. Un tel concentré de Cr(III) peut être non seulement utilisé en tant qu'agent tannant, mais également peut être utilisé dans la préparation de pigments, d'acier inoxydable, de matériaux réfractaires et de catalyseurs.

Il a été observé qu'une grande quantité d'acide sulfurique est requise pour extraire le Cr(III), ce qui augmente le coût d'extraction du chrome. Pour contrer ce problème, la solubilisation du chrome a été étudiée par un procédé de biolixiviation utilisant des bactéries oxydant le soufre élémentaire en acide sulfurique. Le dénombrement des bactéries oxydant le soufre élémentaire a montré que les thiobacilles acidophiles contribuent davantage à la réduction du pH dans les boues de tannerie que les thiobacilles peu-acidophiles. Malgré l'atteinte d'une concentration élevée en Cr(III) (aussi élevée que 5 930 mg/L), aucun effet toxique n'a été décelé sur les bactéries oxydant le soufre (thiobacilles). De plus, les bactéries oxydant le soufre élémentaire ont pu vivre dans les boues de tannerie à un pH aussi faible que 0.48 à 21°C. Une concentration en solides de 60 g/L a pu être utilisée avec succès, toutefois, une concentration de 40 g/L s'avère être la teneur optimale en solides pour l'opération du procédé de biolixiviation. D'autre part, les essais effectués ont montré que la concentration optimale, d'un point de vue économique, de soufre élémentaire ajouté pour la biolixiviation du Cr(III) se situe à 20 g/L. L'efficacité d'extraction du chrome par le procédé biologique s'est avérée comparable à celle du procédé chimique avec l'acide sulfurique, tandis que le coût des produits chimiques requis pour le procédé biologique est seulement 28 % de celui du procédé chimique. Cette étude constitue donc la première démonstration de l'efficacité de la biolixiviation avec soufre élémentaire pour l'extraction du chrome des boues de tannerie.

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SYNTHÈSE

1 SYNTHÈSE

1.1 Revue de la littérature

1.1.1 Production des boues de tannerie

Le chrome trivalent, typiquement le sulfate hydraté de Cr(III), est utilisé en grande quantité dans l'industrie de tannage des peaux. Les tanneries consomment environ 32 % des composés chromés distribués dans le commerce mondial (Walsh et John, 1996). Cependant, près de 50 % des sels chromiques produits par les tanneries sont rejetés sous forme de boues ou d'eaux usées (Tiravanti *et al.,* 1997).

La fabrication du cuir tanné par le Cr(III) comprend plusieurs d'étapes. Les peaux sont d'abord préparées par des traitements mécaniques et chimiques. Ces opérations produisent beaucoup d'effluents contenant des teneurs élevées en DBO, en protéines insolubles, en sels et en sulfures à un pH élevé (> 11) (Walsh et John, 1996).

Après ces opérations, le tannage comme tel est exécuté. Les peaux sont tambourinées dans une solution de réactif tannant (8.9 à 17.8 g/L de Cr(III), 33 % de l'alcalinité de Schorlemmer, pH 2.0 à 3.8) (Randall, 1985).

Les effluents basiques et acides sont habituellement mélangés afin de les neutraliser. Ce processus entraîne la précipitation de composés métalliques (Walsh et John, 1996) et donne naissance aux boues de tannerie. Ces boues sont habituellement déshydratées mécaniquement avant leur disposition finale.

1.1.2 Enfouissement et incinération des boues de tannerie

Malgré la concentration très élevée en Cr(III) dans les boues de tannerie, la plupart de ces résidus industriels sont encore disposés par enfouissement et ce, par manque de méthodes appropriées de traitement. L'incinération, quoique rarement utilisée, constitue aussi une voie de disposition des boues de tannerie. La plupart des méthodes d'incinération rapportées dans les brevets entraînent l'émission de gaz toxiques. Récemment, une technologie améliorée d'incinération, appelée Enersludge, a été développée en Allemagne (Skrypski-Mantele et Bride, 1995). Avec cette technologie, la plupart des métaux se retrouvent dans les cendres sous forme de sulfures. Un tel procédé nécessite cependant des équipements coûteux peu compatibles avec l'exploitation d'une tannerie.

1.1.3 Méthodes d'enlèvement du chrome des boues de tannerie

Macchi *et al.* (1991) ont étudié les effets du type d'acide (HCl, HNO_3 et H_2SO_4) et du pH sur l'extraction du Cr(III) à partir des boues de tannerie. Aucune différence significative n'a été observée avec l'emploi des différents acides. Cette étude a montré que la solubilisation du Cr(III) s'accroît avec la réduction du pH. Près 90 % du Cr(III) dans les boues a été extrait à pH 1. Chuan et Liu (1996) ont étudié l'influence du potentiel d'oxydo-réduction sur la mise en solution du Cr(III) à partir des boues de tannerie. Ces chercheurs ont également établi qu'à pH 4.2, la solubilité du Cr(III) diminue avec la hausse du potentiel d'oxydo-réduction de 0 à 470 mV. Ils ont aussi conclu que la réaction de précipitation-dissolution contrôle le comportement du Cr(III) dans les boues de tannerie. Les autres facteurs contrôlant la mise en solution du chrome et des autres métaux dans les boues de tannerie ne semblent pas avoir été étudiés.

1.1.4 Méthodes de séparation du chrome des boues de tannerie

La récupération du Cr(III) dans les boues de tannerie peut présenter un intérêt économique considérant les fortes teneurs en chrome dans ce résidu. De plus, la récupération du chrome est évidemment souhaitable du point de vue environnemental. La récupération du chrome dans les boues de tannerie est toutefois rendu compliquée par la présence d'autres métaux dont : Al, Fe(III), Ca, Mg, et Zn. L'espèce majeure de fer dans les boues de tannerie est le Fe(III), alors que la teneur en Fe(II) est habituellement très basse. En plus du Cr(III), les autres métaux, surtout le Al(III) et le Fe(III), peuvent aussi être adsorbés sur les peaux lors du tannage et ont ainsi des effets défavorables sur la qualité des cuirs. Par exemple, la présence de sels d'aluminium dans le réactif tannant peut sécher le cuir, ce qui rendra celui-ci dur et corné (Randall, 1985). Bien sûr, la présence de faibles teneurs en autres métaux, surtout le Ca et le Mg, dans le réactif tannant ne nuit pas au traitement, puisque ceux-ci sont moins adsorbés par les peaux animales. Ces métaux (Ca et Mg) sont d'ailleurs généralement peu retenus par les biomasses (Blais *et al.,* 1999). Les travaux antérieurs ont donc visé principalement la séparation du Cr(III), du fer et de l'aluminium. Les méthodes suivantes ont été étudiées pour séparer le Cr(III) des autres métaux dans les lixiviats acides des boues de tannerie ou dans les eaux usées de tannerie.

1.1.4.1 Séparation du chrome des autres métaux par oxydation du Cr(III)

Macchi *et al.* (1991) ont séparé le Cr(III) des autres métaux dans le lixiviat acide des boues de tannerie en oxydant le Cr(III) en Cr(VI) au moyen de H_2O_2 à pH 10. Le schéma du procédé est présenté à la Figure 1.1. Les problèmes majeurs liés à ce procédé sont les suivants:

1. Dans ce procédé, le Cr(III) est oxydé en Cr(VI), lequel est très toxique. Du Cr(VI) est inévitablement déchargé à l'environnement avec les précipités et les eaux usées produites à partir de ce procédé;

2. Il a été rapporté que le rendement d'oxydation du Cr(III) dépend de la concentration en Fe et en Mg dans la solution. Si le ratio molaire (Fe+Mg)/Cr est de 0.8, le ratio molaire H_2O_2/Cr est alors de 7 et le rendement d'oxydation se situe à environ 83 %; Si le ratio molaire (Fe+Mg)/Cr est de 8, le ratio molaire H_2O_2/Cr sera alors de 80 et le rendement d'oxydation chutera à 70 %. En général, le rendement d'oxydation du Cr(III) est bas et beaucoup de H_2O_2 est consommé pour l'oxydation du Cr(III). Ceci résulte en un coût élevé pour le traitement des boues de tannerie;

3. Une résine échangeuse d'ions est nécessaire également pour séparer le Cr(VI) du Ca et du Mg.

4. Le dioxide de soufre, un gaz toxique, est utilisé afin de convertir le Cr(VI) en Cr(III).

1.1.4.2 Séparation du chrome des autres métaux par échange ionique

Tiravanti *et al.* (1997) ont rapporté la séparation du Cr(III) du Fe(III) et de l'Al par une résine d'échange cationique (Purolite C106). Le Cr(III), le Al(III) et le Fe(III) dans la solution sont adsorbés sur la résine entre pH 8.5 et 9. Ensuite, un éluant alcalin (0.15 M H_2O_2, 1 M NaCl, 0.1 M NaOH, pH 12) est passé dans le colonne. Une fraction du Cr(III) adsorbé sur la résine est oxydée en anions CrO_4^{2-} et est élué du système. Le Al(III) est aussi converti en l'$Al(OH)_4^-$ et est libéré de la colonne. Seulement le Fe(III) demeure retenu sur la résine. En ajustant par la suite le pH de l'éluat à 8.5 le $Al(OH)_4^-$ présent dans l'éluat peut être précipité sous forme de l'$Al(OH)_3$ et ainsi séparé du CrO_4^{2-}. Les problèmes majeurs inhérents à cette méthode sont les suivants :

1. Le Cr(III) doit être oxydé en Cr(VI) afin de régénérer la résine et aussi séparer le Cr(III) de Al et Fe;

2. La vitesse d'adsorption du Cr(III) sur la résine est lente;

3. L'opération d'adsorption doit être exécutée dans une gamme étroite de pH, soit de 8.5 à 9;

4. Le rendement de l'oxydation du Cr(III) et la consommation du H_2O_2 n'ont pas été rapportés;

5. Les substances organiques (les protéines, les acides graisseux des chaînes longues, phénols) et l'oxydant (H_2O_2) peuvent polluer et oxyder la résine. Ceci raccourcit la durée de vie de la résine;

6. Ce procédé requiert une quantité appréciable de résine d'échange d'ion, ce qui fait en sorte d'entraîner des coûts d'opération élevés.

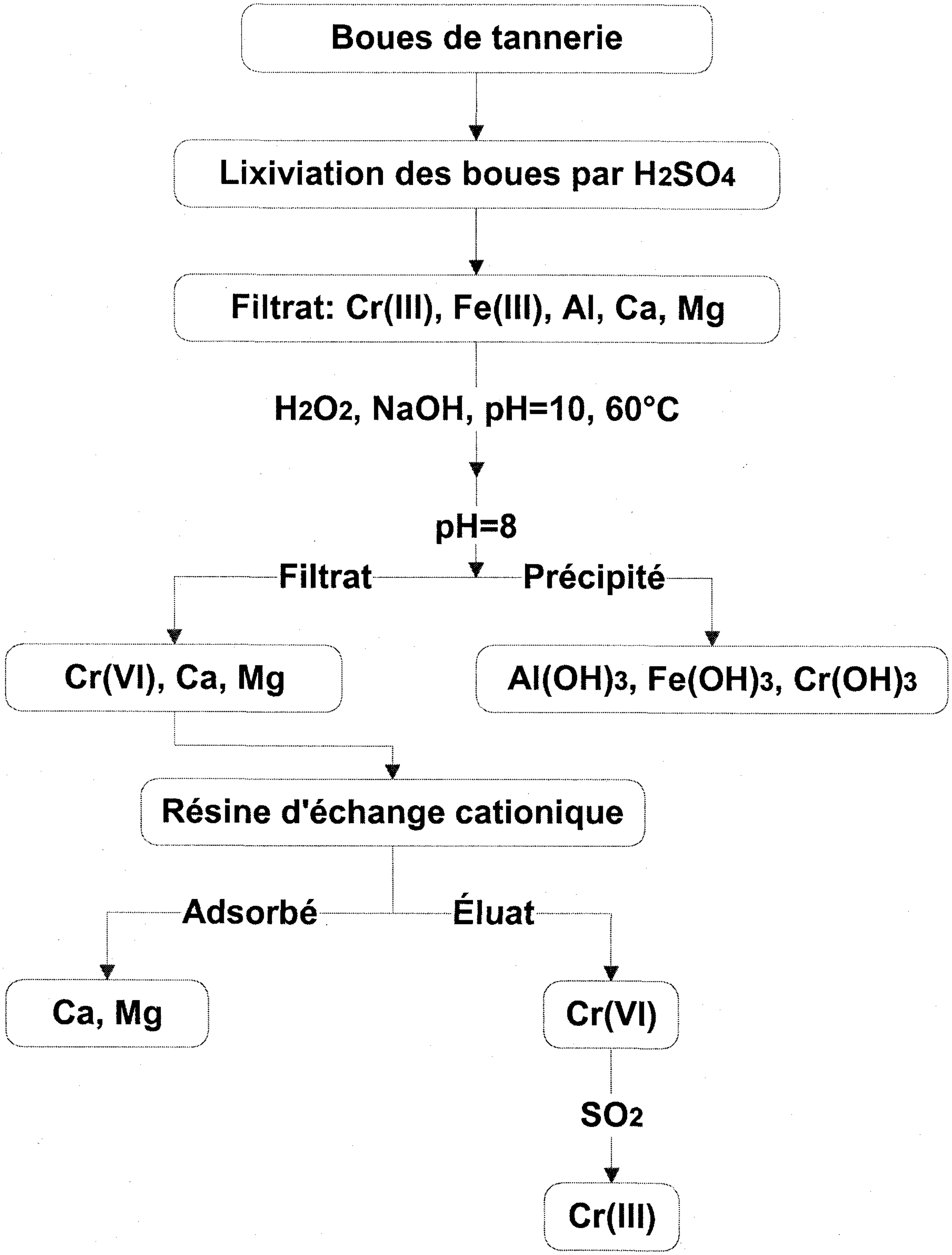

Figure 1.1 **Procédé de l'isolement du Cr(III) suggéré par Macchi et al. (1991)**

1.1.4.3 Séparation du Cr(III) de l'Al et du Fe(III) par le réactif organique cupferron

Majone (1986) a rapporté la séparation du Cr(III) de l'Al(III) et du Fe(III) dans les eaux usées de tannerie. La séparation a été faite au moyen du réactif organique cupferron. Seulement l'Al et le Fe(III) peuvent former des précipités stœchiométriques avec le cupferron. Le Cr(III) n'est pas précipité dans ce cas. Les réactions de précipitation ont lieu entre pH 2.5 et pH 4.0. Les réactions sont complétées en une demi-heure et les précipités de l'Al et du Fe peuvent être enlevés facilement par filtration. La récupération du cupferron peut être réalisée en redissolvant les précipités formés dans une solution alcaline. Le pourcentage de récupération varie de 50 % à 80 %. Le pourcentage de récupération diminue avec la hausse de la concentration de fer. Ce procédé pourrait être prometteur si le pourcentage de récupération pouvait être augmenté. Il faut noter toutefois que le cupferron est un produit toxique.

1.1.5 Propriétés et préparation du réactif tannant

Le sulfate alcalin hydraté du Cr(III) est employé largement comme réactif tannant du cuir. Ce type du sel est hydrolysé et le pH de la solution se situe aux environs de 2. L'ion pentaaquohydrochro(III) $[Cr(H_2O)_5(OH)]^{2+}$ est habituellement formé dans une telle solution. La réaction correspondante est la suivante: $[Cr(H_2O)_6]^{3+}+OH = [Cr(H_2O)_5(OH)]^{2+}+H^+$ (Habashi, 1997). La formule du sulfate alcalin du Cr(III) se définie parfois par $Cr(OH)SO_4$. La propriété du réactif tannant est habituellement représentée par son alcalinité de Schorlemmer. Le réactif tannant doit avoir une alcalinité de Schorlemmer de 33 % ou plus. L'alcalinité de Schorlemmer d'une solution peut être mesurée au laboratoire selon une méthode recommandée (ASTM, 1996). Le pH du réactif tannant en solution a une influence importante sur le tannage des peaux. Le pH favorable au tannage des peaux se situe entre 2.0 et 3.8. À un pH plus élevé, une précipitation du composé de chrome(III) a lieu. Le processus tannant est ainsi empêché lorsque le pH de la solution est supérieur à 4.5. À un pH plus faible, le Cr(III) n'est pas adsorbé sur les peaux

(Randall, 1986). Le poids du Cr(III) utilisé est de 5 % à 10 % de celui des peaux. Cela équivaut à une solution contentant de 8.9 à 17.8 g/L de Cr(III) (Panswad *et al.*, 1995).

Les réactifs tannants se divisent en deux types; L'un est une poudre et l'autre est une solution. Afin de faciliter le transport, le réactif tannant est habituellement fabriqué et distribué en poudre. Cependant, la solubilité de la poudre tannante dans l'eau est faible. Des substances organiques doivent donc être ajoutées à la poudre tannante afin d'augmenter sa solubilité (Habashi, 1997). D'autre part, la fabrication du réactif tannant en solution est plus simple. Notamment, le réactif tannant en solution fabriqué à partir du Cr(III) récupéré des boues de tannerie peut être utilisé directement pour le tannage des peaux (Panswad *et al.*, 1995).

1.1.6 Utilisation des composés de chrome (III)

Le chrome (III) est utilisé dans les alliages ferreux et non ferreux, ainsi que dans divers produits chimiques. Le chrome augmente la durabilité et la résistance aux impacts et réduit la corrosion et l'usure des alliages. Les alliages ferreux, principalement les aciers inoxydables, représentent la majeure partie de la consommation. Les produits chimiques du chrome (III) sont également largement utilisés dans d'autres industries. La plus grande quantité est consommée pour fabriquer des pigments pour les peintures et les encres. D'autres applications incluent le tannage des cuirs, l'inhibition de la corrosion des métaux, les colorants du textile, les catalyseurs, etc.

1.1.7 Toxicologie et santé

Seuls les composés hexavalents de chrome sont actifs biologiquement. Le chrome métallique et les composés trivalents, y compris ceux dans les minéraux de chrome, ne sont ni irritants, ni mutagéniques, ni cancérogéniques (Habashi, 1997).

1.1.7.1 Effets aiguës

Les effets d'une plus longue exposition aux composés hexavalents de chrome varient de l'irritation de la membrane muqueuse nasale à la formation des ulcères et des perforations du septum nasal (Habashi, 1997). Une concentration plus élevée en Cr(VI) irrite la membrane muqueuse bronchique, menant de ce fait à la bronchite. La pénétration des particules de chrome hexavalent dans de petits défauts de peau cause des ulcères qui guérissent difficilement. L'absorption du Cr(VI) cause des inflammations intestinales sérieuses, parfois avec perte de sang (Habashi, 1997).

1.1.7.2 Effets chroniques

L'irritation chroniques de la membrane muqueuse nasale peut mener à son atrophie. La bronchite chronique a été enregistrée après une exposition à long terme aux composés hexavalent de chrome (Habashi, 1997). Les composés hexavalents de chrome sont capables de sensibiliser la peau fortement, qui peut mener aux eczemas chroniques, en particulier quand la source est la poussière de ciment contenant du chrome (VI).

1.1.7.3 Cancérogénicité

Beaucoup d'expériences sur des animaux ont été effectués pour tester la cancérogénicité des composés de chrome. Ceux-ci incluent l'injection sous-cutanée, l'inhalation, l'instillation intra-trachéale, ainsi que l'introduction de granules dans l'arbre bronchique (Habashi, 1997). Selon ces expériences, les composés hexavalents du chrome doivent être classés comme étant cancérogènes.

1.2 Objectifs de recherche

La présence de teneurs élevées en Cr(III) dans les boues de tannerie représente un risque potentiel pour l'environnement. Une oxydation du Cr(III) en Cr(VI) catalysée par le MnO_2 présent dans les sols a d'ailleurs été rapportée précédemment (Eary et Rai, 1987; Nakayama *et al.,* 1981). Toutefois, la plupart des boues de tannerie dans le monde sont encore disposées par enfouissement par manque de méthodes appropriées de valorisation. Et ce, même si l'enfouissement est de plus en plus remis en question à cause de la saturation progressive des sites de disposition.

La récupération du Cr(III) des boues de tannerie est une voie prometteuse de valorisation de ce résidu industriel. Un tel procédé comprend habituellement trois étapes :

1. La mise en solution du Cr(III) des boues de tannerie;
2. La séparation du Cr(III) des autres métaux également solubilisés;
3. La transformation du Cr(III) isolé en un réactif tannant.

D'après les discussions précédentes, les problèmes rencontrés aux étapes (1) et (2) sont résumés ci-dessous.

Les problèmes associés à l'étape (1):

1. Peu de travaux ont été menés pour établir les conditions optimales de mise en solution du Cr(III) à partir des boues de tannerie par la lixiviation chimique;
2. Une consommation excessive d'acide est requise pendant la lixiviation chimique;
3. Il n'existe pas d'information concernant les précipités générés lors du processus de lixiviation du chrome.

Les problèmes inhérents à l'étape (2):

1. Jusqu'à présent, la plupart des méthodes proposées emploient l'oxydation du Cr(III) en Cr(VI) au moyen de H_2O_2 et ce, afin de séparer le Cr(III) des autres métaux. Le Cr(VI) est très toxique et est préoccupant pour l'environnement;
2. Le rendement d'oxydation du Cr(III) est souvent faible et beaucoup de H_2O_2 est consommé. Ceci résulte en un coût élevé pour le traitement des boues de tannerie;

3. Le dioxide de soufre, un gaz toxique, est habituellement utilisé pour convertir le Cr(VI) au Cr(III);

4. La plupart des méthodes de séparation proposées adoptent des résines échangeuses d'ions afin de séparer le chrome des autres métaux. Un tel procédé de séparation est habituellement coûteux;

5. Lors de la séparation de Al, Fe(III) et de Cr(III) par le réactif organique cupferron, le pourcentage de récupération du cupferron est faible à cause de la présence du Fe(III).

Le présent projet de doctorat vise donc à développer une nouvelle méthode simple, efficace et économique pour enlever et récupérer le Cr(III) des boues de tannerie.

1.2.1 Objectifs spécifiques

Les objectifs spécifiques associés à l'étude et au développement des concepts technologiques peuvent être résumés ainsi :

1. Déterminer les conditions optimales pour l'extraction chimique du Cr(III) des boues de tannerie par les acides minéraux;

2. Étudier à l'aide de calculs thermodynamiques la formation des divers complexes et précipités et ce, afin de cibler les conditions optimales pour l'extraction chimique et la séparation chimique des métaux;

3. Développer une nouvelle méthode pour la séparation du Cr(III) des autres métaux;

4. Développer une nouvelle méthode pour l'extraction microbienne du Cr(III) des boues de tannerie afin de diminuer le coût de l'extraction.

1.2.1.1 Déterminer les conditions optimales pour l'extraction du Cr(III) des boues de tannerie

L'enlèvement et la récupération du chrome des boues de tannerie nécessitent invariablement une mise en solution de ce métal. Pour cette étape, l'objectif visé consiste à obtenir la meilleure solubilisation du chrome en minimisant le plus possible la mise en solution des autres métaux et éléments constituant les boues de tannerie.

En ce qui concerne la lixiviation en milieu acide, les paramètres à optimiser sont le type d'acide utilisé, le pH de réaction, le temps d'extraction, la température et la concentration en solides des boues. La consommation d'acide représente un aspect important à considérer, ainsi que la possibilité de ré-utilisation de l'acide.

1.2.1.2 Étudier à l'aide de calculs thermodynamiques la formation des divers complexes et précipités

La mise au point des procédés discutés précédemment requiert impérativement de pouvoir prédire les conditions optimales (le pH, la température, la concentration en solides) dans lesquelles les métaux peuvent être soit solubilisés ou encore précipités.

Bien que les conditions appropriées de lixiviation puissent être trouvées par les moyens expérimentaux, les facteurs (la formation des précipités des métaux, l'adsorption des métaux sur des solides des boues) qui déterminent ces conditions de lixiviation optimales sont inconnus.

Les calculs thermodynamiques seront donc employés pour prédire le comportement des métaux lors de l'étape de lixiviation chimique des boues de tannerie. En autre, cette approche permet :

1. D'explorer les complexes et les précipités de métaux pouvant se former pendant le processus de lixiviation;

2. D'étudier l'influence des forces ioniques en jeu lors de l'étape de lixiviation sur la formation des diverses espèces chimiques.

D'autre part, les calculs thermodynamiques peuvent également être exploités pour la prédiction des précipités générés lors des étapes de séparation des métaux. Cette approche peut, entre autres, permettre de rencontrer l'objectif suivant:

Déterminer le pH, la concentration en solides et la température auxquels le Cr(III) et l'Al peuvent être séparés des autres métaux.

1.2.1.3 Développer une nouvelle méthode pour la séparation du Cr(III) des autres métaux

La plupart des méthodes répertoriées dans la littérature nécessitent l'oxydation du Cr(III) en Cr(VI) au moyen de H_2O_2 et ce, afin de séparer le Cr(III) des autres métaux. Afin d'éviter cette transformation, il faut développer de nouvelles méthodes pour séparer le Cr(III) des autres métaux.

1.2.1.4 Développer une nouvelle méthode pour l'extraction microbienne du Cr(III) des boues de tannerie

Une grande quantité d'acide sulfurique est nécessaire pour extraire le Cr(III) à partir des boues de tannerie. Il est donc nécessaire d'explorer une autre voie plus économique pour extraire le Cr(III) des boues de tannerie. L'enlèvement des métaux présents dans les boues d'épuration municipales a été étudié par utilisation de bactéries oxydant le soufre élémentaire (Tyagi *et al.,* 1988, 1993, 1994, 1996, 1997; Blais *et al.,* 1992a, b, c, 1993). Tyagi *et al.* (1988) ont montré que les coûts des produits chimiques associés à la biolixiviation des métaux par les bactéries oxydant le soufre étaient 80 % plus faibles que ceux associés à la lixiviation chimique. Cette méthode de biolixiviation doit donc être étudiée pour l'extraction du chrome (III) des boues de tannerie.

1.3 Matériels et méthodes

Les informations concernant la méthodologie sont décrites dans les six articles issus de cette recherche (voir chapitres 2 à 7).

1.4 Résultats et discussion

Les travaux réalisés jusqu'à présent ont permis d'étudier adéquatement le procédé , soit 1) la lixiviation chimique des métaux des boues de tannerie , 2) la prédiction de la formation des précipités des métaux pendant la lixiviation chimique basé sur les calculs thermodynamiques, 3) l'isolement du Cr(III) des autres métaux des boues de tannerie et 4) la biolixiviation du Cr(III) et des autres métaux des boues de tannerie par les bactéries indigènes oxydant le soufre élémentaire. Les résultats expérimentaux sont présentés dans les articles. Les sections suivantes discutent sommairement de ces résultats.

1.4.1 Lixiviation chimique des métaux des boues de tannerie

Macchi *et al.* (1991) ont trouvé que le type d'acides minéraux (HCl, HNO_3 et H_2SO_4) n'a aucun effet sur l'extraction du Cr(III) à partir des boues séchées de tannerie et qu'environ 90 % du Cr(III) peut être extrait à pH 1. Ces résultats sont similaires à la présente étude. Il est suggéré que l'adsorption et la liaison du Cr(III) sur les matières colloïdales organiques insolubles, ainsi que la formation des précipités des métaux constituent deux raisons pour la perte du Cr(III) pendant le procédé de lixiviation.

Il semble que les rendements d'extraction des autres métaux nuisibles (Al, Fe, Ca, Mg et Zn) n'ont pas été étudiés auparavant. L'essai d'extraction avec trois types des acides (HCl, HNO_3 et H_2SO_4) n'a pas montré des différences apparentes sur les rendements d'extraction du Fe, de l'Al, du Mg et du Zn. Les meilleurs rendements de solubilisation du Cr(III) ont été atteints par utilisation de l'acide sulfurique. Il y avait une grande différence de solubilisation du Ca avec les différents acides (10 % de solubilisation du Ca avec le H_2SO_4, 70 à 80 % avec le HCl ou avec le HNO_3). Le Ca est probablement enlevé comme précipité de $CaSO_4 \cdot 2H_2O$ lors de l'emploi du H_2SO_4 ce qui est un avantage indéniable.

1.4.2 Prédiction de la formation des précipités des métaux pendant la lixiviation chimique basé sur les calculs thermodynamiques

La confirmation des espèces de précipités de métaux par des moyens expérimentaux est très difficile. Les précipités tendent à être amorphes ($Cr(OH)_3$, $CrPO_4$ et $AlPO_4 \cdot 2H_2O$, par exemple) à la température ambiante et peuvent être facilement adsorbés par les autres solides insolubles. La quantité de précipités peut changer selon des conditions de fonctionnement d'un système. D'autre part, les données thermodynamiques (constante d'équilibre d'activité de la réaction de précipitation, par exemple) de presque toutes les réactions de précipitation des métaux sont disponibles dans la littérature. Les concentrations en ions précipités dans la solution aqueuse dans laquelle quelques réactions de précipitation ont eu lieu peut être déterminées avec précision par des méthodes chimiques. En principe, basé sur des données thermodynamiques et des concentrations ioniques mesurées, quelques espèces de précipités de métaux peuvent être déterminées ou prédites. L'objectif de la présente étude était de prédire thermodynamiquement la formation des précipités des métaux. Cette information a pu aider à développer une stratégie pour la séparation des métaux dans le lixiviat (la séparation du Ca et du Mg de Cr(III), par exemple).

Bien que des logiciels tel que MINEQL et HYDRAQL ont été développés pour étudier les espèces de précipités dans des solutions aqueuses, les conditions spécifiques suivantes du lixiviat de tannerie ont limité l'utilisation de ces logiciels.

- Présentement, il n'y a pas de traitement spécial qui présente progressivement le calcul de l'énergie libre de Gibbs $\Delta G=RT\ln(Qc/Kc)$ d'une réaction de précipitation dans une solution d'électrolyte dans laquelle l'effet de la concentration ionique n'est pas négligeable;

- Il n'est pas possible de suivre les calculs thermodynamiques d'une réaction de précipitation de manière progressive avec ces logiciels. Le processus du calcul thermodynamique est particulièrement compliqué, quelques approximations doivent être prises en compte. Il n'est pas possible de connaître comment ces approximations sont faites avec ces logiciels. Ainsi, la signification physique des résultats issus de ces logiciels n'est pas très claire;

1.4.3 Isolement du Cr(III) des autres métaux des boues de tannerie

Les boues de tannerie contiennent habituellement une grande quantité de métaux nuisibles (Al, Fe, Ca, Mg et Zn). La présence de ces métaux dans l'agent tannant nuira inévitablement au tannage des peaux. Il est donc essentiel d'isoler le Cr(III) des autres métaux solubilisés à partir des boues de tannerie. Après l'isolement du Cr(III) d'autres métaux dans les extraits acides des boues de tannerie, le Cr(III) isolé est obtenu sous la forme de précipités de $Cr(OH)_3$. Ce précipité sera dissous avec l'acide sulfurique et la solution obtenue et pourra ainsi être utilisée en tant qu'agent tannant. Bien que l'isolement du Cr(III) d'autres métaux des boues de tannerie ou des eaux usées de tannerie a été étudié par différents chercheurs en Italie (Randall, 1985; Majone, 1986; Macchi *et al.*, 1991; Tiravanti *et al.* 1997), aucun d'eux n'a mentionné les concentrations maximales tolérables de métaux nuisibles (Al, Fe, Ca, Mg et Zn) dans les agents tannants. En revanche, Panswad *et al.* (1995) précipitaient le Cr(III) des eaux usées de tannerie (contenant probablement une grande quantité de métaux nuisibles) avec le MgO et le précipité obtenu (contenant Al, Fe, Ca, Mg et Zn) a été dissous avec l'acide sulfurique concentré pour la préparation de l'agent tannant. Cette solution a été diluée et puis utilisée directement dans le processus de tannage en tant qu'agent tannant en Thaïlande. Ce procédé n'a pas comporté l'isolement du Cr(III). Donc, il semble que les concentrations tolérables d'autres métaux varient beaucoup selon les différentes tanneries. Cependant, il est évident que les cuirs de haute qualité exigent que l'agent tannant contienne très peu d'autres métaux.

Le précipité de $Cr(OH)_3$ obtenu dans cette étude peut être utilisé en tant qu'agent tannant, mais également peut être utilisé dans la préparation des pigments, de l'acier inoxydable, des matériaux réfractaires et des catalyseurs. Pour ces diverses applications, il est également préférable de réduire les teneurs en autres métaux dans le précipité de $Cr(OH)_3$. Par exemple, le contenu en Cr(III) dans les pigments varie entre 96 % à 99 %, selon la catégorie du pigment (Habashi, 1997). Les pigments de haute qualité contiennent donc moins d'autres métaux.

1.4.4 Biolixiviation du Cr(III) et des autres métaux des boues de tannerie par les indigènes bactéries oxydant soufre élémentaire

Les études récentes ont démontré que l'oxydation du soufre élémentaire dans les boues d'épuration est accomplie par une croissance successive de thiobacilles peu-acidophiles et acidophiles (Blais *et al.,* 1992c). Plusieurs espèces de thiobacilles peu-acidophiles participent à l'acidification des boues, mais *Thiobacillus thioparus* est l'espèce la plus importante. D'autre part, *Thiobacillus thiooxidans* et *Thiobacillus ferrooxidans* sont les deux principales espèces acidophiles impliquées dans l'oxydation du soufre élémentaire dans les boues (Blais *et al.,* 1993). Dans les boues d'épuration, les thiobacilles peu-acidophiles peuvent diminuer le pH initial des boues (7.0 à 8.5) à une valeur entre 4.0 et 4.5. À ce pH, la diminution de pH devient plus lente. Les thiobacilles acidophiles commencent à croître à ce pH et diminuent le pH à des valeurs en-dessous de 2.0. Ce phénomène a également été observé dans les boues de tannerie. Le pH du lixiviat de tannerie a diminué lentement de 7.0 à 5.0, tandis que le pH a diminué rapidement de 5.0 à 1.3 ou moins. La diminution de pH dans les boues de tannerie était beaucoup plus lente dans la première étape (la diminution du pH de 7.0 à 5.0) que dans les boues d'épuration.

Les thiobacilles sont des bactéries aérobies strictes (à part *Thiobacillus denitrificans*). La plupart des espèces de thiobacilles, dont *T. ferrooxidans*, *T. thiooxidans* et *T. thioparus* utilisent le CO_2 en tant que leur source unique de carbone (Doelle, 1975). Ils obtiennent l'énergie de l'oxydation chimique de substances inorganiques (Rittenberg, 1969). Les présents travaux ont montré que la concentration élevée en substances organiques dans les boues de tannerie n'a pas empêché la croissance des thiobacilles. Le mécanisme d'oxydation du soufre élémentaire par *T. thioparus* et *T. thiooxidans* a été étudié. Le produit initial de l'oxydation du soufre a été identifié comme étant le sulfite.

$$S + O_2 + H_2O \rightarrow 2H^+ + SO_3^{2-} \qquad (1.1)$$

Par la suite, le sulfite est oxydé en sulfate. Tyagi *et al.* (1994) ont étudié la formation d'autres intermédiaires possibles de réaction ($S_2O_3^{2-}$, $S_3O_6^{2-}$ et $S_4O_6^{2-}$) et constaté que ceux-ci n'ont pas été formés.

1.5 Conclusions

D'abord, les travaux réalisés dans cette étude ont permis d'étudier les effets de divers facteurs sur la mise en solution par des acides minéraux du Cr(III) et des autres métaux à partir des boues de tannerie. Le but de cette partie de la recherche consistait à identifier des conditions optimales dans lesquelles plus de Cr(III) et moins des autres métaux sont solubilisés. Les conclusions suivantes peuvent être tirées de ce travail:

- Trois types d'acides minéraux ont été comparés, soit HCl, HNO_3 et H_2SO_4. Les meilleurs rendements de solubilisation du chrome ont été atteints avec le H_2SO_4, lequel est également le réactif le plus économique;

- La consommation de l'acide sulfurique requise peut être déterminée d'après l'équation $\ln Q = -0.0335pH^3 + 0.3458pH^2 - 1.3pH + 8.0218$. Le Q représente le poids de l'acide sulfurique (kg) consommé par tonne métrique de boues séchées;

- La concentration maximale de calcium dans le lixiviat est atteinte entre 10 et 20 min, tandis que pour les autres métaux, plus de deux heures sont nécessaires afin d'obtenir les rendements maximaux;

- Le rendement de lixiviation du chrome diminue de 90 % à 85 % lorsque le pH augmente de 0.4 à 1.3. De pH 1.3 à 3.0, ce rendement diminue de 85 % à 70 %. Le rendement chute à environ 35 % quand le pH est près de 3.5. Un pH se situant entre 2.0 et 3.0 est jugé optimal considérant les rendements de solubilisation du chrome et les besoins en acide sulfurique;

- La concentration optimale en solides totaux pour l'extraction du Cr(III) se situe entre 75 et 80 g/L. Dans ce cas, plus de Cr(III) et moins de Ca sont solubilisés;

- La concentration maximale en solides suggérée pour la filtration adéquate des boues se situe aux environs de 100 g/L. Lorsque la concentration en solides est supérieure, la séparation solide/liquide par filtration devient très difficile. La séparation doit alors être exécutée par centrifugation;

- À l'exception du Ca, les rendements de lixiviation des autres métaux ne montrent aucune différence remarquable pour les boues séchées et humides. L'extraction du Cr(III) des boues humides est donc préférée du point de vue économique;
- Le rendement de lixiviation du chrome diminue lorsque la température augmente. Donc, une température basse, par exemple 25°C, est favorable à l'extraction du Cr(III).

Secondairement, cette étude a porté sur l'identification au moyen de calculs thermodynamiques des précipités se formant probablement pendant le processus de lixiviation chimique des boues. Les conclusions suivantes peuvent être tirées de cette étude :

- Les précipités possibles dans le processus de lixiviation chimique sont (am)$Cr(OH)_3$, (am)$CrPO_4$, (am)$Fe(OH)_3$, α-FeOOH (goethite), $FePO_4 \cdot 2H_2O$, (am)$AlPO_4 \cdot 2H_2O$ et $CaSO_4 \cdot 2H_2O$ (gypse). La formation de ces précipités a été soutenue par de nombreuses expériences;
- Les solubilités de ces précipités diminuent en fonction de la concentration en solides dans les boues (ou la force ionique de lixiviat). Ce résultat est en d'accord avec des phénomènes expérimentaux observés;
- La séparation de Cr(III), Al et de Ca, Mg, Zn, Fe(II) peut être effectuée entre pH 5.5 à 7.0 et 80°C.

Troisièmement, une expérience à petite échelle a été effectuée pour isoler le Cr(III) des autres métaux à partir de l'extrait acide des boues de tannerie. Les conclusions suivantes peuvent être tirées :

- Un procédé simple en trois étapes est proposé pour la séparation du Cr(III) des autres métaux nuisibles (Al, Fe, Ca, Mg, Zn) présents dans l'extrait acide (lixiviat ou filtrat) des boues de tannerie;
- Les rendements globaux d'enlèvement des métaux obtenus dans un cas typique sont les suivants: 77 % Al, 84 % Fe, 99 % Ca, 99 % Mg et 61 % Zn. Au total, environ 42 % du Cr(III) est enlevé sous forme de précipités;
- La quantité de cupferron requise dans ce procédé pour enlever l'Al, le Fe et le Zn est réduite de plus de neuf fois en comparaison avec la méthode proposée dans la littérature;
- Le procédé de séparation est simple puisqu'il ne comporte pas l'oxydation de Cr(III) et l'utilisation de résines échangeuses d'ions.

Quatrièment, afin de calculer le bilan de matière du procédé dans son entier et fournir une base pour l'évaluation économique du procédé, un essai pilote a été réalisé au laboratoire. Un composé organique, le cupferron, n'a pas été utilisé dans cet essai pilote prenant en compte le coût élevé de ce composé. Cependant, un procédé en trois étapes supplémentaires a été employé lors de cet essai pilote afin de récupérer plus de Cr(III). Les rendements globaux d'enlèvement des métaux obtenus sont les suivants: 76 % Al, 69 % Fe, 97 % Ca, 97 % Mg et -50% Zn. Environ 44 % du Cr(III) présent initialement dans les boues de tannerie a été récupéré. Les taux molaires relatifs d'Al, du Ca, du Cr, du Fe, du Mg et du Zn dans le produit final (étape 3 + étape 6) sont respectivement de 3.83, 1.79, 100, 0.79, 3.28 et 0.22.

Une partie de ce projet de doctorat a porté sur l'étude de la biolixiviation du chrome à partir des boues de tannerie. Plus spécifiquement, une partie de la recherche a porté sur l'étude de l'effet de la concentration de soufre élémentaire ajouté aux boues de tannerie sur la biolixiviation du chrome en utilisant des bactéries oxydant le soufre élémentaire. Cette étude comprend l'évaluation de l'effet de la concentration en soufre sur le pH final de l'échantillon, le temps de lixiviation, les rendements de lixiviation des métaux, la concentration de sulfates produits, ainsi que les teneurs en solides résiduels. Des essais de biolixiviation ont été effectués avec des concentrations en soufre élémentaire variant entre 5 et 40 g/L. La concentration de solides des boues était fixée à 40 g/L. Les conclusions suivantes peuvent être tirées de ce travail :

- Les résultats ont montré que le pH des boues diminue plus rapidement lorsque la concentration initiale en soufre dans les boues est plus élevée et que le pH final obtenu est également plus bas. La période de temps requise pour atteindre le pH minimal était toutefois presque identique dans tous les cas, soit environ 15 jours;
- L'efficacité de lixiviation du Cr(III), de l'Al et du Fe, ainsi que la concentration en SO_4^{2-} a augmenté avec la hausse de la concentration initiale en soufre élémentaire. Cependant, l'efficacité de lixiviation du Zn, du Ca et du Mg a été moins affectée par la concentration initiale en soufre;
- La concentration optimale, d'un point de vue économique, de soufre élémentaire ajouté pour la biolixiviation du Cr(III) se situe à 20 g/L;
- Pendant la biolixiviation, les teneurs en matières en suspension totales et volatiles des boues diminuent fortement;
- Le dénombrement des bactéries oxydant le soufre élémentaire a montré que les thiobacilles acidophiles contribuent davantage à la réduction du pH dans les boues de tannerie que les thiobacilles peu-acidophiles;
- Les bactéries oxydant le soufre élémentaire ont pu vivre dans les boues de tannerie à un pH aussi faible que 0.48 à 21°C.

Finalement, une recherche portant sur l'étude de l'effet de la concentration en solides des boues sur la biolixiviation du Cr(III) et des autres métaux des boues de tannerie a été effectuée. Ces travaux comprennent l'étude de l'effet de la concentration en solides des boues sur le pH final de l'échantillon, le temps de lixiviation, les rendements de lixiviation des métaux, la concentration de sulfates produits et la teneur en solides résiduels. De plus, une comparaison entre la biolixiviation et la lixiviation chimique des métaux des boues de tannerie a été réalisée. Des essais de biolixiviation ont été effectués avec des concentrations en solides de boues variant entre 13 et 60 g/L. La concentration de soufre élémentaire ajouté aux boues était fixée à 30 g/L. Les conclusions suivantes peuvent être tirées de ce travail :

- Le pH final des boues, après 25 jours de biolixiviation, avec différentes concentrations de solides se situait aux environs de 1.3 dans tous les cas;
- Le temps requis pour atteindre le pH minimal est fonction de la teneur en solides des boues selon la relation mathématique suivante : Jours = 0.4354 C (solides, g/L) + 1.8106;
- La concentration optimale en solides des boues pour la lixiviation maximale des métaux se situe à 40 g/L. Dans ce cas, les rendements de solubilisation suivants sont atteints : 87 % du Cr(III), 73 % de l'Al, 72 % du Fe, 62 % du Mg et 73 % du Zn;
- L'efficacité d'extraction du Cr(III) avec le procédé de biolixiviation est presque identique à celle obtenue par le procédé chimique, tandis que le coût des produits chimiques requis pour le procédé biologique est seulement 28 % de celui du procédé chimique;
- Les bactéries oxydant le soufre élémentaire tolèrent une concentration en Cr(III) aussi élevée que 5930 mg/L à pH 1.3.

1.6 Recommandations

Les travaux effectués dans le cadre de ce doctorat ont porté essentiellement sur la mise au point d'un procédé permettant, dans un premier temps, la lixiviation chimique ou biologique du chrome des boues de tannerie et, dans un second temps, l'isolement du Cr des autres métaux nuisibles (Al, Ca, Mg, Fe, Zn) à partir de l'extrait acide obtenu. Les travaux suggérés porteraient donc sur les étapes en aval, soit la préparation du réactif tannant à partir du Cr(III) isolé, ainsi que l'essai dans une tannerie du réactif tannant préparé. Il serait aussi utile d'explorer les possibilités d'extraire une partie des contaminants (principalement le Ca et le Mg) par lavage en milieu aqueux et non-acide, avant de procéder à la mise en solution du chrome par lixiviation chimique ou biologique. Une étude à l'échelle du pilote pré-industriel serait également requise afin d'obtenir les critères de design de la technologie pour une éventuelle implication à l'échelle réelle.

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CHAPITRE 2

EXTRACTION OF CR(III) AND OTHER METALS FROM TANNERY SLUDGE BY MINERAL ACIDS

EXTRACTION OF Cr(III) AND OTHER METALS FROM TANNERY SLUDGE BY MINERAL ACIDS

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2 EXTRACTION OF CR(III) AND OTHER METALS FROM TANNERY SLUDGE BY MINERAL ACIDS

2.1 Résumé

Une recherche exhaustive portant sur les conditions d'extraction du Cr(III) et des autres métaux des boues de tannerie utilisant des acides minéraux a été exécutée. L'effet de divers facteurs (le temps d'extraction, le type d'acides minéraux, la consommation de l'acide, le pH, la concentration en solides des boues, la température et le type des boues) sur les rendements de lixiviation des métaux a été étudié. Les résultats indiquent que le temps requis pour l'extraction de la plupart des métaux était de 2 h à 25°C. Cette étude a aussi montré que l'acide sulfurique constitue l'acide inorganique le plus intéressant pour l'extraction du chrome à partir des boues de tannerie. Une relation entre la consommation de l'acide et le pH a été établie pour différentes concentrations en solides des boues. Les différents tests effectués ont montré que le rendement de lixiviation du chrome varie avec le pH et dont la gamme optimale pour l'extraction du chrome se situe entre 2.0 et 3.0. De même, selon les tests réalisés la concentration optimale en solides des boues pour l'extraction du Cr(III) se situe aux environs de 75-80 g/L. L'adsorption et la liaison des métaux sur les matières colloïdales organiques insolubles, ainsi que la formation de précipités métalliques constituent deux causes probables de la diminution du rendement d'extraction des métaux avec la hausse de la concentration en solides des boues. Les essais de lixiviation conduits à différentes températures ont montré une baisse du rendement d'extraction avec la hausse de la température des boues. D'autre part, le type des boues traitées (humides ou séchées) n'a aucun effet sur le rendement de lixiviation du Cr(III).

2.2 Abstract

A comprehensive investigation on the extraction conditions of Cr(III) and other metals from tannery sludge using mineral acids was performed. The effect of various factors (the extraction time, the type of mineral acid, the consumption of acid, pH, sludge solids concentration, temperature, and the type of sludge) was studied on the leaching yield of metals. The results indicate that the metal extraction time for most of the metals was 2 h at 25°C. The most suitable acid for Cr(III) extraction was sulphuric acid. A relationship for the acid requirement to adjust different sludge pH at varying sludge solids concentration was established. Leaching yield of chromium varied with sludge pH and the suitable pH for Cr(III) extraction was between 2.0 to 3.0. The optimum sludge solids concentration for Cr(III) extraction was 78.5 g/L. The leaching yield of Cr(III) decreased with the increased temperature. The type of sludge (wet or dry) has no effect on the leaching yield of Cr(III). The metal adsorption and bonding on the insoluble organic colloid matter as well as the formation of metal precipitates may be two possible reasons for the decreased extraction yield of metals with increased solids concentration.

Key words: Chromium extraction, tannery sludge, sludge solids, chemical leaching.

2.3 Introduction

Current studies relating to the treatment of tannery sludge or tannery wastewater have focused on the recovery of Cr(III) [1, 2, 3, 4]. Macchi *et al.* [1] reported that the type of mineral acids (HCl, HNO_3 and H_2SO_4) has no effect on Cr(III) extraction from dry tannery sludge and about 90 % of Cr(III) could be extracted at pH 1. Panswad *et al.* [3] reported that 98 % of Cr(III) from tannery sludge could be extracted using sulphuric acid. Chuan and Liu [5] studied the influence of oxidation reduction potential (ORP) on the release of Cr(III) from tannery sludges. They found that the dissolved Cr(III) concentration decreased as ORP increased (0-470 mV) at pH 4.2. The dissolved Cr concentration was relatively low at pH 8.0 and at different ORP (-220 to 250 mV). They concluded that precipitation-dissolution reactions controlled the release behaviour of Cr.

Past research on leaching of tannery sludge has focused on solubilisation of Cr(III). However, to facilitate the recovery of Cr(III) from the leachate, higher concentrations of Cr(III) were desirable, while other metal concentrations in the leachate should be minimised. This will minimise the interference caused by the other metals in the recovery of Cr. In order to find suitable Cr(III) extraction conditions, different from previous work reported in the literature, the effect of process conditions on the extraction yield of Cr(III) as well as other metals was studied in this work. The literature on tannery sludge leaching is also scanty on the effect of operating conditions (sludge solids concentration, leaching time, temperature, the type of sludge - dry or wet, and acid requirement) on metal leaching. Studies carried out [6, 7, 8] on wastewater sludge demonstrated that the metal solubilization efficiency was strongly affected by the sludge solids concentration. In contrast to wastewater sludge, tannery sludge contains a large amount of Cr(III) and less organic matter. It has been reported that 10-20% Cr(III) in tannery effluent was bonded to organic ligands and 80 to 90 % Cr(III) existed in inorganic form [9]. The metal-organics bonding was thought to be the major problem for the removal of Cr(III) from leather scraps [10]. In fact, Cr(III) behaves as a typical strong Lewis acid and readily forms complexes with a variety of organic and inorganic ligands [11]. Moreover, Cr(III) is one of the most readily absorbed metals by the biomass (bacteria, fungi, wood chips) in acidic aqueous solutions [12]. Hence, the presence of organic matter may affect the leaching of Cr(III) as well as the solid-liquid separation (filtration or centrifugation) after the leaching. Therefore, the influence of sludge solids concentrations as well as sludge type (dry and wet) on the extraction of Cr(III) and the solid-liquid separation was studied. The influence of extraction temperature was also studied.

2.4 Materials and methods

2.4.1 Samples of tannery sludge

The sample of dehydrated (mechanical press) tannery sludge was procured from "La Tannerie des Ruisseaux" in Rivière-du-Loup (Québec). This sludge contained 69.74 % of water. The sludge was stored at 4°C. A part of the sludge sample was dried at 104°C for 48 h before use.

2.4.2 Digestion of the tannery sludge

Two samples of the dry sludge were digested. In addition, a blank was also performed. The samples (0.5 g each) were placed in two Teflon beakers (100 mL capacity each). Fifteen mL of concentrated HNO_3 was added to each sludge sample and the blank sample. Then the beakers were placed on a hot plate for digestion. When the solution in the beaker was evaporated to near dryness, an additional 15 mL of concentrated HNO_3 was added to each beaker and the heating was continued. After 1 h, 10 mL of HCl was added to each beaker. The heating was continued until the solution became clear. After cooling, the solution was filtered through Whatman GF/C filter and diluted to 100 mL with 0.2 % HNO_3. The corresponding blank values were subtracted for each element analysis. Each element content came from the average analysis of two samples.

Experiments were performed in 500 mL in polyethylene flasks with stoppers at different sludge solids concentration to establish the quantity of sulphuric acid required to adjust the pH. A known weight of the dry sludge was suspended in 150 mL of water to obtain the desired concentration of sludge solids. The mixture was stirred immediately at room temperature (21°± 2°C) on a shaker at 200 rpm. The pH was recorded when a constant reading was observed. Sulphuric acid (50 % v/v) was added to adjust the desired pH. The volume of the acid used was recorded. The acid requirement was calculated to adjust the following pH at different sludge solids concentration: 9.81, 5.73, 5.62, 5.13, 3.92, 1.88, 1.21, 1.05, 0.88, 0.73, 0.61, 0.48 and 0.40. The exact acid strength was determined by titration.

2.4.3 Metal extraction experiment

A known weight of the sludge was placed in a 500 mL polyethylene flask with a stopper. Mineral acid (150 mL) was added to the flask. The amount of acid required to adjust the pH was determined from the acid requirement curve. This solution was placed immediately in a controlled environment incubator shaker (New Brunswick scientific Co. INC., EDISON, N.J. U.S.A) at 25°C and 200 rpm for 5 days. Samples (2 mL each) were drawn at different times (10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 6 h, 1 d, 2 d, 3 d, 4 d and 5 d) and then filtered or centrifuged. Centrifugation was performed only for the samples whose sludge solids concentration was greater than 100 g/L. The filtration was performed by vacuum filtration using a conventional suction flask and Whatman GF/C filter paper. The filtrate was used to determine dissolved metal concentration and the pH value. Metal extraction experiments at different temperatures (25°C, 43°C, 60°C and 80°C) were performed as before. A shaking water bath (controlled temperature) was used to study the metal leaching at 40 to 80°C. Different sludge solids concentration was obtained by suspending different amounts of dry sludge in the acid solution.

2.4.4 Chemical analysis

ICP Perkin Elmer Optima 3000 and Varian Spectr AA·20 atomic absorption spectrometer was used to measure the metal (Cr, Al, Fe, Ca, Mg, Zn, Na, K) concentration in the digested solution and the leachate. Cr^{6+} concentration in the digested solution was determined by the S-diphenylcarbazide method [13]. Fe^{2+} concentration was measured by the phenanthroline method [13]. Orthophosphate concentration was analysed by the ascorbic acid method [13]. SO_4^{2-} and Cl^- concentration in the leachate were determined by ion chromatography (DIONEX). The water content was obtained from the average weight loss of five sludge samples at 104°C in 48 h. The volatile organic matter content was obtained from the average weight loss of the dried sludge samples at 550°C over 48 h.

2.5 Results and discussion

The results of chemical analysis of the tannery sludge are provided in Table 2.1. The predominant species of Fe and Cr are Fe(III) and Cr(III).

2.5.1 Influence of acid type on the extraction yield of metals

The extraction test with three different kinds of acids (HCl, HNO_3 and H_2SO_4) did not show apparent differences on the extraction yield of Fe, Al, Mg and Zn (Table 2.2). The solubilisation of Cr was better with sulphuric acid. There was a large difference for Ca solubilisation with the type of acid used (10 % with H_2SO_4, 70 to 80 % with HCl or HNO_3). Ca is probably removed as the precipitate of $CaSO_4 \cdot 2H_2O$ when H_2SO_4 was used for metal extraction. The leachate is directly destined to metal separation and Cr(III) recovery, higher amount of Cr(III) and less of Ca in the leachate is desirable. Therefore, H_2SO_4 is preferred due to better solubilization of Cr and less solubilization of Ca. Moreover, H_2SO_4 is the least expensive among these three types of acids. In addition, Ca is not a toxic element, therefore, residual sludge solids with Ca can be disposed without the environmental risk.

2.5.2 Acid requirement for the extraction

The amount of sulphuric acid required to adjust the different sludge pH is presented in Figure 2.1. These curves, which correspond to different sludge solids concentrations, appear to overlap. It suggests that the amount of sulphuric acid required at a given pH is independent of initial sludge solids concentration. Acid requirement exhibits a relation with pH (Figure 2.1).

2.5.3 Influence of extraction time on the extraction yield of metals

Plots of metal solubilization versus time at pH 1.3 and 3.0 are presented in Figures 2.2 and 2.3, respectively. Except for Ca, the leaching yield (% metal solubilization) of metals reached a maximum in 2 to 3 h. Maximum solubilization of Ca was achieved in 10 to 20 min irrespective of pH.

2.5.4 Influence of pH and sludge solids concentration on the extraction yield of metals

The influence of pH and sludge solids concentration on the leaching yield of different metals is presented in Figures 2.4 through 2.6 and Table 2.3. When pH increased from 0.4 to 1.0, the leaching yield of Cr decreased from 90 to 80 % (Table 2.3 and Figure 2.4). The Cr solubilization yield decreased from 80 to 70 % with an increase in pH from 1.3 to 3.0 (Figure 2.4). The Cr yield dropped steeply to about 35 % when pH was about 3.4 (Table 2.2). A large quantity of acid is required to adjust the pH to less than 1 (Figure 2.1). Therefore, pH 1 to 3 is advisable for effective Cr extraction. The preferred pH should be between 2.0 to 3.0 due to low sulphuric acid requirement and reasonable metal solubilization yield.

The effect of sludge solids concentration was studied in the range of 19.6 g/L to 140 g/L. When the sludge solids concentration increased from 19.6 g/L to 78.5 g/L, Cr leaching yield slightly decreased (Figure 2.4). The average value of Cr leaching yield in this solids concentration range was 83 % at pH 1.3 and 72 % at pH 3.0. At a sludge solids concentration of 100 g/L, the Cr leaching yield decreased to 66 % at pH 1.3 and 60 % at pH 3. The leaching yield of Ca decreased significantly as the sludge solids concentration increased (Figure 2.4). The leaching yield of Ca was about 35 % at a sludge solids concentration of 19.6 g/L and 4 % at 140 g/L. The leaching yield of other metals such as Fe, Al, Mg and Zn varied but not to a large extent (Figures 2.4 to 2.6). The suitable sludge solids concentration for Cr(III) extraction is about 78.5 (g/L). In this case, more Cr(III) and less Ca could be extracted.

2.5.5 Influence of sludge type (dry or wet) on the extraction yields of metals

The results on the metal extraction yield are presented in Table 2.3. Except for Ca, the leaching yield of other metals did not show a significant difference between dry and wet sludge. Therefore, the Cr(III) extraction using wet sludge should be preferred from an economic viewpoint.

2.5.6 Influence of temperature on the extraction yields of metals

The leaching yield of Cr decreased with the increased temperature (Table 2.3). This is probably due to the formation of $Cr(OH)_3$ and $CrPO_4$ [13]. The solubility of $Cr(OH)_3$ and $CrPO_4$ decreases with an increase in temperature [15, 16]. Thus, a low temperature is preferable for the extraction of Cr(III).

This work (Table 2.3) and that of Mącchi et al. [1] showed that the highest leaching yield of Cr(III) was about 90% even if the pH of the solution was 0.4. Approximately 10% of Cr(III) that could not be extracted. To understand this phenomenon, an experiment was conducted where the insoluble solids were determined. The results are presented in Table 2.4.

The residual solids (insoluble solids) increased with initial sludge solids concentration (Table 2.4). 37 % insoluble solids was left in the final leaching mixture when initial sludge concentration was 100 g/L. The residual organic matter probably adsorbed some metals or formed strong chemical bonds with them. Thus some metals could not be released into the leaching solution. Cr(III) is one of the most readily adsorbed metals by the biomass in the acidic solutions [11]. Hence, the presence of insoluble sludge solids is probably an important factor that results in the metal loss during the extraction process. Thus decreased yield of Cr leaching at a sludge solids concentration of 78.5 g/L to 100 g/L (Figure 2.4) may be due to binding of metals with the residual sludge solids.

In addition, some metal may also precipitate during the leaching process [14] and hence decrease the metal solubilization. The formation of $Cr(OH)_3$ (s) and $CrPO_4$ in the leaching process was predicted by means of thermodynamic calculations [14]. Therefore, it is inferred that $Cr(OH)_3$ (s) and $CrPO_4$ were probably formed in the leaching process, which resulted in the corresponding decrease of the leaching yield of Cr(III).

At 100 g/L sludge solids concentration and above, filtration of samples was difficult. The residual insoluble solids after leaching caused this problem. However, a good separation could be performed by centrifugation. Therefore, the maximum suggested sludge solids concentration for filtration after leaching is less than 100 g/L. The residual (insoluble sludge solids) concentration increased with initial sludge solids concentration (Table 2.4). A part of the insoluble solids may be formed in the form of non-filterable organic colloids, which makes filtration difficult. The concentration of insoluble solids in the liquid phase increased with the increase in sludge solids concentration. The filtration thus became more and more difficult.

2.6 Conclusions

This work studied the effects of various factors on the extraction of Cr(III) and other metals from the tannery sludge using mineral acids. The following conclusions can be drawn from this work.

- H_2SO_4 is the most suitable acid for the extraction of Cr(III), because most of Ca can be removed as precipitates of $CaSO_4$;
- The maximum leaching of metals was usually achieved in 2-3h;
- Suitable pH for Cr(III) extraction is between pH 1.0 and 3.0;
- The suitable sludge solids concentration for Cr(III) extraction is about 78.5 g/L;
- The leaching yields of metals did not show significant difference for dry or wet sludge;
- The leaching yield of Cr(III) decreased with the increased temperature.

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Table 2.1 Composition of the dry tannery sludge

Parameters	Concentration (% w/w)
Cr(III)	12.80
Cr(VI)	0.004
Al	1.063
Fe(III)	0.339
Fe(II)	0.014
Ca	4.980
Mg	5.795
Zn	0.022
K	0.009
Na	2.262
Orthophosphate	0.114
Volatile organic matter	43.4

Table 2.2 **Influence of acid type on metal solubilization (total sludge solids - 20 g·L^{-1}, 25°C, 200 rpm, 3 h leaching time)**

	Solubilization yield (%)											
	H_2SO_4				HNO_3				HCl			
pH	1.03	2.02	2.91	3.41	0.84	0.96	2.91	3.23	0.64	2.45	3.02	3.55
Cr	80.7	81.7	72.4	37.5	71.8	69.4	73.0	58.1	74.7	73.1	74.6	36.4
Al	80.1	78.9	68.2	65.9	80.4	78.1	77.0	57.9	77.0	78.3	75.1	55.6
Fe	73.8	80.0	65.2	59.6	63.8	64.2	61.1	48.3	66.0	57.9	68.0	54.6
Ca	11.8	11.1	11.6	9.68	72.8	74.4	81.7	90.0	83.2	76.3	87.1	86.9
Mg	75.6	78.8	69.1	68.5	71.9	74.5	79.6	77.0	84.5	76.5	77.1	76.4
Zn	65.1	63.3	59.3	55.4	64.9	66.4	62.8	53.1	64.8	59.4	55.8	57.7

Table 2.3 Effect of sludge type and temperature on metal solubilization

Sludge	Solids (g·L^{-1})	pH	T (^{o}C)	Solubilization yield (%)					
				Cr	Al	Fe	Ca	Mg	Zn
Dry	20.2	0.4	25	91.4	72.2	73.4	48.5	91.3	94.7
Wet	20.2	0.4	25	90.9	82.3	87.0	56.0	89.6	96.7
Dry	60.5	0.6	25	79.9	80.2	69.1	33.4	85.9	79.7
Wet	60.5	0.6	25	80.0	79.7	68.0	46.7	81.2	76.1
Dry	100	1.3	25	65.7	65.1	59.9	6.1	67.4	57.4
Dry	100	1.3	43	63.0	48.7	55.8	7.3	64.3	61.9
Dry	100	1.3	60	55.3	51.1	62.5	5.9	60.9	64.9
Dry	60.0	0.7	25	85.8	-	-	-	-	-
Dry	60.0	0.7	43	80.4	-	-	-	-	-
Dry	60.0	0.7	80	73.1	-	-	-	-	-
Dry	60.0	1.7	25	79.6	-	-	-	-	-
Dry	60.0	1.7	43	76.6	-	-	-	-	-
Dry	60.0	1.7	80	68.2	-	-	-	-	-
Dry	60.0	2.6	25	66.0	-	-	-	-	-
Dry	60.0	2.6	43	60.0	-	-	-	-	-
Dry	60.0	2.6	80	52.6	-	-	-	-	-

Table 2.4 **Residual insoluble solids in the leaching mixtures (25°C, 200 rpm, pH=1.3, 5 days)**

Initial sludge solids concentration (g·L-1)	Residual solids (%)
39.5	18
100	37
200	63

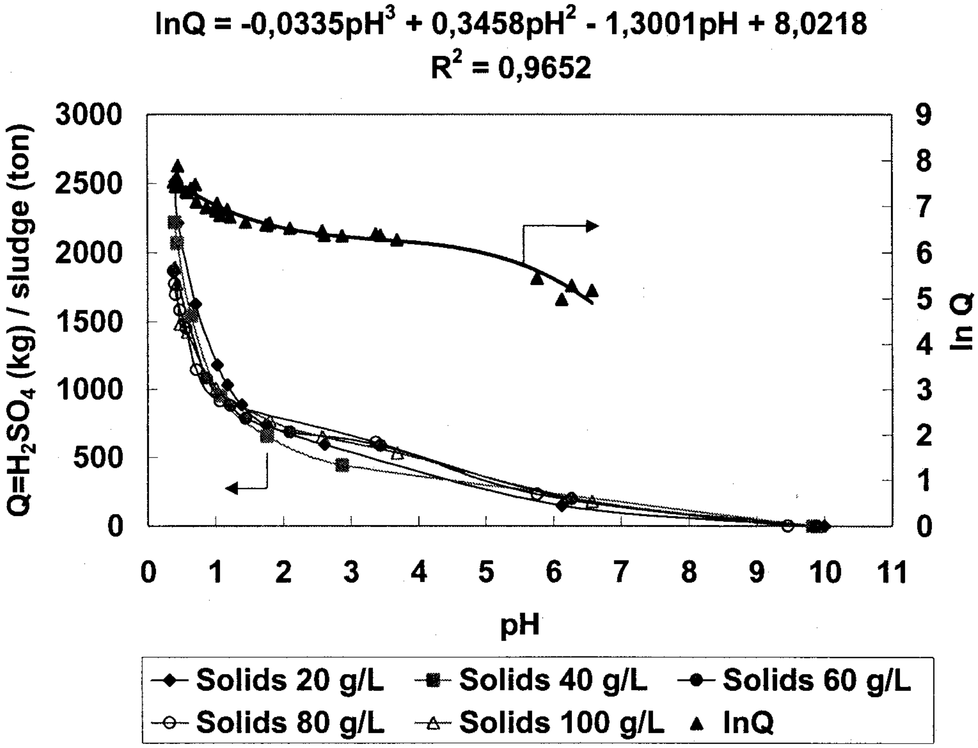

Figure 2.1 **Curve of acid consumption of the dry tannery sludge (25°C, 200rpm)**

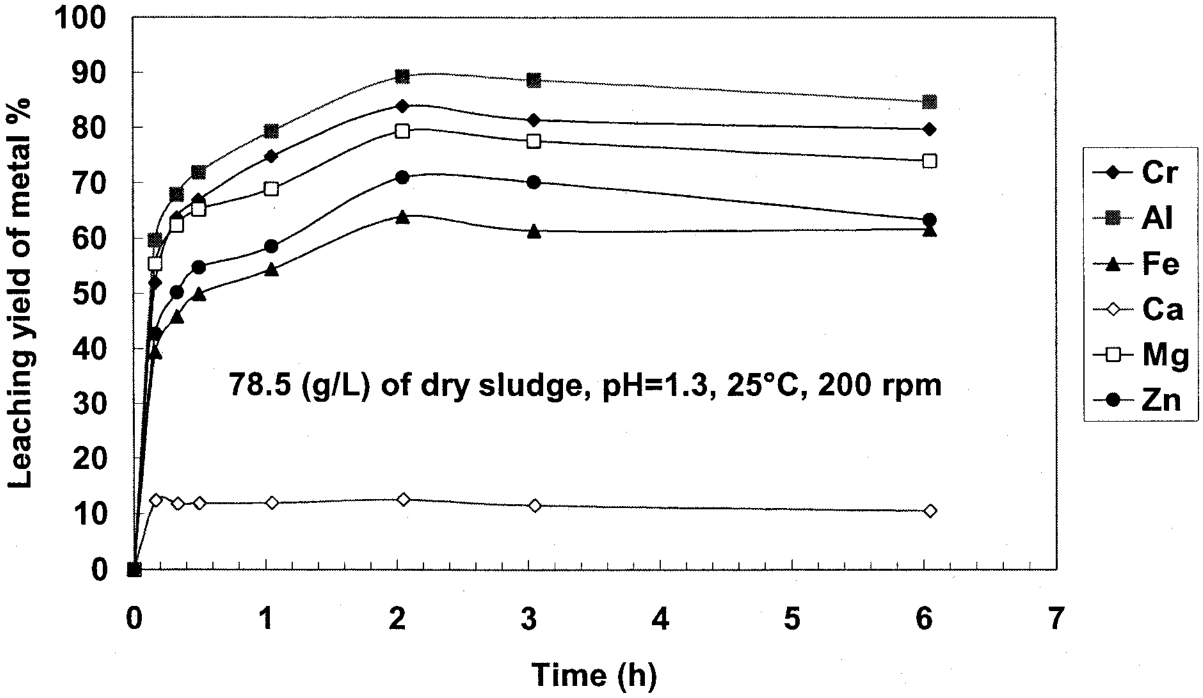

Figure 2.2 Variation of the leaching yield of metals with time

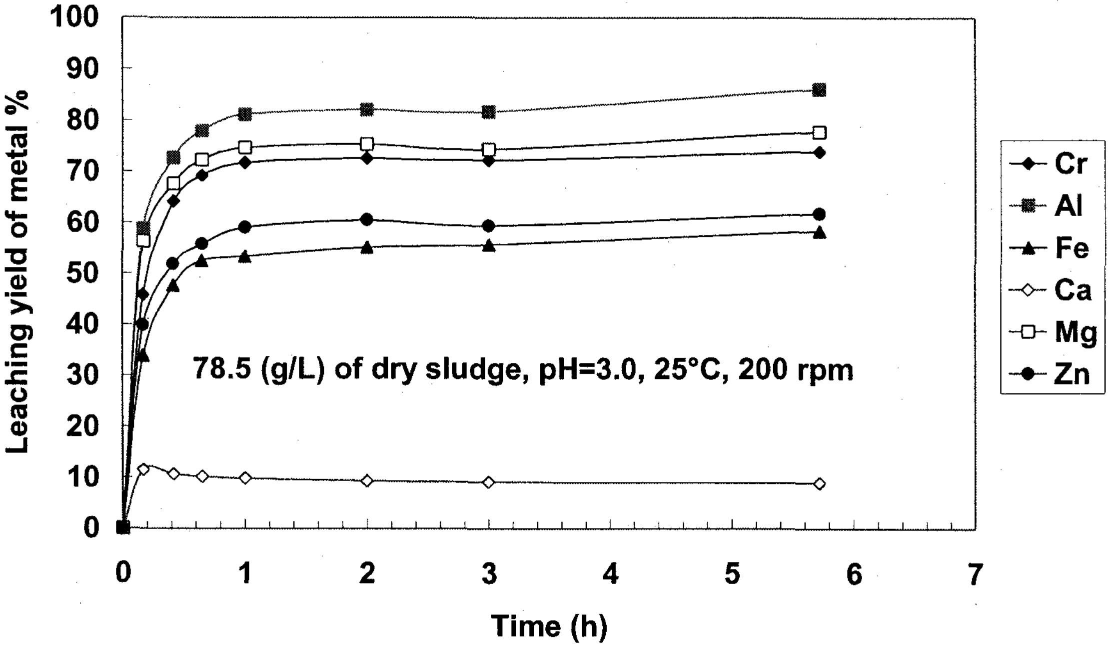

Figure 2.3 **Variation of the leaching yield of metals with time**

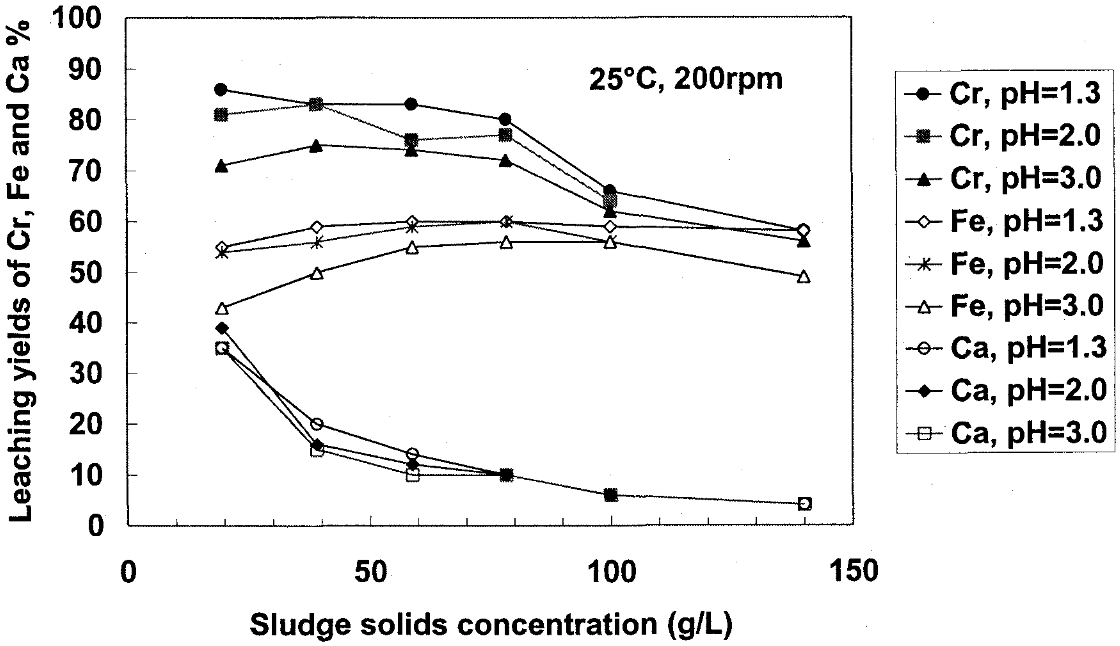

Figure 2.4 **Variation of leaching yields of Cr, Fe & Ca with solids concentration and pH**

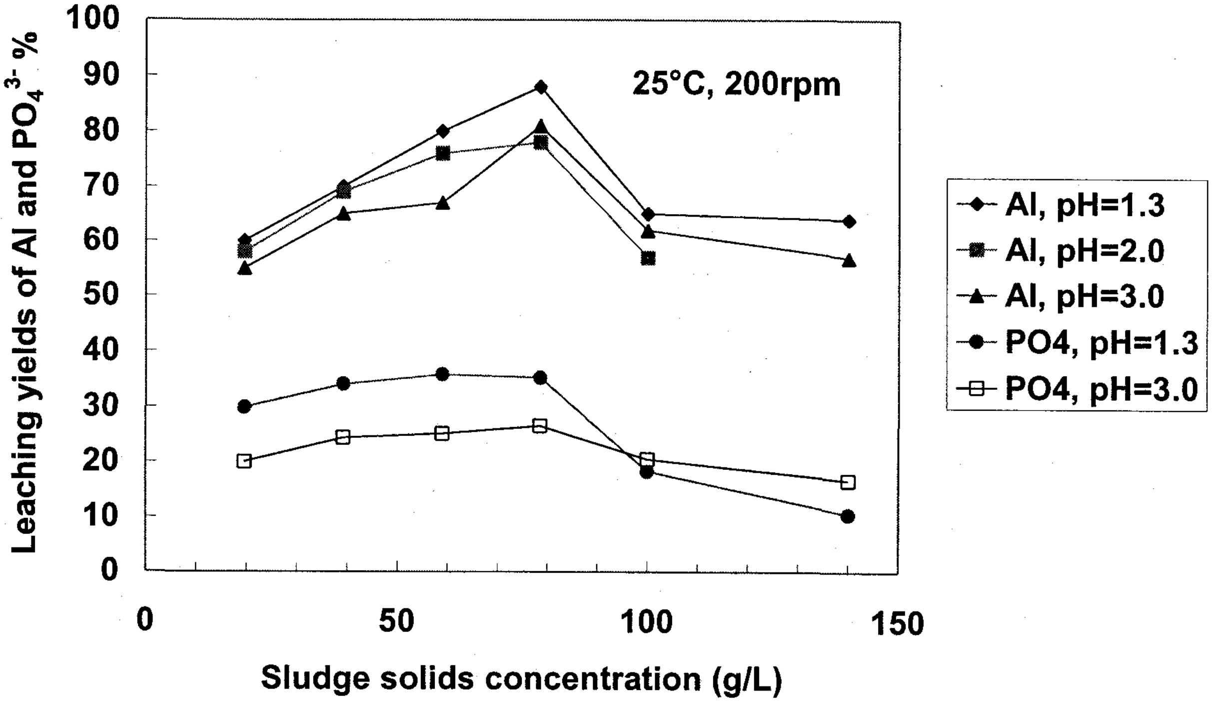

Figure 2.5 Variation of leaching yields of Al and PO_4^{3-} with solids concentration and pH

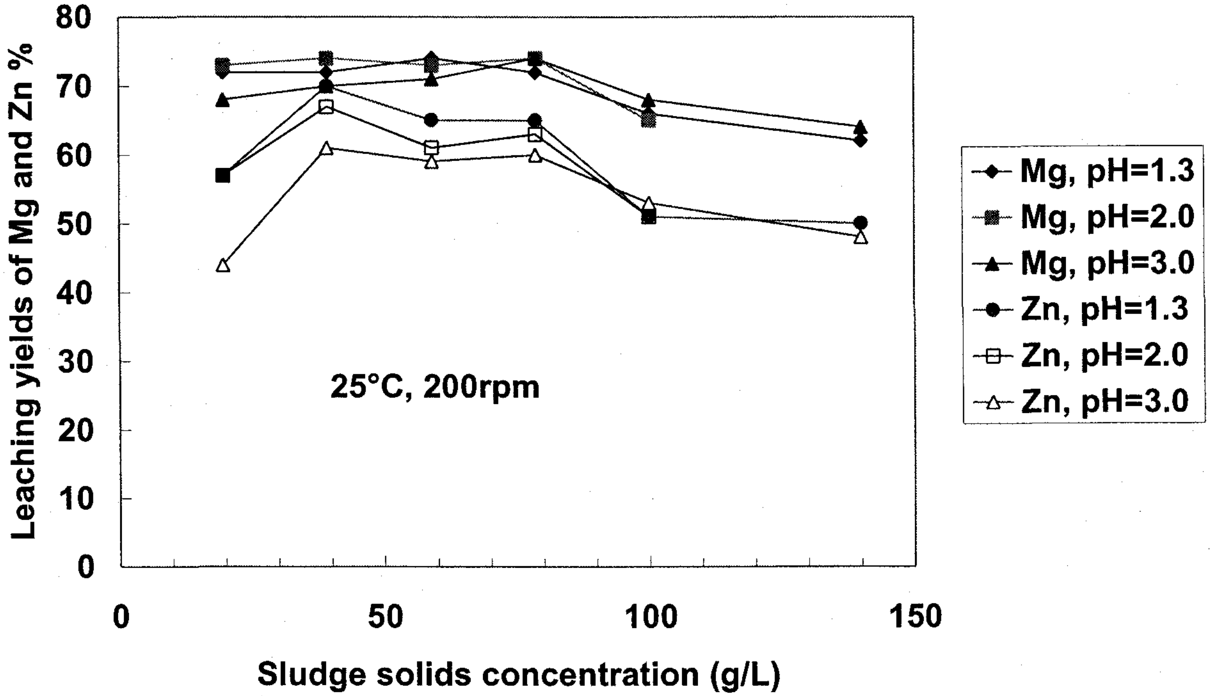

Figure 2.6 Variation of leaching yields of Mg and Zn with solids concentration and pH

CHAPITRE 3

PREDICTION OF METAL PRECIPITATES IN TANNERY SLUDGE LEACHATE BASED ON THERMODYNAMIC CALCULATIONS

PREDICTION OF METAL PRECIPITATES IN TANNERY SLUDGE LEACHATE BASED ON THERMODYNAMIC CALCULATIONS

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3 PREDICTION OF METAL PRECIPITATES IN TANNERY SLUDGE LEACHATE BASED ON THERMODYNAMIC CALCULATIONS

3.1 Résumé

Des calculs thermodynamiques ont été exécutés afin de prévoir la formation des précipités de métaux pendant la lixiviation des boues de tannerie. L'énergie libre de Gibbs ($\Delta G = RT\ln(Qc/Kc)$) de précipitation a été employée pour examiner la formation des précipités pendant le procédé de lixiviation. Les constantes d'équilibre d'activité (Ka) de diverses précipitations ont été tirées de la littérature. Les valeurs de Ka ont été corrigées pour obtenir les valeurs correspondantes du produit de concentration (Qc) et de la constante d'équilibre de concentration (Kc) en utilisant les coefficients d'activité (γ) d'ions. Les coefficients d'activité d'ions ont été calculés en utilisant l'équation de Davies $\text{Ln}\,\gamma_i = -1.172\, Z_i^2\,((I^{0.5} / (1 + I^{0.5})) - 0.3\, I)$ (la solution aqueuse, 25°C, 1 atm, $I > 0.3$ mol/kg). Les valeurs de la force ionique (I) aux différentes concentrations en solides des boues et aux différents pH ont été obtenues en mesurant les concentrations des principales espèces ioniques dans les lixiviats. Les calculs thermodynamiques ont proposé que les précipités possibles formés pendant le procédé de lixiviation étaient le $Cr(OH)_3$, le $CrPO_4$, le (am)$Fe(OH)_3$, le α-FeOOH (goethite), le $FePO_4{\cdot}2H_2O$, le $AlPO_4{\cdot}2H_2O$ et le $CaSO_4{\cdot}2H_2O$ (gypse). Les solubilités de ces précipités diminuent avec la hausse de la force ionique (ou la concentration en solides des boues). Les résultats des calculs ont été appuyés par les observations expérimentales.

3.2 Abstract

Thermodynamic calculations were performed in order to predict the formation of metal precipitates during the tannery sludge leaching. Gibbs free energy $\Delta G = RT\ln (Q_c/K_c)$ of precipitation reaction was used to examine the formation of precipitates during the leaching process. The values of activity equilibrium constant (K_a) of various precipitation reactions were adopted from the literature. The K_a values were corrected to obtain the corresponding values of concentration product (Q_c) and concentration equilibrium constant (K_c) using the activity coefficients (γ) of the ions. The activity coefficients (γ) of the ions was calculated using Davies equation $\mathrm{Ln}\, \gamma_i = -1.172\, Z_i^2\, ((I^{0.5} / (1 + I^{0.5})) - 0.3\, I)$ (aqueous solution, 25°C, 1 atm, $I > 0.3$ mol/kg). The values of ionic strength (I) at different sludge solids concentration and leaching pH were obtained by measuring the concentration of all ionic species in the leachate. The thermodynamic calculations indicated that the possible metal precipitates formed during the leaching process were $Cr(OH)_3$, $CrPO_4$, (am)$Fe(OH)_3$, α-FeOOH (goethite), $FePO_4{\cdot}2H_2O$, $AlPO_4{\cdot}2H_2O$, $CaSO_4{\cdot}2H_2O$ (gypsum). The solubility of these precipitates were found to decrease with the increase in the ionic strength (or sludge solids concentration). The results of computations were supported by the experimental observations.

Key words: Thermodynamic model, metal precipitates, tannery sludge, metal leaching.

3.3 Introduction

In order to recover Cr(III) from a tannery sludge, the sludge was leached with sulphuric acid (Shen *et al.*, 2000). The aim of the sludge leaching was to maximise the Cr(III) solubilisation and to minimise other metal solubilisation. This will favour the separation of Cr(III) from other metals in the leachate. This demands the needs to find the suitable leaching conditions. Although suitable leaching conditions may be found by experimental means [1], the factors (formation of metal precipitates, adsorption of metals on sludge solids) that determine these optimum leaching conditions are unknown. It was found that the highest leaching yield of Cr(III) was about 90 % even if the pH of the solution was 0.4. There is still 10 % of Cr(III) that could not be extracted. The chromium precipitation was thought to be responsible for this loss. In addition, it was observed that the leaching yield of Cr decreased as the temperature increased. It was also found that $CaSO_4$ precipitates were probably formed in the sludge leaching process. All these observations indicate that the precipitation of metals probably took place during the leaching process and thus affected the leaching yield of metals. Therefore, it is important to know under what conditions metals precipitate during the tannery sludge leaching process. This will help in understanding the leaching process as well as developing the optimum conditions for leaching.

Confirming the species of metal precipitates by experimental means is very difficult. The precipitates tend to be amorphous at ambient temperature and may be easily adsorbed by other insoluble solids. The amount of precipitates may vary depending on operating conditions of a system. On the other hand, the thermodynamic data (activity equilibrium constant of the precipitation reaction, for example) of almost all metals precipitation reactions are available in the literature. The concentration of precipitated ions in the aqueous solution in which some precipitation reactions have taken place can be determined precisely by laboratory chemical methods. In principle, based on thermodynamic data and measured ionic concentrations, some metal precipitate species can be determined or predicted. The objective of the present study was to predict thermodynamically the formation of metals precipitates. This information could help to develop a strategy for metal separation from the leachate.

3.4 Thermodynamic Model

The main purpose of thermodynamic calculations is to solve the following problems: a) at what pH and sludge solids concentration, a precipitate can form in the leaching process, and b) the influence of ionic strength of leaching solution on the solubility of metal precipitates.

All possible precipitation reactions that could occur during the tannery sludge leaching process in accordance with the literature [2, 3, 4, 5] are listed in Table 3.1.

Let us consider precipitation reaction no.4 in Table 3.1.

$$FePO_4 \cdot 2H_2O(s) = Fe^{3+} + H_2PO_4^- + 2OH^- \qquad (3.1)$$

It is assumed that if this precipitation reaction took place before the leaching process attains its equilibrium state (metal solubilization reaches maximum), the leaching solution should be saturated with respect to $FePO_4.2H_2O(s)$. In general, Gibbs free energy (Stumm and Morgan, 1981) which is given by Equations (3.2) and (3.3) can predict the formation of precipitates.

$$\Delta G = RTln(Q_c/K_c) \qquad (3.2)$$

$$K_c = K_a/ Q_r \qquad (3.3)$$

where,

ΔG – Gibbs free energy of the precipitation reaction (J);

R – Universal gas constant (equals to 8.314 $J \cdot K^{-1} \cdot mol^{-1}$);

T – Temperature (^oK);

K_a – Activity equilibrium constant of the precipitation reaction. It is a constant at a given temperature and pressure. LogK_a values for possible precipitation reactions in the tannery sludge leaching process are given in Table 3.1;

K_c – Concentration equilibrium constant. It is a constant at a given temperature, pressure and ionic strength. In an infinitely dilute solution (ionic strength $I = 0$), $K_c = K_a$. In an electrolytic solution (ionic strength $I \neq 0$), $K_c \neq K_a$;

Q_c – Concentration product of precipitated ions in leachate. For Equation (3.1), Q_c is given by $[Fe^{3+}]$ $[H_2PO_4^-]$ $[OH^-]^2$. The details on the calculation of K_c and Q_c are provided later in the text;

Q_r – Activity-coefficient product for individual precipitation reaction. For the reaction described by equation (1), Q_r can be obtained by Equation (3.4).

$$Q_r = \gamma(Fe^{3+})\gamma(H_2PO_4^-)\gamma(OH^-)^2 \qquad (3.4)$$

where γ is the activity coefficient of an individual ion and can be calculated by Davies equation (Equation 3.5).

$$Ln\gamma_i = -1.172Z_i^2((I^{0.5}/(1+I^{0.5}))-0.3I)$$

$$\textit{(aqueous solution, 25°C, 1 atm, } I > 0.3 \textit{ mol/kg)} \qquad (3.5)$$

where I is the ionic strength. The method of calculation of I in tannery sludge leachate is presented in the next section.

By combining Equations (3.3) to (3.5), we have

$$LogK_c = Log(K_a) + 0.509*(3^2+1^2+2*1^2)\ ((I^{0.5}/(1+I^{0.5}))-0.3I) \qquad (3.6)$$

Log(K_c) values and thus Log(Q_c/K_c) of all possible precipitation reactions can be calculated as illustrated in following sections.

The state of saturation of the leachate with respect to any precipitation reaction may be interpreted in the following way:

If $Q_c/K_c = 1$ or $Log(Q_c/K_c) = 0$, then $\Delta G = 0$, the reaction reaches equilibrium (saturated);

If $Q_c/K_c > 1$ or $Log(Q_c/K_c) > 0$, then $\Delta G > 0$, the reaction proceeds to the left (oversaturated and implies that the precipitation reaction took place during the leaching process);

If $Q_c/K_c < 1$ or $Log(Q_c/K_c) < 0$, then $\Delta G < 0$, reaction proceeds to the right (undersaturated).

3.5 Calculation of ionic strength (I) of the tannery sludge leachate

The ionic strength (I) of the leachate can be calculated according to equation (3.7).

$$I = (1/2)\ \Sigma (c_i z_i^2) \qquad (3.7)$$

where c_i is molality of individual ionic species. z_i is the charge number of an ion.

The value of c in Equation (3.7) may be approximately obtained from the measured element concentrations in the leachate and K_a values for complex reactions given in Table 3.2 (assuming I = 0). For example, c value for species Fe^{3+} in a leachate is given by $c(Fe^{3+})$. It can be approximately calculated by the following formulas.

$$Fe^{3+} + OH^- = Fe(OH)^{2+},\ K_{11,\,a} \qquad (3.8)$$

$$Fe^{3+} + 2OH^- = Fe(OH)_2^{+},\ K_{12,\,a} \qquad (3.9)$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3^{0},\ K_{13,a} \qquad (3.10)$$

Where, $K_{11,\,a}$, $K_{12,\,a}$ and $K_{13,a}$ are activity equilibrium constants of the complex reactions (Table 3.2) and may be approximately written as,

$$K_{11,\,a} = c(Fe(OH)^{2+}) \,/\, c(Fe^{3+})\ c(OH^-) \qquad (3.11)$$

$$K_{12,a} = c(Fe(OH)_2^+) / c(Fe^{3+}) (c(OH^-))^2 \qquad (3.12)$$

$$K_{13,a} = c(Fe(OH)_3^0) / c(Fe^{3+}) (c(OH^-))^3 \qquad (3.13)$$

The total Fe(III) concentration $C(Fe(III))_T$ may be written as,

$$c(Fe(III))_T = c(Fe^{3+}) + c(Fe(OH)^{2+}) + c(Fe(OH)_2^+) + c(Fe(OH)_3^0) =$$

$$c(Fe^{3+}) (1 + K_{11,a}\, c(OH^-) + K_{12,a}(c(OH^-))^2 + K_{13,a}(c(OH^-))^3) \qquad (3.14)$$

The total Fe (III) concentration ($c(Fe(III))_T$) in the leachate was measured in the laboratory [1]. $c(OH^-)$ can be obtained from pH value of the leachate. Thus, the concentration of the species ($c(Fe^{3+})$) can be obtained from Equation (3.14). Once $c(Fe^{3+})$ is obtained, $c(Fe(OH)^{2+})$, $c(Fe(OH)_2^+)$ and $c(Fe(OH)_3^0)$ can be calculated from equations (3.11), (3.12) and (3.13), respectively. Similarly, the approximate concentrations of other ionic species that participate in the complex reactions (Table 3.2) can be calculated. The c values of Ca, Mg, Zn, Cl^- and Na for the calculation of the ionic strength (I) came directly from the measured concentrations in the laboratory [1]. These ions did not take part in complex reactions.

The total value of I in the leachate at different sludge solids concentration was calculated using Equation (3.7). The values of I thus obtained at pH 1.3 and 3 are presented in Figures 3.1 and 3.2, respectively. It should be noted that the ionic strength (I) for the tannery sludge leachate at different solids concentration and pH is more than 0.3 (Figures 3.1 and 3.2). Based on this observation ($I > 0.3$) mol/kg as suggested by Morel and Hering [6], Davis equation (Equation 3.5) can be used to approximately calculate the activity coefficient of individual ions in the tannery sludge leachate.

3.6 Calculation of Qc and Kc

In order to obtain the concentration product (Q_c) of the precipitated ions, the precise concentration of all dissolved ions should be known.

The concentration of some dissolved ions (Ca^{2+}, Mg^{2+}, Zn^{2+}, Na^+ and Cl^-) was obtained directly from the laboratory measured values. Some dissolved ions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, Fe^{3+}, Al^{3+}, Cr^{3+}) took part in different complex reactions during the leaching process and are given in Table 3.2. In this case the measured value is the total concentration in different species. The concentration of individual species can not be measured in the laboratory. For example, the measured value of $[Fe(III)]_T=[Fe^{3+}]+[Fe(OH)^{2+}]+[Fe(OH)_2^+]+[Fe(OH)_3^0]$. Therefore, their concentrations can only be obtained by calculations. The calculation of the concentration of these ions is somewhat similar to that performed for the calculation of the ionic strength. However, to obtain a precise concentration of Fe(III) species, K_a must be replaced by K_c in equation (3.14). The precise calculation of the concentration of Fe^{3+} species (defined as [Fe(III)]) is based on: (a) the measured concentration of Fe^{3+}, (b) K_a values for complex reactions (Table 3.2), and (c) the ionic strength (I) of the leachate (Figures 3.1 and 3.2). For example, $[Fe^{3+}]$ in the leachate was calculated by the following formulas.

$$Fe^{3+}+OH^- = Fe(OH)^{2+},\ K_{11,\,c} \qquad (3.15)$$

$$Fe^{3+}+2OH^- = Fe(OH)_2^+,\ K_{12,\,c} \qquad (3.16)$$

$$Fe^{3+}+3OH^- = Fe(OH)_3^0,\ K_{13,c} \qquad (3.17)$$

Where, $K_{11,\,c}$, $K_{12,\,c}$ and $K_{13,c}$ are concentration equilibrium constants and may be written as

$$K_{11,\,c}=[Fe(OH)^{2+}]/[Fe^{3+}][OH^-] \qquad (3.18)$$

$$K_{12,\,c}=[Fe(OH)_2^+]/[Fe^{3+}][OH^-]^2 \qquad (3.19)$$

$$K_{13,c}=[Fe(OH)_3^0]/[Fe^{3+}][OH^-]^3 \qquad (3.20)$$

The total Fe^{3+} concentration $[Fe(III)]_T$ may be written as,

$$[Fe(III)]_T= [Fe^{3+}]+[Fe(OH)^{2+}]+[Fe(OH)_2^+]+[Fe(OH)_3^0] =$$

$$[Fe^{3+}](1+K_{11,c}[OH^-]+ K_{12,c}[OH^-]^2+ K_{13,c}[OH^-]^3) \qquad (3.21)$$

Total ferric concentration $[Fe(III)]_T$ in the leachate was measured in the laboratory and $[OH^-]$ was obtained from the pH value of the leachate (pH 1.3 or 3.0). In order to calculate $[Fe^{3+}]$ in the leachate, the required values of $K_{11,c}$, $K_{12,c}$ and $K_{13,c}$ were calculated. For example, $K_{11,c}$ value was calculated from the following equation.

$$K_{11,\,a} = a(Fe(OH)^{2+}) / a(Fe^{3+})\, a(OH^-) =$$

$$([Fe(OH)^{2+}]/[Fe^{3+}][\,OH^-])(\gamma(Fe(OH)^{2+})/\gamma(Fe^{3+})\gamma(\,OH^-)) =$$

$$K_{11,\,c}\,(\gamma(Fe(OH)^{2+})/\gamma(Fe^{3+})\gamma(\,OH^-)) \qquad (3.22)$$

where, $a(Fe(OH)^{2+})$, $a(Fe^{3+})$ and $a(OH^-)$ are activities. $K_{11,\,a}$ is the activity equilibrium constant (Table 3.2). $\gamma(Fe\ (OH)\ ^{2+})$, $\gamma(Fe^{3+})$ and $\gamma(OH^-)$ are activity coefficients. These activity coefficients were calculated by Davies equation (Equation (3.5)). Hence, $[Fe^{3+}]$ was obtained from Equations (3.5) and (3.18) to (3.21). Similarly, the precise concentration of other precipitated ions (Table 3.1) (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, Fe^{3+}, Al^{3+} and Cr^{3+}) in leachate was calculated. Thus, the Q_c values for each precipitation reaction (given in Table 3.1) was calculated. The K_c values for the precipitation reactions were obtained from Equation (3.6). The values of log (Q_c/K_c) for each precipitation reaction in Table 3.1 at different conditions (pH and sludge solids concentration) were thus obtained. The values of $\log K_c$ and $\log(Q_c/K_c)$ thus calculated at various sludge solids concentration and pH (1.3 and 3.0) are presented in Figures 3.1 to 3.4.

3.7 Formation of precipitates during tannery sludge leaching process

Log (Q_c/K_c) values of precipitation reactions No 1, 2, 3, 4, 5, 7, 9 (Table 3.1) at pH 1.3 and pH 3.0 are presented in Figures 3 and 4, respectively. The values of Log (Q_c/K_c) at pH 3.0 are greater than zero (Figure 3.4). The only exception is Ca that exhibits Log (Q_c/K_c) value less than 0 at sludge solids concentration ≤ 40 g/L. The corresponding values for other reactions such as reactions No 6 and 10 to 18 (Table 3.1) were calculated and found to be less than zero. Based on these calculations various species that could precipitate at different sludge solids concentration and pH are listed in Table 3.3. This indicates that the possible metal precipitates formed during the leaching process are (am)

$Cr(OH)_3$, (am) $CrPO_4$, (am)$Fe(OH)_3$, α-FeO(OH) (goethite), $FePO_4 \cdot 2H_2O$, (am) $AlPO_4 \cdot 2H_2O$, and $CaSO_4 \cdot 2H_2O$ (gypsum) (Table 3.3).

At pH 1.3, $Cr(OH)_3$ did not form (Figure 3.3). $Cr(OH)_3$ can form when solution pH value is 3.0 for all sludge solids concentration. $CrPO_4$ can form at pH 1.3 when sludge solids concentration is more than 78.5 g/L. $CrPO_4$ was predicted to be precipitated at all sludge solids concentrations at pH 3.0. $AlPO_4$ can form at pH 1.3 and sludge solids concentration 140 g/L. At pH 3.0, $AlPO_4$ was precipitated at all sludge solids concentration studied. $Fe(OH)_3$ can form at pH 3.0 and all sludge solids concentration studied. α-FeO(OH) (goethite) can form at pH 1.3 and at sludge solids concentration more than 39.2 g/L. At pH=3.0, α-FeO(OH) was predicted to be precipitated at all sludge solids concentrations studied. $FePO_4$ can form at pH 1.3 or 3.0 at all sludge solids concentration studied. At pH 3.0, $CaSO_4 \cdot 2H_2O$ can form when sludge solids concentration is more than 39.2 g/L. At pH 1.3, $CaSO_4 \cdot 2H_2O$ can form at all sludge solids concentrations used. In general, a higher pH value (pH 3.0) and a higher sludge solids concentration facilitate the formation of precipitates.

3.8 Experimental proof of the formation of precipitates

Precipitates of $Cr(OH)_3$, $CrPO_4$ and $AlPO_4 \cdot 2H_2O$ do not exist in crystal form [7, 8]. Therefore, X ray diffraction method can not be used to verify the existence of these precipitates. However, the precipitates obtained based on the thermodynamic calculations may be corroborated with the experimental results obtained on metal solubilization at different sludge solids concentration and pH [1].

The most direct proof for the formation of $CaSO_4 \cdot 2H_2O$ precipitate is the low leaching yield of Ca. About 10 % Ca was solubilized using sulphuric acid as extractant [1]. In contrast, Ca leaching yields was 70 to 80 % using HNO_3 or HCl as extracting agents. The laboratory results indicated that in most of the cases the leaching yield of metals was in the following order: Al ≅ Mg > Cr ≅ Zn >Fe >Ca [1]. In addition, Ca concentration in the leachate did not vary to a large extent with sludge solids concentration at a given pH (Figure 3.5). It suggested that there was a precipitation reaction that controlled the concentration of Ca in the leaching solution. Solution pH has very little effect on Ca solubilization. The leaching yield of Ca decreased significantly as sludge solids concentration increased [1]. This was due to the increased SO_4^{2-} concentration required to adjust solution pH at larger solids concentration. On the other hand, a high yield of Ca solubilization occurred when HNO_3 or HCl was used to leach the sludge.

The leaching yield of orthophosphate (PO_4^{3-}) was lower than 35 % [1]. This phenomenon was probably caused by the formation of phosphate precipitates such as $FePO_4{\cdot}2H_2O$, $AlPO_4{\cdot}2H_2O$ and $CrPO_4$ (Table 3.3). It should be noted that $FePO_4{\cdot}2H_2O$ might form at pH 1.3 for all solids concentration studied. $CrPO_4$ might form at pH 1.3 only when sludge solids concentration is more than 78.5 g/L. $FePO_4{\cdot}2H_2O$, $AlPO_4{\cdot}2H_2O$ and $CrPO_4$ can form at pH 3.0 for all solids concentration used. Therefore, the formation of $CrPO_4$ and $AlPO_4$ at pH 3.0 is likely to be responsible for the difference of phosphate concentration between pH 3.0 and pH 1.3 when solids concentration is less than 78.5 g/L (Table 3.4). $AlPO_4{\cdot}2H_2O$ is the sole precipitated species of Al. This may explain the slight difference of the leaching yield of Al between pH 1.3 and pH 3.0 (Table 3.4).

$FePO_4{\cdot}2H_2O$ and α-FeO(OH) (goethite) can form at pH 1.3 and pH 3.0 (Table 3.3). At pH 1.3, $FePO_4{\cdot}2H_2O$, α-FeO(OH) (goethite) and $CaSO_4{\cdot}2H_2O$ precipitates can form at almost all sludge solids concentrations. Hence, Fe(III) loss as precipitates might be higher among the metals Cr, Al, Mg, Zn, Fe and Ca. Actually, the leaching yield of Fe(III) is next to calcium as described before.

Both the leaching yield of Cr(III) and its concentration have a significant difference at pH 1.3 and pH 3.0 ([1], Table 3.4). The pH value has less effect on the leaching yield of Zn [1]. These phenomena are most likely relevant to the presence of $Cr(OH)_3$ and the absence of $Zn(OH)_2$. This can be illustrated as follows.

Although the precipitate of $CrPO_4$ may cause the concentration difference of Cr(III) at different pH values, however, it does not cause a large difference as observed in Table 3.4 This is due to the fact that the difference of PO_4^{3-} concentration between pH 1.3 and pH 3.0 is much less than that of Cr(III) (Table 3.4). Moreover, total content of orthophosphate in the sludge is low, 0.114 %. [1]. According to the thermodynamic calculation (Table 3.3), there are only two types of Cr(III) precipitates, $CrPO_4$, and $Cr(OH)_3$. Therefore, $Cr(OH)_3$ is probably the main Cr(III) precipitate in the leaching process. There is no $Cr(OH)_3$ at pH 1.3. $Cr(OH)_3$ can form only at pH 3.0 (Table 3.3). Hence, the formation of $Cr(OH)_3$ caused the significant difference of solubilised Cr(III) concentrations between pH 3.0 and 1.3 as observed in Table 3.4.

Further, the solubility of $CrPO_4$ and $Cr(OH)_3$ decreases with increase in temperature [8, 9]. Hence Cr leaching yield will decrease with temperature. This is in agreement with the experimental observations of Shen *et al.* [1].

From Table 3.3, it is observed that at pH 1.3 and sludge solids concentration of 58.9 g/L or less, FePO4 precipitates whereas CrPO4 does not. Therefore, it is inferred that more Fe could be removed without the loss of chromium by adding additional phosphate to the leaching mixture under the above leaching conditions. In order to verify this finding, an experiment was conducted at 40 g/L and 100 g/L sludge solids concentration and the sludge was fortified with KH_2PO_4. The results obtained on Cr and Fe concentration in leachate are presented in Table 3.5.

From Table 3.5, it is observed that at pH 1.3 and a sludge solids concentration less than 58.9 g/L, $FePO_4$ precipitates whereas $CrPO_4$ does not. The concentration of Fe in leachate decreased with KH_2PO_4, whereas Cr concentration remains almost constant. At 100 g/L sludge solids concentration, the concentration of Cr as well as Fe in the leachate decreased with the addition of KH_2PO_4. Therefore, it is inferred that more Fe could be removed without the loss of chromium by adding additional phosphate to the leaching mixture under the above leaching conditions.

The solubilization of Cr(III) can also be explained as follows. It is reasonable to assume that the principal form of precipitates in the leaching process is $Cr(OH)_3$ and main soluble Cr(III) species in the leaching solution are Cr^{3+}, $Cr(OH)^{2+}$ $Cr(OH)_2^{+}$ and $Cr(OH)_3^{0}$ [8].

$$Cr(OH)_3\,(s)+3H^{+}\rightarrow Cr^{3+}+3H_2O,\ Ks_{10} \qquad (3.23)$$

$$Cr(OH)_3\,(s)+2H^+ \rightarrow Cr(OH)^{2+}+2H_2O,\ Ks_{11} \tag{3.24}$$

$$Cr(OH)_3\,(s)+H^+ \rightarrow Cr(OH)_2^{\ +}+H_2O,\ Ks_{12} \tag{3.25}$$

$$Cr(OH)_3\,(s) \rightarrow Cr(OH)_3^{\ 0},\ Ks_{13} \tag{3.26}$$

Total soluble Cr(III) can be expressed by the equation.

$$[Cr^{3+}]_T = K_{s10}[H^+]^3 + K_{s11}[H^+]^2 + K_{s12}[H^+] + Ks_{13} \tag{3.27}$$

$[Cr^{3+}]_T$ represents the total measured Cr(III). K_{s10}, K_{s11}, K_{s12} and K_{s13} are equilibrium constants. This equation illustrates that more soluble Cr(III) can be obtained at a lower pH (pH 1.3).

Since there are no precipitates of Mg, the leaching yield of Mg is high [1]. Moreover, both pH and sludge solids concentration have very little influence on the leaching yield of Mg.

Thus summarising the above discussion, the precipitates predicted from thermodynamic calculations may be used to explain the leaching phenomena of various metals (Ca, Mg, Al, Fe, Cr, and Zn) and orthophosphate in the leachate.

3.9 Effect of ionic strength on the solubility of precipitates

The activity equilibrium constants (K_a) of precipitation reactions (Table 3.1) are corrected to obtain concentration equilibrium constants (K_c) according to the ionic strengths of leaching solution and the K_c values are presented in Figures 3.1 and 3.2. The concentration equilibrium constants (K_c) of these precipitates are generally higher than their corresponding activity equilibrium constants K_a ($K_a = K_c$, at zero solids concentration or $I = 0$, Figures 3.1 and 3.2). The K_c value decreased with increased sludge solids concentration. The K_c values of most of the precipitates become even less than their corresponding K_a values when sludge concentration is 140 g/L. The smaller the K_c value, the smaller is the solubility of corresponding precipitate. Therefore, the solubility of these precipitates decreased as sludge solids concentration (or the ionic strength I of the leachate) increased. In fact, the leaching yield of some metals (Cr, Fe, Al, Ca) indeed decreased as sludge concentration increased in most of the cases [1]. Chuan and Liu [10] reported that precipitation-dissolution reaction controlled the release behaviour of Cr(III) from tannery sludge. Similar situation occurred in the case of other metals such as Fe, Al and Ca as shown by thermodynamic calculations. Thus, the decrease of leaching yield of four metals (Cr, Fe, Al & Ca) with the increased sludge concentration is likely to be partially caused by the decrease of the solubility of their precipitates. Hence, the thermodynamic calculations can explain the variation of solubility of above precipitates with sludge solids concentration.

3.10 Effects of dissolved organic matter from tannery sludge on the ionic strength

The dissolved organic matters may react with dissolved Cr(III) to form complexes. These complex reactions will compete for the dissolved Cr(III) with the precipitation reaction and therefore may affect the thermodynamic calculations. Chuan and Liu (1996) reported the effects of organic matter from tannery sludge on the leaching of Cr(III). They found that the concentration of dissolved Cr(III) from the leaching of tannery sludge appeared to be controlled by the solubility of Cr(III) rather than an adsorption-desorption reaction. Experimental results also showed that solubilisation of Cr(III) in the leaching process was near the theoretical solubility [11, 12]. Chuan and Liu [10] thought that this could be attributed to the fact that dissolved TOC concentration was relatively low under acidic conditions, or the long equilibration period had rendered biodegradable fraction of soluble TOC non-existent [10] (Chuan and Liu, 1996). Therefore, the dissolved organic matter has little effect on the leaching of Cr(III) from tannery sludge. Hence, the effect of dissolved organic matter on thermodynamic calculations was neglected.

3.11 Conclusions

Thermodynamic computations based on the Gibbs free energy, $\Delta G = RT\ln(Q_c/K_c)$, were performed to predict the possible metal precipitates formed during tannery sludge leaching process. The results indicated that the possible metal precipitates formed during the leaching process were (am) $Cr(OH)_3$, (am) $CrPO_4$, (am)$Fe(OH)_3$, α-FeOOH (goethite), $FePO_4 \cdot 2H_2O$, (am) $AlPO_4 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$ (gypsum). According to thermodynamic calculations, the solubility of these precipitates was found to decrease with the increase in the ionic strength (or sludge solids concentration). The computed results were supported by experimental observations.

3.12 Acknowledgements

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Table 3.1 **Possible precipitation reactions in the tannery sludge leaching process (T=25°C, I=0)**

No	Possible precipitation reactions	$Log_{10}Ka$	References
1	$Cr(OH)_3(s) = Cr^{3+} + 3OH^-$	-37.4	[13]
2	$CrPO_4(s) + 2H_2O = Cr^{3+} + H_2PO_4^- + 2OH^-$	-31.07	[14]
3	$(am)Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	2.5	[3]
4	$FePO_4.2H_2O(s) = Fe^{3+} + H_2PO_4^- + 2OH^-$	-35.65	[14]
5	α-$FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	2.5	[3]
6	$(am)Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	10.8	[3]
7	$AlPO_4.2H_2O(s) = Al^{3+} + H_2PO_4^- + 2OH^-$	-30.52	[14]
8	$Ca(OH)_2(s) = Ca^{2+} + 2OH^-$	-5.2	[15]
9	$CaSO_4.2H_2O(s) = Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.6	[3]
10	$CaHPO_4(s) = Ca^{2+} + HPO_4^{2-}$	-6.6	[3]
11	$Ca_{10}(PO_4)_6(OH)_2(s) = 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	-114	[3]
12	$Ca_3(PO_4)_2(s) = 3Ca^{2+} + 2PO_4^{3-}$	-28.9	[3]
13	$Ca_4H(PO_4)_3(s) = 4Ca^{2+} + 3PO_4^{3-} + H^+$	-46.9	[3]
14	$Mg(OH)_2(s) = Mg^{2+} + 2OH^-$	-11.6	[15]
15	$MgHPO_4(s) = Mg^{2+} + HPO_4^{2-}$	-2.5	[3]
16	$Mg_3(PO_4)_2(s) = 3Mg^{2+} + 2PO_4^{3-}$	-23.18	[3]
17	$Zn(OH)_2(s) = Zn^{2+} + 2OH^-$	-15.5	[3]
18	$Zn_3(PO_4)_2(s) = 3Zn^{2+} + 2PO_4^{3-}$	-31.94	[14]

Table 3.2 **$LogK_a$ values of the possible complex reactions in the tannery sludge leaching process (T=25°C, I=0)**

Complex reactions	$Log_{10}Ka$	References
$H_3PO_4 = PO_4^{3-} + 3H^+$	-21.71	[14]
$H_2PO_4^- = PO_4^{3-} + 2H^+$	-19.55	[14]
$HPO_4^{2-} = PO_4^{3-} + H^+$	-12.35	[14]
$HSO_4^- = SO_4^{2-} + H^+$	-1.99	[16]
$Fe^{3+} + OH^- = Fe(OH)^{2+}$	11.81	[15]
$Fe^{3+} + 2OH^- = Fe(OH)_2^+$	22.33	[15]
$Fe^{3+} + 3OH^- = Fe(OH)_3^0$	31.8	[15]
$Al^{3+} + OH^- = Al(OH)^{2+}$	9.03	[15]
$Al^{3+} + 2OH^- = Al(OH)_2^+$	18.7	[15]
$Al^{3+} + 3OH^- = Al(OH)_3^0$	27	[15]
$Cr^{3+} + OH^- = Cr(OH)^{2+}$	10.0	[17]
$Cr^{3+} + 2OH^- = Cr(OH)_2^+$	18.35	[17]
$Cr^{3+} + 3OH^- = Cr(OH)_3^0$	34.00	[17]

Table 3.3 **Precipitates predicted in the leaching process of tannery sludge according to thermodynamic calculations**

Sludge solids concentration	Predicted precipitates	
($g \cdot L^{-1}$)	pH 1.3	pH 3.0
19.6	$CaSO_4$, $FePO_4$	$AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$
39.2	$CaSO_4$, FeOOH, $FePO_4$	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$
58.9	$CaSO_4$, FeOOH, $FePO_4$	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$
78.5	$CaSO_4$, FeOOH, $FePO_4$, $CrPO_4$	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$
100	$CaSO_4$, FeOOH, $FePO_4$, $CrPO_4$	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$
140	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $CrPO_4$	$CaSO_4$, $AlPO_4$, FeOOH, $FePO_4$, $Fe(OH)_3$, $CrPO_4$, $Cr(OH)_3$

Table 3.4 **Concentration difference (mM) of elements between pH 1.3 and pH 3.0 in the leaching solutions (element concentration at pH 1.3 minus that at pH 3.0)**

Element	Sludge solids concentration (g·L^{-1})					
	19.6	39.2	58.9	78.5	100	140
Cr	7.307	9.538	17.73	19.88	13.38	2.231
Al	0.537	0.748	3.967	1.633	1.703	4.593
Fe	0.144	0.186	0.402	0.404	0.35	1.021
Ca	1.153	0.555	3.463	1.863	0.26	0.315
Mg	0.329	1.523	5.805	2.140	11.36	-16.79
Zn	0.0091	0.0198	0.0122	0.015	0.018	0
Na	1.957	-2.087	5	3.652	4.696	-3.478
PO_4^{3-}	0.0257	0.0524	0.0936	0.102	-0.026	-0.149
SO_4^{2-}	4.14	6.7	11.97	17.2	7.97	14.32
Cl^-	-0.089	-0.022	-0.099	-0.016	0.031	-0.001

Table 3.5 Solubilisation of Cr and Fe (mg L^{-1}) at different concentrations of KH_2PO_4 and sludge solids

Added KH_2PO_4 ($g \cdot L^{-1}$)	40 g sludge solids L^{-1}*		100 g sludge solids L^{-1}*	
	Cr	Fe	Cr	Fe
0	4001	133	9472	221
0.27	3990	104	9372	200
0.56	3996	93	9285	203

*The amount of added KH_2PO_4 was so designed that the precipitate of $CrPO_4$ did not form at this concentration according to the thermodynamic calculations.

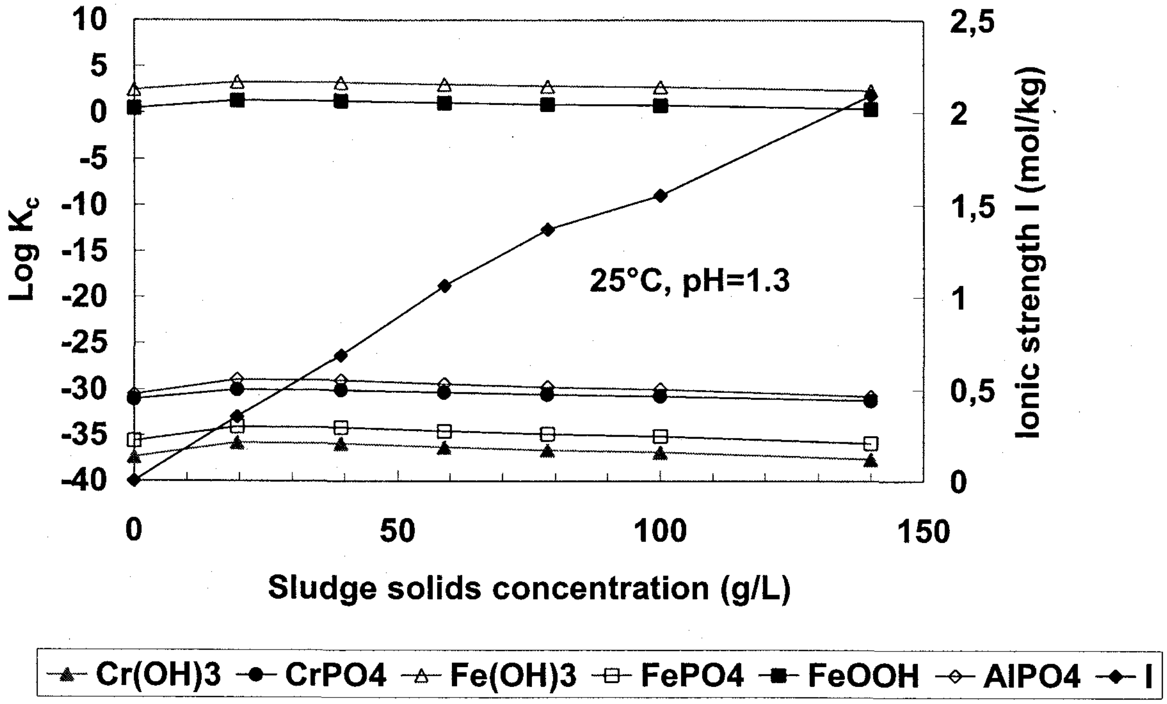

Figure 3.1 Variation of LogK_c and ionic strength I with sludge solids concentration

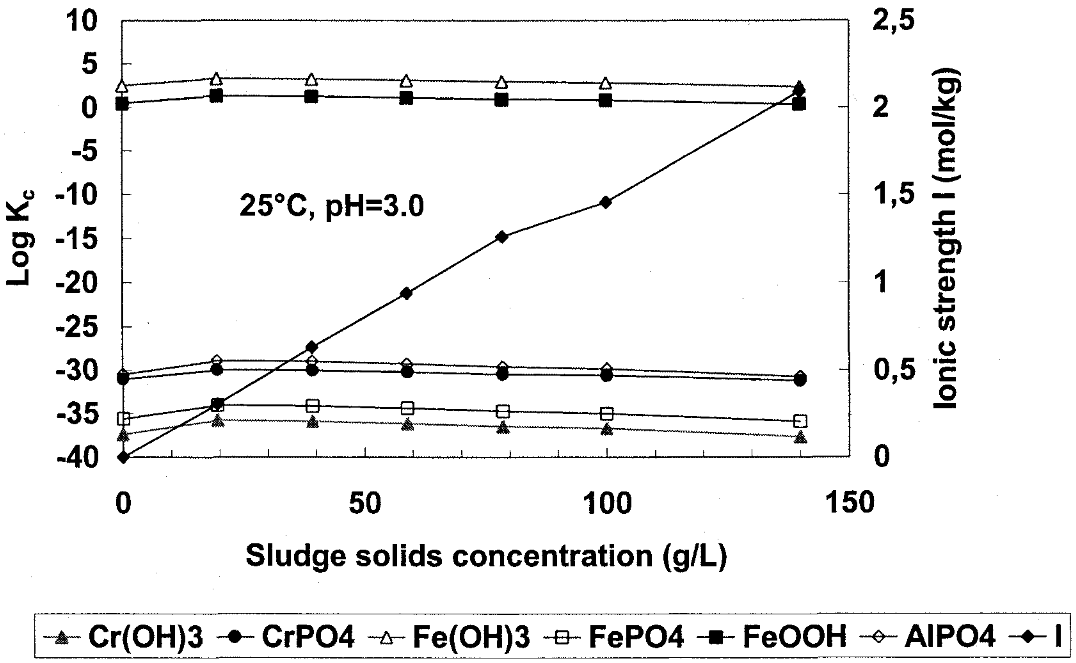

Figure 3.2 Variation of LogK$_c$ and ionic strength I with sludge solids concentration

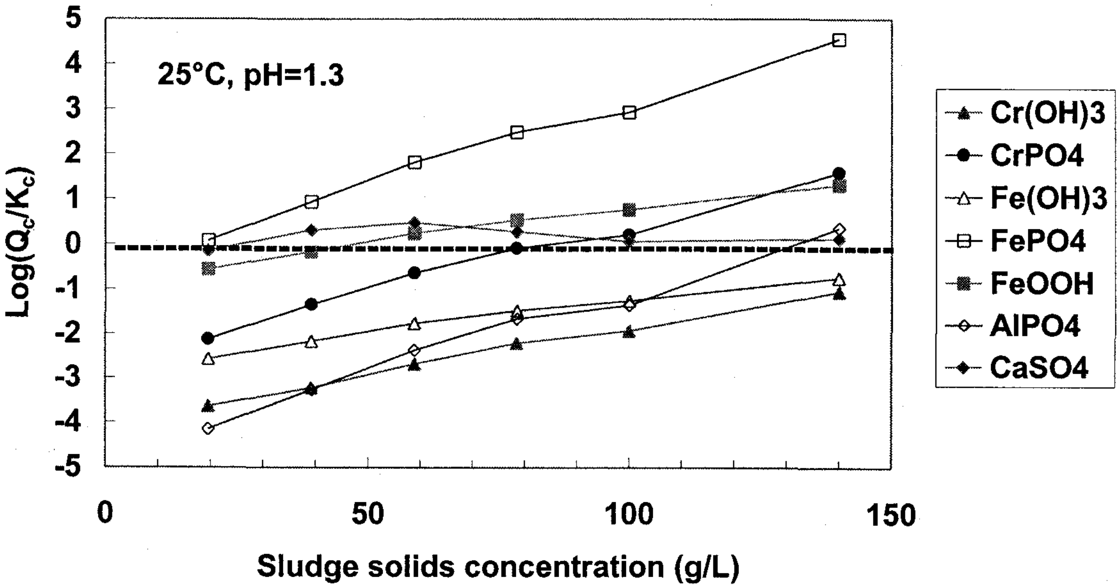

Figure 3.3 Variation of Log(Q_c/K_c) with sludge solids concentration

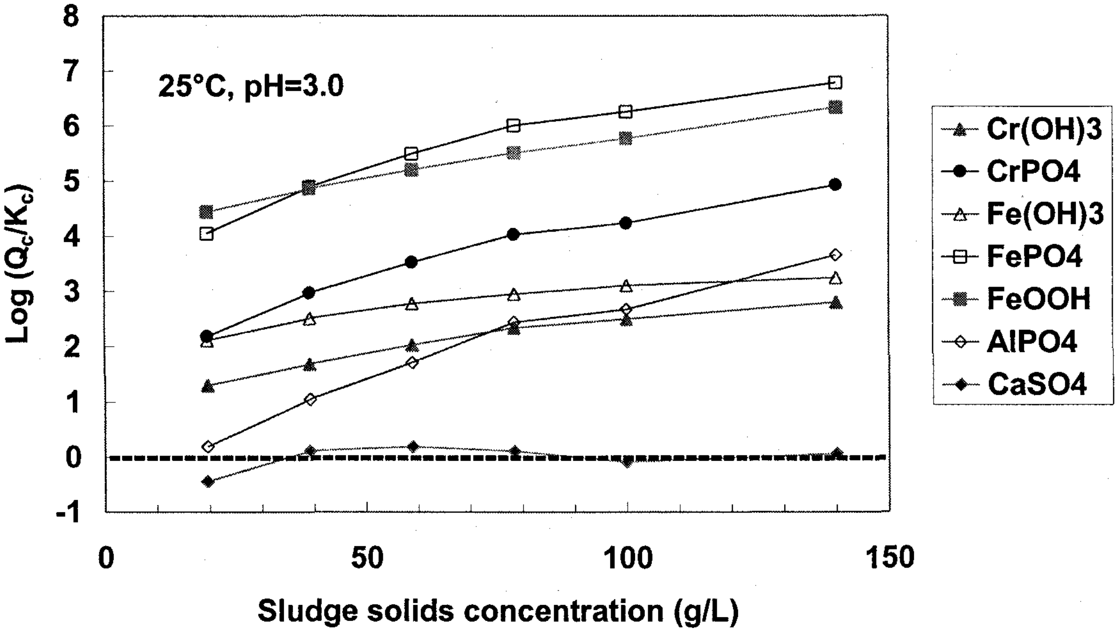

Figure 3.4 Variation of Log(Q_c/K_c) with sludge solids concentration

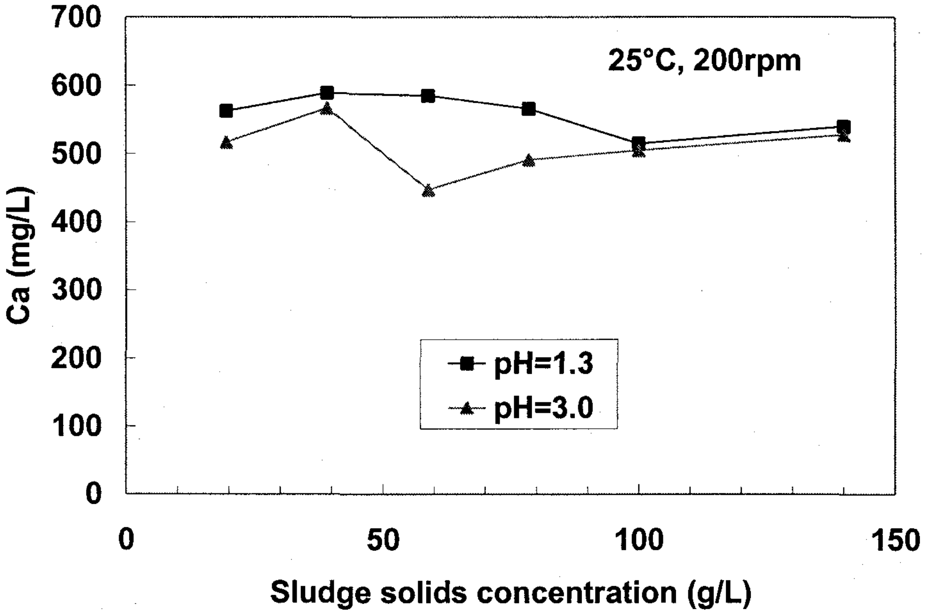

Figure 3.5 Variation of Ca concentration with sludge solids concentration

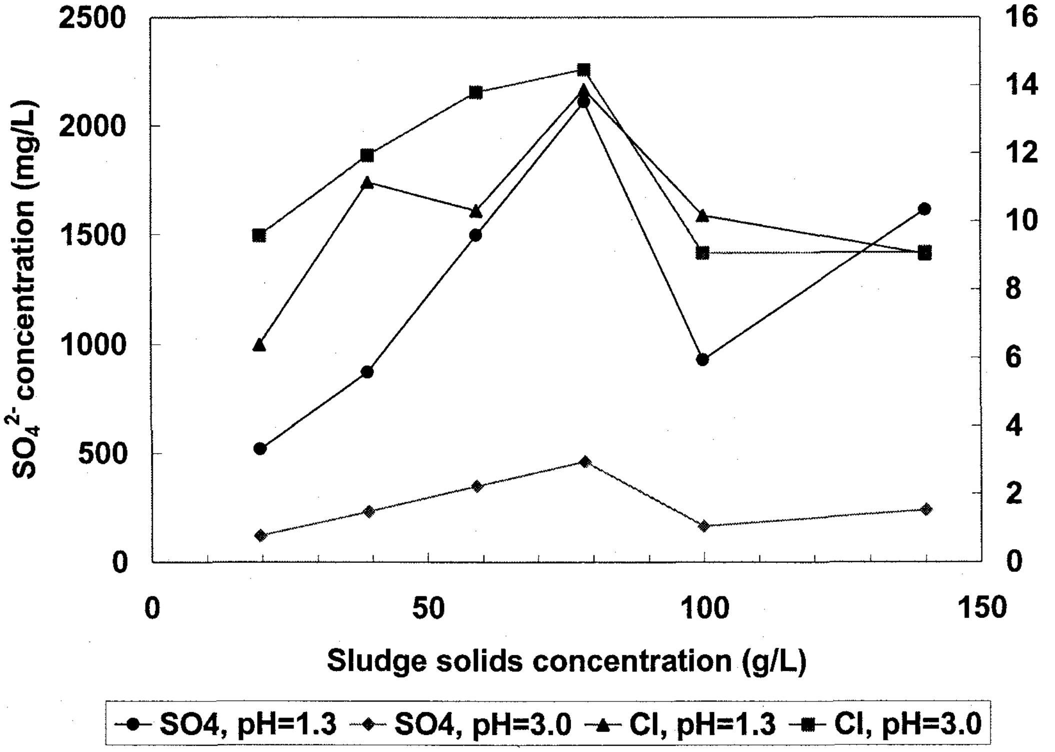

Figure 3.6 **Variation of SO_4^{2-} and Cl^- concentration with sludge solids concentration**

CHAPITRE 4

CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

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4 CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

4.1 Résumé

Les concentrations élevées en Al, en Fe, en Ca, en Mg et en Zn dans l'agent tannant sont nuisibles aux propriétés du cuir tanné. Pour faciliter l'enlèvement du chrome des boues de tannerie et recycler le chrome comme agent tannant, ces cinq métaux doit d'abord être enlevés autant que possible de l'extrait acide des boues de tannerie. Ce travail propose un procédé en trois étapes pour la séparation du Cr(III) de ces métaux nuisibles présents dans l'extrait acide (le lixiviat) des boues de tannerie. Lors de l'étape 1, le lixiviat est dilué de manière appropriée et l'Al est enlevé efficacement par précipitation sous forme d'hydroxyde à 21°C par ajustement du pH du lixiviat entre 4.6 et 4.8. Le taux optimal de dilution pour le lixiviat ayant une concentration en solides de 80 g/L se situe à 6.3. Dans ces conditions, 50 à 80 % d'Al, 30 à 40 % du Fe et 22 à 40 % du Cr sont enlevés et le taux de discrimination de l'Al au Cr se situe entre 2.0 et 2.2, selon le pH. Dans l'étape 2, le Al et le Fe restant dans le filtrat après l'étape 1 sont éliminés davantage à 21°C en réagissant avec un agent organique le cupferron. Les précipitations du cupferron avec tous les métaux peuvent être accomplies rapidement, soit en moins de 10 minutes. Le pH optimal pour l'enlèvement de l'Al, du Fe et du Zn se situe entre 3.0 et 4.8. Le rapport molaire optimum du cupferron à la somme de l'Al, du Fe et du Zn se situe entre 2.8 et 4.0. Dans ces conditions, environ 90 % du Fe, 80 % de l'Al, 70 % du Zn et 7 % du Cr sont précipités. Pendant l'étape 2, la plupart du Fe, de l'Al et du Zn dans le lixiviat initial de boues de tannerie sont séparés du Cr(III), du Ca et du Mg. Lors de l'étape 3, le Ca et le Mg laissés dans le filtrat après l'étape 2 ont été séparés du Cr(III) en ajustant le pH du filtrat à 7.0 avec une solution d'hydroxyde de sodium à 21°C. Les efficacités d'enlèvement du Cr(III), du Ca et du Mg sont respectivement de 99.6 %, 13.7 % et 4.9 %. Après l'étape 3, les pourcentages molaires d'Al, du Ca, du Cr, du Fe, du Mg et du Zn dans le précipité formé à pH 7.0 et 21°C dans un cas typique sont respectivement de 2.94, 0.06, 95.65, 0.30, 1.01 et 0.04. Les efficacités globales d'enlèvement des métaux obtenus

dans un cas typique sont les suivantes: 77 % Al, 84.4 % Fe, 99.2 % Ca, 98.5 % Mg et 61 % Zn. Au total,près de 42 % du Cr(III) (étape 1 + étape 2) est enlevé par précipitation. Le précipité d'hydroxyde de Cr(III) (à partir de l'étape 1) peut être récupéré efficacement par la méthode conventionnelle d'oxydation. Le cupferron épuisé en tant que cupferrate peut être récupéré et réutilisé. Le procédé de séparation est simple puisqu'il ne comporte pas l'oxydation du Cr(III) et l'utilisation de résines échangeuses d'ions.

4.2 Abstract

High concentrations of Al, Fe, Ca, Mg and Zn in the tanning agent are detrimental to the properties of tanned leather. To facilitate removal of chromium from the tannery sludge and recycle to the tanning agent, first these five metals must be removed as much as possible from the acid extract of tannery sludge. This work proposes a three step process for the separation of Cr(III) from these interfering elements metals present in the acid extract (leachate) of tannery sludge. In step 1, the leachate was appropriately diluted and the Al was efficiently removed by precipitation in the form of hydroxide at 21°C and adjusting the pH between 4.6 and 4.8. The optimum dilution ratio for the tannery sludge leachate at a solids concentration 80 g/L was 6.3. Under the above operating conditions, 50 to 80 % of Al, 30 to 40 % of Fe and 22 to 40 % of Cr were removed and the discrimination ratio between Al to Cr was between 2.0 and 2.2, depending on the pH. In step 2, the Al and Fe that remained in the filtrate after step 1 were further reduced at 21°C by reacting with an organic agent cupferron (Y). The precipitation reactions of cupferron with all of metals were completed in 10 min. The optimum pH for the removal of Al, Fe and Zn was between 3 and 4.83. The optimum molar ratio of cupferron to the sum of Al, Fe and Zn was between 2.78 to 4. Under these operating conditions, about 90 % of Fe, 80 % of Al, 70 % of Zn and 7 % of Cr were precipitated. During step 2, most of Fe, Al and Zn originally present in the tannery leachate were separated from Cr(III), Ca and Mg. In step 3, the Ca and Mg left in the filtrate after step 2 were separated from Cr(III) by adjusting the pH of the filtrate to 7.0 with the solution of sodium hydroxide at 21°C. The removal efficiency of Cr(III), Ca and Mg were 99.6 %, 13.7 % and 4.9 %. After step 3, the molar percentages of Al, Ca, Cr, Fe, Mg and Zn in the precipitate formed at pH 7.0 and 21°C in a typical case were 2.94, 0.055, 95.649, 0.302, 1.013 and 0.041 respectively. The overall removal efficiencies of the targeted metals in a typical case were as follows: Al – 77 %, Fe - 84.4 %, Ca - 99.2 %, Mg - 98.5 % and Zn – 61 %. About 42 % of Cr(III) in total (step 1 + step 2) was removed as precipitates with other metals. The hydroxide precipitates of Cr(III) (from step 1) can be recovered efficiently by the conventional oxidation method. The spent cupferrons as cupferrates can be recovered and recycled.

The separation process was simple since it does not involve the oxidation of Cr(III) and the use of ionic exchange resin.

Key words: Tannery sludge, acid extract, removal of Al, Fe, Ca, Mg and Zn, Cr(III) recovery, cupferron.

4.3 Introduction

The trivalent chromium, typically basic hydrated chromic sulfate, is utilized in a large quantity in the tanning of hides. Leather tanning consumes about 32% of the total world trade of chromium compounds (Walsh and John, 1996). However, about 50% of chromium salts from the production process are disposed with the tannery sludge or tannery wastewater (Tiravanti *et al.,* 1997). Despite of the extreme high content of Cr(III) in the tannery sludge (about 13 % w/w on a dry basis, Table 4.1), most of the tannery sludge is still disposed in landfills due to the absence of suitable treatment method. The recovery of Cr(III) and its reuse in the tanning process has economical interest and reduces Cr(III) release in the environment. However, the reuse of Cr(III) in the tanning process is strongly dependent on the separation of Cr(III) from other interfering metals such as Fe, Mg, Al, Ca, and Zn (Macchi *et al.,* 1991). High concentration of these five metals in the tanning agent is detrimental to the properties of tanned leather (Randall, 1985). In order to separate Cr(III) from other metals, most of previously reported methods for chromium recovery employed H_2O_2 to oxidize Cr(III) to Cr(VI) in alkaline solution at 60°C (Macchi *et al.,* 1991; Tiravanti *et al.,* 1997). It was found that for molar ratios of (Fe+Mg)/Cr in the acid leachate 0.81 and 8.2, the required H_2O_2/Cr molar ratios were 7 and 80 respectively. The corresponding oxidation efficiencies of Cr(III) were 83% and 70 % respectively (Macchi *et al.,* 1991). Therefore, at least 20 to 30 % of Cr(III) in the acid extract could not be recovered while large amount of H_2O_2 was consumed in this process. Expensive cationic exchange resin was also needed to separate Cr(VI) from Ca and Mg. The use of these agents and materials greatly increased the recovery cost. Moreover, the process produced Cr(VI) that was very toxic to the environment. After separation of Cr(VI) from other metals, SO_2 (a toxic gas) was usually needed to reduce Cr(VI) to Cr(III) for preparing the tanning agent. To alleviate these unfavorable factors brought about by the Cr(III) oxidation method, the isolation of Cr(III) by the non-oxidation means was preferable.

Majone (1986) reported that organic agent cupferron could be used as a selective precipitating agent for Fe and Al. Cupferron is a solid, soluble in water at room temperature and is widely used in analytical chemistry as a specific complexing agent for some metals such as Fe(III) and Cu(II). It was reported that cupferron (Y) could react stoichiometrically with Al and Fe(III) in the tannery leachate to form insoluble complexes in the form of MY_3 and Cr(III) was left in the residual solution (Majone, 1986). The acid extract of tannery sludge was directly treated with solid cupferron at pH 3. More than 99 % of Fe and Al were removed as precipitates while less than 12 % of Cr(III) was removed at the same time. The disadvantages of this method was that only part of the expensive cupferron could be recovered as described by Majone (1986). Also, a large amount of cupferron was required to precipitate Al and Fe, especially for Al, because the molar concentration of Al was about six times that of Fe. The reported recovery efficiency of cupferron was relatively low.

In the present study, a new process scheme was developed to reduce the amount of cupferron required for the precipitation of Al and Fe. The influence of the molar ratio of cupferron to the sum of Al, Fe and Zn on the metal removal efficiency was also investigated. Furthermore this work also proposes a method to separate Cr(III) from Ca and Mg following removal of Al, Fe and Zn from the tannery leachate.

4.4 Materials and methods

4.4.1 Samples of tannery sludge

The sample of dehydrated (filter-press) tannery sludge was procured from “La Tannerie des Ruisseaux” in Rivière-du-loup (Québec, Canada). The sludge contained 69.7 % of water and was stored at 4°C. A part of the sludge sample was dried at 104°C for 48 h before use.

4.4.2 Digestion of the tannery sludge and the precipitates

The weighted samples (0.02 to 0.5 g) were placed in two covered Teflon beakers (100 mL capacity each). A control sample was also carried through the process. Fifteen mL of concentrated HNO_3 was added to each sludge and the blank sample. Then the beakers were placed on a hot plate for digestion. When the solution in the beaker was evaporated to near dryness, an additional 15 mL of concentrated HNO_3 was added to each beaker while heating was continued. After 1 h, 10 mL of HCl was added to each sample. The heating continued until the solution became clear. After cooling, the solution was filtered through Whatman GF/C filter and diluted to 100 mL with 0.2 % HNO_3. The corresponding control values were subtracted for each element analysis. Each metal concentration was calculated as average of the analytical result of the two samples.

4.4.3 Acid extraction of the tannery sludge

Eighty grams of dried tannery sludge was placed in a 2000 mL capacity flask. One liter of acid solution containing 44.5 mL of concentrated sulfuric acid was added to the flask gradually. This solution was agitated in a shaker controlled at 200 rpm and 21°C for 3 days. The mixture was centrifuged at 4000 rpm for 20 min to separate solids from the aqueous phase. After centrifugation the liquid was filtered through GF/C filter to remove the fine insoluble solids in the liquid. The pH of this tannery leachate was 1.01. Metal concentrations of Al, Ca, Cr, Fe, Mg and Zn in the leachate were 792, 632, 11500, 250, 3840 and 16 mg/L, respectively.

4.4.4 Removal of aluminium and iron by the hydroxide precipitation (step 1)

Three aliquots of above acid extract (leachate) were diluted by 4, 6.3 and 8.0 times with Millipore reagent water. The pH values of diluted leachates were around 1.8. These three diluted leachate samples along with original leachate sample were used in this experiment. 160 mL portions of each leachate sample (diluted and original), were placed in a glass beaker of 500 mL. Then to reach a desired pH range between 1.01 to 12.59, 12 N or 3 N NaOH was added drop by drop to each solution under constant stirring at 21°C. At the desired pH, 1.5 mL of sample was drawn and immediately filtered. The filtration was performed by vacuum filtration using a conventional suction flask and Whatman GF/C filter paper. The filtrate was used to determine the remaining dissolved metal concentration.

4.4.5 Removal of residual Al, Fe, and Zn by cupferron precipitation (step 2)

The filtrate obtained after precipitation of Al and Fe was subsequently used to study the effect of time, pH and cupferron (N-Nitroso-N-phenylhydroxylamine ammonium salt, (I)) concentration.

4.4.6 Effect of time on the metals removal by cupferron

After removing part of Al and Fe at pH 4.37 (in step 1) by hydroxide precipitation, the remaining metals concentrations in one of the filtrates were as follows: [Al] = 73.5 mg/L, [Ca]= 81.5 mg/L, [Cr] = 1530 mg/L, [Fe] = 30.5 mg/L, [Mg] = 548 mg/L and [Zn] = 2.5 mg/L. An aliquot of 45 mL of was withdrawn from the filtrate. Then, 0.0552 g of solid cupferron was added directly to the sample. The molar ratio of cupferron to the sum of Al, Fe and Zn was 2.4. The mixture was put in a shaker at 21°C and 150 rpm. Samples of 1.5 mL were drawn sequentially from the supernatant of the mixture at 10, 25, 45, 60, 95 and 145 min. The samples were filtered through GF/C filter and the residual metal concentrations in the filtrate were measured.

4.4.7 Effect of pH on the removal of metals by cupferron

After removing a part of Al and Fe at pH 4.51 by hydroxide precipitation (step 1), the metals concentrations in a typical filtrate were as follows: [Al] = 80 mg/L, [Ca]= 82 mg/L, [Cr] = 1586 mg/L, [Fe] = 31.5 mg/L, [Mg] = 560 mg/L and [Zn] = 2.5 mg/L. Five aliquots of 20 mL each were individually transferred into clean flasks. The pH of these solutions were adjusted with 10 % HCl to 1.99, 2.26, 3.13, 3.50 and 4.16. Then, 0.0227 g of solid cupferron was directly added to each solution. The molar ratio of cupferron to the sum of Al, Fe and Zn was 4.07 for each solution. The stoichiometrical molar ratio required for Al, Fe and Zn suggested by the literature was about 3.0. An excess of molar ratio was used to make sure that cupferron concentration was not limiting the reaction. The mixture was agitated in a shaker at 21°C and 150 rpm. After 30 min of agitation, the mixture was filtered through GF/C filter. The residual metal concentrations in the filtrate were measured.

4.4.8 Effect of the amount of cupferron on the removal of metals

After removing Al and Fe at pH 4.83 by hydroxide precipitation (step 1), the metals concentrations in the filtrate were as follows: [Al] = 63.5 mg/L, [Ca]= 123 mg/L, [Cr] = 1810 mg/L, [Fe] = 34.9 mg/L, [Mg] = 905 mg/L and [Zn] = 3.3 mg/L. Four aliquots of the solutions, each having a volume of 20 mL, were individually transferred into a clean flask. Then, portions of of solid cupferron 0.0126, 0.0189, 0.0262 and 0.0382 g were added directly to the solutions. The molar ratio of cupferron to the sum of Al, Fe and Zn in solution were 1.34, 2.00, 2.78 and 4.05. The solutions were agitated in a shaker at 21°C and 150 rpm. After 30 min of agitation, the mixture was filtered through GF/C filter. The residual metals concentrations in the filtrate were measured.

4.4.9 Removal of Mg and Ca by precipitation (step 3)

After removing Al and Fe at pH 4.83 by hydroxide precipitation (step 1), the metals concentrations in the filtrate were as follows: [Al] = 63 mg/L, [Ca]= 121 mg/L, [Cr] = 1810 mg/L, [Fe] = 34.9 mg/L, [Mg] = 903 mg/L and [Zn] = 3.3 mg/L. A 70 mL aliquot of this filtrate was treated with 0.1505 g of solid cupferron (step 2). The mixture was agitated in a shaker at 21°C and 150 rpm. After 30 min of agitation, the mixture was filtered through GF/C filter. The residual metal concentrations in the filtrate were measured. After that, the filtrate obtained was equally divided into three portions of 20 ml each. The pHs of three solutions were adjusted individually to 6.42, 6.96 and 7.52 with 12 N or 3 N NaOH. The samples were filtered through GF/C filters. The residual metal concentrations in the filtrates were measured. The precipitates retained on the filters were dried at 104°C for 24 h. The dried precipitates were weighed and digested as described above. Metals concentrations of the digested solutions were measured.

4.4.10 Chemical analysis

The pH of the solutions was monitored by a ORION Model 420A pH meter calibrated by three standard buffer solution (pH 4.00, 5.00 and 7.00) during each experiment. Varian VISTA AX CCD Simultaneous ICP-AES was used to measure the dissolved metal (Cr, Al, Fe, Ca, Mg and Zn) concentrations. Cr^{6+} concentration in the digested solutions was determined by the S-diphenylcarbazide method (APHA, 1989). Fe^{2+} concentration was measured by the Phenanthroline method (APHA, 1989). Orthophosphate concentration was analyzed by the ascorbic acid method (APHA, 1989). Total carbon, total nitrogen and total sulfur in the solid powder (>80 mesh) of dried tannery sludge were determined with CARLO ERBA INSTRUMENTS NA 1500 NITROGEN/CARBON/SULPHUR ANALYZER. Water content was obtained from the average weight loss of 5 sludge samples at 104°C over 48 h. The volatile organic matter content was obtained from the average weight loss of the dried sludge samples at 550°C over 48 h.

4.5 Results and discussion

The results of chemical analysis of the tannery sludge are listed in Table 4.1. The predominant species of Fe and Cr are respectively Fe(III) and Cr(III).

4.5.1 Removal of aluminium and iron by hydroxide precipitation (step 1)

The effect of pH on the leachate metal concentrations at different dilutions is presented in Figures 4.1 to 4.4. Below pH 4.2, the concentration of Cr, Al and Fe in solution decreased slowly with the increase of pH. Between pH 4.2 and 5.0, the concentration of Cr, Al and Fe decreased steeply (Figure 4.1). The pattern of change of Al, Fe and Cr concentration with pH was different for different dilution. This resulted in a larger difference in the removal efficiencies between Al and Cr at different dilution. Figure 4.5 depicts the ratio of removal efficiency of Al and Fe relative to Cr. When the leachate was not diluted, the removal ratio of Al to Cr was 1.24 at pH 4.59. When the leachate was diluted 4 times, the ratio was 1.49 at pH 4.67. When the leachate was diluted 6.3 times, the ratio was 2.21 at pH 4.68 and 50 % of Al was removed at this pH. When the leachate was diluted 8 times, the removal ratio of Al and Cr was 2.31 at pH 4.59. Thus, the removal ratio of Al to Cr increased with the dilution of leachate. The dilution higher than 8 did not increase the ratio of removal efficiency of Al to Cr. The removal ratio of Fe to Cr increased slowly as compared with the Al/Cr ratio with dilution of the leachate. The results indicate a 6.3, optimum dilution for the maximum removal of Al and Fe. In this case (for 6.3 times diluted sample), the initial concentrations of Cr, Al, Fe, Ca, Mg and Zn were 1640, 110, 35.5, 83.5, 568 and 2.5 mg/L respectively, and initial pH was 1.79. An acid extract of similar composition could be obtained by leaching tannery sludge with solids concentration of about 15 g/L.

The reason for the increase of the ratio of removal efficiency of Al to Cr with dilution was not very clear. One of the possible explanations was that the concentration product $Qc = [Cr^{3+}][OH^-]^3$, at a given pH, for the dissolution reaction $Cr(OH)_3 \Leftrightarrow Cr^{3+} + 3OH^-$ decreased with dilution. The Gibbs free energy of this reaction $\Delta G = RT\ln(Q_c/K_c)$ was thus reduced. K_c is the concentration equilibrium constant at a given temperature, pressure and ionic strength (Shen *et al.,* 2000). According to chemical thermodynamics a chemical reaction always shifts to a forward direction if Gibbs free energy (ΔG) is less than zero. Therefore, with dilution this reaction had a tendency to proceed in the forward direction (i.e. equilibrium shifted to the right). It means that less Cr^{3+} was precipitated at a given pH after dilution. In addition, because the molar concentration of Cr(III) in the leachate was larger than Al, the decreasing value of Cr(III) concentration due to dilution was larger than Al. This resulted in a larger decrease in ΔG for the reaction $Cr(OH)_3 \Leftrightarrow Cr^{3+} + 3OH^-$ as compared to the reaction $Al(OH)_3 \Leftrightarrow Al^{3+} + 3OH^-$. Therefore, after dilution, the tendency for Cr(III) to form precipitate $Cr(OH)_3$ was low relative to Al. That is to say that dilution resulted in a larger decrease of Gibbs free energy (ΔG) for the dissolution reaction of $Cr(OH)_3$ relative to the dissolution reaction of $Al(OH)_3$. Thus, after dilution the tendency for Cr(III) to form precipitate $Cr(OH)_3$ was low relative to Al.

The removal ratio of Al to Cr at different dilution increased with increase of pH. The optimum pH for the maximum removal of Al from the leachate was between 4.6 to 4.8 (Figure 4.5). At this pH range, 50 to 80 % of Al, 30 to 40 % of Fe and 22 to 40 % of Cr was removed at the optimum dilution rate of 6.3.

The pH had no influence on the removal of zinc in the pH range of 1 to 5. However, this was not important, because the molar concentration of Zn in the leachate was very low and could be removed by cupferron. This will be discussed in a later section.

4.5.2 Further removal of aluminum, iron and zinc by cupferron (step 2)

After step 1, an organic reagent cupferron (N-Nitroso-N-phenylhydroxylamine ammonium salt, (I)) was used to remove aluminium, iron and zinc. It was found in step 1 that Zn was difficult to remove efficiently as its hydroxide precipitate up to pH 8.0 (Figures 4.1 to 4.4).

4.5.3 Effect of time on the removal of metals by cupferron

Figure 4.6 presents the effect of time on the metal removal. It is apparent that the removal of all metals reached a plateau within 10 min.

4.5.4 Effect of pH on the removal of metals by cupferron

Figure 4.7 depicts the effect of the initial pH on removal efficiency of metals. About 90 % of Fe was removed between pH 1.99 and 4.16. About 80 % of Al was removed between pH 2.26 and 4.16. Zn removal efficiency was above 70 % between pH 3.13 and 4.16. About 7 % of Cr, 6 % of Mg and 4 % of Ca were also removed between pH 1.99 and 4.16. It seemed that Zn could only be removed efficiently at a pH above 3.0 (Figure 4.7). Therefore, the suitable pH for the simultaneous removal of Al, Fe and Zn was between 3 and 4.16. It was also found that the removal efficiencies of metals at pH 4.83 (Figure 4.8) were similar to those at pH 4.16 (Figure 4.7). Therefore, the optimal pH for the removal of Al, Fe and Zn falls between 3 and 4.83. This suggests that after the removal of Al as hydroxide precipitate at pH 4.6 to 4.8 in step 1, the solid cupferron may be added directly to the filtrate without the need of adjusting the pH value of the filtrate.

Similar amounts of Al and Cr were precipitated by cupferron at pH 2.26, 3.13, 3.50 and 4.16 (Table 4.2). Thus, cupferron had the same reaction efficiency for Al and Cr. This conclusion was contrary to a previous report of Majone (1986), who found that cupferron could precipitate Al and Fe present in tannery leachate while leaving Cr(III) in the residual solution.

Zn removal from tannery leachate by cupferron had not been reported earlier. It was also found in step 1 that Zn was difficult to be removed efficiently as its hydroxide precipitates only gradually up to pH 8.0 (Figures 4.1 to 4.4). However, in step 2 Zn was probably precipitated by cupferron and thus removed (Figures 4.4 and 4.5). Zn adsorption on cupferron-metal precipitates is unlikely because removal of Zn (with the precipitate) in step 1 was not observed (Figures 4.1 to 4.4).

4.5.5 Effect of the amount of cupferron on the removal of metals

Figure 4.8 presents the effect of the molar ratio of cupferron to the sum of Al, Fe and Zn on the metal removal. The removal efficiencies of Fe and Al showed a marked increase when the molar ratio was increased from 1.34 to 2.0 and a slow increase in removal efficiency when the molar ratio increased from 2 to 4. The removal efficiency of zinc showed an appreciable increase when the molar ratio increased from 2 to 2.78. Therefore, the optimum molar ratio of cupferron to the sum of Al, Fe and Zn for the removal of Al, Fe and Zn falls between 2.78 and 4.

4.5.6 Removal of Mg and Ca by precipitation (step 3)

In the previous two steps, most of Al, Fe and Zn in the tannery leachate were removed as precipitates (hydroxides and cupferrates). The significant residual metals in the filtrate were Cr(III), Ca and Mg. Table 4.3 presents the results of the separation of Mg and Ca from Cr(III) in the filtrate. At pH 6.42 to 7.52, most of the residual small amount of Al, Fe and Zn and large amount of Cr(III) were converted into insoluble precipitates. Some of the metals (Ca, Mg) were also entrapped in the foams generated. The removal efficiency of Ca and Mg increased with increasing pH. The removal efficiency increased substantially between pH 6.96 and 7.52 (Table 4.3). Correspondingly, the contents (mole %) of Ca and Mg in the precipitates increased with pH. The Ca and Mg content in precipitates increased substantially between pH 6.96 and 7.52 (Table 4.3). The removal efficiency of Cr(III) showed an appreciable increase from pH 6.42 to 6.96 (Table 4.3). Therefore, the optimum separation of Ca and Mg from Cr(III) is apparent at pH 6.96. At pH 6.96, less Cr(III) remained in the filtrate while less Ca and Mg were precipitated.

At about pH 4.0, some foam was formed. The amount of foam increased with pH. During filtration, precipitates could be carried by the solution whereas foams did not move with solution, thus were left over in the beaker. Portions of the foam were sampled. The samples were dried and digested as precipitates. Table 4.4 presents the chemical composition of foams as well as the precipitates collected from the same sample and at the same pH. The contents of Cr, Al and Fe were higher in the precipitates, while the contents of Ca and Mg in the foams were much higher than that in the precipitates. This may explain the low Ca and Mg contents in the precipitates at pH 6.42 and 6.96, although the removal efficiencies of Ca and Mg were not proportional (Table 4.3). The molar ratio of Ca and Mg between foams and precipitates were 10.12 and 10.18 respectively (Table 4.4). It means that Ca and Mg had similar distributional behavior between foams and precipitates. Total carbon in the tannery sludge was high (14.96 %, Table 4.1). The presence of long chain organic molecules could be the reason for foam formation. These long chain molecules could act as surfactants.

The solution in step 3 may also contain residual cupferron from step 2. This may influence the separation of Ca and Mg in step 3. In fact, only small amount of Ca and Mg was found in the precipitates at pH below 7 (Tables 4.3 and 4.4). Therefore, it was thought that most of the Ca and Mg from the solution was adsorbed on the precipitates or occluded in the foams and precipitates of metals (Cr(III) and Al) without forming the precipitates themselves. This contention was also supported by thermodynamic claculations (Shen *et al.,* 2000). In thermodynamic calculations it was shown that Ca and Mg in the tannery leachate, obtained by leaching the sludge with solids concentration less than 80 g/L, could not be precipitated as hydroxides or carbonates at a pH below 7.

4.5.7 Separation efficiency of the whole process

Figure 4.9 presents a typical block diagram of the whole separation process of Cr(III) from Al, Fe, Ca, Mg and Zn. The overall results of the process are presented in Table 4.5 where molar ratio of metals relative to Cr(III) in the tannery leachate is presented. Their differences are due to their removal efficiencies from the tannery leachate. About 99 % of Ca and Mg, 77 % of Al, 84 % of Fe and 60 % of Zn were removed in this separation process. About 37.3 % of Cr(III) was retained as hydroxide precipitates and with foams at pH 4.8 (in step 1). About 4.4 % of Cr(III) was retained as Cr(III)-cupferron precipitate (step 2). So in total about 42 % of Cr(III) was retained with the precipitates in the whole separation process. The 37.3 % Cr(III) of hydroxide precipitates at pH 4.8 may be recovered efficiently by the oxidation method (Macchi *et al.,* 1991), since the molar ratio of (Mg+Fe)/Cr in the precipitate is very low (0.052, Table 4.4). In this case, significantly less H_2O_2 would be required compared with the Cr oxidation in the original leachate at pH 1 (Figures 4.4 to 4.6) and a high oxidation efficiency of Cr(III) could be obtained.

The concentration of Al and Fe in the leachate (without dilution) at pH 1.79 was 792 mg/L (or 29.33 mmol/L) and 250 mg/L (or 4.81 mmol/L), respectively. The amount of cupferron required to precipitate Al and Fe was about 102.4 mmol/L. After step 1, the pH became 4.83 and the concentration of Al and Fe was 86.4 mg/L (or 3.2 mmol/L) and 24.65 mg/L (or 0.474 mmol/L), respectively. The amount of cupferron required to precipitate Al and Fe would be 11.02 mmol/L. Thus the amount of cupferron required was reduced by more than 9 times.

It was reported that about 50 % to 80 % of cupferron could be recovered by dissolving the cupferron at about pH 10 based on the reaction $AlY_3 + 3OH^- \rightarrow Al(OH)_3 + 3Y^-$ and $FeY_3 + 3OH^- \rightarrow Fe(OH)_3 + 3Y^-$ (Majone, 1986). However, the principal problem in the recovery of cupferron was the dissolution of $Al(OH)_3$ at about pH 10, i.e. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$. Soluble $Al(OH)_4^-$ could co-exist with Y^- (cupferron) in the solution (Majone, 1986). This resulted in the failure of cupferron recovery. However, we did not observe appreciable dissolution of $Al(OH)_3$ precipitate in the studied solutions up to pH 12 (Figures 4.1 and 4.3). This is probably due to the fact that metals (Al, Cr(III), Fe and Zn.) concentration and chemical composition of the leachates in the present work are different from those in the work of Majone (1986). Therefore, cupferron recovery at pH 10 may be possible. Thus, the future work should be focused to study the recovery of cupferron.

After Cr(III) isolation, the final precipitate in the Figure 4.9 could be dissolved directly in sulfuric acid for preparing the tanning agent.

4.6 Conclusions

This study proposed a simpler three step process for the separation of Cr(III) from interfering elements (Al, Fe, Ca, Mg, Zn) in the tannery leachate. It involves dilution and precipitation of Al, Fe and Zn at pH 4.6-4.8. The second step involves the precipitation of residual Al, Fe and Zn with cupferron. The third step involves the precipitation of Chromium and the separation of Ca and Mg from chromium. The removal efficiencies of interfering metals for the whole separation process were as follows: Al 77 %, Fe 84 %, Ca 99 %, Mg 99 % and Zn 61 %. About 42 % of Cr(III) was also retained with the precipitates in these processes. The amount of cupferron required to remove Al, Fe and Zn in this process was reduced more than 9 times.

4.7 Acknowledgements

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Table 4.1 Composition of the dry tannery sludge

Parameters	Concentration (% w/w)
Cr(III)	12.80
Cr(VI)	0.004
Al	1.063
Fe(III)	0.339
Fe(II)	0.014
Ca	4.980
Mg	5.795
Zn	0.022
K	0.009
Na	2.262
Orthophosphate	0.114
Total carbon	14.957
Total nitrogen	1.349
Total sulfur	< 0.5
Volatile organic matter	43.4

Table 4.2 Mole numbers of metals precipitated with cupferron at different pH

pH	Al	Ca	Cr	Fe	Mg	Zn
2.26	4.82E-05	1.25E-06	3.75E-05	1.04E-05	2.80E-05	1.53E-07
3.13	4.71E-05	1.75E-06	5.10E-05	1.02E-05	3.04E-05	6.12E-07
3.50	4.67E-05	7.49E-07	4.63E-05	1.02E-05	1.93E-05	6.12E-07
4.16	4.89E-05	7.49E-07	6.12E-05	1.0E-05	2.49E-05	5.20E-07

Table 4.3 Separation of Ca and Mg from Cr(III) by filtration at different pH

	pH	Al	Ca	Cr	Fe	Mg	Zn
Initial concentration (mg/L)*	4.83	21.19	118.8	1714	5.966	886.6	0.996
Removal efficiency of metal from the leachate by precipitation (%)	6.42	100	6.985	96.15	95.76	2.428	95.18
	6.96	100	13.70	98.74	99.83	4.946	99.83
	7.52	100	24.82	99.76	96.28	13.85	98.33
Metal in the precipitate (Molar percentage)	6.42	3.157	0.066	95.89	0.354	0.459	0.071
	6.96	2.940	0.055	95.65	0.302	1.013	0.041
	7.52	2.761	0.460	90.69	0.282	5.754	0.049

* Metal concentration after step 1 and step 2.

Table 4.4 Metal distribution in solution, precipitate and foam at pH 4.83 and 21°C

	Unit	pH	Al	Ca	Cr	Fe	Mg	Zn
Atomic weight			26.78	40.08	51.99	55.84	24.30	65.38
Initial concentration	(mg/L)	1.67	191.8	140.9	2899	60.51	980.5	4.041
Metal concentration in the filtrate	(mg/L)	4.83	21.19	118.8	1714	5.966	886.6	0.996
Metal in the foams	(W (%))	4.83	1.278	0.197	12.61	0.301	1.706	0.012
Metal in the precipitates	(W (%))	4.83	3.056	0.035	23.02	0.594	0.306	0.012
Metal in the foams	(relative molar ratio)	4.83	19.67	2.024	100	2.222	28.947	0.077
Metal in the precipitates	(relative molar ratio)	4.83	25.77	0.200	100	2.401	2.842	0.040

Table 4.5 **Relative removal efficiency of metals for the whole process in the specific case (Figure 4.9)**

		Al	Ca	Cr	Fe	Mg	Zn
Metal molar ratio relative to Cr	Tannery leachate	13.35	7.12	100	2.02	71.42	0.11
	Final precipitate	3.07	0.057	100	0.316	1.06	0.043
Relative removal efficiency (%)		77.00	99.20		84.36	98.52	60.91

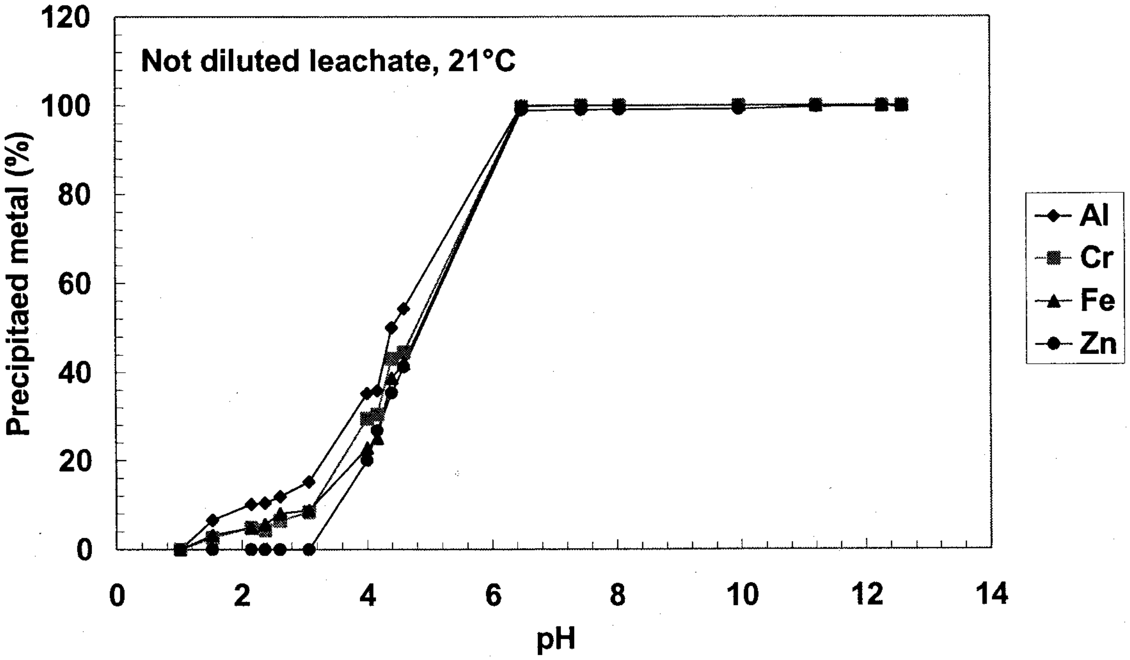

Figure 4.1 Variation of percentage of precipitated metal in the leachate with pH

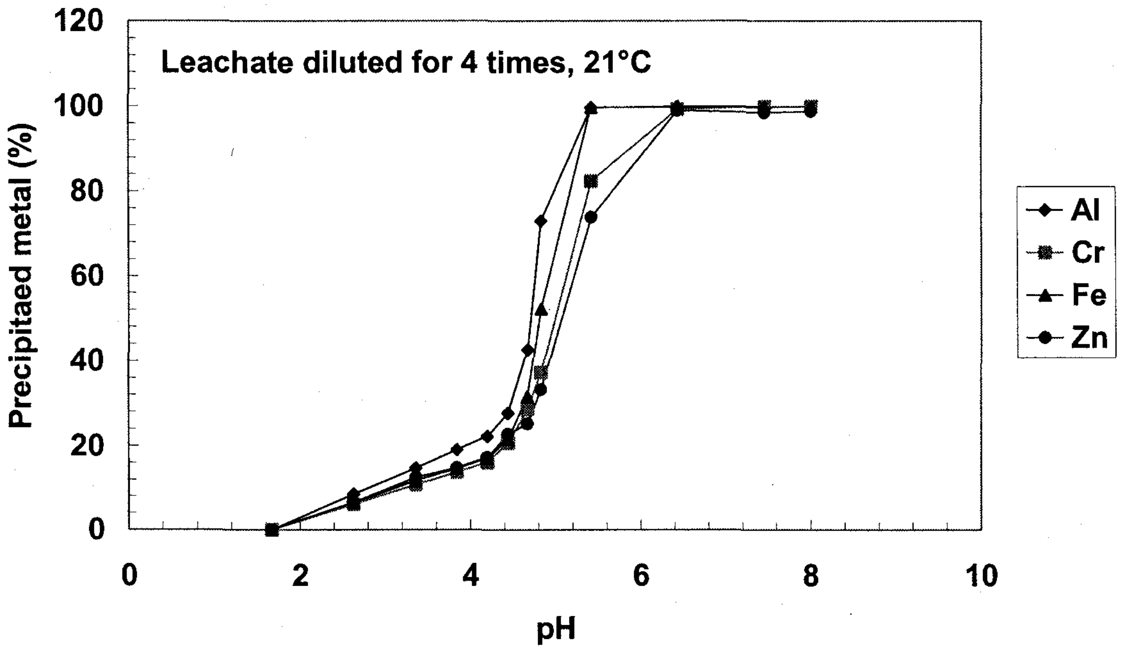

Figure 4.2 Variation of percentage of precipitated metal in the leachate with pH

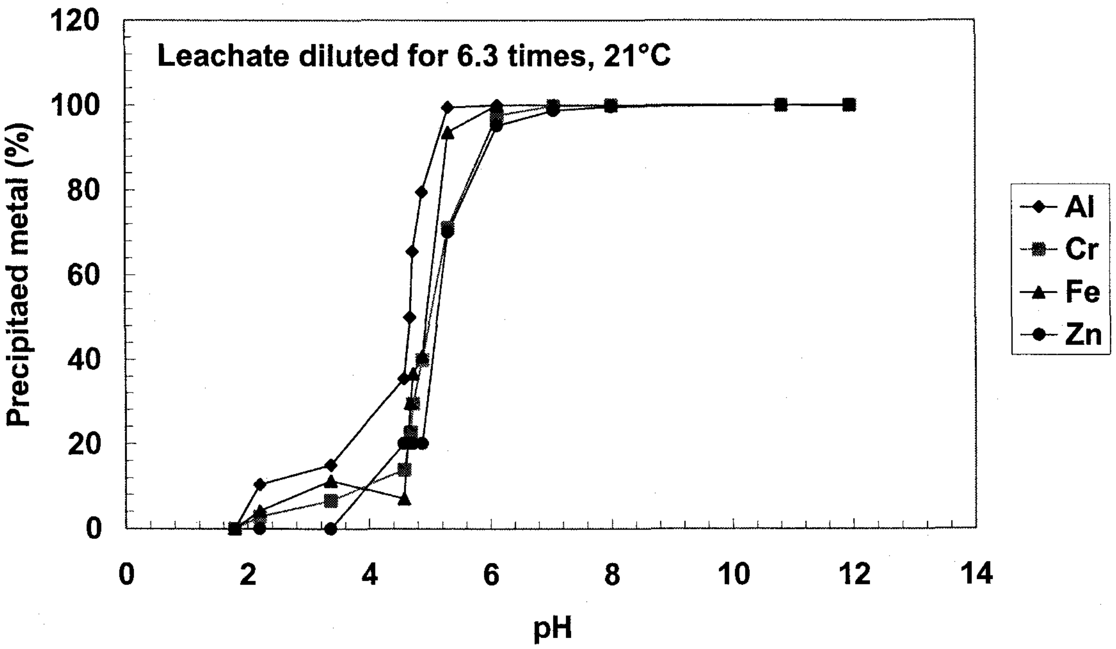

Figure 4.3 Variation of percentage of precipitated metal in the leachate with pH

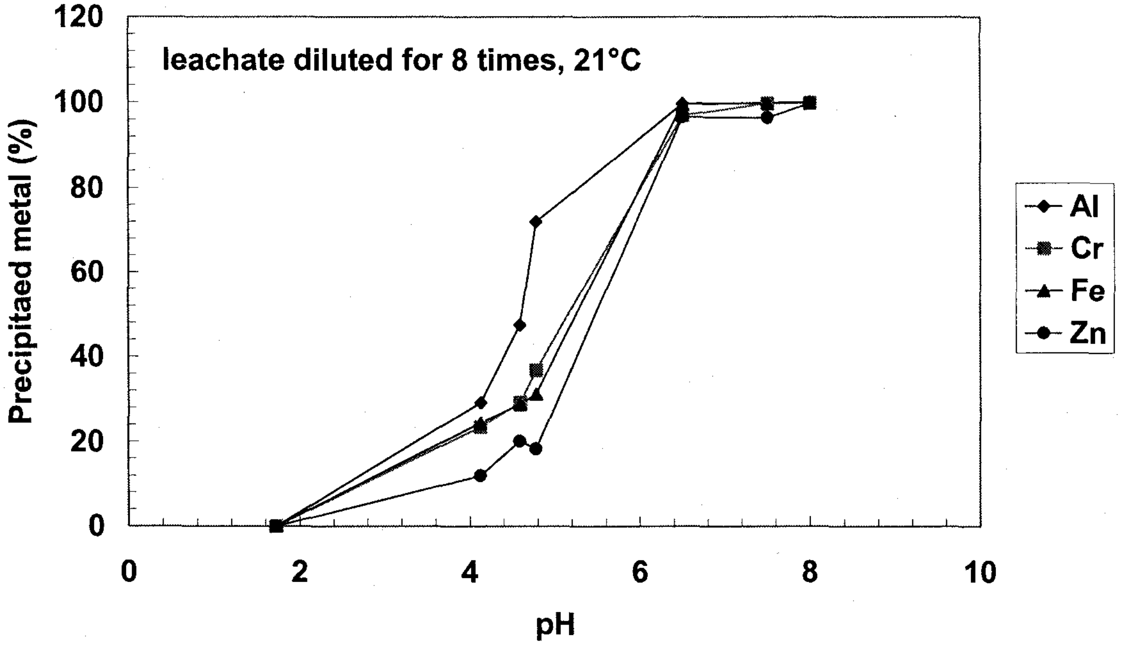

Figure 4.4 Variation of percentage of precipitated metal in the leachate with pH

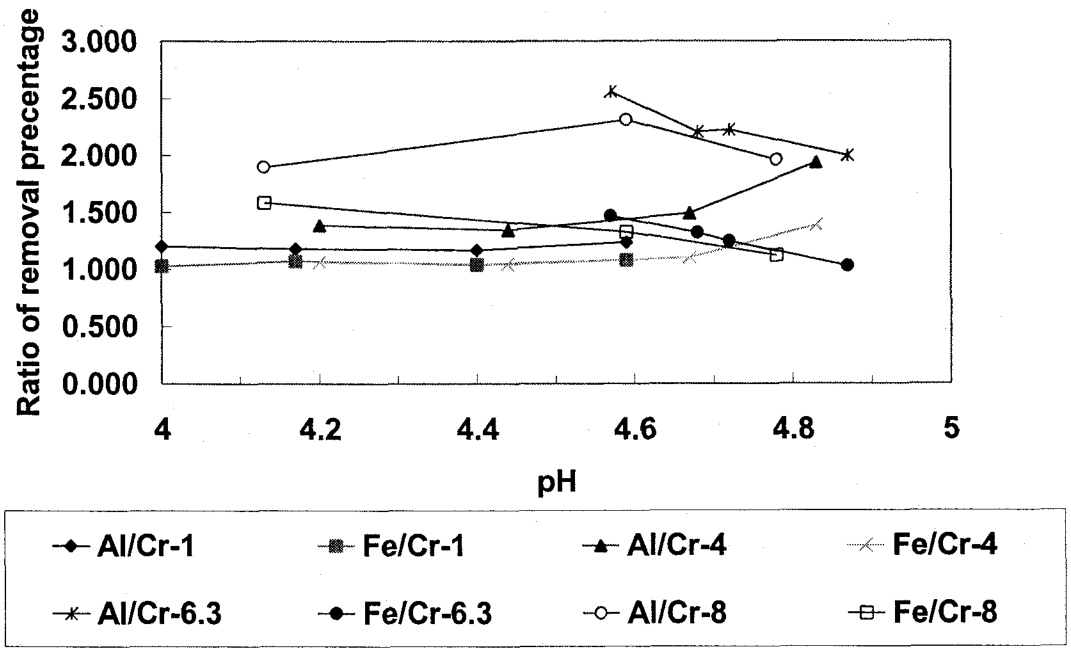

Figure 4.5 **Variation of ratio of removal efficiency of Al or Fe to Cr for the leachates at different dilution and 21°C with pH. The metal concentrations of non-diluted leachate was 792, 250 and 11514 mg/L for Al, Fe and Cr, respectively. The numbers in the legend represent the dilution times of leachate**

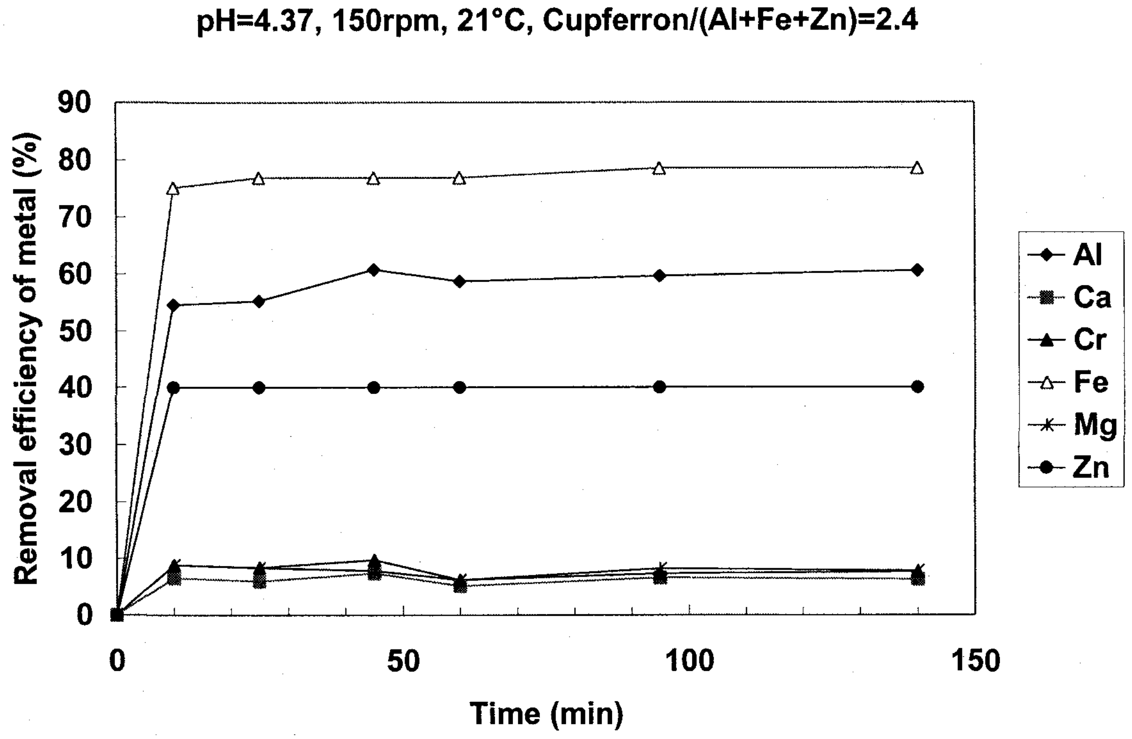

Figure 4.6 **Influence of reaction time on the metal precipitation with cupferron. The respective initial metal concentrations of Al, Ca, Cr, Fe, Mg and Zn at pH 4.37 was 73.5, 81.5, 1527, 30.5, 548 and 2.5 mg/L**

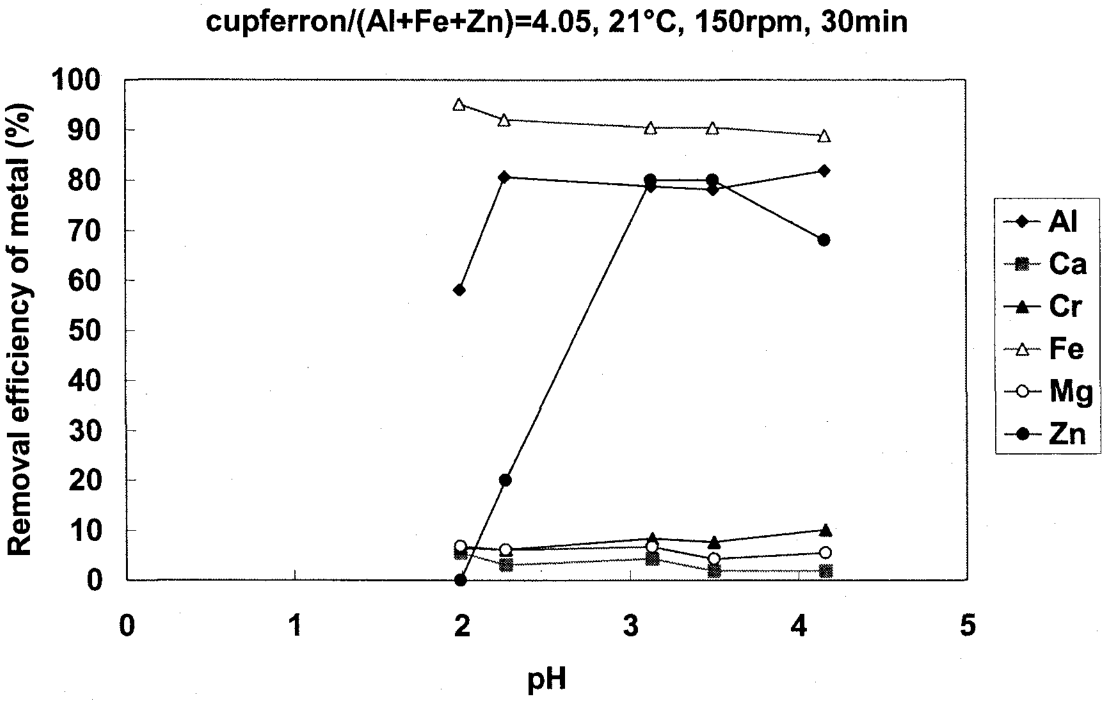

Figure 4.7 Influence of pH on the metal precipitation with cupferron. The respective initial metal concentrations of Al, Ca, Cr, Fe, Mg and Zn at pH 4.51 was 80, 82, 1585, 31.5, 560 and 2.5 mg/L

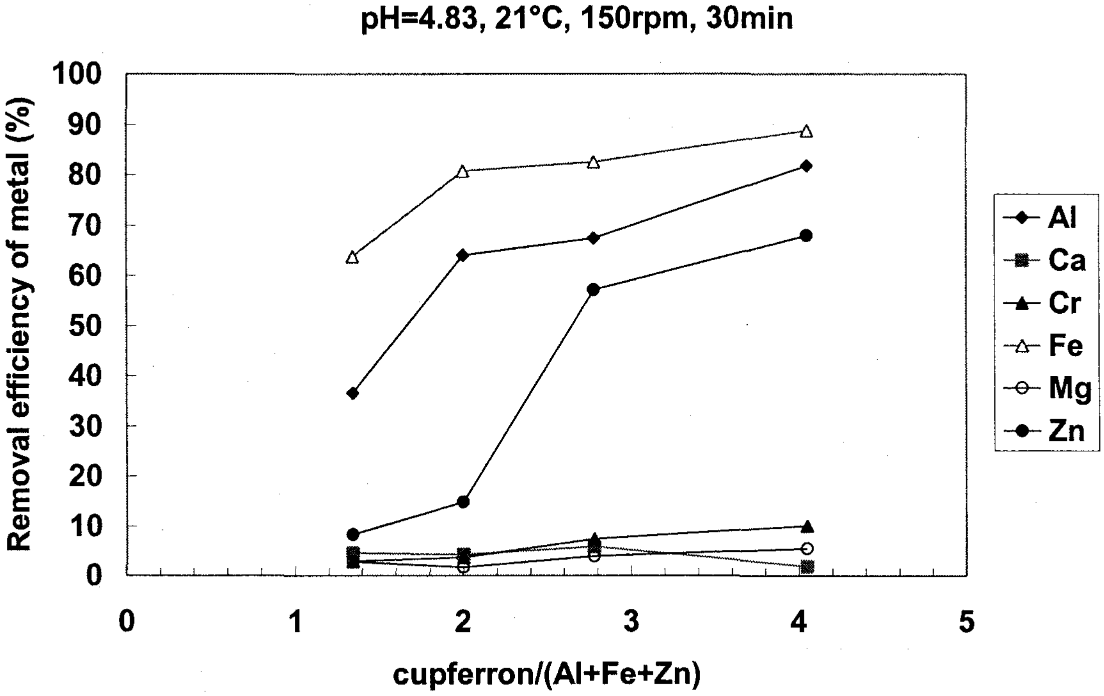

Figure 4.8 Variation of removal efficiency of metal with the molar ratio of cupferron to the sum of Al, Fe and Zn. The respective initial metal concentrations of Al, Ca, Cr, Fe, Mg and Zn was 63, 121, 1809, 35, 903 and 3.3 mg/L

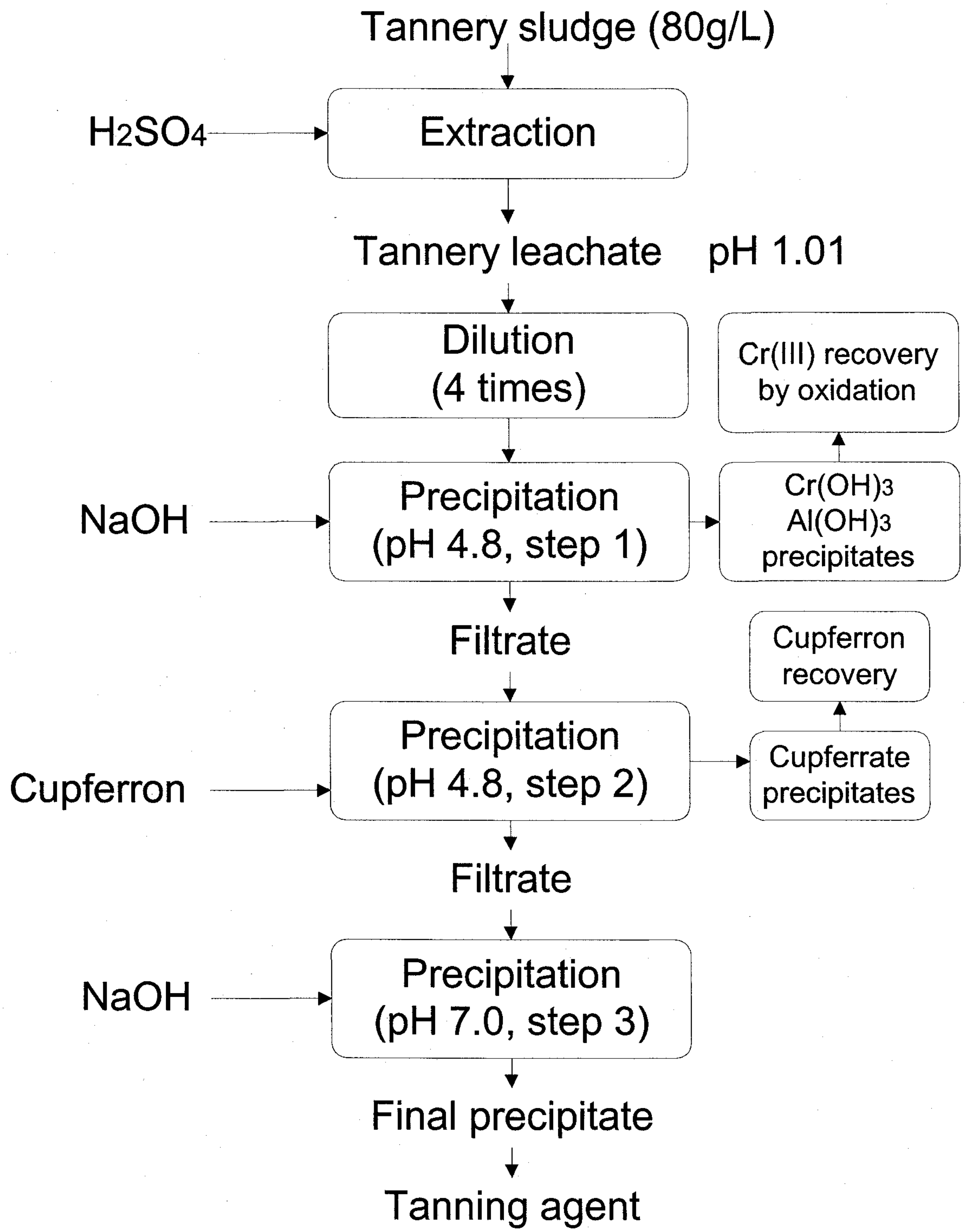

Figure 4.9 Block diagram of separation of Cr(III) from other metals in the tannery leachate

CHAPITRE 5

LABORATORY PILOT TEST OF CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

LABORATORY PILOT TEST OF CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

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5 LABORATORY PILOT TEST OF CHROMIUM (III) ISOLATION FROM ACID EXTRACT OF TANNERY SLUDGE

5.1 Résumé

Les concentrations élevées d'Al, de Fe, de Ca, de Mg et de Zn dans l'agent tannant sont nuisibles aux propriétés du cuir tanné. Pour recycler le Cr(III) des boues de tannerie comme agent tannant, ces cinq métaux doivent être enlevés de l'extrait acide obtenu en traitant les boues de tannerie avec l'acide sulfurique. Une nouvelle approche a été développée pour recycler le Cr(III) et enlever les autres métaux. Sommairement, cet essai pilote inclut un processus simple en six étapes pour l'extraction des métaux des boues de tannerie et pour la séparation subséquente du Cr(III) des éléments nuisibles (Al, Fe, Ca, Mg et Zn) présents dans l'extrait acide (filtrat). Lors de l'étape 1, les métaux sont solubilisés à partir des boues de tannerie avec de l'acide sulfurique à pH 1 à 2. Une filtration est alors effectuée pour séparer les solides résiduels et le liquide. La deuxième étape inclut la dilution du filtrat et la précipitation de l'Al et du Fe à pH 4.8. La troisième étape inclut la précipitation du Cr (III) à pH 7.0 pour séparer le Ca et le Mg du Cr (III). En conséquence, un précipité contenant moins de métaux nuisibles est obtenu dans la troisième étape. Afin de récupérer plus de Cr(III), le précipité obtenu dans l'étape 2 est dissous de nouveau avec l'acide sulfurique lors de la quatrième étape. Les cinquièmes et sixièmes étapes sont semblables aux deuxièmes et troisième étapes respectivement, sauf que le pH dans la sixième étape est ajusté à 8.3 au lieu de 7.0. Après la sixième étape, un précipité contenant moins de métaux nuisibles est également obtenu. Un rendement global de récupération du Cr de 44 % a été obtenu dans le produit final (étape 3 + étape 6). La concentration en Cr dans ce produit est de 32.5 % et le rapport des concentrations des métaux nuisibles par rapport au Cr ((Al + Fe + Ca + Mg + Zn)/5Cr) est inférieur ou égal à 0.02.

5.2 Abstract

High concentrations of Al, Fe, Ca, Mg and Zn in the tanning agent are detrimental to the properties of tanned leather. To recycle the Cr(III) from the tannery sludge to the tanning agent, these five metals must be removed from the acid extract obtained by sulfuric-acid treatment of tannery sludge. A new approach has been developed to recycle the Cr(III) and to remove the other metals. Summarily, this pilot test includes a simple six steps process for the extraction of metals from tannery sludge and the following separation of Cr(III) from interfering elements (Al, Fe, Ca, Mg, Zn) in the acid extract (or filtrate). In step 1, metals were extracted from tannery sludge with sulfuric acid at about pH 1-2. A filtration was then performed to separate the residual solids and the liquid. The second step involves the dilution of filtrate and the precipitation of Al and Fe at pH 4.8. The third step involves the precipitation of Cr (III) at pH 7.0 for the separation of Ca and Mg from Cr (III). As a result, a precipitate containing less interfering metals was obtained in the third step. In order to recover more Cr(III), the precipitate obtained in step 2 was dissolved once again with sulfuric acid in the fourth step. The fifth and sixth steps were similar to the second and third steps respectively, except that the pH in the sixth step was adjusted to 8.3 not 7.0. After the sixth step, a precipitate containing less interfering metals was also obtained. A 44 % of Cr recovery yield was obtained in the final product. The Cr concentration in this product was 32.5 % and the ratio of interfering metals to Cr concentration was inferior or equal to 0.02.

Key words: Tannery sludge, chromium, leaching, precipitation, metals, acid extract, sulfuric acid, sodium hydroxide.

5.3 Introduction

The recovery of Cr(III) and its reuse in the tanning process has economical interest and reduces Cr(III) release in the environment. However, the reuse of Cr(III) in the tanning process is strongly dependent on the separation of Cr(III) from other interfering metals such as Fe, Mg, Al, Ca and Zn (Macchi *et al.,*1991). High concentrations of these five metals in the tanning agent is detrimental to the properties of tanned leather (Randall, 1985).

Most of previously reported methods for chromium recovery employed H_2O_2 to oxidize Cr(III) to Cr(VI) in alkaline solution (Macchi *et al.,*1991; Tiravanti *et al.,* 1997). It was found that at least 20 to 30% of Cr(III) in the acid extract could not be oxidized while large amount of H_2O_2 was consumed in this process (Macchi *et al.,*1991). Expensive cationic exchange resin was also needed to separate Cr(VI) from Ca and Mg. The use of these agents and materials greatly increased the recovery cost. Moreover, the process produced Cr(VI) that was very toxic to the environment. After separation of Cr(VI) from other metals, SO_2 (a toxic gas) was usually needed to reduce Cr(VI) to Cr(III) for preparing the tanning agent. To alleviate these unfavorable factors brought about by the Cr(III) oxidation method, the isolation of Cr(III) by a non-oxidation means was preferable.

Small-scale experiments have been carried out to isolate Cr(III) from acid extract of tannery sludge (Shen *et al.,* 2001 a). That work proposed a three step process for the separation of Cr(III) from these interfering elements metals present in the acid extract (leachate) of tannery sludge. In step 1, the leachate was appropriately diluted and the Al was efficiently removed by precipitation in the form of hydroxide by adjusting the pH between 4.6 and 4.8 at 21°C. The optimum dilution ratio for the tannery sludge leachate, obtained by leaching tannery sludge solids concentration 80 g/L) was 6.3. Under the above operating conditions, 50-80 % of Al, 30-40% of Fe and 22-40% of Cr were removed and the discrimination ratio between Al to Cr was between 2.0 and 2.2, depending on the pH. In step 2, the Al and Fe that remained in the filtrate after step 1 were further reduced by reacting with an organic agent cupferron (Y) at 21°C. The precipitation reactions of cupferron with all of metals were completed in 10 minutes. The optimum pH for the removal of Al, Fe and Zn was between 3 and 4.83. The optimum molar ratio of cupferron to the sum of Al, Fe and Zn was between 2.78 to 4. Under these operating conditions, about 90% of Fe, 80% of Al, 70% of Zn and 7% of Cr were precipitated. During step 2, most of Fe, Al and Zn originally present in the tannery leachate were separated from Cr(III), Ca and Mg. In step 3, the Ca and Mg left in the filtrate after step 2 were separated from Cr(III) by adjusting the pH of the filtrate to 7.0 with the solution of sodium hydroxide at 21°C. The removal efficiency of Cr(III), Ca and Mg were 99.6%, 13.7% and 4.9%. After step 3, the molar percentages of Al, Ca, Cr, Fe, Mg and Zn in the precipitate formed at pH 7.0 and 21°C in a typical case were 2.9, 0.06, 95.6, 0.3, 1.0 and 0.04 respectively. The overall removal efficiencies of the targeted metals in a typical case were as follows: Al - 77%, Fe - 84.4%, Ca - 99.2%, Mg - 98.5% and Zn - 61%. About 42% of Cr(III) in total (step 1 + step 2) was lost as precipitates with other metals.

The above process did not involve the oxidation of Cr(III) and the use of ionic exchange resin. In order to calculate the mass balance of various metals and provide a basis for economical evaluation of the process, a laboratory-pilot test was run in this work. Different from the past small-scale tests, expensive cupferron was not used in this pilot test. . Moreover, an extra three-step process was introduced in this pilot test to recover more Cr(III) from the tannery sludge.

5.4 Materials and methods

5.4.1 Sampling of tannery sludge

The sample of dehydrated (filter-press) tannery sludge was procured from "La Tannerie des Ruisseaux" in Rivière-du-loup (Québec, Canada). The sludge contained 30.3 % of total solids and was stored at 4°C. A part of the sludge sample was dried at 104°C for 48 h before use.

5.4.2 Pilot test for chromium (III) isolation in the acid extract of tannery sludge

5.4.2.1 Metal extraction from tannery sludge by sulfuric acid (Step 1)

A mass of 451 g of dried tannery sludge was placed in a 20 L capacity polyethylene reactor. Ten liters of acid solution containing 248 mL of concentrated sulfuric acid was added to the reactor gradually. This solution was mixed with an agitator with a rotational speed of 200 rpm at 21°C for 1 day. After that, the mixture was left stationary for one night to settle undissolved solids. The mixture was then filtered through Whatman No. 3 filter paper at a diameter of 18.5 cm to separate solids from the aqueous phase. After filtration, the residual solids was termed as **precipitate A** and the liquid was marked as **filtrate A**. The whole precipitate A was dried at 104°C and then weighed.

5.4.2.2 Removal of aluminium and iron by hydroxide precipitation (Step 2)

Filtrate A was transferred to a 40 L capacity polyethylene reactor. Twenty liters of Millipore water was added to this reactor to dilute the filtrate 'A' by three times. To reach the desired pH 4.80, 25.8 N NaOH was added drop by drop to the diluted filtrate under constant stirring at 21°C. At pH 4.80, the agitation was continued for 3 h. After that, the mixture was left stationary overnight to settle the formed precipitate. The mixture was then filtered as described previously to separate solids from the aqueous phase. After filtration the residual solids was termed as **precipitate B** and the liquid was called as **filtrate B**. The whole precipitate B was dried at 104°C and then weighed.

5.4.2.3 Removal of Mg and Ca by precipitation (step 3)

To reach the desired pH 7.0, 25.8 N NaOH was added drop by drop to the filtrate B under constant stirring at 21°C. At pH 7.0, the agitation was continued for 3 h. After that, the mixture was left stationary overnight to settle the formed precipitate. The mixture was then filtered as described previously. After filtration the residual solids was termed as **precipitate C** and the liquid was called as **filtrate C**. The whole precipitate C was dried at 104°C and then weighed.

5.4.2.4 Metal extraction from precipitate B (Step 4)

A mass of 165 g of dried precipitate B was placed in a 20 L capacity reactor. About 10.5 L of acid solution containing 65 mL of concentrated sulfuric acid was gradually added to the reactor. This solution was agitated with an agitator with a rotational speed of 500 rpm at 21°C for 1 day. After that, the mixture was left stationary for one night to settle undissolved solids. The mixture was then filtered as described previously. After filtration the residual solids was termed as **precipitate D** and the liquid was marked as **filtrate D**. The whole precipitate D was dried at 104°C and then weighed.

5.4.2.5 Removal of aluminium and iron from filtrate D by the hydroxide precipitation (Step 5)

To reach the desired pH 4.80, 25.8 N NaOH was added drop by drop to above filtrate D under constant stirring at 21°C. At pH 4.80, the agitation was continued for 3 h. After that, the mixture was left stationary overnight to settle the formed precipitate. The mixture was then filtered as described previously. After filtration the residual solids was termed as **precipitate E** and the liquid was called as **filtrate E**. The whole precipitate E was dried at 104°C and then weighed.

5.4.2.6 Removal of Mg and Ca from filtrate E by precipitation (step 6)

In this case pH 8.0 was used for precipitation because the content of Ca and Mg in precipitate B was much less than in filtrate B, thus the removal of Ca and Mg in step 6 was not so important as in step 3. On the other hand, considering the higher residual Cr(III) concentration in filtrate C at pH 7.0, the pH was then increased from 7.0 to 8.0 in order to decrease the residual Cr(III) concentration in filtrate F of step 6. However, if the pH was increased too high such as 9.0, more Ca and Mg would have precipitaed. Therefore, pH 8.0 was selected to investigate that if residual Cr(III) concentration could be further decreased by increasing pH from 7.0 to 8.0, To reach the desired pH 8.0, 25.8 N NaOH was added drop by drop to above filtrate E under constant stirring at 21°C. At pH 8.3, the agitation was continued for 3 h. After that, the mixture was left stationary overnight to deposit the formed precipitate. The mixture was then filtered as described previously. After filtration the residual solids was termed as **precipitate F** and the liquid was called as **filtrate F**. The whole precipitate F was dried at 104°C and then weighed.

5.4.3 Digestion of tannery sludge and precipitates

The digestion of samples was carried out according to the method recommended by Chuan and Liu (1996). A few concentrated HNO_3 and HCl were sequentially added to the duplicate samples (about 0.30 g) and the duplicate blanks at about 150°C. After cooling, the solution was filtered through Whatman GF/C filter and diluted to 100 mL with 0.2 % HNO_3. The corresponding blank values were subtracted for each element analysis. Each metal concentration was calculated as average of the analytical result of the two samples.

5.4.4 Chemical analysis

The pH of the solutions was monitored by a Orion Model 420A pH meter. Varian VISTA AX CCD Simultaneous ICP-AES was used to measure the dissolved metal (Cr, Al, Fe, Ca, Mg and Zn) concentrations. Cr(VI) concentration in the digested solutions was determined by the S-diphenylcarbazide method (3500-Cr, D, APHA, 1989). Fe(II) concentration was measured by the phenanthroline method (3500-Fe, D, APHA, 1989). Orthophosphate concentration was analyzed by the ascorbic acid method (4500-P, E, APHA, 1989). A part of the solids of dried tannery sludge was pulverized and passed through a sieve of 80 mesh. Total carbon, total nitrogen and total sulfur in the solid powder (particle size inferior to 80 mesh) of tannery sludge were determined with Carlo Erba Instruments NA 1500 Nitrogen/Carbon/Sulphur Analyzer. Water content was obtained from the average weight loss of five sludge samples at 104°C over 48 h. The volatile organic matter content was obtained from the average weight loss of the dried sludge samples at 550°C over 48 h.

5.5 Results and discussion

The results of chemical analysis of the tannery sludge are listed in Table 1. The predominant species of Fe and Cr are Fe(III) and Cr(III), respectively. The flow chart of the process and the mass balance is presented in Figure 1. According to the metal concentrations measured in various filtrates and the total volume of each filtrate (Table 2), the weight of elements (Al, Fe, Cr, Ca, Mg and Zn) in each solution was obtained and presented in Figure 1. From the element contents measured in the digested precipitates and the total weight of each precipitate (Table 3), the total weight of elements in each precipitate was calculated and also presented in Figure 1. The quantities of metals in the filtrates and precipitates are given in terms of grams of metal per metric ton of tannery sludge treated.

The distribution of chromium and interfering metals (Al, Ca, Fe, Mg and Zn) in the different filtrates and precipitates is presented in Figure 2. The percentages are calculated on the basis of the metal quantity measured in the initial tannery sludge.

Table 4 includes the values of the ratio of the individual metal concentration to chromium concentration in the different filtrates and precipitates as well as the values for the initial tannery sludge and the final reusable product (precipitates C and F) as tanning agent ($Cr_2(SO_4)_3 \cdot 6H_2O$).

5.5.1 Metal extraction from tannery sludge by sulfuric acid (Step 1)

Chemical leaching of metals from tannery sludge was realized in step 1. According to the distribution of metals (Figure 1), 86.6 % of Al, 24.4 % of Ca, 100.2 % of Cr, 83.1 % of Fe, 85.0 % of Mg and 109.4 % of Zn originally present in the tannery sludge were found in the filtrate A. The concentration of solubilized Cr in filtrate A has reached 6.34 g/L (Table 2). On the other hand, the mass balance reveals that 7.4 % of Al, 96.7 % of Ca, 7.7 % of Cr, 21.2 % of Fe, 16.1 % of Mg and 17.0 % of Zn remain in the residual sludge (precipitate A). At pH 1.51 and sludge solids concentration 45 g/L, the precipitates of $CaSO_4 \cdot 2H_2O$, are probably formed according to the thermodynamic calculations (Shen *et al.,* 2001b). This explains the lower leaching efficiency of Ca . The other reasons for the reduction in leaching efficiency of all metals (Al, Ca, Cr, Fe , Mg and Zn) may be due to the presence of undissolved sludge solids bonding with metals, metal adsorption on the undissolved sludge solids or the formed precipitates and metal occlusion during the formation of the precipitates (Shen *et al.,* 2001b). The metal leaching step causes an appreciable reduction of the sludge solids. The dry mass of the precipitate A (residual tannery sludge after leaching) was only 168 g (Table 3), when the initial mass of the tannery sludge was 451 g. This removal corresponds to a reduction of 62.7 % of the solids. The residual sludge contains only 26.3 g Cr/kg (Table 3) when the initial Cr concentration in the tannery sludge was 128 g Cr/kg (Table 1). The precipitate A (residual sludge) was discarded as it had low concentration of Cr. Filtrate A was further used for processing to recover Cr.

5.5.2 Removal of aluminium and iron by the hydroxide precipitation (Step 2)

A recent study showed that the optimal pH for the removal of Al and Fe from tannery sludge leachate was 4.60-4.80 (Shen *et al.,* 2000a). Dilution (3X) and neutralization to pH 4.8 of the diluted filtrate A were carried out in step 2. The precipitates B formed contains a large proportion of Al (79.4 %), Cr (66.4 %) and Fe (79.5 %) previously present in the filtrate A, while most of the Ca and Mg are still in solution (filtrate B) (Figure 1). The dilution and partial neutralization of the filtrate A has resulted in a decrease of the soluble Cr concentration from 6.34 g Cr/L to 0.75 g Cr/L in the filtrate B (Table 2).

The dry mass of the precipitate B (166 g) is not negligible because it's approximately equal to the dry weight of the treated sludge (168 g of precipitate A). The precipitate B contains a very high concentration of Cr, 230 g/kg (Table 3) and therefore was subjected to metal leaching to further recover Cr in step 4. The relative deviation in mass balance at level B was low: Al (-0.1%), Ca (-5.5%), Cr (0.05%), Fe (10.35%), Mg (-7.44%) and Zn (-1.72%).

5.5.3 Removal of Mg and Ca by precipitation (step 3)

In step 3, the filtrate B was neutralized at pH 7.0 . This step has resulted in the formation of a very rich Cr precipitate (precipitate C) containing 33.5 % (w/w) of Cr (Table 3). The dry mass of the precipitate C (54.4 g) was relatively small in comparison to the initial weight of tannery sludge treated (451 g). The final soluble Cr concentration in filtrate C was only 9.6 mg/L and was discarded.

After step 3, most of Cr, Al, Fe and Zn from filtrate B were removed and existed in precipitate C while the Ca and Mg contents in the precipitate C were small. Since the amounts of Al, Fe and Zn relative to Cr in the filtrate B were very small, the amounts of Al, Fe and Zn relative to Cr in the precipitate C were also very small (Table 4).

Therefore, after step 3, Cr(III) may be assumed to be isolated (final product) from other metals (Al, Ca, Fe, Mg and Zn) from the acid extract (filtrate A). Hence, Cr(III) isolation in this work was much simpler than Cr(III) oxidation methods (Macchi *et al.,* 1991; Tiravanti *et al.,* 1997). However, only 31.6 % of Cr was recovered up to step 3 (Figure 1). According to thermodynamic calculations, Ca and Mg can not be removed as precipitate at a pH below 7.0, but they can be removed as precipitates of $CaCO_3$ and $MgCO_3$ at pH 8.0 (Shen *et al.*, 2001b). This explains why most of Ca and Mg were not removed in step 2 (pH 4.8) and step 3 (pH 7.0). Small removal of Ca and Mg was probably due to their adsorption on the precipitates of Cr, Al and Fe during steps 2 and 3. The relative deviation in mass balance at level C was: Al (-18.5%), Ca (-3.07%), Cr (-5.47%), Fe (-4.58%), Mg (-0.96%) and Zn (-11.09%).

5.5.4 Metal extraction from precipitate B (Step 4)

As mentioned before, only 31.6 % of Cr was isolated after step 3. Most of Cr (66.4 %) was lost in the precipitate B (Figure 2). In order to recover more Cr, the precipitate B was redissolved with sulfuric acid at pH 1.7 in step 4. The leaching efficiency of Cr was much less than step 1 and 43.2 % of Cr was lost in precipitate D. The dry mass of the precipitate D is 93.7 g and the Cr content was 266 g Cr/kg (Table 3). The soluble Cr concentration reached in filtrate D was 1.25 g/L. The precipitate D was discarded for disposal.

The low efficiency of Cr solubilization may be due to the formation of aged hydrated chromic oxide or aged hydrated chromium (III) sulfate when drying the precipitate B at 104°C. The $Cr(OH)_3$ formed at a pH below 4.8 (step 2) is generally supposed to be a colloidal hydrated oxides (Mellor, 1931; Habashi, 1997). The specimens of Cr(III) hydroxide prepared by precipitation with alkali in the cold from violet Cr(III) salt solution have a composition corresponding to $Cr_2O_3{\cdot}9H_2O$ (Habashi, 1997). Upon careful heating, dehydration occurs in steps and compounds containing 8, 5, 3, and 1 mol of water are formed. The density increased as the water content falls. Above 50°C, conversion to a gelatinous green aging product occurs, and the solubility and chemical reactivity decrease greatly. Chromium (III) oxide Cr_2O_3 does not dissolve in water, acid, alkali, or alcohols (Habashi, 1997).

In addition, Chromium (III) sulfate $[Cr(H_2O)_6]_2(SO_4)_3$ gives off water on heating and above 70°C it is converted , with further loss of water, into a dark-green crystalline pentadecahydrate. As the water content diminishes, the solubility decreases (Habashi, 1997). The dark-green solid was observed after heating at 104°C in this work.

Fe(III) can form co-precipitate $(Fe, Cr)_3(OH)_3$ with Cr(III) (Sass and Rai, 1987). In freshly precipitated Cr(III) hydroxides a crystalline phase isomorphic with bayerite $[Al(OH)_3]$ is observed (Habashi, 1997). Therefore, Al(III) was also likely to form co-precipitate with Al(III). Thus, the formation of co-precipitates $(Al, Fe, Cr)_3(OH)_3$ probably explained the low leaching efficiency of Al and Fe in step 4.

The contents of Ca and Mg in precipitate B were low. Thus, Ca concentration in the obtained filtrate D should be low. Moreover, the concentration was probably lower than that required to form the precipitate of $CaSO_4{\cdot}2H_2O$. Hence, most of leached Ca in filtrate D probably did not form the precipitate of $CaSO_4{\cdot}2H_2O$. This explains higher leaching efficiency of Ca in filtrate D.

At level D, relative deviations in mass balance of Ca and Zn were –19.37% and –49.79%, respectively. This was probably caused by adsorption during the filtration or by analytical error, since Ca and Zn content were low in level D. Small adsorption or analytical error will result in a large relative deviation in Ca or Zn.

5.5.5 Removal of aluminium and iron from filtrate D by the hydroxide precipitation (Step 5)

The filtrate D has been neutralized to pH 4.8 by addition of sodium hydroxide. This has resulted in a large removal of Al and Fe in precipitate E. A proportion of only 4.4 % of total Cr has also precipited (Figure 1). The dry mass of the precipitate E was 21.0 g and it contained 121 g Cr/kg (Table 3). The soluble Cr concentration in filtrate E was 0.92 g/L, whereas it was 1.25 g/L before neutralization (Table 2).

At level E, the relative deviations in mass balance of Al, Fe and Zn were –34% , –38% and 14% , respectively. Due to their low concentration, adsorption and/or a small analytical error will result in a large relative deviation.

5.5.6 Removal of Mg and Ca from filtrate E by precipitation (step 6)

The final step included the neutralization to pH 8.3 of the filtrate E. After this step, almost all Cr, Al, Fe and Zn from filtrate E were removed and existed in precipitate F. Meanwhile, the removal percentage of Ca and Mg in the precipitate F is much higher than in the precipitate C of step 3 (Fig. 1). This is due to the fact that Ca and Mg can be removed as precipitates of $CaCO_3$ and $MgCO_3$ at a pH above 8.0, according to the thermodynamic calculations (Shen *et al.,* 2001b).

It should be noted that the residual Cr(III) concentration in filtrate C (pH 7.0) and filtrate F (pH 8.3) was respectively 9.6 and 0.1 mg/L. Therefore, pH 8.3 seemed to be appropriate for the removal of Cr(III). The filtrate F was safer for disposal. However, part of Ca and Mg was also brought in precipitate F as impurities. Therefore, a compromised pH such as pH 7.5 may be more appropriate for the separation of Ca and Mg from Cr(III) as well as the disposal of final filtrate.

Except for levels A and C, metal adsorption on filter paper during filtration or analytical error are two possible reasons resulting in the large relative deviations of mass balance for the level in which metal content is low in precipitate or filtrate.

5.5.7 Ratio of metal concentration to chromium concentration in exit products

The ratios of metal concentration relative to Cr concentration in the initial tannery sludge, different precipitates and filtrates obtained at different steps of the process are presented in Table 4. There is the least impurities in precipitate C (final product). Precipitate F (final product) is the second most pure product. Relative to the original tannery sludge, the removal efficiencies of Al, Ca, Fe, Mg and Zn are 81.6 %, 96.8 %, 64.8 %, 97.7 % and −108.2, respectively for precipitate C and are 62.1 %, 95.7 %, 80.8 %, 94.1 % and 42.3 %, respectively for precipitate F. The amount of Zn in precipitate C increased by 1.1 times relative to original sludge. However, the amount of Zn in original sludge is very small. Therefore, the amount of increased Zn is negligible. Moreover, Zn could be removed by cupferron (Shen *et al.,* 2001a).

The final reusable product includes the combined precipitates C and F. Table 4 shows the values of concentration ratio of other individual metal to Cr for this product which are very good (inferior or equal to 0.02). Relative to the tannery sludge, the removal efficiency of Al, Ca, Fe, Mg and Zn in final product (combined precipitates C and F) is 76.0 %, 96.5 %, 69.3 %, 96.6 % and −50 %, respectively.

The removal factor ((Me/Cr) of the initial tannery sludge / (Me/Cr) of the final product) of the interfering metals relatively to the Cr concentration is also given in Table 4. Me represent metals (Al, Ca, Fe, Mg and Zn). The process has allowed producing a reusable product containing 28.2 and 29.5 times less Ca/Cr and Mg/Cr ratio than the initial tannery sludge. The removal of Al and Fe is also interesting with Al/Cr and Fe/Cr ratio values of 4.2 and 3.2, respectively. The removal efficiency of individual interfering metal (Al, Fe, Ca and Mg) in this pilot test was very close to the corresponding value obtained in previous small-scale experiments (Shen et al, 2001 a). Thus the process can be scaled-up using these pilot plant data.

5.5.8 Distribution of metals in the final reusable product

The weight and percentage distributions of metals in the final product reusable as tanning agent is presented in Figure 1. About 44.5 % of Cr(III) (56.9 kg Cr(III)/ton of treated tannery sludge) originally present in the tannery sludge was measured in the final product (combined precipitates C and F). Meantime, 10.7 % of Al (1.13 kg/ton), 1.6 % of Ca (0.78 kg/ton), 13.7 % of Fe (0.49 kg/ton), 1.5 % of Mg (0.88 kg/ton) and 73.2 % of Zn (0.16 kg/ton) were also present in these two precipitates.

The dry mass of the final product corresponds to 17.5 % of the weight of the treated tannery sludge (Table 3) (78.9/451=17.5 %). The Cr content in the final product is equal to 325 g Cr/kg of dry mass (32.5 % w/w). The concentrations of interfering metals have been reduced to the following values: 6.5 g Al/kg, 4.5 g Ca/kg, 2.3 g Fe/kg, 5.0 g Mg/kg and 0.9 g Zn/kg.

The summary of mass balance of the inputs and outputs (metals recovered) in the process is also presented in Figure 1. The input values only include the quantities of metals measured in the original tannery sludge. The output values include the quantities of metals determined in the precipitates A, C, D, E, F and in the filtrates C and F. The output/input ratio values (Figure 1) for Al, Ca, Cr, Fe, Mg and Zn are good with values situated between 0.83 and 1.18.

5.5.9 Chemical consumption

During this study, the acid consumption required for the process was equal to 1.23 metric tons (m.t.) of sulfuric acid/m.t. of sludge treated. By using a unitary cost of 80 \$/m.t. H_2SO_4 (93 %), this corresponds to a cost of approximately 105 \$Can/m.t. of sludge treated. The sodium hydroxide used during this research was equal to 0.67 m.t./m.t. of sludge treated. Then, by using a maximum estimated cost of 4140\$Can/m.t. NaOH, the cost for alkali could be estimated to 2773 \$Can/m.t. of sludge treated. Thus, the total cost of chemicals was 4245 \$Can/m.t. of sludge treated. Chemical cost is about 30% of the total operating cost (maintenance, utilities, labour) of a plant with an approximate capacity 3000 tons hides per year. The cost of chemicals will become more important if the capacity of tanning plant is further increased (Fig 1). The treatment of one metric tons of dry sludge gave 56.90 kg of Cr(III). One kg of Cr(III) was equal to 4.81 kg of tanning agent ($Cr_2(SO_4)_3{\cdot}6H_2O$). The estimated sale price of one kg of tanning agent was 181.9 \$Can. Thus the total sale price of tanning agent was 49756 \$Can, which can be realized by treating one metric ton of dry sludge. The ratio of the sale price of recovered tanning agent and the chemicals consumption was 11.72 (49756\$/4245\$). The ratio of sale price and total operating cost of the plant is estimated to be 3.5. Thus the Cr recovery process was an economical process. However, the ratio of output/input can further be increased by further improvement in the recovery of Cr. The efforts are continued in this direction.

5.6 Conclusions

This study proposed a simple six steps process for the extraction of metals from tannery sludge and the following separation of Cr(III) from interfering elements (Al, Fe, Ca, Mg, Zn) in the acid extract (or filtrate). It involves metal extraction from tannery sludge with sulfuric acid at about pH 1-2. The second step involves dilution of filtrate and precipitation of Al and Fe at pH 4.8. The third step involves the precipitation of chromium (III) and the separation of Ca and Mg from chromium (III) at pH 7.0. As a result, a precipitate containing less interfering metals was obtained in the third step.

In order to recover more Cr(III), the precipitate obtained in step 2 was dissolved with sulfuric acid in the fourth step. The fifth and sixth steps were similar to the second and third steps respectively, except that the pH in the sixth step was adjusted to 8.27 not 7.0. After the sixth step, a precipitate containing less interfering metals was also obtained.

About 44.5 % of Cr(III) present in the tannery sludge was found in the final reusable product as tanning agent. The dry mass of the final product corresponds to 17.5 % of the weight of the original tannery sludge and the Cr content in that final product is 325 g Cr/kg of dry mass. The concentrations of interfering metals were reduced to the following values: 6.5 g Al/kg, 4.5 g Ca/kg, 2.3 g Fe/kg, 5.0 g Mg/kg and 0.9 g Zn/kg of dry mass.

5.7 Acknowledgements

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Table 5.1 Composition of the dry tannery sludge

Parameters	Concentration (mg/kg)
Cr(III)	128 000
Cr(VI)	40
Al	10 600
Fe(III)	3 390
Fe(II)	140
Ca	49 800
Mg	58 000
Zn	220
K	90
Na	22 600
Orthophosphate	1 140
Total carbon	150 000
Total nitrogen	13 500
Total sulfur	< 5 000
Volatile organic matter	434 000

Table 5.2 Metal contents in the filtrates

Filtrates	Volume (L)	pH	Metal concentration in solution (mg/L)					
			Al	Ca	Cr	Fe	Mg	Zn
A	9.12	1.5	454	602	6 340	145	2435	11.9
B	26.2	4.8	13.0	179	746	7.3	745	2.8
C	26.0	7.0	0.0	166	9.6	0.2	736	0.0
D	10.5	1.7	138	36.7	1 250	40.4	86.0	0.7
E	10.5	4.8	20.7	34.6	915	3.8	78.0	0.6
F	10.5	8.3	0.0	17.7	0.1	0.0	45.0	0.0

Table 5.3 Metal contents in the precipitates

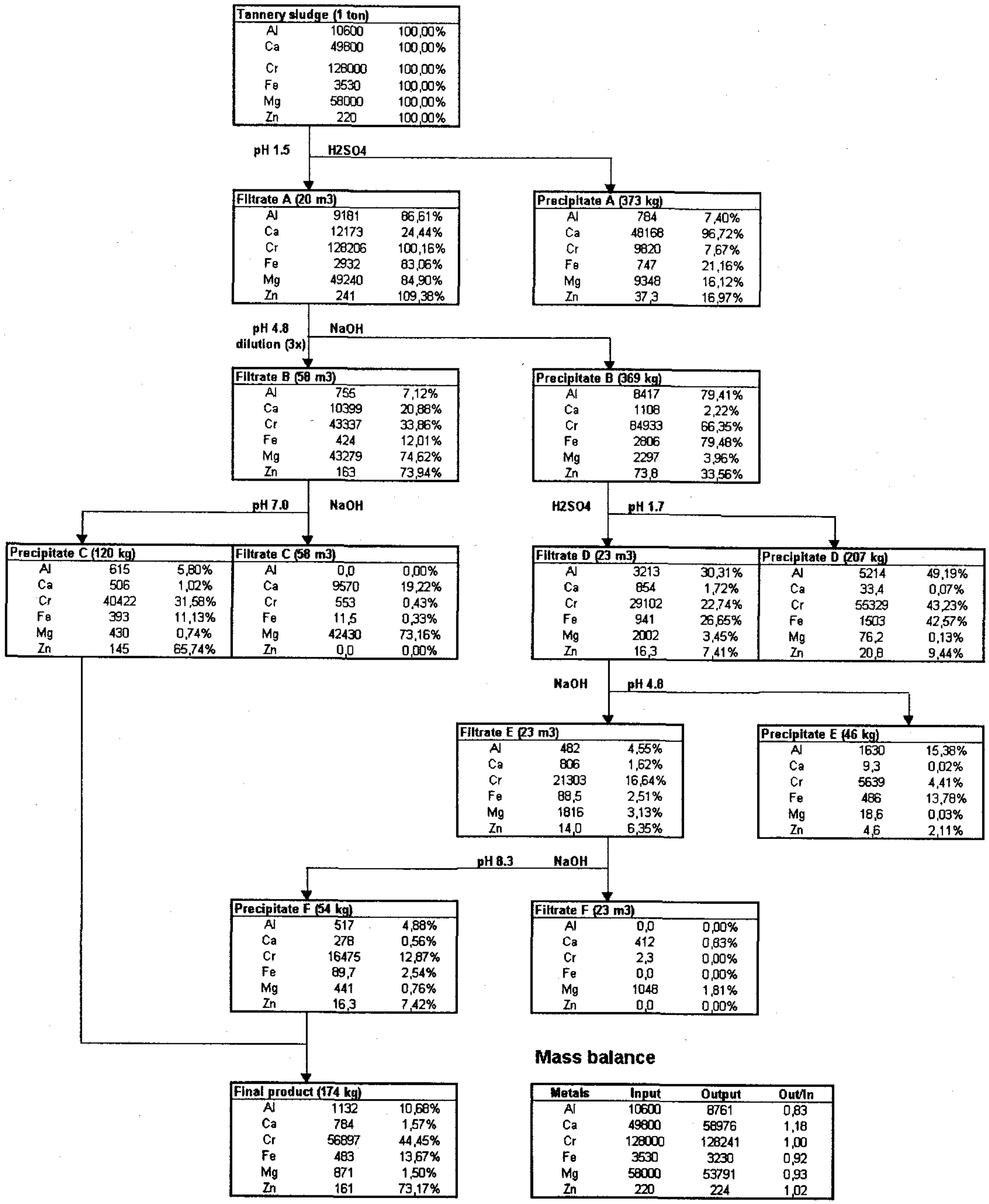
Precipitates	Dry mass (g)	Metal concentration (mg/kg)					
		Al	Ca	Cr	Fe	Mg	Zn
A	168	2 100	129000	26 300	2 000	25 034	< 100
B	166	22 800	3 000	230 060	7 600	6 223	200
C	54.36	5 100	4 200	335 363	3 259	3 566	1 200
D	93.7	25 100	161	266 338	7 234	367	< 100
E	21.0	35 100	200	121 400	10 472	400	< 100
F	24.55	9 500	5 100	302 656	1 648	8 100	300
Final product	78.9	6 470	4 480	325 187	2 758	4977	920

Table 5.4 **Ratio of metal concentration to chromium concentration in the final filtrates and precipitates generated by the process**

Fraction	Concentration ratio				
	Al/Cr	Ca/Cr	Fe/Cr	Mg/Cr	Zn/Cr
Tannery sludge	0.083	0.389	0.028	0.453	0.002
Precipitate A	0.080	4.905	0.076	0.952	0.004
Precipitate C	0.015	0.013	0.010	0.011	0.004
Precipitate D	0.094	0.001	0.027	0.001	0.000
Precipitate E	0.289	0.002	0.086	0.003	0.001
Precipitate F	0.031	0.017	0.005	0.027	0.001
Filtrate C	0.000	17.29	0.021	76.66	0.000
Filtrate F	0.000	177.0	0.000	450.0	0.000
Final product	0.020	0.014	0.008	0.015	0.003
(Me/Cr) i /(Me/Cr) f	4.163	28.24	3.252	29.61	0.608

(Me/Cr)i represents the metal ratio to Cr in input tannery sludge
(Me/Cr)f represents metal to Cr ratio in the final product.

*Combined precipitates C and F



Tannery sludge (1 ton)		
Al	10600	100,00%
Ca	49800	100,00%
Cr	128000	100,00%
Fe	3530	100,00%
Mg	58000	100,00%
Zn	220	100,00%

Filtrate A (20 m3)		
Al	9181	86,61%
Ca	12173	24,44%
Cr	128206	100,16%
Fe	2932	83,06%
Mg	49240	84,90%
Zn	241	109,38%

Precipitate A (373 kg)		
Al	784	7,40%
Ca	48168	96,72%
Cr	9820	7,67%
Fe	747	21,16%
Mg	9348	16,12%
Zn	37,3	16,97%

Filtrate B (58 m3)		
Al	756	7,12%
Ca	10399	20,88%
Cr	43337	33,86%
Fe	424	12,01%
Mg	43279	74,62%
Zn	163	73,94%

Precipitate B (369 kg)		
Al	8417	79,41%
Ca	1108	2,22%
Cr	84933	66,35%
Fe	2806	79,48%
Mg	2297	3,96%
Zn	73,8	33,56%

Precipitate C (120 kg)		
Al	615	5,80%
Ca	506	1,02%
Cr	40422	31,58%
Fe	393	11,13%
Mg	430	0,74%
Zn	145	65,74%

Filtrate C (58 m3)		
Al	0,0	0,00%
Ca	9570	19,22%
Cr	553	0,43%
Fe	11,5	0,33%
Mg	42430	73,16%
Zn	0,0	0,00%

Filtrate D (23 m3)		
Al	3213	30,31%
Ca	854	1,72%
Cr	29102	22,74%
Fe	941	26,65%
Mg	2002	3,45%
Zn	16,3	7,41%

Precipitate D (207 kg)		
Al	5214	49,19%
Ca	33,4	0,07%
Cr	55329	43,23%
Fe	1503	42,57%
Mg	76,2	0,13%
Zn	20,8	9,44%

Filtrate E (23 m3)		
Al	482	4,55%
Ca	806	1,62%
Cr	21303	16,64%
Fe	88,5	2,51%
Mg	1816	3,13%
Zn	14,0	6,35%

Precipitate E (46 kg)		
Al	1630	15,38%
Ca	9,3	0,02%
Cr	5639	4,41%
Fe	486	13,78%
Mg	18,6	0,03%
Zn	4,6	2,11%

Precipitate F (54 kg)		
Al	517	4,88%
Ca	278	0,56%
Cr	16475	12,87%
Fe	89,7	2,54%
Mg	441	0,76%
Zn	16,3	7,42%

Filtrate F (23 m3)		
Al	0,0	0,00%
Ca	412	0,83%
Cr	2,3	0,00%
Fe	0,0	0,00%
Mg	1048	1,81%
Zn	0,0	0,00%

Final product (174 kg)		
Al	1132	10,68%
Ca	784	1,57%
Cr	56897	44,45%
Fe	483	13,67%
Mg	871	1,50%
Zn	161	73,17%

Mass balance

Metals	Input	Output	Out/In
Al	10600	8761	0,83
Ca	49800	58976	1,18
Cr	128000	128241	1,00
Fe	3530	3230	0,92
Mg	58000	53791	0,93
Zn	220	224	1,02

Figure 5.1 **Schematic flow sheet of the process and mass balance in grams of metals in the filtrates and precipitates per metric ton of sludge and in weight percentage**

CHAPITRE 6

BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA — EFFECT OF SLUDGE SOLIDS CONCENTRATION

BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA — EFFECT OF SLUDGE SOLIDS CONCENTRATION

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6 BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA – EFFECT OF SLUDGE SOLIDS CONCENTRATION

6.1 Résumé

Cette étude porte sur l'effet de la concentration en solides des boues de tannerie sur la biolixiviation du chrome en utilisant des bactéries oxydant le soufre élémentaire. Des essais de biolixiviation ont été effectués avec des concentrations en solides de boues variant entre 13 et 60 g/L. La concentration de soufre élémentaire ajouté aux boues était fixée à 30 g/L. Après 25 jours de biolixiviation, le pH des boues ayant différentes concentrations de solides se situait aux environs de 1.3. Le temps requis pour atteindre ce pH est toutefois fonction de la teneur en solides des boues selon la relation mathématique suivante : Jours = 0.4354 C (solides, g/L) + 1.8106. La concentration optimale en solides des boues pour la lixiviation maximale des métaux se situe à 40 g/L. Dans ce cas, les rendements de solubilisation suivants sont atteints : 87 % du Cr(III), 73 % de l'Al, 72 % du Fe, 62 % du Mg et 73 % du Zn. Pendant la biolixiviation, les teneurs en matières en suspension totales et volatiles des boues diminuent considérablement. D'autre part, les bactéries oxydant le soufre élémentaire tolèrent une concentration en Cr(III) aussi élevée que 5930 mg/L à pH 1.3. Finalement, les efficacités de lixiviation du Cr(III), de l'Al et du Fe du procédé de biolixiviation sont semblables à celles mesurées par lixiviation chimique avec de l'acide sulfurique.

6.2 Abstract

An investigation on the effect of sludge solids concentration on bioleaching of Cr(III) and other metals from tannery sludge by indigenous sulphur-oxidizing bacteria was carried out. The sludge solids concentrations ranged from 13 to 60 g/L. The concentration of elemental sulphur was fixed at 30 g/L. The results showed that the lowest pH reached after 25 days of bioleaching at all studied sludge solids concentration was about 1.3. The optimum sludge solids concentration for maximum metal leaching from tannery sludge was 40 g/L and about 87 % of Cr(III), 73 % of Al, 72 % of Fe, 62 % of Mg and 73 % of Zn could be leached in this case. During bioleaching, the concentrations of total and volatile suspended solids of the tannery sludge significantly decreased. The sulphur-oxidizing bacteria could tolerate a Cr(III) concentration as high as 5 930 mg/L at pH 1.3. The leaching efficiencies of Cr(III), Al, Fe for both chemical leaching and bioleaching of tannery sludge were similar at pH 1.3. The leaching efficiency of Ca, Mg and Zn in both leaching processes were identical for pH values in the range of 1.3 to 3.0.

Key words: Tannery sludge, chromium, bioleaching, metals, sludge solids, sulphur-oxidizing microorganisms, thiobacilli.

6.3 Introduction

The trivalent chromium, typically basic hydrated chromic sulphate, is utilised in large quantity in the tanning of hides. Leather tanning consumes about 32 % of total world trade in chromium compounds (Walsh and John, 1996). However, about 50 % of chromium salts used in the production process are disposed in tannery sludge or tannery wastewater (Tiravanti *et al.,* 1997). Despite of the extreme high content of Cr(III) in the tannery sludge (about 13 % w/w on a dry basis, Table 1), most of tannery sludge is still disposed in landfill due to the absence of a suitable treatment method. The oxidation of Cr(III) to very toxic Cr(VI) catalyzed by MnO_2 in the soils has been reported (Eary and Rai, 1987; Nakayama *et al.,* 1981). Moreover, this oxidation could be enhanced by the chelation of Cr(III) with organic ligands in the tannery sludge and soil (James and Bartlett, 1983). Therefore, the landfill of tannery sludge constitutes a considerable potential menace to the environment. The current studies relating to the treatment of tannery sludge or tannery wastewater have focused on the recovery of Cr(III) (Macchi *et al.,* 1991; Skrypski-Mantele and Bridle, 1995; Panswad *et al.,* 1995, Tiravanti *et al.,* 1997, Shen *et al.*, 2001 a). The recovery of Cr(III) and its reuse in the tanning process has the economical interest considering high content of Cr(III) in tannery sludge and annual astonishing consumption in the Cr(III)-containing tanning agent around the world. More important, this process can greatly reduce Cr(III) release to the environment. The first step of Cr(III) recovery is the extraction of Cr(III) from tannery sludge. The chemical leaching of Cr(III) and other metals from tannery sludge by mineral acids has been studied (Macchi *et al.*, 1991; Panswad *et al.,* 1995; Chuan and Liu 1996; Shen *et al.*, 2001 b). It was found that a large amount of sulphuric acid was required to extract Cr(III) from tannery sludge (Shen *et al.,* 2001 b). Therefore, it could be useful to develop other economical way to extract Cr(III) from tannery sludge.

Removing metals from sewage sludge by bioleaching (mainly by sulphur-oxidizing bacteria) have been studied extensively (Tyagi *et al.*, 1988, 1993, 1996, 1997; Blais *et al.*, 1992 a, 1992 b). Tyagi *et al.* (1988) observed that the bioleaching of metals by sulphur-oxidizing bacteria was 80 % cheaper than the chemical leaching of acid-consuming due to a less requirement for acid and lime in the former method. In this process the added elemental sulphur was oxidised by mixed sulphur oxidising microorganisms to sulphuric acid. The pH of the sludge decreased from near 7 to about 1.0. The metals were solubilised as a result of sludge acidification. Moreover, the bioleaching process destroys indicator bacteria (due to pH reduction) to a level normally found in the agricultural soil, and contributes substantially toward the reduction of volatile organic matters in the sludge (Blais *et al.,* 1992 a). Thus, this process is capable of carrying out simultaneous sludge digestion and metal leaching.

It seemed that extracting Cr(III) from tannery sludge by bioleaching was never reported before. Maybe it was thought that high Cr(III) concentration, especially in the case of high sludge solids concentration, in the tannery leachate would have strong toxic effect on the microbiological activity of metal-leaching bacteria. The economic analysis of bioleaching revealed that sewage sludge having lower sludge solids concentration incurred higher treatment cost (Sreekrishnan and Tyagi, 1994; Sreekrishnan *et al.,* 1996). This is due to an increase in the volume of handled sludge whilst dealing with a sludge having low solids concentration. In addition, the cost of sludge conditioning and dehydration with plate and frame filter press are reduced with increased sludge solids concentration. Thus, the bioleaching of Cr(III) from tannery sludge at a high solids concentration is highly desirable from an economic viewpoint.

The objective of the present work is to study the microbial leaching process at different sludge solids concentration for the solubilization of Cr(III) and other metals in tannery sludge using indigenous sulphur oxidising microorganisms.

6.4 Materials and methods

6.4.1 Tannery sludge samples and digestion of the samples

The dehydrated (filter-press) tannery sludge sample was obtained from “La Tannerie des Ruisseaux” in Rivière-du-loup (Québec, Canada). The sludge contained 30.3 % of total solids and was stored at 4°C. A part of the sludge sample was dried at 104°C for 48 h before use.

The digestion of sludge samples was carried out according to the method recommended by Chuan and Liu (1996). Two samples (0.3 g each) of the dry sludge were digested. A blank was also performed. The solution obtained after sludge digestion was filtered through Whatman GF/C filter and diluted to 100 mL with 0.2 % HNO_3. The corresponding blank values were subtracted for each element analysis. Each metal concentration was calculated as an average of the two samples.

6.4.2 Bioleaching of metals at different sludge solids concentrations

The sulphur oxidising mixed culture was acclimated in the tannery sludge according to the method described by Jain and Tyagi (1992) for municipal sludge. The acclimated mixed sulphur oxidising microorganisms comprise of Thiobacillus strains (*Thiobacillus thioparus* and *Thiobacillus thiooxidans*) that are responsible for the pH reduction (Shen et al., 2001 d).

Different quantities of tannery sludge were suspended in five Erlenmeyer flasks containing 100 mL of Millipore water to make final solids concentrations of 13, 20, 30, 40 and 60 g/L. After shaking at 150 rpm and 21°C for two hours, the mixtures had a pH about 9.0. The pH of each solid suspension in flasks was adjusted to 7.0 using 1.8M H_2SO_4. Six mL of acclimated mixed culture was added to each flask. Each flask was amended with 3 g of tyndallized elemental sulphur powder. A control flask containing 100 mL of 40 g/L of dry tannery sludge was autoclaved at 121°C for 20 min. Tyndallized sulphur powder was added (3.0 g) to the flask. The initial pH of this flask was 7.05. This sample was used as a control to investigate if a chemical oxidation of elemental sulphur occurred during the experiment. The six flasks were placed in a gyratory shaking incubator at 170 rpm and 21°C. The solution pH in each flask was measured and 2 mL samples from each flask were drawn at a regular interval. The samples were immediately centrifuged at 10 000 x *g* for 15 min. The supernatant was used to determine dissolved metals concentrations. After bioleaching, the treated sludge was recovered to determine the residual total suspended solids (TSS) and residual volatile suspended solids (VSS) according to APHA (1989).

6.4.3 Chemical analysis

The pH of the solutions was monitored by a Orion Model 420A pH meter. Varian VISTA AX CCD Simultaneous ICP-AES (inductively coupled plasma—atomic emission spectrometer) was used to measure soluble metals and sulphates. Cr(VI) concentration was determined by the S-diphenylcarbazide method (3500-Cr, D, APHA, 1989). Fe(II) concentration was measured by the phenanthroline method (3500-Fe, D, APHA, 1989). Orthophosphate concentration was analyzed by the ascorbic acid method (4500-P, APHA, 1989). Total carbon, total nitrogen and total sulfur in the solid powder (particle size inferior to 80 mesh) of tannery sludge were determined with Carlo Erba Instruments NA 1500 Nitrogen/Carbon/Sulphur Analyzer. Water content was obtained from the average weight loss of five sludge samples at 104°C over 48 h. The volatile organic matter content was obtained from the average weight loss of the dried sludge samples at 550°C over 48 h.

6.5 Results and discussion

6.5.1 Chemical composition of the tannery sludge

The Chemical composition of the tannery sludge was presented in Table 1. The predominant species of Cr and Fe are Cr(III) and Fe(III), respectively. In addition, Al, Fe, Ca , Mg and Zn are also present in this sludge.

6.5.2 Effect of sludge solids concentration on final sludge pH and leaching time

The variation of sludge pH during bioleaching of the tannery sludge is presented in Figure 1. The final pH at sludge solids concentration 13, 20, 30, 40 and 60 g/L was 1.29, 1.22, 1.44, 1.43 and 1.57, respectively. Therefore, there was no appreciable difference in final sludge pH for the different sludge solids concentration. The required time to arrive at the final pH was 6.8, 9.8, 13.8, 21 and 25.8 days respectively corresponding to the sludge solids concentration 13, 20, 30, 40 and 60 g/L. The required time to arrive at final pH increased with increasing sludge solids concentration and exhibit an approximately linear relationship: Days = 0.4198 C(solids, g/L) + 1.7475. The pH of the control (without sulphur addition) remained at about 7 during the experiment (Fig. 1). It indicates that the chemical oxidation of elemental sulphur did not occur during the experiment.

Similar to these results on tannery sludge, municipal sludge solids concentration had no appreciable effect on final sludge pH during bioleaching (Tyagi *et al.,* 1997). However, the required time to arrive at a final pH during bioleaching of municipal sludge and tannery sludge was different. The time required to achieve final pH for tannery sludge and sewage sludge at sludge solids concentration of 13 g/L was 6.8 and 8 days respectively, and 13.8 and 9 days respectively at sludge solids concentration of 30 g/L (Tyagi *et al.,* 1997).

6.5.3 Effect of sludge solids concentration on metal leaching efficiencies

6.5.3.1 Chromium (III), Aluminium and Iron

The effect of sludge solids concentration on leaching efficiencies (amount of metal solubilized/initial amount of metal in sludge) of Cr(III), Al and Fe are shown in Figures 2, 3 and 4 respectively. The leaching efficiencies of these metals showed a similar trend. The leaching efficiencies of Cr, Al and Fe showed an appreciable value when sludge pH was below 2.9 and increased steeply with decreasing pH at the pH range of 2.9 to 1.2. The final leaching efficiencies of metals at sludge solids concentration of 13, 20, 30, 40 and 60 g/L were: Cr(III) - 91.5, 91.8, 91.6, 87.2 , 74.4 %; Al – 74.5, 77.5, 77.8, 71.8 and 65.9%; Fe –76.1, 83.4, 69.7, 74.3, and 57.6 , respectively. More than 74 % of Cr(III), >65% of Al and >51.6% of Fe could be leached at sludge pH below 1.6. Therefore, the optimum pH for bioleaching of Cr(III), Al and Fe was below 1.6. The final leaching efficiency of Cr(III), Al and Fe began to decrease appreciably at solids concentration of 60 g/L. There was no appreciable difference in the leaching efficiency of these metals at 13 to 40 g/L of tannery sludge. Since a higher sludge solids concentration should be preferred from an economic viewpoint (Sreekrishnan and Tyagi, 1994; Sreekrishnan *et al.,* 1996), the optimum sludge solids concentration for bioleaching of Cr(III), Al and Fe from tannery sludge was 40 g/L.

Previous studies (Blais et al., 1992 b) showed that approximately 16 % of Cr , 5% of Fe and 15% of Al could be solubilized from municipal sludge at pH 2.0. The sludge solids concentration used was 20-22 g/L with initial Cr, Fe and Al concentration of 116, 487 and 475 mg/L, respectively. The corresponding solubilization efficiencies from tannery sludge at 20 g/L solids concentration and pH 2.0 for Cr, Fe and Al were also of the same order. The Cr in municipal sludge could not be solubilized until the sludge pH decreased to below 2.5 (Blais *et al.,* 1992 b). Cr solubilization from tannery sludge was observed at a pH below 3.0. Thus, considering the similar leaching efficiencies of Fe and Al achieved in two kinds of sludges under similar leaching condition, it can be suggested that the sludge properties do not affect the leaching efficiencies of Fe and Al. For the tannery sludge at pH 2, higher sludge solids concentration gave higher leaching efficiencies of Cr, Fe and Al (Figures 2, 3 and 4). Since a longer leaching time was required to arrive at the same pH 2 at higher tannery sludge solids concentration (Figure 1), the higher leaching efficiency of Cr, Fe and Al were probably caused by a longer leaching time.

6.5.3.2 Calcium

The effect of sludge solids concentration on leaching efficiency of Ca is presented in Figure 5. The leaching of Ca showed a different trend than that of Cr, Al and Fe. In general, Ca leaching efficiency was less affected by pH at each sludge solids concentration. The leaching efficiency between pH 5.5 and 2.0 did not change appreciably. The average leaching efficiency of Ca at the end of leaching process was about 33, 24, 21, 14 and 10 % respectively corresponding to sludge solids concentration of 13, 20, 30, 40 and 60 g/L. The Ca solubilization efficiency decreased with increased sludge solids concentration and could be explained by the increase of sulphate concentration resulting in the formation of sparingly soluble $CaSO_4{\cdot}2H_2O$. This was due to increased H_2SO_4 amount required to achieve the same final pH (about 1.2) with increasing sludge solids concentration. Similar phenomena were also observed in chemical leaching of tannery sludge (Shen *et al.,* 2001 b).

6.5.3.3 Magnesium)

The effect of sludge solids concentration on leaching efficiency of Mg is presented in Figure 6. Mg leaching efficiency was less affected by sludge solids concentration. The final leaching efficiency of Mg for all solids concentration was about 60 %. The Mg leaching efficiency increased slowly with decreasing pH.

6.5.3.4 Zinc

The effect of sludge solids concentration on leaching efficiency of Zn is presented in Figure 7. Zn leaching efficiency showed an appreciable value when sludge pH was below 4.0. The leaching efficiency of Zn increased linearly with decreasing pH in the range of 4.0 to 1.2. Zn leaching efficiency was less affected by sludge solids concentration. The final leaching efficiency of Zn for all solids concentration was about 65 %. In earlier studies on municipal sludge showed that Zn began to dissolve at pH 4.0 and its leaching efficiency increased linearly with decreasing pH (Blais *et al.,* 1992 b). A similar result was also observed in the tannery sludge (Figure 7).

Generally for tannery sludge and sewage sludge, Ca and Mg could be leached at a higher pH about 6.0 to 7.0. Zn could be leached at a pH about 4.0. Cr, Al and Fe could be leached at a pH about 3.0. Therefore, Ca and Mg were the first to leach out followed by Zn. Cr, Al and Fe were the last to leach out. This may be related to the adsorption capacity of different metals. Ca, Mg and Zn were the most easily desorbed metals among Pb, Cr, Cu, Al, Fe, Ni, Cd, Mn, Zn, Mg and Ca from different biomass (Blais *et al.,* 1999).

Another possible reason for low leaching efficiencies of Cr, Al and Fe at a pH 3.0 was the presence of more undissolved sludge solids than at pH 1.3. These undissolved sludge solids probably carried Cr, Al and Fe.

The third possible reason for low leaching efficiencies of Cr, Al and Fe at pH 3.0 was the formation of hydroxide and phosphate precipitates of Cr(III), Al and Fe at this pH. Based on thermodynamic calculations, it was found that α-FeOOH (goethite), (am)$Fe(OH)_3$, (am) $Cr(OH)_3$, $FePO_4{\cdot}2H_2O$, (am)$AlPO_4{\cdot}2H_2O$, (am)$FePO_4{\cdot}2H_2O$ were likely to form at a pH range of 1.3 to 3.0 and at a sludge solids concentration range of 19.6 to 58.9 g/L during the chemical leaching of the tannery sludge (Shen *et al.,* 2001 c). Moreover, the possibility of formation of these precipitates generally increased with increasing pH.

Once the metals are solubulized, Cr must be recovered from the leachate to recycle in the tanning process. This necessitates isolation of Cr from other metals (Fe, Mg, Ca, Zn). One of the methods used to recover Cr is the oxidation of Cr(III) to Cr(VI) using H_2O_2. In order to minimise the consumption of H_2O_2 and to enhance the recovery efficiency of Cr, the molar ratio of (Fe+Mg)/Cr in the leachate should be minimum (Macchi et al., 1991). Figures 2 to 4 show that Cr, Al and Fe are not solubilized until pH 3.0. Ca solubilization at a given solid concentration remains almost constant in the pH range of 5.5 to 3 (Fig. 5), whereas Mg solubilization remains almost constant irrespective of solids concentration in the same pH range (5.5 to 3) (Fig. 6). This indicates that the concentration of Mg and Ca in the final leachate can be minimised by conducting the leaching process in two steps. The first step involves the leaching of sludge up to a pH 4.0 and thus removing a substantial amount of Mg (55%) and Ca (15%). After first step, the solids can be separated from the leachate and suspended in fresh water to continue the leaching to pH 1.5 to obtain a leachate with substantially low concentrations of Mg and Ca. Based on the calculations at 40 g/L solids concentration from the results shown in Figs 2-7, the molar ratio of (Fe+Mg)/Cr can be reduced by 50%. The two step bioleaching can be accomplished by acclimating two different sulphur oxidising bacteria that grow in different pH range (neutrophilic, pH range 8-4 and acidophilic, pH range 4-1) (Jain and Tyagi, 1992). Further studies are continued in this direction.

6.5.4 Effect of sludge solids concentration on sulphate concentration

The effect of sludge solids concentration on the concentration of soluble sulphates is presented in Figure 8. The concentration of soluble sulphates at a given sludge solids concentration increased slowly with decreasing pH in the range of 6.6 to 2.9 followed by an abrupt increase in the pH range of 2.9 to 1.2. This implied that more H_2SO_4 was produced at this pH range (2.9-1.5). The pH reduction resulted in desorption of metals, dissociation of metal-organic complexes and solubilization of metal precipitates. This explained a sharp increase in the leaching efficiencies of Cr(III), Al and Fe(III) at pH range 3.0 to 1.2 (Figures 2 to 4). The concentration of soluble sulphates increased with increasing sludge solids concentration at this pH range. This was due to an increased H_2SO_4 concentration required to adjust solution pH at higher sludge solids concentration.

6.5.5 Effect of bioleaching on residual sludge solids concentration

After bioleaching, the residual suspended solids in tannery sludge are composed of three parts. The undissolved original sludge solids, precipitates formed during bioleaching such as $CaSO_4 \cdot 2H_2O$, $FePO_4$, FeOOH (Shen *et al.,* 2001 c) and the non-oxidised elemental sulphur. The melting point and boiling point of pure elemental sulphur are 115 and 444°C, respectively. Hence, elemental sulphur is not volatile at 104°C but is at 550°C. It indicates that un-oxidized sulphur is included in the residual suspended solids (TSS) as well as in the volatile suspended solids (VSS).

The effect of initial sludge solids concentration on the residual sludge suspended solids is shown in Table 2. During bioleaching the TSS and VSS concentrations decreased. Moreover, the percent reduction of TSS and VSS increased with increased sludge solids concentration. Similar phenomenon was also observed in bioleaching of sewage sludge (Tyagi *et al.,* 1997). Comparatively, low percent reduction of TSS at low sludge solids concentration was probably due to the presence of higher residual (non-oxidised) elemental sulphur. Therefore, at low solids concentration low quantity of sulphur may be added to achieve the same final sludge pH (pH 1.2) as that obtained at a higher sludge solids concentration. The decrease of TSS and VSS concentrations could also be explained by the solubilization of the initial suspended solids of the tannery sludge and also by microbiological digestion of organic matter present in the sludge. Low reduction of VSS at low sludge solids concentration was probably due to the shorter leaching time that was not sufficient for biodegradation.

6.5.6 Metal tolerance by the sulphur-oxidizing bacteria

The final metal concentration in the leachate and the average metal solubilization rate (digits in parenthesis) is presented in Table 3. The metals solubilization rates (metal concentration/total leaching time) for Al, Cr, Fe, Mg, and Zn did not change appreciably with sludge solids concentration. At sludge solids concentration of 60 g/L and pH 1.3, soluble Cr(III) concentration in tannery sludge was as high as 5 930 mg/L and the Cr solubilisation rate was almost similar as observed at low metal concentrations. At this Cr(III) concentration, a large number of living sulphur-oxidizing bacteria were still observed under microscope. Hence, these bacteria could endure a high Cr(III) concentration.

6.5.7 Relative metal molar ratio in the final leachate

Relative metal molar ratios in the final leachates obtained during microbial leaching (Table 3) and chemical leaching (at 80 g/L solids concentration) of tannery sludge are very similar (Table 3). The molar ratios of Al relative to Cr in the final bioleaching leachates (leachate obtained through bacterial leaching) are higher than the corresponding values of Fe but similar in two leachates. Thus, Al which is one of the most interfering elements in the isolation of Cr(III) (for a possible recycle) is present in both the leachates in the same order. Thus, from this viewpoint, two leachates have almost similar characteristics.

6.5.8 Comparison between bioleaching and chemical leaching of tannery sludge

A comprehensive investigation on the leaching of Cr(III) and other metals from the tannery sludge using mineral acids was carried out by Shen *et al.*(2001 b). The average chemical leaching efficiencies of Cr, Al, Fe, Mg and Zn at sludge solids concentration range of 19.6 to 78.5 g/L were 83, 72, 60, 70 and 65 % respectively at pH 1.3 and 72, 65, 50, 70 and 57 % respectively at pH 3.0. The average bioleaching efficiency of Cr, Al, Fe, Mg and Zn at sludge solids concentration range of 13 to 60 g/L was 87, 73, 72, 62 and 73 % respectively when pH reached about 1.3 and 10, 15, 5, 55 and 40 % respectively when pH reached about 3.0.

Chemical and bioleaching efficiencies of Cr, Al, Fe, Mg and Zn were close at pH 1.3. But the bioleaching efficiencies of Cr, Al and Fe at pH 3.0 were much lower than corresponding values in chemical leaching process. Thus during the bioleaching process when pH 3.0 is reached, low amount of Cr was solubilized (compared to chemical leaching at pH 3) and a substantial amount Mg was solubilized suggesting that a two step bioleaching process (as discussed before) shall lead in a substantial reduction of (Fe+Mg)/Cr molar ratio. This will facilitate recovery of Cr from the leachate for a possible recycle for tanning. The bioleaching efficiency of Ca decreased with increasing sludge solids concentration and the efficiency was less affected by pH. This result was similar to that observed in chemical leaching of Ca (Shen *et al.,* 2001 b). The chemical leaching efficiency of Ca was about 40 and 12 % at sludge solids concentration of 19.6 and 80 g/L, respectively. The bioleaching efficiency of Ca was about 35 and 10 % at solids concentration of 13 and 60 g/L, respectively. Both chemical leaching and bioleaching efficiencies of Ca were close at similar sludge solids concentration.

6.6 Conclusions

An investigation on the effects of sludge solids concentration on the metal bioleaching from tannery sludge by the sludge indigenous sulphur-oxidizing bacteria was performed. The following conclusions were drawn from this study.

1. The final pH at all solids concentration (13 to 60 g/L) was between 1.3 – 1.5. Chemical oxidation of elemental sulphur was insignificant during the experiments.

2. The required time to achieve the final pH had an approximate linear relationship with sludge solids concentration.

3. The leaching efficiency of Cr, Al and Fe increased with increasing sludge solids concentration at around pH 2. The preferred sludge solids concentration was 40 g/L and about 87 % of Cr(III), 73 % of Al, 72 % of Fe, 62 % of Mg and 73 % of Zn could be leached at this concentration. The leaching efficiency of Mg and

Zn was less affected by sludge solids concentration. In contrast, the leaching efficiency of Ca decreased with increasing sludge solids concentration.

4. The concentrations of total suspended solids and volatile suspended solids appreciably decreased. Reduction of solids was higher at higher solids concentration.

5. The leaching efficiency of Cr(III), Al and Fe for both chemical leaching and microbial leaching of tannery sludge was approximately the same at pH 1.3, but there was a remarkable difference at a higher pH 3.0. The leaching efficiency of Ca, Mg and Zn for both the leaching processes were independent of pH in the range of 1.3 to 3.0.

6. The sulphur-oxidizing bacteria could tolerate a Cr(III) concentration as high as 5930 mg/L at pH 1.3.

7. Relative metal molar ratios in the final leachates obtained from both microbial and chemical leaching of tannery sludge were very similar.

6.7 Acknowledgements

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Table 6.1 Composition of the dry tannery sludge

Parameters	Concentration (% w/w)
Cr(III)	12.80
Cr(VI)	0.004
Al	1.063
Fe(III)	0.339
Fe(II)	0.014
Ca	4.980
Mg	5.795
Zn	0.022
K	0.009
Na	2.262
Orthophosphate	0.114
Total carbon	14.96
Total nitrogen	1.349
Total sulphur	< 0.5
Volatile organic matter	43.4

Table 6.2 Variation of solids concentration in tannery sludge during bioleaching

TSS (g/L)			VSS (g/L)		
Initial (g/L)	Final (g/L)	Reduction (%)	Initial (g/L)	Final (g/L)	Reduction (%)
13.1	12.5	5.0	5.70	5.03	11.8
20.0	17.2	14.3	8.68	7.59	12.6
29.9	24.2	19.0	13.0	9.20	29.1
39.9	30.6	23.4	17.3	9.65	44.3
59.7	41.6	30.3	25.9	11.0	57.7

Table 6.3 Final tannery sludge leachate composition

Solids	Metals					
(g/L)	Al	Ca	Cr	Fe	Mg	Zn
			Soluble metal concentration (mg/L)			
13	114 (16.7)	494(72)	1690(247)	38.8(5.7)	527(77)	2.35(0.34)
20	172 (17.5)	527(54)	2450(250)	61.6(6.3)	812(83)	3.41(0.34)
30	261 (18.9)	540(39)	3690(267)	77.7(5.6)	1120(81)	4.90(0.35)
40	322 (15.3)	538(26)	4700(223)	111(5.3)	1550(74)	6.41(0.3)
60	437 (16.9)	512(20)	5930(230)	127(4.9)	2050(79)	8.08(0.3)
			Metal molar ratio relative to Cr			
13	13.0	37.9	100	2.14	66.6	0.11
20	13.5	27.9	100	2.34	70.9	0.11
30	13.6	19.0	100	1.96	64.8	0.11
40	13.2	14.8	100	2.19	70.3	0.11
60	14.2	11.2	100	1.99	74.0	0.11
80*	13.4	7.1	100	2.02	71.4	0.11

* Data abstracted from the result of chemical leaching of tannery sludge (Shen et al., 2001 a)

- Digits in parenthesis represent the metals solubilization rates (mg/L/day)

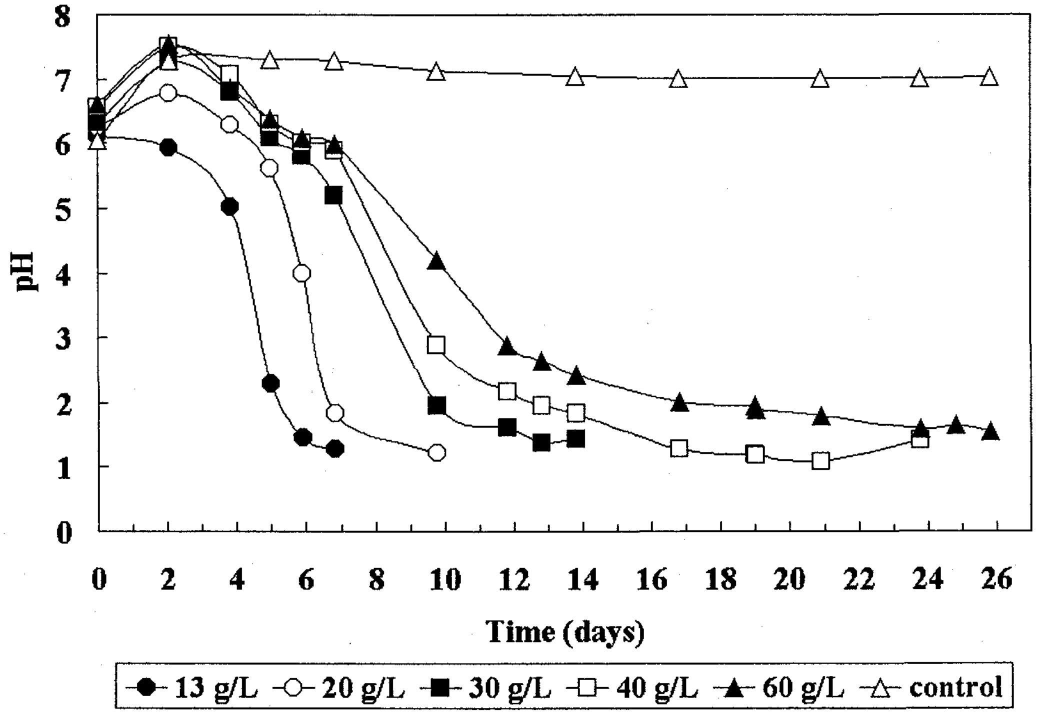

Figure 6.1 Variation of sludge pH during bioleaching of tannery sludge using different sludge solids concentration

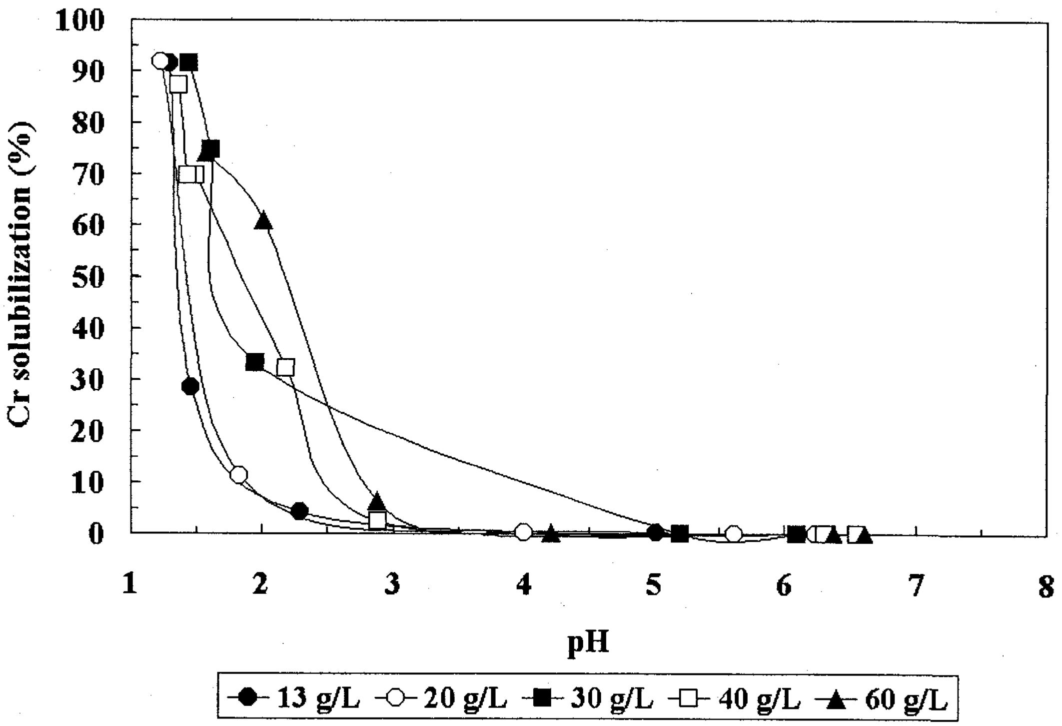

Figure 6.2 **Variation of Cr(III) leaching efficiency during bioleaching of tannery sludge**

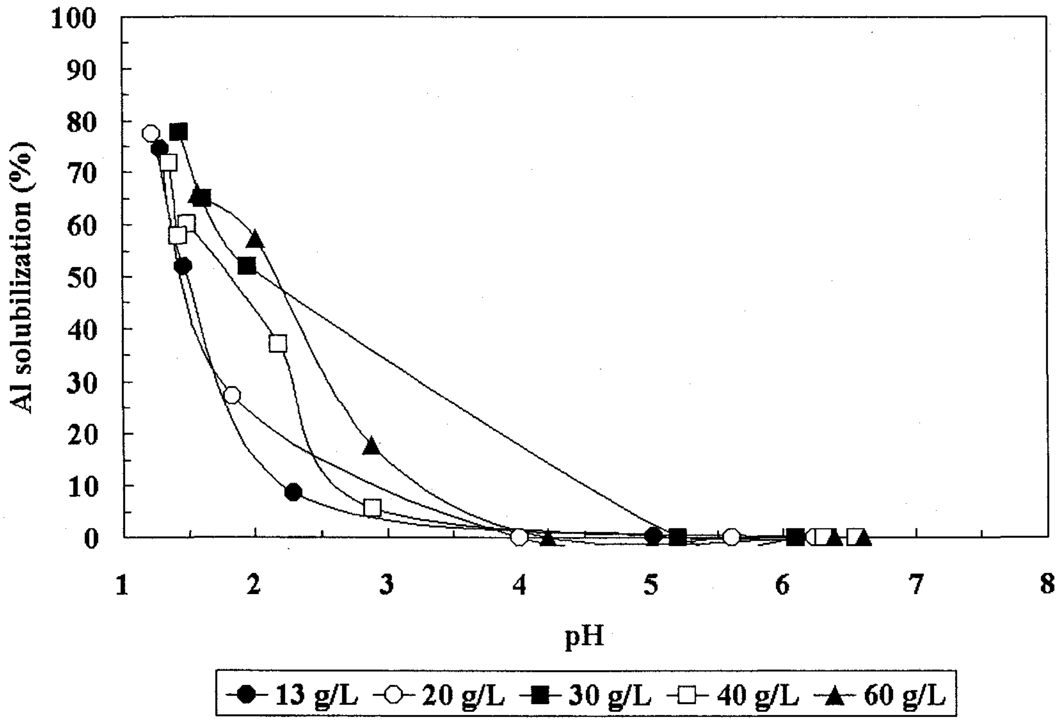

Figure 6.3 **Variation of Al leaching efficiency during bioleaching of tannery sludge**

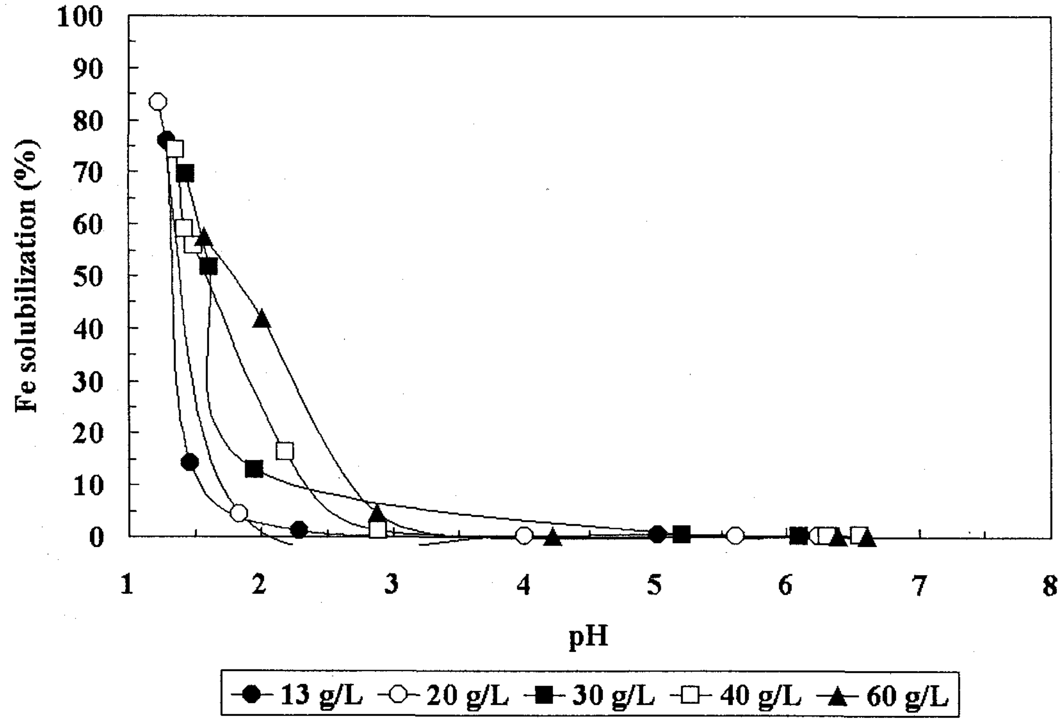

Figure 6.4 Variation of Fe leaching efficiency during bioleaching of tannery sludge

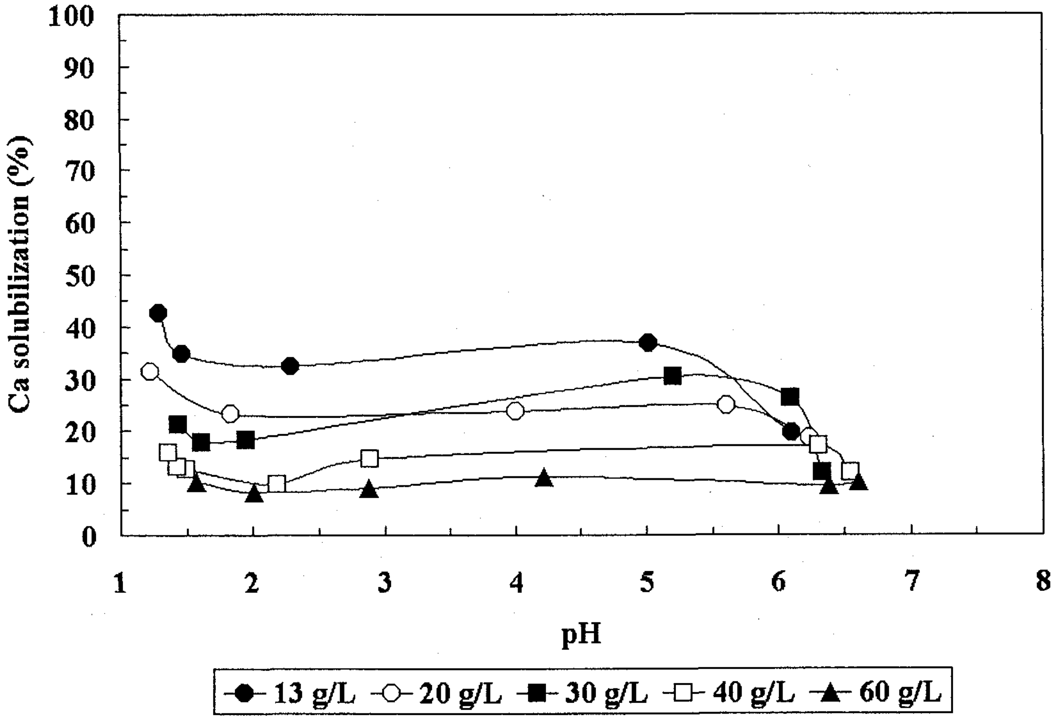

Figure 6.5 **Variation of Ca leaching efficiency during bioleaching of tannery sludge**

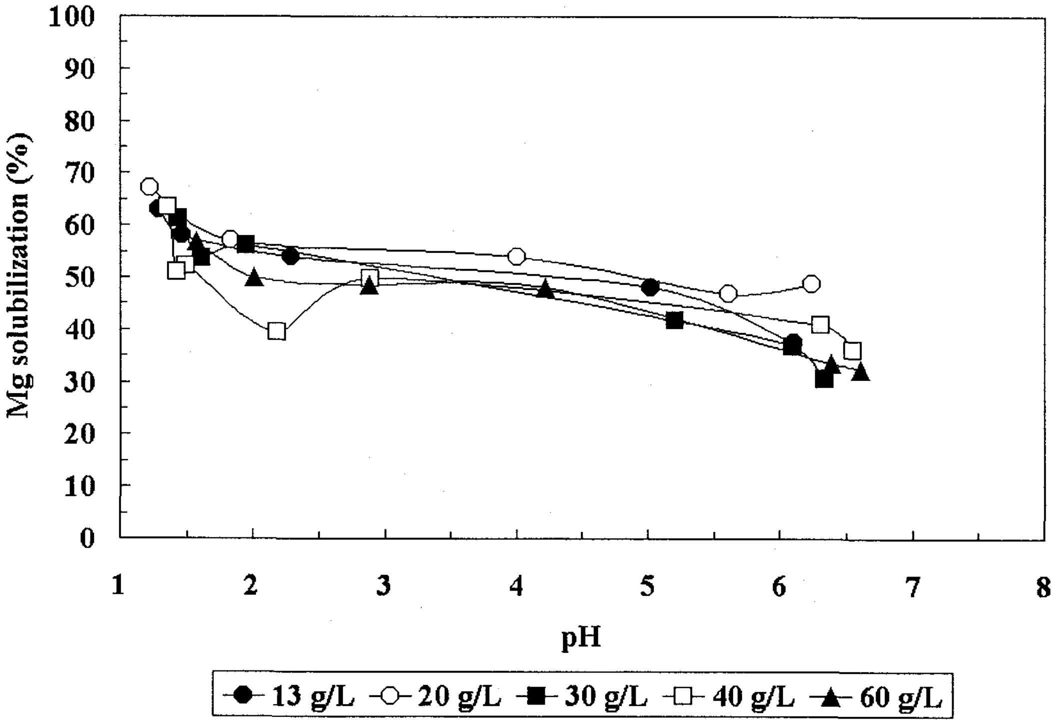

Figure 6.6 Variation of Mg leaching efficiency during bioleaching of tannery sludge

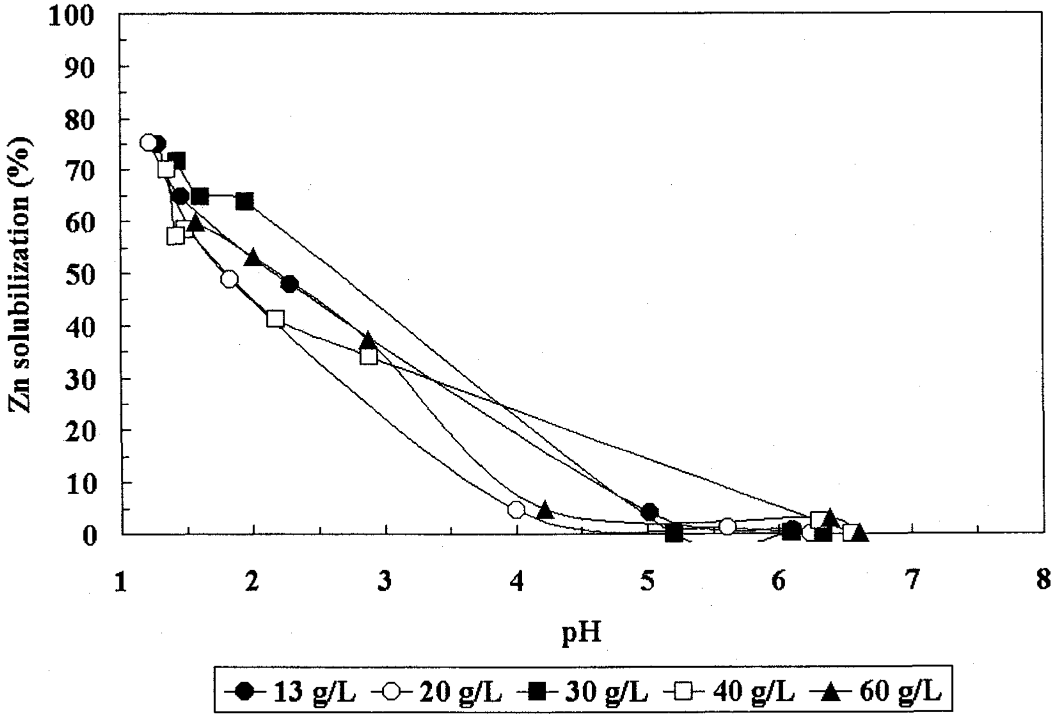

Figure 6.7 Variation of Zn leaching efficiency during bioleaching of tannery sludge

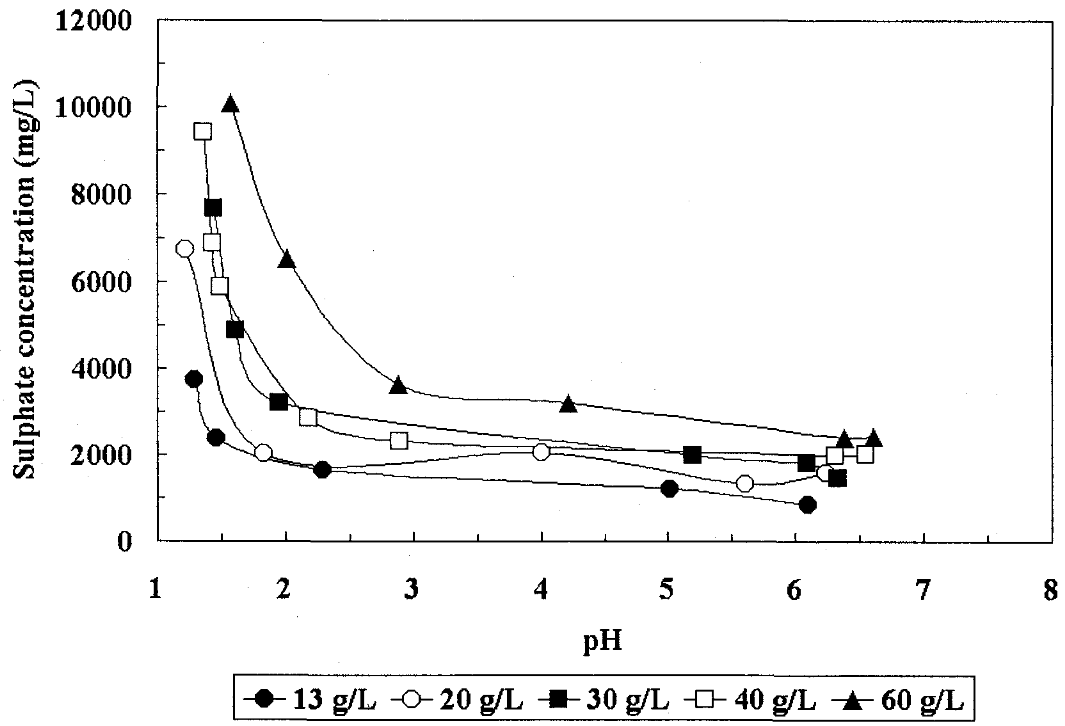

Figure 6.8 **Variation of sulphate concentration with pH during bioleaching of tannery sludge**

CHAPITRE 7

BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA — EFFECT OF ELEMENTAL SULPHUR CONCENTRATION

BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA — EFFECT OF ELEMENTAL SULPHUR CONCENTRATION

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7 BACTERIAL LEACHING OF METALS FROM TANNERY SLUDGE BY INDIGENOUS SULPHUR-OXIDIZING BACTERIA – EFFECT OF ELEMENTAL SULPHUR CONCENTRATION

7.1 Résumé

Cette étude traite de l'effet de la concentration de soufre élémentaire ajouté aux boues de tannerie sur la biolixiviation du chrome en utilisant des bactéries oxydant le soufre élémentaire. Des essais de biolixiviation ont été effectués avec des concentrations en soufre élémentaire variant entre 5 et 40 g/L. La concentration de solides des boues était fixée à 40 g/L. Les résultats ont montré que le pH des boues diminue plus rapidement lorsque la concentration initiale en soufre dans les boues est plus élevée et que le pH final obtenu est également plus bas. La période de temps requise pour atteindre le pH minimal était toutefois presque identique dans tous les cas, soit environ 15 jours. L'efficacité de lixiviation du Cr(III), de l'Al et du Fe, ainsi que la concentration en SO_4^{2-} a augmenté avec la hausse de la concentration initiale en soufre élémentaire. Cependant, l'efficacité de lixiviation du Zn, du Ca et du Mg a été moins affectée par la concentration initiale en soufre. La concentration optimale, d'un point de vue économique, de soufre élémentaire ajouté pour la biolixiviation du Cr(III) se situe à 20 g/L. Pendant la biolixiviation, les teneurs en matières en suspension totales et volatiles des boues diminuent considérablement. Le dénombrement des bactéries oxydant le soufre élémentaire a montré que les thiobacilles acidophiles contribuent davantage à la réduction du pH dans les boues de tannerie que les thiobacilles peu-acidophiles. Les bactéries oxydant le soufre élémentaire ont pu vivre dans les boues de tannerie à un pH aussi faible que 0.48 à 21°C.

7.2 Abstract

An investigation on the effect of elemental sulphur concentration on bioleaching of Cr(III) and other metals from tannery sludge by sludge indigenous sulphur-oxidizing bacteria was performed. Elemental sulphur concentrations ranging from 5 to 40 g/L were tested during this study. The sludge solids concentration was fixed at 40 g/L. The results showed that the sludge pH decrease was faster and sharper with increased sulphur concentration. The time required to achieve the final pH (the lowest pH) was about 15 days irrespective of sulphur concentration. The leaching efficiencies of Cr(III), Al and Fe, and the SO_4^{2-} production increased with increasing initial sulphur concentration. However, the leaching efficiencies of Zn, Ca and Mg were less affected by initial sulphur concentration. The preferred sulphur concentration for Cr leaching was 20 g/L from an economic viewpoint. The total and volatile suspended solids decreased during the process. The measurements of sulfur-oxidizing bacteria showed that less acidophilic thiobacilli and acidophilic thiobacilli contributed to the pH reduction in tannery sludge. The sulphur-oxidizing bacteria could survive in tannery sludge at a pH as low as 0.5 at 21°C.

Key words: Tannery sludge, chromium, bioleaching, metals, sulphur, sulphur-oxidizing microorganisms, thiobacilli.

7.3 Introduction

The current studies relating to the treatment of tannery sludge or tannery wastewater have focused on the recovery of Cr(III) (Macchi *et al.,* 1991; Skrypski-Mantele and Bridle, 1995; Panswad *et al.,* 1995, Tiravanti *et al.,* 1997, Shen *et al.*, 2001 a). The recovery of Cr(III) and its reuse in the tanning process has the economical interest considering high content of Cr(III) in tannery sludge and annual astonishing consumption of Cr(III)-containing tanning agents around the world. More important, this process can greatly reduce Cr(III) release to the environment. The first step of Cr(III) recovery is to extract Cr(III) from tannery sludge. The chemical leaching of Cr(III) and other metals from tannery sludge by mineral acids has been studied (Macchi *et al.,* 1991; Panswad *et al.,* 1995; Chuan and Liu 1996; Shen *et al.,* 2001 b). It was found that a large amount of sulphuric acid was required to extract Cr(III) from tannery sludge (Shen *et al.,* 2001 b). Therefore, it is necessary to develop other economical ways to extract Cr(III) from tannery sludge.

Removing metals from sewage sludge by bioleaching (mainly by sulphur-oxidizing bacteria) have been studied extensively (Tyagi *et al.,* 1988, 1993, 1996, 1997; Blais *et al.,* 1992a, 1992b, 1993). Tyagi *et al.* (1988) observed that the bioleaching of metals by sulphur-oxidizing bacteria was 80 % cheaper than the chemical leaching by acid-consuming due to use of acid and lime in the former method. The economic analysis of bioleaching process revealed that sewage sludge having lower sludge solids concentration incurred higher treatment cost (Sreekrishnan *et al.,* 1994). Hence, metal bioleaching from sewage sludge should preferably to be performed at a higher sludge solids concentration. We have investigated the effect of sludge solids concentration on the metal bioleaching from tannery sludge. The optimal solids concentration was found to be near 40 g/L.

The objective of the present work is to study the effect of elemental sulphur concentration on the bioleaching of Cr(III) and other metals from tannery sludge by indigenous sulphur-oxidizing bacteria. If the sulphur concentration is lower, the produced acid may be less and the pH decrease may not be sufficient to solubilize metals in the tannery sludge. On the other hand, if sulphur concentration is too high, a part of sulphur may not be oxidised in the tannery sludge and the residual (non-oxidised) sulphur may pose problems in the residual sludge disposal. Moreover, a sufficiently low pH (less than 1.0) may not enhance the leaching efficiency. The maximum metal leaching efficiency during chemical leaching was generally achieved at pH of about 1.0 (Shen *et al.,* 2001 b). Therefore, it is necessary to find an optimal sulphur concentration for metal bioleaching.

7.4 Materials and Methods

7.4.1 Tannery sludge samples and digestion of the samples

The dehydrated (filter-press) tannery sludge sample was obtained from “La Tannerie des Ruisseaux” in Rivière-du-loup (Québec, Canada). The sludge contained 30.3 % of total solids and was stored at 4°C. A part of the sludge sample was dried at 104°C for 48 h before use.

The digestion of sludge samples was carried out according to the method recommended by Chuan and Liu (1996). Two samples (0.3 g each) of the dry sludge were digested. A blank was also performed. The solution obtained after sludge digestion was filtered through Whatman GF/C filter and diluted to 100 mL with 0.2 % HNO_3. The corresponding blank values were subtracted for each element analysis. Each metal concentration was calculated as an average of the two samples.

7.4.2 Effect of sulphur concentration on the metal leaching

About 13.2 g of fresh tannery sludge was suspended in each of six Erlenmeyer flasks (500 mL capacity) containing 100 mL of Millipore water. After shaking at 150 rpm and 21°C for two hours, the mixtures had a pH of 9.0. The sludge solids concentration in these six samples was about 40 g/L (on a dry basis). H_2SO_4 (1.8 M) was added to each of the six samples to adjust pH from 9.0 to 6.0-7.0. Five mL of inoculum containing acclimatized indigenous sulphur-oxidizing bacteria was added to each sample. The acclimation of sulphur-oxidizing bacteria in tannery sludge was carried out in a similar way as reported by Jain and Tyagi (1992). After that, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 g of tyndallized sulphur powder were added to six flasks, and these additons lead to sulphur concentrations of 5, 10, 15, 20, 30 and 40 g/L in the samples, respectively.

These six flasks were placed in a gyratory shaking incubator at 170 rpm and 21°C. The solution pH in each flask was measured and 2 mL samples from each flask were drawn at a regular interval. The samples were immediately centrifuged at 10 000 x *g* for 15 min. The supernatant was used to determine dissolved metal concentrations. After bacterial leaching, the treated sludge was recovered to determine the residual total suspended solids (TSS) (dried at 104°C) and residual volatile suspended solids (VSS) (dried at 550°C) according to APHA *et al.* (1989).

7.4.3 Measurement of the thiobacilli in the tannery sludge at different pH

The thiobacilli count during the bacterial leaching process of tannery sludge was carried out by a plate count technique using the $S_2O_3^{2-}$ synthetic salt agar medium for less-acidophilic (pH 7.0) and acidophilic (pH 4.0) thiobacilli described by Laishley *et al.* (1988) and Reynolds *et al.* (1981). Sludge samples were diluted serially by vortex mixing 0.5 mL of sludge with 4.5 mL of sterile NaCl saline solution (8.6 g/L). After that, 0.1 mL of diluted sample was drawn and spread with sterile glass L-rods over each of quadruplicate plates. These thiobacilli plates were incubated at 28°C until clear colonies appeared on the plate.

7.4.4 Chemical analysis

An Orion Model 420A pH meter was used to monitor the pH of the solutions. Varian VISTA AX CCD Simultaneous ICP-AES was used to measure soluble metals and sulphate. Cr(VI) concentration was determined by the S-diphenylcarbazide method (3500-Cr, D, APHA *et al.,* 1989). Fe(II) concentration was measured by the phenanthroline method (3500-Fe, D, APHA *et al.,* 1989). Orthophosphate concentration was analyzed by the ascorbic acid method (4500-P, APHA *et al.,* 1989). Total carbon, total nitrogen and total sulfur in the solid powder (particle size inferior to 80 mesh) of tannery sludge were determined with Carlo Erba Instruments NA 1500 Nitrogen/Carbon/Sulphur Analyzer. Water content was obtained from the average weight loss of five sludge samples at 104°C over 48 h. The volatile organic matter content was obtained from the average weight loss of the dried sludge samples at 550°C over 48 h.

7.5 Results and discussion

7.5.1 Effect of sulphur concentration on final sludge pH and leaching time

Figure 1 presents the variation of pH with time for the tannery sludge containing different sulphur concentrations. The final pH reached was 3.2 and 2.9 when sulphur concentrations were 5 and 10 g/L, respectively. There was an important decrease in the final sludge pH from 2.9 to 1.4 corresponding to an increase in the sulphur concentration from 10 to 15 g/L. The final pH was about 1.2 for the sludge samples whose sulphur concentrations were 15, 20 and 30 g/L. The final pH decreased to 0.5 when sulphur concentration was 40 g/L. The pH drop was faster and sharper when initial sulphur concentration was higher. The final pH was also lower with higher sulphur concentration. The time required to achieve the final pH (the lowest pH) was about 15 days irrespective of sulphur concentration. A similar phenomenon was also observed in the case of municipal sludge (Sreekrishnan *et al.,* 1996).

7.5.2 Effect of sulphur concentration on metal leaching efficiencies

7.5.2.1 Chromium (III)

The results of chemical analysis of the tannery sludge are provided in Table 1. The predominant species of Fe and Cr are Fe(III) and Cr(III), respectively.

The effect of sulphur concentration on leaching efficiency of Cr(III) is presented in Figure 2. The final leaching efficiency of Cr(III) and the final pH at sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L was 7.0, 39.2, 60.2, 91.7, 90.7 94.6 % and 3.2, 2.9, 1.4, 1.2, 1.1 and 0.5, respectively. The leaching efficiency of Cr(III) began to increase remarkably with increasing sulphur concentration at sulphur concentration, particularly after sulphur of 15 g/L. Cr leaching efficiency was close to maximum (about 91 %) when sulphur concentration was 20 g/L. Therefore, the preferred sulphur concentration for Cr(III) leaching was 20 g/L with sludge solids concentration of 40 g/L. The time required to attain the maximum leaching efficiency of Cr(III) was 26.7, 24.0, 16.9, 16.9, 15.7 and 14.8 days respectively corresponding to sulphur concentrations of 5, 10, 15, 20, 30 and 40 g/L. Cr(III) leaching efficiency reached the maximum, in shorter time, when sulphur concentration was increased. For the sludge samples whose sulphur concentration was 15 g/L or higher, the maximum Cr(III) leaching efficienciy was attained once the final and lowest pH was reached (15th day). However, for the sludge samples whose sulphur concentration was less than 15 g/L, the leaching efficieny of Cr(III) attained the maximum at about 26th day, even though the final pH was reached on 15th day. This may be due to the fact that metal dissociation from tannery sludge into solution is a function of time at a given pH. More time is required for metal dissociation at a higher pH or at a lower sulphur concentration.

7.5.2.2 Aluminium

The effect of sulphur concentration on leaching efficiency of Al is presented in Figure 3. The final leaching efficiency of Al at sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L, was 17.9, 53.5, 62.5, 83.0, 83.3 and 79.5 %, respectively. Al leaching efficiency increased with increased sulphur concentration, however, there was a remarkable increase in leaching efficiency at sulphur concentration of 15 g/L and higher. Also, at higher sulphur concentration, Al solubilized at a faster rate (Fig. 3). The solubilization efficiency was close to the maximum, about 80 %, when sulphur concentration was above 20 g/L.

The time required to attain the maximum or final leaching efficiency of Al was 26.7, 20.7, 16.9, 16.9, 13.9 and 14.8 days, respectively, corresponding to sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L. The final value of Al leaching efficiency was attained in a shorter time as the sulphur concentration was increased. For the sludge samples with sulphur concentration 15 to 40 g/L, the leaching efficiency of Al attained maximum once the final pH (the lowest pH, in 15 days) was reached. However, for the sludge samples whose sulphur concentration was lower than 15 g/L, the leaching efficiency of Al attained maximum on 21st day even though the final pH (the lowest pH) was reached on 15th day. This was due to the fact that longer time is required to solubilize Al at higher pH, as was the case with Cr.

7.5.2.3 Iron (III)

The effect of sulphur concentration on leaching efficiency of Fe is shown in Figure 4. The final leaching maximum efficiency of Fe at sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L, was 2.2, 22.3, 35.5, 62.4, 77.2 and 78.8 %, respectively. The leaching efficiency of Fe increased with increasing sulphur concentration. The leaching efficiency of Fe approached a maximum, about 77 %, when sulphur concentration was 30 g/L.

The time required to attain the maximum leaching efficiency of Fe was 20.8, 24.0, 16.9, 16.9, 15.7 and 14.8 days, respectively, corresponding to sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L. The leaching efficiency of Fe attained a maximum value in a shorter time when the sulphur concentration was increased. For the sludge samples whose sulphur concentration was >15 g/L, the leaching efficiency of Fe also attained maximum once the final pH (exactly the lowest pH) was reached (on 15th day). However, for the sludge samples whose sulphur concentration was 5 and 10 g/L, the leaching efficiency of Fe attained a maximum on 24th day even though the final pH (the lowest pH) was reached on 15th day.

7.5.2.4 Calcium

The effect of sulphur concentration on leaching efficiency of Ca is presented in Figure 5. The final (maximum) leaching efficiency of Ca at sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L, was 16.3, 17.8, 13.5, 13.7, 16.3 and 19.0 %, respectively. The final leaching efficiency of Ca was close, about 16 % for all the samples. The precipitate of $CaSO_4 \cdot 2H_2O$ was likely to be formed at sludge solids concentration of 40 g/L (Shen *et al.,* 2001 b). Therefore, the Ca solubilisation was limited by the precipitation equilibrium and the final leaching efficiency of Ca was thus close for all the samples. It should be noted that the initial Ca leaching efficiency of all the samples was also low. This is due to the fact that some sulphuric acid was added to the sludge samples to adjust the pH from 9 to 6-7 at the beginning of the experiment and thus the precipitates of $CaSO_4 \cdot 2H_2O$ were also formed.

For the sludge sample whose sulphur concentration was 10 g/L, the Ca leaching efficiency decreased from 31% to 20% with time in 12.7 days and then remained constant. Otherwise, Ca leaching efficiency in all other samples remained almost constant with time. It indicates that most of the Ca had dissociated from tannery sludge during the adjustment of sample pH from 9 to 6-7.

In general, except for 10g/L sulphur concentration sample the final pH did not affect the final leaching efficiency of Ca. The average leaching efficiency of Ca was about 16 % at different sulphur concentrations.

7.5.2.5 Magnesium

Mg leaching efficiencies at different sulphur concentrations were almost same all the time (Figure 6). It indicates that Mg leaching efficiency was not affected much by sulphur concentration in the leaching process. Mg leaching efficiencies of all samples increased slowly with time from about 40 %, in the beginning, to about 70 % at the end. The final leaching efficiency of Mg at sulphur concentration of 5, 10, 15, 20, 30, 40 g/L was 70.7, 61.8, 60.2, 80.7, 70.7 and 78.0 %, respectively.

7.5.2.6 Zinc

The maximum leaching efficiency of Zn at sulphur concentration of 5, 10, 15, 20, 30 and 40 g/L, was 53.8, 61.8, 60.2, 80.7, 70.7 and 78.0 %, respectively, and the time required to attain the efficiency was 26.7, 20.7, 16.9, 15.9, 13.8 and 14.8 days, respectively (Figure 7). Hence, Zn leaching efficiency increased slightly with increasing sulphur concentration. Zn leaching efficiency attained the maximum in a shorter time when the sulphur concentration was increased.

7.5.3 Effect of sulphur concentration on concentration of soluble sulphate

The effect of sulphur concentration on the concentration of soluble sulphates is presented in Figure 8. The maximum final concentration of soluble sulphates at sulphur concentration 5, 10, 15, 20, 30, 40g/L was 3 090, 3 470, 5 600, 8 530, 8 560 and 9 230 mg/L, respectively, and the time required to attain these concentrations was 26.7, 26.7, 16.9, 16.9, 26.7 and 16.9 days, respectively. With increasing sulphur concentration, the concentration of soluble sulphates also attained a maximum value in a shorter time. This was due to a larger sulphur surface available to bacteria for colonisation at a higher sulphur concentration. Higher amount of elemental sulphur was oxidised to sulphuric acid as the initial sulphur concentration was increased. It should be noted that the soluble sulphate was only a part of the oxidised elemental sulphur. The rest of the oxidized sulphur probably existed in the form of undissolved precipitates such as $CaSO_4{\cdot}2H_2O$ (Shen *et al.,* 2001 c).

7.5.4 Variation of the sulfur-oxidizing microorganisms

The less-acidophilic and acidophilic *thiobacilli* were considered as the main sulphur-oxidising bacteria in sewage sludge (Blais *et al.,* 1993). Therefore, enumeration of *thiobacilli* in the tannery sludge during the leaching process was used to study the effect of biological activity of the *thiobacilli* on pH.

The pH of tannery sludge decreased from 6-7 to 1-2 in the bioleaching process. A lag in pH decrease from 6-7 to 5 was observed (Figure 1). A similar phenomenon also occurred in the aerobically digested municipal sludge (Blais *et al.,* 1992a). For municipal sludge, the acidification takes place in two steps: an initial decrease in pH from 7 to 4-5 by less-acidophilic thiobacilli followed by a lag in bacterial growth and a further pH reduction from 4-5 to 2 or below by the acidophilic thiobacilli (Blais *et al.,* 1992 a, 1992 b, 1993). To explain the phenomenon that occurred in tannery sludge, the enumeration of two groups of sulphur-oxidizing thiobacilli was carried out and the results were presented in Figure 9. As explained before, a lag in pH decrease from 6.7-7.2 to 5.2 in 9.8 days was observed for the tannery sludge. From 3.9th day to 9.8th day, the concentration of less-acidophilic thiobacilli remained at a constant level 10^9 CFU/ml, meanwhile the concentration of acidophilic thiobacilli increased appreciably. The concentration of acidophilic thiobacilli stayed at a maximum level, 2×10^8 CFU/ml, between 9.8th and 11th day. From 9.8th to 11th day, the sludge pH showed a most rapid drop- a pH reduction from 5.2 to 2.0 in about 1 day. During this period, the concentration of less-acidophilic thiobacilli decreased rapidly. Once pH decreased to 2.0 on 11th day, the concentration of acidophilic thiobacilli began to decrease. On the 13.9th day (pH 1.2), the concentrations of less-acidophilic and acidophilic thiobacilli decreased to 10^6 and 2 x 10^6 CFU/ml, respectively. After 13.9th day, the concentration of acidophilic thiobacilli increased with time and reached a value of 2.5 x 10^7 CFU/ml on 26.8th day. From 13.9th day to 26.8th day, the concentrations of less-acidophilic *thiobacilli* decreased very slowly with time and reached a value of 4.5 x 10^5 CFU/ml on 26.8th day.

The pH of tannery sludge decreased slowly from pH 7.0 to 5.0, then the pH decreased further (abruptly) from 5.0 to 1.2 or below. The pH decrease of tannery sludge in the first stage (the pH reduction from 7.0 to 5.0) was much slower than that was observed in the municipal sludge. One possible explanation is that elemental sulphur was more slowly dissolved in the tannery sludge than in the municipal sludge due to less organic substances in the tannery sludge. Another possible explanation is that less-acidophilic thiobacilli grew more slowly in tannery sludge than in sewage sludge due to the presence of high concentration of Cr(III) and other metals, which may inhibit the growth of less-acidophilic thiobacilli.

7.5.5 Effect of sulphur concentration on amount of residual solids

After bioleaching the residual suspended solids in tannery sludge are composed of three parts: The first part is undissolved original sludge solids, the second is formed precipitates during bioleaching, such as $CaSO_4 \cdot 2H_2O$, $FePO_4$, FeOOH (Shen *et al.,* 2001 c); and the third is the non-oxidised elemental sulphur. The melting point and the boiling point of pure elemental sulphur are 115 and 444°C, respectively. Hence, elemental sulphur is not volatilizable at 104°C, but volatilize at 550°C. This suggests that non-oxidised sulphur is present in the residual total suspended solids (TSS), but not in the residual volatile suspended solids (VSS).

After bioleaching, total suspended solids and residual volatile suspended solids concentration decreased for all samples (Table 2). Also, the reduction (or degradation) of TSS decreased with increased sulphur concentration. This was probably due to increased unoxidized amount of sulphur in the residual TSS with increased initial sulphur concentration. In contrast, the reduction of VSS increased with increased initial sulphur concentration. This was probably due to additional organic matter that became soluble, during bioleaching, as the initial sulphur concentration was increased. Finally, a lower final pH was achieved, with higher initial sulphur concentrations that resulted in increased solublisation of organic matter.

7.6 Conclusions

The following conclusions could be drawn from this research.

1. The time required to achieve final pH was close to 15 days. The pH drop was faster and sharper when the initial sulphur concentration was higher.

2. The leaching efficiencies of Cr(III), Al, Fe, and the concentration of soluble sulphate increased with initial sulphur concentration. However, the leaching efficiencies of Zn, Ca and Mg were less affected by the initial sulphur concentration. The preferred elemental sulphur concentration for Cr leaching from tannery sludge with 40 g/L of sludge solids was 20 g/L.

3. During bioleaching, total suspended solids and volatile suspended solids concentration decreased. The reduction of total suspended solids (TSS) decreased with increased sulphur concentration. This was due to increased amount of unoxidized sulphur with increased initial sulphur concentration. In contrast, the reduction of volatile suspended solids (VSS) increased with increased initial sulphur concentration. This was due to solubilization or degradation of organic matter that became soluble during bioleaching as initial sulphur concentration was increased. A final lower pH was achieved with increased initial sulphur concentration and this lead to further solubiliztion of organic matter.

There was a lag in pH decrease between pH 6-7 and 5. This was probably due to a slower growth of acidophilic thiobacilli at pH > 5. The leaching pH showed a most rapid drop from 5 to 2 or below.

7.7 Acknowledgements

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Table 7.1 Composition of the dry tannery sludge

Parameters	Concentration (% w/w)
Cr(III)	12.80
Cr(VI)	0.004
Al	1.063
Fe(III)	0.339
Fe(II)	0.014
Ca	4.980
Mg	5.795
Zn	0.022
K	0.009
Na	2.262
Orthophosphate	0.114
Total carbon	14.96
Total nitrogen	1.349
Total sulphur	< 0.5
Volatile organic matter	43.4

Table 7.2 **Solids variation in tannery sludge during bioleaching**

Solids		Sulphur concentration (g/L)			
		10	20	30	40
TSS	Initial (g/L)	40.3	40.0	40.0	40.0
	Final (g/L)	28.0	27.5	30.6	37.2
	Reduction (%)	30.5	31.3	23.5	7.0
VSS	Initial (g/L)	17.5	17.4	17.4	17.4
	Final (g/L)	16.2	10.4	8.95	9.32
	Reduction (%)	7.1	40.1	48.4	46.4

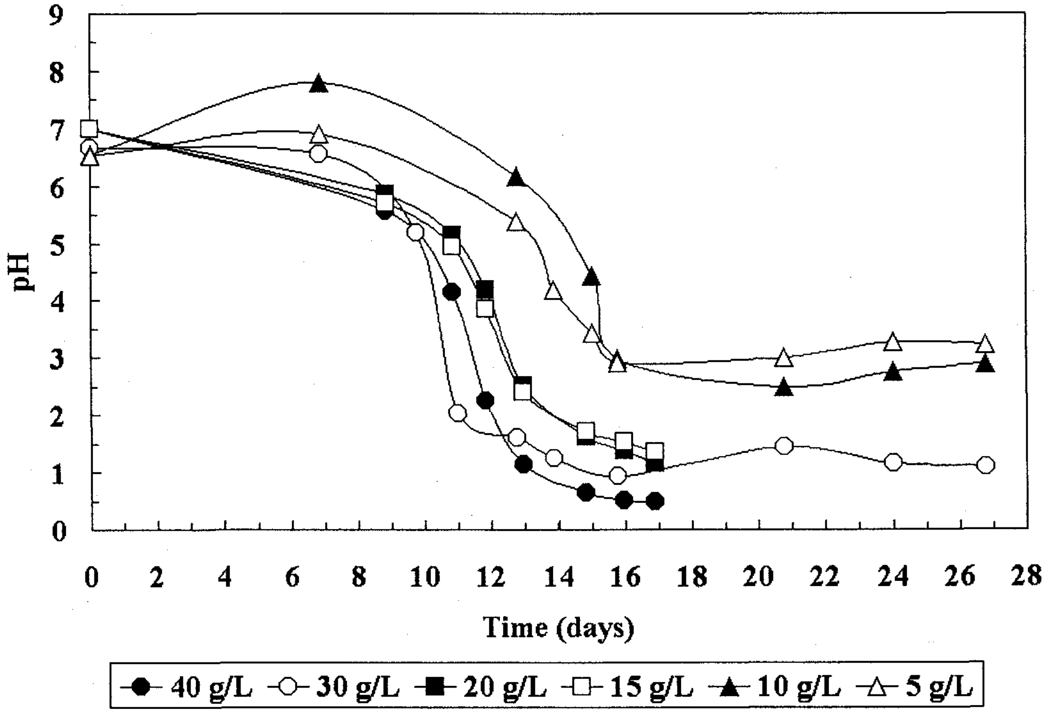

Figure 7.1 **Variation of sludge pH during bioleaching of tannery sludge using different sulphur concentrations**

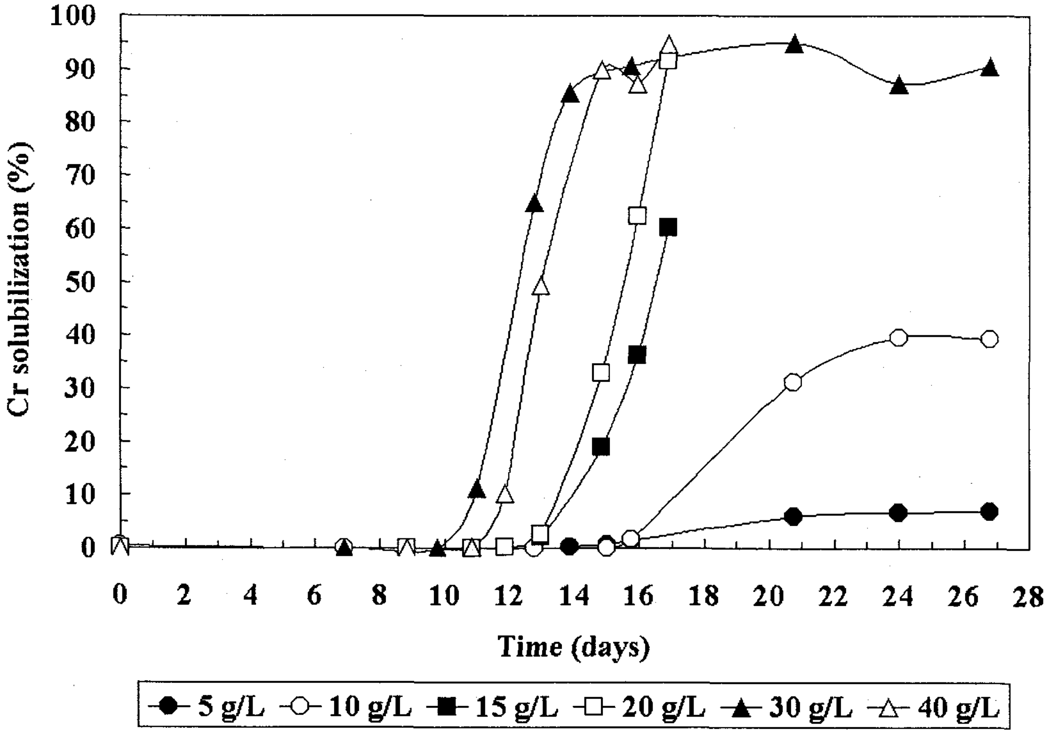

Figure 7.2 **Variation of Cr(III) leaching efficiency during bioleaching of tannery sludge**

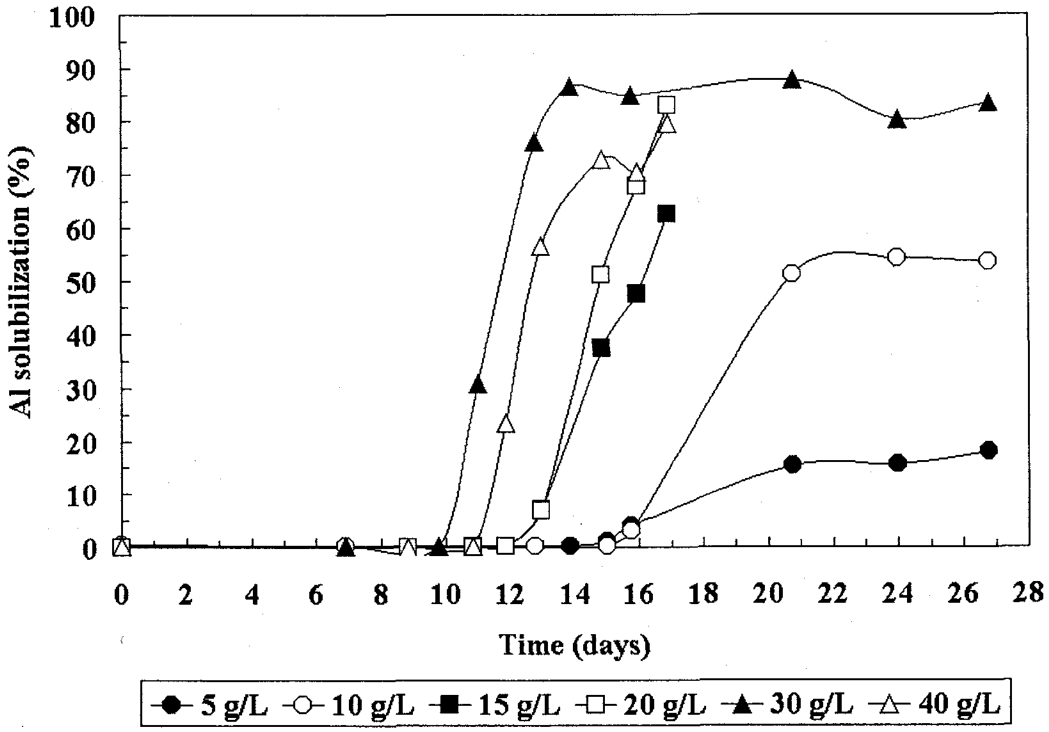

Figure 7.3 **Variation of Al leaching efficiency during bioleaching of tannery sludge**

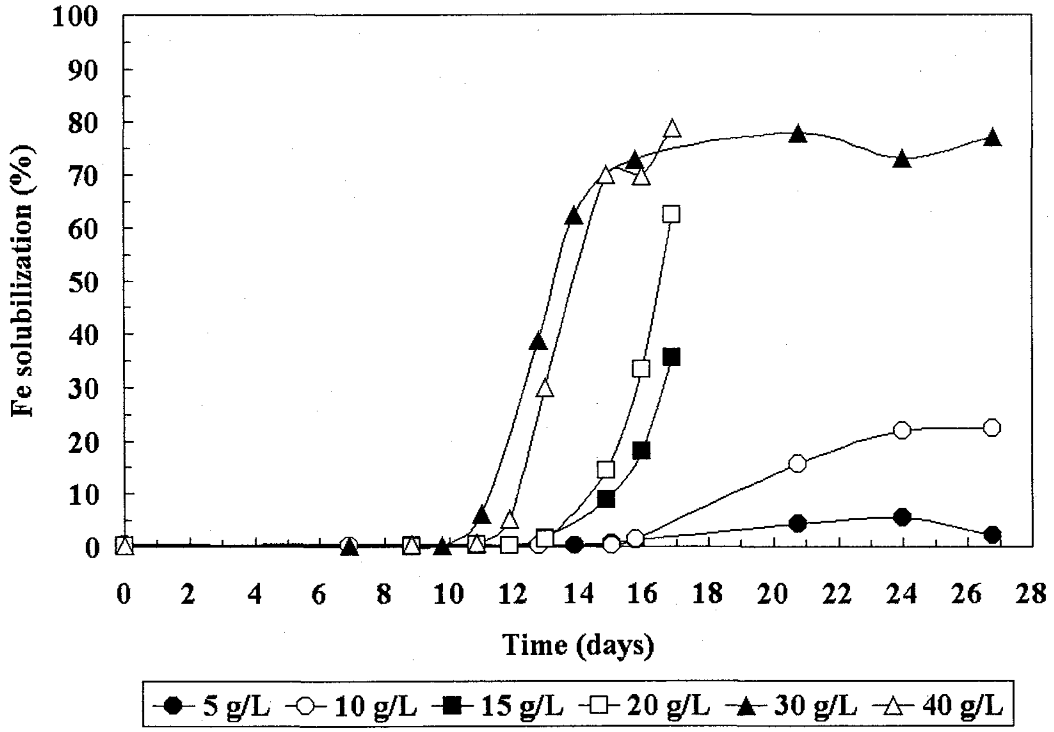

Figure 7.4 Variation of Fe leaching efficiency during bioleaching of tannery sludge

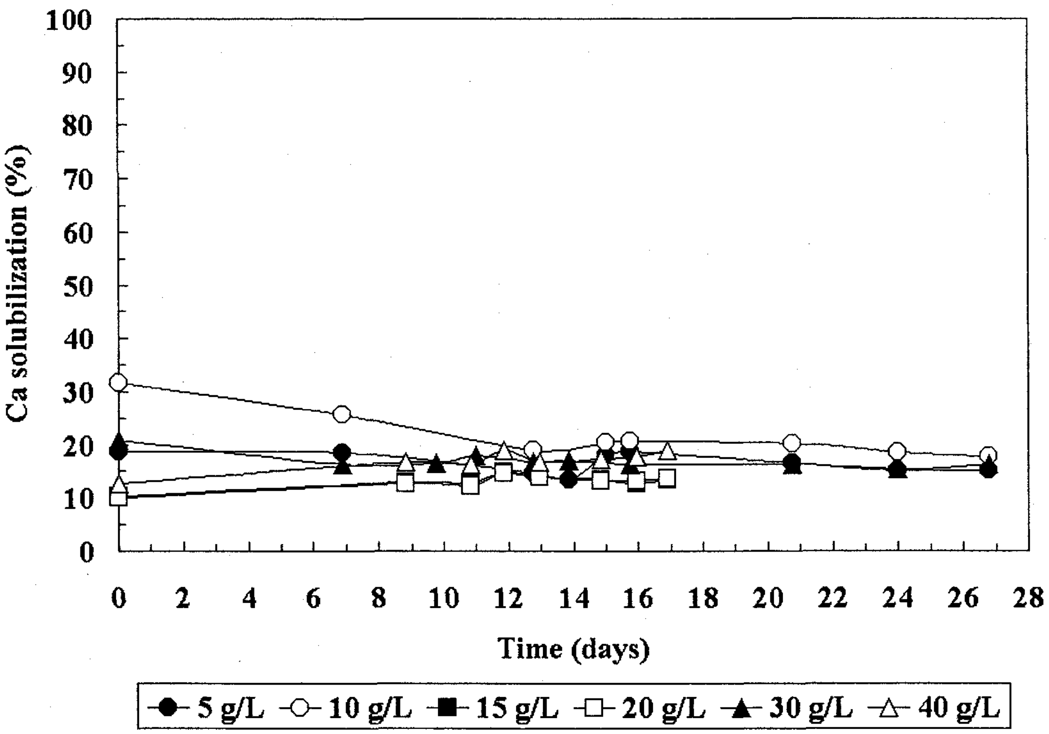

Figure 7.5 **Variation of Ca leaching efficiency during bioleaching of tannery sludge**

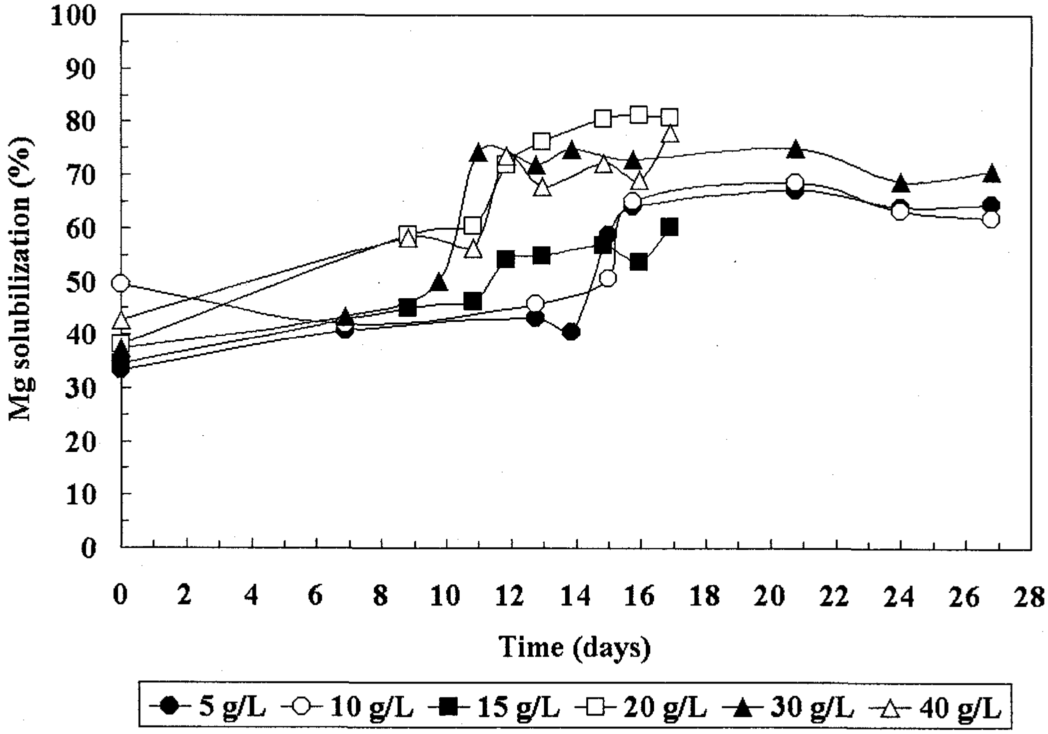

Figure 7.6 **Variation of Mg leaching efficiency during bioleaching of tannery sludge**

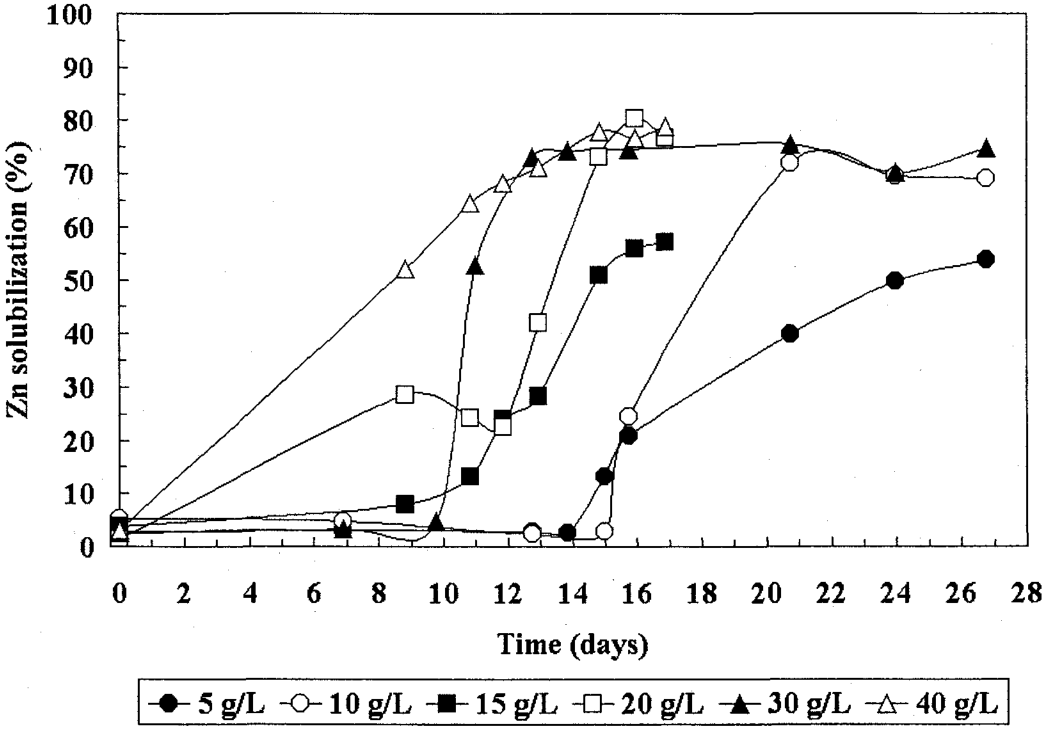

Figure 7.7 Variation of Zn leaching efficiency during bioleaching of tannery sludge

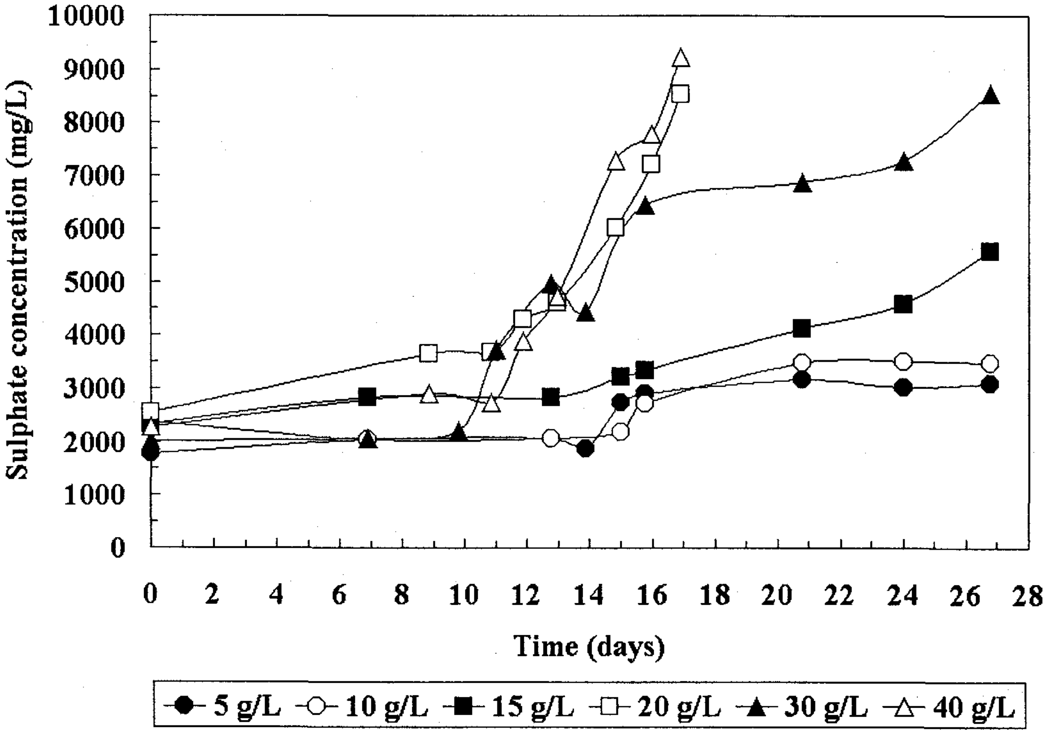

Figure 7.8 Variation of sulphate concentration with pH during bioleaching of tannery sludge

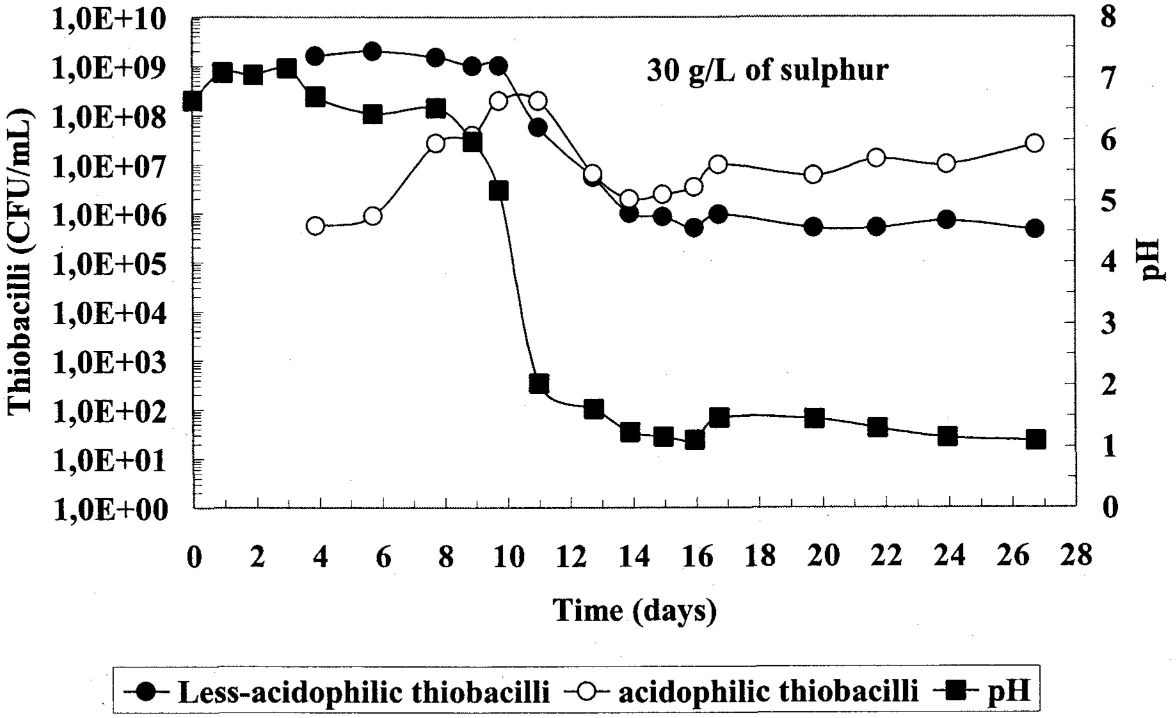

Figure 7.9 Variation of sulphur-oxidizing bacteria (less-acidophilic and acidophilic thiobacilli) during bioleaching of tannery sludge

Annexe

Données des figures

Fig 2.1

Solides	pH	Vol d'acide/mL	Poids d'acide/g	Kg acide / ton boues	
20g/L	10	0	0	0	
	6,13	0,5	0,4438	147,736	4,99543
	2,61	2	1,7752	590,945	6,38172
	1,75	2,5	2,219	738,682	6,60487
	1,39	3	2,6628	886,418	6,78719
	1,18	3,5	3,1066	1034,15	6,94134
	1,03	4	3,5504	1181,89	7,07487
	0,71	5,5	4,8818	1625,1	7,39332
	0,45	7,5	6,657	2216,05	7,70348
	0,41	8,5	7,5446	2511,52	7,82864
40g/L	9,83	0	0	0	
	2,87	3	2,6628	443,357	6,09437
	1,76	4,45	3,94982	657,646	6,48867
	1,07	6,45	5,72502	953,217	6,85984
	0,64	10,45	9,27542	1544,36	7,34236
	0,44	14	12,4264	2069	7,63482
	0,4	15	13,314	2216,78	7,70381
60g/L	9,88	0	0	0	
	6,27	2	1,7752	197,266	5,28455
	3,44	5,95	5,28122	586,867	6,3748
	2,1	6,95	6,16882	685,501	6,53015
	1,45	7,95	7,05642	784,134	6,66458
	1,22	8,95	7,94402	882,767	6,78306
	0,87	10,95	9,71922	1080,03	6,98475
	0,39	18,95	16,82	1869,1	7,53321
80g/L	9,46	0	0	0	
	5,76	3	2,6628	231,548	5,44479
	3,37	7,9	7,01204	609,743	6,41304
	1,07	11,85	10,5181	914,614	6,8185
	0,72	14,8	13,1365	1142,3	7,0408
	0,57	18,75	16,6425	1447,17	7,27737
	0,48	20,5	18,1958	1582,24	7,3666
	0,42	22	19,5272	1698,02	7,43722
	0,4	23	20,4148	1775,2	7,48167
100g/L	9,9	0	0	0	
	6,57	3	2,6628	177,52	5,17908
	3,68	9	7,9884	532,56	6,2777
	2,58	11	9,7636	650,907	6,47837
	1,8	13	11,5388	769,253	6,64542
	1,01	17	15,0892	1005,95	6,91368
	0,59	24	21,3024	1420,16	7,25852
	0,48	25	22,19	1479,33	7,29935
	0,43	30	26,628	1775,2	7,48167
	0,4	32	28,4032	1893,55	7,54621

Fig2.2

Solides 78.5 (g/L)		Cr	Al	Fe	Ca	Mg	Zn
Time/min	Time/h	C/100					
10	0,16666	54,52	5,206	1,143	5,073	26,35	0,076
20	0,33333	68,03	6,025	1,355	4,877	30,16	0,091
30	0,5	72,8	6,506	1,502	5,003	32,11	0,101
63	1,05	82,88	7,299	1,666	5,129	34,57	0,11
123	2,05	94,8	8,379	1,993	5,493	40,58	0,136
183	3,05	93,72	8,472	1,953	5,144	40,43	0,137
363	6,05	93,5	8,256	1,998	4,767	39,28	0,126
1440	24	93,47	8,076	2,043	4,492	39,05	0,125
2947	49,1166	94,75	8,156	2,134	4,303	39,94	0,128
4371	72,85	96,17	8,203	2,125	4,092	39,3	0,126
5742	95,7	95,79	8,266	2,151	4,151	40,45	0,13
7250	120,833	83,87	7,055	1,916	3,553	34,78	0,116

Fig 2.3

Solides 78.5 (g/L)		Cr	Al	Fe	Ca	Mg	Zn
Time/min	Time/h	C/100					
10	0,166	48,11	5,126	0,984	4,71	26,8	0,071
25	0,416	68,58	6,458	1,409	4,423	32,71	0,094
39	0,65	75,3	7,05	1,581	4,317	35,63	0,103
60	1	79,53	7,479	1,636	4,245	37,47	0,111
120	2	82,01	7,709	1,724	4,131	38,56	0,116
180	3	83,16	7,815	1,772	4,092	38,76	0,116
343	5,7166	86,75	8,399	1,893	4,102	41,33	0,123
1440	24	83,92	7,987	1,809	3,798	39,64	0,115
2917	48,616	84,1	8,024	1,817	3,593	39,61	0,117
4340	72,333	88,75	8,414	1,919	3,804	41,49	0,124
5712	95,2	88,07	8,559	1,924	3,856	41,8	0,125
7220	120,333	91,03	9,081	2,041	3,894	44,72	0,13

Fig 2.4 to Fig. 2.6

pH=1.3	19,6	39,2	58,9	78,5	100	140	Solides(g/L)
Cr	86	83	83	80	66	58	
Al	60	70	80	88	65	64	
Fe	55	59	60	60	59	58	
Ca	35	20	14	10	6	4	
Mg	72	72	74	72	66	62	
Zn	57	70	65	65	51	50	
P	29,88	34,02	35,79	35,24	18,21	10,41	
Na	93,56	78,19	86,41	84,4	66,27	73,93	
K	61,07	48,99	42,77	39,65	36,12	32,44	
pH=2.0	19,6	39,2	58,9	78,5	100		
Cr	81	83	76	77	64		
Al	58	69	76	78	57		
Fe	54	56	59	60	56		
Ca	39	16	12	10	6		
Mg	73	74	73	74	65		
Zn	57	67	61	63	51		
pH=3.0	19,6	39,2	58,9	78,5	100	140	
Cr	71	75	74	72	62	56	
Al	55	65	67	81	62	57	
Fe	43	50	55	56	56	49	
Ca	35	15	10	10	6	4	
Mg	68	70	71	74	68	64	
Zn	44	61	59	60	53	48	
P	20,02	24,4	25,13	26,56	20,46	16,63	
Na	84,25	82,93	80,61	81,92	63,89	72,74	
K	60,98	39,21	37,13	37,97	33,31	33,47	

Fig 3.1

				pH=1.3			
Solid (g/L)	0	19,6	39,2	58,9	78,5	100	140
I	0	0,351	0,684	1,062	1,368	1,551	2,094
$Cr(OH)_3$	-37,4	-35,8	-35,92	-36,27	-36,63	-36,86	-37,62
$CrPO_4$	-31,07	-30	-30,08	-30,31	-30,55	-30,71	-31,22
$Fe(OH)_3$	2,5	3,3	3,24	3,07	2,89	2,77	2,39
$FePO_4$	-35,65	-34,05	-34,17	-34,52	-34,88	-35,11	-35,87
FeOOH	0,5	1,3	1,24	1,07	0,89	0,77	0,39
$AlPO_4$	-30,52	-28,92	-29,04	-29,39	-29,75	-29,98	-30,74

Fig 3.2

				pH=3.0			
Solid (g/L)	0	19,6	39,2	58,9	78,5	100	140
I	0	0,304	0,631	0,938	1,257	1,454	2,093
$Cr(OH)_3$	-37,4	-35,81	-35,88	-36,14	-36,49	-36,73	-37,62
$CrPO_4$	-31,07	-30,01	-30,05	-30,23	-30,46	-30,63	-31,21
$Fe(OH)_3$	2,5	3,29	3,26	3,13	2,95	2,83	2,39
$FePO_4$	-35,65	-34,06	-34,13	-34,39	-34,74	-34,99	-35,87
FeOOH	0,5	1,29	1,26	1,13	0,95	0,83	0,39
$AlPO_4$	-30,52	-28,93	-29	-29,25	-29,61	-29,86	-30,74

Fig 3.3

		8	PH=1.3			
Solid (g/L)	19,6	39,2	58,9	78,5	100	140
$Cr(OH)_3$	-3,64016	-3,2204	-2,68403	-2,21824	-1,9431	-1,05552
$CrPO_4$	-2,13077	-1,34679	-0,63827	-0,09259	0,210853	1,586925
$Fe(OH)_3$	-2,57187	-2,17718	-1,77211	-1,48413	-1,25964	-0,74715
$FePO_4$	0,082785	0,936695	1,811662	2,478566	2,924279	4,559524
FeOOH	-0,56384	-0,16749	0,243038	0,538825	0,767082	1,320977
$AlPO_4$	-4,1549	-3,27003	-2,37161	-1,66756	-1,36351	0,3638
$CaSO_4$	-0,14691	0,319938	0,473925	0,283979	0,067443	0,122871

Fig 3.4

			pH=3.0			
Solid (g/L)	19,6	39,2	58,9	78,5	100	140
$Cr(OH)_3$	1,294246	1,677151	2,034227	2,33967	2,494071	2,795129
$CrPO_4$	2,180671	2,961731	3,52047	4,029465	4,233478	4,927375
$Fe(OH)_3$	2,109173	2,507028	2,773296	2,951532	3,101059	3,240799
$FePO_4$	4,048791	4,884801	5,491653	6,009189	6,261784	6,791031
FeOOH	4,440421	4,857103	5,204641	5,513895	5,766602	6,343912
$AlPO_4$	0,190248	1,048286	1,711048	2,432649	2,668386	3,657152
$CaSO_4$	-0,44009	0,11227	0,192289	0,110253	-0,08991	0,067815

Fig 3.5 to 3.6

			9 PH=1.3			
Solid (g/L)	19,6	39,2	58,9	78,5	100	140
Cr (mg/L)	2383	4799	7368	9350	10260	13912
Al	142	331,3	593,5	825,6	844,8	1285,2
Fe	41,4	90	153,4	199,8	258,4	387,6
Ca	562,9	588,9	585,4	565,5	514,8	539,6
Mg	913	1848	2961	3928	5244	6672
Zn	2,7	7	9,5	12,6	15,2	20
PO_4^{3-}	7,36	17,41	28,32	36,77	25,28	20,92
SO_4^{2-}	518,4	873,6	1497,6	2112	929,28	1612,8
Cl^-	6,4	11,15	10,3	13,88	10,16	9,02
Na	458	795	1359	1750	1828	2952
K	1,2	2	2,7	3,3	4	4,2
			pH=3.0			
Solid (g/L)	19,6	39,2	58,9	78,5	100	140
Cr	2003	4303	6446	8316	9564	13796
Al	127,5	311,1	486,4	781,5	798,8	1161,2
Fe	33,3	79,6	130,9	177,2	238,8	330,4
Ca	516,8	566,7	446,9	491	504,4	527
Mg	905	1811	2820	3876	4968	7080
Zn	2,1	5,7	8,7	11,6	14	20
PO_4^{3-}	4,94	12,48	19,52	27,18	27,72	34,88
SO_4^{2-}	120,96	230,4	348,48	460,8	164,16	238,08
Cl^-	9,57	11,93	13,8	14,47	9,06	9,07
Na	413	843	1244	1666	1720	3032
K	1,2	1,6	2,3	3,1	3,6	4,6

Fig. 4.1

pH	Al	Ca	Cr	Fe	Mg	Zn
1,01	0	0	0	0	0	0
1,53	6,57	2,88	2,64	3,20	5,62	0,00
2,15	10,10	5,75	4,90	4,80	6,66	0,00
2,37	10,35	5,43	4,34	5,60	6,92	0,00
2,61	11,87	7,67	6,50	8,00	9,11	0,00
3,07	15,15	9,27	8,41	8,80	10,41	0,00
4	35,19	32,52	29,56	22,83	27,25	20,00
4,17	35,82	34,30	30,50	25,10	29,23	26,75
4,4	50,08	46,74	43,16	38,76	42,31	35,41
4,59	54,33	44,21	44,60	42,12	39,57	41,35
6,48	99,97	46,34	99,83	99,93	45,60	98,88
7,44	100,00	57,99	99,97	99,96	51,56	98,96
8,05	100,00	71,57	99,99	100,00	64,20	99,09
9,97	100,00	95,69	99,98	99,98	92,49	99,18
11,21	100,00	99,49	99,99	99,99	99,80	99,64
12,27	99,88	99,94	99,98	99,94	99,98	99,82
12,59	99,94	100,00	99,97	100,00	100,00	99,73

Fig. 4.2

pH	Al	Ca	Cr	Fe	Mg	Zn
1,67	0,00	0,00	0,00	0,00	0,00	0,00
2,63	8,41	5,69	6,07	6,45	7,00	6,52
3,36	14,63	10,08	10,68	11,66	12,34	12,41
3,84	19,02	12,85	13,72	14,57	15,82	14,74
4,2	22,17	14,99	15,99	16,99	18,44	17,18
4,44	27,65	19,95	20,63	21,56	22,79	22,68
4,67	42,56	20,88	28,64	31,53	24,33	25,11
4,83	72,92	22,61	37,32	52,18	26,62	33,19
5,42	99,67	27,59	82,34	99,75	26,47	73,77
6,44	99,94	29,58	99,21	99,75	27,28	99,01
7,46	99,92	33,14	99,88	99,75	28,41	98,52
8,01	99,93	50,30	99,95	99,90	33,04	98,76

Fig 4.3

pH	Al	Ca	Cr	Fe	Mg	Zn
1,79	0,00	0,00	0,00	0,00	0,00	0,00
2,2	10,45	6,70	2,83	4,23	10,48	0,00
3,36	15,00	13,97	6,64	11,27	20,41	0,00
4,57	35,45	13,41	13,85	7,04	18,44	20,00
4,68	50,00	16,20	22,68	29,58	19,94	20,00
4,72	65,45	17,32	29,47	36,62	24,67	20,00
4,87	79,55	14,53	39,85	40,85	19,31	20,00
5,3	99,55	24,30	71,08	93,66	30,38	70,00
6,11	100,00	28,49	97,62	100,00	30,97	95,20
7,05	100,00	32,96	99,79	100,00	32,86	98,80
8	100,00	37,43	99,97	100,00	34,44	99,60
10,81	100,00	98,93	99,99	100,00	98,61	100,00
11,94	99,88	100,00	99,98	100,00	100,00	100,00

Fig 4.4

pH	Al	Ca	Cr	Fe	Mg	Zn
1,72	0,00	0,00	0,00	0,00	0,00	0,00
4,13	29,15	19,35	23,39	24,38	24,86	11,95
4,59	47,46	20,20	29,17	28,65	23,89	19,94
4,78	71,94	11,02	36,75	31,14	13,81	18,19
6,5	99,66	21,81	96,97	99,67	22,48	96,61
7,5	99,93	26,92	99,69	99,75	30,27	96,42
8	100,00	35,02	99,85	99,93	30,40	99,73

Fig 4.5

pH	Al/Cr	Fe/Cr
4	1,199	1,025
4,17	1,178	1,071
4,4	1,167	1,039
4,59	1,237	1,079
4,2	1,386	1,063
4,44	1,340	1,045
4,67	1,486	1,101
4,83	1,934	1,384
4,57	2,560	1,467
4,68	2,205	1,316
4,72	2,221	1,243
4,87	1,996	1,025
4,13	1,895	1,585
4,59	2,313	1,325
4,78	1,958	1,119

Fig 4.6

Time/min	Al	Ca	Cr	Fe	Mg	Zn
0	0	0	0	0	0	0
10	54,63	6,56	8,85	75,24	8,79	40
25	55,31	5,95	8,4	76,89	8,33	40
45	60,75	7,4	9,74	76,89	7,79	40
60	58,71	5,11	6,21	76,89	6,15	40
95	59,67	6,63	7,29	78,52	8,26	40
140	60,54	6,36	7,68	78,52	7,85	40

Fig 4.7

pH	Al	Ca	Cr	Fe	Mg	Zn
1,99	58,13	5,49	6,40	95,24	6,79	0,00
2,26	80,63	3,05	6,15	92,06	6,07	20,00
3,13	78,75	4,27	8,36	90,48	6,61	80,00
3,5	78,13	1,83	7,60	90,48	4,20	80,00
4,16	81,85	1,83	10,03	88,79	5,40	68,05

Fig 4.8

Cupferron/(Al+Fe+Zn)	Al	Ca	Cr	Fe	Mg	Zn
1,34	36,58	4,56	2,93	63,79	2,76	8,29
2	64,03	4,17	3,65	80,81	1,73	14,78
2,78	67,44	5,83	7,39	82,59	3,87	57,15
4,05	81,85	1,83	10,03	88,79	5,40	68,05

Fig 6.1

Sample	NC-1	NC-2	NC-3	NC-4	NC-5	control
Solid (g/L)	13	20	30	40	60	40
Days	pH	pH	pH	pH	pH	pH
0	6,1	6,24	6,33	6,55	6,61	6,05
2,07	5,92	6,77	7,26	7,5	7,54	7,28
3,83	5,02	6,29	6,8	7,08	6,86	7,3
4,98	2,29	5,61	6,09	6,31	6,38	7,28
5,92	1,46	4	5,8	6,01	6,09	7,13
6,83	1,29	1,83	5,2	5,89	5,99	7,06
9,79		1,22	1,95	2,89	4,21	7,02
11,83			1,61	2,18	2,88	7,02
12,83			1,39	1,96	2,64	7,01
13,81			1,44	1,83	2,43	7,03
16,79				1,29	2,01	
18,98				1,21	1,95	
19,02				1,18	1,9	
20,92				1,09	1,79	
23,79				1,43	1,6	
24,81					1,65	
25,81					1,57	

Fig 6.2 to 6.9

Solides	pH	Al	Ca	Cr	Fe	Mg	Zn	SO_4^{2-}
60 g/L	6,61	0,00	10,19	0,00	0,12	32,32	0,26	2450,30
	6,38	0,00	9,58	0,03	0,18	33,65	3,18	2397,20
	4,21	0,00	11,33	0,16	0,35	47,98	4,80	3212,80
	2,88	17,78	9,15	6,50	4,77	48,58	37,34	3645,60
	2,01	57,23	8,44	61,00	41,94	50,06	53,09	6542,20
	1,57	65,95	10,23	74,38	57,61	56,87	59,76	10087,40
	pH	Al	Ca	Cr	Fe	Mg	Zn	SO_4^{2-}
40 g/L	6,55	0,00	11,89	0,01	0,38	35,99	0,00	2016,70
	6,31	0,00	17,22	0,03	0,15	40,91	2,52	2014,70
	2,89	5,73	14,79	2,46	1,26	49,78	34,02	2330,20
	2,18	36,97	9,80	32,19	16,43	39,41	41,25	2841,00
	1,49	59,97	12,64	69,75	55,96	52,30	58,33	5869,09
	1,43	57,83	13,16	69,76	59,07	51,09	57,05	6876,20
	1,36	71,82	15,90	87,22	74,33	63,37	70,10	9418,20
	pH	Al	Ca	Cr	Fe	Mg	Zn	SO_4^{2-}
30 g/L	6,33	0,00	11,91	0,00	0,20	30,59	0,00	1466,20
	6,09	0,00	26,16	0,00	0,16	36,72	0,29	1819,70
	5,2	0,00	30,39	0,12	0,42	41,65	0,00	1985,94
	1,95	51,95	18,44	33,11	13,03	56,11	63,68	3211,60
	1,61	64,88	17,78	74,72	51,64	53,78	64,59	4891,40
	1,44	77,78	21,32	91,56	69,72	61,30	71,53	7675,80
	pH	Al	Ca	Cr	Fe	Mg	Zn	SO_4^{2-}
20 g/L	6,24	0,00	18,70	0,01	0,27	48,87	0,00	1576,70
	5,61	0,00	24,70	0,01	0,21	46,76	1,23	1330,90
	4	0,00	23,71	0,23	0,36	53,91	4,54	2051,70
	1,83	27,26	23,19	11,28	4,50	57,12	48,86	2026,00
	1,22	77,48	31,41	91,76	83,39	67,19	75,16	6730,20
	pH	Al	Ca	Cr	Fe	Mg	Zn	SO_4^{2-}
13 g/L	6,1	0,00	19,60	0,01	0,23	37,44	0,78	858,59
	5,02	0,31	36,65	0,30	0,52	48,01	4,13	1218,70
	2,29	8,59	32,36	4,15	1,31	54,00	47,76	1640,30
	1,46	51,92	34,75	28,44	14,22	58,13	64,60	2392,00
	1,29	74,44	42,59	91,54	76,10	63,00	74,98	3744,20

Fig. 7.1 to 7.8

Soufure (g/L)	Days	pH	Al	Ca	Cr	Fe	Mg	Zn
40	0	7	0,173	12,708	0,031	0,303	42,799	3,083
	8,84	5,57	0,093	16,732	0,099	0,402	58,253	51,920
	10,84	4,14	0,186	16,263	0,202	0,803	56,333	64,608
	11,84	2,26	23,451	18,879	10,279	5,193	73,584	68,260
	12,96	1,14	56,508	16,710	49,392	29,969	67,965	71,172
	14,84	0,65	73,004	17,330	89,961	70,040	72,064	77,957
	15,96	0,52	70,530	17,789	87,410	69,826	69,115	76,849
	16,9	0,48	79,508	18,985	94,697	78,863	77,986	78,912
20	0	7	0,037	10,085	0,030	0,205	38,206	1,356
	8,84	5,85	0,081	12,765	0,060	0,119	58,860	28,505
	10,84	5,14	0,089	12,162	0,039	0,557	60,487	24,152
	11,84	4,18	0,175	14,668	0,192	0,222	72,022	22,574
	12,96	2,51	7,061	13,948	2,587	1,554	76,147	42,051
	14,84	1,63	51,170	13,146	32,783	14,444	80,671	73,171
	15,96	1,39	67,777	13,161	62,263	33,387	81,339	80,374
	16,9	1,16	83,085	13,750	91,705	62,460	80,774	76,854
15	0	7	0,048	10,421	0,042	0,195	34,526	3,786
	8,84	5,71	0,110	12,976	0,068	0,228	45,177	7,991
	10,84	4,95	0,173	12,668	0,103	0,183	46,243	13,144
	11,84	3,86	0,223	14,947	0,239	0,235	54,134	23,983
	12,96	2,41	7,076	14,006	2,186	1,663	54,937	28,260
	14,84	1,71	37,435	13,523	18,845	8,870	56,735	50,731
	15,96	1,53	47,486	12,773	36,288	17,953	53,788	55,805
	16,9	1,37	62,587	13,541	60,254	35,518	60,218	57,075

Fig 7.1 to 7.8 continued

Soufure (g/L)	Days	pH	Al	Ca	Cr	Fe	Mg	Zn
30	0	6,65	0,207	20,965	0,035	0,138	37,387	2,561
	6,875	6,56	0,189	16,325	0,021	0,224	43,307	3,371
	9,771	5,18	0,305	16,626	0,036	0,268	50,068	4,783
	11	2,03	30,929	17,901	11,270	6,233	74,388	52,687
	12,77	1,61	76,246	16,895	64,959	38,955	72,004	73,234
	13,87	1,24	86,652	17,111	85,634	62,413	74,887	74,307
	15,771	0,93	84,842	16,307	90,669	72,971	72,942	74,616
	20,77	1,45	87,877	16,423	94,846	77,998	75,108	75,656
	24	1,15	80,431	15,371	87,401	73,257	68,714	70,182
	26,77	1,09	83,341	16,274	90,742	77,202	70,711	74,887
5	0	6,53	0,188	18,692	0,053	0,229	33,327	2,921
	6,875	6,9	0,190	18,565	0,022	0,173	40,746	3,202
	12,77	5,39	0,124	14,680	0,033	0,291	43,235	2,933
	13,87	4,19	0,261	13,537	0,190	0,345	40,534	2,560
	15	3,43	1,251	17,973	0,645	0,606	58,853	13,298
	15,771	2,92	4,186	18,646	1,437	1,209	64,094	20,932
	20,77	3,01	15,237	16,637	6,013	4,428	67,064	39,796
	24	3,27	15,635	15,085	6,691	5,546	63,916	49,561
	26,77	3,23	17,875	15,097	6,955	2,238	64,403	53,822
10	0	6,54	0,567	31,666	0,527	0,493	49,400	5,380
	6,875	7,79	0,284	25,749	0,032	0,196	41,893	4,706
	12,77	6,16	0,150	19,059	0,036	0,192	45,804	2,387
	15	4,44	0,201	20,358	0,106	0,275	50,705	2,784
	15,771	2,98	3,160	20,531	1,693	1,434	64,998	24,549
	20,77	2,49	51,052	20,256	31,162	15,555	68,533	71,904
	24	2,77	54,139	18,506	39,575	21,784	63,371	69,478
	26,77	2,89	53,524	17,838	39,268	22,301	61,831	69,158

Fig 7.9

Days	pH	CFU / yel(6,0)	CFU / yel(3,0)
0	6,65		
0,958	7,1		
1,916	7,06		
3	7,17		
3,896	6,71	1,6E+09	550000
5,729	6,43	2E+09	900000
7,75	6,52	1,5E+09	27500000
8,916	5,98	1E+09	40000000
9,75	5,18	1,01E+09	2E+08
11	2,03	58000000	2E+08
12,75	1,61	5500000	6500000
13,896	1,24	1000000	2000000
14,958	1,16	850000	2450000
15,958	1,11	500000	3500000
16,75	1,47	950000	10000000
19,75	1,45	500000	6000000
21,75	1,3	500000	12900000
23,958	1,15	700000	10000000
26,75	1,09	450000	25000000

REPROGRAPHIE DE LA REMISE FINALE DU MÉMOIRE OU DE LA THÈSE

Lors de la remise finale de mon mémoire ou de ma thèse, les photocopies ont été effectuées par :

l'étudiant(e) : ☒ *Les photocopies effectuées par l'étudiant(e) seront sous sa responsabilité.*

Shaobo Shen	Shaobo Shen
Nom	Signature

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Boursier ou non-boursier: Non boursier