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Leaching and recovery of molybdenum, nickel and cobalt from metals recycling plants mineral sludges

Mirjana Vemic

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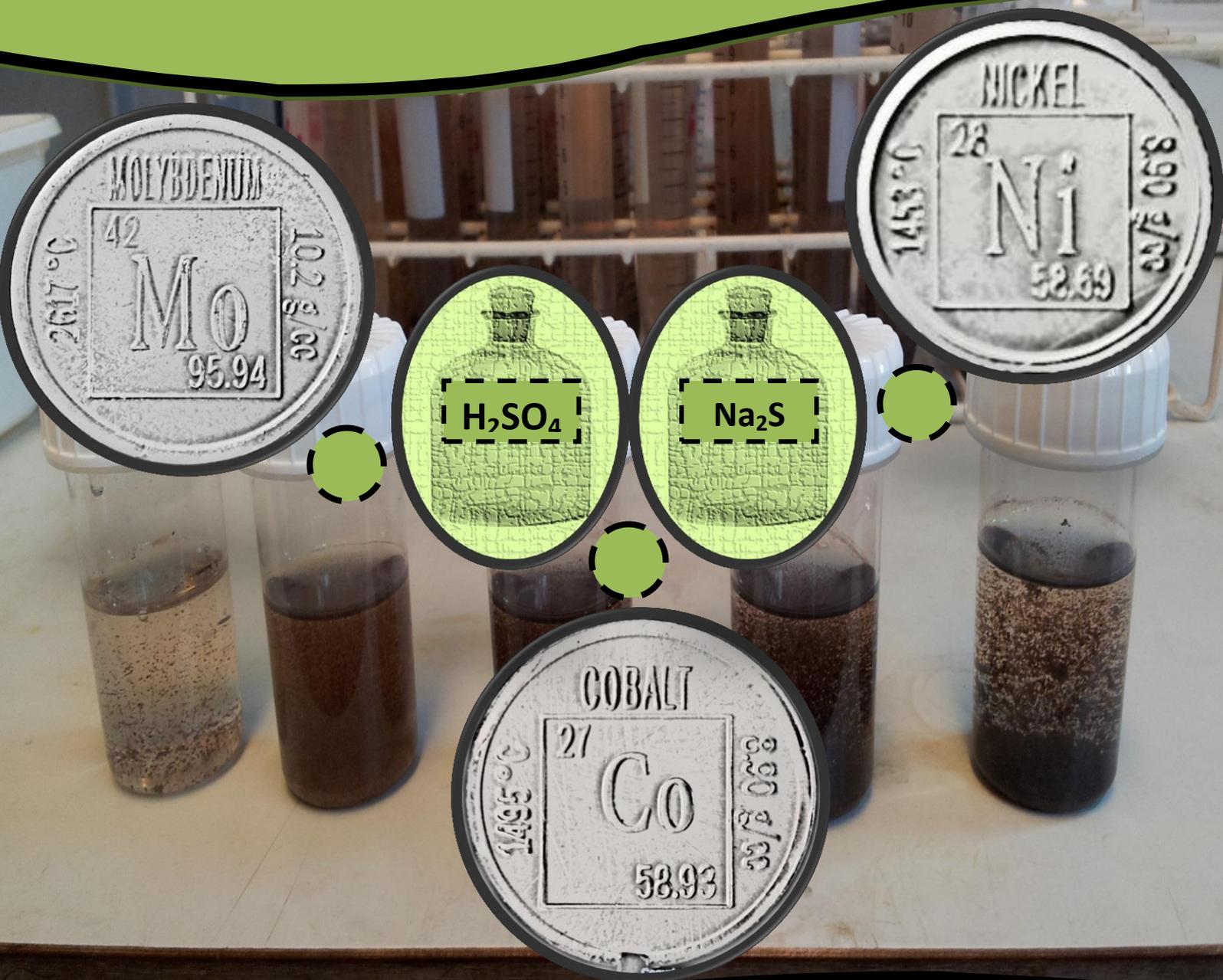
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Leaching and recovery of Mo, Ni and Co from metals recycling plants mineral sludges



Mirjana VEMIC

**Leaching and recovery of
Mo, Ni and Co from metals
recycling plants mineral
sludges**

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Spécialité : Science et Technique de l'Environnement



Dottore di Ricerca in Tecnologie Ambientali



Degree of Doctor in Environmental Technology

Thèse – Tesi di Dottorato – PhD thesis

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Leaching and recovery of Mo, Ni and Co from metals recycling plants mineral sludges

To be defended October 26th, 2015

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Summary

In view of the on-going depletion of the natural resources taking place worldwide, the high price, high demand and future shortage of the primary mineral resources for Mo, Ni and Co it is extremely important to implement metals recycling/recovery/reuse from semi-finished products, by-products, secondary materials and wastes, including hazardous waste (*i.e.* spent catalysts, mineral sludges). Furthermore, there is a need to utilize more efficient technologies to recover metals from wastes/secondary resources in order to minimize capital outlay, environmental impact and to respond to the metal increased demand.

Among the different secondary resources, spent catalysts and mineral sludges generated at the spent catalysts recycling plants could be a very good secondary resource, as they contain high concentrations of different metals (especially Mo, Ni and Co). Therefore, they should be viewed as a resource, not as a waste.

In our study we are dealing with the catalyst, metallic oxide and battery recycling plant mineral sludge. This type of material contains high concentrations of different metals. However, to the best of our knowledge, speciation, leaching and recovery of Mo, Ni and Co from this type of material were not investigated before.

Mineral sludge was minutely characterized where pH, Loss On Ignition (LOI), Toxicity Characteristic Leaching Procedure (TCLP), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS), Total Metal Content (TMC) and Sequential Extraction (SE) were performed.

Based on the mineral sludge characterization results the leaching rate and yields of Mo, Ni and Co from mineral sludge sample were quantified. Different leaching reagents (stand-alone acids (nitric, sulfuric and hydrochloric) and acid mixtures (*aqua regia* (nitric + hydrochloric (1:3)), nitric + sulfuric (1:1) and nitric + sulfuric + hydrochloric (2:1:1)) were investigated at changing operational parameters (solid to liquid ratio, leaching time and temperature), in order to understand the leaching features and select the suitable leaching reagent which achieves the highest metal leaching yields. Sulfuric acid (H_2SO_4) was found to be the leachant with the highest metal leaching potential. The optimal leaching conditions were a three stage successive leaching, temperature 80°C , leaching time 2 h and S/L ratio 0.25 g L^{-1} . Under these conditions, the leaching yields from our mineral sludge sample reached 85.5, 40.5 and 93.8% for Mo, Ni and Co, respectively.

Target metals recovery from synthetic and real acidic leachate of a mineral sludge from a metal recycling was investigated with Na_2S solution. At first, the operational parameters (metal sulfide ratio (M/S) 0.1 - 1, agitation speed 0 - 100 rpm, contact time 15 - 120 min, and pH 1 - 5) were optimized in batch conditions on synthetic metal leachate (0.5 M HNO_3 , Mo = 101.6 mg L^{-1} , Ni = 70.8 mg L^{-1} , Co = 27.1 mg L^{-1}) with a $0.1 \text{ M Na}_2\text{S}$ solution. Additionally, recovery of the target metals was theoretically simulated with a chemical equilibrium model (Visual MINTEQ 3.0). The optimized Na_2S precipitation of metals from the synthetic metal leachate resulted in the potential selective recovery of Mo as oxide at pH 1 (98% by modelling, 95.1% experimental), after simultaneous precipitation of Ni and Co as sulfide at pH 4 (100% by modelling, 98% experimental). Metal precipitation from the real acidic leachate ($18 \text{ M H}_2\text{SO}_4$, Mo = $10,160 \text{ mg L}^{-1}$, Ni = $7,082 \text{ mg L}^{-1}$, Co = $2,711 \text{ mg L}^{-1}$) of mineral sludge was performed with $1 \text{ M Na}_2\text{S}$, and resulted in a maximal Mo recovery at pH 2 (50.3%), while maximal recoveries of Ni and Co were at pH 4 (56.0 and 59.7%, respectively). Real acidic leachate gave a lower metals recovery

efficiency, which can be attributed to various factors such as changes in the pH, nature of leachant, co-precipitation of Zn and competition for S^{2-} ions.

Résumé

Compte tenu du prix élevé, de la forte demande et de la pénurie future des ressources minérales de métaux critiques ou précieux, il est extrêmement important de mettre en œuvre des méthodes de recyclage de ces métaux par la récupération et la réutilisation de matériaux secondaires et des déchets, y compris les déchets dangereux (c'est à dire des catalyseurs pétrochimiques usagés ou boues minérales). En outre, il est nécessaire d'utiliser des technologies plus efficaces pour récupérer des métaux à partir de ces ressources secondaires afin de minimiser les investissements, l'impact environnemental et également répondre à l'augmentation de la demande d'éléments comme le nickel (Ni), le cobalt (Co) et le molybdène (Mo).

Parmi les différentes ressources secondaires, les catalyseurs usagés et les boues minérales générés par les usines de recyclage métallurgique peuvent être une très bonne ressource secondaire, parce qu'ils contiennent des concentrations élevées de différents métaux (en particulier Mo, Ni et Co). Par conséquent, ils doivent être considérés comme une ressource et non comme un déchet.

Dans notre étude, nous nous sommes intéressés à des boues métallurgiques provenant d'un site traitant des catalyseurs pétrochimiques, des oxydes métalliques et réalisant le recyclage des batteries et piles. Ce type de matériau contient de fortes concentrations de métaux différents. Cependant, l'étude de la minéralogie, de la lixiviation et de la récupération d'éléments critiques ou précieux à partir de ce type de matériel n'a pas été réalisée jusqu'à maintenant.

Différentes boues minérales ont été minutieusement caractérisées pour déterminer leur pH, la perte au feu (LOI), leur toxicité déterminée par une procédure de lixiviation (type TCLP), la diffraction des rayons X (XRD), la microscopie électronique à balayage (SEM) avec dispersion d'énergie des rayons X spectroscopie (EDS) et leur composition élémentaire totale (TMC). Des extractions séquentielles (SE) ont également été réalisées pour estimer la mobilité potentielle des éléments critiques ou précieux en fonction des conditions physico-chimiques (pH et potentiel d'oxydo-réduction).

Sur la base des résultats de caractérisations physico-chimiques et minéralogiques des boues minérales, les rendements d'extraction de Mo, Ni et Co à partir de l'échantillon de boue minérale ont été quantifiés. Différents réactifs de lixiviation (acide simple (nitrique, sulfurique ou chlorhydrique) et les mélanges d'acides (eau régale (nitrique + chlorhydrique (1:3)), nitrique + sulfurique (1:1) et nitrique + sulfurique + chlorhydrique (2:1:1)) ont été étudiés. Il s'agissait également de faire varier les paramètres de fonctionnement (ratio solide / liquide (S/L), le temps de lixiviation et la température), afin de comprendre les caractéristiques de lixiviation et sélectionner le réactif de lixiviation approprié qui permet d'atteindre les plus hauts rendements de lixiviation de éléments cibles de notre étude. L'acide sulfurique (H_2SO_4) a été trouvé comme le produit de lixiviation avec le potentiel de lixiviation des métaux les plus élevés. Les conditions de lixiviation optimales étaient une lixiviation comportant trois étapes successives, à une température de $80^\circ C$, pendant 2 h, et à un ratio S/L de 0.25 g L^{-1} . Dans ces conditions, les rendements de lixiviation à partir de notre échantillon de boue minérale a atteint 85.5, 40.5 et 93.8% pour Mo, Ni et Co, respectivement.

La récupération des éléments cibles (Ni, Co et Mo) à partir de lixiviats acides synthétique ou de lixiviats acides réels obtenus à partir d'une boue minérale a été étudiée avec une solution de Na_2S . Dans un premier temps, les paramètres opératoires (ratio molaire métaux / sulfure (M/S) variant de 0.1 à 1, la vitesse d'agitation de 0 à 100 tours par minute, le temps de contact de 15 à 120 min,

et un pH variant de 1 à 5) ont été optimisées dans des conditions de traitement en mode batch sur le lixiviat synthétique (0.5 M HNO_3 , $\text{Mo} = 101.6 \text{ mg L}^{-1}$, $\text{Ni} = 70.8 \text{ mg L}^{-1}$, $\text{Co} = 27.1 \text{ mg L}^{-1}$) avec une solution 0.1 M de Na_2S . De plus, la récupération des métaux cibles a été théoriquement simulée avec un modèle d'équilibre chimique (Visual MINTEQ 3.0). La précipitation Na_2S optimisée de métaux à partir de la solution de lixiviation de métal synthétique a abouti à la récupération sélective potentiel de Mo sous forme d'oxyde à pH 1 (98% par modélisation, 95.1% expérimental), après précipitation simultanée de Ni et Co sous forme de sulfure à un pH de 4 (100% par la modélisation, 98% expérimentale). Cependant la précipitation des métaux à partir de lixiviats acides obtenus à partir des boues minérales ($18 \text{ M H}_2\text{SO}_4$, $\text{Mo} = 10,160 \text{ mg L}^{-1}$, $\text{Ni} = 7,082 \text{ mg L}^{-1}$, $\text{Co} = 2,711 \text{ mg L}^{-1}$) a été réalisée avec $1 \text{ M Na}_2\text{S}$, et a permis une récupération maximale de Mo à pH 2 (50.3%), tandis que les recouvrements maximales de Ni et Co a été accompli a pH 4 (56.0 et 59.7%, respectivement). Les moins bons rendements de récupération des métaux obtenu pour les lixiviats acides générés à partir des boues minérales peut être attribué à divers facteurs tels que: i) les changements pH, ii) la nature de lixiviation, et iii) co-précipitation de Zn et la compétition en cations pour la formation de complexes avec les ions sulfures.

Sommario

Riguardo dell'esaurimento in corso delle risorse naturali che si svolgono a livello mondiale, il prezzo alto, richiesta alta e la scarsità futura delle risorse minerali primarie per Mo, Ni e Co è estremamente importante per implementare il riciclo/recupero/riutilizzo dei metalli da prodotti semi-finiti, sottoprodotti, materiali secondari e scarti, incluso i rifiuti pericolosi (cioè catalizzatori esausti, fanghi minerali). Inoltre, ci sta un bisogno di utilizzare le tecnologie più efficienti per recuperare metalli da rifiuti/risorse secondarie per ridurre gli investimenti, impatto ambientale e rispondere alla richiesta alta per i metalli.

Tra le diverse risorse secondarie, i catalizzatori esausti e fanghi minerali generati agli impianti di riciclaggio dei catalizzatori esausti potrebbero essere una secondaria risorsa molto buona, come loro contengono concentrazioni alte di metalli diversi (soprattutto Mo, Ni e Co). Perciò, loro dovrebbero essere visti come una risorsa, non come un rifiuto.

Nel nostro studio noi stiamo trattando con il catalizzatore, ossidi metallici e fanghi minerali generati agli impianti di riciclaggio delle batterie. Questo tipo di materiale contiene concentrazioni alte di metalli diversi. Comunque, al meglio delle nostre conoscenze attuali speciazione, lisciviazione e recupero di Mo, Ni e Co, da questo tipo di materiale non fu investigato prima.

Fango minerale è stato minutamente caratterizzato cui pH, Perdita alla combustione (LOI), Caratteristica di Tossicità Leaching Procedura (TCLP), Diffrazione di raggi X (XRD), Microscopia elettronica a scansione (SEM) con dispersione di energia di raggio X spectroscopy (EDS), Contenuto del Metallo Totale (TMC) e di Estrazione Sequenziale (SE) sono stati eseguiti.

Sulla base dei risultati di caratterizzazione dei fanghi minerali il tasso di lisciviazione e le rese di Mo, Ni e Co dal campione di fango minerale sono stati quantificati. Diverse reagenti lisciviazione (stand-alone (acidi nitrico, solforico e cloridrico) e miscele di acidi (acqua regia (nitrico + cloridrico (1:3)), nitrico + solforico (1:1) e nitrico + solforico + cloridrico (2:1:1)) sono stati indagati a modificare i parametri operativi (il rapporto solido-liquido, tempo di lisciviazione e temperatura), per capire le caratteristiche di lisciviazione e selezionare il reagente lisciviazione adatto di raggiungere i massimi rendimenti di lisciviazione metallo. Acido solforico (H_2SO_4) è stato trovato essere il leachant con il più alto potenziale lisciviazione metallo. Le condizioni ottimali lisciviazione erano una lisciviazione a tre stadi successivi, temperatura di $80^\circ C$, tempo di lisciviazione 2 ore e un rapporto S/L di 0.25 g L^{-1} . In tali condizioni, le rese lisciviazione dal nostro campione di fango minerale hanno raggiunto 85.5, 40.5 e 93.8% per Mo, Ni e Co, rispettivamente.

Recupero dei metalli da percolato sintetico ed quello acido vero di un fango minerale da un riciclaggio di metalli è stato studiato con una soluzione Na_2S . All'inizio i parametri operativi (rapporto solfuro metallico (M/S) 0.1 - 1, con velocità di agitazione 0 - 100 rpm, il tempo di contatto 15-120 min, e pH 1 - 5) sono state ottimizzate in condizioni di lotto sul percolato metallo sintetico (0.5 M HNO_3 , Mo = 101.6 mg L^{-1} , Ni = 70.8 mg L^{-1} , Co = 27.1 mg L^{-1}) con una soluzione 0.1 M Na_2S . Inoltre, il recupero dei metalli bersaglio è stato teoricamente simulato con un modello di equilibrio chimico (Visual Minteq 3.0). La precipitazione di Na_2S ottimizzata dei metalli dal percolato di metallo sintetico portato nel potenziale recupero selettivo di Mo come ossido a pH 1 (98% calcolata mediante modellazione, 95.1% sperimentale), dopo precipitazione simultanea di Ni e Co come solfuro a pH 4 (100% calcolata mediante modellazione, 98%

sperimentale). La precipitazione del metallo dal percolato vero acido (18 M H_2SO_4 , Mo = 10,160 mg L^{-1} , Ni = 7,082 mg L^{-1} , Co = 2,711 mg L^{-1}) di fango minerale è stata eseguita con 1 M Na_2S , e ha portato un massimo recupero di Mo a pH 2 (50.3%), mentre i massimi recuperi di Ni e Co erano a pH 4 (56.0 e 59.7%, rispettivamente). Il percolato acido vero diede ad un'efficienza di ricupero di metalli più bassa, che può essere attribuita ai vari fattori come le variazioni del pH, la natura di dilavante, co-precipitazione di Zn e la competizione per S^{2-} ioni.

Samenvatting

In het licht van de huidige uitputting van de natuurlijke hulpbronnen die wereldwijd plaatsvindt, de hoge prijs, hoge vraag en toekomstige tekort aan primaire mineralen voor Mo, Ni en Co is het uiterst belangrijk om metalen te hergebruiken door middel van recycling/terugwinning/hergebruik van semi-afgewerkte producten, bijproducten, secundaire materialen en afval, met inbegrip van gevaarlijke afvalstoffen (dwz afgewerkte katalysatoren, mineraal slib). Verder is er behoefte aan efficiëntere technologieën te gebruiken om metalen uit afval/secundaire grondstoffen terug te winnen, milieu-impact te minimaliseren en om te reageren op de toegenomen vraag naar metalen.

De verschillende secundaire grondstoffen, afgewerkte katalysatoren en mineraal slibsoorten die vrijkomen kunnen een zeer goede secundaire hulpbron blijken te zijn, omdat ze hoge concentraties van verschillende metalen (vooral Mo, Ni en Co) bevatten. Daarom moeten ze worden beschouwd als een bron, niet als afval.

In ons onderzoek hebben we te maken met de katalysator, metaaloxide en uit batterij recycle voortgekomen mineraal slib. Dit type materiaal bevat hoge concentraties van verschillende metalen. Echter, naar ons weten, is het in kaart brengen, uitspoeling en terugwinning van dit soort materiaal niet eerder onderzocht.

Mineraal slib werd minutieus gekenmerkt wavoor pH, gloeiverlies (LOI), Toxiciteit uitloogprocedure voor (TCLP), X-ray diffractie (XRD), Scanning Electron Microscopy (SEM) met energie-dispersieve X-ray spectroscopy (EDS), Total Metal gehalte (TMC) en sequentiële extractie (SE) werden uitgevoerd.

Op basis van de resultaten van de karakterisering van het mineraal slib en van de uitloging ervan werden de opbrengsten van Mo, Ni en Co uit minerale slibmonsters gekwantificeerd. Verschillende uitlogings reagentia (stand-alone zuren (salpeterzuur, zwavelzuur en zoutzuur) en zure mengsels (koningswater (salpeter- + zoutzuur (1:3)), salpeterzuur + zwavelzuur (1:1) en salpeterzuur + zwavelzuur + zoutzuur (2:1:1)) werden onderzocht op verandering van operationele parameters (vaste naar vloeibare verhouding, uitlogings tijd en temperatuur), teneinde de uitlogings functies te verduidelijken en selecteert de geschikte uitloging reagens die de hoogste metaaluitloging opbrengst bereikt. Zwavelzuur (H_2SO_4) is de leachant die het beste metalen uitspoelt. De optimale uitlogings omstandigheden waren drie opeenvolgende uitlogingen, temperatuur 80°C , uitloging tijd 2 uur en S/L-verhouding 0.25 g L^{-1} . Onder deze omstandigheden was de opbrengst van de uitlogingen van onze minerale slibmonster 85.5, 40.5 en 93.8% voor Mo, Ni en Co, respectievelijk.

Target metalen terugwinning van synthetische en werkelijk zure percolaat van een mineraal slib met recycling van een metaal werd onderzocht met Na_2S oplossing. De operationele parameters (metaalsulfide verhouding (M / S) 0.1 - 1, roersnelheid 0 - 100 rpm, contacttijd 15 - 120 min, en pH 1 - 5), de batch omstandigheden van synthetische metalen percolaat (0.5 M HNO_3 , Mo = 101.6 mg L^{-1} , Ni = 70.8 mg L^{-1} , Co = 27.1 mg L^{-1}) werden uitgevoerd met een $0.1 \text{ M Na}_2\text{S}$ oplossing. Daarnaast werd de recovery van de doelgroep metalen theoretisch gesimuleerd met een chemisch evenwichts model (Visual Minteq 3.0). De geoptimaliseerde Na_2S precipitatie van metalen uit de synthetische metalen percolaat resulteerde in de potentiële selectieve terugwinning van Mo als oxide bij pH 1 (98% door modellering, 95.1% experimenteel) na gelijktijdige precipitatie van Ni en Co als sulfide bij pH 4 (100% door modellering, 98% experimenteel). Metalen precipitatie uit het echte zure percolaat ($18 \text{ M H}_2\text{SO}_4$, Mo = 10,160 mg

L^{-1} , Ni = 7,082 mg L^{-1} , Co = 2,711 mg L^{-1}) minerale slib werd uitgevoerd met 1 M Na_2S , en resulteerde in een maximale Mo herstel bij pH 2 (50.3%), terwijl de maximale recuperatie van Ni en Co bij pH 4 (56.0 en 59.7%, respectievelijk) waren. Het echte zuur percolaat gaf een lagere metalen herstelcapaciteit die kunnen worden toegeschreven aan verschillende factoren, zoals: i) veranderingen in de pH, ii) de aard van leachant, en iii) co-precipitatie van Zn en concurrentie S^{2-} ionen.

CHAPTER 1

Introduction

Chapter 1

At every stage of the production and consumption cycle of essential and consumer items, whether intermediate or the finished products, certain contaminants (*i.e.* organic and/or inorganic compounds) are invariably generated which have various degree of toxicity to the living organisms including human beings (Asghari et al., 2013a,b; Lee and Pandey, 2012). In 23rd October 2001 European directive No. 2001/81/CE restricted the emissions of pollutants such as sulfur dioxide, nitrogen oxides, etc. into the atmosphere (Kar et al., 2004). Consequently, levels of sulfur in petrol's and diesels should not exceed 10 ppm as from 2009. The result of this directive is a significant increase in the amount of used catalysts, which are used in greater numbers by oil companies to achieve the threshold fixed by the European Commission (Kar et al., 2004).

By definition, catalyst is an element in a chemical reaction that participates in the reaction but is not used up (Silvy, 2004). Catalysts are composed of an aluminous or silica base on which metal oxides are deposited, *e.g.* molybdenum and nickel oxide, known as nickel-molybdenum catalysts (NiMo), molybdenum and cobalt oxide, known as cobalt-molybdenum catalysts (CoMo), tungsten and nickel oxide, known as nickel-tungsten catalysts (NiW) (Kar et al., 2004; Marafi and Stanislaus, 2003).

As the catalyst is used, it wears out and can no longer extract all the harmful elements. This is known as a used catalyst (Marafi and Stanislaus, 2007). The used catalysts therefore contain the elements they are composed of (alumina, sometimes silica, molybdenum, nickel, phosphorus, copper, etc.) and the harmful elements captured during the refining process (sulfur, carbon, hydrocarbons, nickel, vanadium, arsenic, etc.) (Silvy, 2004). Numerous harmful effects are associated with used catalysts: nickel, molybdenum, vanadium and tungsten in the form of sulfur compounds are extremely toxic to humans (carcinogenic, mutagenic and affecting reproduction) and the environment (highly mobile) if they get into the food chain or nature (Marafi and Stanislaus, 2008a,b). If the sulfur is not captured, it can cause acid rain or salt waste to contaminate surface and underground water (Zeng and Cheng, 2009a). The heavy and light hydrocarbons can affect the air, the water and the soil if they are not treated. The toxicology of poisonous elements such as arsenic, selenium or fluoride in low concentration is well-known (Zeng and Cheng, 2009b).

Disposal of spent catalyst represent an increasing environmental problem due to the metallic content, being considered as hazardous waste (Zeng and Cheng, 2009a,b). The cost for safe disposal of this hazardous material is quite high in terms of the amount of waste produced and the limited storage capacity of landfills and/or dumpsites (Silvy, 2004). Therefore, concepts of reutilization and recycling of materials are appearing in order to minimize the wastes (Sayilgan et al., 2009a). Furthermore, substitution of raw materials by the recycled products provides both reduction in production costs and the preservation of raw materials, thus environmental protection (Sayilgan et al., 2009b).

1.1. Problem description

In order to achieve recycling of large amounts of incoming used catalysts, the recycling plant (study area of PhD research) designed a process allowing the recovery of precious metals from used NiMo, CoMo and NiW catalysts (thus they have second life in the refinery), and thus they are transformed into new raw materials. For this process, the recycling of used catalysts is based on smart combinations of hydrometallurgical and pyrometallurgical processes.

Although the recycling process(es) have demonstrated to be successful in handling catalysts recycling, the recycling plant encounter specific problems such as rainfall, causing the runoff of metal-laden particles from the plant site and storage areas. Runoff water containing metals is collected *via* an adequate piping network and then channeled to the collection reservoir for processing at the wastewater treatment plant prior to ultimate discharge into the nearby aquatic system. Along with the runoff particles, dusts are also transported that tends to form a mineral sludge containing various compositions and concentrations of inorganic contaminants. Under such a situation, the recycling plant is forced to choose between two commonly practiced options, namely ultimate sludge disposal (a relatively high-cost option), or the recovery of the sludge output (yielding revenue generation from the economic value of certain metals). Since some metals like Mo, Ni, Co, Cr, Zn and W present in the sludge are especially valuable to the recycling plant (both economically and ecologically) and given their increased demand and future shortfall within primary sources, the prime focus of our research was on these metal species.

This PhD research aimed to experimentally test various speciation, leaching and recovery processes: their principle, applicability, methods of predicting and improving of their

performance in the treatment of metals from contaminated sludges. Since Mo is metal of primary importance to the recycling plant (economically and ecologically), this PhD research was mainly focused on recovery of Mo and additionally on recovery of other metals such as Ni and Co.

1.2. Objectives

The main objective of this research is *“to develop an appropriate hydrometallurgical approach for optimal metals recovery from mineral sludges generated at a metal recycling plant”*.

The specific objectives are:

1. Bibliographic researches about Mo general characteristics, speciation, leaching and recovery.

The synthesis of this work is done through a review article.

2. To study the general characterization and metals speciation of the mineral sludge samples.

- a) To investigate physical and chemical characteristics of the minerals sludge samples.
- b) To investigate the total metals concentrations of minerals sludge samples and to appoint the metals that are exceeding sludge quality guidelines.
- c) To investigate the mineral composition of the metals (Mo, Ni, Co, Cr, Zn and W) in the mineral sludge samples.
- d) To investigate for which sludge extraction fraction (acid soluble, reducible, oxidizable and residual) are metals showing the highest bonding affinities in the mineral sludge samples.
- e) To investigate mineral sludge samples toxicity characteristics and to evaluate their acceptance for the landfill disposal based on the Compliance and TLCP tests.

3. To study the metals leaching properties of the mineral sludge samples.

- a) To define the appropriate leachants to be tested for determining the metals leaching potential of the mineral sludge samples.
- b) To investigate the appropriate solid to leachant ratio to obtain the highest metals leaching yields.
- c) To investigate the optimum leaching time for achieving the highest metals leaching yields.
- d) To investigate the optimum temperature for achieving the highest metals leaching yields.

- e) To investigate the mineral composition of the mineral sludge samples after performing the leaching experiments.
 - f) To appoint the leachant with the highest metals leaching potential.
4. To study the metals recovery properties of the mineral sludge samples.
- a) To define the appropriate recovery experiments to be evaluated for the metals recovery potential of the mineral sludge samples.
 - b) To set up a batch recovery tests for the metals precipitation with Na_2S from the synthetically prepared metal leachate.
 - c) To test the effect of different operational parameters (metal to sulfide ratio, agitation speed, contact time and pH) for the optimal metal sulfide/oxide precipitation from the synthetically prepared metal leachate.
 - d) To investigate the characteristics of the metal sulfide/oxide precipitates (settleability, x-ray diffraction, scanning electron microscopy, total metal concentrations).
 - e) To compare the experimental metal sulfide/oxide precipitation data with Visual MINTEQ modelling.
 - f) To investigate the metal recovery properties of the real acidic metals leachate under the defined optimal metal sulfide/oxide precipitation conditions.

1.3. Structure of thesis

The present dissertation comprises six chapters. The following paragraphs outline the content of the chapters (Figure 1.1).

Chapter 1 gives a general overview of the research, including background, problem description, research objectives and the thesis structure.

Chapter 2 gives a literature review about molybdenum general characteristics, leaching, bioleaching and recovery from the spent catalysts.

Chapter 3 investigates the general characteristics of the mineral sludge samples generated at the metal recycling plant.

Chapter 4 investigates the metals leaching potential of different acids/acid mixtures under the effect of different operational parameters.

Chapter 5 investigates the target metals precipitation with Na_2S from synthetic and real metals leachate under the effect of different operational parameters, coupled with Visual MINTEQ modelling.

Chapter 6 addresses the future shortages of the target metals, summarizes and draws conclusions on gained knowledge about their recovery from the secondary resources and gives recommendations for future perspectives.

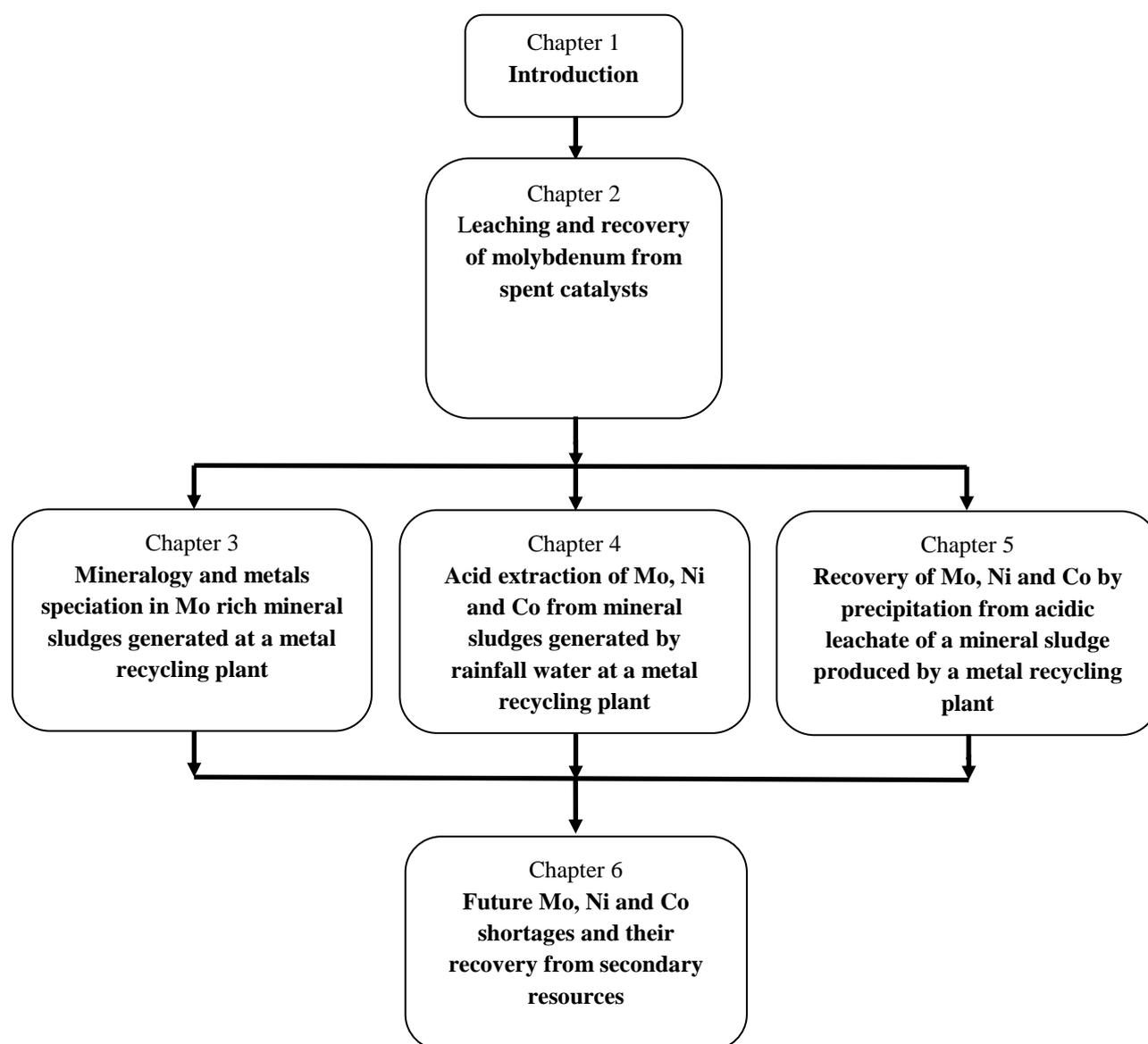


Figure 1.1. Overview of the PhD thesis.

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CHAPTER 2

Leaching and recovery of molybdenum from spent catalysts

This chapter has been submitted as:

Vemic, M., Bordas, F., Guibaud, G., Lens, P.N.L., van Hullebusch, E.D., 2015. Leaching and recovery of molybdenum from spent catalysts. *Springer Book: Sustainable Technologies for Heavy Metal Removal from Soils, Solid Wastes and Wastewater, in revision.*

Chapter 2

Spent catalysts are generated in large quantities as solid waste on a yearly basis. Due to their hazardous nature, environmental regulations for discarded spent catalysts are very strict. Consequently, from ecological and economical view point, metals recovery from spent catalysts is very important. Molybdenum (Mo) is one of the elements present in spent catalysts at high concentrations. The rapidly growing demands for Mo and its products create a need to develop novel recovery processes from secondary resources, *i.e.* spent catalysts, as there is a projected shortage of the primary resources for this element. This paper overviews the general characteristics of Mo along with the research conducted over the last years concerning Mo chemical leaching (with strong inorganic acids, sodium hydroxide, hydrogen peroxide and acid mixtures), bioleaching (with bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Acidianus brierleyi* or fungi *Penicillium simplicissimum* and *Aspergillus niger*), and recovery technologies (precipitation, adsorption, ion exchange, solvent extraction) from spent catalysts.

2.1. Introduction

Molybdenum (Mo) is valuable element to all living organisms because of its functional role in cofactors in various bacterial, plant, and animal enzymes (Giussani, 2011), and its specific geochemical behavior. Mo also has widespread industrial importance (Pyrzynska, 2007). On account of its high melting point, high strength at higher temperatures, high thermal conductivity and good corrosion resistance (Pyrzynska, 2007), Mo is extensively used in a variety of industrial processes (Figure 2.1a) (Aydin et al., 2012; Das et al., 2007).

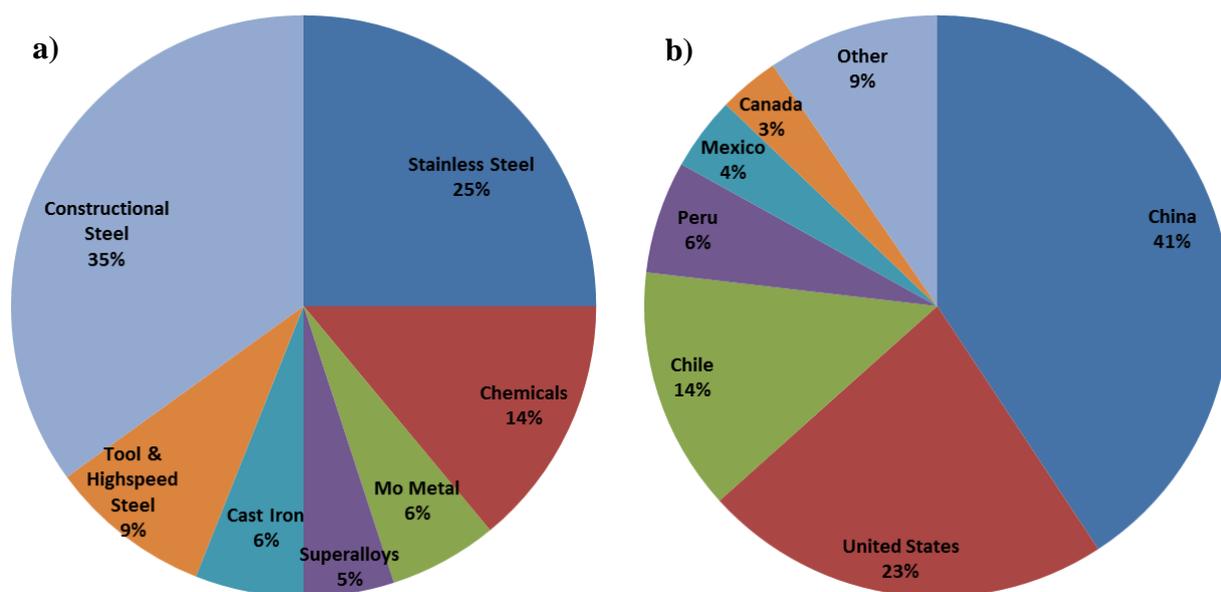


Figure 2.1. Molybdenum application in industry (a) and molybdenum world production (b) (U.S. Geological Survey, 2014).

Among all other industrial uses, Mo catalysts are vastly utilized in petroleum desulfurization to minimize sulfur dioxide emissions from combustion of fuel (Asghari et al., 2013; Cibati et al., 2013; Kar et al., 2004; Zeng and Cheng, 2009b). Mo also has its use in alloys, corrosion inhibitors, flame retardants and lubricants (Van Gestel et al., 2012).

Mo world production (Figure 2.2) increased over the years and was estimated 270,000 tons in 2013, with the largest producers being China (110,000 t), United States (61,000 t), Chile (36,500 t), Peru (16,900 t), Mexico (11,000 t) and Canada (9,000 t) (Figure 2.1b) (U.S. Geological Survey, 2014). Mo is an expensive element. The average market price of Mo oxide is around 21,433 € t⁻¹ in 2014 (www.infomine.com). In 2013, Mo produced at 11 mines valued 1 billion euros (U.S. Geological Survey, 2014).

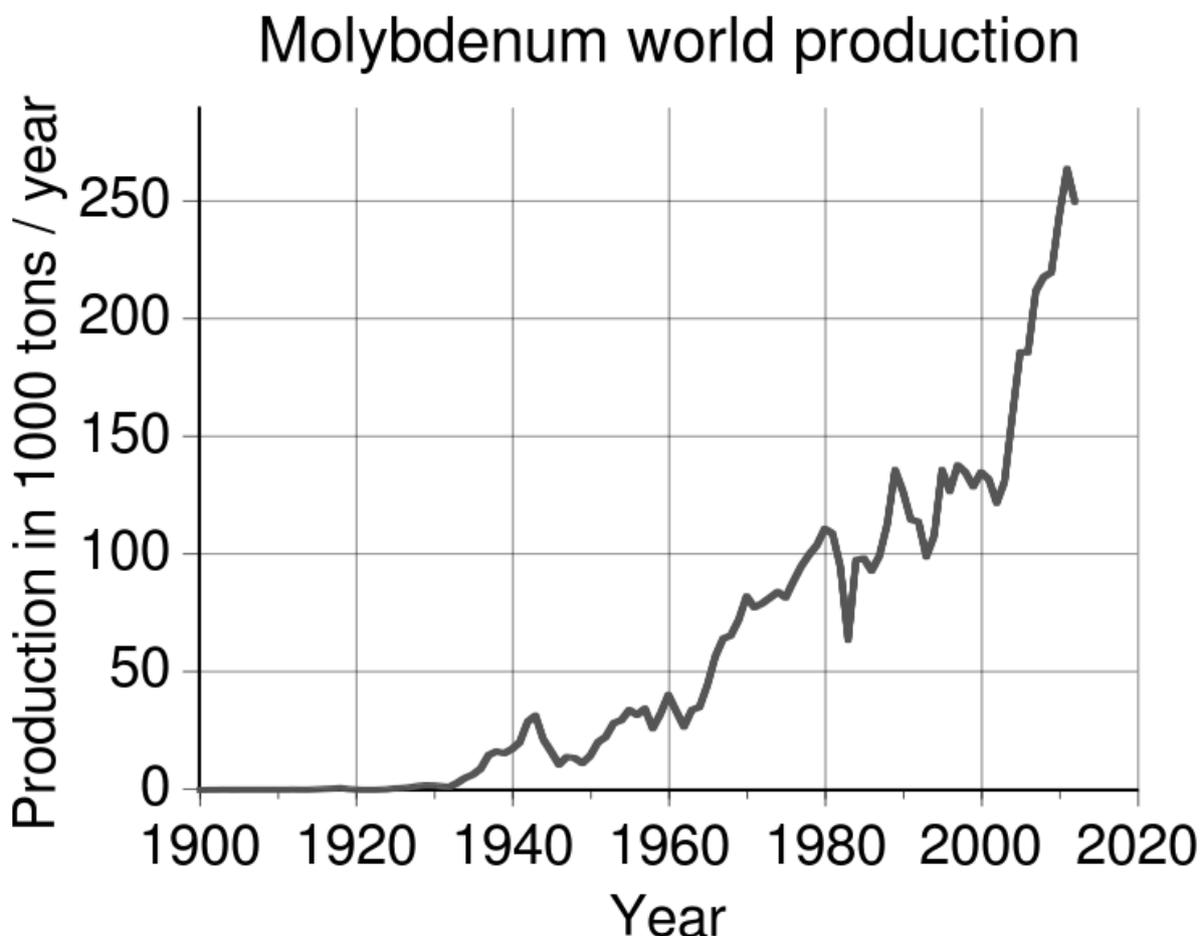


Figure 2.2. World production of molybdenum over the years (adapted from www.imoa.info).

The high demand, high price and projected future shortage of the Mo primary mineral resources creates a need to develop secondary resources and to find more beneficial ways of Mo recovery from industrial waste materials, especially spent catalysts (Marafi et al., 2007). Spent catalysts discarded by industries are undoubtedly very important, because of the inherent metals (Mo, Ni, Co, Zn, Cr, Fe, Al, W etc.) (Erust et al., 2013; Marafi et al., 2007). Worldwide generated amount of spent catalysts is in the range of 150,000 - 170,000 tons year⁻¹ (Amiri et al., 2011; Bharadwaj and Ting, 2013; Marafi and Stanislaus, 2008a,b). This large quantity of spent catalysts could potentially be a suitable secondary resource of Mo. However, the information found in the literature about Mo leaching and recovery from spent catalysts is scattered and as to our best knowledge no review article was developed concerning the summary of available options. Therefore, this chapter overviews different Mo leaching and the recovery techniques from spent catalysts.

2.2. General characteristics of molybdenum

2.2.1. Origin, abundance and production of molybdenum

Mo is a trace element in the Earth's crust and its estimated abundance is in the range of 0.05 - 40 mg kg⁻¹, with average of 1.5 mg kg⁻¹ (Aydin et al., 2012; Das et al., 2007; Kabata-Pendias and Mukherjee, 2007; Zemberyova et al., 2010). Mo general characteristics are presented in Table 2.1. Despite the fact that Mo is found in minerals such as powellite (CaMoO₄), wulfenite (PbMoO₄) and molybdite (MoO₃) (oxidation state VI), Mo primary source is molybdenite (MoS₂) (oxidation state IV) (Viera et al., 2007). Mo occurs as a major component (more than 60%) in MoS₂, while the percentage of its presence in the minerals such as pyrite (FeS₂), galena (PbS) and sphalerite (ZnS) is variable (Smedley et al., 2013).

Table 2.1. General characteristics of molybdenum (Kabata-Pendias and Mukherjee, 2007).

Name, symbol, number	Molybdenum, Mo, 42
Element category	Transition metal
Mendeleev table position	Group 6
Atomic mass	95.95
Density	10.28 g cm ⁻³
Melting temperature	2623°C
Boiling temperature	4639°C
Thermal expansion	4.8 × 10 ⁻⁶ /K at 25°C
Thermal conductivity	138 W/m K at 20°C
Oxidation states	-I, -II, I, II, III, IV, V and VI
Isotopes	⁹² Mo, ⁹³ Mo, ⁹⁴ Mo, ⁹⁵ Mo, ⁹⁶ Mo, ⁹⁷ Mo, ⁹⁸ Mo, ⁹⁹ Mo and ¹⁰⁰ Mo

Mo production flow sheet is presented in Figure 2.3. Mo is obtained as a primary product from its high-grade sulfide ore, molybdenite, through oxidative roasting, purification of calcine, followed by hydrogen reduction of Mo oxide (MoO₃) (Kim et al., 2008).

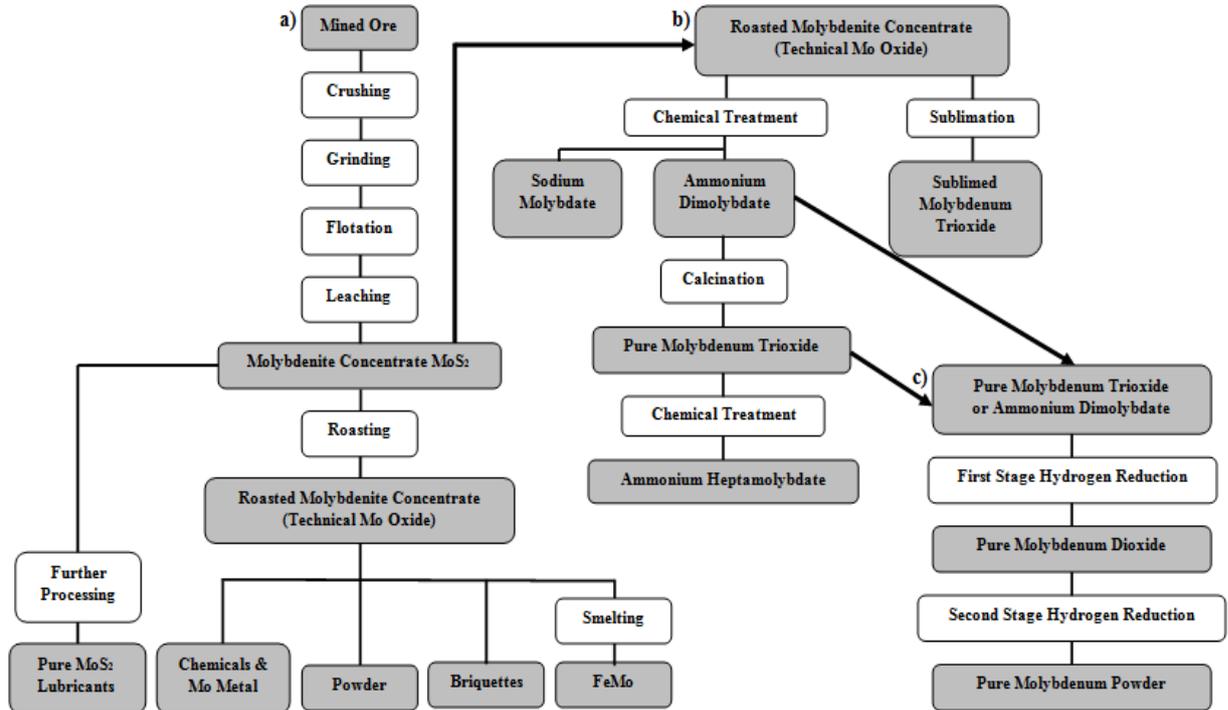
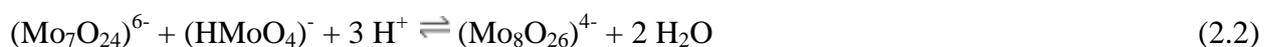


Figure 2.3. Molybdenum production: a) Molybdenum processing flow sheet; b) Molybdenum upgrading from Technical Oxide; c) Molybdenum metal powder production (modified from www.imoa.info).

2.2.2. Equilibria and complexes of molybdenum

Figure 2.4 presents equilibria of Mo (VI) in aqueous solutions (Lee et al., 2011). Table 2.2 lists the complex formation constants of Mo (VI) and formation constants for some new Mo (VI) containing species (Lee et al., 2011). When Mo concentrations exceed $10^{-3} \text{ mol L}^{-1}$ at $\text{pH} > 6$, the dominant species is the tetrahedral $(\text{MoO}_4)^{2-}$ ion (www.imoa.info). An interesting feature shown by Mo is its polymerization (Xiong et al., 2011). Polymerization condensation occurs when the pH is slowly decreased from 6.5 to 2.0, (Zeng and Cheng, 2009a,b), giving at pH 5 - 6 heptamolybdate $(\text{Mo}_7\text{O}_{24})^{6-}$ ion (Eq. 1), and at pH 3 - 5 octamolybdate $(\text{Mo}_8\text{O}_{26})^{4-}$ ion (Eq. 2) (www.imoa.info):



A further pH decrease leads to anionic polymers with probably 16 - 18 Mo atoms (Zeng and Cheng, 2009a,b).

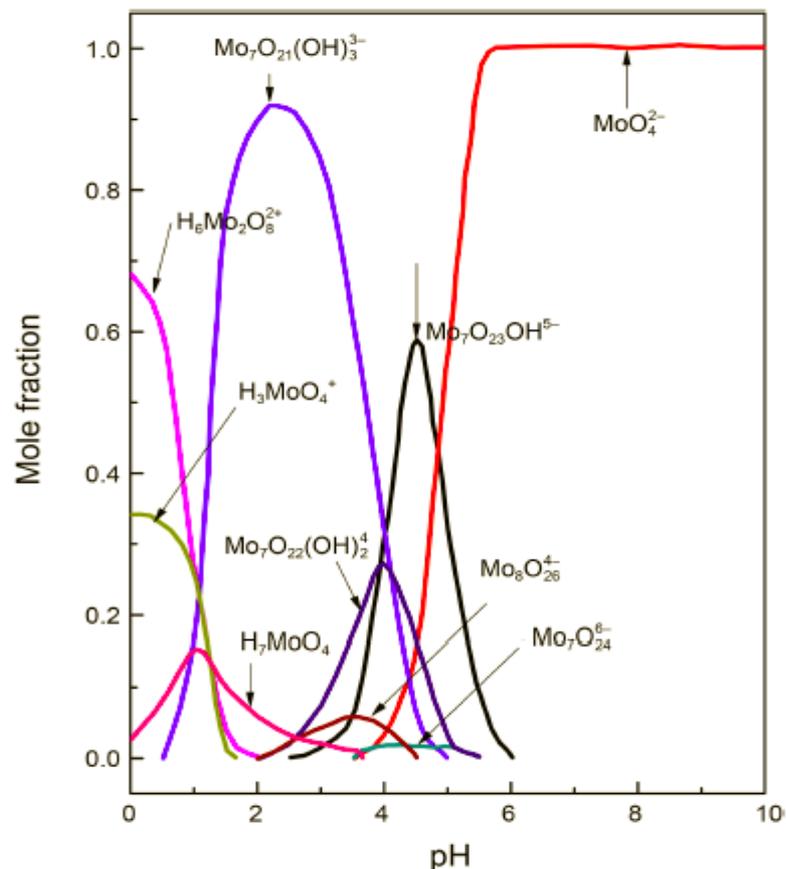


Figure 2.4. Distribution diagram of molybdenum chemical species in aqueous phase as a function of pH (adapted from Lee et al., 2011).

Table 2.2. Stability constants for the formation of complexes of Mo (IV) (0.01 M) in aqueous solution at 25°C (modified from Lee et al., 2011).

Formula	Reaction	Log K
H_3MoO_4^+	$\text{MoO}_4^{2-} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{MoO}_4^+$	$\log K_1 = 8.4$
MoO_2OH^+	$\text{MoO}_4^{2-} + 3\text{H}^+ \leftrightarrow \text{MoO}_2\text{OH}^+ + \text{H}_2\text{O}$	$\log K_2 = 8$
$\text{Mo}_2\text{O}_5\text{OH}^+$	$2\text{MoO}_4^{2-} + 5\text{H}^+ \leftrightarrow \text{Mo}_2\text{O}_5\text{OH}^+ + 2\text{H}_2\text{O}$	$\log K_3 = 18$
$\text{Mo}_2\text{O}_2(\text{OH})_6^{2+}$	$2\text{MoO}_4^{2-} + 6\text{H}^+ \leftrightarrow \text{Mo}_2\text{O}_2(\text{OH})_6^{2+}$	$\log K_4 = 19$
$\text{Mo}_7\text{O}_{24}^{6-}$	$7\text{MoO}_4^{2-} + 8\text{H}^+ \leftrightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$	$\log K_5 = 52$
$\text{Mo}_8\text{O}_{26}^{4-}$	$8\text{MoO}_4^{2-} + 12\text{H}^+ \leftrightarrow \text{Mo}_8\text{O}_{26}^{4-} + 6\text{H}_2\text{O}$	$\log K_6 = 71$
$\text{Mo}_{18}\text{O}_{56}^{4-}$	$18\text{MoO}_4^{2-} + 32\text{H}^+ \leftrightarrow \text{Mo}_{18}\text{O}_{56}^{4-} + 16\text{H}_2\text{O}$	$\log K_7 = 171$
HMoO_4^-	$\text{MoO}_4^{2-} + \text{H}^+ \leftrightarrow \text{HMoO}_4^-$	$\log K_8 = 3.6$
$\text{HMo}_7\text{O}_{24}^{5-}$	$7\text{MoO}_4^{2-} + 9\text{H}^+ \leftrightarrow \text{HMo}_7\text{O}_{24}^{5-} + 4\text{H}_2\text{O}$	$\log K_9 = 57$
$\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$	$7\text{MoO}_4^{2-} + 10\text{H}^+ \leftrightarrow \text{H}_2\text{Mo}_7\text{O}_{24}^{4-} + 4\text{H}_2\text{O}$	$\log K_{10} = 60$
$\text{H}_3\text{Mo}_7\text{O}_{24}^{3-}$	$7\text{MoO}_4^{2-} + 11\text{H}^+ \leftrightarrow \text{H}_3\text{Mo}_7\text{O}_{24}^{3-} + 4\text{H}_2\text{O}$	$\log K_{11} = 62$
$\text{Mo}_7\text{O}_{24}\text{OH}^{7-}$	$7\text{MoO}_4^{2-} + 7\text{H}^+ \leftrightarrow \text{Mo}_7\text{O}_{24}\text{OH}^{7-} + 3\text{H}_2\text{O}$	$\log K_{12} = 46$
$\text{H}_2\text{Mo}_6\text{O}_{21}^{4-}$	$6\text{MoO}_4^{2-} + 8\text{H}^+ \leftrightarrow \text{H}_2\text{Mo}_6\text{O}_{21}^{4-} + 3\text{H}_2\text{O}$	$\log K_{13} = 49$
$\text{H}_3\text{Mo}_8\text{O}_{28}^{5-}$	$8\text{MoO}_4^{2-} + 11\text{H}^+ \leftrightarrow \text{H}_3\text{Mo}_8\text{O}_{28}^{5-} + 4\text{H}_2\text{O}$	$\log K_{14} = 67$
$\text{HMo}_{13}\text{O}_{42}^{5-}$	$13\text{MoO}_4^{2-} + 21\text{H}^+ \leftrightarrow \text{HMo}_{13}\text{O}_{42}^{5-} + 10\text{H}_2\text{O}$	$\log K_{15} = 119$
MoO_3	$\text{MoO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{MoO}_3 + \text{H}_2\text{O}$	$\log K_{16} = 7.2$
H_2MoO_4	$\text{MoO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{MoO}_4$	$\log K_{17} = 7.4$

Mo creates vast number of complexes in different valences (hydrochloric, oxalic, thiocyanic and phosphoric molybdates) (Zeng and Cheng, 2009a). Complexes with hexavalent Mo, Mo trioxide and molybdic acid, are the most significant ones (Zeng and Cheng, 2009b). As a result of the activity of alkalis on MoO_3 , molybdate ion MoO_4^{2-} is formed (Zeng and Cheng, 2009a,b). Mo salts such as di-, and tri-molybdates can be produced by changing the quantities of MoO_3 and alkalis.

Mo (IV) is predominant in reducing conditions, while Mo (VI) in predominant in oxidizing environments. Cationic species of MoO_2 are formed at pH 2.0. In stronger acid solutions (~ 6 N HCl), neutral MoO_2Cl_2 complexes are created (Zeng and Cheng, 2009b). In a solution with 2 - 3 N HCl and H_2SO_4 , anionic $\text{MoO}_2\text{Cl}_3^-$ and $\text{MoO}_2(\text{SO}_4)_2^{2-}$ complexes are existent (Zeng and Cheng, 2009a).

2.2.3. *Molybdenum in catalysts*

Due to the continued world supply of crude oil and limited availability of low-sulfur crudes, catalysts increase in their use. Catalysts not only allow for economical fuel refining but also contribute to a safer environment through lower sulfur emissions (Zeng and Cheng, 2009a,b). The most common catalysts are made up of oxides of Mo and Co (or Ni) on γ -alumina support (Cibati, 2011). Mo based catalysts are commonly composed of 10 - 30% Mo, 10 - 12% C, 8 - 12% S, 1 - 12% V, 1 - 6% Co, 0.5 - 6% Ni and the basis is γ -alumina (Kar et al., 2004; Marafi et al., 2007; Zeng and Cheng, 2009a,b).

The Mo based catalysts are usually prepared by soaking support solutions in which alumina is dissolved with salts of Mo, Co and Ni, after which the material is calcined at 600°C to obtain the oxides (Marafi et al., 2010a,b). Mo oxides (MoO_3) presence in catalysts was verified in study by Cedeño-Caero and Alvarez-Amparan (2014). The Ni and Co oxides exercise a promoting effect on the activity of the catalytic system $\text{MoO}_3\text{-Al}_2\text{O}_3$ (Cedeño-Caero and Alvarez-Amparan, 2014; Cibati, 2011). However, the catalysts efficiency is maximal when they are in the form of sulfides. For this reason an initial addition of H_2S gas is needed to get MoS_2 and CoS compounds that are active in catalysis. The component that catalyses the reaction is the MoS_2 , activated by Co, which limits the sintering of the crystals (Cibati, 2011).

As a consequence of fouling of the active catalyst surface by deposition of coke and metals, catalysts have a tendency to quickly deactivate (Marafi and Stanislaus, 2003). The quantity of metal-fouled spent catalysts from residue hydroprocessing units has increased significantly worldwide due to a rapid growth in the residual oil upgrading capacity by hydroprocessing (Marafi and Stanislaus, 2003). Spent hydrodesulphurization (HDS) catalysts account for nearly one-third of the entire worldwide catalyst utilization (Zeng and Cheng, 2009a,b), therefore, they could be a considerable secondary resource of Mo.

Spent catalyst characterization is an important part of the evaluation process when determining the ultimate fate of the catalyst and which leaching and/or recovery technique is the most suitable for metal recovery. Unfortunately, very few studies have been performed concerning spent catalysts characterization (Furimsky, 1996; Mishra et al., 2007). Mo and Ni are not uniformly spread in a middle section of spent catalyst (Asghari et al., 2013b). In the non-treated spent catalyst, Ni is concentrated in the surface layer, while Mo is concentrated in the lobe centre

(Asghari et al., 2013b). The pre-treating process triggers a migration of Mo and Ni toward the centre of the pellet (Asghari et al., 2013b). SEM-EDX analysis of the spent catalyst by Mishra et al. (2009) confirmed that Mo matrix is firmly fixed inside of a sulfur matrix, thereby having an additional diffusion barrier (Asghari et al., 2013b).

2.3. Chemical leaching of molybdenum from spent catalysts

Chemical leaching of metals is a process of extracting their minerals from a solid into the liquid phase caused by inorganic/organic leachants. This process is influenced by mineral dissolution, desorption and complexation processes due to the effect of pH, redox etc. Metal leaching is influenced by parameters such as type of leachant, particle size, presence of chelating agents, S/L ratio, temperature, contact time, stirring and pH. An optimal chelating agent displays a high leaching efficiency, a high selectivity for the target element, a high solubility and a high thermodynamic stability of the formed complex (De Souza Pereira, 2011; Goel et al., 2009; Kim et al., 2008). Since the 1970s, research on Mo leaching from industrial wastes has attracted more attention and the metal leaching with a variety of reagents such as H₂SO₄ (Kim et al., 2009a,b), HNO₃ (Khoshnevisan et al., 2012; Sastre et al., 2002; Smirnov et al., 2010), HCl (Banda et al., 2013a), NaOH (Ghosh et al., 2015; Huang et al., 2014; Rojas-Rodríguez et al., 2012; Ruiz et al., 2011a), H₂O₂ (Park et al., 2006a,b; Park et al., 2008; Ruiz et al., 2011b), NaClO (Liu et al., 2011) and chemical mixtures (Barik et al., 2012a,b; De Lima et al., 2005; Lai et al., 2008; Park et al., 2007) have been developed one after another. Table 2.3 overviews Mo leaching technologies from spent catalysts along with the achieved leaching yields.

Table 2.3. Overview of molybdenum leaching methods from spent catalysts and molybdenum leaching yield (%) achieved.

Type of treatment	Leaching agent	Temperature (°C)	Time (h)	Other conditions	Mo leaching yield (%)	Reference
Sulfuric acid leaching	2% v/v H ₂ SO ₄	95	1	Baking at 200-450°C, pulp density 5% (w/v)	90	Kim et al., 2009a
	2% v/v H ₂ SO ₄	80	1	Baking at 400°C, pulp density 5% (w/v)	96	Kim et al., 2009b
Nitric acid leaching	3.5 - 4.0% v/v HNO ₃	150	0.5	Pulp density 10% (w/v)	92	Khoshnevisan et al., 2012
Hydrochloric acid leaching	10% v/v HCl	90	1	250 µm particle size, pulp density 5% (w/v)	97	Banda et al., 2013a
Sodium hydroxide leaching	8% v/v NaOH	60	4	Roasting at 700°C for 20 min	90	Ruiz et al., 2011a
	5% v/v NaOH	160	2	Pulp density 4% (w/v), 300 rpm	96	Huang et al., 2014
	20% v/v NaOH	25	2	200 rpm	95	Rojas-Rodríguez et al., 2012
Hydrogen peroxide leaching	6% v/v H ₂ O ₂	25	1	Pulp density of 10% (w/v)	85	Park et al., 2006b
	40 g L ⁻¹ Na ₂ CO ₃					
	10% v/v H ₂ O ₂ , 85 g L ⁻¹ Na ₂ CO ₃	25	1	Pulp density 20% (w/v)	84	Park et al., 2006a
	12% v/v H ₂ O ₂	60	1	pH 1.3, stoichiometric factor 2.4	90	Ruiz et al., 2011b
Leaching using mixtures of chemicals	5% v/v H ₂ SO ₄ , 25% v/v HNO ₃	50	5	Particle size 51 - 70 µm	99	Barik et al., 2012b
	5% v/v H ₂ SO ₄ , 17% v/v H ₂ O ₂	50	5	Particle size 51 - 70 µm	99	Barik et al., 2012a
	6% v/v H ₂ SO ₄ , 30 g L ⁻¹ Na ₂ CO ₃	90	1	Pulp density 10% (w/v)	98	Park et al., 2007
	HNO ₃ /H ₂ SO ₄ /HCl (2:1:1)	70	1	Pulp density 4% (w/v)	90	Lai et al., 2008
Combination of chemical leaching and bioleaching	<i>Acidithiobacillus ferrooxidans</i> , 30 g L ⁻¹ (NH ₄) ₂ CO ₃	35	40 h	Initial ferrous ion of 2 g L ⁻¹ , initial pH of 2, pulp density of 10% (w/v), particle size of 106±45 µm	99	Pradhan et al., 2013

2.3.1. Sulfuric acid leaching

The possibility of Mo leaching from spent catalysts using H₂SO₄ has been evaluated by numerous studies. For instance, in one study, dissolution of metals from a pre-oxidized refinery plant spent Co-Mo/Al₂O₃ catalyst was investigated using H₂SO₄ baking (200 - 450°C) followed by a leaching process (Kim et al., 2009a). Spent catalyst contained 9.92% Mo, 40% Al, 2.28%

Co, 2.5% C and trace amounts of other elements such as Fe, Ni, S and P (Kim et al., 2009a). The percentage of metals dissolution has been studied under the influence of different parameters (time, temperature and catalyst-to-acid ratio). This study showed that the metal dissolution increased with the increase in baking temperature (up to 300°C), while it decreased with the further temperature increase (Kim et al., 2009a). More than 90% of Mo could be dissolved from the spent catalyst, under optimal leaching conditions (pulp density 5% (w/v) and 2% (v/v) H₂SO₄ at 95°C for 60 min) (Kim et al., 2009a).

In another study (Kim et al., 2009b), spent catalyst that contained a different composition than the previous one (11.6% Mo, 27.1% Al, 2.5% Ni, 9.7% S, 4.8% C, 1.9% P, 0.4% Si and trace amounts of Co and Fe), H₂SO₄ baking was investigated at 200 - 450°C, also followed by the leaching process. This time the various baking parameters such as baking temperature, H₂SO₄ concentration and baking duration were optimized according to the 23 full factorial methods for maximum dissolutions of Mo, Al and Ni during leaching. Under optimal baking conditions (400°C, 1.28 stoichiometric H₂SO₄, 1h), more than 96% of Mo was dissolved from the spent catalyst with 2% (v/v) H₂SO₄ at 80°C (Kim et al., 2009b). Carbon and sulfur analyses of the baked samples and leaching residues indicated only 10 - 15% of residual hydrocarbons reacted during acid baking, while most of the sulfur (assumed to be metal sulfides) was converted into soluble sulfates/oxy-sulfates (Kim et al., 2009b). By comparison, in both studies, direct H₂SO₄ leaching of the catalyst resulted in low dissolution of Mo, even with excess of acid, thus revealing the valuable effect of H₂SO₄ acid baking (Kim et al., 2009a,b).

2.3.2. Nitric acid leaching

HNO₃ is a successful oxidant in different leaching processes (Barik et al., 2012b; Khoshnevisan et al., 2012; Sastre et al., 2002; Smirnov et al., 2010). Additionally, the use of HNO₃ and HNO₃/H₂SO₄ mixtures as leachants result in fast metal extraction from spent catalysts (Barik et al., 2012b; Sastre et al., 2002). The effects of oxygen pressure, stirring speed, pulp density, acid concentration and temperature on the Mo leaching rate from spent catalyst were investigated by Khoshnevisan et al. (2012). The HNO₃ concentration was an important parameter in pressure leaching (PO₂ = 965.3 kPa) of the molybdenite concentrate (Khoshnevisan et al., 2012). At least 3.5 - 4% (v/v) HNO₃ was required for the leaching of a 100 g L⁻¹ molybdenite concentrate (containing 92% of molybdenite) (Khoshnevisan et al., 2012). 85% of the reacted molybdenite

precipitated as molybdic oxide, whereas the remaining 15% was dissolved in the liquor (Khoshnevisan et al., 2012).

2.3.3. Hydrochloric acid leaching

The dissolution behavior of metals in spent catalysts was investigated with respect to the HCl concentration, time and pulp density (Banda et al., 2013b). From the study it was concluded that the particle size had negligible effect, whereas the reaction temperature had a great effect on the metal leaching efficiency (Banda et al., 2013b). Under the optimum leaching conditions (10% (v/v) HCl, 90°C, 250 µm particle size, pulp density 5% (w/v) and 60 min reaction time), it was possible to dissolve 97% of Mo (Banda et al., 2013b).

2.3.4. Sodium hydroxide leaching

Mo leaching from industrially roasted (800°C for 20 min) spent CoMo/Al₂O₃ catalysts with NaOH was reported by Ruiz et al. (2011b). To achieve more than 85% leaching yields of Mo, the process was optimized by 23 factorial experimental designs. Temperature, amount of NaOH, and leaching time were the investigated parameters. Regrettably, even with the optimal leaching conditions established by the factorial design, Mo leaching yield never exceeded 60% due to an unfinished catalyst roasting (Ruiz et al., 2011b). Furthermore, leaching of an unroasted catalyst (comprised of 23.9% Al, 11% Mo, 7.9% S, 6.3% C and 2.9% Co) was investigated using a central composite design (CCD) (Ruiz et al., 2011b). With the changed thermal conditions (700°C for 20 min) and by applying the optimal NaOH leaching conditions (8% (v/v) NaOH for 4 h at 60°C), it was feasible to leach out more than 90% of Mo from spent catalyst (Ruiz et al., 2011b).

Metal extraction from the spent Mo-Ni/Al₂O₃ catalyst was investigated by Huang et al. (2014). First, acidic oxide MoO₃ was selectively extracted by alkali leaching and then amphoteric Al₂O₃ was dissolved by caustic soda autoclaving (Huang et al., 2014). The results showed that caustic autoclaving at low NaOH/Mo ratio could selectively extract Mo without significant dissolution of the matrix (Huang et al., 2014). Under the optimum operating conditions of temperature 160°C, 5% (v/v) NaOH, pulp density 4% (w/v), time 120 min and stirring speed 300 rpm, over 96% of Mo was leached out (Huang et al., 2014). In the other study (Rojas-

Rodríguez et al., 2012), under the optimal leaching conditions (20% v/v NaOH, room temperature, 2 h) about 95% recovery of Mo was achieved.

2.3.5. Hydrogen peroxide leaching

Park et al. (2006a) investigated a hydrometallurgical processing of spent HDS catalyst for Mo recovery using a H₂O₂ and Na₂CO₃ mixture. Under the optimum leaching conditions (6% (v/v) H₂O₂, 40 g L⁻¹ Na₂CO₃, room temperature, 1 h) about 85% leaching of Mo was achieved (Park et al., 2006a). Similarly, the large scale leaching of spent catalyst, under optimum conditions: pulp density 20% (w/v), 10% (v/v) H₂O₂, 85 g L⁻¹ Na₂CO₃ and 1 h reaction, resulted in a leaching efficiency of 84% Mo (Park et al., 2006b).

Ruiz et al. (2011b) conducted a study on the feasibility of the oxidative leaching of Mo and Co sulfides contained in a spent HDS catalyst using H₂O₂. The oxidative leaching of the CoMo/Al₂O₃ spent catalyst was performed with previous grinding. In a single-step, at pH = 1.3, a pulp density 7.5% (w/v), and 12% (v/v) H₂O₂, it was possible to leach out 90% of Mo from the spent catalyst (Ruiz et al., 2011b). It was suggested that an increase of surface area and phase transformation under mechanical activation was responsible for the improved leaching recovery of Mo (Liu et al., 2011).

2.3.6. Leaching using mixtures of chemicals

As acid mixtures are commonly used in hydrometallurgical processes for the purpose of metal leaching, multiple studies are reported in the literature (Barik et al., 2012b). For instance, Mo and Co extraction from spent petroleum catalyst (Co-Mo/Al₂O₃) was examined utilizing H₂SO₄ and HNO₃ mixture (Barik et al., 2012b). While standalone H₂SO₄ was not effective as a leachant, the mixture of H₂SO₄ and HNO₃ resulted in significant recovery of both Mo and Co (Barik et al., 2012b). Under the optimal leaching conditions (5% (v/v) H₂SO₄, 25% (v/v) HNO₃, pulp density 10% (w/v), particle size 51 - 70 μm, temperature 50°C and contact time 5 h), 99.7% of Mo was leached out from spent catalyst (Barik et al., 2012b).

Barik et al. (2012a) investigated the extraction behavior of Mo, Co and Al with sulfuric acid. Spent catalyst had the following composition: 9.93% Mo, 2.24% Co, 24.09% Al and 9.12% S (Barik et al., 2012a). Similarly to the previous study, Mo, Co and Al extraction with only

H₂SO₄ was low (21.3%, 56.1% and 8.2%, respectively) because of the oxide minerals dissolution (Barik et al., 2012a). Addition of oxidants was required in order to dissolve elemental sulfur and sulfide minerals, hence the effect of different oxidants was investigated for possible increase in metal extraction (Barik et al., 2012a). Based on the extraction efficiency, these oxidants are ordered as follows: H₂O₂ > HNO₃ > NaClO₃ > NaOCl (Barik et al., 2012a). Under optimum leaching conditions (5% (v/v) H₂SO₄, 17% (v/v) H₂O₂, pulp density 1% (w/v), particle size 51 - 70 μm, temperature 50°C and time 2 h), Mo was extracted with efficiency of 99.8% (Barik et al., 2012a).

Park et al. (2007) reported a two stage alkali/acid leaching process to selectively target Mo and Co/Ni. During the leaching process, roasted spent catalyst (at 500°C) was primarily treated with alkali solutions (30 g L⁻¹ Na₂CO₃ at 90°C for 1 h with pulp density 10% (w/v)) to remove Mo, and then with sulfuric acid (6% (v/v) H₂SO₄ at 90°C for 1 h with pulp density 10% (w/v)), resulting in a Ni and Co rich solution (Park et al., 2007; Zeng and Cheng, 2009a,b). Leaching efficiencies of up to 98% for Mo were achieved (Park et al., 2007; Zeng and Cheng, 2009a,b).

De Lima et al. (2005) described Mo, Ni, Co and Al leaching from spent CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts (roasted at 500°C for 5 h) (Barik et al., 2012b). Experiments were carried out combining one, two or three chemicals, using 15 mL of each reagent (De Lima et al., 2005). The following fluoride chemicals were used: 37 wt% (~ 20 mol L⁻¹) HF, NaF, KF, NH₄F and NH₄HF₂ (De Lima et al., 2005). Other solubilizing agents employed were: HCl (12 mol L⁻¹), HNO₃ (16 mol L⁻¹), H₂SO₄ (10 mol L⁻¹) and H₂O₂ (36 wt%) (De Lima et al., 2005). Catalyst mass was fixed at 1.0 g and experiments were performed in Teflon® beakers, under 200 rpm at 50 - 60°C (De Lima et al., 2005). These conditions allowed leaching efficiency of more than 95% of Mo at 60°C after 1 h (Barik et al., 2012b; De Lima et al., 2005).

In another study, recovering of valuable metals from spent HDS catalysts using a combined acid-leaching was investigated (Marafi et al., 2010a,b). An acid solution consisting of concentrated HNO₃/H₂SO₄/HCl with a volume ratio of 2:1:1 was found to be better than the other tested solutions (HNO₃/H₂SO₄ = 1:1) to leach the metals out of the HDS catalysts (Lai et al., 2008). For the three-acid mixture, the best pulp density and time were 4% (w/v) and 1 h, respectively, at 70°C (Lai et al., 2008). Under these conditions, the Mo leaching yields in the 1st step of leaching reached 90% (Lai et al., 2008).

2.3.7. Evaluation of chemical leaching of molybdenum from spent catalysts

Hydrometallurgical approaches such as chemical leaching give Mo leaching yields of more than 90%. In spite of the good metal leaching efficiencies of chemical leaching, the leaching process itself requires continuous control, the use of high temperatures and the addition of large amounts of acid to regulate the pH and large alkali amounts (such as NaOH) to neutralize the waste at the end of the leaching process (Asghari et al., 2013b; Zeng and Cheng, 2009a,b). It is crucial that other important factors are also taken into account, *e.g.* costs associated with handling by-products (*i.e.* toxic gases) (Kar et al., 2004; Marafi et al., 2010a,b). Therefore, the methods which are established on utilization of strong acids need rigorous safety precautions (Marafi et al., 2010a,b). Among all chemical leachants, sulfuric acid appear to be the optimal option since all of the target metals dissolve rapidly due to its high oxidising power (Marafi et al., 2010). Although the acid mixtures showed notable advancement in the leaching efficiency in comparison with the standalone acids, the high acid utilization and high cost present a drawback (Barik et al., 2012b; Marafi et al., 2010a,b).

2.4. Bioleaching of molybdenum from spent catalysts

Bioleaching of waste has become increasingly important in recent years, due to its vast potential, simplicity and eco-friendly operation (Chen et al., 2011; Nasernejad et al., 1999). Bioleaching utilizes the potential of different microorganisms to mobilize and leach out metals from solid materials (Asghari et al., 2013b; Lee and Pandey, 2012). Soluble and extractable elements can be recovered due to the ability of microorganisms (bacteria and fungi) to modify solid compounds, via the production of organic or inorganic acids (Amiri et al., 2011; Beolchini et al., 2010; Villa-Gomez et al., 2014a,b). Two bacterial metal leaching mechanisms have been suggested in the literature (Bayat and Sari, 2010). Firstly (Eq. 3), bacteria interact directly with the minerals and increase the speed of mineral dissolution (biological mechanism):



The second mechanism involves bacterial oxidation of Fe^{2+} to Fe^{3+} (Eq. 4) and subsequent chemical leaching of metal-bearing minerals by Fe^{3+} (Eq. 5) (Bayat and Sari, 2010). During this indirect (chemical) mechanism, Fe^{3+} produced by the bacteria plays a crucial role in metal solubilisation (Bayat and Sari, 2010).



The reaction presented in Eq. (4) needs the involvement of bacteria, while Eq. (5) is a entirely chemical process (Bayat and Sari, 2010). Since Fe^{2+} created in the chemical reaction (Eq. 5) is reused to the iron oxidizing conversion (Eq. 4), large quantity of heavy metals can be continuously leached out from solid substrates (Bayat and Sari, 2010).

Table 2.4 overviews Mo bioleaching from spent catalysts along with its extraction efficiency. Literature shows that a lot of investigations (Amiri et al., 2011; Amiri et al., 2012; Asghari et al., 2013a; Aung and Ting, 2005; Beolchini et al., 2010; Beolchini et al., 2012; Bharadwaj et al., 2013; Brandl et al., 2001; Chen et al., 2006b; Chen et al., 2011; Cibati et al., 2013; Donati et al., 1992; Gerayeli et al., 2013; Gholami et al., 2011; Gholami et al., 2012; Huisman et al., 2006; Kaksonen et al., 2007; Lee and Pandey, 2012; Mishra et al., 2008; Nasernejad et al., 1999; Pathak, et al., 2009; Pradhan et al., 2010; Pradhan et al., 2013; Santhiya and Ting, 2005; Shahrabi-Farahani et al., 2014; Srichandan et al, 2014; Villa-Gomez et al., 2014a,b) have been performed on Mo extracting from spent catalysts with mesophilic bacteria, but ended up with low Mo leaching yields (less than 70%) and relatively long leaching cycles (more than 1 day, usually 20 days). In spent catalysts Mo is strongly bound on the alumina support in the form of a $\text{MoO}_3/\text{MoS}_2$ (Asghari et al., 2013b; Cibati, 2011). As the Mo matrix is implanted inside the sulfur matrix, the attacking species need to penetrate through the sulfur species thus having an extra diffusion barrier (Kononova et al., 2003). Additionally, Mo is a toxic element to some bacteria (*Acidithiobacillus ferrooxidans*), and concentrations as low as 1.5 - 2 mg L⁻¹ of Mo are enough to inhibit the microorganism (Nasernejad et al., 1999). Therefore, the Mo speciation in the spent catalysts and its potential toxicity towards the microorganisms are the possible reasons why the bioleaching of Mo from spent catalysts is less effective than the bioleaching of other metals.

Table 2.4. Overview of molybdenum bioleaching processes from spent catalysts using different microorganisms and molybdenum recovery (%) achieved.

Type of treatment	Microorganism used	Temp. (°C)	Time (days)	Other conditions	Mo bioleaching yield (%)	Reference
Bioleaching with bacteria	<i>A. ferrooxidans</i>	30	30	pH 1.8 - 2.0	84	Gholami et al., 2011
	<i>A. thiooxidans</i>	30	30	pH 3.9 - 4.4	95	Gholami et al., 2011
	<i>A. ferrooxidans</i>	30	5	Pulp density 5% (w/v), 20 g L ⁻¹ elemental sulfur	46	Mishra et al., 2008
	<i>A. ferrooxidans</i>	30	21	175 rpm	40	Beolchini et al., 2010
	<i>A. ferrooxidans</i>	35	1.5	Ferrous ion 2 g L ⁻¹ , pH 2, pulp density 10% (w/v)	53	Pradhan et al., 2013
	<i>A. ferrooxidans</i>	35	7	Pulp density 0.9% (w/v), particle size 60.7 µm, aeration rate 209 mL min ⁻¹	87	Shahrabi-Farahani et al., 2014
	<i>Acidianus brierleyi</i>	30	6	Pulp density 1% (w/v)	67	Bharadwaj et al., 2013
Bioleaching with fungi	<i>Penicillium simplicissimum</i>	30	5	Pulp density 4% (w/v), sucrose (90 g L ⁻¹), NaNO ₃ (2 g L ⁻¹), yeast extract (0.36 g L ⁻¹)	98	Amiri et al., 2011
	<i>Aspergillus niger</i>	30	5	Particle size 150 - 212 µm, sucrose 93.8 g L ⁻¹ , pulp density 3% (w/v) and pH 7	99	Amiri et al., 2012
	<i>Aspergillus niger</i>	30	1	pH of 5.0, rotation speed of 115 rpm, 12% inoculum	69	Gholami et al., 2012

2.4.1. Bioleaching with bacteria

Iron/sulfur oxidizing bacteria (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) are commonly used microorganisms for metal bioleaching. *A. ferrooxidans* and *A. thiooxidans* were used for Mo, Co, Ni and Al mobilization from the spent catalysts in batch cultures (Gholami et al., 2011). After indirect bioleaching using *A. ferrooxidans*, maximum extraction efficiencies of 84% Mo were achieved after 30 days at pH 1.8 - 2.0 (Gholami et al., 2011). The highest Mo extraction efficiencies using *A. thiooxidans* were 95% after 30 days at pH 3.9 - 4.4. The same two bacteria were used in another study for bioleaching of the exhaust catalyst that was rich in Mo (4.4. mg g⁻¹), Ni (4.5 mg g⁻¹) and V (9.4 mg g⁻¹) (Beolchini et al., 2010). However, the observed Mo extraction efficiencies (30 - 40%) were not as high as those for Ni and V (83% and 90%, respectively), as Ni and V dissolution kinetics were faster than that of Mo

(Gholami et al., 2010). The achieved results have evidenced that metal solubilisation is strongly affected by the metal speciation and dissolution in the solid matrix (Beolchini et al., 2012).

Metals bioleaching from spent catalysts was attempted in two stage process (Mishra et al., 2008). First stage included change of elemental sulfur particles into sulfuric acid via oxidation process by *A. ferrooxidans* (Mishra et al., 2008). In the second stage, acidic medium (sulfuric acid) was used for the Mo, Ni and V extraction (Mishra et al., 2008). At pulp density 5% (w/v) of spent catalyst and 20 g L⁻¹ elemental sulfur, 46.3% Mo was recovered after 7 days (Mishra et al., 2008).

Beolchini et al. (2012) conducted a bioleaching study with *A. ferrooxidans* where the experiments were performed in autoclaved 250 mL Pyrex flasks filled to a volume of 100 mL. Incubation was carried out at 30°C and at 175 rpm horizontal shaking, for a maximum of 21 days using the 9 K medium ((NH₄)₂SO₄, 3.0 g; KCl, 0.1 g; K₂HPO₄, 0.5 g; MgSO₄ × 7H₂O, 0.5 g; Ca(NO₃)₂, 0.01 g; deionized water, 1,000 mL; and concentrated H₂SO₄, 2.5 mL (pH 2.5)) (Beolchini et al., 2012). The reported bioleaching yield of Mo was 40% (Beolchini et al., 2012). A bioleaching study with *A. ferrooxidans* where Mo, Ni and V were leached out from spent catalyst was reported by Pradhan et al. (2013). Under best bioleaching condition (initial Fe 2 g L⁻¹, initial pH 2, pulp density 10% (w/v) and temperature 35°C), the Mo leaching efficiency was 53 % (Pradhan et al., 2013).

Hydrocracking spent catalyst bioleaching of metals (Mo, Ni, Al) was studied in a column bioreactor with *A. thiooxidans* (Shahrabi-Farahani et al., 2014). The experiments were performed in a CCD in order to appoint the best conditions: particle size, pulp density and aeration rate were selected for investigation (Shahrabi-Farahani et al., 2014). The best values of variables were a pulp density of 0.9% (w/v), particle size of 60.7 µm, and aeration rate of 209 mL min⁻¹ to get simultaneous maximum recovery of three metals (Shahrabi-Farahani et al., 2014). The results displayed that at best conditions, a maximal Mo extraction after 7 days of batch processing in the bioreactor was 87% (Shahrabi-Farahani et al., 2014).

In the literature, other types of bacteria were also used for bioleaching. For instance, spent hydrotreating catalyst bioleaching by the thermophillic archae *Acidianus brierleyi* was studied (Bharadwaj and Ting, 2013). The spent catalyst was characterized, and the effect of pretreatment on two-step leaching was investigated at 1% w/v pulp density (Bharadwaj and Ting, 2013). Pretreatment (decoking) affected the solubility of metals via oxidization of the metal sulfides

(Bharadwaj and Ting, 2013). Close to 100% metal extraction efficiency was reached for Mo, Ni, Fe, and 67% for Al. Chemical (*i.e.* abiotic) leaching with bacterially produced H₂SO₄ resulted in lower leaching efficiencies (only up to 30%) (Bharadwaj and Ting, 2013).

2.4.2. Bioleaching with fungi

Bioleaching with fungi is ground on their capacity to transform solid compounds, *via* an indirect mechanism by the production of organic or inorganic acids, into soluble elements that can be recovered (Amiri et al., 2011). The most active leaching fungi, which have been isolated and used, are from the genera *Penicillium* or *Aspergillus* (Amiri et al., 2011; Amiri et al., 2012; Gholami et al., 2012; Santhiya and Ting, 2005). Amiri et al. (2011) applied statistically based experimental designs (CCD) to screen and optimize the bioleaching of spent hydrocracking catalyst by *Penicillium simplicissimum*. The combined effect of different variables (pulp density, sucrose, NaNO₃ and yeast extract concentrations) on metal bioleaching was investigated (Amiri et al., 2011). The optimal values of the variables for maximum metal bioleaching were pulp density (4.0% (w/v)), sucrose (90 g L⁻¹), NaNO₃ (2 g L⁻¹) and yeast extract (0.36 g L⁻¹) (Amiri et al., 2011). The maximal predicted Mo extraction efficiency was 97.6%. This value was consistent with the experimental values (98.8 ± 0.9% Mo) (Amiri et al., 2011).

The kinetics of bioleaching of Mo, Ni, and Al from spent hydrocracking catalyst using *Aspergillus niger* was also studied (Amiri et al., 2012). The four most effective bioleaching variables were selected as follows: particle size 150 - 212 μm, sucrose 93.8 g L⁻¹, pulp density 3% (w/v) and pH 7 (Amiri et al., 2012). The maximum metal leaching efficiencies were 99.5% Mo (Amiri et al., 2012).

Bioleaching experiments in batch cultures using *Aspergillus niger* in a one-step process to mobilize Mo, Co and Ni from hazardous spent catalysts were also carried out by Gholami et al. (2012). Maximal Mo extraction efficiencies of 69% were achieved at a pH of 5.0, a temperature of 30°C, a pulp density of 2 g L⁻¹, a rotation speed of 115 rpm, and using a 12% inoculum (Gholami et al., 2012).

2.4.3. Combination of chemical leaching and bioleaching

To leach out Mo, Ni and V present in spent refinery catalyst, two step leaching experiments were carried out (Pradhan et al., 2013). Firstly, bioleaching was applied where Mo was leached out with a maximum recovery of 53% at optimized bioleaching conditions of an initial ferrous concentration of 2 g L^{-1} , initial pH of 2, pulp density of 10% (w/v), particle size of $106 \pm 45 \text{ }\mu\text{m}$ and a temperature of 35°C (Pradhan et al., 2013). Given that the quantity of leached Mo was low, a second leaching step using $(\text{NH}_4)_2\text{CO}_3$, Na_2CO_3 or H_2SO_4 was applied on the bioleached residue (Pradhan et al., 2013). With respect to Mo extraction, in the second leaching step, leaching with 30 g L^{-1} $(\text{NH}_4)_2\text{CO}_3$ obtained the best results (Pradhan et al., 2013). The percentage of extracted Mo by combining the first step and the second step with 30 g L^{-1} $(\text{NH}_4)_2\text{CO}_3$ was 99% (Pradhan et al., 2013).

2.4.4. Evaluation of bioleaching of molybdenum from spent catalysts

In comparison with chemical leaching, bioleaching can offer attractive features, especially considering environmental issues (Beolchini et al., 2010); processes are more cost efficient (they can be performed at mild conditions), simpler (there is no need for a complex machinery) and more environmentally friendly than their chemical counterparts (Asghari et al., 2013b; Zeng and Cheng, 2009a,b). Some of the disadvantages are that bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo are rather low (less than 70%). The bioleaching process requires only 1/5th of the cost of the chemicals needed for leaching and recovery of metals compared to the traditional chemical methods (Pathak et al., 2009). Bioleaching processes are less costly in terms of chemical cost, but could prove costly in terms of capital cost, energy cost and maintenance cost associated with them (Pathak et al., 2009). In addition to the costs of chemicals, the costs of mixing, aeration, construction of holding tank and operational maintenance will have to be added to the total cost for carrying out a satisfactory cost analysis (Pathak et al., 2009).

2.5. Molybdenum recovery from spent catalysts

Following the solubilisation of Mo via (bio)leaching Mo recovery technologies have been summarized (Table 2.5). Precipitation (Chen et al., 2006a; Cibati et al., 2013; Mishra et al., 2007; Park et al., 2006a,b), activated carbon (Afkhami and Conway, 2002; Bostick et al., 2003;

Derakhshi et al., 2009; Dodbiba et al., 2011; Guibal et al., 1998; Gustafsson, 2003; Namasivayam and Sureshkumar, 2009; Pagnanelli et al., 2011; Ryden et al., 1987), ion exchange (Henry and Lierde, 1998; Kononova et al., 2003; Nguyen et al., 2013a,b; Nguyen and Lee, 2014) and solvent extraction (Banda et al., 2012; Banda et al., 2013b; Barik et al., 2014; Guan et al., 2012; Lozano and Godinez, 2003; Mishra et al., 2010; Miura et al., 2001; Parhi et al., 2011; Park et al., 2010; Sahu et al., 2013; Zeng and Cheng, 2010; Zhang et al., 1996) are used for Mo recovery from leach liquors. Mo purification and recovery from leach liquors that simultaneously contain other extractable metals is difficult due to co-precipitation. In this case selective recovery of metals under the controlled manipulation of operational parameters (especially pH) needs to be applied.

Table 2.5. Overview of molybdenum recovery technologies from spent catalysts and molybdenum recovery (%) achieved.

Type of treatment	Recovery agent	Temperature (°C)	Time (h)	pH	Mo recovery yield (%) achieved	Reference
Precipitation	Biogenic H ₂ S	25	5	2	36-72	Cibati et al., 2013
	Ammonia	90	5	2	97	Park et al., 2006a,b
	Barium hydroxide and barium aluminate	25	24	5	92	Chen et al., 2006a
Adsorption	Activated carbon	25	3	2	99	Park et al., 2006b
Ion exchange	Acrylic anion exchanger's AN-108P and AN-108TP	25	24	2	99	Kononova et al., 2003
	Diphonix and AG1-x8	25	24	1.2	99	Nguyen et al., 2013a,b; Nguyen and Lee, 2014
Solvent extraction	Alamine® 304-1	25	4	2	99	Pahri et al., 2011
	LIX® 973 N	25	5	1	99	Barik et al., 2014
	LIX® 84-I and Cyanex 272	25	4	2	99	Park et al., 2010

2.5.1. Precipitation

2.5.1.1. Sulfide precipitation

Precipitation is designed to precipitate metals by surpassing their solubility limits. Additional recovery can be achieved by co-precipitation or adsorption on the precipitate during the precipitation reaction. Sulfidogenic bioreactors have been utilized to recover metals from different metal-containing waters (Cibati et al., 2013; Zeng and Cheng, 2009a,b). Cibati et al. (2013) assessed the feasibility of using biogenic H_2S to selectively precipitate Mo, Ni, Co and V from synthetic spent refinery catalyst leach liquor containing 15.3 g L^{-1} Mo, 4.9 g L^{-1} Ni, 2.4 g L^{-1} Co and 7.6 g L^{-1} V. The average sulfate reduction rate in the ABR was $130\text{ mg L}^{-1}\text{ d}^{-1}$ and the average dissolved sulfide concentration was 190 mg L^{-1} (Cibati et al., 2013). Biogenic H_2S eased the selective precipitation of MoS_2 (oxidation state IV) at pH 2 with recoveries of 36 - 72% (Cibati et al., 2013).

2.5.1.2. Ammonium salt precipitation

Precipitation of Mo from a leach solution containing 22.0 g L^{-1} Mo, 0.015 g L^{-1} Ni, 0.82 g L^{-1} Al and 8 mg L^{-1} V was investigated by Park et al. (2006a,b). An ammonium molybdate product of 97.3% purity was obtained (Park et al., 2006a,b). To convert Mo to ammonium molybdate $(NH_4)_2MoO_4$ the solution was neutralized with ammonia at pH 11 (Zeng and Cheng, 2009a). Subsequently, the solution was acidified by HCl to pH 2 and heated up to 90°C to enable the formation of ammonium molybdate precipitates (Zeng and Cheng, 2009a).

2.5.1.3. Barium hydroxide and barium aluminate precipitation

Selective precipitation of Mo from spent catalysts alkaline leachate was investigated by adding barium hydroxide and barium aluminate (Chen et al., 2006a; Zeng and Cheng, 2009a,b). Mo precipitated with 92.6% efficiency at 80°C for 40 min (Chen et al., 2006a; Zeng and Cheng, 2009a,b). The precipitation of Mo is more favorable when its concentration in solution is high (above 30 g L^{-1}) (Chen et al., 2006a; Zeng and Cheng, 2009a,b).

2.5.2. Adsorption

Various adsorbents, such as granular-activated carbon (Derakhshi et al., 2009; Namasivayam and Sangeetha, 2006; Pagnanelli et al., 2011), pyrite (Bostick et al., 2003; Namasivayam and Sureshkumar, 2009), ferrihydrite (Gustafsson, 2003), high-area carbon cloth (Afkhani and Conway, 2002), chitosan beans (Guibal et al., 1998), ferric oxide gel (Ryden et al., 1987) and iron based adsorbents (Dodbiba et al., 2011) have been used for the adsorption of Mo (VI) from aqueous solution.

Activated carbon adsorption in order to recover Mo from spent catalyst acid leach liquors was investigated by Pagnanelli et al. (2011). Kinetic tests showed that the speed of adsorption is dependent on the quantity of Mo in solution (Pagnanelli et al., 2011). Equilibrium adsorption experiments displayed that Mo buildup has a bell-shaped behavior as pH changes, with a maximum adsorption capacity of around pH 5 (Pagnanelli et al., 2011). Sorption tests, performed in a column reactor utilizing leachate with a Mo concentration of 3.06 g L^{-1} , demonstrated that Mo can be removed from leachate with removal efficiency of 99% (Pagnanelli et al., 2011).

Adsorption/desorption method to recover Mo as molybdenum trioxide after leaching spent HDS catalysts with sodium carbonate and hydrogen peroxide was studied by Park et al. (2006b). With best adsorption conditions (pH 0.75, 3 h and pulp density 40% (w/v)), the quantity of Mo absorbed by a gram of activated carbon was 48.8 mg (Park et al., 2006b; Zeng and Cheng, 2009b). With a pulp density 30% (w/v) and 15% (v/v) NH_4OH at pH 9.5 for 3 h, nearly all Mo was desorbed (Zeng and Cheng, 2009b).

2.5.3. Ion exchange

Ion exchange is a common technology for purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral ion exchangers (Henry and Lierde, 1998; Kononova et al., 2003). Kononova et al. (2003) investigated the Mo adsorption abilities of the acrylic anion exchanger's AN-108P and AN-108TP. The Mo recovery was conducted under static (batch experiment) and dynamic (columns) conditions (Kononova et al., 2003). In the batch experiments, the resin amounts (0.1 g, dry substance) were pre-swollen for 4 h in water with a regulated pH value, and subsequently, they were agitated in $\text{Na}_2\text{MoO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ (HNO_3) solutions for 24 h (Kononova et al., 2003). The quantity of resin mass to the solution volume was 1:200 (Kononova et al., 2003). The Mo quantity in the resins was

deliberated from the difference between initial and equilibrium concentrations of the molybdate ions in solution (Kononova et al., 2003). The Mo was desorbed by 15% aqueous ammonia solution (Kononova et al., 2003). As a result, ammonium molybdate solution (72-155 g L⁻¹ Mo) was acquired (Kononova et al., 2003). After the performed filtration Mo desorption degree was 99.9% (Kononova et al., 2003).

In other studies, Nguyen et al. (2013a,b; 2014) tried separation of Mo and V from a HCl and H₂SO₄ solution containing 0.2 g L⁻¹ Mo (VI) and 0.2 g L⁻¹ V (V) using ion exchange. The loading behavior of the two metals from moderate to strong acid solution was investigated using cationic (Diphonix®) and anionic (AG1-x8) resins (Nguyen and Lee, 2013a). The highest separation factor was obtained by ion exchange with AG1-x8 from the H₂SO₄ acid solution at pH 1.2, where no V was loaded (Nguyen and Lee, 2013a). The loading capacity of AG1-x8 for Mo from the H₂SO₄ solution at pH 1.2 was 176 mg g⁻¹ (Nguyen and Lee, 2013a). Continuous column experiments demonstrated complete separation of the metals by selectively loading Mo from the feed (Nguyen and Lee, 2013a).

2.5.4. Solvent extraction

A considerable effort has been made to recover Mo and V from aqueous solutions by solvent extraction using various extractants such as alamine® 336 (Lozano and Godinez, 2003; Miura et al., 2001; Sahu et al., 2013), alamine® 304 (Parhi et al., 2011), alamine® 308 (Sahu et al., 2013; Zeng and Cheng, 2010), trialkylamine (Banda et al., 2012), tributyl phosphate (TBP) and tris (2-ethylhexyl) amine (TEHA) (Banda et al., 2013b), LIX® (Guan et al., 2012), Cyanex 272 (Park et al., 2007), tri-alkyl phosphine oxide (TRPO) and tributyl phosphate (TBP) (Guan et al., 2012). A number of investigations indicated that Mo could be extracted selectively from an aqueous solution containing various other metals by chelating the extractants such as LIX® 63 (solvent extraction reagent, water insoluble 5,8-diethyl-7-hydroxy-dodecan-6-oxime) at low and high acidities (Barik et al., 2014; Mishra et al., 2010; Park et al., 2010; Sahu et al., 2013; Zhang et al., 1996).

Parhi et al. (2011) showed that complete extraction and recovery of Mo as MoO₃ with a purity close to 100% was possible from the spent catalyst leach solution by using 10% (v/v) of Alamine® 304-1 in kerosene at pH 2.0 (Banda et al., 2012). In another study (Zeng and Cheng, 2010), the separation and recovery of Mo and Co from the synthetically prepared chloride leach

liquors of petroleum refining catalyst has been tested by using trioctylphosphine oxide (TOPO) and Alamine® 308 as extractants. The synthetically prepared leach liquor contained Mo (394 mg L^{-1}), Al (1782 mg L^{-1}) and Co (119 mg L^{-1}) in 3 M HCl (Zeng and Cheng, 2010). The separation of Mo from Co and Al was achieved with 0.05 M TOPO and selective recovery of Mo was attained with a combination of 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$ (Zeng and Cheng, 2010). Mo recovery of close to 100% was obtained from the synthetic chloride leach liquors (Kislik, 2012).

Barik et al. (2014) studied leachates acquired by the acid leaching of spent HDS catalysts (containing 10.7 g L^{-1} Mo, 2.4 g L^{-1} Co and 3.8 g L^{-1} Al) for the separation and recovery of Mo (VI) utilizing solvent extraction by LIX® 973 N. Extraction of Mo (VI) increased from 13.9 to 96.7% with an increase in the extractant concentration from 2.5 to 30.0% (v/v) using 30% LIX® 973 N in kerosene with feed pH 1.0 and a phase ratio of organic to aqueous (O:A) ratio of 1:1 (Barik et al., 2014). The McCabe-Thiele plot for Mo (VI) extraction with 30% LIX® 973 N illustrated 2-stages at a 2:3 (O:A) phase ratio and the loaded organic contained 16.0 g L^{-1} Mo (VI) demonstrating complete (99.9%) extraction (Barik et al., 2014). Stripping of Mo (VI) from the loaded organic phase was carried out with different $(\text{NH}_4)_2\text{CO}_3$ concentrations and resulted in a maximum stripping efficiency of 98.5% (Barik et al., 2014).

The baking-leaching-solvent extraction process was investigated (Park et al., 2012), to recover Mo from waste petroleum catalyst. With optimal baking conditions (30°C , 1.2 stoichiometric H_2SO_4 and baking time 1 h), and low acid leaching conditions (95°C , 2% (v/v) H_2SO_4 , pulp density 5% (w/v) and leaching time 30 min), nearly 96% Mo was dissolved (Park et al., 2012). Obtained leachate was further subjected to the solvent extraction of Mo (VI) by LIX® 84-I, followed by aluminum using Na-Cyanex 272 (Park et al., 2012). A quantitative extraction of Mo (VI) was obtained in 2-stage at an A:O ratio of 1:1 with 40% LIX® 84-I and 2-stages at a 1:1 phase ratio with 60% neutralized Cyanex 272, respectively (Park et al., 2012). By using 20% NH_4OH , Mo (VI) concentration in the strip solution were enhanced up to 1.5 times and 3 times when using two and three stages, respectively (Park et al., 2012).

A detailed study on Mo and V separation of from spent catalyst leach solution (composed of 7.2% MoO_3 , 1.7% V_2O_5 , 3.7% NiO, 54.3% Al_2O_3 and 2.3% SiO_2) was performed by Sahu et al. (2013). The catalyst roasted under oxidizing atmosphere at a temperature of about 550°C and leaching in diluted sulphuric acid to solubilize Mo, V, Ni and part of the Al (Sahu et al., 2013).

Metals from the leach solution were separated by solvent extraction using alamine® 304 (Sahu et al., 2013). Different parameters such as initial pH of the aqueous feed, organic to aqueous ratio (O:A) and solvent concentration were optimized until almost complete extraction and recoveries of 99.7% and 99.2% were obtained for Mo and V, respectively (Sahu et al., 2013).

2.5.5. Evaluation of recovery of molybdenum from spent catalysts

Precipitation, adsorption, ion exchange and solvent extraction are the commonly applied technologies for Mo recovery and purification from spent catalyst leach solutions (Banda et al., 2012; Marafi and Stanislaus 2008a,b; Zeng and Cheng, 2009a,b). The use of traditional recovery approaches, such as precipitation and adsorption, offers simple operations and good Mo recovery (more than 90%), but high purities of Mo are very hard to achieve by these technologies (Pagnanelli et al., 2011). Ion exchange and solvent extraction, offer a useful means for almost complete recovery of high purity Mo. However, these methods are very expensive and their scale of application in industry is limited (Kononova et al., 2003; Zeng and Cheng, 2010). Among all these techniques, solvent extraction is one that is mostly used in hydrometallurgy for commercial production of high purity metals (Zeng and Cheng, 2009a,b).

2.6. Conclusion

In the presented review various methods of leaching, bioleaching and recovery of Mo from spent catalysts are summarized. This chapter gives better understanding of the alternatives for leaching and recovery of Mo from spent catalysts and the gained knowledge will allow more informed decision making when it comes to handling of spent catalysts. The summarized results display that the Mo leaching and recovery efficiency utilizing various methods is similar. Thus, it may not be straightforward to determine a method of choice. Also, material requirements on the design and construction of equipment used for the leaching and recovery are rather different. Fluctuations in the market prices for the Mo and its concentration in the spent catalysts are important factors which influence the economic viability of metal recovery from spent catalysts. Therefore, future studies should be more focused on the assessment of the Mo speciation in spent catalysts which can indicate the ease of its leachability and recovery from the spent catalysts and help better decision making in term of a technique of choice.

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CHAPTER 3

Mineralogy and metals speciation in Mo rich mineral sludges generated at a metal recycling plant

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Chapter 3

In France, more than 250 million metric tons of sludges need to be treated each year. These sludges are either dumped on the landfills or reused as secondary resources in order to preserve natural resources. A large portions of these sludges are mineral sludges, originating from metal recycling plants. In order to estimate their metal recovery potential, these mineral sludges were characterized. Four types of mineral sludge samples were collected from a metal recycling plant (3 from the recycling plant storage areas (bulk storage, barrel storage and storage shed) and 1 from the collection basin). The sludges were characterized, wherein the Mo, Ni, Cr, Co, Zn and W content and speciation were quantified. The samples had pH values between 5.9 and 10.3 with organic matter contents varying between 6.3% (storage shed) and 29.5% (bulk storage) (at 500°C), and between 4.6% (storage shed) and 42.6% (bulk storage) (900°C). Based on their leaching properties, the four mineral sludge samples (in the case of Mo) and the bulk storage sludge (in the case of Ni and Zn) were classified as potentially hazardous regarding the EN 12457-1 and EN 12457-2 method. Mineralogical results reveal that both bulk storage and the storage shed give the highest contributions to the metal content of the collection basin sample. Sequential extraction of the collection basin samples indicated that Mo is bound to the oxidizable and residual fraction, while Ni, Cr and Co were bound to the residual fraction, and Zn to the soluble acid fraction, respectively. W tends to be equally distributed among all extracted fractions. A strong correlation existed between Mo and Co, as well as between Ni, Zn and Cr, respectively.

3.1. Introduction

Significant volumes of industrial mineral wastes, such as sludges, are produced yearly around the world. In France, more than 250 million metric tons of overall sludges need to be treated each year (Veolia, 2013). A large amounts of these sludges are mineral sludges generated at a metal recycling plants, oil and gas industries, etc. As an example, oil production processes generate an estimated 200,000 metric tons of mineral sludges each year (U.S. EPA, 1993). Utilization of industrial waste sludges as a secondary resource for metal recovery is an appropriate solution of how to manage the waste sludge generation effectively in order to meet stringent environmental quality standards, and at the same time, to sustain the metal reserves for our future generations (Gholami et al., 2012).

The rapid proliferation in the demand for metals such as molybdenum, nickel, tungsten and vanadium (attributed to the world's increasing use of metals), implies that primary mineral supplies are falling short of meeting demand, thus resulting in an increased utilization of secondary mineral sources (Sayilgan et al., 2009a,b; Zeng and Cheng, 2009a). A wide array of recycling processes, such as pyro-metallurgical and hydro-metallurgical processes have been applied to recover these metals from various waste materials (Marafi and Stanislaus, 2008; Zeng and Cheng, 2009a; Zeng and Cheng, 2009b; Pagnanelli et al., 2011).

Although the recycling process(es) have been shown to be successful in handling metal-laden or mineral-laden sludges, recycling plants may still encounter specific problems such as rainfall induced runoff of metal-laden particles from the plant site or storage areas. Such metal contaminated runoff water is usually collected *via* an adequate piping network and channeled to a collection reservoir for processing at a wastewater treatment plant prior to discharge. Along with the runoff particles, dusts are also transported and tend to form a mineral sludge containing various inorganic contaminants. The recycling plant(s) are forced to choose between two commonly practiced options: ultimate sludge disposal (a relatively high-cost option) or the recovery of metals from the sludge (yielding revenue from the economic value of the recovered metals).

The prime focus of this research was on the elements Mo, Ni, Cr, Co, Zn and W, which are present in mineral sludges and are valuable to the recycling plant(s) given their increased demand and potential future shortfall within primary sources. This research was conducted on mineral sludge samples collected from a recycling plant designed primarily for catalyst, metal oxide and battery recycling. The main aim of this research was to understand the mineralogy and metal recovery potential of mineral sludges generated at a recycling plant. The specific objectives were targeted towards: (i) general characterization of mineral sludge samples, (ii) determination of their total metal content, (iii) metal fractionation of mineral sludge samples, (iv) identification of samples mineralogy, and (v) leaching test of the mineral sludges.

3.2. Materials and methods

3.2.1. Site description and sample collection

In the recycling plant, rainfall runoff is drained *via* a network into the collection reservoir and then processed at the wastewater treatment plant prior to discharge into the adjacent stream.

Along with runoff particles, dust particles were also transported, forming a thick mineral-rich sludge that contains various concentrations and proportions of inorganic contaminants. For the purpose of this research, 4 mineral sludge samples were collected from the recycling plant site and storage areas (Figure 3.1). This collection step was performed over a 2-week period (April 12th to April 26th 2012). One mineral sludge sample was collected from the rainwater drainage basin covering the entire recycling plant area, while three other samples were collected in a nearby barrel storage area, bulk storage area and storage shed area, respectively.

The sample collection protocol involved partial obstruction of the network channels to create a sedimentation zone (for the collection basin sample) or the placement of a trap in the water collection system manhole (for the barrel storage, bulk storage and storage shed areas). The samples were air-dried and sieved on a 2 mm mesh in accordance with the ISO 11464 (2006) standards.

All experimental protocols were conducted at least twice using three replicates, and all chemicals used in this study were of analytical grade. The solutions were prepared in ultra-pure water (Milli-Q system: resistivity = 18.2 M Ω .cm, Total Organic Carbon \leq 10 $\mu\text{g L}^{-1}$). All glassware and containers were previously rinsed in 10% (v/v) nitric acid solution.

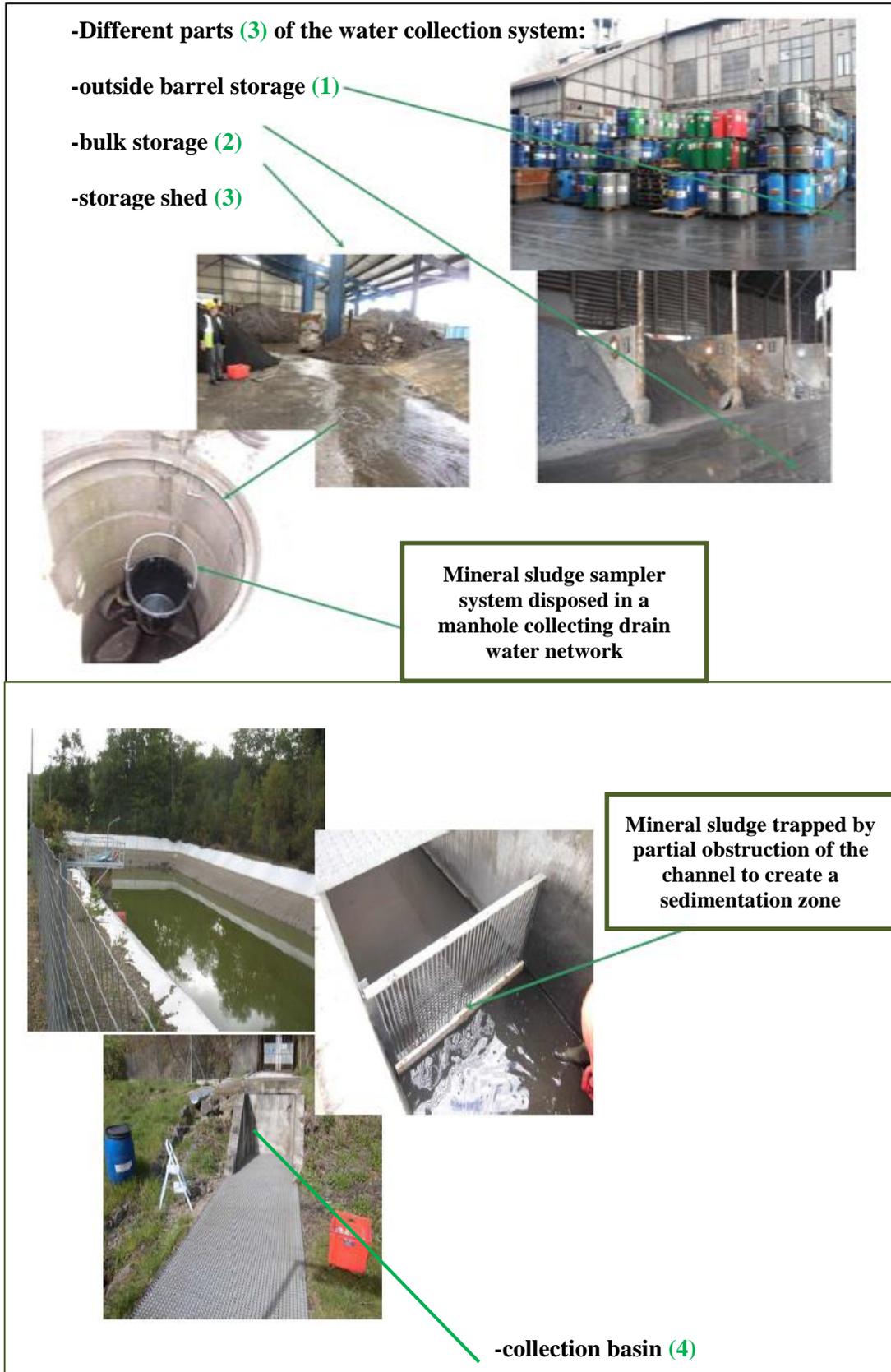


Figure 3.1. Sampling locations and collection protocol of recycling plant mineral sludge samples.

3.2.2. General characteristics of the samples

3.2.2.1. pH

The pH of the mineral sludge samples was measured according to the EN ISO 3696 (1997) standard procedure, which requires suspending 10 g of the dry mineral sludge sample in 50 mL volume of ultra-pure water. Test portions were placed in polyethylene bottles and suspensions were shaken for 1 h using an orbital shaker (IKA Labortechnik K550 Digital). The suspensions were then filtered using 0.45 µm Whatman acetate filters, and the filtrate pH was measured using a Crison GLP 22 pH-meter (previously calibrated with two buffers, pH 4.0 and 7.0, respectively, at 20°C).

3.2.2.2. Loss on ignition (LOI) tests

The LOI (TC WI, 2003) analyses were carried out in a Protistor 16 A furnace with a thermostatic temperature control at 500°C (for 4 h) and 900°C (for 16 h), respectively. Special care was taken to ensure that no humidity remained in the samples before the start of individual experiments. The empty crucibles and mineral sludge samples were dried overnight at 105°C before weighing. The sample weights used for LOI testing were approximately 10 g. The weight loss on ignition provided a rough approximation of the amounts of total organic matter (at 500°C) and carbonates (at 900°C) present in the solid fraction of the sample (APHA, 2005).

3.2.2.3. Particle size separation and distribution of the collection basin sludge sample

Mineral sludge samples from the collection basin (~400 g) were sieved, yielding the following size fractionation: < 200 µm, 200 - 400 µm, 400 - 630 µm, 630 - 800 µm, 800 µm - 1 mm, 1 - 1.6 mm, and < 2 mm. The sample weights in each fraction were determined after sieving.

3.2.3. Total metal content (TMC) of the mineral sludge samples

In order to perform total metal analysis, ~0.1 g of dry sludge (using three replicates from each sample) was digested in a microwave system (Anton Paar 3000), containing HNO₃ (5 mL), HCl (2 mL) and HF (1 mL). A 1 hour digestion (power: 1,600 W, temperature: 210°C, pressure: 40 bar) was followed by free fluoride ion complexation (power: 900 W, temperature: 210°C, pressure: 40 bar) with saturated boric acid solution (6 mL). The samples were subsequently

transferred into 50 mL flasks and filled with ultra-pure water. Each sample was filtered (0.45 μm Whatman acetate filters) and stored at 4°C prior to TMC analysis.

3.2.4. Sample mineralogy

3.2.4.1. X-ray diffraction (XRD)

Mineral sludge samples were powdered to perform XRD analysis. X-ray diffraction patterns were obtained using a Bruker-AXS D 5005 powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda_{\text{K}\alpha} = 0.154186 \text{ nm}$) and a graphite back-monochromator. These patterns were determined with a dwell time of 2 s and 2θ step of 0.04° .

3.2.4.2. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS)

Mineral sludge samples (size < 2 mm) were placed on microscopic glass slides, covered with resin and polished prior to conducting the SEM analysis. Sample morphology was investigated using scanning electron micrographs (SEM, Philips XL 30, 20 kV, SERMIEL - Université de Limoges, France) coupled to an Energy Dispersive X-ray Spectroscopy (EDS) device.

3.2.5. Sequential extractions (SE)

Table 3.1 lists the experimental parameters used for the sequential extraction of metals (Perez-Cid *et al.*, 1998). The extraction solutions were prepared from high-quality reagents by dissolving them in ultra-pure water. The samples were treated in 40 mL capacity polyethylene tubes, by placing 0.25 g of mineral sludge sample (two replicates from each sample) with a particle size < 2 mm. Metals were extracted using an ultrasonic probe (Bandelin GM 70) by applying a 20 W sonication power for a different time (see Table 3.1) in each sequential extraction step. The extracts were centrifuged at $\times 3000 \text{ g}$ for 15 min (Jouan KR 22i) and transferred into 50 mL flasks filled with ultra-pure water. Each sample was filtered (0.45 μm Whatman filters) and then stored at 4°C prior to analysis.

Table 3.1. Experimental conditions adopted in an ultrasound accelerated sequential extraction procedure for metal speciation in mineral sludge (Perez-Cid et al., 1998).

Fraction	Extraction agent	Extraction conditions	
		Ultrasound time	Power
F1: Acid soluble	20 mL HOAc (0.11 mol L ⁻¹)	7 min	20 W
F2: Reducible	20 mL NH ₂ OH.HCl (0.1 mol L ⁻¹ , pH = 2)	7 min	20 W
F3: Oxidizable	10 mL H ₂ O ₂ (30%, pH = 2), followed by 25 mL NH ₄ OAc (1 mol L ⁻¹ , pH = 2)	2 min and 6 min	20 W
F4: Residual	HNO ₃ /HCl/HF, in 5:2:1 ratio	40 min	1600 W microwave-assisted digestion

3.2.6. Leaching of the mineral sludges

The leaching properties of the mineral sludge samples were assessed according to standard procedures in order to classify the various mineral sludge samples as inert, hazardous or non-hazardous. Compliance with EN 12457-1 and -2 standards (European Landfill legislation, EU Council, 2003) and TCLP (Environmental Protection Agency, US-EPA, 1999) tests were conducted under the following conditions: i. Compliance 2 L kg⁻¹, pH free, 250 rpm, 24 h; ii. Compliance 10 L kg⁻¹, pH free, 250 rpm, 24 h; iii. TCLP 20 L kg⁻¹, pH 4.9, 100 rpm, 18 h.

All experiments were performed in batch systems (150 mL polyethylene bottles) under continuous stirring on an orbital shaker (IKA Labortechnik K550 Digital, 250 rpm) at ambient temperature (21° ± 1°C). After leaching, each sample was filtered (0.45 µm Whatman filters), acidified to pH 2.0 (HNO₃) and then stored at 4°C prior to analysis.

3.2.7. Analytical and quality control

The total metal content in the mineral sludge extracts were analyzed using flame atomic absorption spectrometry (Varian SpectrAA 220). Blanks were included in each experimental and analytical run. During analytical runs, after every ten samples, a standard sample was analyzed to check the deviations of the standards used. When the metal concentrations from sequential extractions were measured, the matrix effect was taken into account (*i.e.* standards prepared using extraction solutions instead of ultra-pure water). In addition to the determination of total metal concentrations of the six afore-mentioned primary elements, the total metal analysis on mineral sludge samples was also performed by ACME Analytical Laboratories in targeting metals such as Mn, V, Al, Fe, Na and Ca. The results were subjected to statistical analysis, using the statistical tool-pack from MS-Excel 2007. A correlation analyses were carried out using Pearson's correlation coefficients, while multiple regression analysis was carried out using the same tool-pack in order to determine the level of statistical significance (*p* value).

3.3. Results

3.3.1. Origin of metals contained in the mineral sludge samples

Table 3.2 presents the main elements (in %) contained in the various waste products stored at the recycling plant. Metals contained in the mineral sludge samples originate from various materials stored in designated areas at the recycling plant: spent catalysts, metal oxides, metal hydroxide muds, batteries and accumulators, and an array of co-products used for recycling processes.

Metal oxides account for nearly 40%, spent catalysts nearly 38%, batteries and accumulators almost 16%, metal hydroxide mud around 2% and recycling co-products around 4% (in weight terms) of the total quantity of mineral wastes processed by the recycling plant. The bulk storage area constitutes the main *on-site* location for storing spent catalysts, metal oxides, metal hydroxide mud and recycling co-products. A portion of the metal oxides is also stored in the shed area, while batteries and accumulators are mainly housed in the barrel storage area.

Mineralogy and metals speciation in Mo rich mineral sludges generated at a metal recycling plant

Table 3.2. Main elements contained in the various waste products stored at the recycling plant.

Element (%)	Catalysts (38%)	Metal oxides (40%)	Hydroxide muds (2%)	Batteries and accumulators (16%)
Ni	0-20	0-10	0-20	-
Co	0-10	0-10	0-10	-
Mo	0-20	0-15	0-25	-
Al	0-40	0-10	0-40	-
Si	0-1	0-10	0-30	-
V	0-30	-	-	-
Mn	-	-	-	1-30
Fe	-	40-85	0-10	2-25
Cr	-	0-10	0-10	-
Zn	-	-	0-25	10-45
Ca	-	-	0-40	-
Mg	-	-	0-20	-
K	-	-	-	0-20
C	-	-	-	0-20
S	0-15	-	-	-
Cl	-	-	-	0-13

3.3.2. General samples characteristics

3.3.2.1. pH

The pH of mineral sludge samples (Table 3.3) indicates values of 5.9 (bulk storage), 7.8 (barrel storage), 8.4 (collection basin), and 10.3 (storage shed).

Table 3.3. Total metal concentrations (in mg g⁻¹), Loss on Ignition (%) and pH for the mineral sludge samples (n = 3).

Analyte	Mo	Ni	Zn	Cr	Co	W	LOI (500°C)	LOI (900°C)	pH
Barrel storage area	13.2±0.4	13.2±0.6	11.5±0.3	6.5±0.2	2.6±0.1	11.1±0.3	13.8±0.2	16.8±0.2	7.8
Bulk storage area	52.4±0.8	8.9±0.3	1.3±0.1	1.6±0.2	10.4±0.1	3.2±0.1	29.5±0.7	42.6±0.4	5.9
Storage shed area	7.6±0.5	21.6±0.7	13.6±0.2	23.9±0.5	2.4±0.1	1.3±0.1	6.3±0.1	4.6±0.3	10.3
Collection basin	11.9±0.1	17.5±0.2	7.2±0.2	11.2±0.1	2.9±0.4	6.6±0.1	8.4±0.2	8.6±0.2	8.4
Allowable limits*	0.075	0.42	7.5	3.0	4.3	-			

* Maximum metal concentrations in industrial waste or sludge (adapted from U.S. EPA, 1993).

† No allowable limits available

3.3.2.2. Loss on ignition (LOI)

A LOI was performed at 500°C for 4 h and again at 900°C for 16 h (Table 3.3). The results obtained show that values for the volatile component of mineral sludge samples vary over a wide range: between 6.3% (storage shed) and 29.5% (bulk storage) for the 500°C LOI, and between 4.6% (storage shed) and 42.6% (bulk storage) for the 900°C LOI. The statistical analysis reveals, however, no statistical differences between the LOI performed at 500°C and 900°C (Pearson's correlation coefficient = 0.99, *p* one-tail = 0.18, *p* two-tail = 0.36).

3.3.2.3. Particle size separation and distribution of the collection basin sludge sample

A sieving analysis of the collection basin sludge sample yielded the following mass distribution (in %) among the various sieving fractions: 17.2% (< 200 µm), 20.2% (200-400 µm), 14.6% (400-630 µm), 11.6% (630-800 µm), 12% (800 µm - 1 mm), 20.7% (1-1.6 mm), and 3.7% (1.6-2 mm). These percentages show that our sample is distributed among all size fractions, with < 200 µm, 200 - 400 µm, 400 - 630 µm and 1 - 1.6 mm containing the highest main sample percentages. The coarse fraction excluded during sample pretreatment (> 2 mm) was small (just a few percent) and contained among other things wood, plastic, iron and plant residues.

3.3.3. Total metal content (TMC) of the mineral sludge samples

The total metal content in the mineral sludge samples is listed in Table 3.3. The highest concentrations for Mo (possibly from Doped alumina) and Co were found in the bulk storage sludge at a concentration of 52.4 mg g⁻¹ and 10.4 mg g⁻¹, respectively; while their lowest

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concentrations occurred in the storage shed sludge with 7.6 mg g^{-1} and 2.4 mg g^{-1} , respectively. In contrast, the lowest Ni, Zn and Cr concentrations were found in the bulk storage sample with 8.9, 1.3 and 1.6 mg g^{-1} , respectively. The highest concentrations of these three metals were identified in storage shed sludge with 21.6, 13.6 and 23.9 mg g^{-1} , respectively. The lowest concentration of W was measured in the storage shed sample (1.3 mg g^{-1}), while the highest concentration was found in the barrel storage (11.1 mg g^{-1}).

The total metal analysis on mineral sludge samples shows that this sludge contains significant amounts of other metals as well (Table 3.4), with the elements Mn, V, Al, Fe, Na and Ca being present in high concentrations. The elements were found to be present in mineral form during the solid characterization (Table 3.6).

Table 3.4. Total metal contents (mg g^{-1}) in the 4 mineral sludge samples, tested using *aqua regia* digestion and ICP-MS analysis. The standard deviation varies between 2 and 5% depending on the element considered.

Analyte	Cu	Pb	Mn	As	Cd	V	La	Ba	Al	Na	K	Fe	Ca
Barrel storage	1.3	0.5	3.9	0.2	0.5	0.6	0.2	0.4	20	0.9	0.7	70	50
Bulk storage	0.2	0.7	0.9	0.1	0.7	1	0.1	0.2	30	0.7	0.4	20	20
Storage shed	0.5	0.1	6.1	0.04	0.3	0.5	1	0.5	50	11.5	0.8	90	110
Collection basin	0.6	0.2	3.8	0.07	0.2	0.9	0.7	0.3	60	1.6	0.9	50	100

The collection basin samples were sieved over the various sizes and the total metal concentrations were determined in every sieved fraction (Table 3.5). The highest metal concentrations were present mostly in the fine and 1 - 1.6 mm fractions, while the larger 1.6 - 2 mm fraction contains far less metals.

Table 3.5. Average ($n = 3$) of total metal contents (mg g^{-1}), along with standard deviations, for the collection basin mineral sludge sample relative to particle size distribution fractions.

Analyte	Mo	Ni	Zn	Cr	Co	W
< 200 μm	3.0 \pm 0.8	6.3 \pm 0.7	2.9 \pm 0.4	3.9 \pm 0.7	1.3 \pm 0.2	1.7 \pm 0.1
200-400 μm	2.0 \pm 0.7	4.2 \pm 0.5	1.9 \pm 0.5	1.8 \pm 0.2	0.6 \pm 0.0	1.2 \pm 0.1
400-630 μm	1.5 \pm 0.1	3.3 \pm 0.3	0.9 \pm 0.1	1.9 \pm 0.2	0.3 \pm 0.1	0.7 \pm 0.2
630-800 μm	1.4 \pm 0.2	1.1 \pm 0.0	0.4 \pm 0.4	0.9 \pm 0.9	0.2 \pm 0.2	0.2 \pm 0.2
800 μm - 1 mm	1.2 \pm 0.3	0.5 \pm 0.1	0.2 \pm 0.1	0.7 \pm 0.4	0.1 \pm 0.0	0.1 \pm 0.1
1-1.6 mm	2.8 \pm 0.2	1.0 \pm 0.1	0.8 \pm 0.1	1.4 \pm 0.3	0.3 \pm 0.4	1.3 \pm 0.3
1.6-2 mm	0.5 \pm 0.2	0.2 \pm 0.2	0.1 \pm 0.1	0.3 \pm 0.4	0.1 \pm 0.0	0.1 \pm 0.4
Sum (sieved collection basin sample)	12.5 \pm 0.4	16.5 \pm 0.3	7.3 \pm 0.2	10.8 \pm 0.4	2.9 \pm 0.1	5.3 \pm 0.2
"Raw" collection basin sample	11.9 \pm 0.1	17.5 \pm 0.2	7.2 \pm 0.2	11.2 \pm 0.1	2.9 \pm 0.4	6.6 \pm 0.1

3.3.4. Samples mineralogy

Table 3.6 demonstrates that each mineral sludge sample exhibits a somewhat different crystalline mineral phase composition. The relative proportion of mineralogical phases was derived directly from XRD and SEM-EDS investigations according to their frequency of occurrence for a given surface. A number of similarities, however, have helped to determine the mineral contribution of various recycling plant sampling sites to the mineral composition in the collection basin sample. This way, it was determined which sampling site gave the largest runoff of mineral sludges to the collection basin sample.

All three samples (barrel storage, bulk storage and storage shed) contribute with Hematite and Chlorite to the mineral content in the collection basin sample. Fe-Zr-oxides, Quartz and Moissanite originate mainly from barrel storage and storage shed samples. Only bulk storage contributes to the collection basin sample with Doped alumina, Boehmite and Feldspar, while only barrel storage contributes with Ni-oxides and Mn-oxides.

Table 3.6. Major mineralogical phases, as detected in the studied mineral sludge samples. Components are classified according to their relative proportions from XRD and SEM-EDS investigations (the predominant elements are presented within brackets).

Barrel storage	Bulk storage	Storage shed	Collection basin
Fe-Zr-oxides (Fe, Zr)	Doped alumina (Mo, V, Zr)	Quartz (Si)	Fe-Zr-oxides (Fe, Zr)
Chromite (Fe, Cr)	Sulfate-Zr (S, Zr)	Moissanite (Si, C)	Doped alumina (Mo, V, Zr)
Quartz (Si)	Chromite (Fe, Cr)	Hematite (Fe)	Boehmite (Al)
Moissanite (Si, C)	Cumingtonite (Mg, Fe, Si)	Fe-Zr-oxides (Fe, Zr)	Hematite (Fe)
Zr-oxides (Zr)	Feldspar (Si, Al, K, Na, Ca)	Glass phases (Si, Fe, Ca, Mg)	Quartz (Si)
Glass phases (Si, Fe, Ca, Mg)	Glass phases (Si, Fe, Ca)	Chlorite (Cl)	Moissanite (Si, C)
Hematite (Fe)	Hematite (Fe)	Ti-oxides (Ti)	Ni-oxides (Ni)
Mn-oxides	Boehmite (Al)	Bustamite (Ca, Mn, Si)	Feldspar (Si, Al, K, Na, Ca)
Magnetite (Fe)	Chlorite (Cl)		Mn-oxides (Mn)
Chlorite (Cl)	Kalsilite (K, Al, Si)		Chlorite (Cl)
W-oxides (W)			
Carbonate (C)			
Ni-oxides (Ni)			
Ti-oxides (Ti)			
Scheelite (Ca, W)			
Trevorite (Ni, Fe)			
Mg-oxides (Mg)			

3.3.5. Sequential extractions (SE)

Sequential extraction of the collection basin mineral sludge sample indicated that Mo is present in the highest percentages in the oxidizable (45.1%) and residual (50.9%) extraction fractions (Figure 3.2d). On the other hand, Ni, Cr and Co are mainly extracted from the residual fraction (86.7, 96.2 and 78.6%, respectively), while Zn was found mostly bound to the acid-soluble fraction (55.5%). W is distributed across all fractions (acid soluble, reducible, oxidizable and residual), but in the highest percentage in the residual extraction fraction (41.6%). Bulk storage, barrel storage and storage shed minerals sludge samples (Figures 3.2a, 3.2b and 3.2c), have a similar distribution pattern across the sludge extraction fractions as the collection basin sample.

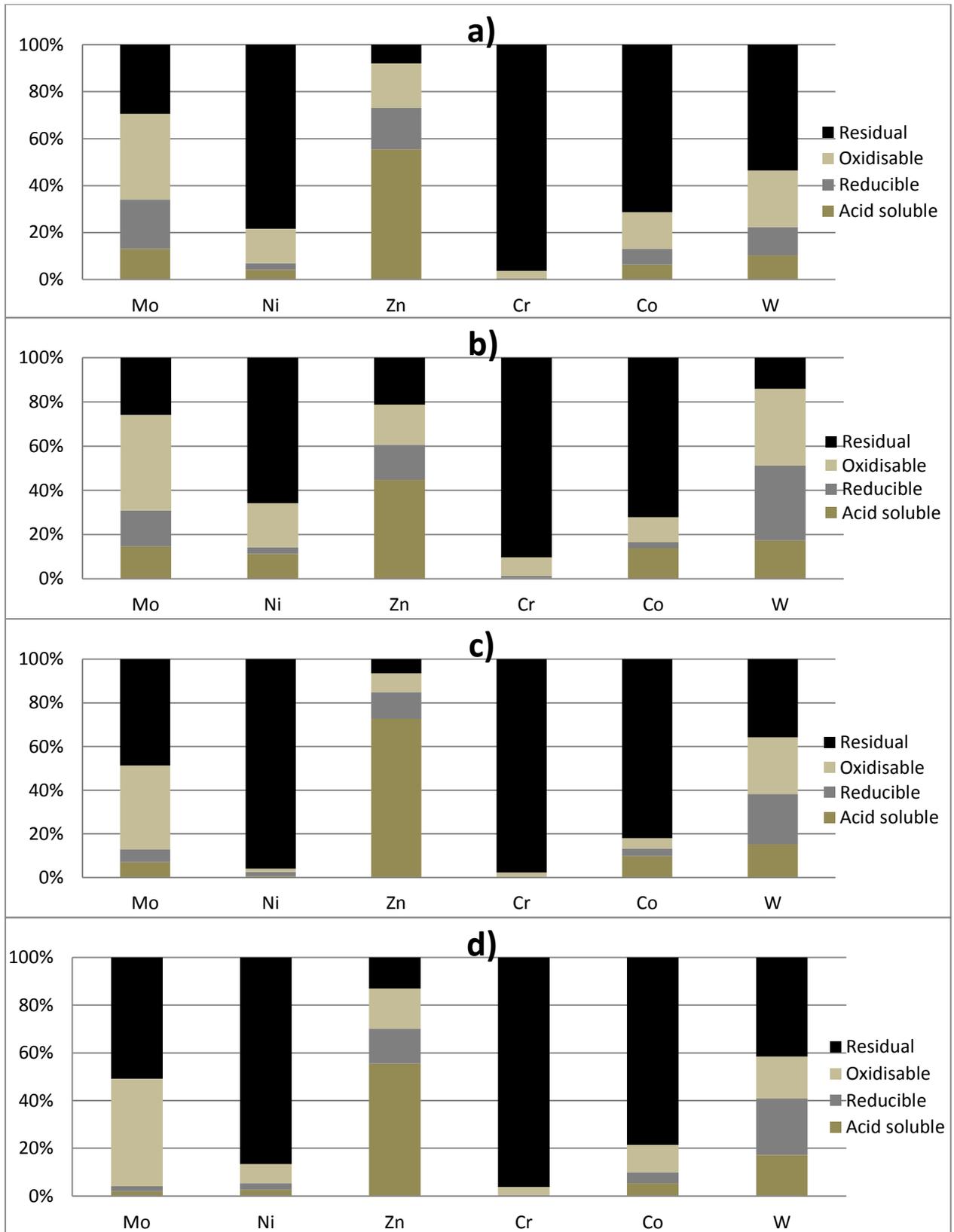


Figure 3.2. Metal fractionation by sequential extraction in the 4 mineral sludge samples (%): a) barrel storage; b) bulk storage; c) storage shed; and d) collection basin.

3.3.6. Leaching of the mineral sludges

The results from the leaching experiments were compared with the regulatory limits on acceptable waste at landfills for inert, non-hazardous and hazardous waste, along with the regulatory limits on Total Threshold Limit Concentrations (TTLC) (see Table 3.7).

Table 3.7. Experimental conditions and metal contents (in mg kg⁻¹) obtained from Compliance and TCLP tests for mineral sludge samples (with ultra-pure water leaching solution). Also displayed are the regulatory limits (mg kg⁻¹) on acceptable waste at landfills for inert, non-hazardous and hazardous wastes as well as the limits on Total Threshold Limit Concentrations (TTLC).

Experiments		Analyte	Mo	Ni	Zn	Cr	Co	W
Compliance tests	2 L kg ⁻¹ , 24 h, pH free, 250 rpm	Barrel storage	65.1	0.0	0.1	0.0	0.2	2.4
		Bulk storage	769	350	19.7	0.0	411	0.0
		Storage shed	299	0.0	0.0	0.0	0.4	4.9
		Collection basin	166	0.0	0.1	0.0	0.3	135
	10 L kg ⁻¹ , 24 h, pH free, 250 rpm	Barrel storage	95.8	0.0	0.1	0.0	0.1	0.0
		Bulk storage	708	204	16.7	0.0	314	8.7
		Storage shed	311	0.0	0.1	0.0	0.2	0.0
		Collection basin	49.8	0.0	0.1	0.0	0.3	59.5
TCLP test	20 L kg ⁻¹ , 18 h, pH 4.9, 100 rpm	Barrel storage	435	403	268	0.0	52.6	0.0
		Bulk storage	4096	2039	494	0.0	3149	208
		Storage shed	508	484	3007	0.0	121	0.0
		Collection basin	425	3971	3117	0.0	488	150
Regulatory limits	Inert waste	Compliance 2 L kg ⁻¹	0.3	0.2	2	0.2	-	-
		Compliance 10 L kg ⁻¹	0.5	0.4	4	0.5	-	-
	Non-hazardous waste	Compliance 2 L kg ⁻¹	5	5	25	4	-	-
		Compliance 10 L kg ⁻¹	10	10	50	10	-	-
	Hazardous waste	Compliance 2 L kg ⁻¹	20	20	90	25	-	-
		Compliance 10 L kg ⁻¹	30	40	200	70	-	-
	TTLC	TCLP 20 L kg ⁻¹	3500	2000	5000	2500	8000	-

LEGEND:

Inert waste

Not compared

Non-hazardous waste

Hazardous waste

Exceeds TTLC limits

Measured Mo concentrations indicate that all mineral sludge samples (barrel storage, bulk storage, storage shed and collection basin) contain hazardous waste since the concentrations of all samples exceed the landfill regulatory limits. Furthermore, when Mo concentrations are

compared with TTLC, findings show that bulk storage also exceeds the regulatory limits, with Mo concentration of 4096 mg kg^{-1} .

Both the Ni and Zn concentrations indicate that for the two compliance tests (2 L kg^{-1} and 10 L kg^{-1}), three samples (barrel storage, storage shed and collection basin) can be considered as inert waste. In contrast, the bulk storage sample is considered as a hazardous waste in the case of Ni ($2 \text{ L kg}^{-1} = 350 \text{ mg kg}^{-1}$; $10 \text{ L kg}^{-1} = 204 \text{ mg kg}^{-1}$) and non-hazardous for Zn ($2 \text{ L kg}^{-1} = 19.7 \text{ mg kg}^{-1}$; $10 \text{ L kg}^{-1} = 16.7 \text{ mg kg}^{-1}$). For the TCLP test on the other hand, all samples can be considered as hazardous since their concentrations exceed the regulatory limits. In comparison with TTLC regulations, all samples lie below the regulatory limits as regards to Zn, while Ni concentrations indicate that the sludge samples from bulk storage and the collection basin exceed regulatory limits (with Ni concentrations of 2039 mg kg^{-1} and 3971 mg kg^{-1} , respectively). Consequently, these Ni containing samples cannot be disposed at landfills without adequate treatment due to potential environmental impacts.

When assessing the concentrations of chromium (Cr), all mineral sludge samples can be considered as inert wastes given that the results of all samples lie below the regulatory threshold (for both landfill and TTLC). In the case of cobalt (Co) and tungsten (W), no regulatory limits are available.

3.4. Discussion

3.4.1. General characteristics of mineral sludge samples

Mineral sludge has often been considered as a non-reactive material due to the low solubility of their solid phases, *viz.* silicates, oxides, and glassy forms (Pareuil et al., 2010a). However, the release of metal elements from mineral sludges is governed by their physicochemical properties, *i.e.* dissolution of metal-bearing silicates and glass, precipitation of secondary phases, and sulfide oxidation (Parsons et al., 2001). This dissolution process is capable of polluting the surrounding compartments of a conventional landfill, such as soils, groundwater, sediments, drainage networks and reservoirs (Pareuil et al., 2010b). The origin of metals in mineral sludge displays a correlation with the mineral sludge characteristics. Due to the complex composition of this mineral sludge (not strictly a catalyst sludge or hydroxide sludge, but rather a combination of both), our results are not easily comparable with those of other studies as their characterization was performed on a raw spent catalyst material (Zeng and Cheng, 2009a,b).

Looking at the physicochemical properties of the mineral sludge samples investigated, their wide range of pH values (greater than 4 pH-units) may be explained by the fact that each sampling site contains a different composition of stored material, thus generating differences in pH. The different material compositions are confirmed by the presence of different metal concentrations (Table 3.3) and crystalline mineral phases in the sludge samples investigated (Table 3.6).

The sludges LOI can be explained by the presence of organic compounds, sulfur and activated carbon, as well as by the instability of certain mineral phases (*e.g.* carbonates) (Capobianco and Carpenter, 1989). The fact that the runoff water, along with domestic wastewater from the recycling plant, is drained into the collection reservoir is causing an increase of the organic content of the mineral sludges. When comparing the LOI performed at 500 and 900°C, the differences in results obtained are very low, except for the bulk storage sludge. This difference may be explained by the variety in material composition and the fact that bulk storage sludge contains some minerals not present in the other sludge samples, such as Cummingtonite ((Mg,Fe)₇Si₈O₂₂(OH)₂) and Kalsilite (KAlSiO₄) (Table 3.6), which can only be dissociated and evaporated at high temperatures like 900°C (Capobianco and Carpenter, 1989).

The mineralogical analysis (Table 3.6) shows that both the bulk storage and the storage shed areas contribute the most to the metal content present in the collection basin mineral sludge and that the main mineral contribution of Mo is coming from the bulk storage in the form of doped alumina. This is due to the fact that the bulk storage area and storage shed area are the main *on-site* locations (Section 3.3.1) for more than 80% of recycling plant materials (spent catalysts, metal oxides, metal hydroxide mud and recycling co-products).

Spent catalysts are typically composed of Al and Si with Co, Mo, Ni, V and W oxides. Following their use, these catalysts may contain additional elements, such as S, C, V, Ni and As (Barik et al., 2012; Pradhan et al., 2010, 2013; Lai et al., 2008). Metal oxides stem from metallic residues, which themselves mainly contain Fe, Co, Mo, Al, Si, Cr and Ni. Metal hydroxide mud is composed of a mixture of solid and metal oxide-bearing impurities, primarily composed of Ni, Co, Mo, Al, Si, Cr, Fe, Ca, Mg and Zn. Batteries and accumulators basically contain Fe, graphite carbon, Zn, Mg, K, Cl and Hg, while recycling co-products usually contain coke, activated carbon, alumina and slag.

The origin of metals in mineral sludge displays a correlation with sludge characterization. Due to the complex composition of this mineral sludge (not strictly a catalyst sludge or hydroxide sludge, but rather a combination of both), our results are not easily comparable with those of other studies as their characterization was performed on a raw spent catalyst material (Zeng and Cheng, 2009a,b).

3.4.2. Total metal content of mineral sludge samples

The total metal analysis results were compared with the regulatory limits used to determine the maximum permissible metal concentrations in industrial waste or sludge (Table 3.3, adapted from U.S. EPA, 1993). With respect to sludge regulations, our four samples exceed the permissible limits for Mo and Ni, which suggests that samples containing Mo and Ni might pose an environmental hazard if left untreated. Zinc exceeds regulatory limits in barrel storage and storage shed, while its concentration in the bulk storage (1.3 mg g^{-1}) and the collection basin (7.2 mg g^{-1}) does not surpass the regulatory limits. Chromium surpasses limits in all samples, except in the bulk storage sample (1.6 mg g^{-1}). Cobalt only fails to respect the limits in the bulk storage sludge, while the other three samples feature metal concentrations below the allowable limits. In the case of W, no regulatory limits are available. The highest W concentrations were found in the barrel storage (11.1 mg g^{-1}) and collection basin (6.6 mg g^{-1}) samples, which indicate that W in the collection basin sample probably originates from the barrel storage sludge. The latter was confirmed by the solid characterization of the mineral sludge samples, which showed that W-rich minerals (W-oxides and Scheelite) are present only in the barrel storage sample (Table 3.6).

3.4.3. Sequential extraction

Sequential extraction of mineral sludge samples provide detailed data on the potential mobility of metals in soils/sludges. Sequential extraction methods may provide useful information on the association of metals with different soil/sludge phases. In this study, the studied metals are mainly present in the residual extraction fraction of the mineral sludge samples (Figure 3.2), suggesting that leaching and recovery will require more energy demanding processes. In a study conducted by Aydin et al. (2012), the most abundant form of Mo in sludge samples was the sulfide fraction. Relative abundances of the remaining fractions followed the order: residual > reducible > oxidizable > exchangeable > carbonate > water soluble. In another study done by

Zemberyova et al. (2010), Mo was associated with the organic matter and sulfides fraction in the sludge.

When observing the figures obtained from the sequential extraction (Figure 3.2), the "fingerprints" of the minerals from the barrel storage and the bulk storage sludges seem similar, while on the other hand the "fingerprints" of sludges from the storage shed and collection basin were similar. The latter suggests that the storage shed might constitute the main source of collection basin mineral sludge. However, mineralogical data (Table 3.6) indicate that the bulk storage, storage shed and collection basin samples have a similar mineral composition. This implies that the bulk storage and storage shed together contribute to the formation of the collection basin mineral sludge.

When results from the sum of the SE fractions are compared with results from total metal concentrations, no significant differences (Pearson's correlation coefficient = 0.95, p one-tail = 0.13, p two-tail = 0.26) can be found for any of the measured metals. A correlation analysis reveals that Mo is highly correlated with Co, while Ni, Zn and Cr show a strong correlation between each other. One possible reason for this is the primary association of these metals in the recycled materials, *i.e.* significant amounts of CoMo or NiMo catalysts and batteries containing Ni and Zn are processed in the recycling plant.

3.4.4. Metal leaching of the mineral sludge samples

The presence of heavy metals in mineral-rich sludge, even at low concentrations, can cause detrimental effects on the ecosystem due to their accumulative behavior and phyto-toxicity effects (McGrath et al., 2010). The toxicity of any substance in sludge is determined by its bioavailability (Barik et al., 2012). The strength of binding in the case of cationic elements varies across sludges as a consequence of differences in sludge properties such as pH or cation exchange capacity (McGrath et al., 2010). In the case of anionic species, a key factor controlling their toxicity is the binding strength of the positively charged sludge components such as amorphous Fe and Al oxides and clays, because the partitioning of oxyanions towards the sludge solid phase from the sludge solution reduces both the bioavailability for mobilisation and the uptake by biota (Aydin et al., 2012). Besides sludge components, other important factors controlling the partitioning of metals/metalloids in sludge include the characteristics of the sludge solution and the speciation of elements in that solution (Zemberyova et al., 2010).

Solution pH, the presence of inorganic and organic ligands as well as other anions may also influence the metal bioavailability (McGrath et al., 2010).

In all cases, environmental toxicity and safety must be investigated to prevent damaging effects on the environment. The European Landfill legislation (EU Council, 2003) recommends EN 12457-1 (2002) and EN 12457-2 (2002) as standard procedures for metal-contaminated sludges and provides threshold values that allow classifying the solid material as either "inert", "non-hazardous" or "hazardous". The U.S. Environmental Protection Agency adopted the Toxicity Characteristic Leaching Procedure (TCLP) test (US-EPA, 1999), which makes use of a buffering solution in order to determine whether the waste quantities meet or exceed regulatory limits as well as to evaluate the potential risk of contamination by landfill waste (Lee and Pandey, 2012).

The fact that all our mineral sludge samples exceed the allowable landfill sludge regulations limits of Mo and Ni (Table 3.7) indicates that samples containing Mo and Ni might present a possible danger for the environment. Exposure of human beings to Mo and Ni concentrations above the trace level may occur in mining and refining operations and in the chemical and metallurgical industries. In checking for possible Mo and Ni toxicity, it is important to know where and in what form toxic effects may occur. As reported by Kabata-Pendias and Mukherjee (2007) in a study conducted on experimental animals some of the effects that Mo toxicity causes are loss of weight, harmful changes in the liver, kidneys, and bones as well as diminution of the strength of conditioned reflexes.

When taking into account the above considerations, the mineral sludge samples containing Mo and Ni cannot be discharged into landfills without prior treatment due to the damage that their high concentrations can potentially cause to the environment (Zeng and Cheng, 2009a,b). The use of this type of sludges, that are highly contaminated with metals, as a secondary resource for metal recovery could reduce the amount of the sludges that have to be yearly disposed on the landfills and at the same time reduce the costs of their disposal.

3.5. Conclusion

This work investigated the metal fractionation of the mineral sludge samples originating from a catalyst, metallic oxide and battery recycling plant to provide insight in the elemental concentration levels, mineral composition and metal recovery potential of these mineral sludges.

The investigated mineral sludge samples have a heterogeneous composition, reflecting the materials stored on-site. All mineral sludge samples exceed the allowable landfill sludge regulatory limits of Mo and Ni, indicating that uncontrolled disposal of these mineral sludges present a possible danger for the environment.

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CHAPTER 4

Acid extraction of molybdenum, nickel and cobalt from mineral sludge generated by rainfall water at a metal recycling plant

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Chapter 4

This study investigated the leaching yields of Mo, Ni and Co from a mineral sludge of a metal recycling plant generated by rainfalls. The investigated mineral sludge had a complex heterogeneous composition, consisting of particles of settled soil combined with the metal bearing particles (produced by catalysts, metallic oxides and battery recycling). The leaching potential of different leaching reagents (stand-alone strong acids (HNO₃ (68%), H₂SO₄ (98%) and HCl (36%)) and acid mixtures (*aqua regia* (nitric + hydrochloric (1:3)), nitric + sulfuric (1:1) and nitric + sulfuric + hydrochloric (2:1:1))) was investigated at changing operational parameters (solid - liquid (S/L) ratio, leaching time and temperature), in order to select the leaching reagent which achieves the highest metal leaching yields. Sulfuric acid (98% H₂SO₄) was found to be the leachant with the highest metal leaching potential. The optimal leaching conditions were a three stage successive leaching at 80 °C with a leaching time of 2 h and S/L ratio 0.25 g L⁻¹. Under these conditions, the achieved mineral sludge sample leaching yields were 85.5, 40.5 and 93.8% for Mo, Ni and Co, respectively. The higher metal leaching potential of H₂SO₄ in comparison with the other strong acids/acid mixtures is attributed to the fact that H₂SO₄ is a diacidic compound, thus it has more H⁺ ions, resulting in its stronger oxidising power and corrosiveness.

4.1. Introduction

Molybdenum (Mo), nickel (Ni) and cobalt (Co) are important metals for human activities and industry in general (Marafi et al., 2007). In order to meet the rapidly growing demands for these metals and their products, the metal industries have increased their production and output (Pradhan et al., 2013). In view of the anticipated shortage of primary resources for these metals in the near future, it is a prerequisite to exploit secondary resources (Marafi et al., 2007). Among the different secondary resources, spent catalysts discarded from industries are undoubtedly very important, due to the presence of inherent metals (Mo, Ni, Co, Al, V, W, Zn, Cr, Fe, etc.) (Marafi and Stanislaus, 2003; Silvy, 2004). Catalysts have the tendency to lose their activity with time by overheating, carbon and sulfur deposition and contamination with metals, and are ultimately discarded as waste (De Lima et al., 2005; Marafi and Stanislaus, 2008a). Waste catalysts are regarded as hazardous by the U.S. Environmental Protection Agency due to their metal content (U.S. EPA, 2003).

About 150 - 170 kilotons of exhausted catalysts are produced every year in the world (Marafi and Stanislaus, 2008b). Two alternatives can be considered for their treatment: proper preservation in order not to contaminate the environment (industrial waste collector, containers etc.) or recovery of metals with economic value (Bayat and Sari, 2010). The latter is often chosen as a prospective alternative because the valuable metals can be recovered and subsequently reused (Pradhan et al., 2010).

Different pyrometallurgical and hydrometallurgical processes have been developed to recover metals from metal containing wastes (Zeng and Cheng, 2009a,b). For pyrometallurgical processes, the gas emissions due to incineration at high temperatures ($> 600^{\circ}\text{C}$) and high energy demands are major drawbacks (Pagnanelli et al., 2011). On the other hand, hydrometallurgy processes, such as chemical leaching, have been widely applied for metals recovery due to their flexibility, environmentally-friendliness and energy-saving characteristics (Sayilgan et al., 2009).

Chemical leaching of metals is a process of extracting their minerals from a solid into the liquid phase using inorganic/organic leachants. This process is influenced by the mineral dissolution rates, desorption and complexation processes due to the effect of pH, temperature, pulp density (S/L), particle size and redox (Lai et al., 2008). Metals leaching from wastes is generally carried out by acidification of waste matrices (Bayat and Sari, 2010). Acid-leaching is usually applied to obtain high metal leaching yields because of its high oxidability (Lai et al., 2008). The process of acid-leaching involves the addition of strong inorganic acids to the waste followed by mixing. The waste pH is brought to 1.5 - 2.0; conditions under which many of the metals present in the waste could be solubilized (Bayat and Sari, 2010). Metal leaching is influenced by parameters such as type of leachant, particle size, presence of chelating agents, S/L ratio, temperature, contact time, stirring and pH. An optimal chelating agent displays a high leaching efficiency, a high selectivity for the target metal, a high solubility and a high thermodynamic stability of the formed complex (De Souza Pereira et al., 2011).

The attempts of using a variety of leaching reagents such as H_2SO_4 (Barik et al., 2012b; Kim et al., 2009a,b), HNO_3 (Khoshnevisan et al., 2012; Smirnov et al., 2010), HCl (Banda et al., 2013) and chemical acid mixtures (Barik et al., 2012a; Lai et al., 2008) to leach out metals from spent catalysts have been developed one after another. Leaching of heavy metals has been also investigated in very similar matrices, for example in industrial galvanic sludge (Świerk et al.,

2007). However, the main focus of their study was on Cr, Cu and Ni leaching, in comparison with our study where we focus on the leaching potential of Mo, Ni and Co.

Our investigated mineral sludge had a complex heterogeneous composition, consisting of particles of settled soil combined with the particles of metals (produced by catalysts, metallic oxides and batteries recycling). The study area of this research, *i.e.* metal recycling plant, generates metal-laden particles of rainfall induced runoff from the plant site and storage areas. This metal contaminated runoff water is collected *via* an adequate piping network and channeled to a collection reservoir. Along with the runoff particles, dusts are also transported and form a mineral sludge containing various inorganic contaminants. The recycling plant is forced to choose between two commonly practiced options: ultimate sludge disposal (a relatively high-cost option due to high metal concentrations) or the recovery of metals from the mineral sludge (yielding revenue from the economic value of the recovered metals). Due to its high metal content, this mineral sludge could be a good secondary resource for recovery of the valuable metals Mo, Ni and Co. Therefore, this mineral sludge needed to be thoroughly tested and its metal leaching conditions optimized.

The objective of this study was to elucidate the potential of different leaching reagents to leach out valuable metals (Mo, Ni and Co) from a mineral sludge originating from a metal recycling plant. Different acids/acid mixtures were investigated in order to select the leachant with the highest metals leaching potential. The effects of leaching time, temperature and S/L ratio (dry weight of mineral sludge sample/volume of leachant, expressed in g L^{-1}) were investigated by performing batch experiments. Since the metals (Mo, Ni and Co) present in the mineral sludge are especially valuable to the recycling plant (both economically and ecologically), our research placed great emphasis on recovering these metals, with the specific emphasis on Mo leaching.

4.2. Materials and methods

4.2.1. Mineral sludge

A mineral sludge sample was collected in the rainfall water collection reservoir from a catalyst, metallic oxide and battery recycling plant, and characterized in detail by Vemic et al. (2015). The sample was collected over a 2 week period from the rainwater drainage collection basin covering the entire industrial area. The sample collection protocol involved partial obstruction of the network channel to create a sedimentation zone for the collection basin sample. The collected

mineral sludge was air-dried and sieved on a 2 mm mesh, in accordance with the ISO 11464 (2006) standard, and stored at 4°C. In study presented by Vemic et al. (2015), particles with the smallest size were found to contain the highest metal content. Therefore, in order to get the smallest particle size and to increase the surface area of the mineral sludge sample for the purpose of metal leaching, the sample was grinded and a particle size of < 105 µm was used throughout the study.

Metals contained in the mineral sludge sample originate from various materials stored in designated areas at the recycling plant: spent catalysts, metal oxides, metal hydroxide muds, batteries and accumulators, and an array of co-products used for recycling processes. Metal oxides account for nearly 40%, spent catalysts nearly 38%, batteries and accumulators almost 16%, metal hydroxide mud around 2% and recycling co-products around 4% (in weight terms) of the total quantity of mineral wastes processed by the recycling plant.

4.2.2. Total metal content (TMC) of the mineral sludge sample

For the total metal analysis, ~ 0.1 g of dry mineral sludge (using three replicates from the collection basin sample) was digested in a microwave system (Anton Paar 3000), containing HNO₃ (5 mL), HCl (2 mL) and HF (1 mL). A 1 hour digestion (power: 1,600 W, temperature: 210°C, pressure: 40 bar) was followed by free fluoride ion complexation with saturated boric acid (6 mL) (power 900 W, temperature 210°C, pressure 40 bar) (Vemic et al., 2013). The samples were subsequently transferred into 50 mL flasks and filled with ultra-pure water. Each sample was filtered using 0.45 µm Whatman filters and stored at 4°C prior to analysis.

4.2.3. Mineral sludge leaching properties

4.2.3.1. Testing the leaching properties of different acids/acid mixtures under the optimal leaching conditions from the literature

Three types of concentrated stand-alone strong acids (HNO₃ (68%), H₂SO₄ (98%) and HCl (36%)), hereafter referred as A, B and C, respectively, along with three concentrated acid mixtures (*aqua regia* (HNO₃+HCl (1:3)), HNO₃+H₂SO₄ (1:1) and HNO₃+H₂SO₄+HCl (2:1:1)), hereafter referred as D, E and F, respectively, were used to extract metals from the mineral sludge samples. The above mentioned acids/acid mixtures were chosen leachants based on the mineral sludge characterization results presented by Vemic et al. (2015) and similar studies from

the literature (Barik et al., 2012a; Ferella et al., 2011; Lai et al., 2008; Zeng and Cheng, 2009a,b). Furthermore, they are commonly used leaching agents in hydrometallurgical processes. The starting S/L ratio (1 g L^{-1}), time (2 h) and temperature (60°C) were set based on the optimal metal leaching conditions found in the literature (Barik et al., 2012a; Lai et al., 2008; Zeng and Cheng, 2009a,b). Experiments were performed in batch systems (50 mL polyethylene bottles) under continuous stirring conditions on an orbital shaker (IKA Labortechnik K550 Digital, 250 rpm, circular motion). After leaching, each sample was filtered through $0.45 \mu\text{m}$ Whatman filters to remove the solid residues, diluted to 100 mL using ultra-pure water and then stored at 4°C prior to analysis.

4.2.3.2. Testing the effect of S/L ratio ($0.25 - 50 \text{ g L}^{-1}$)

The effect of S/L ratio (0.25, 0.5, 0.75, 1, 5, 10, 20, 30, 40 and 50 g L^{-1}) on the metal leaching efficiency was tested in 10 mL acid/acid mixture at a temperature of 60°C and a leaching time of 2 h. The leaching experiments and the processing of the obtained leachate were conducted as explained in section 4.2.3.1.

4.2.3.3. Testing the effect of time (1 - 5 h)

The effect of leaching time (1, 2, 3, 4 and 5 h) on the metal leaching efficiency was tested by keeping the best S/L ratio from previous experiment (0.25 g L^{-1}) and the temperature (60°C) at constant values. The leaching experiments and the processing of the obtained leachate were conducted as explained in the section 4.2.3.1.

4.2.3.4. Optimisation of metal leaching with acid B under the effect of temperature (20 - 100°C)

Temperatures of 20, 30, 40, 50, 60, 70, 80, 90 and 100°C , were tested in order to further optimize the metal leaching yields of acid B (98% H_2SO_4). The experiments were performed in the shaking (circular motion, 250 rpm) thermo-water bath (GFL 1086) in order to achieve desired temperatures. The optimal S/L ratio (0.25 g L^{-1}) and optimal leaching time (2 h) from previous experiments were kept constant.

4.2.3.5. Successive metal leaching experiment

For the successive metal leaching experiment the leaching conditions were as follows: temperature 80°C, S/L ratio 0.25 g L⁻¹, time 2 h and three step leaching process. After performing the experiment one time, the sample was centrifuged, supernatant was taken for the analysis and the remaining mineral sludge sample was used in the next leaching step. This process was repeated three times.

4.2.4. Mineral sludge sample mineralogy before and after leaching

4.2.4.1. X-ray diffraction (XRD)

Mineralogical analyses of samples were performed by powder x-ray diffraction using a Bruker-AXS (Siemens) D5005 powder diffractometer (Cu, 40kV, 40 mA) from 5 to 65 (2-theta) at 1.5/min.

4.2.4.2. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS)

Mineral sludge sample was placed on microscopic glass slide, covered with resin and polished prior to conducting the SEM analysis. Sample morphology was investigated using a scanning electron micrographs (SEM, Philips XL 30, 20 kV, SERMIEL - Université de Limoges, France) coupled to an Energy Dispersive X-ray Spectroscopy (EDS) device.

4.2.5. Analytical and quality control

All experiments were conducted at least twice using three replicates, and all chemicals used in this study were of analytical grade. The solutions were prepared in ultra-pure water (Milli-Q system: resistivity = 18.2 MΩ.cm, Total Organic Carbon ≤ 10 µg L⁻¹). All glassware and containers were previously decontaminated in 10% (v/v) nitric acid. The total metal content in the mineral sludge extracts was analyzed using flame atomic absorption spectrometry (FAAS, Varian SpectrAA 220). The FAAS system was calibrated before each experimental run. The relative standard deviations of replicate analyses were below a control level of 5%. Blanks were included in each experimental and analytical run. During the analytical runs, after every ten samples, analysis of a standard sample was performed. The method detection limit (MDL) was

estimated by repeatedly analyzing a predefined quality control solution and by performing replicate analysis of FAAS measurements.

4.3. Results

4.3.1. Total metal content (TMC) of the collection basin mineral sludge sample

With respect to the industrial waste/sludge regulations (U.S. EPA, 1993), the sample from this study exceeds the allowable limits for Mo and Ni (with metal concentrations of 11.9 and 17.5 mg g⁻¹, respectively), which suggests that the sample might pose significant environmental hazards if disposed untreated. On the other hand, Co (2.9 mg g⁻¹) concentrations did not surpass the regulatory limits (Table 4.1). The results presented in Table 4.1 are representative of the mineral sludge produced in the industrial site according to the result of several measurement campaigns.

Table 4.1. Average (n = 3) total metal content (mg g⁻¹) with standard deviation, for the collection basin mineral sludge along with respective allowable limits.

Sample (mg g ⁻¹)	Mo	Ni	Co
Collection basin sludge	11.9 ± 0.1	17.5 ± 0.2	2.9 ± 0.4
Allowable limits for industrial waste or sludge (U.S. EPA, 1993)	0.075	0.42	4.3

4.3.2. Strong acids/acid mixtures leaching performances under the optimal metal leaching conditions from the literature

In contrast to the weak acids employed in the toxicity characteristic leaching procedure (TCLP), while testing potential metal leaching in the environment in our previous study (Vemic et al., 2015), in this study strong acids/acid mixtures were used to extract metals from the collection basin mineral sludge sample. Under the optimal metal leaching conditions from the literature (S/L ratio 1 g L⁻¹, time 2 h and temperature 60°C), the target metals reached leaching yields 5.7% (acid B), 12.4% (acid F) and 19.5% (acid B) for Mo, Ni and Co, respectively (Figure 4.1). Even so the achieved leaching yields were low we can notice that Mo and Co exhibited their highest leaching yields under the leaching effect of acid B, while Ni exhibited its highest leaching yields with acid F. As leachants B and F achieved better leaching yields of target metals compared to leachants A, C, D and E, we decided to perform our subsequent experiments using these two leachants.

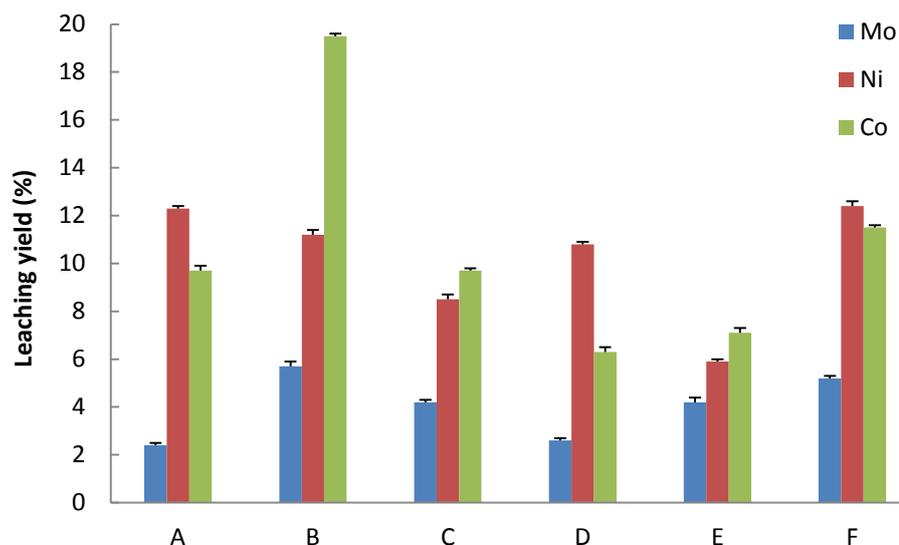


Figure 4.1. Metal leaching yields (%) from the collection basin mineral sludge under the optimal leaching conditions from the literature (S/L ratio = 1 g L⁻¹, Time = 2 h, Temperature = 60°C). A - HNO₃, B - H₂SO₄, C - HCl, D - HNO₃+HCl (1:3), E - HNO₃+H₂SO₄ (1:1) and F - HNO₃+H₂SO₄+HCl (2:1:1). Average of three replicates.

4.3.3. Effect of S/L ratio (0.25 - 50 g L⁻¹) on the metal leaching yields

The metal leaching yields decreased with an increasing S/L ratio from 0.25 to 50 g L⁻¹ (Figure 4.2), possibly due to the increased acid neutralisation capacity of the solid material, which was also reported in the literature (Barik et al., 2012a,b; Lai et al., 2008). At the first testing of the effect of the S/L ratio (1 - 50 g L⁻¹), the highest metal leaching yields of target metals were achieved at the S/L ratio of 1 g L⁻¹. Mo and Co leaching efficiencies were again slightly better with acid B (H₂SO₄), while Ni leaching efficiency was better with acid mixture F.

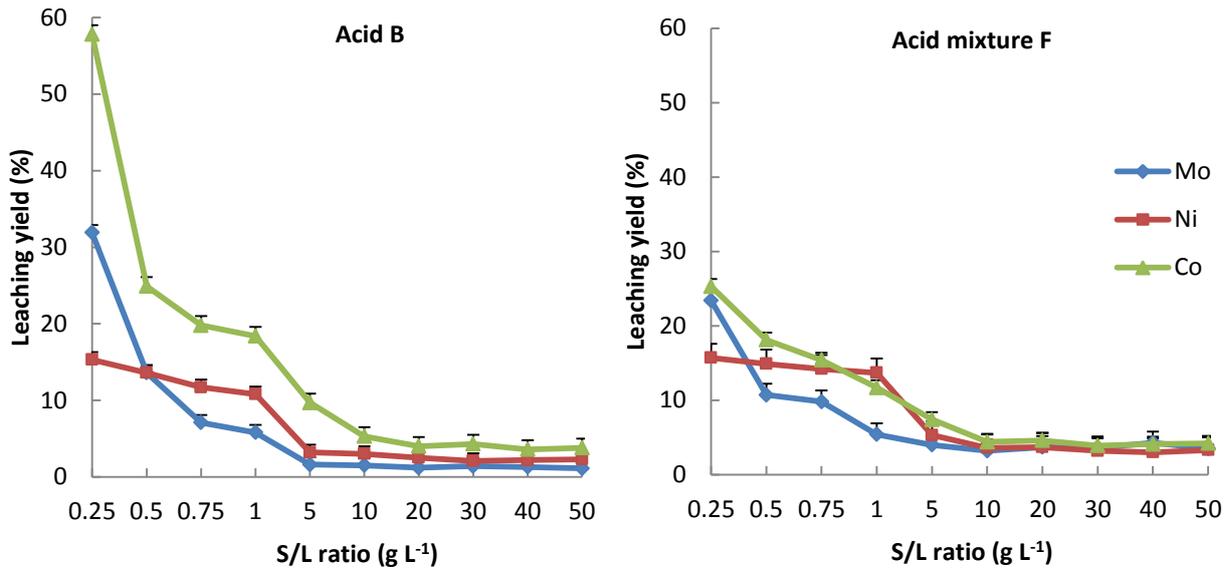


Figure 4.2. Metal leaching yields (%) from the collection basin mineral sludge for the S/L ratio of 0.25 - 50 g L⁻¹ (Time = 2 h, Temperature = 60°C). Three replicates, standard deviation < 0.5%. B - H₂SO₄ and F - HNO₃+H₂SO₄+HCl (2:1:1).

At the second testing of the effect of the S/L ratio (0.25 - 1 g L⁻¹), it was observed that the decrease in the S/L ratio gives a leaching advantage to acid B, as in case of almost all metals (Ni leaching yield difference is negligible, 15.3% in case of acid B and 15.7% in case of acid F), as the leaching yields of acid B were much higher in comparison with acid F (Figure 4.2). The metal leaching yields obtained with acid B were 31.9, 15.3 and 57.8% for Mo, Ni and Co, respectively.

4.3.4. Effect of leaching time (1 - 5 h) on the metal leaching yields

Among the five investigated time profiles (1, 2, 3, 4 and 5 h), the optimal metal leaching time was between 1 and 3 h (Figure 4.3). The metal leaching yields for both acids displayed their peak at ~ 2 h, after which the leaching yields decreased significantly. At the leaching time of 2 h, Mo and Co reached their leaching yields (30.8 and 56.7%, respectively) with acid B, while Ni reached its leaching yields (15.2%) with acid mixture F.

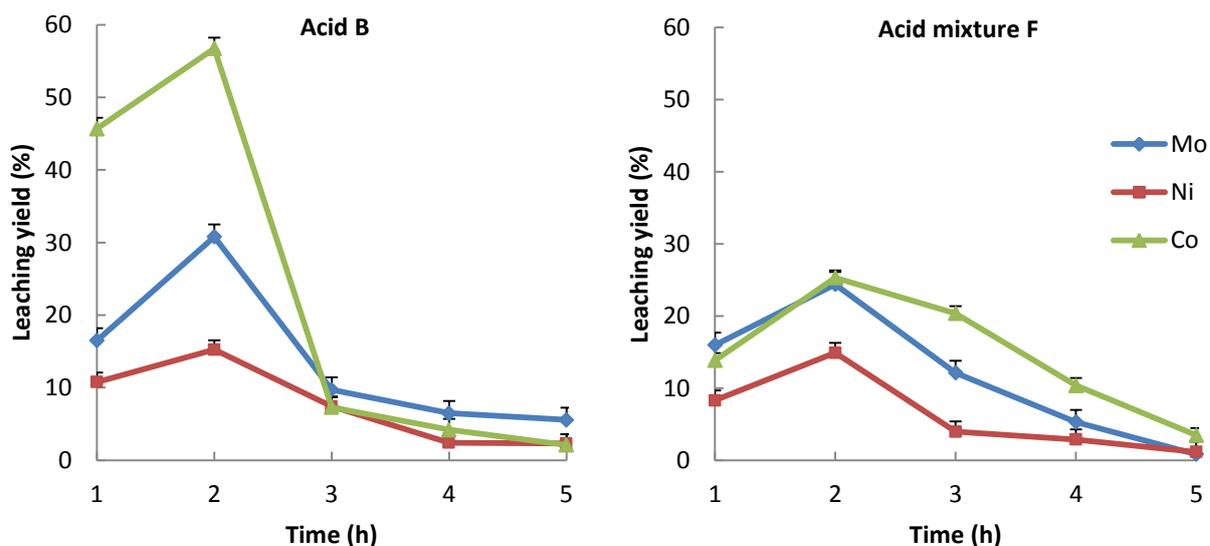


Figure 4.3. Metal leaching yields (%) from the collection basin mineral sludge for the leaching time of 1 - 5 h ($S/L = 1 \text{ g L}^{-1}$, Temperature = 60°C). Three replicates, standard deviation $< 0.5\%$. B - H_2SO_4 and F - $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HCl}$ (2:1:1).

4.3.5. Optimisation of metal leaching with acid B (H_2SO_4) under the effect of temperature (20 - 100°C)

As the temperature rises from 20 - 80°C , the metal leaching efficiency rises as well (Figure 4.4). At 80°C the optimal metal leaching yield with acid B is achieved with a leaching efficiency of 47.9, 19.7 and 80.2% for Mo, Ni and Co, respectively. At temperatures higher than 80°C , the metal leaching yields gradually decrease possibly due to metals reprecipitation affected by the change in solubility product (K_{sp}).

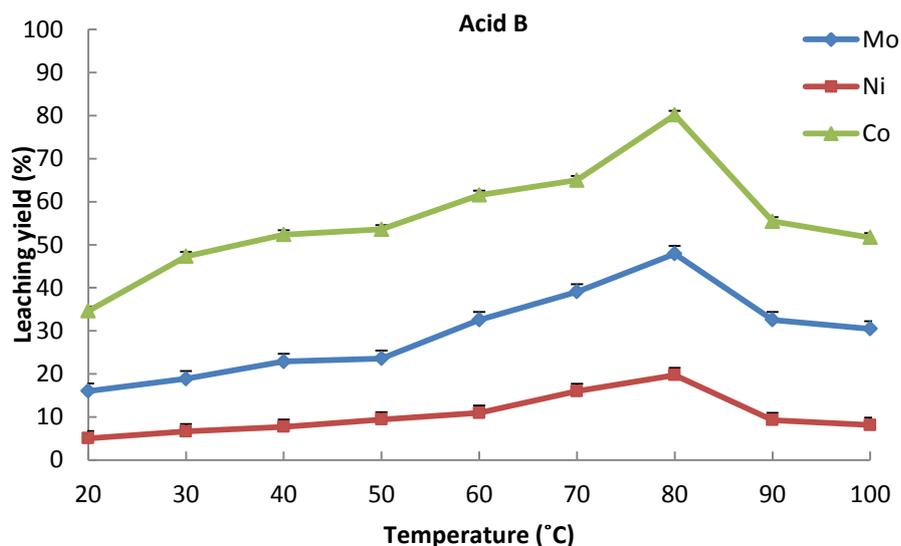


Figure 4.4. Metal leaching yields (%) from the collection basin mineral sludge for the temperature 20 - 100°C (S/L ratio = 0.25 g L⁻¹, Time = 2 h). Three replicates, standard deviation < 0.5%. B - H₂SO₄.

4.3.6. Successive metal leaching with acid B

From the previous experiment, it was observed that at 80 °C the best metal leaching yields with acid B can be achieved. To further optimize these achieved metal leaching yields successive metal leaching was performed on the mineral sludge sample. After first leaching step the metal leaching yields were 46.6, 19.9 and 79.2% for the Mo, Ni and Co, respectively. After the second leaching step the metal leaching yield decreased giving the values of 31.4, 15.4 and 14.6% for Mo, Ni and Co, respectively. In the third leaching step, the metal leaching yields were low, with the values of 7.4 and 5.3% for Mo and Ni, respectively, while no leaching yield of Co was measurable. The obtained results show that during the step 1, the quantity of H₂SO₄ is limiting, therefore the renewal of the extraction solution allowed increase in the metal leaching yields. Summarizing the leaching yields from all three successive leaching steps resulted in vastly improved Mo, Ni and Co leaching, achieving the total leaching efficiencies of 85.5, 40.5 and 93.8%, respectively.

4.3.7. Mineral sludge sample mineralogy before and after leaching

Figure 4.5 compares the mineral composition using XRD analysis of mineral sludge samples before and after leaching treatment with acid B at temperatures of > 80°C. Looking at the XRD

results (Figure 4.5), we noticed that: (i) most of the mineral phases present in the mineral sludge sample before leaching (see Vemic et al., 2015), were dissolved in the leaching liquor after leaching with acid B, (ii) the presence of Quartz, Plagioclases, and Magnetite is evident in the sample after leaching treatment (dome centered near $30^{\circ}2\text{-theta}$), (iii) Jarosite formation was not evidenced as we don't have enough iron in solution to form such a compound, and (iv) the presence of sulfate-based phases (Gypsum) after leaching with acid B is evident.

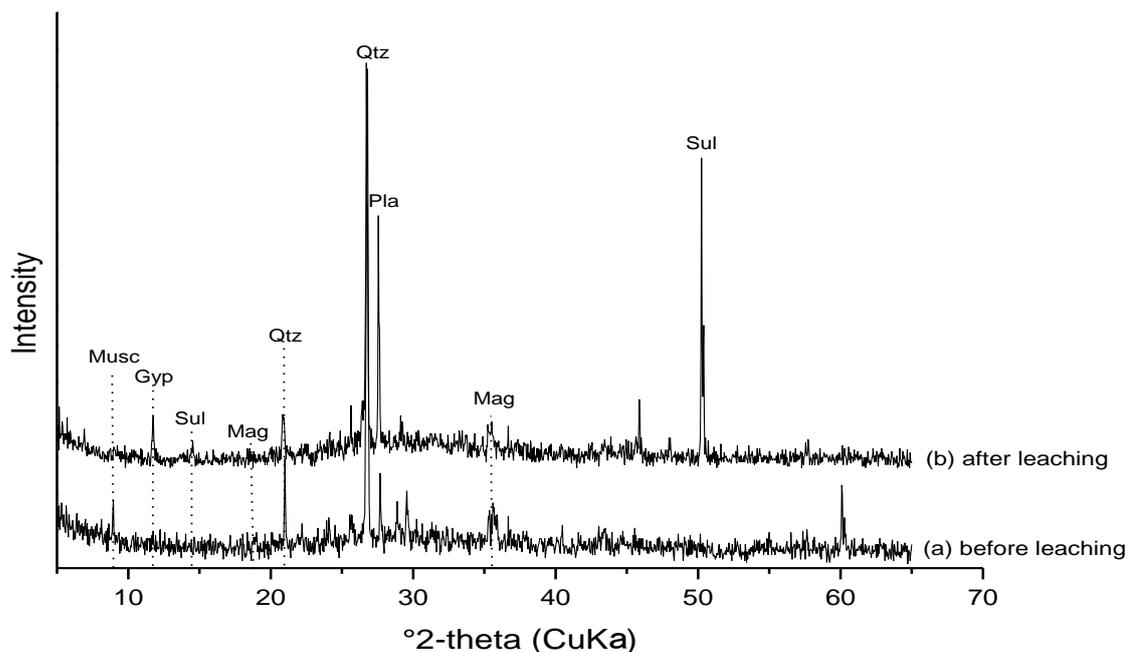


Figure 4.5. XRD patterns of collection basin mineral sludge sample before (a) and after (b) leaching with H_2SO_4 at 80°C . Musc-Muscovite, Gyp-Gypsum, Qtz-Quartz, Pla-Plagioclases, Mag-Magnetite and Sul-Sulfate based phases.

The changes in surface morphology were observed by SEM (Figure 4.6). Data obtained by SEM show the direct impact of the leaching treatment. Indeed, the sample seems to be cleaned after leaching: dissolution of fine particles and alterations coated onto fresh samples (Figures 4.6a and 4.6b compared to Figures 4.6e and 4.6f). Moreover, the surface of each quartz or alumina particle is coated by a developed phase which is described as gypsum (CaSO_4) from the EDS analyses (Figure 4.6h). This fact is in accordance with the XRD data (Figure 4.5). In our sample, gypsum could be acting as a capping agent, and therefore limiting the leachability of the target metals.

The (Cr, Ni, Fe, Mn) particles of about 5 to 40 μm size is evidenced (Figures 4.6c and 4.6g). presence of some metallic-rich Some particles are also composed by Zn, Zr, Mo or W. Figure 4.6g also shows that the matrix was corroded as the surface layer of the mineral sludge got dehydrated prior to SEM analysis.

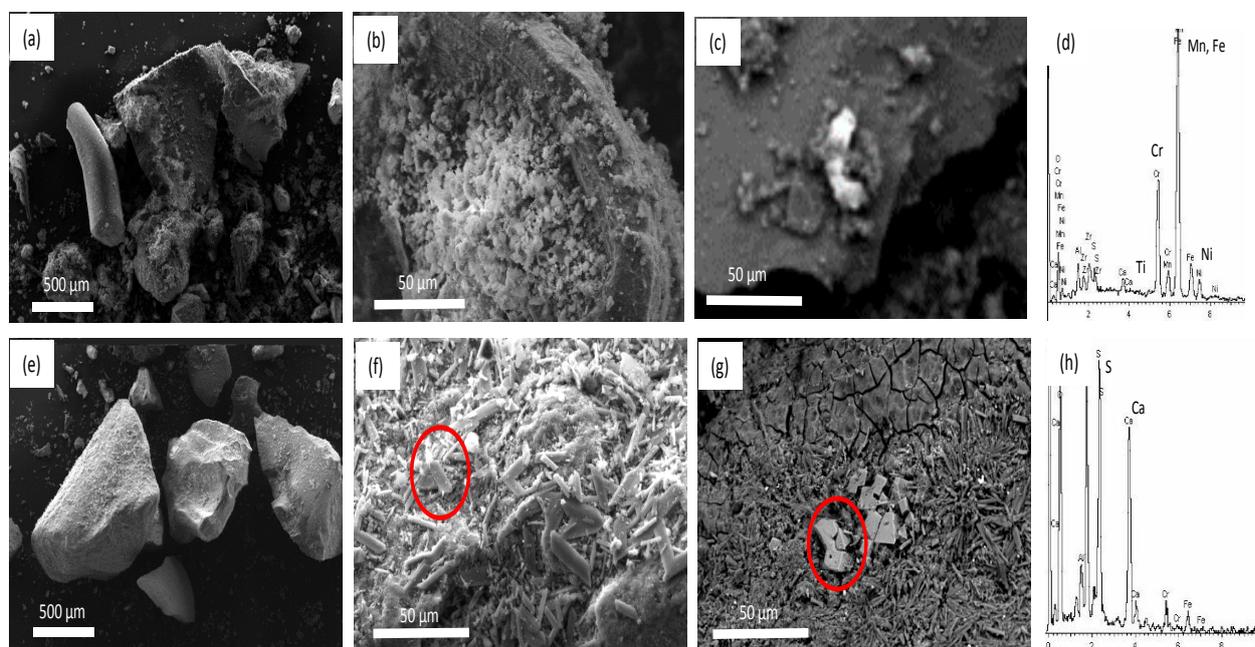


Figure 4.6. SEM micrographs of samples before (a, b, c, d) and after (e, f, g, h) leaching with H_2SO_4 . Figures a, b, e and f were obtained in secondary electrons, while figures c and g were obtained in backscattered electrons. Chemical analyses spectra by EDS performed onto red circles are reported in figure h.

4.4. Discussion

4.4.1. Link between mineral sludge fractionation data and the choice of metal leaching agents

Metals (Mo, Ni, Co) contained in the rainfall collection basin mineral sludge sample originate from various materials stored in designed areas at the recycling plant: spent catalysts, metal oxides, metal hydroxide mud, batteries, accumulators, and an array of co-products used for recycling processes (Vemic et al., 2015). The metals and metalloids fractionation of the mineral sludge sample performed in our previous study (Vemic et al., 2015) indicated that Mo is mostly present in the residual and oxidizable fractions, while Ni and Co are mainly bound to the residual sludge fraction. The fact that the targeted metals are present in a high percentage in the residual sludge fraction means that they are entrapped in the crystalline structures of the particles constituting the sludge, which make these metals very difficult to leach out (Vemic et al., 2015).

Therefore, to access the target metals the crystalline structures have to be destroyed by addition of a strong leaching agent, such as the concentrated inorganic acids used in this study.

The mineralogical data from our previous study (Vemic et al., 2015) showed the presence of mostly metal oxides in our collection basin mineral sludge. Metals are generally leached out from their oxides by acid-leaching as it obtains high metal leaching yields because of its high oxidizing and complexing power (Zeng and Cheng, 2009a,b). Due to this reason and based on the similar studies from the literature (Barik et al., 2012a,b; De Souza Pereira et al., 2011), we decided to test the metal leaching potential of strong inorganic acids/acid mixtures (A-F) on our mineral sludge sample. In addition, we also tested the metal leaching potential of different weak acids (citric, formic, acetic, ascorbic, oxalic) and other chemicals (sodium carbonate, sodium hydroxide, ammonium acetate). However, their metal leaching efficiencies were very low in comparison with those achieved with strong inorganic acids. For the up scaling of the leaching process, the possibility of using the low acid concentrations/high pulp density needs further investigation. However, due to the time limit of this research the possibility for upscaling was not studied.

The general mechanism for direct leaching of metal oxides with strong inorganic acids is based on the fact that the oxides shell and core become rapidly hydroxylated, followed by the successive adsorptions of hydrogen ions, anions of the acid and again hydrogen ions at hydroxylated sites [27]. In our case, when leaching a solid (mineral sludge) with liquid (strong inorganic acid), the desired solid (metals) is extracted to the liquid phase while unleached solid (mineral sludge with unleached metal minerals) remains. The removal of the solid as the liquid penetrates into the particle leads to shrinking of a diameter of unleached core with time [28]. From our previous study [24] we learned that in our mineral sludge sample most of the metals are entrapped in the residual sludge matrix (co-precipitated or part of a mineral structure) which could explain why it is so difficult to leach them out.

Among the six different strong acid leaching reagents (A-F) investigated in our study (Figure 4.1), H_2SO_4 (acid B) was found to be the leachant with the highest metal leaching potential. If we look at the chemical formulas of each single acid, H_2SO_4 breaks down the furthest producing 2 hydrogen ions (H^+) and one sulfate (SO_4^{2-}) ion, resulting in 3 moles of ions/molecules per mole of acid. HNO_3 only forms 2 (1 H^+ and 1 NO_3^-), as does HCl (1 H^+ and one Cl^-). The

concentration of H^+ ions for each acid is $H_2SO_4 = 36.8 \text{ mol L}^{-1}$, $HNO_3 = 15.8 \text{ mol L}^{-1}$ and $HCl = 10.2 \text{ mol L}^{-1}$.

Rates of oxide dissolution are generally observed to be affected by the proton concentration of the reacting solution (Brantley, 2008). Therefore, we can conclude that the better metal leaching efficiency of H_2SO_4 in comparison with the other strong acids could be attributed to the fact that H_2SO_4 is a diacidic compound (two hydrogen atoms), meaning that it has more H^+ ions for the exchange, resulting in its strong oxidising power and corrosiveness (De Souza Pereira et al., 2011). Although, the use of acid mixtures (in case of acid F) showed significant leaching efficiency (the introduction of concentrated HCl to the metal extraction led to the formation of metal-chlorine ion complexes and thus enhanced the metal leaching), compared to the individual acids, the high acid consumption is a drawback (De Lima et al., 2005).

4.4.2. The effect of the different operational parameters on the metal leaching

In the process of metal leaching the two phases (solid and leachant) are in intimate contact; the solute(s) can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid (Abdel-Aal et al., 2004). This depends on the proportion of the soluble constituent present, its distribution throughout the original solid, the nature of the solid, and the original particle size (Ognyanova et al., 2009). Due to the strong corrosive potential of inorganic acids the solid phase may be easily dissolved, therefore solubilizing the target metals. If the soluble material is surrounded by a matrix of insoluble matter, the solvent must diffuse inside to contact and dissolve the soluble material and then diffuse out. In these cases crushing and grinding of the solid material is used to increase the specific surface area allowing the better leaching yields since the soluble portions are made more accessible to the solvent (Kim et al., 2009a). In our study, it was noticed that the target metals leaching efficiencies were significantly improved by crushing the mineral sludge sample from original $< 2 \text{ mm}$ size (metal leaching yields of Mo, Ni and Co were found to be 52.2, 23.7 and 60.6%, respectively), to the particle size of $< 105 \mu\text{m}$ (metal leaching yields of Mo, Ni and Co were found to be 85.5, 40.5 and 93.8%, respectively).

Metal leaching efficiencies in our study also improved with decrease in the S/L ratio, achieving the best metal leaching yields at the S/L ratio 0.25 g L^{-1} (Figure 4.2). The mechanism behind this phenomenon is that with the S/L decrease there are more H^+ ions from the leachant available for

exchange per ion of metal oxide. This statement is additionally confirmed while performing the successive metal leaching experiments (section 4.3.6), where it was observed that the renewal of the extraction solution allowed increase in the metal leaching yields due to the renewal of H^+ ions to react with the remaining ions of metal oxides.

Dissolution of highly soluble minerals has a greater likelihood of becoming transport-limited as compared to low solubility minerals which are likely to be interface-limited (Brantley, 2008). Two regions of dissolution are distinguished based on pH: for $pH < 3.5$, dissolution is controlled by transport while for $pH > 3.5$ the interfacial reaction is slower than transport and the rate is interface-controlled. Above pH 5.5, dissolution is more dependent on the solution chemistry and the mineral precipitation reactions are observed to be significant (Brantley, 2008).

Looking at the effect of time on the metal leaching efficiency, we noticed that at 2 h of leaching time our target metals extraction potentials reach their maximum (Figure 4.3). As we used concentrated inorganic acids/acid mixtures, the leachant/solid reactions are very quick resulting in fast dissolution of metal oxides (1 - 2 h). Possible reasons for a maximal metal leaching efficiency at 2 h of leaching time could be targeted metal precipitation due to the increase in pH over the time (final pH around 6) which probably influenced the solubility of the target metals.

In the literature we observed similar phenomena (Lai et al., 2008). In the study conducted by Lai et al. (2008), an acid solution consisting of concentrated $HNO_3/H_2SO_4/HCl$ with a volume ratio of 2:1:1 was found to be better than the other tested solutions ($HNO_3/H_2SO_4 = 1:1$) to leach the metals out of the spent catalysts. For the three-acid mixture, the best metal leaching efficiency was found to be at a leaching time 2 h, and temperature of $70^\circ C$. Under these conditions, the leaching yields of Mo and Ni reached 90 and 99%, respectively.

The lower metal leaching efficiencies achieved in our study (leaching yields of Mo, Ni and Co reached 85.5, 40.5 and 93.8%, respectively) in comparison to metal leaching efficiencies achieved in study by Lai et al. (2008), could be due to the complex composition of our mineral sludge (not strictly a catalyst sludge or hydroxide sludge, but rather a combination of both). Furthermore, the rather low Ni leaching efficiencies achieved in our study could be attributed to the fact that among all three target metals, Ni is the one that is present in the residual mineral sludge fraction at the highest percentage meaning that much more effort is needed for its extraction. Similarly, in the literature rather low Ni extraction efficiencies were reported: 60%

with H₂SO₄ (Abdel-Aal et al., 2004), 50% with ammoniacal media (Silva et al., 2005), 23% with CH₃COOH (Gzar et al., 2014), and 18% with HCl (Chandhary et al., 1993). The leaching kinetics of Ni investigated by Abdel-Aal et al. (2004) indicated that chemical reactions at the surface of the particles are the rate-controlling processes during the leaching.

The mineralogical results before and after leaching with acid B (Figures 4.5 and 4.6), indicated that at the higher temperatures metals are associated with sulfate phases (some metals might precipitate as metal sulfates), which could be a possible reason why their presence in the leach liquor at higher temperatures is gradually decreasing (Figure 4.4). Additionally, we noticed that due to the metal sulfates precipitation and temperature increase, the mineral sludge becomes more condense and it forms a thick layer on the walls of a glass bottle (used for leaching experiments), thus physically preventing further metal leaching.

4.4.3. Metal recycling plant mineral sludge as a secondary resource for metals

The high price, high demand and future shortage of primary mineral resources for metals such as Mo, Ni and Co, creates the need to develop secondary resources and to find more beneficial ways of metals leaching and recovery from such resources (McGrath et al., 2010a,b; Van Gestel et al., 2012).

Metal leaching from secondary resources (*i.e.* mineral sludges) receive great attention in view of the presence of several metals of economic interest (such as Mo) which are sometimes richer than those of the available natural reserves (ores/minerals). As our mineral sludge sample is highly loaded with metals, the use of this type of sludges as a secondary resource for metal recovery could at the same time reduce the amount of the sludges that have to be yearly disposed in landfills (thus preventing environmental contamination) and reduce the costs of their disposal (Vemic et al., 2015). Additionally, utilization of industrial mineral sludges as a secondary resources for metal recovery is an appropriate solution to manage the continuously increasing waste sludge generation, to reach stringent environmental quality standards, and at the same time, to sustain the metal reserves for our future generations (Kabata-Pendias and Mukherjee, 2007).

4.5. Conclusion

In view of the on-going depletion of the natural resources taking place worldwide it is necessary to implement metals extraction/recycling/recovery/reuse from semi-finished products, by-products, secondary materials and wastes, including hazardous wastes (*i.e.* mineral sludges). This work gives an insight into the metal leaching properties of mineral sludge from a rainfall collection basin (originating from a metal recycling plant) under the effect of strong inorganic acids/acid mixtures. Among the different acids/acid mixtures studied, H₂SO₄ (acid B) was found to be the leachant with the highest metal leaching potential (optimal leaching conditions: three stage successive leaching, a temperature 80 °C, a leaching time 2 h and a S/L ratio 0.25 g L⁻¹), with the leaching efficiency of 85.5, 40.5 and 93.8% for Mo, Ni and Co, respectively. The conducted study demonstrated that metal containing mineral sludges have a great potential to be an important secondary resource for secured supply of contained metals/materials.

4.6. References

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CHAPTER 5

Recovery of molybdenum, nickel and cobalt by precipitation from the acidic leachate of a mineral sludge produced by a metal recycling plant

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Chapter 5

The objective of this study was to investigate the recovery potential of Mo, Ni and Co from synthetic and real acidic leachate of a mineral sludge from a metal recycling plant by sulfide precipitation. At first, the operational parameters (metal sulfide ratio (M/S) 0.1 - 1, agitation speed 0 - 100 rpm, contact time 15 - 120 min, and pH 1 - 5) were optimized in batch conditions on synthetic metal leachate (0.5 M HNO₃, Mo = 101.6 mg L⁻¹, Ni = 70.8 mg L⁻¹, Co = 27.1 mg L⁻¹) with a 0.1 M Na₂S solution. Additionally, recovery of the target metals was theoretically simulated with a chemical equilibrium model (Visual MINTEQ 3.0). The optimized Na₂S precipitation of metals from the synthetic metal leachate resulted in the potential selective recovery of Mo as oxide at pH 1 (98% by modelling, 95.1% experimental), after simultaneous precipitation of Ni and Co as sulfide at pH 4 (100% by modelling, 98% experimental). Metal precipitation from the real acidic leachate (18 M H₂SO₄, Mo = 10,160 mg L⁻¹, Ni = 7,082 mg L⁻¹, Co = 2,711 mg L⁻¹) of mineral sludge was performed with 1 M Na₂S, and resulted in a maximal Mo recovery at pH 2 (50.3%), while maximal recoveries of Ni and Co were at pH 4 (56.0 and 59.7%, respectively). Real acidic leachate gave a lower metals recovery efficiency, which can be attributed to various factors such as changes in the pH, nature of leachant, co-precipitation of Zn and competition for S²⁻ ions.

5.1. Introduction

Molybdenum (Mo), nickel (Ni) and cobalt (Co) are important metals for human activities and industry in general (Pradhan et al., 2013). They are expensive metals. In 2015, the average market price for Mo, Ni and Co was 16,988 € t⁻¹, 12,502 € t⁻¹ and 25,253 € t⁻¹, respectively (www.infomine.com). Due to the high price, high demand and future shortage of the primary mineral resources for Mo, Ni and Co, it is important to recover these metals from secondary resources, *e.g.* spent catalysts (Banda et al., 2013a; Marafi and Stanislaus, 2003; Marafi et al., 2007).

The recovery of metals from spent catalyst leachates can be achieved through various methods (Marafi and Stanislaus, 2008a,b; Zeng and Cheng, 2009a,b), such as sulfide precipitation (Cibati et al., 2013), adsorption (Derakhshi et al., 2009; Pagnanelli et al., 2011), ion exchange (Henry and van Lierde, 1998; Kononova et al., 2003; Nguyen and Lee, 2013; Nguyen and Lee, 2014) and solvent extraction (Banda et al., 2012; Banda et al., 2013b; Mishra et al., 2010).

In hydrometallurgical processes and in the treatment of metal-containing leach liquors, the use of precipitation and selective precipitation for metal recovery has received considerable attention due to its simple operations and lower costs in comparison with the other recovery methods (Lewis, 2010; Reis et al., 2013; Veeken et al., 2003). Among the precipitation methods, sulfide precipitation is commonly used in industry due to its advantages, which include the lower solubility of metal sulfide precipitates, potential for selective metal removal, fast reaction rates, better settling properties and potential for re-use of sulfide precipitates by smelting (Cibati et al., 2011). Sulfide precipitation can be performed using either solid (FeS, CaS), aqueous (Na₂S, NaHS, NH₄S) or gaseous sulfide sources (H₂S) (Lewis, 2010).

Although there have been numerous studies in the literature addressing sulfide precipitation of different metals, such as Zn, Cu, Fe, Pb, Rh, Mn, Co, Ni, V, Cd, Hg, Bi and Ag (Lewis, 2010), only a few studies have addressed sulfide precipitation of Mo despite the interest of this element (Cibati, 2011; Cibati et al., 2013; Freedman, 1963). Cibati et al. (2013) evaluated the feasibility of using biogenic H₂S to selectively precipitate Mo, Ni, Co and V from spent refinery catalyst leach liquor containing 15.3 g L⁻¹ Mo, 4.9 g L⁻¹ Ni, 2.4 g L⁻¹ Co and 7.6 g L⁻¹ V. Biogenic H₂S facilitated the selective precipitation of MoS₂ at pH 2 with recoveries of 36 - 72%. Ni and Co were simultaneously precipitated at pH 3.5 with recovery efficiencies of 23 and 16%, respectively; while V was recovered at pH 6 with recovery efficiencies between 64 - 70%.

In this study, we are dealing with a mineral sludge originating from spent catalysts, metallic oxides and batteries recycling plant. The investigated mineral sludge has a complex heterogeneous composition (a combination of both catalyst and hydroxide sludge), reflecting the materials stored on-site (Vemic et al., 2015). Due to its high metal content, this mineral sludge could be an important secondary resource for recovery of valuable metals (*e.g.* Mo, Ni and Co). However, to the best of our knowledge, the metal recovery potential of this type of material was not yet investigated. Therefore, this mineral sludge needed to be thoroughly tested with classical methods and its metal recovery conditions optimized.

The objective of the present study was to theoretically simulate the sulfidic precipitation of target metals in a chemical equilibrium model (Visual MINTEQ 3.0) and then to experimentally optimize the operational parameters (metal/sulfide ratio (M/S), agitation speed, contact time, and pH), using a synthetic metal leachate (0.5 M HNO₃, Mo = 101.6 mg L⁻¹, Ni = 70.8 mg L⁻¹, Co = 27.1 mg L⁻¹) with a 0.1 M Na₂S solution in batch conditions. For safer operations with lower

sulfide concentrations and lower sulfide gas exposure, the synthetically prepared metal leachate contained a hundred times lower metal concentration than the concentrations present in the real acidic leachate (18 M H₂SO₄, Mo = 10,160 mg L⁻¹, Ni = 7,082 mg L⁻¹, Co = 2,711 mg L⁻¹) of the mineral sludge. Once the operational conditions were optimized, the target metals were precipitated from real metal leachate with 1 M Na₂S solution. Since Mo, Ni and Co are especially valuable to the metal recycling plant (both economically and ecologically), our research placed great emphasis on recovering these metals, with specific emphasis on Mo recovery.

5.2. Materials and methods

5.2.1. Mineral sludge characterization and leaching properties

A sample of mineral sludge from a catalysts, metallic oxides and batteries recycling plant was collected over a 2 week period from the rainwater collection basin covering the entire industrial area (Vemic et al., 2015). In accordance with the ISO 11464 (2006) standard, the sample was air-dried and sieved on a 2 mm mesh. Mineral sludge was characterized in detail where pH, Loss On Ignition (LOI), Compliance with EN 12457-1 and -2 standards (EU Council, 2003), Toxicity Characteristic Leaching Procedure (TCLP; US-EPA, 1999), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Total Metal Content (TMC) and Sequential Extraction (SE) were performed, as described by Vemic et al. (2015).

Based on the characterization of the mineral sludge (Vemic et al., 2015) and similar studies from the literature (Lai et al., 2008; Zeng and Cheng, 2009a,b), the leaching rate and yields of Mo, Ni and Co from the mineral sludge sample were quantified (Vemic et al., accepted in Environmental Technology). When the leaching process was optimized (type of leachant, solid/liquid ratio (S/L), leaching time, temperature, successive leaching), sulfuric acid (H₂SO₄) was found to be the leachant with the highest metal leaching potential. The optimal leaching conditions were a three stage successive leaching at 80°C for 2 h and with a S/L ratio 0.25 g L⁻¹. Under these conditions, the leaching yields from the mineral sludge sample reached 85.5, 40.5 and 93.8% for Mo, Ni and Co, respectively (Vemic et al., accepted in Environmental Technology).

5.2.2. Optimization of recovery of metals from synthetic metal leachate

Batch experiments for sulfide precipitation were conducted to investigate the recovery potential of Mo, Ni and Co from a synthetic metal leachate. For proper metal preservation, the synthetic metal leachate was prepared in 0.5 M HNO₃ and contained a hundred times lower metal concentration (Mo = 101.6 mg L⁻¹, Ni = 70.8 mg L⁻¹, Co = 27.1 mg L⁻¹) than present in the real mineral sludge leachate. Standard stock solutions of Mo, Ni and Co (1000 mg L⁻¹) were prepared from the metallic salts (NH₄)₆Mo₇O₂₂·4H₂O, Ni(NO₃)₂·6H₂O and CoCl₂·6H₂O, respectively. Na₂S (0.1 M) was used for precipitation of the target metals.

The metal recovery potential from the synthetic metal leachate was investigated with different operational parameters: metal sulfide ratio (0.1 to 1 with increase of 0.1), agitation speed (0, 25, 50, 75 and 100 rpm) and contact time (from 15 to 120 min with increase of 15 min). At first, experiments were conducted without controlling pH (starting pH of the synthetic metal leachate was 1). Once the effects of metal sulfide ratio, agitation speed and contact time were optimized, we proceeded with the pH optimization (1 - 5) in order to further increase the metal recovery yields. The effect of pH on the recovery of target metals was theoretically simulated in Visual MINTEQ (section 5.2.3). Temperature was kept constant for all experiments (20 - 25°C). All experiments were conducted in batch systems (50 mL polyethylene bottles) under continuous stirring conditions on an orbital shaker (IKA Labortechnik K550 Digital). After precipitation, each sample was centrifuged at ×3000 g for 15 min (Eppendorf S804), filtered through 0.45 μm Whatman filters and immediately analyzed for metal content.

5.2.3. Visual MINTEQ modelling of the synthetic metal leachate precipitation with Na₂S

The chemical equilibrium model Visual MINTEQ 3.0 (using the standard solubility constant database) was used to simulate the theoretical sulfide precipitation of metals from the synthetic metal leachate. The model simulated equilibrated mass distribution (distribution of components between dissolved, adsorbed and precipitated phases), stoichiometry and mineral components, concentrations and activities of aqueous inorganic species, saturation indices and amount of finite solids. Saturation indices, $SI = \log(IAP/K_s)$, were derived from the calculated ion activity products (IAP) and solubility products (K_s) for the relevant minerals. The speciation of the elements was taken into account and the possible precipitation of new solid phases was

determined based on the thermodynamic equilibrium of the solution being reached at temperatures between 25 - 50°C.

Data inputs in Visual MINTEQ included: $\text{MoO}_4^{2-} = 1.06 \text{ mM}$, $\text{Ni}^{2+} = 1.26 \text{ mM}$, $\text{Co}^{2+} = 0.46 \text{ mM}$, $\text{S}^{2-} = 100 \text{ mM}$, $\text{Na}^+ = 200 \text{ mM}$, $\text{Cl}^- = 0.92 \text{ mM}$, $\text{NO}_3^- = 2.41 \text{ mM}$ and $\text{NH}_4^+ = 0.91 \text{ mM}$. Equilibrium with atmospheric CO_2 was assumed. The activity coefficient was determined using the Debye–Hückel equation. The oversaturated solids were allowed to precipitate, but only after the final equilibrium is reached. The effects of different temperatures (from 20 to 50°C with increase of 5°C) and pH (from 1 to 14 with increase of 1 unit) on the recovery efficiencies of target metals were simulated in the model. The model outputs were used for comparison with experimental data.

5.2.4. Na₂S precipitation of metals from real acidic leachate

Batch Na_2S precipitation experiments were also conducted with real acidic leachate of the mineral sludge from the metal recycling plant under the optimal operational conditions (M/S ratio 0.1, agitation speed 100 rpm, time 75 min and pH 1) determined in the previous experiments. 1 M Na_2S was used. To increase the recovery potential of target metals under the above-mentioned optimal operational conditions, the effect of pH (1, 2, 3, 4 and 5) on the metal recovery from the real acidic leachate was further investigated.

5.2.5. Metal sulfide/oxide precipitates characterization

5.2.5.1. Settleability

After precipitation experiments were performed under optimal operational conditions (M/S ratio 0.1, agitation speed 100 rpm, time 75 min and pH 1), precipitates were poured into a measuring cylinder (50 mL, diameter 2.6 cm, height 20 cm), and the settling properties of the sample were measured for 1 h. The settled precipitate volume was measured every five minutes for the first 30 minutes, and every ten minutes for the remaining time.

5.2.5.2. X-ray diffraction (XRD)

Mineralogical analyses of metal sulfide/oxide precipitates were performed on a Bruker D8 X-ray diffractometer (2.5 to 120° (2-theta) at 1.5°/min).

5.2.5.3. Environmental scanning electron microscopy (ESEM)

The morphology of metal sulfide/oxide precipitates morphology was investigated using Environmental Scanning Electron Micrographs (ESEM, Electro-Scan E3 Phillips, 25 kV, ESD, 8.1 T - Université Paris-Est, France).

5.2.5.4. Total metal content (TMC) of the metal sulfide/oxide precipitates

For the total metal analysis, ~0.5 g of dry metal sulfide/oxide precipitate was digested in a digestion block system (DigiBlock ED16S) containing 68% HNO₃ (3 mL) and 32% HCl (9 mL). After 1 hour digestion (temperature 210°C), the samples were subsequently transferred into 50 mL flasks and filled with ultra-pure water and stored at 4°C prior to total metal analysis.

5.2.6. Analytical and quality control

All analyses were conducted at least twice using three replicates, and all chemicals used in this study were of analytical grade. The solutions were prepared in ultra-pure water (Milli-Q system: resistivity = 18.2 MΩ.cm, Total Organic Carbon ≤ 10 µg L⁻¹). All glassware and containers were previously decontaminated in 10% (v/v) HNO₃. All pH adjustments were done with 0.5 M HCl. The presence of this chemical was considered in Visual MINTEQ simulations.

The metal concentrations were analysed using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Bruker, 820-MS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin Elmer, Optima 8300). The ICP-MS and ICP-OES systems were calibrated before each experimental run. The relative standard deviations of replicate analyses were below a control level of 5%. Blanks were included in each experimental and analytical run. During the analytical runs, after every ten samples, analysis of a standard sample was performed. The method detection limit (MDL) was estimated by repeatedly analyzing a predefined quality control solution and by performing replicate analysis of ICP-MS/ICP-OES measurements.

5.3. Results

5.3.1. Optimization of the Na_2S precipitation from the synthetic leachate

5.3.1.1. Effect of M/S ratio on metal recovery potential

The target metals recovery efficiencies gradually increased with a decreasing M/S ratio from 1 to 0.1 (Figure 5.1). The best target metals recovery efficiencies were achieved with a 0.1 M/S ratio (Figure 5.1). The achieved metal recovery efficiencies were 81.0, 81.3 and 83.6% for Mo, Ni and Co, respectively (Figure 5.1). As the M/S ratio decreases, there are more sulfide ions available per metal ion, resulting in higher metal recovery efficiencies. As per Visual MINTEQ simulations, Ni and Co were recovered in the form of sulfide (NiS_2 and CoS_2), while Mo was recovered in the form of molybdic acid (H_2MoO_4).

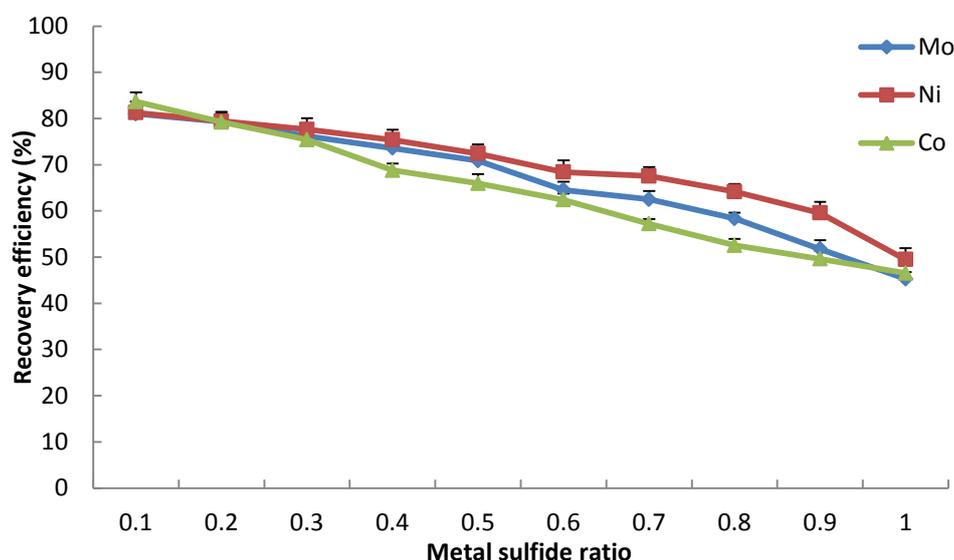


Figure 5.1. Metal recovery efficiencies (%) from the synthetic leachate of mineral sludge from a metal recycling plant by Na_2S precipitation for the M/S ratio of 0.1 - 1 (agitation speed = 100 rpm, time = 120 min, pH = 1). Three replicates, standard deviation < 5%.

5.3.1.2. Effect of agitation speed on metal recovery potential

Recovery efficiencies in static batch conditions (0 rpm) for target metals were 65.1, 68.7 and 63.6% for Mo, Ni and Co, respectively (Figure 5.2). The highest metal recovery efficiencies were obtained under agitation, at 100 rpm with a recovery efficiency of 81.4, 81.7 and 84.4% for Mo, Ni and Co, respectively (Figure 5.2). These results indicate that even if metal precipitation occurs under static batch conditions, there is a roughly 20% increase in the metal recovery

efficiency under agitation conditions. Precipitation of Mo, Ni and Co at agitation speeds exceeding 100 rpm (Figure 5.2) resulted in limited precipitates formation or only very small precipitates (nanometer scale). The visually largest precipitates were formed at 75 rpm.

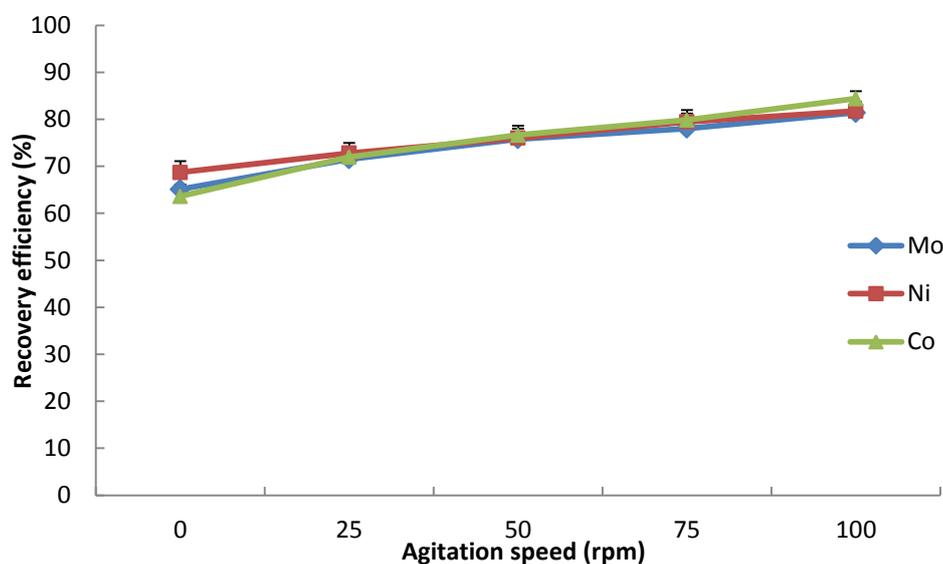


Figure 5.2. Metal recovery efficiencies (%) from the synthetic leachate of mineral sludge from a metal recycling plant using Na_2S precipitation for the agitation speed 0 - 100 rpm (M/S ratio = 0.1, time = 120 min, pH = 1). Three replicates, standard deviation < 5%.

5.3.1.3. Effect of contact time on metal recovery potential

In the time period between 60 and 90 min, recovery efficiency stabilizes and reaches its maximum at 75 min with the recovery efficiencies of 95.2, 96.6 and 95.8% for the Mo, Ni and Co, respectively (Figure 5.3). After 75 min of contact time, the efficiency slowly decreases, possibly due to metal dissolution from the metal sulfide/oxide precipitates and oxidation due to the presence of atmospheric O_2 .

Recovery of Mo, Ni and Co by precipitation from the acidic leachate of a mineral sludge produced by a metal recycling plant

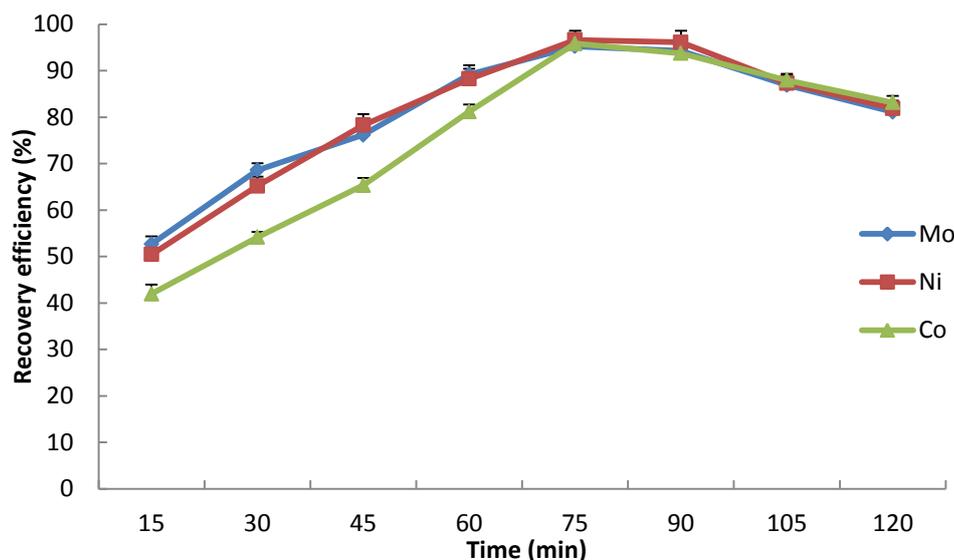


Figure 5.3. Metal recovery efficiencies (%) from the synthetic leachate of mineral sludge from a metal recycling plant by Na_2S precipitation as function of time (M/S ratio = 0.1, agitation speed = 100 rpm, pH = 1). Three replicates, standard deviation < 5%.

5.3.1.4. pH effect on metals recovery potential

Modelling of the synthetic metal leachate precipitation with Na_2S indicated that Ni and Co simultaneously precipitate at all pH values measured with efficiencies of 98 - 100%. Mo can be selectively recovered at pH 1 and pH 2 with recovery efficiencies of 98%. Modelling indicates that Mo, Ni and Co precipitated (SI = 0) in the form of H_2MoO_4 (s), NiS (gamma) and CoS (beta), respectively. In addition to the effect of pH (1 - 14), the effect of seven temperature profiles (from 20 to 50°C) on metal precipitation was modelled. However, simulation results indicated that the temperature does not affect the metal recovery efficiencies (data not shown).

Similarly to the Visual MINTEQ simulations, Na_2S metal precipitation results were obtained under experimental conditions (Figure 5.4), confirming that Ni and Co precipitate at all measured pH values but with the highest percentages (98 - 99%) at pH 3, 4 and 5. However, they precipitate simultaneously, which confirms that these two metals are difficult to selectively precipitate. In case of Mo, it can be selectively recovered at pH 1 and pH 2 with a recovery efficiency of 95.1 and 89.2%, respectively. At the higher pH values (3, 4 and 5), Mo precipitates with < 5%, while the rest remains in solution.

The above mentioned theoretical and experimental results are important as they show that Mo can be selectively recovered (which was confirmed with the metal sulfide/oxide precipitates characterization, see section 5.3.3) by firstly precipitating Ni and Co from the mixed metal synthetic leachate at pH 4, leaving the majority of Mo in solution which can then be recovered at pH 1.

Figure 5.4, in addition, shows the comparison of Mo, Ni and Co experimental precipitation results at different pH values between the synthetic and real metal leachate, where defined pH recovery profiles can be observed.

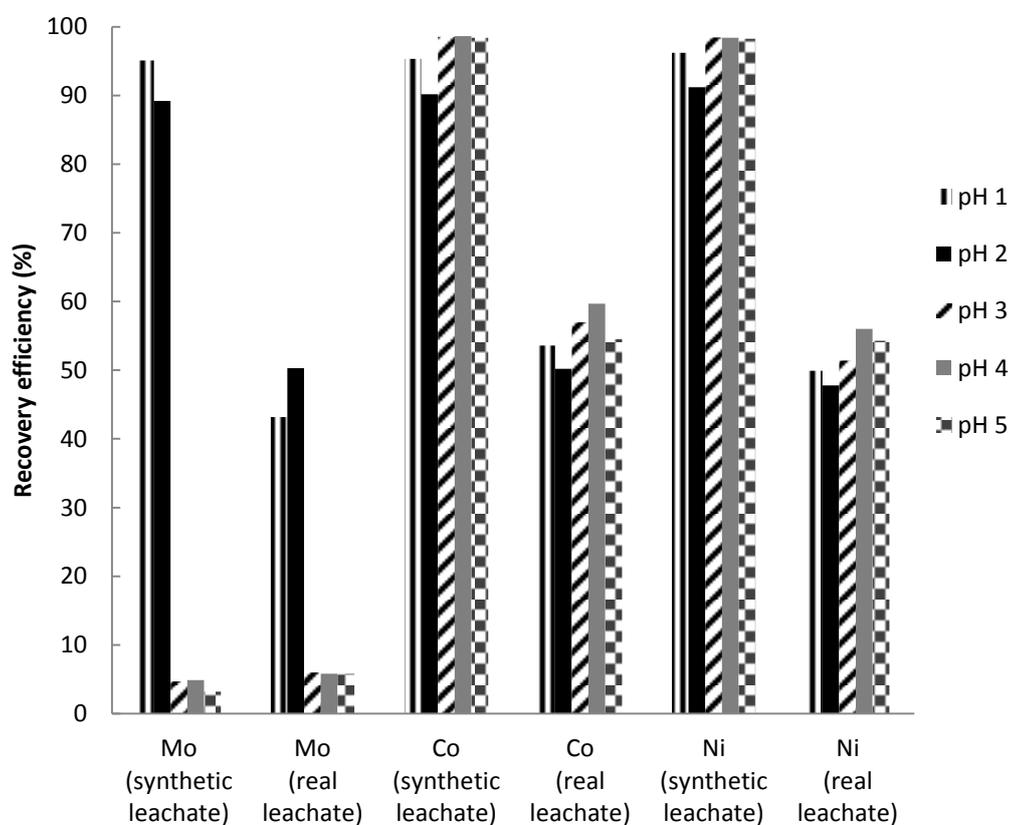


Figure 5.4. Experimentally investigated metal recovery efficiencies (%) from the synthetic and real metal leachate of mineral sludge from a metal recycling plant by Na_2S precipitation for the pH 1 - 5 (M/S ratio = 0.1, agitation speed = 100 rpm, time = 75 min). Three replicates, standard deviation < 5%.

5.3.2. Metal precipitation with Na_2S from the real acidic leachate

Precipitation of the real acidic leachate of mineral sludge with Na_2S under the previously determined optimal operational conditions (M/S ratio = 0.1, agitation speed = 100 rpm, time = 75

min and pH = 1), resulted in recovery efficiencies of only 43.2, 49.9 and 53.6% for Mo, Ni and Co, respectively (Figures 5.4 and 5.5a). Further optimization of the pH (Figures 5.4 and 5.5b) resulted in a maximal recovery of Mo at pH 2 (50.3%), while the maximal recoveries of Ni and Co were at pH 4 (56.0 and 59.7%, respectively).

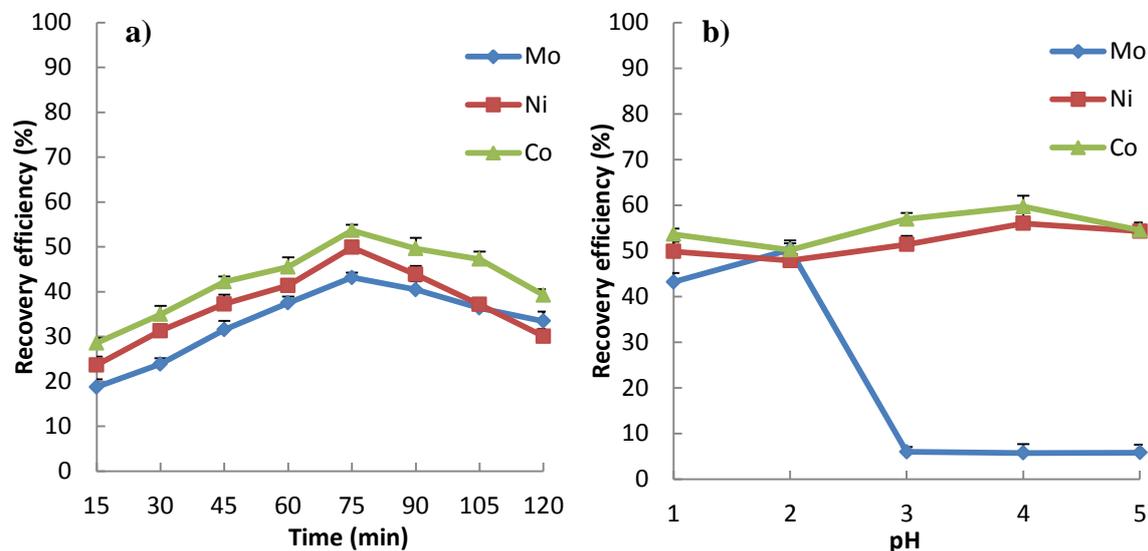


Figure 5.5. a) Metal recovery efficiencies (%) from the real acidic leachate of mineral sludge from a metal recycling plant by Na_2S precipitation for the time 15 - 120 min (M/S ratio = 0.1, agitation speed = 100 rpm, pH = 1). Three replicates, standard deviation < 5%. b) Metal recovery efficiencies (%) from real acidic leachate of mineral sludge from a metal recycling plant by Na_2S precipitation for the pH range 1 - 5 (M/S ratio = 0.1, agitation speed = 100 rpm, time = 75 min). Three replicates, standard deviation < 5%.

5.3.3. Characterization of metal sulfide/oxide precipitates

The metal sulfide/oxide precipitates had good settling properties: after 10 min of settling time the majority (80%) of the precipitate was settled down, while complete settling (200 mL L^{-1}) was observed after 30 min settling time.

Modelling and experimentally obtained Na_2S metal precipitation results (Figure 5.4) indicated that Mo can be selectively recovered at pH 1 after simultaneous precipitation of Ni and Co at pH 4. In order to confirm these findings, Environmental Scanning Electron Microscopy (ESEM), X-ray Diffraction (XRD) and analysis of Total Metal Content (TMC) were performed on metal sulfide/oxide precipitates formed at pH 1, pH 4 and also after simultaneous precipitation of Ni and Co (pH 4) again at pH 1.

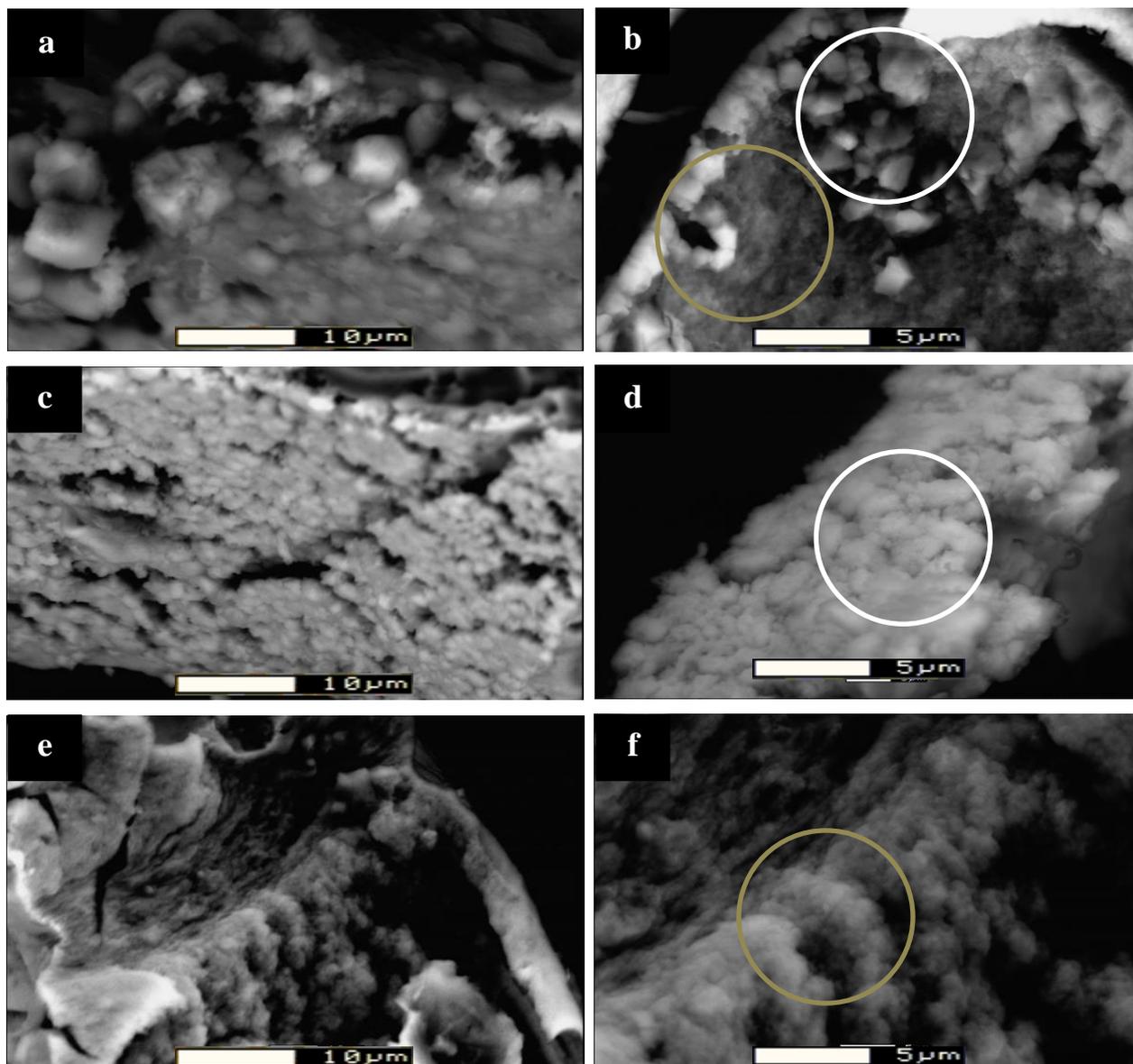


Figure 5.6. Environmental scanning electron micrographs of metal sulfide/oxide precipitates at pH 1 (5.6a and 5.6b), pH 4 (5.6c and 5.6d) and pH 1 (5.6e and 5.6f) after simultaneous precipitation of Ni and Co at pH 4. White circles point out Ni and Co crystals, brown circles Mo crystals.

Different morphologies of precipitates were clearly noticeable. At pH 1 round, edgy precipitates as well as finer, amorphous precipitates (indicating the presence of a mixture of Mo, Ni and Co) were formed (Figures 5.6a and 5.6b). At pH 4 only round, edgy precipitates are present indicating the presence of only Ni and Co (Figures 5.6c and 5.6d), while at pH 1 (after simultaneous precipitation of Ni and Co at pH 4) only fine, amorphous precipitates are present indicating the presence of Mo (Figures 5.6e and 5.6f).

ESEM observations were done on the metal sulfide/oxide precipitates formed with synthetic and real leachate at pH 1, pH 4 and pH 1 after simultaneous precipitation of Ni and Co at pH 4 (Figure 5.7a), all three targeted elements are present as metal sulfide/oxide precipitate at pH 1 (recovery efficiency of 90.0, 92.9 and 88.9% for the Mo, Ni and Co, respectively). At pH 4, only Ni and Co were detected in the metal sulfide/oxide precipitate (recovery efficiency of 92.9 and 88.9%, respectively). The absence of Mo was verified by Visual MINTEQ modelling indicating that Mo is complete in the solution at pH 4. Once the Ni and Co are precipitated at pH 4, Mo can be selectively recovered by lowering the pH to 1 (recovery efficiency of 95%).

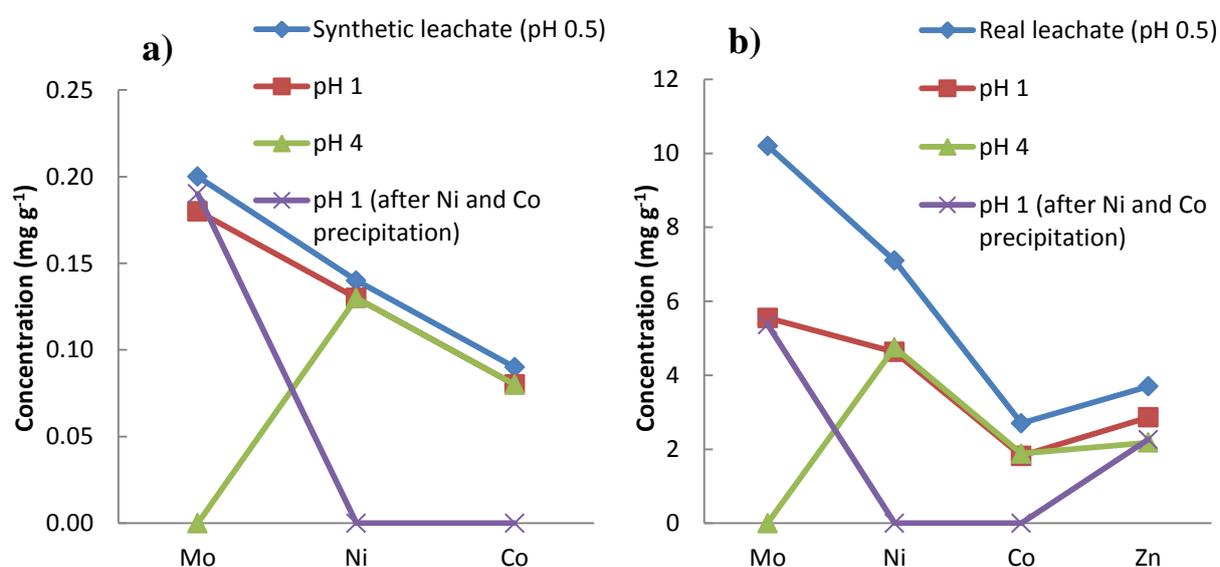


Figure 5.7. Metal concentrations measured in metal sulfide/oxide precipitates from the synthetic (a) and real (b) metal leachate at pH 1, pH 4 and pH 1 after simultaneous precipitation of Ni and Co at pH 4. Three replicates, standard deviation < 5%.

Similar trends are noticed in the case of real acidic metal leachate (Figure 5.7b), with the difference that apart from the three target metals (Mo, Ni and Co), also Zn is detected in the leaching solution and precipitates with the sulfide. The presence of Zn creates competing conditions for sulfide ions, resulting in lower metal recovery efficiencies of the target metals. At pH 1, Mo, Ni, Co and Zn are detected in the metal sulfide/oxide precipitate (recovery efficiencies of 54.4, 65.3, 67.4 and 77.3%, respectively). Similarly to the total metal analysis of the synthetic metal leachate, Mo is absent at pH 4, while Ni, Co and Zn precipitate with recovery efficiencies of 66.9, 69.6 and 58.9%, respectively. Once the Ni and Co are precipitated at pH 4, Mo can be recovered by lowering the pH to 1 (recovery efficiency of 52.6%). Apart from Mo,

the presence of Zn (recovery efficiency of 61.1%) is detected as well at pH 1 after precipitation of Ni and Co.

During the XRD analyses performed on the metal sulfide/oxide precipitates from the synthetic leachate obtained at pH 1, pH 4 and pH 1 after simultaneous precipitation of Ni and Co at pH 4, no crystalline phases of the formed metal sulfides could be identified. Due to the amorphous metal sulfide precipitates in the micrometer range, the XRD peaks were broad which made their identification difficult. Similar findings are reported by Jovanovic et al. (2007), where the nanometric crystal sizes disable the determination of zinc sulfides. On the other hand, in case of metal sulfide/oxide precipitates from the real leachate at pH 1 (Figure 5.8a), pH 4 (Figure 5.8b) and pH 1 after simultaneous precipitation of Ni and Co at pH 4 (Figure 5.8c), mineral crystalline phases were clearly defined. At pH 1, MoO_3 , NiS_2 , CoS_2 and ZnS were detected. At pH 4 NiS_2 , CoS_2 and ZnS were detected, while Mo crystalline mineral phases were absent. At pH 1, after simultaneous precipitation of Co and Ni at pH 4, only crystalline mineral phases of MoO_3 and ZnS were present.

Recovery of Mo, Ni and Co by precipitation from the acidic leachate of a mineral sludge produced by a metal recycling plant

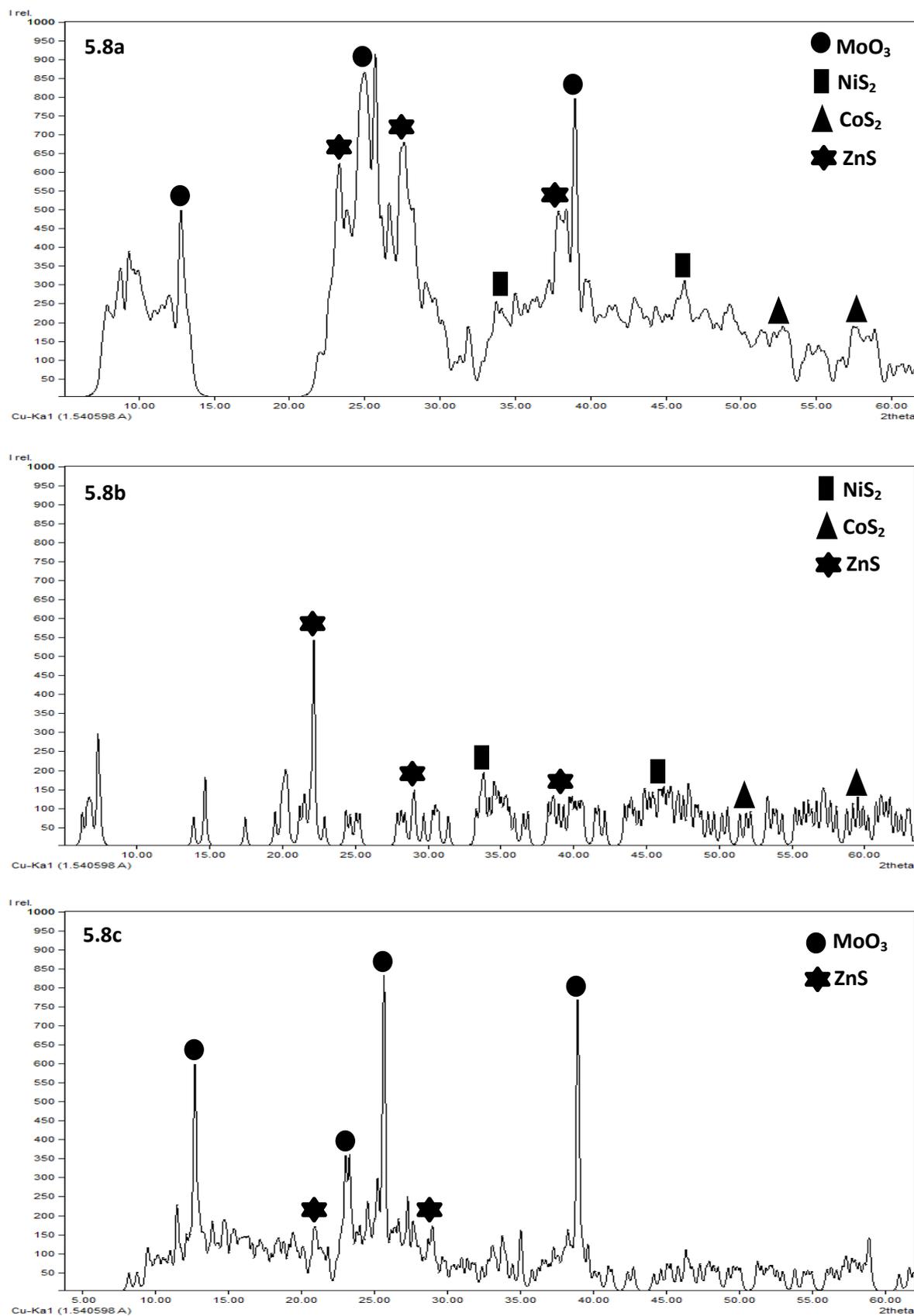


Figure 5.8. Mineral phases detected in the real leachate metal sulfide/oxide precipitates at pH 1 (5.8a), pH 4 (5.8b) and pH 1 after simultaneous precipitation of Ni and Co at pH 4 (5.8c).

5.4. Discussion

5.4.1. *Na₂S precipitation of real acidic leachate of mineral sludge*

This study showed that Na₂S precipitation of real acidic leachate of mineral sludge resulted in metal recovery efficiencies that are roughly 35% lower than the ones achieved while precipitating synthetic metal leachate that contains only the target metals. The lower metal recovery efficiencies achieved with the real acidic metal leachate can be attributed to various factors: i) changes in the pH, ii) nature of the leachant, iii) co-precipitation of Zn and competition for S²⁻ ions, and iv) oxidation of metals at the mineral surfaces.

Changes in the pH during the sulfide precipitation process can affect the target metal solubility, resulting in lower recovery efficiencies (Veeken et al., 2003). Precipitation of metal ions from solution was found to be accompanied by a rapid drop in pH (Lewis, 2010). However, when the surface of the particles is highly charged the particles become hydrophilic and dispersed. As a result, the low removal efficiency and decreasing particle size observed during mixed metal precipitation can be attributed to the highly charged nature of the resulting particles and segregation as the pH of the process increases over time (Al-Tarazi, 2004).

The differences between theoretical (H₂MoO₄ at pH 2) and experimental (MoO₃ at pH 1) results in case of Mo precipitation could be attributed to the fact that the molybdate species in aqueous solutions depends on the Mo concentration and the pH (Mitchell, 1990). At Mo concentrations exceeding 10⁻³ mol L⁻¹ at pH > 6, the predominant species is the tetrahedral [MoO₄]²⁻ ion. As the pH is lowered, the anions become protonated and polymerization condensation occurs giving the heptamolybdate ion [Mo₇O₂₄]⁶⁻ at pH 5 - 6 and the octamolybdate ion [Mo₈O₂₆]⁴⁻ at pH 3 - 5. At pH 2 - 3, the dominant species is molybdic acid (H₂MoO₄), while at pH < 1 Mo trioxide (MoO₃) precipitates. Molybdic acid (H₂MoO₄) refers to a solid, hydrated form of MoO₃ in aqueous solution. H₂MoO₄ precipitates efficiently only when the molarity of the leachate is around or below 0.5 M (Mitchell, 1990). As the molarity of our real metal leachate was 18 M, H₂MoO₄ could not be detected in the obtained precipitates. Instead MoO₃ precipitated, which was indeed detected by XRD analysis (Figure 5.8).

In comparison with the work of Cibati et al. (2013) where Mo was precipitated in the form of MoS₂, Mo precipitated in the form of MoO₃ in our study. In the work of Cibati et al. (2013), the precipitates obtained from solution at pH 2 were analysed by SEM-EDS to determine their

elemental composition. Oxygen (O), sulfur (S) and Mo were the predominant elements in the precipitates (approximately 31%, 28% and 22%, respectively), indicating the precipitation of Mo as sulfides and oxides. In our study, concentrated H_2SO_4 rapidly oxidizes MoS_2 into MoO_3 (Vertes et al., 1976) and it could thus not be detected in the obtained precipitates.

The synthetic metal leachate was prepared in 0.5 M HNO_3 , whereas the concentrated H_2SO_4 (18 M) was used for the leaching. Latter possibly influenced target metals solubility causing some metals to dissolve back into the solution, attributed to the fact that H_2SO_4 has a strong acidic nature (Barik et al., 2012a,b). Due to the strong oxidising power of H_2SO_4 , metal sulfide/oxide precipitates undergo oxidation to metal sulfate salts thus resulting in the decreased target metals recoveries.

Due to the complex composition of the mineral sludge in the real H_2SO_4 metal leachate apart from the target metals (Mo, Ni and Co), other metals such as Zn, Fe, Cr and Ca are present which precipitate with Na_2S as well. The total metal analysis and XRD showed that also Zn was co-precipitating, causing interference and competition for S^{2-} ions, and therefore resulting in less S^{2-} ions available for the precipitation of the target metals. Zinc precipitation at pH 1 (92%) and pH 4 (100%) was confirmed with the Visual MINTEQ modelling. Co-precipitation of other metals (Fe, Cr and Ca) was not detected in significant quantity.

The surface of the metal sulfide/oxide precipitates is highly reactive and begins to oxidize as soon as the mineral is longer in contact with water, if no particular precaution is taken (Lewis and van Hille, 2006). Consequently, it is necessary to ensure minimal oxidation of the metal sulfide/oxide particles during the precipitation step. According to Mokone et al. (2009), non-oxidized metal precipitates have an isoelectric point that lies at low pH. As the extent of oxidation increases, the position of the isoelectric point shifts towards the alkaline side, resulting in lower metal precipitation efficiencies. In addition, the metal sulfide/oxide precipitates are in the nanometer scale and they may not be able to settle down properly, which could explain why Mo, Ni or Co are not fully recovered (Villa Gomez et al., 2015).

5.4.2. Na_2S precipitation of synthetic leachate

The metal sulfide ratio influenced the efficiency of the metal sulfide/oxide precipitation: the metal recovery efficiencies gradually increased with a decreasing M/S ratio (Figure 5.1). This

might be due to an M/S ratio below 1, thus more sulfide ions are available per metal ions, which ensures metal sulfide/oxide precipitation (Kaksonen et al., 2006). In the case where the M/S ratio exceeds 1, there are fewer sulfides available, resulting in a decreased metal sulfide precipitation yield (Kaksonen et al., 2006).

Looking at the effect of the agitation speed (rpm) on the metal sulfide/oxide precipitation (Figure 5.2a), apart from the fact that there is a roughly 20% increase in the metal recovery efficiency under agitation conditions, it was visually observed that the largest precipitates were formed at 75 rpm (Figure 5.2b). Metal precipitation, as a chemical reaction, can occur in seconds forming colloids at nanometer scale (Lewis, 2010). Subsequent, particle growth and hence, metal depletion from solution occurs at a slower rate (Peters et al., 1984).

The physics of nucleation and crystal growth processes involved during metal sulfide/oxide precipitation are rather complex (Bhattacharyya et al., 1979; Lewis and van Hille, 2006; Veeken et al., 2003). Small particles are initially formed in solution and subsequently undergo secondary particle processes such as aggregation and aging (Veeken et al., 2003). The behaviour of the initially formed primary particles during precipitation processes is governed by the interfacial forces between them (Peters et al., 1984). When precipitation of metal ions from solution is enhanced, the level of supersaturation generated increases and thus the rate of primary homogeneous nucleation becomes significantly higher. As a result, the amount of fine particles formed in solution increases (Lewis, 2010). Al-Tarazi (2004) showed that the mass transfer and metal concentration have a considerable influence on the morphology of the particles produced during metal sulfide/oxide precipitation. Depending on the conditions, either nucleation or crystal growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained (Lewis and van Hille, 2006).

When investigating the effect of contact time (Figure 5.3), the addition of sulfide resulted in a very rapid reaction for the synthetic solution, leading to a colour change from transparent to dark brown solution. As the time passed, due to the rapid reaction kinetics the supersaturation ratio remained low and resulted in the formation of amorphous precipitates (Figure 5.2b). The optimal time that achieved the highest metal recovery efficiency was at 75 min (Figure 5.3). The gradual decrease in metal recovery efficiency after 75 min possibly happened due to change of pH which influenced the solubility of metals resulting in metal dissolution from metal sulfide/oxide precipitates.

The pH is an important operational factor as it influences both the solubility of sulfides, and the kinetics of the precipitation processes for selective metal recovery (Lewis, 2010). Visual MINTEQ simulations showed that aqueous sulfide speciation and thus the aqueous concentration of the reactive sulfide species (*i.e.* HS^- and S^{2-}) depends on the pH of the solution. Due to a release of protons the pH of the solution decreases. As the pH of the solution drops, the sulfide speciation equilibrium is reversed and favors aqueous H_2S (Lewis and van Hille, 2006). When this happens, the availability of the reactive HS^- ions in solution decreases and the reaction between the metal ions and HS^- ions is suppressed (Lewis, 2010). While the availability of reactive HS^- ions decreases, the amount of supersaturation necessary for nucleation and growth of particles also decreases. When the pH continues to decrease, the solution becomes depleted of the initially produced supersaturation and aggregation and/or flocculation become inhibited due to lack of the supersaturation required to provide the growth medium for the inter-particle crystalline bridges (Lewis and van Hille, 2006).

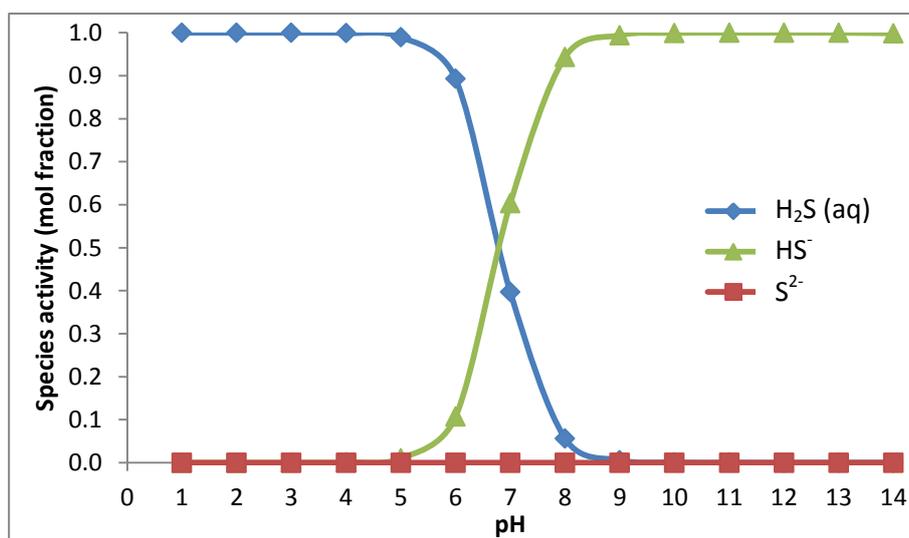


Figure 5.9. pH dependence of sulfide species as simulated in Visual MINTEQ.

The pH determines the solubility of the metal species. Therefore, it determines their availability in solution (Gonzalez-Silva et al., 2009). From our theoretical and laboratory investigations, it was noticed that the controlling of the pH allows selective recovery of Mo at pH 1 (Figure 5.4) after simultaneous precipitation of Ni and Co from the mixed metal synthetic leachate at pH 4. Visual MINTEQ simulations and laboratory investigations indicated that selective precipitation was not possible for Ni and Co because of the similarity of their solubility products: 1.3×10^{-25} - 4×10^{-20} for NiS and 3×10^{-26} - 5×10^{-22} for CoS (Cibati et al., 2013).

5.4.3. Mineral sludge of metal recycling plant as a secondary resource for metals

Metal recovery from secondary resources (*i.e.* mineral sludges) has a great importance in view of the presence of several metals of economic interest (such as Mo) which are sometimes richer than the available natural reserves (ores/minerals). The high price, high demand and future shortage of primary mineral resources for metals such as Mo, Ni and Co creates a need to develop secondary resources and to find more beneficial ways of metals recovery from such resources (McGrath et al., 2010a,b; Van Gestel et al., 2012).

As the investigated mineral sludge sample is highly loaded with metals, the use of this type of sludges as a secondary resource for metal recovery could at the same time reduce the amount of sludges that needs to be disposed off yearly in landfills (thus preventing environmental contamination) and reduce the costs of their disposal (Vemic et al., 2015). Additionally, utilization of industrial mineral sludges as a secondary resource for metal recovery is an appropriate solution to manage the continuously increasing waste sludge generation, to reach stringent environmental quality standards, and at the same time to sustain the metal reserves for our future generations (Kabata-Pendias and Mukherjee, 2007).

5.5. Conclusion

- This work, for the first time, gives an insight into the recovery of Mo, Ni and Co from the acidic leachate of mineral sludge from a metal recycling plant with Na₂S under different operational parameters.
- Optimized Na₂S precipitation of metals from the synthetic metal leachate resulted in the selective recovery of Mo at pH 1 (98% Visual MINTEQ, 95.1% experimental) after simultaneous precipitation of Ni and Co at pH 4 (100% Visual MINTEQ, 98% experimental).
- Metal precipitation from the real acidic leachate resulted in a maximal Mo recovery at pH 2 (50.3%) as Mo oxides, while the maximal recoveries of Ni and Co were at pH 4 (56.0 and 59.7%, respectively) as Ni and Co sulfides.

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CHAPTER 6

Future molybdenum, nickel and cobalt shortages and their recovery from secondary resources

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CHAPTER 6

Numerous industries (*e.g.* metal-finishing, electroplating, electronic, steel and nonferrous processes, petrochemical and the used electronic/household goods), discharge a variety of toxic heavy metals such as Mo, Ni, Co, Cu, Cd, Cr, Zn etc. Metal containing wastes/byproducts of various industries are potential pollutants of human habitation including air, surface and water, if not treated properly. Some metals can be toxic to living organisms. Man, who is on top of the food pyramid, will receive the pre-concentrated metals from plants and animals. Therefore, not only the environment, but also the human beings will suffer of the negative consequences of heavy metal pollution. As environmental regulations become ever more stringent, particularly regarding the disposal of toxic wastes, the costs for ensuring environmental protection continue to rise. In addition, high price, high demand and future shortage of metals such as Mo, Ni and Co create a need to develop novel recovery processes from secondary resources (*i.e.* spent catalysts, mineral sludges, etc.), as there is a projected shortage of the primary resources for these metals. Therefore, there is a need to utilize more efficient technologies to recover metals from wastes/secondary resources in order to minimize capital outlay, environmental impact and to respond to the metal increased demand.

6.1. Scarcity of metals

The move toward new and better technologies means an ever-increasing demand for metals (such as Mo, Ni and Co) that are scarce due to both geology and geopolitics constraints. Earth metal resources are not evenly distributed around the globe (Marafi and Stanislaus, 2008a). For example, China controls 97% of the global rare earth elements production and has active mines and a strong manufacturing demand that has so far been supplying the entire world with these metals (Marafi and Stanislaus, 2008b). The largest producers of Mo are China (~41%), United States (~23%), Chile (~14%), Peru (~16%), Mexico (~4%) and Canada (~2%) (U.S. Geological Survey, 2014; Figure 6.1). On the other side, the largest producers of Ni are Indonesia (~18%), Philippines (~18%), Russia (~10%), Australia (~10%), Canada (~9%) and Brazil (~6%) (U.S. Geological Survey, 2014; Figure 6.1). The largest producers of Co are Congo (~49%), Canada (~7%), China (~6%), Russia (~6%), and Australia (~5%) (U.S. Geological Survey, 2014; Figure 6.1).

Bottom of the ocean, Antarctica and the Arctic contain many different resources available for extraction, including silver, gold, copper, manganese, cobalt, and zinc (Dodson et al., 2012; European Commission, 2010). In these locations the resources are usually found in higher concentrations than in the terrestrial mines. However, the extraction of the resources from such locations is very difficult and limited by transport because the resources are generally not next to the production sites. In addition, the extraction of the resources is very expensive and always imposes high environmental impacts on surrounding areas and ecosystems (European Commission, 2010).

Despite the high price, high demand and future shortage of metals for energy or resource-saving technologies (such as Mo, Ni and Co), very little amounts of these metals are recycled. In 2009, it was estimated that less than one percent of these metals was recovered (Zeng and Cheng, 2009a). Thus, the sustainable handling of wastes/secondary resources is very important to maximize the recovery of metals and to minimize the pollution (Zeng and Cheng, 2009a). It helps reduce the amount of valuable metals being wasted every year. The recovered metals can help cater the needs for generations to come and help preserve the Earth's natural resources for many more years (Zeng and Cheng, 2009b).

6.1.1. Metals criticality in the European context

Securing reliable and undistorted access of certain metals (Mo, Ni and Co) is of growing concern within the Europe and across the globe (Kleijn et al., 2011). Although data are often sparse, available information suggests that current practices are likely to lead to scarcity for some metals in the not-too-distant future (Nansai et al., 2015).

Much of Europe's industry and economy is reliant on international markets to provide access to essential metals. Critical metals have a high economic importance to the Europe combined with a high risk associated with their supply (Peiró et al., 2013). Analysis of the global primary supply of the critical metals identifies around 90% of global supply originated from extra-EU sources, mostly from China (Dodson et al., 2012).

The European Commission published report concluding that certain metals (such as Co and Ni), including rare earths, are critical to the emerging clean energy economy. The first criticality analysis for metals was published in 2010 by an expert group of the European Commission.

Twenty critical raw materials were identified as critical from the list of fifty-four candidate materials (*e.g.* Co, Ni, Cr, Mg, W, In, Ga, etc.). In case of critical metals, European Commission (2010) considers two types of risks: i) the 'supply risk', which takes into account the political-economic stability of the producing countries, the level of concentration of production, the potential for substitution and the recycling rate; and ii) the 'environmental country risk' which addresses the risk that measures might be taken by countries with weak environmental performance in order to protect the environment and, in doing so, endanger the supply of metals to the Europe.

As the report imply, there is serious concern that the spread of green technologies by countries endeavoring to limit their greenhouse gas emissions will inevitably increase demand for the metals in question, leading to a tightening of supply. As we strive to reduce global carbon emissions, it is therefore essential to limit the current growth of metals consumption while still meeting rising demand for them. In other words, in those countries and regions involved in any way with the global flow of the metals in question it is necessary to use these metals more efficiently, that is, less wastefully, to reduce unnecessary mining (Dodson et al., 2012; Kleijn et al., 2011; Reck and Graedel, 2012).

After millennia of products made almost entirely of a handful of metals, modern technology is today using almost every possible metal, but often only once (European Commission, 2010). Therefore, there is a clear need for better design for recycling and for new recycling processes that support the recovery of scarce metals and do not pose risks of adulterating other recycling streams.

6.1.2. Molybdenum, nickel and cobalt world production and uses

Molybdenum (Mo), nickel (Ni) and cobalt (Co) are important metals for human activities and industry in general (Pradhan et al., 2013). They are expensive metals. In 2014 the average market price for Mo, Ni and Co was 21,433 € t⁻¹, 13,847 € t⁻¹ and 24,705 € t⁻¹, respectively (www.infomine.com). World production of Mo, Ni and Co is presented in Figure 6.1.

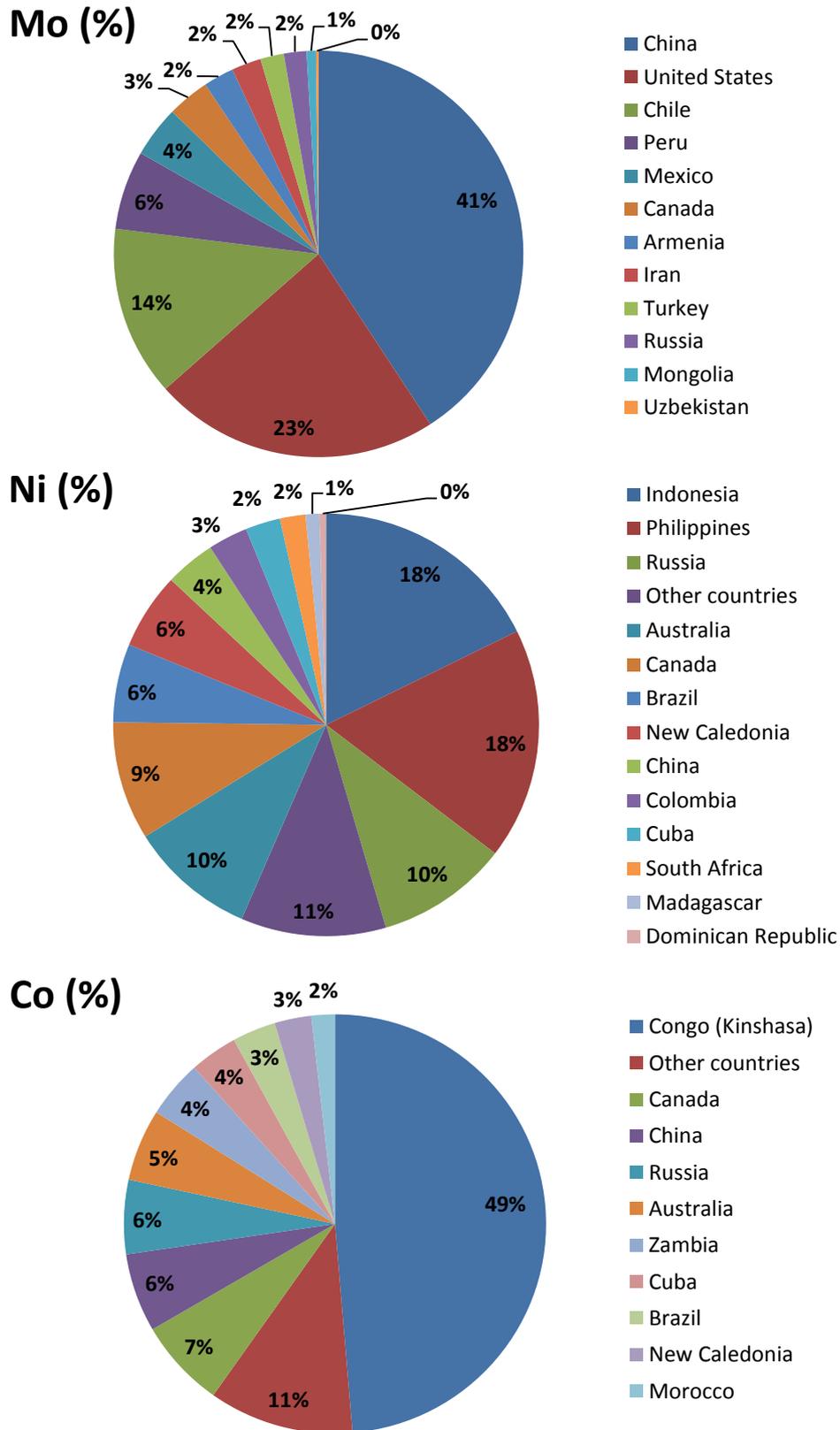


Figure 6.1. World production (%) of molybdenum, nickel and cobalt, based on the U.S. Geological Survey, Mineral Commodity Summaries, 2014.

6.1.2.1. Molybdenum uses and recycling in 2014

Mo is used as a constructional steel, 35%; stainless steel, 25%; chemicals, 14%; high-speed steel, 9%; cast iron, 6%; Mo metal, 6%; superalloys, 5% (U.S. Geological Survey, 2014). In 2014, Mo valued at about 1.1 billion euros was produced at 11 mines. Mo in the form of Mo metal or superalloys was recovered, but the amount was small. Although Mo is not recovered from scrap steel, recycling of steel alloys is significant, and some Mo content is reutilized. The amount of Mo recycled as part of new and old steel and other scrap may be as much as 30% of the apparent supply of Mo (U.S. Geological Survey, 2014).

6.1.2.2. Nickel uses and recycling in 2014

In 2014 (U.S. Geological Survey, 2014), approximately 48% of the primary Ni consumed went into stainless and alloy steel production, 41% into nonferrous alloys and superalloys, 7% into electroplating, and 4% into other uses. End uses were as follows: transportation, 31%; fabricated metal products, 13%; electrical equipment, 12%; petroleum industry, 10%; chemical industry, construction, household appliances, and industrial machinery, 8% each; and other, 2% (U.S. Geological Survey, 2014). The estimated value of apparent primary consumption was 1.4 billion euros. About 82,200 tons of Ni was recovered from purchased scrap in 2014. This represented about 41% of reported secondary plus apparent primary consumption for the year (U.S. Geological Survey, 2014).

6.1.2.3. Cobalt uses and recycling in 2014

In 2014 (U.S. Geological Survey, 2014), about 48% of the Co consumed was used in superalloys, mainly in aircraft gas turbine engines; 9% in cemented carbides for cutting and wear-resistant applications; 16% in various other metallic applications; and 27% in a variety of chemical applications (U.S. Geological Survey, 2014). The total estimated value of Co consumed in 2014 was 200 million euros. In 2014, Co recovered from purchased scrap represented an estimated 26% of Co reported consumption (U.S. Geological Survey, 2014).

6.1.3. Market trends in molybdenum, nickel and cobalt prices

Due to the explosion in demand for Mo, its price (as oxide) increased abruptly in mid-2002, levelling off around 9 € kg⁻¹ in 2003. The temporary closure of some mines in China has pushed the price above 12 € kg⁻¹ (Marafi and Stanislaus, 2008a). During this period, the average price has risen from 11 to almost 31 € kg⁻¹. In 2005, however, the price of MoO₃ stood with some fluctuations, at around 55 € kg⁻¹, while between May 2007 and October 2008 the price has remained more or less constant over 46 € kg⁻¹ (Marafi and Stanislaus, 2008b). In March 2015 the price of Mo oxide fluctuated around 20 € kg⁻¹ (Figure 6.2).

The Co price has been relatively stable until the 70s, then, because of uncertainties in the supply, the price rose more than 62 € kg⁻¹ (Marafi and Stanislaus, 2008b). After an initial stabilization in the 80s (about 15 € kg⁻¹) the price began to rise again in the early 90s to about 46 € kg⁻¹. From 1996 to 2000, prices have always fluctuated between 20 and 35 € kg⁻¹ (Marafi and Stanislaus, 2008a). In March 2015 price of Co fluctuated around 25 € kg⁻¹ (Figure 6.2).

As for the price of Ni, it has fluctuated very similar to those of other metals. In 2005 began a continued prices growth that has reached peak (~ 35 € kg⁻¹) to April 2007, and then begin a slow descent interrupted by some short period of increases (Marafi and Stanislaus, 2008a). The sharp price increase that was recorded for almost two years was due not only to an increase in real demand but also a strong speculation of investment funds that have invested heavily in commodities (Marafi and Stanislaus, 2008b). In March 2015 price of Ni fluctuated around 15 € kg⁻¹ (Figure 6.2).

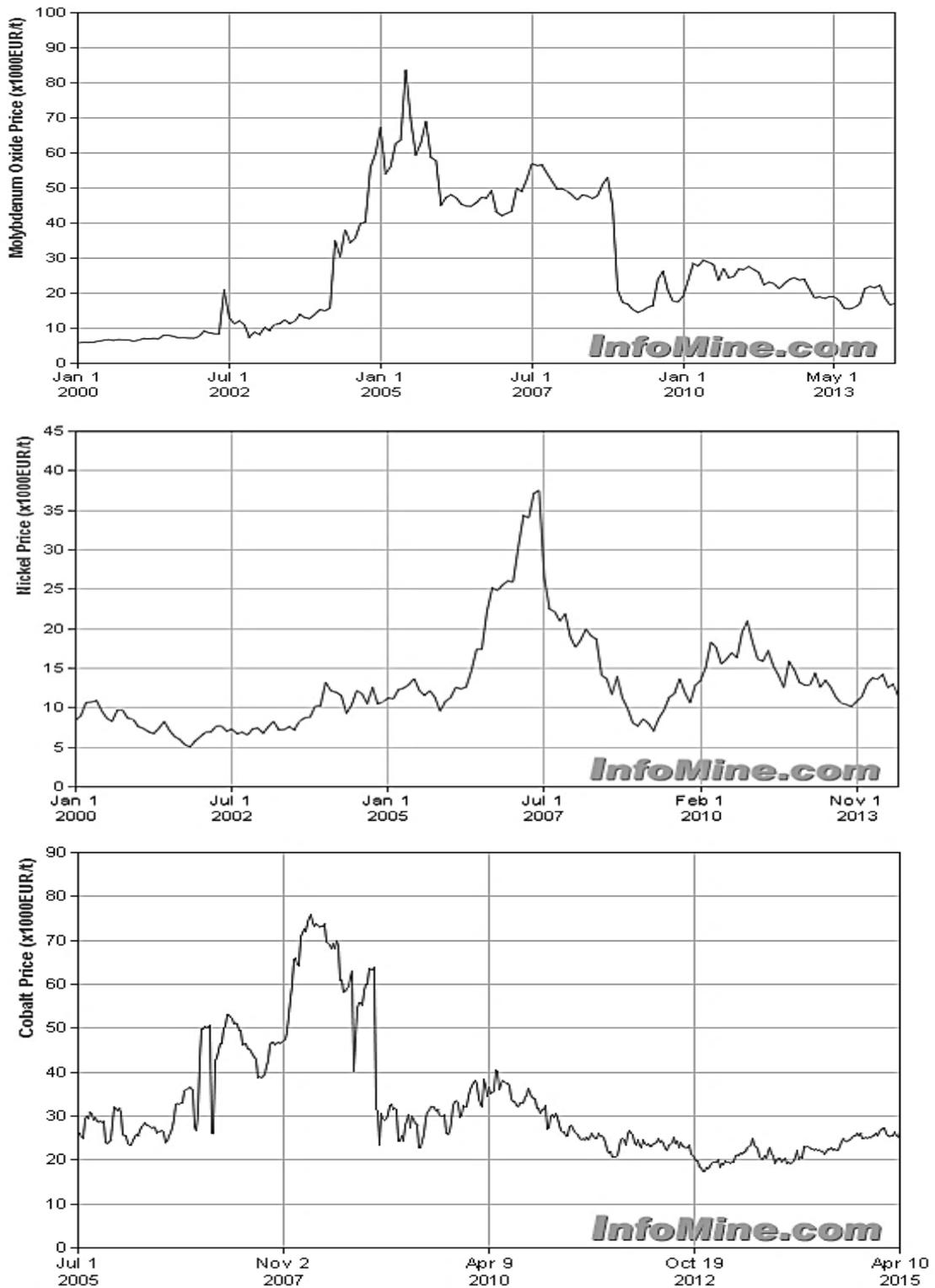


Figure 6.2. Historical prices (€ t^{-1}) of molybdenum, nickel and cobalt (www.infomine.com).

6.2. Spent catalysts as a secondary resource for molybdenum, nickel and cobalt

Due to the high price, high demand and future shortage of the primary mineral resources for Mo, Ni and Co, it is extremely important to develop secondary resources for these metals (Banda et al., 2013a,b).

In view of the on-going depletion of the natural resources taking place worldwide it is necessary to implement metals recycling/recovery/reuse from semi-finished products, by-products, secondary materials and wastes, including hazardous waste (*i.e.* spent catalysts) (Mazurek, 2013). Among the different secondary resources, spent catalysts discarded from industries are undoubtedly very important (Marafi and Stanislaus, 2003; Silvy, 2004). About 150 - 170 kilotons of exhausted catalysts are produced every year in the world (Marafi and Stanislaus, 2008b). The most common catalysts generally consist of 10 - 30% Mo, 1 - 12% V, 1 - 6% Co, 0.5 - 6% Ni, 8 - 12% S, 10 - 12% C and the balance is γ -alumina, which makes them economically viable for recovery of valuable metals (Cibati, 2011).

Recovery of metals from spent catalysts depends on several factors: chemical composition, the price of metals, the environmental directories and the operational costs. Since the cost of transportation and disposal in industrial dumps, the severity of environmental directories, and the price of some metals have been rising, spent catalysts have been recognized as a secondary source of valuable metals (Mazurek, 2013).

The volume of spent catalysts discarded as solid waste has increased significantly in recent years due to the following reasons (Silvy, 2004):

- (i) A rapid growth in the distillates hydrotreating capacity to meet the increasing demand for ultra-low sulfur transportation fuels.
- (ii) Reduced cycle times due to higher severity operations in diesel hydrotreating units.
- (iii) A steady increase in the processing of heavier feedstocks containing higher sulfur and metal contents to distillates by hydrogen addition technology.
- (iv) Rapid deactivation and unavailability of reactivation process for residue hydroprocessing catalysts.

As the world supply of crude oil is further extended and low-sulfur crudes become less available, catalysts increase in their use (Zeng and Cheng, 2009a,b). About 150 - 170 Kt of exhausted

catalysts are produced every year in the world (Marafi and Stanislaus, 2007; Marafi and Stanislaus, 2008a,b; Pagnanelli et al., 2011). After periodical use of the catalysts, due to the poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they become inactive. Catalysts poisoning involves strong chemical interactions of a component of the feed or products with active sites on the catalyst surface (Pagnanelli et al., 2011). Catalysts are also deactivated by sintering which causes loss of active surface area and therefore lowers catalytic activity. In general, catalysts deactivated by thermal degradation, phase separation or phase transformations, cannot be reactivated easily and therefore, replacement is necessary. In such cases, fresh catalysts have to be substituted and the spent catalyst will be discarded as waste material (Pradhan et al., 2013).

Direct dumping of such a waste catalysts, not only causes environmental pollution, but also is associated with the waste of valuable metals. Due to on-going environmental concerns and regulations (USEPA, 2003), the recycling and re-utilization of spent catalysts are important for the protection of environment and recovery of the valuable metals.

The hazardous nature of the spent catalysts is attracting the attention of environmental authorities in many countries and the refiners are experiencing pressures from environmental authorities for safe handling of spent catalysts. Earlier studies on the environmental, disposal and utilization aspects of spent refinery catalysts have been reviewed by Furimsky (1996) and Trimm (1990). Various options such as: (a) minimizing spent catalyst waste generation, (b) utilization to produce new catalysts and other useful materials, (c) recycling through recovery of metals and (d) treatment of spent catalysts for safe disposal, are available to refiners to handle the spent catalyst problem (Mazurek, 2013).

6.3. Mineral sludge as a secondary resource

Apart from spent catalysts, mineral sludges generated at the spent catalysts recycling plants could be a very good secondary resource for metals as well, as they contain high concentrations of different metals (especially Mo, Ni and Co). Therefore, mineral sludges should be viewed as a resource, not as a waste. For example, recovered metals from the mineral sludges can be used to produce useful chemicals or reagents (Furimsky, 1996). Remaining solids of the mineral sludge which are free of heavy metals can be reclassified as non-hazardous and be safe for final disposal or may be used for land reclamation (Furimsky, 1996).

Metal containing mineral sludges may be important secondary resources if processed in eco-friendly manner for secured supply of contained metals/materials (Asghari et al., 2013a). Physical and chemical immobilization of mineral sludge ensure that the hazardous elements are permanently trapped as highly insoluble compounds or encapsulated inside an inert matrix, so that they do not leach out and pollute soil and groundwater. This method may help reduce the pollution problem, but it would suffer when scrutinized for sustainability (Mazurek, 2013).

The methods of recovering metals from mineral sludges can be broadly classified into three groups: (a) physical, (b) chemical and (c) biological methods (Mazurek, 2013). Physical treatment methods are based on the principle of the extraction of the contaminants by physical or physiochemical means. Chemical methods use several types of organic and inorganic solutions, while biological methods use bacteria or plant cells and tissues to remove contaminants (Asghari et al., 2013a).

Potentially usable elements, many of which are scarce and expensive, are forbidden for future use by virtue of the treatment. In fact, they are artificially rendered difficult to recover. Therefore, a more practical approach is needed, which can both minimize the amount of waste generated and maximize the recovery of usable elements from the wastes instead of merely trapping or dumping them (Cibati, 2011).

6.4. Different metal leaching techniques advantages and disadvantages

Prior to target metals recovery, the metal minerals have to be leached out from solid (catalysts, mineral sludge, sediment etc.) into the liquid phase caused by inorganic/organic leachants. Numerous industrial processes, based on hydrometallurgy have been developed to extract metals from spent catalysts. Within the hydrometallurgical methods, acid solutions, with emphasis on sulfuric acid (H_2SO_4), have been widely studied as leachants to extract metals from spent catalysts. To dissolve high percentages of metals (extractions > 90%), concentrated solutions are required (Kim et al., 2009a,b).

In order for a leaching procedure to be satisfactory, it must have a high efficiency in leaching substantially all of the metal ions from solid, by converting it into the metallic or metal ion form in solution (Barik et al., 2012a). The metal must be produced in a form substantially free of contaminants and readily isolable. The leaching efficiency of heavy metals from solids varies

with solids properties and the types of leaching methods used (Barik et al., 2012b). Extracting agents normally used for metal extraction from solids are inorganic acids. Acid leaching or dissolution has proven to be a technically and economically efficient method in extracting of metals. When acid is added to sludge, the heavy metals present in the solid are dissolved and then exist in solution (Lai et al., 2008).

The attempts of using variety of leaching reagents such as H_2SO_4 (Barik et al., 2012b; Kim et al., 2009a,b; Vemic et al., accepted), HNO_3 (Khoshnevisan et al., 2012; Smirnov et al., 2010), HCl (Banda et al., 2013b), NaOH (Huang et al., 2014; Ruiz et al., 2011a), H_2O_2 (Ruiz et al., 2011b) and chemical acid mixtures (Barik et al., 2012a; Lai et al., 2008), in order to leach out different metals from spent catalysts have been reported one after another.

Hydrometallurgical approaches such as chemical leaching give Mo, Ni and Co leaching yields of $> 90\%$ (Vemic et al., accepted; Table 6.1). In spite of the good metal leaching efficiencies of chemical leaching, the leaching process itself requires continuous control, the use of high temperatures and the addition of large amounts of acid/alkali in the leaching process (Zeng and Cheng, 2009a,b). It is essential that other relevant factors also need to be taken into consideration, *e.g.* costs associated with handling by-products, such as liquid streams containing strong acids, toxic gases, etc. (Kar et al., 2004). Therefore, the methods which are based on the use of strong acids require a much higher level of safety precautions. Among all chemical leachants, sulfuric acid seems to be the best option since all of the valuable metals dissolve quickly due to its high oxidizing power. Although the acid mixtures showed significant improvement in the leaching efficiency compared to the individual acids, the high acid consumption and high cost present a drawback (Barik et al., 2012b).

Table 6.1. Advantages and disadvantages of metal leaching and recovery methods.

Method used	Advantages	Disadvantages
Leaching	-Extraction efficiencies of Mo, Ni and Co > 90% -Quick leaching processes	-Processes require continuous controlling, the use of high temperatures and large amounts of leachants -Costly in terms of chemical costs
Bioleaching	-Processes are more cost efficient, simpler and more environmentally friendly -Less costly in terms of chemical costs	-Long leaching processes (up to 20 days) -Extraction efficiencies of Mo, Ni and Co < 70% -Costly in terms of capital, energy and maintenance costs
Recovery	-Simple operations -Recovery efficiencies of Mo, Ni and Co > 90%	-High purities and selectivity are very hard to achieve -Very expensive and application in industry is limited

Apart from chemical leaching, bioleaching is also widely used for valuable metals recovery. In comparison with chemical leaching, bioleaching can offer attractive features, especially considering environmental issues; processes are more cost efficient (they can be performed at mild conditions), simpler (there is no need for a complex machinery) and more environmentally friendly than their chemical counterparts (Zeng and Cheng, 2009a,b; Table 6.1). Some of the disadvantages are that bioleaching has relatively long leaching cycles (usually around 20 days) and extraction efficiencies of Mo, Ni and Co are rather low (< 70%). The bioleaching process requires only 1/5th of the cost of the chemicals required for leaching and recovery of metals compared to the traditional chemical methods (Asghari et al., 2013b). Bioleaching processes are less costly in terms of chemical cost, but could prove costly in terms of capital cost, energy cost and maintenance cost associated with them. In addition to the costs of chemicals, the costs of mixing, aeration, construction of holding tank and operational maintenance will have to be added to the total cost for carrying out a satisfactory cost analysis (Asghari et al., 2013a).

6.5. Different metal recovery techniques advantages and disadvantages

From the hazardous waste management standpoint, it is important not only to leach out the metals from waste but also to develop means to recover them (Cibati et al., 2013). The recovery of metals from the leach liquors can be achieved through various methods (Zeng and Cheng,

2009a,b), such as precipitation (Cibati et al., 2013; Vemic et al., submitted), adsorption (Derakhshi et al., 2009; Pagnanelli et al., 2011), ion exchange (Henry and Lierde, 1998; Kononova et al., 2003; Nguyen and Lee, 2013a,b; Nguyen and Lee, 2014) and solvent extraction (Banda et al., 2012; Banda et al., 2013a; Mishra et al., 2010).

Precipitation, adsorption, ion exchange and solvent extraction are the main applied technologies for the recovery and purification of Mo, Ni and Co in spent catalyst leach solutions (Banda et al., 2012). The use of traditional recovery approaches, such as precipitation and adsorption, offers simple operations and good metals recovery (> 90%), but high purities and selectivity are very hard to achieve by these technologies (Pagnanelli et al., 2011; Table 1). Ion exchange and solvent extraction, offer a useful means for almost complete recovery of high purity of metals. However, these methods are very expensive and their scale of application in industry is limited (Kononova et al., 2003). Among all these techniques, solvent extraction is one that is well-established in hydrometallurgy for commercial production of high purity metals.

6.6. Future perspectives

The challenge of sustainable development at the beginning of the 21st century has become a systemic one, with environmental, social and economic dimensions on an equal footing (Marafi and Stanislaus, 2003). Our contributions need to be systematic, for example through the promotion of resource efficiency, improved materials recycling and life-cycle thinking (Kar, 2004).

It may not be easy to identify a metal leaching/recovery method of choice. Material requirements on the design and construction of equipment used for the leaching and recovery are rather different (Marafi and Stanislaus, 2008b). Fluctuations in the market prices for the metals and their concentration in the secondary resources are important factors which influence the economic viability of metal recovery (Marafi and Stanislaus, 2003). Therefore, future studies should be more focused on the assessment of the metals speciation in secondary resources (catalysts, mineral sludge, sediment etc.), which can indicate the ease of their leachability and recovery and help better decision making in term of a technique of choice (Vemic et al., 2015).

Recycling has become increasingly difficult today and much value is lost due to the growing complexity of products and complex interactions within recycling systems (Marafi and

Stanislaus, 2008b). Recycling of metals can be optimized on an economic and technological basis along product life cycles in the move towards sustainable metals management (Marafi and Stanislaus, 2003). Sustainable metals management requires more than improving recycling rates of selected materials. The whole mind-set on recycling of metals need to be changed, moving away from a material-centric approach to a product-centric approach (Kar, 2004).

The focus needs to be on optimizing the recycling of entire products at their end of life instead of focusing on the individual materials contained in them (Marafi and Stanislaus, 2008a). The global mainstreaming of a product-centric view on recycling will be a remarkable step towards efficient recycling systems, resource efficiency, and a green economy in the context of sustainable development and poverty eradication (Silvy, 2004). Such a transition will depend on the mobilization of everyone in the value chain, from operators in the primary production of metals and metal-containing products to the recycling and collection industry to the consumers. Industry can be the source of driving innovation that maximizes resource efficiency when policy makers draw on their expertise and tools (Marafi and Stanislaus, 2008a).

Only a wide, systemic view of recycling looking at the industrial and economic factors driving recycling can deal with the complexity of interactions between metals (Marafi and Stanislaus, 2008a). Recycling is primarily an economic industrial activity, driven by the value of the recovered metals and materials. An infrastructure for optimized recycling would therefore make use of economic incentives (Marafi and Stanislaus, 2008b). Those economic drivers must align with long term economic goals, such as conserving critical metal resources for future applications, even if their recovery may be currently uneconomic (Kar, 2004). Getting all stakeholders on board is crucial if we want to meet the increasing metal needs of the future in a sustainable way (Silvy, 2004). This is a challenging task for policy makers. A wide, systemic approach based on the solid understanding of the industrial and economic factors driving recycling will be needed. Such a knowledge base will allow to develop a coherent regulatory framework and powerful incentives for all stakeholders to participate in recycling and thus in our transition to a resource efficient society (Silvy, 2004).

It is time that corporations, universities, and governments work together to transform the state of today's metal recycling by demonstrating the need for continuing research on improved technologies, the potential benefits of deployment of the improved technologies now available, and the promise suggested by regulatory and financial initiatives that speak to these challenges.

If as a global society, we can collect and reuse almost everything, design products with optimized recycling in mind, and use transformative technology to make the whole process exemplary, we will be helping to ensure that the materials scientists of the future have for their use the full palette of the wonders of the periodic table, and thereby provide society with increasingly innovative and remarkable products.

6.7. References

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Curriculum Vitae



Mirjana Vemic was born on 1st September, 1986 in Savnik (Montenegro). In the years 2002 - 2005 she finished her high school (Medical High School) and she got admitted to the University of Montenegro for her Bachelor and Specialist studies. From 2005 - 2009 she obtained her Bachelor (Biologist) and Specialist (Ecologist) degrees, and she got selected as one of the students within the NEWEN project (Netherlands and Western Balkan Environmental Network, www.nevenproject.org), to perform her MSc studies in Delft, the Netherlands. From 2009 - 2011 she obtained her MSc degree in Environmental Science (Water Quality Management). From November 2011, she started her PhD in the Joint Doctorate program funded by Erasmus Mundus Joint Doctorate Environmental Technologies for Contaminated Solids, Soils and Sediments (ETeCoS³, www.internationaldoctorate.unicas.it). PhD research was carried out at University Paris-Est (France), University of Limoges (France) and UNESCO-IHE Institute for Water Education (The Netherlands). Most of her research is focused mainly on leaching and recovery of metals from metal recycling plants mineral sludges.

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