This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Liu, Fupeng; Wang, Jinliang; Peng, Chao; Liu, Zhihong; Wilson, Benjamin P.; Lundström, Mari

Recovery and separation of silver and mercury from hazardous zinc refinery residues produced by zinc oxygen pressure leaching

Published in:
Hydrometallurgy

DOI:
[10.1016/j.hydromet.2019.01.017](https://doi.org/10.1016/j.hydromet.2019.01.017)

Published: 01/05/2019

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:

Liu, F., Wang, J., Peng, C., Liu, Z., Wilson, B. P., & Lundström, M. (2019). Recovery and separation of silver and mercury from hazardous zinc refinery residues produced by zinc oxygen pressure leaching. *Hydrometallurgy*, 185, 38-45. <https://doi.org/10.1016/j.hydromet.2019.01.017>

Recovery and separation of silver and mercury from hazardous zinc refinery residues produced by zinc oxygen pressure leaching

Fupeng Liu^{a,b}, Jinliang Wang^a, Zhihong Liu^c, Chao Peng^b, Benjamin P. Wilson^b and Mari Lundström^b

^a Institute of Engineering Research, Jiangxi University of Science and Technology, Ganzhou 341000, China

^b Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering (CMET), School of Chemical Engineering, Aalto University, P.O. Box 12200, FI-00076 AALTO, Finland

^c School of Metallurgy and Environment, Central South University, Changsha 410083, China

Abstract:

Hazardous zinc refinery residues that contain Ag and Hg are a typical complex material obtained from zinc oxygen pressure leaching and currently there are few economically viable methods for disposal or reuse. The research presented here offers an effective approach for the comprehensive recovery of Zn, Fe, Cu, Ag and Hg from this highly toxic waste. During the initial hot-acid leaching stage, leaching efficiencies of 96.3% Zn, 96.0% Fe and 97.5% Cu were obtained, whereas the leaching of Ag and Hg were less than 0.2%. This resulted in the simultaneous separation of Zn, Fe and Cu and the enrichment of Ag and Hg *ca.* 300%. Subsequently, the leaching residues obtained from hot-acid leaching was further leached using acidic thiourea solution (pH = 1). The results of this second leaching step showed the almost 93% of Ag and 98% of Hg could be extracted using 20 g/L thiourea and 4 g/L Fe³⁺, with a L/S ratio of 8 and a temperature of 40 °C for 2 hours. The residue after thiourea leaching could be used as raw material in lead smelting. In the next step based on zinc powder cementation, the recovery of Ag and Hg both reached 99.0% and the cementation residue comprised of 53.1 wt. % Ag and 11.7 wt. % Hg. The main phases present included Ag, Hg₃Ag₂ and Ag₂S and these can be further treated by vacuum distillation in order to separate Hg from Ag. These findings demonstrate that high recoveries of Zn, Fe, Cu, Ag and Hg from the toxic waste could be achieved with stepwise leaching followed by zinc powder cementation. This treatment protocol for toxic zinc refinery residues not only avoids the potential harm to the environment but also significantly improves the economics of the process.

Keywords: Silver; Mercury; Thiourea leaching; Zinc cementation, Toxic zinc refinery residues

1. Introduction

Both Ag and Hg are associated elements in sphalerite, which is a zinc sulfide mineral and an important host mineral for a wide range of precious and hazardous elements (Cook et al., 2009; Liang et al., 2008; Frenzel et al., 2016). Currently, in the traditional combined roast-leach-electrowinning process for zinc hydrometallurgy, some accompanying metals - that include Ga, Ge, In, Hg, Ag - become dispersed to the dust, smelting slag, leachate and leaching residues (Raghavan et al., 1998; Han et al., 2014; Ju et al., 2011; George, et al., 2016; Liu et al., 2017a,b,c). Nevertheless, currently these metals can only be retrieved from zinc sulfide concentrates with low recovery rates that also involve considerable associated costs. More importantly, the sulfur and Hg present within the zinc sulfide concentrate are converted into sulfur dioxide (SO₂) and elemental Hg⁰ during the roasting process, which results in significant environmental challenges if not dealt with effectively.

In contrast, the alternative oxygen pressure leaching technique provides a more efficient way to extract valuable metals, whilst simultaneously reducing the possibilities for SO₂ and Hg vapor emission (Li et al., 2010; Wang et al., 2010). Since the first plant was commissioned in early 1981,

zinc oxygen pressure leaching has seen increasing commercial use in countries including Canada, Germany and China (Ozberk et al., 1995; Jankola, 1995; Boissoneault et al., 1995; Crysa, 1995). In China, the first zinc hydrometallurgical plant to use oxygen pressure leaching – the Danxia smelter, based in North Guangdong province – was commissioned in 2011 and now produces approximately 120,000 Mg of zinc ingots annually. The prime motivation for utilizing oxygen pressure leaching at the Danxia smelter is the recovery of the associated Ga and Ge from the Fankou zinc sulfide concentrate (Liu, 2017a) and a number of novel processes for Ga and Ge recovery have been developed in order to achieve the effective recovery of these elements (Liu, 2017b, c). Unlike Ga and Ge, which are leached into solution during oxygen pressure leaching, the Ag and Hg are mainly enriched within the leaching residues along with S, PbSO₄, SiO₂ and other unreacted sulfides (ZnS, PbS and FeS₂). After flotation using a sulfur thermofiltration processes, the resultant sulfur filter cake mainly contains 40 - 50% elemental sulfur and some sulfides that include Ag₂S, FeS₂, ZnS and PbS (Bolorunduro et al., 2003). Further pretreatment of this sulfur filter cake, leads to a highly toxic zinc refinery residue that contains between 2 - 4 kg/t silver and 0.4 - 0.8 kg/t Hg along with Zn, Cu, Fe, Pb and SiO₂ as the other primary components. Estimates suggest that the annual output of this residue from the Danxia smelter is between 2000 - 3000 tons, which due to the high Hg content is considered as hazardous waste. At present, there are few reports on economically viable methods for its disposal or reuse and consequently, it is necessary to find a solution that allows for both the effective recovery of silver, while minimizing associated mercury emissions. Achievement of this key goal would not only provide appreciable environmental benefits but also enhance the economics of the process.

In order to effectively recover and separate Ag and Hg several processes, related to waste smelting residues or scrap electronic devices, have been developed using different leaching agents. For example, although nitric acid is a highly efficient extractant of Ag from mineral and electronic scrap (Aktas et al., 2010; Yoo et al., 2012), it is unable to achieve the selective leaching of silver, which complicates subsequent purification processes. Alternative processes like cyanidation have previously been widely used in the precious metals extraction industry for more than a century because of its simplicity, effectiveness and economy, however, the toxic cyanide water produced can lead to serious environmental damage (Kondos et al., 1995; Eisler et al., 2004).

To overcome this main disadvantage, alternative non-cyanide systems have been developed which include the utilization of thiosulfate and thiourea (Groenewald et al., 1976; Oncel et al., 2005; Ficeiova et al., 2005; Deutsch et al., 2013; Celep et al., 2018). Thiosulfate leaching is considered a non-toxic process that can effectively recover Au and Ag in the presence of Cu²⁺ (Salinas-Rodríguez et al., 2016). Additionally, this has the added advantage of minimizing the solubility of impurities, whilst allowing both the selective recovery of Ag and reduced consumption of thiosulfate (Petter et al., 2014). Thiosulfate is also effective agent for Hg recovery from mercury-containing oxides (Han et al., 2016) however, as thiosulfate does not dissolve mercury sulfides as readily as silver, the mercury tends to become more dispersed (Oraby et al., 2010). Another drawback is that thiosulfate can only work effectively under alkaline and neutral conditions, which means that for highly acidic leaching residues a large amount of alkali is required for neutralization. The alternative thiourea is generally utilized for the environmental recovery of precious metals from some waste streams due to its low toxicity and strong complexing ability with relevant metals.

Furthermore, the addition of ferric sulfate to the thiourea solution results in a rapid increase of the initial silver leaching kinetics, although the presence of excessive amount of ferric ions leads to the oxidation of thiourea, which increases its overall consumption (Li et al., 2012). In contrast to thiosulfate, thiourea is much more stable under acidic conditions, nonetheless, presence of high levels of impurities like Fe^{3+} , Cu^{2+} and metal oxides has a negative impact in terms of thiourea decomposition, which affects the leaching metal kinetics (Li et al., 2006; Calla-Choque et al., 2016). Consequently, it is necessary that some type of pre-treatment protocol be adopted in order to separate such impurities prior to treatment with thiourea-based chemistries.

In view of the fact that the hazardous zinc refinery residues were produced from high sulfuric acid (180 - 220g/L) leaching process and that the phase composition is complicated, a stepwise leaching process has been developed in this paper. In the first stage, hot-acid leaching is used to selectively leach Zn, Fe and Cu from the toxic waste, which simultaneously leads to the effective enrichment of Hg and Ag within the high silicon-lead residues. This is followed by the second stage, which comprises of thiourea leaching of the Ag-rich residues obtained to remove the Hg and Ag.

Whilst the leaching of Hg and Ag can be achieved simultaneously, the main challenge involves the effective recovery and separation of Hg and Ag as they are both very similar chemically. Methods including activated carbon adsorption (Bunney et al., 2010), cementation with base metals (Lee et al., 1997; Ku et al., 2002), direct electrowinning (Sheya et al., 1988), solvent extraction (Stankovic et al., 2008), sulfide precipitation (Gabby et al., 2013) and ion exchange (Grosse et al., 2003) have all been proposed for the recovery Ag and Hg from aqueous acid solutions. Of these, the cementation process has been widely used in industry for the removal of heavy metals from aqueous solution due to its relative ease of operation, low cost and the feasible recovery of valuable metals. Alternatively, investigations by Lee et al. (1997) on the cementation behavior of Ag and Au with Zn, Al and Fe powder from acidic thiourea solution has demonstrated that recoveries of gold and silver can reach almost 100% after 5 min with 10 g/L Zn powder. In addition, it has also been found that 99% of Hg can be removed from a low Hg (30 mg/L) solution by a similar zinc powder cementation method at pH of 4 (Ku et al., 2002). Following cementation, the mercury can be precipitated along with the silver as a silver/mercury amalgam, which is then subsequently separated into its constituent parts by vacuum distillation (Lee et al., 1981; Iano et al., 2008; Pereira et al., 2010; Sadasiva et al., 2017). Based on these previous findings, the final two stages of the process proposed here involve cementation followed by distillation to achieve the required separation of Hg and Ag.

The objective of this study is the development of a more sustainable process for recovery of Ag from hazardous zinc refinery residues and the methodology proposed not only avoids the large consumption of thiourea, but also achieves the comprehensive recovery of all the valuable metals (Zn, Fe, Ag, Hg) from the toxic material. Moreover, the effective of recovery mercury by this process avoids the potential environmental issues related to this type of waste, whilst demonstrating highlighting the economic viability that offers significant potential for industrial application.

2. Experimental

2.1 Experimental procedure

The hot-acid leaching and thiourea (TU) leaching experiments were conducted in 500 mL and 300 mL round-bottom flasks, with mechanical stirring at 300 rpm, respectively, whilst the temperature was set and controlled by a water bath (DF-101S, Gongyi Yuhua Instrument Co., China). Zinc powder cementation experiments for the recovery of Ag and Hg were initially performed using 100 mL of the resulting leachate in 250 mL conical flasks and then the solution was agitated at 300 rpm whilst being heated to the desired temperature by a water bath. The amount of zinc powder (less than 200 mesh) required was primarily determined by the concentration of Ag and Hg present in leachate after leaching. In order to reduce the consumption of reductant, the zinc powder used was firstly modified by 0.01 g/L NaOH solution for 10 min at an L/S ratio of 4. After each experiment, both residue and filtrate were analyzed and the investigated parameters used at each stage are displayed in Table 1. All chemical reagents utilized were of analytical grade and deionized water was used throughout the experiments for the solution preparation.

Table 1 Main parameters investigated in the experiments.

Experiment	Investigated parameters
First leaching stage	Liquid-to-solid (L/S) (ml/g): 10; Temperature (°C): 95; H ₂ SO ₄ (g/L): 180; Reaction time (min): 120; Cl ⁻ (mg/L): 400
Second leaching stage	L/S (ml/g): 8; Temperature (°C): 20-60; TU (g/L): 2-30; Reaction time (h): 10-180min; Fe ³⁺ : 1-14g/L; pH = 0.2-2.0
Ag and Hg precipitation	Ag ⁺ /Zn mole ratio:1-3; Reaction time (min): 0-15; pH=1-4; Temperature (°C): 30-70;

2.2 Analytical methods

Crystallographic phases present within the samples were identified by a Rigaku-TTRIII X-ray diffractometer (Cu target, K α 1, λ = 0.154 nm), whilst the microstructure and phase compositions of were ascertained via a JSM-6306 Scanning Electron Microscope (SEM) with an EDX-GENESIS 60S Energy Dispersive Spectrometer (EDS). The phase composition of Ag and Hg in the zinc refinery residues were examined by use of a chemical selective dissolution method and the analysis was performed based on the dissolution behavior of Ag and Hg species in different solvents, whereas ethylenediaminetetraacetic acid (EDTA) titration was used to determine the zinc concentrations in the leach solutions. The concentrations of Si in leach residues or solutions were analyzed by silicon molybdenum blue spectrophotometry and extraction separation-benzfluorenone spectrophotometry methods, respectively (Yu et al., 2004). Leach residue and solution Ag, Hg and Fe contents were determined by a Thermo Electron IRIS Intrepid II XSP Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) spectrometer. The thiourea concentration in the leach solution was surmised by the potassium iodate titration method using starch as the indicator (Singh and Verma, 1963).

3. Results and discussion

3.1 Characterization of hazardous zinc refinery residues

Hazardous zinc refinery residues that contained silver and mercury were sourced from a zinc smelter in southern China and were used in the experiments in their as received state, without further treatment. The particle size of the residues was determined by a wet screen analysis, which showed that *ca.* 85% of the particles in the residue were $< 38 \mu\text{m}$ (Table 2).

Table 2 Wet screening result of the hazardous zinc refinery residues (wt. %).

Particle size/ μm	> 180	109-180	75-109	48-75	38-48	< 38
wt. %	0.45	4.46	4.75	3.34	1.77	85.24

The contents of Ag, Hg and other main elements of interest found in the residues are shown in Table 3. As can be seen, the residue contains 0.32 wt. % Ag and 0.06 wt. % Hg respectively, whereas the Zn and Fe content are both 15 wt. %, suggesting that the effective treatment of this waste residue would have a positive impact, both economically and environmentally. From the x-ray diffractogram of leach residues, as shown in Fig. 1, it can be clearly seen that there are several diffraction peaks that are related to zinc ferrite, gypsum, silica and lead sulfate. In contrast, the low concentrations or amorphous state of the other components, within the residue, means that their associated diffraction peaks or presence is not observed. Fig.2 and Table 4 presents the SEM-EDS results of different spots, which confirm the existence of ZnFe_2O_4 , SiO_2 and PbSO_4 as well as the main phases of silver (Ag_2S , AgCl) in the residues. In order to check the main phases of silver and mercury within the residues, a chemical selective dissolution method was utilized. These results (Table 5) confirmed that the main phases of silver in the residue were Ag, Ag_2S and AgCl , whereas mercury was mainly present as HgS , HgO and Hg_2SO_4 , indicating that leaching of Ag and Hg can be challenging.

Fig. 1. XRD pattern of the hazardous zinc refinery residues.

Table 3 Metal contents in the hazardous zinc refinery residues (wt%)

Elements	Ag	Hg	Zn	Pb	Cu	Fe	Si	Ca
Content	0.32	0.062	14.90	5.35	0.50	15.10	6.21	4.20

Fig. 2. Backscattered electron image of hazardous zinc refinery residues.

Table 4 Results of EDS analyses of the spots as shown in Fig. 2.

Spot	1	2	3	4	5	6
Phase	Ag ₂ S, AgCl	Ag ₂ S	ZnFe ₂ O ₄	SiO ₂	SiO ₂ , ZnFe ₂ O ₄	PbSO ₄

Table 5 Phase compositions of the silver and mercury present in the hazardous zinc refinery residues.

Silver phases	wt. %	Distribution / %	Mercury phases	wt. %	Distribution / %
Ag	0.101	31.58	HgS	0.056	81.30
Ag ₂ S	0.184	57.56	HgO	0.007	11.30
Ag ₂ SO ₄	0.005	1.46	Hg ₂ SO ₄	0.003	4.88
Ag ₂ O	0.006	1.78	HgSO ₄	0.001	1.14
AgCl	0.024	7.62	HgCl	0.001	1.38
Total	0.320	100	Total	0.062	100

3.2 Stepwise leaching of Ag and Hg from hazardous zinc refinery residues

It has been previously demonstrated that thiourea is an interesting alternative for extraction of silver under acidic conditions and that the presence of an oxidant like Fe³⁺ or H₂O₂ can enhance the leaching kinetics of silver (Li et al., 2006). On the other hand, an excess of oxidant can also result

in the oxidative decomposition of thiourea during the leaching process, which increases the consumption of thiourea and therefore the process costs. In the initial experiment, a one-step thiourea leaching method was adopted in order to directly treat the waste residue. As can be seen in Fig. 3, the increase in acidity (from pH 1.5 to 1) facilitates the leaching of silver and mercury from 40.7% and 43.2% to 87.5% and 89.4%, respectively. Nevertheless, the leaching of Fe and Cu increased from 16.2% to 33.5% and 39.2% to 60.3% with a further increase in acidity (from pH 1.0 to 0.5). This, in turn, would increase the consumption of thiourea and have a detrimental effect on any subsequent solution purification step (Calla-Choque et al., 2016). Consequently, in order to decrease the adverse effect of impurities on the recovery of Ag and Hg and to improve the recovery of all valuable metals from the waste residues, it was determined that a stepwise leaching process was preferable.

Fig. 3. Effect of sulfuric acid concentration and presence of dissolved cations on the recovery of Ag and Hg ($T = 40\text{ }^{\circ}\text{C}$; $t = 2\text{ h}$; $\text{Fe}^{3+} = 0\text{ g/L}$; $\text{TU} = 30\text{ g/L}$; $\text{L/S} = 8$).

3.2.1 First leaching stage: hot sulfuric acid leaching

The purpose of using hot-acid leaching for the waste residues is to dissolve Zn, Fe and Cu, whilst simultaneously enriching the Ag and Hg that remains. This also has the added benefit of reducing the consumption of thiourea reagent in the subsequent Ag-Hg leaching process. In order to reduce the dissolution of Ag into solutions in this initial stage, sodium chloride was added to the solution to form insoluble AgCl salts and maintain the silver in the residue. The most suitable conditions for the hot sulfuric acid leach were determined to be as follows: 95°C , a sulfuric acid concentration of 180 g/L , chloride ion concentration of 400 mg/L , liquid to solid (L/S) mass ratio of 10, stirring rate of 300 rpm and leaching time of 2 h . The quantity of chloride added to the leach solution is nearly identical to that present in typical zinc hydrometallurgy solutions.

The hot-acid leaching residue components and metal leaching efficiencies are shown in Table 6. The leaching efficiencies of Zn, Fe, Cu and Pb attained were 96.3% , 96.0% , 97.5% , 2.15% ,

respectively, whereas the leaching of Ag and Hg were less than 0.2%. The results shown in Fig. 4 indicate that zinc ferrite was almost completely leached and that the main phases that remained after hot acid leaching comprised of PbSO₄ and gypsum. At the same time, the silver and mercury content in the residue were shown to increase from 0.32% to 1.12% (Ag) and 0.062% to 0.217% (Hg) respectively, an enrichment of *ca.* 300% for these elements.

Table 6 Leaching residue components after hot-acid leaching and the associated metals leaching efficiencies.

Elements	Ag	Zn	Pb	Fe	Si	Cu	Hg	Ca
Content	1.12	1.94	18.40	2.14	20.91	0.04	0.22	13.68
Leaching (%)	0.16	96.30	2.15	96.00	1.80	97.50	<0.1	0.81

Fig. 4. XRD pattern of the leaching residue after the hot-acid leaching.

3.2.2 Second leaching stage: thiourea leaching

3.2.2.1 Effect of ferric concentration

Recent research results demonstrate that thiourea and ferric ion can form relatively stable complex species in acid sulfate solution, which can decrease the decomposition rate of thiourea (TU) and maintain the high potential for Ag and Hg dissolution (Li et al., 2006). In addition, the use of Fe³⁺ as an oxidant can greatly reduce the production cost. The effect of oxidant (Fe³⁺) concentration on the leaching of Ag, Hg, Fe and Zn was examined with a TU concentration of 20 g/L at pH = 1 and the results are shown in Fig. 5. As can be observed, the leaching of Ag and Hg increased with the increase of the ferric concentration until initial Fe³⁺ concentration reached 4 g/L with extraction efficiencies of 93% and 98%, respectively. The presence of Fe³⁺ ions provides oxidant that promotes the oxidation of Ag, Hg and their corresponding sulfide (Eqs. (1) - (4)) (Li

et al., 2012), further increases in the Fe^{3+} concentration resulted in a gradual decrease in the efficiency of the Ag and Hg leaching as the thiourea begins to oxidatively decompose (Eq. (5)). In contrast, the leaching of Zn and Fe remained nearly constant at approximately 3.0% and 1.5%, for all Fe^{3+} concentrations investigated due to the difficulties associated with zinc ferrite dissolution.

Fig. 5. Effect of ferric concentration on the leaching efficiencies of Ag, Hg, Zn and Fe ($T = 40^\circ\text{C}$; $t = 2 \text{ h}$; $L/S = 8$; $\text{TU} = 20 \text{ g/L}$; $\text{pH} = 1$).

3.2.2.2 Effect of pH

The effect of pH on the recovery of the target metals from hot-acid leaching residues was investigated with a solution that contained 20 g/L thiourea and 4 g/L Fe^{3+} , which was heated to 40°C for 2 hours. Results shown in Fig. 6 indicate that the leaching of Ag, Hg, Zn and Fe gradually decreased as the initial pH increased from 0.2 to 2.0. Most notably, the leaching of Ag and Hg showed marked reductions from 95% to 86% (Ag) and 99% to 91% (Hg), when the pH increased from 1 to 2. The main reason for the decrease of Ag and Hg leaching is that the thiourea is more readily decomposed in less acidic solutions. In addition, the Fe^{3+} that is used as an oxidant for Ag, Ag_2S and HgS can also precipitate as $\text{Fe}(\text{OH})_3$ when the pH is higher than 2. Consequently, high acidity facilitates the leaching of both Ag and Hg. Nevertheless, in these investigations the leaching of Zn and Fe was also found to reach relatively high levels at a pH of 0.2 (12% for Zn and 10% for Fe), which results in an unsatisfactory separation of zinc from the silver and mercury. Furthermore, when the subsequent recovery of Ag and Hg via the cementation method is taken into account, a

pH = 1 was considered to offer the optimum level of Ag and Hg extraction from hot-acid leaching residues.

Fig. 6. Effect of initial pH on the leaching efficiencies of Ag, Hg, Zn and Fe ($T = 40\text{ }^{\circ}\text{C}$; $L/S = 8$; $t = 2\text{ h}$; $\text{Fe}^{3+} = 4\text{ g/L}$; $\text{TU} = 20\text{ g/L}$).

3.2.2.3 Effect of thiourea concentration

The effect of thiourea concentration on leaching rates of Ag and Hg was examined by varying the thiourea concentration from 2 g/L to 30 g/L. The results shown in Fig. 7 indicate that the extraction of Ag and Hg increased substantially as the thiourea concentration changed from 2 g/L to 20 g/L - from 40% to 93% for Ag and from 61% to 98% for Hg, respectively. In contrast, a further increase in the thiourea concentration from 20 g/L to 30 g/L, only resulted in minor change in the level of Ag and Hg extracted. The amount of thiourea used is higher than the stoichiometric amount (12 g/L) mainly because thiourea more easily undergoes oxidative decomposed by air and ferric iron in acidic solution. Moreover, the leaching efficiency of Hg is always higher than that of Ag during the leaching process. Under the same conditions, the extraction rates of Zn and Fe were found to be both less than 1% over the thiourea concentration range investigated. This difference in the observed dissolution of Hg, Ag, Zn and Fe is attributed to the complexing abilities of thiourea for each respective metal ion. The complexation reactions between metal ions and thiourea can be outlined as follows (Martell and Smith, 1982):

From the log K of complex reaction, it can be seen why the leaching of Hg is higher than that of the other three metals - Ag, Zn and Fe. After hot-acid leaching, the residual zinc and iron mainly exist as ZnFe_2O_4 (Fig.4) which is difficult to leach under conditions of low acidity and atmospheric temperature, which results in significantly lower levels of Zn and Fe leaching *cf.* Ag and Hg.

Fig. 7. Effect of thiourea concentration on the leaching efficiencies of Ag, Hg, Zn and Fe ($T = 40\text{ }^{\circ}\text{C}$; $L/S = 8$; $t = 2\text{ h}$; $\text{Fe}^{3+} = 4\text{ g/L}$; $\text{pH} = 1$).

3.2.2.4 Effect of leaching time

The effect of leaching time on the recovery of Ag, Hg, Zn and Fe during the second leaching stage are presented in Fig. 8. It can be seen that the leaching of Ag and Hg were both efficient and fast with 81% of the Ag and 86% of the Hg extracted within 60 min from the commencement of leaching, after which maximum extractions of 93% (Ag) and 98% (Hg) achieved after 120 min. A further increase in leaching time to 180 min, lead to a decrease in the level of Ag and Hg extraction probably as a result of the formation of $\text{Ag}[\text{CS}(\text{NH}_2)_2]_3^+$ and $\text{Hg}[\text{CS}(\text{NH}_2)_2]_2^{2+}$ between 10 to 120 min. Furthermore, the oxidation reaction of the $\text{CS}(\text{NH}_2)_2$ with air or ferric ion can also easily occur due to the increase in pH of the solution after 120 min. Under the same experimental conditions, the leaching of Zn was found to increase gradually from 1.6 to 5.8%, which results in thiourea consumption and would complicate subsequent purification. On the other hand, the leaching of Fe remained nearly constant at approximately 1.5% for all leaching times investigated.

Fig. 8. Effect of leaching time on the leaching efficiencies of Ag, Hg, Zn and Fe ($T = 40\text{ }^{\circ}\text{C}$; $L/S = 8$; $TU = 20\text{ g/L}$; $\text{Fe}^{3+} = 4\text{ g/L}$; $\text{pH} = 1$).

3.2.2.5 Effect of temperature

The leaching results obtained at different temperatures ($20 - 60\text{ }^{\circ}\text{C}$) are displayed in Fig. 9. As can be observed, the leaching of Hg shows a marked increase from 62% to 98% as the temperature rises from 20 to $40\text{ }^{\circ}\text{C}$. Nevertheless, further increases in the leaching temperature resulted in a decrease of Hg leaching, which can be attributed to the thermolabile nature of thiourea (Li et al., 2006; Li et al., 2012). In contrast, an increase in temperature had a minimal effect on the levels of Ag, Zn and Fe extracted; leaching of Ag reached a maximum recovery of 93%, under the same conditions, whereas the leaching of Zn and Fe was 3.1% and 1.5%, respectively. This difference in leaching phenomena results from the different mineral phase compositions of Ag, Hg, Fe and Zn present. In the waste residue, more than 80% of Hg exists as HgS and higher temperatures favor the oxidation of HgS to HgCl_2 or HgSO_4 , which in turn promotes the leaching of Hg. In the case of Ag, only 57% exists as AgS phases, thus temperature has less effect on the leaching of silver. Low recoveries of Zn and Fe is because they primarily exist as zinc ferrite, which is difficult to leach under conditions of low temperature and acidity (Leclerc et al., 2003).

Fig. 9. Effect of temperature on the leaching efficiencies of Ag, Hg, Zn and Fe (t = 2 h; $L/S = 8$; TU = 20 g/L; $Fe^{3+} = 4$ g/L; pH = 1)

Based on the above results, the most suitable second stage leaching conditions were determined to be a thiourea concentration of 20 g/L, Fe^{3+} concentration of 4 g/L, L/S ratio of 8 with an initial pH = 1 and a total leaching time of 2h. Under these conditions, it was found that > 93% Ag and 98% Hg could be extracted to give a leach solution with the following composition - 1.30 g/L Ag, 0.27 g/L Hg, 0.075 g/L Zn, 4.083 g/L Fe, 0.012 g/L Pb. Additionally, the residue after thiourea leaching was found to contain approximately 20% Pb, which could be used as raw material in lead smelting.

3.3 Recovery of Ag and Hg by zinc powder cementation

There are many effective methods for recovery of silver and mercury from thiourea solution, including sulfide precipitation, metal cementation, electrolysis etc. In this study, it was decided to utilize a zinc cementation method in order to avoid the introduction of other impurities into the process and allow for the effective subsequent separation of Ag and Hg. The most suitable conditions for the maximum recovery of Ag and Hg were determined to be a reaction temperature of 30 °C, pH 3, silver to zinc mole ratio of 2.2, stirring speed of 200 rpm and reaction time of 5 min. As can be seen from Table 7, under these conditions, the cementation rates of silver and mercury both reached almost 100% and the main reactions of Ag and Hg cementation with Zn can be outlined in Eqs. (10), (11) and (12), respectively. Precipitates obtained from zinc powder cementation contain Ag, Hg_3Ag_2 , $Hg_{0.9}Ag_{1.1}$, Ag_2S as the main phases (Fig.10) and in total comprise of 53.1 wt. % Ag and 11.7 wt. % Hg. The source of the S^{2-} ions required for the formation of Ag_2S are thought to result from the decomposition of thiourea. The solution containing 8 g/L thiourea after cementation of Ag and Hg could be recirculated back into the second stage leaching process.

Table 7 Composition of thiourea solution before (PLS1) and after (PLS2) zinc powder cementation and the precipitation ratio of metals.

No.	pH	Concentration (mg/L)					
		Ag	Hg	Fe	Zn	Pb	Si
PLS1	3.02	1300	270	4083	75	12	82
PLS2	5.12	15	< 1	4014	554	4.1	11

Fig. 10. XRD pattern of the obtained residue after zinc powder cementation.

3.4 Flowsheet development

After zinc powder cementation, the separation of Hg and Ag from the cementation products obtained can be achieved by using vacuum distillation under high temperature. The leftover solution was found to contain 4.1 g/L Fe, 0.5 g/L Zn and 8 g/L TU after Ag and Hg precipitation and this can be recirculated back into thiourea leaching stage. Based on the results of stepwise leaching and zinc powder cementation outlined here, a process flow sheet that allows the recovery of Zn, Fe, Pb, Ag and Hg was developed (Fig.11). Industrial application of this new process could significantly improve the recovery of valuable metals and decrease the thiourea consumption. The amount of thiourea consumed per ton of the zinc refinery residues is reduced from 200 kg/t to 60 kg/t, which means that the new process can save 400 tons thiourea per year for the zinc smelter.

Fig. 11. Proposed flow sheet for recovery silver and mercury from hazardous zinc refinery residues.

4 Conclusions

This research outlines a sustainable method to recover and separate Ag and Hg from toxic zinc refinery residues by a combined multi-stage leaching, zinc powder cementation and vacuum distillation process as summarized in Fig.11.

The hazardous zinc refinery residue contains 0.32% Ag and 0.062% Hg with zinc ferrite, gypsum and lead sulfate found to be the main phases. Silver containing phases in the residue include Ag, Ag₂S and AgCl, whereas, mercury is mainly present as HgS, HgO and Hg₂SO₄, which indicates that leaching of Ag and Hg can be challenging.

In the hot-acid leaching, the leaching efficiencies of Zn, Fe and Cu attained were 96.3%, 96.0% and 97.5%, respectively, whereas the leaching of Ag and Hg were less than 0.2%. This demonstrates that Zn, Fe and Cu can be selectively leached from the toxic waste, whilst Hg and Ag are effectively enriched.

Thiourea leaching resulted in Ag and Hg recoveries of > 90% into solution. In addition, the solid remnants left over were found to be rich in Pb (~20%) and can potential be used as raw material in lead smelting.

Zinc powder cementation is an effective method for the recovery of silver and mercury from the thiourea leaching solution. The residue obtained contains 53 wt. % Ag and 11.7 wt. % Hg composed primarily of Ag, Hg_3Ag_2 and Ag_2S . A final step based on vacuum distillation, would allow the effective separation of Ag and Hg to be achieved.

Almost 400 t thiourea can be saved per year for the zinc smelter by using the stepwise leaching process, which provides not only environmental benefits but also economical improvements on an industrial scale.

Acknowledgements

The authors acknowledge the financial support from the National Nature Science Foundation of China (No.51804141) as well as the Science and Technology Project of the Education Department of Jiangxi Province (GJJ170533). This paper also made use of the Academy of Finland's RawMatTERS Finland Infrastructure (RAMI) based at Aalto University. In addition, special thanks go to staff at the Danxia smelter for providing the zinc refinery wastes used in this study as well as for Antti Porvali for his support.

References

- Aktas S., Morcali, M. H., Yucel, O., 2010. Silver Recovery from Waste Radiographic Films by Cementation and Reduction. *Canadian Metallurgical Quarterly* 49(2), 147-154.
- Bolorunduro, S.A., Dreisinger, D.B., Weert, G.V., 2003. Fundamental study of silver deportment during the pressure oxidation of sulfide ores and concentrates. *Minerals Engineering* 16, 965-708
- Boissoneault, M., Gagnon, S., Henning, R., Lachance, E., Vecchiarelli, M., 1995. Improvement in pressure leaching At Kidd Creek. *Hydrometallurgy* 39, 79-90.
- Bunney, K., Jeffrey, M.I., Pleysier, R., and Breuer, P. L., 2010. Selective elution of gold, silver, and mercury cyanide from activated carbon. *Minerals & Metallurgical Processing* 27(4), 205-211.
- Calla-Choque, D., Nava-Alonso, F., Fuentes-Aceituno, J. C., 2016. Acid decomposition and thiourea leaching of silver from hazardous jarosite residues: Effect of some cations on the stability of the thiourea system. *Journal of Hazardous Materials* 317, 440-448.
- Celep, O., Altinkaya, P., Yazici, E.Y., Deveci, H., 2018. Thiosulphate leaching of silver from an arsenical refractory ore. *Minerals Engineering*, 122, 285-295.

- Crysa, D. B., 1995. Zinc pressure leaching at HBMS. *Hydrometallurgy* 39, 71-77.
- Cook, N. J., Ciobanu, C. L., Pring, A., Skinner, W., Danyushevsky, L., Shimizu, M., Saini-Eidukat, B., Melcher, F., 2009. Trace and minor elements in sphalerite: A LA-ICP-MS study, *Geochim. Cosmochim. Acta* 73, 4761-4791.
- Deutsch, J. L., Dreisinger, D. B., 2013. Silver sulfide leaching with thiosulphate in the presence of additives Part II: Ferric complexes and the application to silver sulfide ore. *Hydrometallurgy* 137, 165-172.
- Eisler, R., Wiemeyer, S. N., 2004. Cyanide Hazards to Plants and Animals from Gold Mining and Related Water Issues. *Rev Environ Contam Toxicol* 183, 21–54.
- Ficeriová, J., Baláž, P., Villachica, C.L., 2005. Thiosulfate leaching of silver, gold and bismuth from a complex sulfide concentrates. *Hydrometallurgy* 77(1-2), 35-39.
- Frenzel, M., Hirsch, T., Gutzmer, J., 2016. Gallium, germanium, indium, and other trace and minor elements in sphalerite as a function of deposit type-A meta-analysis. *Ore Geol. Rev.* 76, 52-78.
- Gabby, K. L., Eisele, T. C., 2013. Selective removal of mercury using zinc sulfide. *Minerals and Metallurgical Processing* 30(2), 91-94.
- George, L. L., Cook, N. J., Ciobanu, C. L., 2016. Partitioning of trace elements in co-crystallized sphalerite–galena–chalcopyrite hydrothermal ores. *Ore Geol. Rev.* 77, 97-116.
- Groenewald, T., 1976. The dissolution of gold in acidic solutions of thiourea. *Hydrometallurgy* 1, 277–290.
- Grosse, A. C., Dicoski, G. W., Shaw, M. J., Haddad, P. R., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 69, 1-21.
- Han, H. S., Sun, W., Hu, Y. H., Jia, B. L., Tang, H. H., 2014. Anglesite and silver recovery from jarosite residues through roasting and sulfidization-flotation in zinc hydrometallurgy. *Journal of Hazardous Materials* 278, 49-54.
- Han, C., Wang, W., Xie, F., 2016. Study on the leaching of mercuric oxides with thiosulfate solutions. *Metals* 6(9), 206-213.
- Iano, F. G., Sobrinho, O. S., Silva, T. L., Pereira, M. A., Figueiredo, P. J. M., Alberguini, P. J. M. F., 2008. Optimizing the procedure for mercury recovery from dental amalgam. *Brazilian Oral Research* 22(2), 119-124.
- Jankola, W. A., 1995. Zinc pressure leaching at Cominco. *Hydrometallurgy* 39, 63-70.
- Ju, S., Zhang, Y., Zhang, Y., Xue, P., Wang, Y., 2011. Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy. *Journal of Hazardous Materials* 192, 554 – 558.

- Kondos, P. D., Deschênes, G., Morrison, R. M., 1995. Process optimization studies in gold cyanidation. *Hydrometallurgy* 39 (1-3), 235-250.
- Ku, Y., Wu, M. H., Shen, Y. S., 2002. Mercury removal from aqueous solution by zinc cementation, *Waste Management* 22, 721-726.
- Leclerc, N., Meux, E., Lecuire, J. M., 2003. Hydrometallurgical extraction of zinc from zinc ferrites. *Hydrometallurgy* 70 (1-3), 175-183.
- Lee, C. W., Fung, K. W., 1981. Recovery of silver and mercury from dental amalgam waste. *Resource Recovery and Conservation* 5, 363-371.
- Lee, H. Y., Kim, S. G., Oh, J. K., 1997. Cementation behavior of gold and silver onto Zn, Al, and Fe powders from acid thiourea solutions. *Canadian Metallurgical Quarterly* 36(3), 149-155.
- Liang, D. Q., Wang, J. K., Wang, Y. H., Jiang, J. B., Wang, F., 2008. Recovery of silver and zinc by acid pressure oxidative leaching of silver-bearing. *Int. J. Miner. Process* 89, 60-64.
- Liu, F. P., Liu, Z. H., Li, Y. H., Wilson, B. P., Lundström, M., 2017a. Behavior of gallium and germanium associated with zinc sulfide concentrate in oxygen pressure leaching. *Physicochem. Probl. Miner. Process.* 53(2), 1047-1060.
- Liu, F. P., Liu, Z. H., Li, Y. H., Wilson, B. P., Lundström, M., 2017b. Recovery and separation of gallium (III) and germanium (IV) from zinc refinery residues: Part I: Leaching and iron(III) removal. *Hydrometallurgy* 169, 564-570.
- Liu, F. P., Liu, Z. H., Li, Y. H., Wilson, B. P., Lundström, M., 2017c. Recovery and separation of gallium (III) and germanium (IV) from zinc refinery residues: Part II: Leaching and iron(III) removal. *Hydrometallurgy* 171, 149-156.
- Li, G. H., Feng, X. B., Li, Z. G., Qiu, G. L., Shang, L. H., Liang, P., Wang, D. Y., Yang, Y. K., 2010. Mercury emission to atmosphere from primary Zn production in China. *Science of the Total Environment* 408, 4607-4612.
- Li, J. S., Miller, J. D., 2006. A review of gold leaching in acid thiourea solutions, *Mineral processing & Extractive Metall. Rev.* 27, 177-214.
- Li, J. Y., Xu, X. L., Liu, W. Q., 2012. Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. *Waste Management* 32, 1209-1212.
- Martell, A. E. and Smith, R. M., 1982. Critical stability constants. Plenum Press, New York, USA, 384-385.
- Oncel, M.S., Ince, M., Bayramoglu, M., 2005. Leaching of silver from solid waste using ultrasound assisted thiourea method. *Ultrasonics Sonochemistry* 12, 237-242.

- Oraby, E. A., Jeffrey, M. I., Browner, R. E., 2010. The deportment of mercury during thiosulfate leaching and resin-in-pulp recovery of gold from ores. *Minerals and Metallurgical Processing* 27(4), 184-189.
- Ozberk, E., Jankola, W. A., Vecchiarelli, M., Krysa, B. D., 1995. Commercial operations of the Sherritt zinc pressure leach process. *Hydrometallurgy* 39, 49-52.
- Pereira, H. A., Iano, F. G., da Silva T. L., de Oliveira, R. C., de Menezes, M. L., Buzalaf, M. A., 2010. Recovery of silver residues from dental amalgam. *Journal of Applied Oral Science* 18(2), 121-126.
- Petter, P. M. H., Vert, H. M., Bernardes, A. M. 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. *Waste Management* 34, 475-482.
- Raghavan, R., Mohanan, P. K., Patnaik, S. C., 1998. Innovative processing technique to produce zinc concentrate from zinc leach residue with simultaneous recovery of lead and silver. *Hydrometallurgy* 48, 225-237.
- Sadasiva, K., Rayar, S., Manu, U., Senthilkumar, K., Daya, S., Anushaa, N., 2017. Recovery of mercury from dental amalgam scrap-Indian perspective. *Journal of Pharmacy and Bioallied Sciences* (1), 79-81.
- Salinas-Rodríguez, E., Hernández-Ávila, J., Rivera-Landero, I., Cerecedo-Sáen, E., Reyes-Valderrama, M. I., Correa-Cruz, M., Rubio-Mihi, D., 2016. Leaching of silver contained in mining tailings, using sodiumthiosulphate: A kinetic study. *Hydrometallurgy* 160, 6-11.
- Sheya, S. A. N., Maysilles, J. H., Sandberg, R. G., 1988. Selective Electrowinning of Mercury From Gold Cyanide Solutions. U.S. Bureau of Mines Report, Salt Lake City Research Center, Salt Lake City, UT, USA.
- Singh, B., Verma, B., 1963. Thiourea and its organic derivatives, *Fresenius J. Anal. Chem.* 194(2), 112-115.
- Stankovic, V., Outarra, L., Zonnevillje, F., Comninellis, Ch., 2008. Solvent extraction of silver from nitric acid solutions by calix[4]arene amide derivatives. *Separation and Purification Technology* 61, 366-374.
- Wang, S. X., Song, J. X., Li, G. H., Wu, Y., Zhang L., Wan Q., Streets D. G., Chin C. K., Hao J. M., 2010. Estimating mercury emissions from a zinc smelter in relation to China's mercury control policies. *Environmental Pollution* 158, 3347-3353.
- Yu, L., Fu, B., 2004. *Handbook of Nonferrous Metallurgical Analysis*. Metallurgical Industry Press, Beijing, 252-255, 338-340. (in Chinese)
- Yoo, K., Lee, J., Lee, K., Kim, M., Kim, S., Pandey, B. D., 2012. Recovery of Sn, Ag and Cu from Waste Pb-Free Solder Using Nitric Acid Leaching. *Materials Transactions* 53 (12), 2175-2180.