Selective metal recovery from jarosite residue by leaching with acid-equilibrated ionic liquids and precipitation-stripping

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Abstract

Recovery of valuable metals from industrial process residues is complex because those metals are often present in very low concentrations and often locked in complex matrices. Hence it is important to develop a process that selectively recovers the metal(s) of interest, while the undesired metals remain in the solid residue. Conventional pyrometallurgical and hydrometallurgical routes suffer from high cost and poor selectivity. In this work, a solvometallurgical approach was investigated for the selective leaching of lead and zinc from iron-rich jarosite of the zinc industry. Solvometallurgy uses organic solvents rather than water in order to reduce energy, acid and water consumption and to improve selectivity and reactivity. The screening of different solvometallurgical lixiviants showed that the presence of chloride anions in the lixiviant was crucial for leaching of lead. The ionic liquids Aliquat 336 ([A336][Cl]) and Cyphos IL 101 ([C101][Cl]), after equilibration with HCl, leached more lead and zinc compared to the other lixiviants. [A336][Cl] and [C101][Cl] equilibrated with 0.5 mol L^{-1} HCl, were selected for the optimisation study due to their higher selectivity towards lead and zinc and lower co-dissolution of iron, compared to the same ionic liquids equilibrated with a higher concentration of HCl. At optimised leaching conditions, the metal/iron mass ratio increased from 1/4 for Pb/Fe, and from 1/7 for Zn/Fe in the initial jarosite, to over 2/1 and 1/2, in the leachate, respectively. The dissolved metals were recovered by selective precipitation-stripping with an aqueous ammonia solution. Finally, the corresponding flowsheets were developed for the recovery of zinc and lead for both [A336][Cl] and [C101][Cl].

Keywords: basic extractants; iron-rich sludges; lead leaching; zinc leaching; solvometallurgy

Introduction

Currently, 75–80% of the world's zinc metal production is produced via hydrometallurgical processes.[1–4] This is about 8 million tons annually. Pure zinc metal is produced via a process combining roasting of sphalerite (ZnS) ore to an impure zinc oxide (ZnO) called "zinc calcine" followed by leaching of the calcine in different steps by sulfuric acid and electrowinning.[5] After the leaching process, a precipitation step is applied to remove the co-dissolved iron impurities from the solution. In the "jarosite" process, iron is removed from the leach liquor by precipitation as jarosite, which is a basic iron(III) sulfate complex $MFe_3(SO_4)_2(OH)_6$.[6,7] However, some amounts of lead, zinc, and valuable metals such as indium and germanium are co-precipitated along with iron upon the formation of jarosite. A plant producing 150,000 tons of metallic zinc annually generates about 125,000 tons of jarosite.[4] India, the European Union and China annually produce about 0.25, 0.60 and 1 million tons of jarosite, respectively.[8–10] Due to the high production rate and large generated volume, jarosite not only requires a lot of space for storage, but a large amount of valuable metals are lost with it and thus never return back to the value chain.

Much research has focused on the valorization of industrial process residues including jarosite as a material for construction and ceramic applications.[11–15] However, recovery of the valuable metals prior to their application as construction and ceramic materials was not considered. Hence these approaches result in a great loss of valuable metals. The recovery of metals from jarosite, like other industrial process residue, is complex because the relevant metals are present in low concentrations and often locked in complex matrices (sulphides, oxides, phosphates or silicates).[16] There are few examples of metal recovery from jarosite on a commercial scale. The Onsan Refinery of Korea Zinc used Top Submerged Lancing (TSL) Technology to recover 82% Zn, 92% Pb, 86% Ag and 61% Cu.[17] In China, some factories recovered about 75% Zn, 68% Pb, and 80% Ge by fuming the residue in a rotary kiln, using a mass of coal as heat source.[10]

However, these pyrometallurgical processes applied to industrial residues with low concentration of valuable metals cause air pollution during fuming, and have high fixed investment and operation costs. Other studies applied hydrometallurgical routes to recover valuable metals from jarosite.[17–23] Rusen et al. (2008) recovered 71.9% Zn and 98.9% Pb using acid leaching (H_2SO_4) followed by brine (NaCl) leaching.[17] Turan et al. (2004) extracted 86% of Zn and 89% of Pb from the residue via H_2SO_4 blending and roasting, followed by water leaching and NaCl leaching.[19] Ju et al. (2011) developed a roasting–NH_4Cl–alkali leaching process where more than 95% of the Zn, Pb, Cu, Cd, and Ag can be recovered from jarosite.[10] These hydrometallurgical routes are cheaper and considered to be cleaner compared to the pyrometallurgical routes, but they still have disadvantages. The most important disadvantage is their poor selectivity towards the target metals over iron. The co-dissolution of iron during the leaching process should be limited as much as possible to avoid high consumption of chemicals and to simplify the downstream purification processes.

However, by replacing the aqueous phase in hydrometallurgical processes by organic solvents, it is possible to attain high reactivity and selectivity because non-hydrated anions have a greater affinity to bind to some metal ions and the lack of water's high solvating power makes it impossible for some metals to enter into the solution, if they do not have sufficient affinity for the anions in the organic solution. This new approach to extractive metallurgy, based on the use of organic solvents instead of an aqueous phase, is called "solvometallurgy".[16]

This work presents the development of a novel solvometallurgical process to selectively recover lead and zinc from jarosite of the zinc industry. A suitable lixiviant was chosen after an initial screening test, based on the leaching efficiencies of lead and zinc and the selectivity towards these metals over iron. Finally, the recovery of the dissolved metals from the organic leachate (stripping) was studied.

Experimental

Chemicals

Jarosite was kindly provided by a European zinc producing company. Acetic acid (AnalR NORMAPUR, 100%), ammonia solution (≥25 wt% NH_3 in water, AnalR NORMAPUR) and hydrochloric acid (37 wt% HCl in water) were purchased from VWR Chemicals (Leuven, Belgium). Formic acid (99–100% pure), nitric acid (65 wt% HNO_3 in water), tri-*n*-butyl phosphate (TBP, >99 wt%) and praseodymium standard (1000 mg L^{-1}, 2–5 wt% HNO_3) were purchased from Chem-Lab NV (Zedelgem, Belgium). Versatic Acid 10 was obtained from Resolution Europe B.V. (Hoogvliet, The Netherlands). Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101, >97%) and bis(2,4,4-dimethylpentyl) phosphinic acid (Cyanex® 272, >85%) were obtained from Cytec Industries (Niagara Falls, Ontario, Canada). Aliquat® 336 (trialkylmethylammonium chloride-based commercial mixture with trioctylmethylammonium chloride as the main component, 88.2–90.6%) was purchased from Sigma-Aldrich (Diegem, Belgium). Di-(2-ethylhexyl)phosphoric acid (D2EHPA, >95%) and 1-octanol (99%) and Triton X-100 were supplied by Acros Organics (Geel, Belgium). Absolute ethanol was obtained from Fisher Scientific (Loughborough, United Kingdom). The silicone solution in isopropanol for the treatment of the TXRF quartz glass carriers was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). All chemicals were used as received without any further purification.

Instrumentation

The jarosite sludge (as received) was dried in an oven at 110 °C for 24 h. The dried material was crushed and milled using a vibratory ring mill (Retsch RS200) for 30 s at 1000 rpm. Since the obtained powder sample may collect some moisture from the environment during the milling and sample handling prior to leaching experiment, the moisture content (MC%) of the final residue after milling was determined on the basis of its mass loss after drying in an oven at 110 °C for 48 h. The drying time was doubled compared to the first drying process to make sure that all the free water adsorbed on the surface of the powders was evaporated. The MC% was calculated according to equation (1).

$$MC(\%)=\frac{m_F - m_I}{m_F} \times 100 \qquad (1)$$

where m_F is the mass of the residue (g) after drying and m_I is the mass of the residue (g) before drying.

The morphology of the finely-milled powder was examined by scanning electron microscopy (SEM) using a Philips XL30 model (Philips, Amsterdam, The Netherlands) at an accelerating voltage of 10 keV. The powder sample was coated with a 10 nm platinum layer to avoid charging issues related to insulating sample.[24] The mineralogy was determined by powder X-ray diffraction (XRD) analysis using a Bruker D2 Phaser diffractometer (Bruker, Billerica, MA, USA). Diffractograms were recorded in the measurement range of 10 – 80° 2θ using CuK_α radiation and applying an acceleration voltage of 45 kV, a current of 30 mA, a step size of 0.020° and a counting time of 2.5 s per step. The raw data were processed with the X'pert HighScore Plus PANalytical software. The metal content of the jarosite was determined after fully dissolving 10 mg of the milled sample in 10 mL of a 2/3 (v/v) mixture of 37 wt% HCl and 65 wt% HNO_3 solution using microwave-assisted acid digestion (Speedwave Xpert, Berghof, Germany). Nitric acid is a preferred mineral acid for microwave digestion because of its safe manipulation, facility of purification and oxidative characteristics.[25] The acid mixture of HCl and HNO_3 was necessary for complete dissolution of the residue. The sample dissolution via microwave digestion was done in triplicates to check the reproducibility of the composition. The metal concentrations in each of the digested acid solution were measured in triplicate by Total-Reflection X-ray Fluorescence (TXRF, Bruker S2 Picofox, Bruker, Billerica, MA, USA) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 8300, Perkin Elmer, Waltham, MA, USA) for comparison. The particle size distribution of the milled jarosite was determined by dispersing the residue in water and measuring with a laser particle size analyser (Mastersizer 3000, Malvern, Worcestershire, UK) in liquid mode. The leaching was carried out by shaking and heating using a laboratory shaker (Thermoshaker TMS-300, Nemus Life AB, Lund, Sweden).

Methodology

The lixiviants Cyphos IL 101, Aliquat 336, 1-octanol, and TBP were equilibrated with an aqueous HCl (0.5−12 mol L^{-1}) or HNO_3 (6 mol L^{-1}) solution prior to use for solvoleaching. The equilibration was performed by mixing the lixiviant and the HCl solution in a glass vial, forming a biphasic mixture with a volume phase ratio of 1:1, and stirring at 60 °C for 1 h at 2000 rpm in a laboratory shaker. The intensive shaking at 2000 rpm was done to ensure that equilibration is reached.[26] After the equilibration, the separation between the organic and aqueous phases was accelerated by centrifugation at 5000 rpm for 20 min in a Heraeus Labofuge 200 centrifuge. The organic and aqueous phases were taken out separately with a micropipette and kept in different vials. The nitrate analogues of Cyphos IL 101 or Aliquat 336 were prepared by a metathesis reaction between the ionic liquid and a 2.5 mol L^{-1} KNO_3 solution in 3 equilibration contacts with a volume phase ratio of 1:1, followed by washing three times with aqueous HNO_3 solution of pH 3−4.

For the leaching experiments, the solid material and lixiviant were mixed in 4 mL glass vials and agitated in the laboratory thermoshaker. The initial screening of lixiviants was performed using the following operation conditions: a liquid-to-solid ratio (L/S) of 10 mL g^{-1}, a temperature of 60 °C, a contact time of 2 h and a shaking speed of 2000 rpm. Once the most suitable lixiviants were selected, these operation conditions were further optimised. Finally, the leaching system was scaled up using a 250 mL separatory funnel and stirred by placing it sideways on a heating plate (IKA RCT classic). The leachate was separated from the solid residue through centrifugation (5300 rpm, 30 min). The finer particles suspended in the leachate were further separated by a syringe filter made of a polyester membrane (Chromafil® PET, 0.45 µm pore size).

For TXRF analysis, the sample was 10 times diluted with ethanol to minimize the matrix effects and a known amount of praseodymium internal standard (1000 mg L^{-1}) was added for quantification.[27] A quartz glass carrier was made hydrophobic by drying a 30 µL of a silicon solution in isopropanol (SERVA) on its surface and, finally, 2.5 µL of the diluted sample was pipetted on a quartz glass carrier and dried in oven for 30 minute at 60°C for analysis. The leaching efficiency E_L *(%)* was calculated according to equation (2):

$$E_L(\%) = \frac{c_M \text{ x } v_{LIX}}{m_I \text{ x } c_I} \times 100 \qquad (2)$$

where c_M is the metal concentration in the leachate after leaching (mg L^{-1}), v_{LIX} is the volume of lixiviant used for leaching (L), m_I is the mass of the solid material used for leaching (kg), and c_I is the concentration of the metal in the jarosite before leaching (mg kg^{-1}).

The selectivity S towards lead or zinc over iron was calculated for the solid jarosite and for the leachate according to equation (3):

$$S = \frac{c_{\mathrm{M}}}{c_{\mathrm{Fe}}} \quad (3)$$

where c_{M} is the concentration of lead or zinc (mg kg^{-1} or mg L^{-1}) and c_{Fe} is the concentration of iron (mg kg^{-1} or mg L^{-1}). The preferred case is $S > 1$ because then, the concentration of lead or zinc is higher than that of iron. If the $S = 1$, then the concentration of lead or zinc is equal to that of iron. A low values of S (less than 1) is unwanted as it means that the concentration of the desired metals is lower than that of iron.

For the stripping experiments, the metal-loaded leachate was contacted with an aqueous ammonia solution (0.025 or 2 mol L^{-1}) in a glass vial using a volume phase ratio of 1:1 (commonly written as phase ratio $\Theta = 1$) and stirred in a thermoshaker at 60 °C at 1500 rpm for 1 h. The phase separation was aided by centrifugation and the precipitates were filtered using polyester syringe filters. The metal concentrations in the organic phase were analysed by TXRF using the same methodology as described above. Similarly, the metal concentrations in the aqueous phase were analysed via TXRF, but the liquid was diluted with 5 vol% Triton X-100 in water instead of ethanol.[27] The stripping efficiency E_{S} (%) and the precipitation efficiency E_{P} (%) were calculated according to equations (4) and (5):

$$E_{\mathrm{S}}(\%) = \frac{c_{\mathrm{S}}}{c_{\mathrm{L}}} \times 100 \quad (4)$$

$$E_{\mathrm{P}}(\%) = \frac{c_{\mathrm{L}} - c_{\mathrm{S.L}} - c_{\mathrm{S}}}{c_{\mathrm{L}}} \times 100 \quad (5)$$

where c_{L} is the concentration of the metal in the leachate before stripping, expressed in mg L^{-1}, c_{S} is the concentration of the stripped metal in the aqueous phase after stripping, expressed in mg L^{-1}, and $c_{\mathrm{S.L}}$ is the concentration of the metal remaining in the stripped leachate, expressed in mg L^{-1}.

Results and discussion

Characterization of jarosite

The jarosite, which was provided as a sludge, was characterized after drying and milling into a fine powder (Figure 1). The moisture content of the dried and milled residue was 1.22% of the dried mass. The particle size ranged from 0.3 to 20 µm, although 90% of the particles were smaller than 1.95 µm (Figure S1). The elemental composition of the residue is shown in the Table 1. The elemental composition studied in triplicate varied by less than 5% from the mean, which indicates that the elements are well-dispersed throughout the sample and the composition is representative. The XRD pattern of the jarosite sample revealed that the main metal phases were natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), anglesite ($PbSO_4$) and sphalerite (ZnS) (Figure 2). The phases of the other metals were not detected in the XRD pattern. It is most likely because of their low concentration and good dispersion in the sample, which result in no or very little X-ray diffraction.

Table 1: Elemental composition of milled jarosite residue

Metal	S	Fe	Pb	Zn	Ca	Na	Al	Mg	K	Si	Cu	Other*
[g/kg]	280	174	40	24	25	18	5.7	3.0	2.5	1.5	0.90	2.44

* Others include Ba, Sr, Sn, P and B.

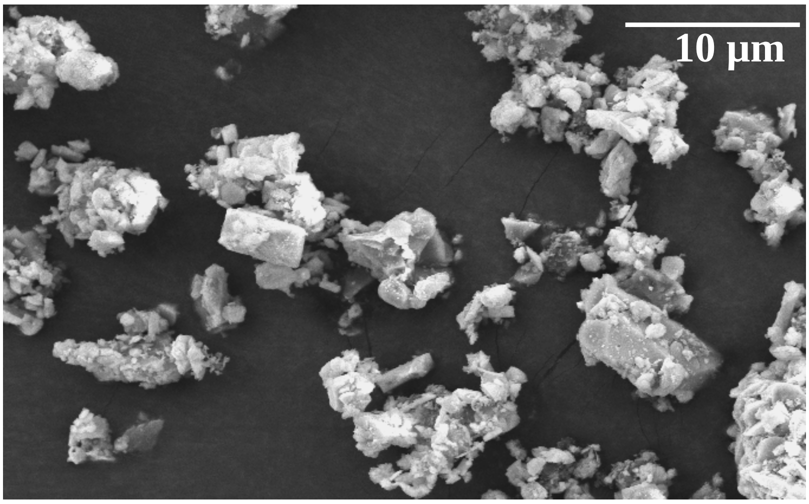

Figure 1: SEM micrograph of jarosite after drying (110 °C, 24 h) and milling (30 s, 1000 rpm).

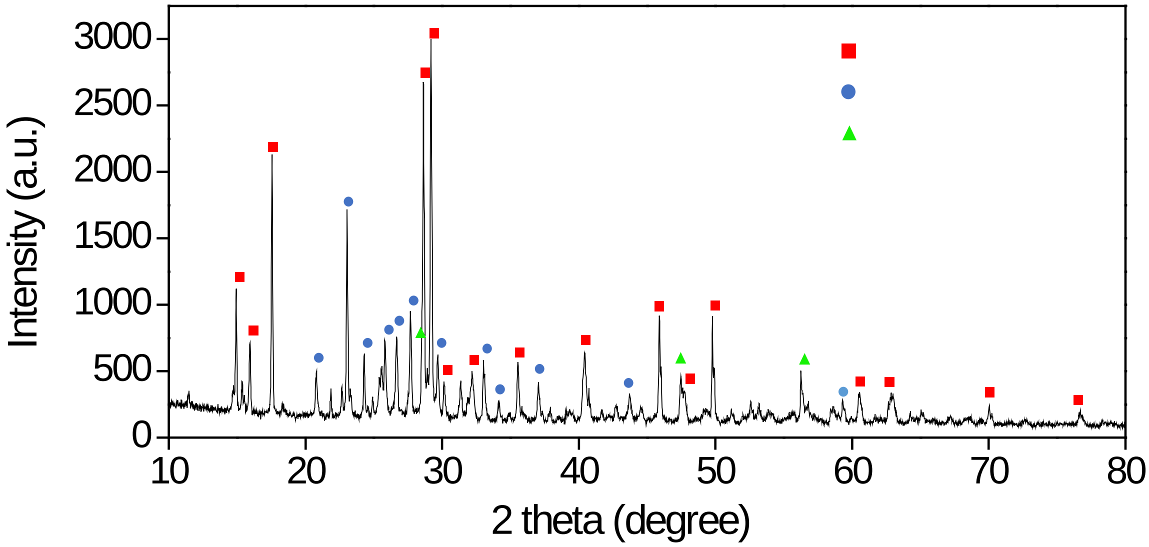

Figure 2: XRD pattern of jarosite after drying (110 °C, 24 h) and milling (30 s, 1000 rpm).

Comparison of solvometallurgical lixiviants

Various solvometallurgical lixiviants were compared in order to determine their suitability for the leaching of lead and zinc from jarosite. The tested lixiviants include organic acids with carboxylic and phosphoric acid functional groups, alcohols containing dissolved mineral acids and acidic, basic and neutral extractants equilibrated with mineral acids (Table S1). Leaching with solutions of mineral acids (HCl, H_2SO_4, HNO_3) in alcohols such as ethanol is reported to be an effective solvometallurgical approach.[28,29] A promising system of *n*-octanol equilibrated with HCl has been developed to chemically attack resistant ores such as titanomagnetite.[30] Organic acids and acidic extractants, such as formic acid, acetic acid, D2EHPA, Versatic Acid 10 and Cyanex 272, can be applied directly for solvent leaching of a solid material, without the need of adding a mineral acid.[16] For example, Versatic Acid 10 is already known to be effective in recovering zinc from chloride-containing solid zinc waste residues.[31] Neutral extractants such as tri-*n*-butylphosphate (TBP) are poor lixiviants, but TBP equilibrated with mineral acids has been found to be a powerful lixiviant.[31,33] Similarly, basic extractants such as [C101][Cl] and [A336][Cl] combined with mineral acids have shown to be good lixiviants.[34] It should be noted that [C101][Cl] and [A336][Cl] can also be considered as ionic liquids. Therefore, [C101][Cl] and [A336][Cl] will be hereafter referred to as ionic liquids.

The ideal lixiviant should achieve a high recovery of zinc and lead and a limited co-dissolution of iron. The experimental results showed that the organic acids, namely formic acid, acetic acid and Versatic Acid 10, and the acidic extractants D2EHPA, Cyanex 272 (unequilibrated) and Cyanex 272 (equilibrated with water) all leached a small amount of zinc (<6%), but no lead (Table 2). Similarly, the ionic liquids [A336][NO_3] and [C101][NO_3] equilibrated with 5 mol L^{-1} HNO_3 leached a small amount of zinc (<7%) but no lead. The poor leaching of zinc and lead by these lixiviants could be due to the fact that zinc is present in jarosite as ZnS and lead as $PbSO_4$, whereas the lixiviants were previously used for leaching metals in oxide phases. On the other hand, the neutral extractant TBP equilibrated with 12 mol L^{-1} HCl leached both lead (4%) and zinc (40%). Likewise, ethanol containing 1.2 mol L^{-1} HCl and 1-octanol containing 5.4 mol L^{-1} HCl also leached both lead (3%) and zinc (28%) but pure ethanol without dissolved HCl did not leach any lead (Table 2). Since the lixiviants that leached lead were the ones that contained chloride anions, it is obvious that the presence of this anion is crucial. Lead(II) forms the insoluble $PbCl_2$ at low chloride concentrations in water, while it forms the soluble $[PbCl_4]^{2-}$ complex in concentrated chloride solutions, according to the equations (6), (7), and (8).[19,35,36] The exact chloride concentration for forming insoluble $PbCl_2$ or soluble $[PbCl_4]^{2-}$ can vary from one system to another, depending on conditions such as the type of chloride sources (NaCl, $CaCl_2$, HCl), complexity of the solution (single-metal or multi-metal), mineral type of lead ($PbSO_4$, PbO, $PbCO_3$, etc.), temperature and kinetics.[37] A high chloride concentration is crucial for the dissolution of lead.

$$\mathrm{Pb^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons PbCl_2(s)} \qquad (6)$$

$$\mathrm{PbCl_2(aq) + Cl^{-}(aq) \rightleftharpoons [PbCl_3]^{-}(aq)} \qquad (7)$$

$$\mathrm{[PbCl_3]^{-}(aq) + Cl^{-}(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)} \qquad (8)$$

The ionic liquids [C101][Cl] and [A336][Cl] equilibrated with 12 mol L^{-1} HCl leached more lead (51% and 66%, respectively) than any of the other tested chloride-containing lixiviants, which could be explained by the higher chloride concentration in the ionic liquids. Furthermore, these ionic liquids contain cationic counter-ions, which means that they can more easily accommodate anionic species such as $[PbCl_4]^{2-}$ than molecular solvents such as 1-octanol. Based on the results in Table 2, TBP, [A336][Cl] and [C101][Cl] equilibrated with HCl were selected as the most promising lixiviants. The leaching of lead and zinc by [A336][Cl] and

[C101][Cl] equilibrated with HCl can be expressed with equations (9) and that of iron by equations (9) and (10).[34]

$$2[\mathrm{Q}][\mathrm{Cl}] + 2\mathrm{HCl} + \mathrm{M}^{2+} \rightarrow [\mathrm{Q}]_2[\mathrm{MCl}_4] + 2\ \mathrm{H}^+ \qquad (9)$$

$$[\mathrm{Q}][\mathrm{Cl}] + 3\mathrm{HCl} + \mathrm{M}^{3+} \rightarrow [\mathrm{Q}][\mathrm{MCl}_4] + 3\ \mathrm{H}^+ \qquad (10)$$

where Q is the cation of the ionic liquid and M is Pb, Zn or Fe.

Table 2: Leaching efficiency (E_L %) of lead, zinc and iron from jarosite by various lixiviants.[§] The chemical structure of the lixiviants can be found in Table S1.

Lixiviant	Pb (E_L%)	Zn (E_L%)	Fe (E_L%)
Formic acid (undiluted)	0	4.70	11.98
Acetic acid (undiluted)	0	0.65	5.33
Versatic Acid 10 (undiluted)	0	0.02	0.04
Di-(2-ethylhexyl)phosphoric acid (D2EHPA) (undiluted)	0	1.26	3.30
Cyanex 272 (equilibrated with water)	0	5.74	0.85
Cyanex 272 (non-equilibrated)	0	1.59	0.5
[A336][NO_3] (equilibrated with 5 mol L^{-1} HNO_3)	0	6.70	1.18
[C101][NO3] (equilibrated with 5 mol L^{-1} HNO_3)	0	1.04	0.01
Ethanol (undiluted)	0	2.85	3.64
1.2 mol L^{-1} HCl in ethanol	0.29	29.27	19.67
5.4 mol L^{-1} HCl in 1-octanol	2.96	28.10	62.81
TBP (equilibrated with 12 mol L^{-1} HCl)	4.22	39.48	89.85
[A336][Cl] (equilibrated with 12 mol L^{-1} HCl)	66.11	56.00	81.38
[C101][Cl] (equilibrated with 12 mol L^{-1} HCl)	51.06	66.14	87.42

[§] Leaching parameters: leaching time 2 h, 60 °C, 2000 rpm, L/S ratio 10 mL g^{-1}.

Effect of HCl concentration used for equilibration

The selected lixiviants [A336][Cl], [C101][Cl] and TBP were equilibrated with different concentrations of HCl to study their subsequent effect on the dissolution of metals from jarosite. For [A336][Cl] and [C101][Cl], the effect of HCl concentration used for equilibration was very similar (Figure 3a, b). The leaching efficiency of lead, zinc and iron generally increased with increasing HCl concentration except for lead which reached a peak at 6 mol L^{-1} and then decreased with increasing HCl concentration. The decrease in the leaching efficiency of lead at a HCl concentration higher than 6 mol L^{-1} was not expected as high concentrations of Cl^- normally increases its leaching efficiency by forming $[PbCl_4]^{2-}$ complexes. This could be explained by the fact that jarosite is not a single-metal residue and there could be competition for Cl^- anions from iron and zinc in the residue. The existence of competition for Cl^- ion can be further supported by the fact that the leaching efficiency for iron and zinc continuously increased after 6 mol L^{-1} HCl concentration, showing higher affinities for these metals than for lead. For [A336][Cl] and [C101][Cl], the highest leaching efficiency of lead was achieved at 6 mol L^{-1} with 74% and 88%, and the highest leaching efficiency for zinc was achieved at 12 mol L^{-1} with 56 and 66%, respectively. The leaching efficiency of iron increased more than that of lead and zinc with increasing HCl concentration. It has to be noted that since the iron content in jarosite is much higher than the zinc or lead content, the same percentage increase in the leaching efficiencies of iron, zinc and lead results in a larger amount of iron being leached compared to zinc and lead. At 0.5 mol L^{-1} HCl concentration, [A336][Cl] and [C101][Cl] leached more lead than zinc and iron. Hence the selectivity for lead was high compared to zinc and iron. When the HCl concentration was increased, the leaching of iron increased much more than that of lead and zinc. Hence, the selectivity towards lead and zinc over iron was significantly reduced at high HCl concentration due to greater co-dissolution of iron. Figure 4 clearly shows the decrease in the selectivity towards lead and zinc over iron when the HCl concentration was increased. Regarding TBP, the leaching of lead was very low at all HCl concentrations compared to that of [A336][Cl] and [C101][Cl] (Figure 3c). This is mostly likely because TBP is a neutral extractant and does not have cations to counter balance anionic complexes like $[PbCl_4]^{2-}$. The concentrations of lead, zinc and iron in the leachates are shown in Tables S2−4.

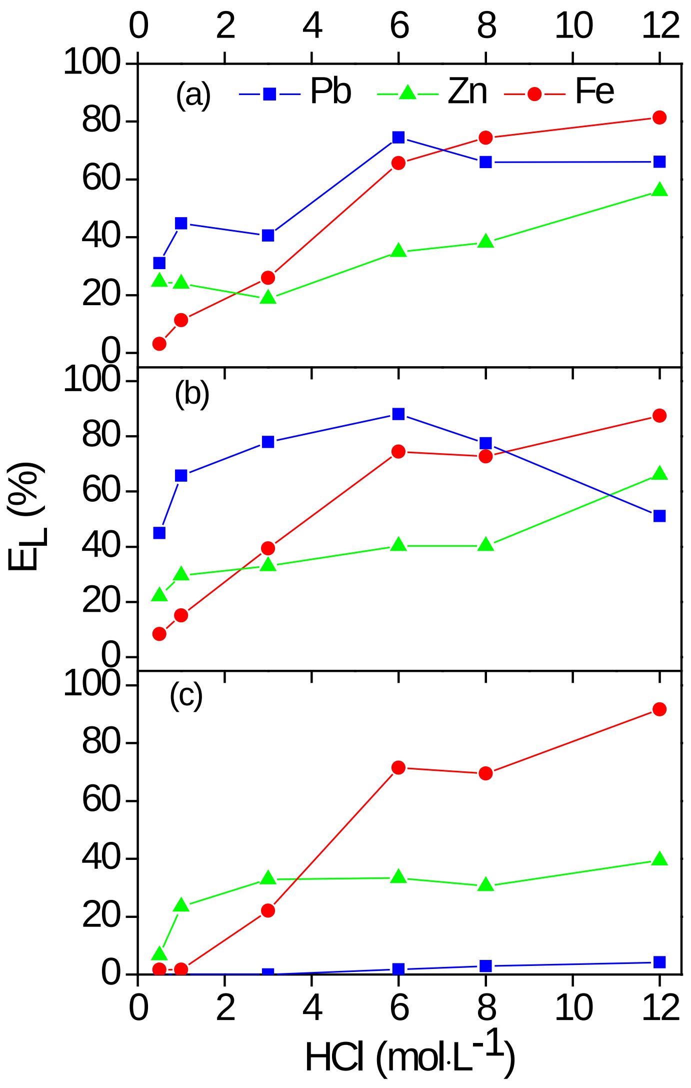

Figure 3: Leaching efficiency E_L (%) of Pb (■), Zn(▲) and Fe(●) from jarosite by (a) [A336][Cl], (b) [C101][Cl] and (c) TBP equilibrated with different HCl concentrations. Leaching parameters: L/S ratio 10 mL g^{-1}, leaching time 2 h, 60 °C, 2000 rpm.

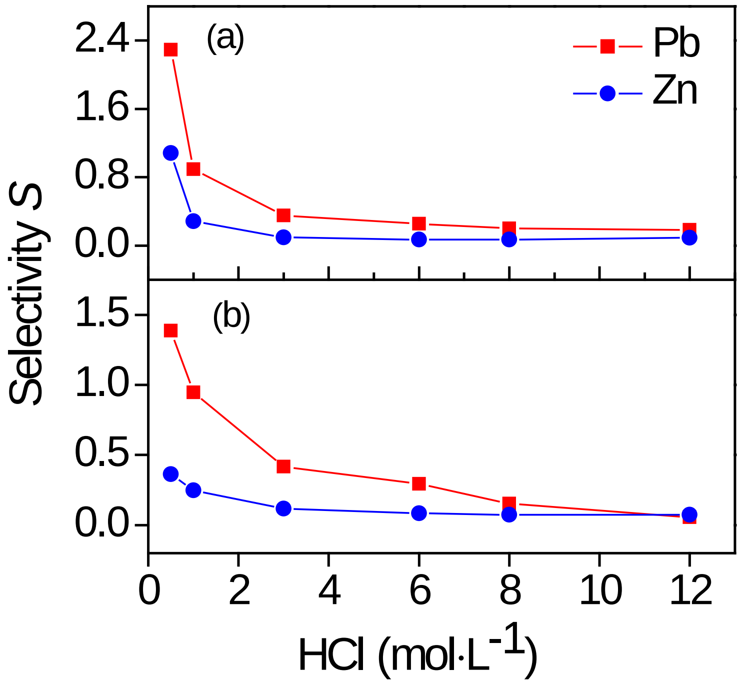

Figure 4: The selectivity *S* (Pb/Fe or Zn/Fe ratio) towards Pb (■) and Zn(●) over Fe, after leaching jarosite using (a) [A336][Cl] and (b) [C101][Cl] equilibrated with different HCl concentrations.

Although equilibrating [C101][Cl] and [A336][Cl] with a higher HCl concentration leached more lead and zinc, it also decreased their selectivity against iron. The co-dissolution of iron would interfere in the downstream processes of the metal recovery. Therefore, the ionic liquids equilibrated with 0.5 mol L^{-1} HCl were chosen as the most suitable lixiviants due to their better selectivity against iron. TBP equilibrated with HCl was a poor lixiviant for lead and thus, it was not studied further.

Optimisation and upscaling

The leaching parameters such as temperature, liquid-to-solid ratio, residence time and stirring speed were optimised for [C101][Cl] and [A336][Cl] equilibrated with 0.5 mol L^{-1} HCl. The best leaching and selectivity values (Table 3) were achieved at L/S of 15 mL g^{-1}, 45 °C, 2 h leaching time and a stirring speed of 1500 rpm (Figure S2−5). In the jarosite, iron is the main component, having a concentration higher than lead ($S = 0.24$) and zinc ($S = 0.14$). After solvometallurgical leaching, the lead concentration ($S > 1.74$) in the leachate surpassed the iron concentration and, although Zn ($S \approx 0.45$) is still less concentrated than iron, the difference decreased compared to the original ratio in the jarosite, leading to an enrichment of zinc from $S = 0.14$ to $S \approx 0.45$. The metal concentrations in the leachate are shown in Table S5.

Table 3: Leaching efficiencies and selectivity of lead, zinc and iron for jarosite at the optimised conditions[§].

Lixiviants	Pb		Zn		Fe
	E_L (%)	S	E_L (%)	S	E_L(%)
[A336][Cl] (eq. with 0.5 mol L^{-1} HCl)	62	1.90	27	0.50	7
[C101][Cl] (eq. with 0.5 mol L^{-1} HCl)	73	1.74	31	0.43	10

[§] Leaching parameters: L/S ratio 15 mL g^{-1}, 2 h, 45 °C, 1500 rpm

The scalability of the leaching results by [A336][Cl] and [C101][Cl] equilibrated with 0.5 mol L^{-1} HCl was investigated by increasing the mass of the jarosite used for leaching from 0.1 to 10 g and by increasing the lixiviant volume from 1 to 100 mL. Upscaling the experiments resulted in a slight decrease of the leaching efficiency of lead by [A336][Cl] and [C101][Cl] equilibrated with 0.5 mol L^{-1} HCl which is most likely because the L/S ratio was decreased from 15 to 10 (Table S6). A lower L/S of 10 was preferred because it reduces the cost of the process from an industrial perspective. Besides the slight decrease in the leaching efficiency of lead, the leaching efficiencies and selectivity of the other metals remained similar. The leaching of jarosite by [A336][Cl] and [C101][Cl] equilibrated with 0.5 mol L^{-1} HCl can therefore be upscaled.

Metal recovery by selective precipitation-stripping

Wellens et al. (2014) successfully stripped zinc and iron from a [C101][Cl] leachate by using 2.67 mol L^{-1} NH_3 solution.[34] Therefore, the recovery of dissolved metals from the [C101][Cl] leachate produced during the upscaling test was investigated by stripping with different concentrations of NH_3 in water. Three distinct phases were present after the stripping process: 1) a liquid organic phase, 2) a liquid aqueous phase and 3) a solid precipitate. At low range of NH_3 concentrations, from 0.0015 to 0.025 mol L^{-1} NH_3, only about 30% of iron remained in the organic phase. The rest was either precipitated (30%) or stripped to the aqueous phase (40%) (Figure 5a–c). Lead and zinc were neither stripped nor precipitated at those NH_3 concentrations. The iron in the organic and aqueous liquid phases continued to precipitate when the NH_3 concentration was increased from 0.025 mol L^{-1}, until complete precipitation of iron occurred at ≥1 mol L^{-1} NH_3 concentration. Similarly, lead started to precipitate at NH_3 concentrations above 0.025 mol L^{-1} and nearly 100% was precipitated by using 0.48 mol L^{-1} NH_3. Interestingly, lead was never present in the aqueous liquor, denoting the preference to precipitate or remain dissolved in the organic phase. The pH of the aqueous phase was monitored during the stripping (Table 4). The poor solubility of Pb(II) in aqueous solution at acidic pH could be explained by the fact that it is, in general, hardly soluble in solutions with a low chloride concentration. Moreover, the solubility of Pb(II) in HCl solution is lower than in $CaCl_2$ or NaCl solution.[37] The very limited solubility in basic pH range is due to the formation of insoluble $(PbOH)_2$.[38] On the other hand, zinc began to strip to the aqueous phase when the NH_3 concentration was increased above 0.32 mol L^{-1}, reaching 100% stripping at 2 mol L^{-1} NH_3 concentration. A certain amount of zinc also precipitated at 0.32 to 1 mol L^{-1} NH_3

concentration but it solubilised back in the aqueous solution at higher NH_3 concentrations. This odd behavior of zinc occurs because the Zn(II) ion forms insoluble $Zn(OH)_2$ in alkaline conditions, but it readily dissolves in excess of NH_3 owing to the formation of $[Zn(NH_3)_4]^{2+}$ ion.[39] In general, when contacting the HCl-containing ionic liquid with an aqueous solution, HCl was stripped to the aqueous phase. The strip solutions with a low NH_3 concentration ($\leq$0.05 mol L^{-1}) became acidic after stripping because the protons from the stripped HCl were present in excess and fully neutralized all the OH^- ions in the NH_3 solution (Table 4Table 4). On the other hand, stripping with NH_3 concentrations higher than 1 mol L^{-1} resulted in a decrease of the pH but the solution remained basic since the OH^- concentration in these NH_3 solutions was higher than the concentration of protons from the stripped HCl solution.

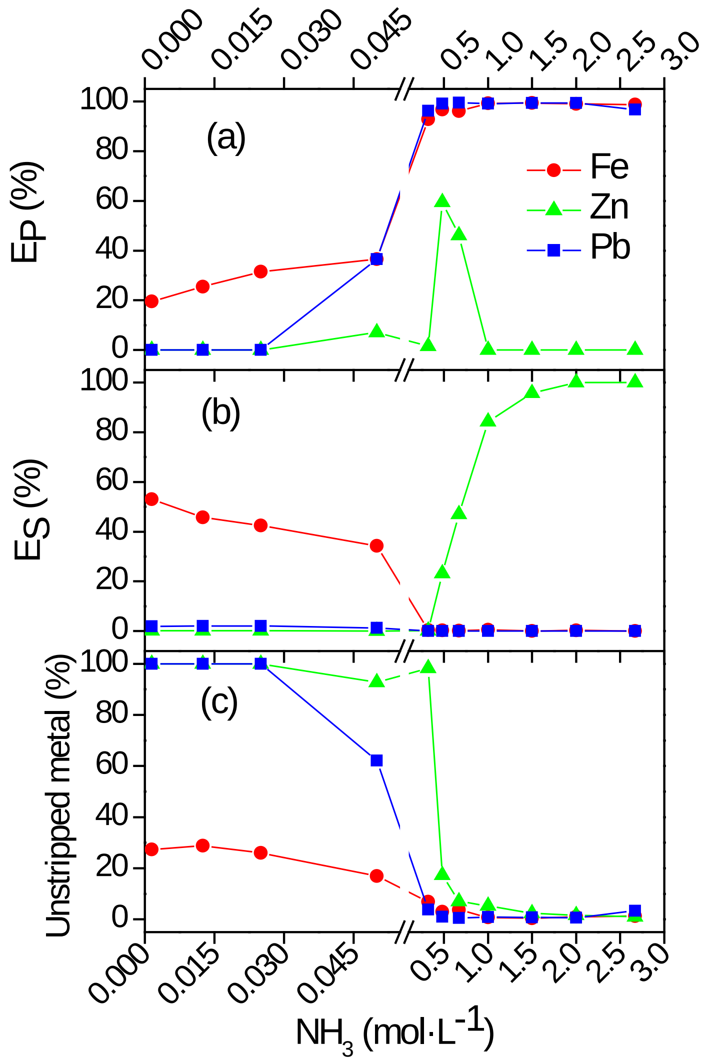

Figure 5: (a) The precipitating efficiency E_P (%), (b) the stripping efficiency E_S (%) and (c) the metals remaining in the stripped leachate (%) of Pb (■), Zn(▲) and Fe(●) from [C101][Cl] leachate to the aqueous phase when contacted with solutions with varying NH_3 concentration. Stripping parameters: volume phase ratio Θ = 1 (mL/mL), 1 h, 60 °C, 1500 rpm.

Table 4: pH of the different NH_3 solutions before and after contacting with the [C101][Cl] leachate.

NH_3 [mol L^{-1}]	pH (before)	pH (after)
0.0015	8.86	1.63
0.0125	10.17	1.76
0.025	10.58	1.86
0.05	10.86	2.08
–	–	–
1	11.73	9.74
1.5	11.77	10.20
2	11.87	10.30
2.67	11.94	10.61

Based on the results above, a two-step cumulative stripping process was proposed to selectively recover lead and zinc from [C101][Cl] leachate. This process consisted of stripping with 0.025 mol L^{-1} NH_3 solution and then with a 2 mol L^{-1} NH_3 solution. The first step with 0.025 mol L^{-1} NH_3, to separate iron apart from the lead and zinc in the organic phase, stripped 34% of iron to the aqueous phase while 31% of iron precipitated (Table S7). The second stripping step was done with a 2 mol L^{-1} NH_3 solution to strip 100% of zinc to the aqueous solution and to precipitate 100% of the lead along with the remaining 35% of the unstripped iron. Unlike what happened with the [C101][Cl] leachate, contacting the [A336][Cl] leachate with a 0.025 mol L^{-1} NH_3 solution precipitated both iron and lead together. Since selective recovery of lead was not possible for the [A336][Cl] leachate, one-step stripping with a 2 mol L^{-1} NH_3 solution was carried out where 100% of the lead and 100% of the iron were precipitated together, and 100% of the zinc was stripped selectively to the aqueous solution (Table S8).

After recovering lead, zinc and iron, the ionic liquid can be used for leaching a new batch of jarosite. A schematic representation of the leaching and subsequent recovery of the metal ions from the [C101][Cl] and [A336][Cl] leachate is shown in Figure 6.

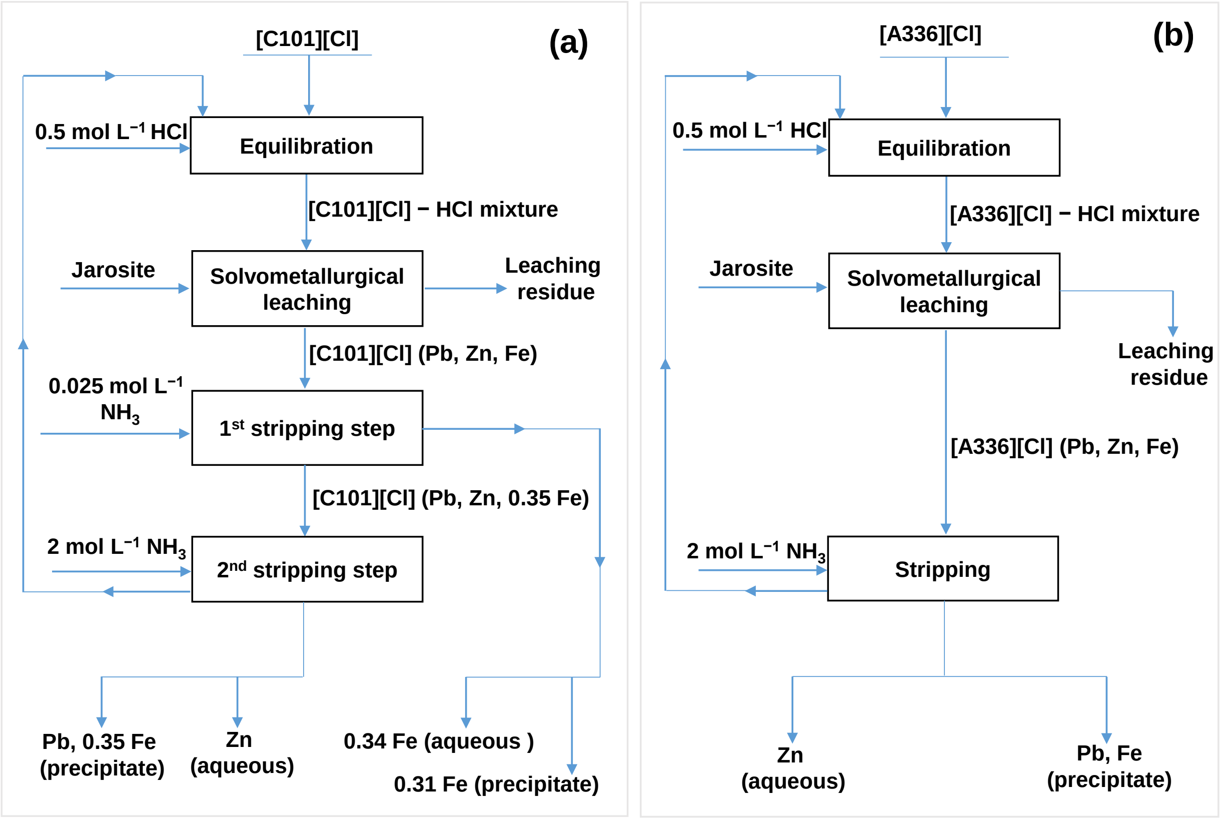

Figure 6: Flow chart for the recovery of lead, zinc and iron from jarosite by using (a) [C101][Cl] and (b) [A336][Cl] equilibrated with 0.5 mol L^{-1} HCl.

Conclusions

Solvometallurgical leaching was applied on a real jarosite residue from the zinc industry to selectively recover lead and zinc over iron. The presence of chloride in the lixiviant was crucial for the leaching of lead. The ionic liquids [A336][Cl] and [C101][Cl] equilibrated with HCl leached the highest amount of lead and zinc. This is due to the presence of high chloride concentration which resulted in the formation of the $[PbCl_4]^{2-}$ complexes and the presence of cations to counterbalance the dissolved anionic metal complexes. The selectivity towards lead and zinc over iron was strongly influenced by the concentration of HCl used for equilibrating the ionic liquids. The leaching efficiency of lead, zinc and iron generally increased with increasing HCl concentration but the selectivity decreased with increasing HCl concentration. The most selective leaching of lead and zinc over iron took place when the [A336][Cl] and [C101][Cl] were equilibrated with 0.5 mol L^{-1} HCl. The leaching system could be upscaled from 0.1 to 10 g with minimal change in leaching efficiency and selectivity. The selective recovery of the dissolved metals from the [A336][Cl] and [C101][Cl] leachates was done by precipitation-stripping with aqueous NH_3 solutions. A two-step stripping with a 0.025 mol L^{-1} NH_3 solution and a 2 mol L^{-1} NH_3 solution was performed to recover the metals from the [C101][Cl] leachate. In this way, the majority of iron was separated from lead and zinc in the first step. In the second stripping step, lead and the remaining iron were precipitated , while zinc was fully separated from lead and iron by stripping to the aqueous phase. A one-step stripping with a 2 mol L^{-1} NH_3 solution was carried out for the [A336][Cl] leachate. In this case, a precipitate containing lead and iron and an aqueous strip solution containing zinc were immediately obtained.

Associated content

Supporting Information

The supporting information includes a density plot of the particle size distribution of the jarosite (Figure S1), a table with the chemical structures of tested lixiviants for leaching jarosite (Table S1), tables of metal concentrations in the leachate after leaching jarosite with [A336][Cl], [C101][Cl] and TBP with different HCl concentrations (Table S2−4), plots of the influence of the shaking speed, temperature, contact time and liquid-to-solid ratio on the leaching efficiency of lead, zinc and iron (Figure S2−5), and a tables of metal concentration in the leachate at optimised conditions (Table S5), a table of leaching efficiencies and selectivity after upscaling

(Table S6), tables of the stripping efficiency and precipitating efficiency during the cumulative stripping of [C101][Cl] and [A336][Cl] leachate (Table S7-8).

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Notes

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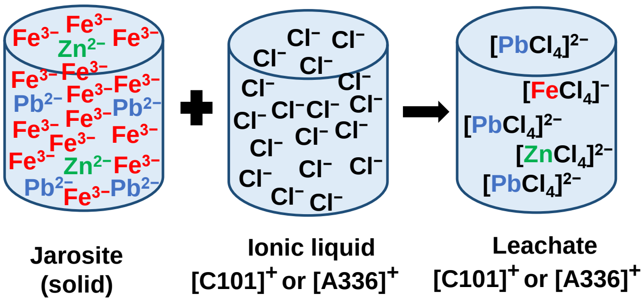
TOC graphic



Synopsis

The ionic liquids [C101][Cl] and [A336][Cl] equilibrated with 0.5 mol L^{-1} HCl showed good leaching efficiency and selectivity for lead and zinc from iron-rich jarosite residue of the zinc industry.