

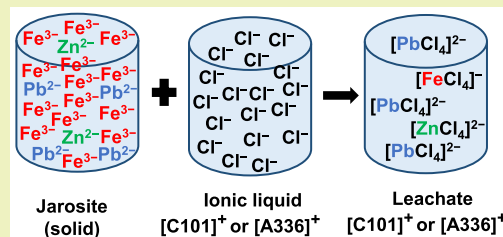
Selective Metal Recovery from Jarosite Residue by Leaching with Acid-Equilibrated Ionic Liquids and Precipitation-Stripping

Thupten Palden,¹ Mercedes Regadío,¹ Bieke Onghena,¹ and Koen Binnemans^{1*}

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, P.O. Box 2404, B-3001, Leuven, Belgium

Supporting Information

ABSTRACT: The recovery of valuable metals from industrial process residues is complex because those metals are often present in very low concentrations and 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 the 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 optimization study because of their higher selectivity toward lead and zinc and lower codissolution of iron, compared to the same ionic liquids equilibrated with a higher concentration of HCl. At optimized 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 codissolved 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 coprecipitated 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} Owing 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 that of other industrial process residues, is complex because the relevant metals are present in low concentrations and often locked in complex matrices (sulfides, 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 (H₂SO₄) followed by brine (NaCl) leaching.¹⁷ Turan et al. (2004) extracted 86% of Zn and 89% of Pb from the residue via H₂SO₄ blending and roasting, followed by water leaching and NaCl leaching.¹⁹ Ju et al. (2011) developed a roasting–

Received: November 14, 2018

Revised: January 13, 2019

Published: January 16, 2019

NH₄Cl–alkali leaching process where more than 95% of the Zn, Pb, Cu, Cd, and Ag is 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 toward the target metals over iron. The codissolution 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 hydro-metallurgical processes by organic solvents, it is possible to attain high reactivity and selectivity because nonhydrated 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 "solvo-metallurgy".¹⁶

This work presents the development of a novel solvo-metallurgical 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 toward these metals over iron. Finally, the recovery of the dissolved metals from the organic leachate (stripping) was studied.

■ EXPERIMENTAL SECTION

Chemicals. Jarosite was kindly provided by a European zinc producing company. Acetic acid (AnalR NORMAPUR, 100%), ammonia solution (≥ 25 wt % NH₃ 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 % HNO₃ in water), tri-*n*-butyl phosphite (TBP, >99 wt %) and praseodymium standard (1000 mg L⁻¹, 2–5 wt % HNO₃) 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 triethylmethylammonium 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 isopropyl alcohol 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 the 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 eq 1.

$$\text{MC}(\%) = \frac{m_i - m_f}{m_f} \cdot 100 \quad (1)$$

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 the 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° 2 θ using Cu K 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 % HNO₃ 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 HNO₃ was necessary for complete dissolution of the residue. The sample dissolution via microwave digestion was done in triplicate 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, PerkinElmer, 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 analyzer (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 HNO₃ (6 mol L⁻¹) solution prior to use for solvo-leaching. 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 KNO₃ solution in three equilibration contacts with a volume phase ratio of 1:1, followed by washing three times with an aqueous HNO₃ 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 optimized. 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 μ m 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 30 μ L of a silicon solution in isopropyl alcohol (SERVA) on its surface and, finally, 2.5 μ L of the diluted sample was pipetted on the quartz glass carrier. The sample on the glass carrier was dried in an oven for 30

min at 60 °C for analysis. The leaching efficiency $E_L(\%)$ was calculated according to eq 2:

$$E_L(\%) = \frac{c_M v_{LIX}}{m_i c_1} \cdot 100 \quad (2)$$

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_1 is the concentration of the metal in the jarosite before leaching (mg kg^{-1}).

The selectivity S toward lead or zinc over iron was calculated for the solid jarosite and for the leachate according to eq 3:

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

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 $S = 1$, then the concentration of lead or zinc is equal to that of iron. A low value 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 analyzed by TXRF using the same methodology as described above. Similarly, the metal concentrations in the aqueous phase were analyzed 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 eqs 4 and 5:

$$E_s(\%) = \frac{c_s}{c_L} \cdot 100 \quad (4)$$

$$E_p(\%) = \frac{c_L - c_{S,L} - c_s}{c_L} \cdot 100 \quad (5)$$

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 $c_{S,L}$ 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, from which a SEM micrograph was taken

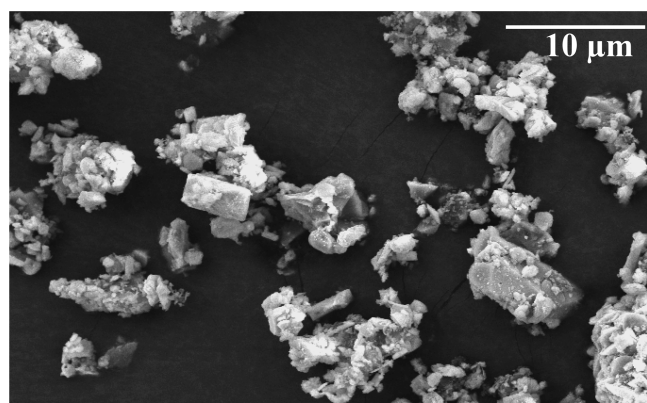


Figure 1. SEM micrograph of jarosite after drying (110 °C, 24 h) and milling (30 s, 1000 rpm).

(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 ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), 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.

Comparison of Solvometallurgical Lixivants. Various solvometallurgical lixivants were compared in order to determine their suitability for the leaching of lead and zinc from jarosite. The tested lixivants 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 lixivants, but TBP equilibrated with mineral acids has been found to be a powerful lixiviant.^{32,33} Similarly, basic extractants such as [C101][Cl] and [A336][Cl] combined with mineral acids have shown to be good lixivants.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 codissolution 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][NO₃] and [C101][NO₃] 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 lixivants could occur because zinc is present in jarosite as ZnS and lead as PbSO_4 , whereas the lixivants 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 lixivants 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 $[\text{PbCl}_4]^{2-}$ complex in

Table 1. Elemental Composition of Milled Jarosite Residue

metal	S	Fe	Pb	Zn	Ca	Na	Al	Mg	K	Si	Cu	other ^a
g/kg	280	174	40	24	25	18	5.7	3.0	2.5	1.5	0.90	2.44

^aOthers include Ba, Sr, Sn, P, and B.

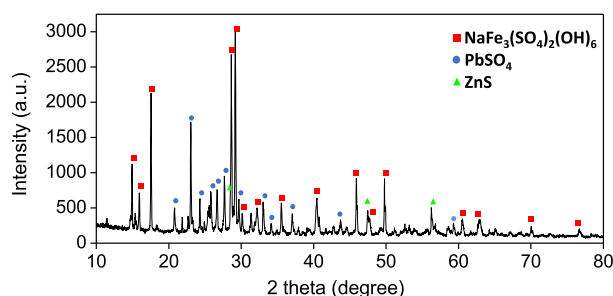


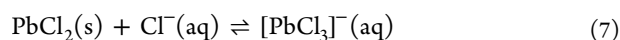
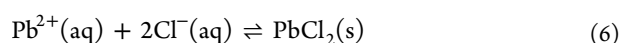
Figure 2. XRD pattern of jarosite after drying (110 °C, 24 h) and milling (30 s, 1000 rpm).

Table 2. Leaching Efficiency (E_L %) of Lead, Zinc, and Iron from Jarosite by Various Lixiviants^a

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 (nonequilibrated)	0	1.59	0.5
[A336][NO ₃] (equilibrated with 5 mol L ⁻¹ HNO ₃)	0	6.70	1.18
[C101][NO ₃] (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

^aLeaching parameters: leaching time 2 h, 60 °C, 2000 rpm, L/S ratio 10 mL g⁻¹. The chemical structure of the lixivants can be found in Table S1

concentrated chloride solutions, according to the eqs 6, 7, and 8.^{19,35,36} The exact chloride concentration for forming insoluble PbCl₂ or soluble [PbCl₄]²⁻ can vary from one system to another, depending on conditions such as the type of chloride sources (NaCl, CaCl₂, HCl), complexity of the solution (single-metal or multimetal), mineral type of lead (PbSO₄, PbO, PbCO₃, etc.), temperature, and kinetics.³⁷ A high chloride concentration is crucial for the dissolution of lead.



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

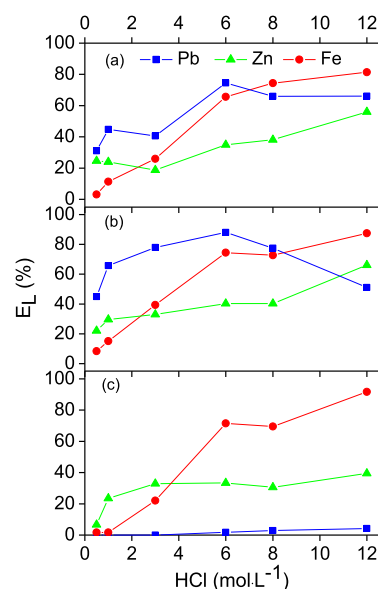


Figure 3. Leaching efficiency E_L (%) of Pb (blue ■), Zn (green ▲), and Fe (red ●) from jarosite by (a) [A336][Cl], (b) [C101][Cl], and (c) TBP equilibrated with different HCl concentrations. Leaching parameters: L/S ratio 10 mL g⁻¹, leaching time 2 h, 60 °C, 2000 rpm.

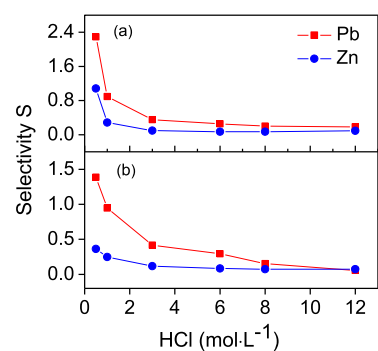


Figure 4. Selectivity S (Pb/Fe or Zn/Fe ratio) toward Pb (red ■) and Zn (blue ●) over Fe, after leaching jarosite using (a) [A336][Cl] and (b) [C101][Cl] equilibrated with different HCl concentrations.

Table 3. Leaching Efficiencies and Selectivity of Lead, Zinc, and Iron for Jarosite at the Optimized Conditions^a

lixivants	Pb		Zn		Fe
	E_L (%)	S	E_L (%)	S	E_L (%)
[A336][Cl] (with 0.5 mol L ⁻¹ HCl)	62	1.90	27	0.50	7
[C101][Cl] (with 0.5 mol L ⁻¹ HCl)	73	1.74	31	0.43	10

^aLeaching parameters: L/S ratio, 15 mL g⁻¹; 2 h; 45 °C; 1500 rpm.

lixivants, which could be explained by the higher chloride concentration in the ionic liquids. Furthermore, these ionic liquids contain cationic counterions, which means that they can more easily accommodate anionic species such as [PbCl₄]²⁻ than molecular solvents such as 1-octanol. On the

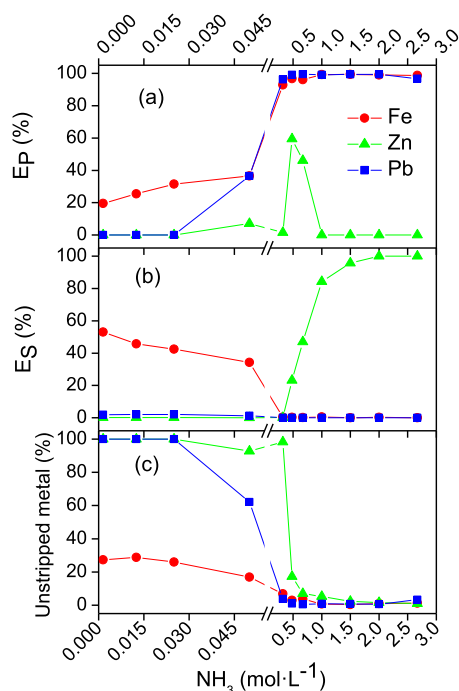
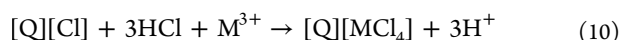
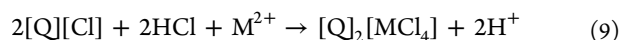


Figure 5. (a) The precipitating efficiency E_p (%), (b) the stripping efficiency E_s (%), and (c) the metals remaining in the stripped leachate (%) of Pb (blue ■), Zn (green ▲), and Fe (red ●) from [C101][Cl] leachate to the aqueous phase when contacted with solutions with varying NH_3 concentration. Stripping parameters: volume phase ratio $\Theta = 1$ (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

basis of the results in Table 2, TBP, [A336][Cl], and [C101][Cl] equilibrated with HCl were selected as the most promising lixivants. The leaching of lead and zinc by [A336][Cl] and [C101][Cl] equilibrated with HCl can be expressed with eq 9 and that of iron by eqs 9 and 10.³⁴



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

Effect of HCl Concentration Used for Equilibration.

The selected lixivants [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 [PbCl₄]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⁻ ions 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 toward lead and zinc over iron was significantly reduced at high HCl concentration due to greater codissolution of iron. Figure 4 clearly shows the decrease in the selectivity toward 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 most likely because TBP is a neutral extractant and does not have cations to counter balance anionic complexes such as [PbCl₄]²⁻. The concentrations of lead, zinc, and iron in the leachates are shown in Tables S2–S4.

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 codissolution 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 lixivants due to their better selectivity against iron. TBP equilibrated with HCl was a poor lixiviant for lead, and thus it was not studied further.

Optimization and Upscaling. The leaching parameters such as temperature, liquid-to-solid ratio, residence time, and stirring speed were optimized 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 (Figures S2–S5). 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 in the leachate surpassed the iron concentration ($S > 1.74$) and, although Zn is still less concentrated than iron ($S \approx 0.45$), the difference decreased compared to the original ratio in the jarosite ($S = 0.14$). The metal concentrations in the leachate are shown in Table S5.

The scalability of the leaching results by [A336][Cl] and [C101][Cl] equilibrated with 0.5 mol L⁻¹ HCl was

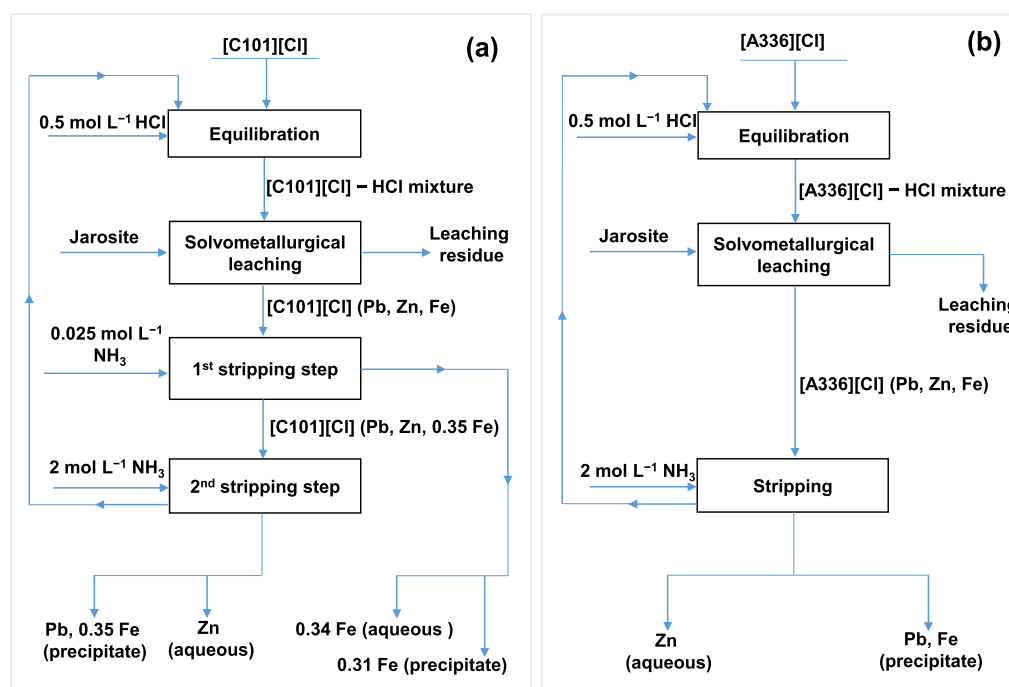


Figure 6. Flowchart for the recovery of lead, zinc, and iron from jarosite by using (a) [C101][Cl] and (b) [A336][Cl] equilibrated with 0.5 mol L⁻¹ HCl.

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 NH₃ 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 NH₃ 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 a low range of NH₃ concentrations, from 0.0015 to 0.025 mol L⁻¹ NH₃, 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 NH₃ concentrations. The iron in the organic and aqueous liquid phases continued to precipitate when the NH₃ concentration was increased from 0.025 mol L⁻¹, until complete precipitation of iron occurred at ≥1 mol L⁻¹ NH₃ concentration. Similarly, lead started to precipitate at NH₃ concentrations above 0.025 mol L⁻¹ and nearly 100% was precipitated by using 0.48 mol L⁻¹ NH₃. 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 CaCl₂ or NaCl solution.³⁷ The very limited solubility in the 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 NH₃ concentration was increased above 0.32 mol L⁻¹, reaching 100% stripping at 2 mol L⁻¹ NH₃ concentration. A certain amount of zinc also precipitated at 0.32 to 1 mol L⁻¹ NH₃ concentration but it solubilized back in the aqueous solution at higher NH₃ 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 NH₃ owing to the formation of [Zn(NH₃)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 NH₃ concentration (≤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 NH₃ solution (Table 4). On the other hand, stripping with NH₃ 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 NH₃ solutions was higher than the concentration of protons from the stripped HCl solution.

On the basis of 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 NH₃ solution and then with a 2 mol L⁻¹ NH₃ solution. The first step with 0.025 mol L⁻¹ NH₃, 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 NH₃ 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 NH₃ 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 NH₃ solution was carried out in which 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.

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 a high chloride concentration which resulted in the formation of the [PbCl₄]²⁻ complexes and the presence of cations to counterbalance the dissolved anionic metal complexes. The selectivity toward 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 NH₃ solutions. A two-step stripping with a 0.025 mol L⁻¹ NH₃ solution and a 2 mol L⁻¹ NH₃ 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 NH₃ 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 is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05938.

Density plot of the particle size distribution of the jarosite (Figure S1); chemical structures of tested lixiviants for leaching jarosite (Table S1); metal concentrations in the leachate after leaching jarosite with [A336][Cl], [C101][Cl], and TBP with different HCl concentrations (Table S2–S4); 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 (Figures S2–S5); metal

concentration in the leachate at optimized conditions (Table S5); leaching efficiencies and selectivity after upscaling (Table S6); stripping efficiency and precipitating efficiency during the cumulative stripping of [C101][Cl] and [A336][Cl] leachate (Tables S7–S8) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: Koen.Binnemans@kuleuven.be. Phone: +3216327446.

ORCID

Thupten Palden: 0000-0003-0284-7427

Mercedes Regadío: 0000-0002-0406-6416

Bieke Onghena: 0000-0002-8809-0842

Koen Binnemans: 0000-0003-4768-3606

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research received funding from the European Commission's H2020—Marie Skłodowska Curie Actions (MSCA)—Innovative Training Networks within the SOCRATES project under the Grant Agreement No. 721385 (Project website: <http://etn-socrates.eu>). The authors thank Dr. Mehmet Ali Recai Onal from KU Leuven for helping with the SEM and XRD measurements. The authors would also like to thank Nikos Nikolopoulos from Utrecht University for sharing the characterization information on jarosite for comparison. This work reflects only the authors' view, exempting the Commission from any liability.

REFERENCES

- (1) Wang, Y.; Yang, H.; Zhang, W.; Song, R.; Jiang, B. Study on recovery of lead, zinc, iron from jarosite residues and simultaneous sulfur fixation by direct reduction. *Physicochem. Probl. Miner. Process.* **2018**, *54* (2), 517–526.
- (2) Liu, C.; Ju, S. H.; Zhang, L. B.; Srinivasakannan, C.; Peng, J. H.; Le, T. Q. X.; Guo, Z. Y. Recovery of valuable metals from jarosite by sulphuric acid roasting using microwave and water leaching. *Can. Metall. Q.* **2017**, *56* (1), 1–9.
- (3) Wang, Y.; Yang, H.; Jiang, B.; Song, R.; Zhang, W. Comprehensive recovery of lead, zinc, and iron from hazardous jarosite residues using direct reduction followed by magnetic separation. *Int. J. Miner., Metall. Mater.* **2018**, *25* (2), 123–130.
- (4) Dutrizac, J. E.; Jambor, J. L. Jarosites and their application in hydrometallurgy. *Rev. Mineral. Geochem.* **2000**, *40* (1), 405–452.
- (5) Arregui, B.; Gordon, A. R.; Steintvelt, G. The jarosite process—past, present, and future. In *Lead–Zinc–Tin '80*; Cigan, J. M., Mackey, T. S., O'Keefe, T. J., Eds.; TMS–AIME: New York, 1979; p 97.
- (6) Dutrizac, J. The behavior of impurities during jarosite precipitation. *Hydrometall. Process Fundam.* **1984**, *10*, 125–169.
- (7) Dutrizac, J. Jarosite-type compounds and their application in the metallurgical industry. *J. Metals.* **1982**, *35*, A70–A70.
- (8) Pappu, A.; Saxena, M.; Asolekar, S. R. Jarosite characteristics and its utilisation potentials. *Sci. Total Environ.* **2006**, *359*, 232–243.
- (9) Romero, M.; Rincon, Ma. J. Microstructural characterisations of a goethite waste from zinc hydrometallurgical process. *Mater. Lett.* **1997**, *31*, 67–73.
- (10) Ju, S. H.; Zhang, Y. F.; Zhang, Y.; Xue, P. Y.; Wang, Y. H. Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy. *J. Hazard. Mater.* **2011**, *192* (2), 554–558.

- (11) Asokan, P.; Saxena, M.; Asolekar, S. Recycling hazardous jarosite waste using coal combustion residues. *Mater. Charact.* **2010**, *61* (12), 1342–1355.
- (12) Asokan, P.; Saxena, M.; Asolekar, S. R. Hazardous jarosite use in developing non-hazardous product for engineering application. *J. Hazard. Mater.* **2006**, *137*, 1589–1599.
- (13) Pelino, M. Recycling of zinc-hydrometallurgy wastes in glass and glass ceramic materials. *Waste Manage.* **2000**, *20*, 561–568.
- (14) Piscicella, P.; Crisucci, S.; Karamanov, A.; Pelino, M. Chemical durability of glasses obtained by vitrification of industrial wastes. *Waste Manage.* **2001**, *21*, 1–9.
- (15) Mehra, P.; Gupta, R. C.; Thomas, B. S. Properties of concrete containing jarosite as a partial substitute for fine aggregate. *J. Cleaner Prod.* **2016**, *120*, 241–248.
- (16) Binnemans, K.; Jones, P. T. Solvometallurgy: An Emerging Branch of Extractive Metallurgy. *J. Sust. Metall.* **2017**, *3*, 570–600.
- (17) Hoang, J.; Reuter, M. A.; Matuszewicz, R.; Hughes, S.; Piret, N. Top submerged lance direct zinc smelting. *Miner. Eng.* **2009**, *22*, 742–751.
- (18) Ruşen, A.; Sunkar, A. S.; Topkaya, Y. A. Zinc and lead extraction from Çinkur leach residues by using hydrometallurgical method. *Hydrometallurgy* **2008**, *93*, 45–50.
- (19) Turan, M. D.; Altundogan, H. S.; Tumen, F. Recovery of zinc and lead from zinc plant residue. *Hydrometallurgy* **2004**, *75*, 169–176.
- (20) Chen, Y. M.; Tang, M. T.; Yang, S. H.; He, J.; Tang, C. B.; Yang, J. G.; Lu, J. Y. Novel technique of decomposition of ammonium jarosite bearing indium in NaOH medium. *Chin. J. Nonferrous Met.* **2009**, *19* (7), 1322–1331.
- (21) Han, H. S.; Sun, W.; Hu, Y. H.; Jia, B. L.; Tang, H. H. Anglesite and silver recovery from jarosite residues through roasting and sulfidization–flotation in zinc hydrometallurgy. *J. Hazard. Mater.* **2014**, *278*, 49–54.
- (22) Malenga, E. N.; Bafubiandi, A. M.; Nheta, W. Alkaline leaching of nickel bearing ammonium jarosite precipitate using KOH, NaOH and NH₄OH in the presence of EDTA and Na₂S. *Hydrometallurgy* **2015**, *155*, 69–78.
- (23) Xue, P. Y.; Ju, S. H.; Zhang, Y. F.; Wang, X. W. Recovery of valuable metals by leaching of roasted jarosite residue. *Chin. J. Process Eng.* **2011**, *11* (1), 56–60.
- (24) Goldstein, J. I.; Newbury, D. E. *Scanning Electron Microscopy and X-Ray Microanalysis*, 3rd ed.; Springer: New York, 2003.
- (25) Silva, S. G.; Oliveira, P. V.; Rocha, F. R. P. A Green Analytical Procedure for Determination of Copper and Iron in Plant Materials after Cloud Point Extraction. *J. Braz. Chem. Soc.* **2010**, *21* (2), 234–239.
- (26) Riaño, S.; Binnemans, K. Extraction and Separation of Neodymium and Dysprosium from Used NdFeB Magnets: An Application of Ionic Liquids in Solvent Extraction towards the Recycling of Magnets. *Green Chem.* **2015**, *17* (5), 2931–2942.
- (27) Regadío, M.; Riaño, S.; Binnemans, K.; Vander Hoogerstraete, T. Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence. *Anal. Chem.* **2017**, *89*, 4595–4603.
- (28) Ozdemir, S.; Girgin, I. Decomposition of scheelite in acid-alcohol solutions. *Miner. Eng.* **1991**, *4*, 179–184.
- (29) Jana, R.; Singh, D.; Roy, S. Hydrochloric acid leaching of sea nodules with methanol and ethanol addition. *Mater. Trans., JIM* **1993**, *34*, 593–598.
- (30) Kopkova, E. K.; Shchelokova, E. A.; Gromov, P. B. Processing of titanomagnetite concentrate with a hydrochloric extract of n-octanol. *Hydrometallurgy* **2015**, *156*, 21–27.
- (31) Thorsen, G.; Grislingås, A.; Steintveit, G. Recovery of Zinc from Zinc Ash and Flue Dusts by Hydrometallurgical Processing. *JOM* **1981**, *33*, 24–29.
- (32) Duan, W.; Zhu, L.; Jing, S.; Zhu, Y.; Chen, J. Study on properties of TBP-HNO₃ complex used for direct dissolution of lanthanide and actinide oxides in supercritical fluid CO₂. *Chin. J. Chem.* **2007**, *25*, 319–322.
- (33) Kumar, B.; Kumar, S.; Sampath, M.; Sivakumar, D.; Kamachi-Mudali, U.; Natarajan, R. Direct dissolution of UO₂ and in situ extraction by TBP-HNO₃ and TiAP-HNO₃ organic solutions at atmospheric pressure. *J. Radioanal. Nucl. Chem.* **2011**, *288*, 443–445.
- (34) Wellens, S.; Vander Hoogerstraete, T.; Möller, C.; Thijs, B.; Luyten, J.; Binnemans, K. Dissolution of metal oxides in an acid-saturated ionic liquid solution and investigation of the back-extraction behaviour to the aqueous phase. *Hydrometallurgy* **2014**, *144*, 27–33.
- (35) Farahmand, F.; Moradkhani, D.; Safarzadeh, M. S.; Rashchi, F. Brine leaching of lead-bearing zinc plant residues: process optimization using orthogonal array design methodology. *Hydrometallurgy* **2009**, *95*, 316–324.
- (36) Guo, Z. H.; Pan, F. K.; Xiao, X. Y.; Zhang, L.; Jiang, K. Q. Optimization of brine leaching of metals from hydrometallurgical residue. *Trans. Nonferrous Met. Soc. China* **2010**, *20*, 2000–2005.
- (37) Holdich, R. G.; Lawson, G. J. The solubility of aqueous lead chloride solutions. *Hydrometallurgy* **1987**, *19*, 199–208.
- (38) Monhemius, A. J. Precipitation Diagrams for Metal Hydroxides Sulfides Arsenates and Phosphates. *Trans. Inst. Min. Metall.* **1977**, *86* (C), 202–206.
- (39) Vogel, A. I.; Svehla, G. *Vogel's Textbook of Macro and semimicro qualitative inorganic analysis*; Longman: London, 1979.