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## Methanesulfonic acid: a sustainable acidic solvent for recovering metals from jarosite residue of the zinc industry†

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Methanesulfonic acid (MSA) is a green acid with a remarkably high solubility for several speciality and base metals including lead, making it an interesting leaching agent for metals. MSA is safer and less toxic than the mineral acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) currently employed for leaching metals from primary and secondary sources. In this study, MSA was tested for the leaching of lead and zinc from iron-rich jarosite residue of the zinc industry. The leaching of lead, zinc and iron increased as a function of the MSA concentration in water up to 90 vol% MSA. Higher MSA concentrations resulted in precipitate formation due to the limited solubility of the iron and zinc methanesulfonate salts in water-lean MSA. Leaching with pure MSA resulted in a pregnant leach solution (PLS) comprising most of the lead and zinc, and a precipitate comprising the majority of the iron and a fraction of the zinc originally present in the jarosite. The optimization of the leaching conditions showed that increasing the liquid-to-solid ratio or temperature increased the leaching efficiencies of the metals, especially of lead. The leaching at optimized conditions was successfully performed on a larger scale using a temperature-controlled batch leaching reactor. 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 2.66/1 and 1/2, in the PLS, respectively. The remaining MSA in the PLS was recovered by vacuum distillation and successfully reused for three leaching cycles.

Key words: jarosite; metal recovery; methanesulfonic acid; selective leaching; solvometallurgy

### Introduction

Methanesulfonic acid (MSA) is a strong organic acid that is considered to be a green solvent.<sup>1,2</sup> The combination of its favorable physical and chemical properties makes MSA a suitable solvent for development of sustainable processes. It has a very low vapor pressure and high boiling point, and no dangerous volatile compounds evolve from the liquid under normal operational conditions.<sup>1-3</sup> The toxicity of MSA is relatively low compared to many commercially available acids. For instance, the LD<sub>50</sub> (oral, cat) of MSA is reported to be 1158 mg kg<sup>-1</sup> compared to 238–277 mg kg<sup>-1</sup> for hydrochloric acid.<sup>4</sup> It is readily biodegradable with a sulfate and carbon dioxide as the degradation products.<sup>1,2</sup> MSA is considered to be a natural product, and it is part of the natural sulfur cycle.<sup>5</sup> MSA is a strong acid with a pK<sub>a</sub> of -1.19 which is close to that of nitric acid (pK<sub>a</sub> = -1.3) and sulfuric acid (pK<sub>a1</sub> = -3) and higher than that of other organic acids such as formic acid (pK<sub>a</sub> = 3.82), acetic acid (pK<sub>a</sub> = 4.76) and citric acid (pK<sub>a1</sub> = 3.09).<sup>6</sup> The application of this strong acid as a commercial chemical is based on the fact that it is a non-oxidizing, highly conductive acid and that metal methanesulfonate salts are highly soluble in water.<sup>1,2,7</sup> As a result it has become the electrolyte of choice for many electrochemical processes, especially for

electrodeposition of tin and lead.<sup>1</sup> Moreover, MSA has many prospective applications in catalysis<sup>1,7-12</sup>, and as solvent for polymer synthesis and depolymerization.<sup>13,14</sup> With its beneficial physical and chemical properties, MSA is also a valuable candidate as reagent in extractive metallurgy, but it has been very little explored to date. MSA's high acidity and its ability to dissolve metal salts make it promising for the leaching of metals from primary and secondary metal sources.

Wu et al. achieved quantitative dissolution of lead from galena concentrate using a ferric methanesulfonate solution.<sup>15</sup> Feng et al. fully leached copper from malachite and zinc from smithsonite concentrates by using an MSA solution.<sup>16,17</sup> Hidalgo et al. leached copper from chalcopyrite using MSA solution containing ferric chloride as an oxidant.<sup>18</sup> Zhang et al. studied the dissolution kinetics of the zinc ore mineral hemimorphite in MSA.<sup>19</sup> These studies are largely of fundamental nature, targeting the leaching of one specific metal from an ore concentrate, which does not necessarily represent the complex composition of ores treated by the metallurgical industries. These studies also lack the downstream processing of the pregnant leach solutions (PLS). Gijsemans et al. used concentrated MSA to leach rare-earth elements terbium, cerium and lanthanum from real lamp phosphor waste residue where yttrium and europium were previously removed.<sup>20</sup> This is the first and only study where concentrated MSA was applied as a leaching agent for the recycling of metals from real waste streams. However, the authors diluted the PLS containing unreacted MSA by 40 times with water to recover the dissolved metals via solvent extraction, and this makes recovery of MSA very difficult.

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In this paper, we describe the development of a novel solvometallurgical process to recover lead and zinc from iron-rich jarosite residue using MSA as a leaching agent.<sup>21</sup> Jarosite is a solid residue generated by the zinc metallurgical industry.<sup>22,23-25</sup> The residue contains iron as the main component and some lead, zinc, and low concentrations of valuable metals such as indium, germanium and silver. Storage of jarosite in tailings ponds has some environmental issues and it is becoming increasingly difficult to get license to open new jarosite tailing ponds. These issues could be prevented by valorizing jarosite, by recovering of valuable metals and using the remaining residue in, for instance, building materials.<sup>26,27</sup>

## Experimental

### Chemicals

Methanesulfonic acid (99.5%) was purchased from Carl Roth (Karlsruhe, Germany). Hydrochloric acid (37%) was purchased from VWR Chemicals (Haasrode, Belgium). Elemental iron ( $\geq 99\%$ , reduced fine powder), elemental lead ( $\geq 99\%$ , 325 mesh), elemental zinc ( $\geq 98\%$ ,  $< 10 \mu\text{m}$ , dust), iron(II,III) oxide ( $95\%$ ,  $< 5 \mu\text{m}$ ), lead(II) oxide ( $+99\%$ ) and zinc(II) oxide ( $> 99\%$  pure) were purchased from Sigma-Aldrich (Diegem, Belgium). Tri-*n*-octylamine (TOA, 98%), di-(2-ethylhexyl)phosphoric acid (D2EHPA,  $> 95\%$ ) and Triton X-100 were supplied by Acros Organics (Geel, Belgium). Absolute ethanol and sulfuric acid ( $> 95\%$ ) was obtained from Fisher Scientific (Loughborough, United Kingdom). Nitric acid (65%), tri-*n*-butyl phosphate (TBP,  $> 99 \text{ wt}\%$ ) and praseodymium standard ( $1000 \text{ mg L}^{-1}$ , 2–5 wt%  $\text{HNO}_3$ ) were purchased from Chem-Lab NV (Zedelgem, Belgium). Cyanex 923 was provided by Cytec Industries (Ontario, Canada). The silicone solution in isopropanol for the treatment of the total-reflection X-ray fluorescence spectroscopy (TXRF) quartz glass carriers was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). All chemicals were used as received without any further purification. Jarosite was kindly provided by a European zinc producing company.

### Instrumentation

The characterization techniques used for the milled jarosite were reported in a previous article by the same authors.<sup>22</sup> The leaching was carried on a RCT classic heating plate (IKA). The phase disengagement between the solid and liquid after leaching was carried out by centrifugation using Heraeus Labofuge 200. The metal concentrations in the liquid phases were measured in duplicate by TXRF spectroscopy using a Bruker S2 Picofox spectrometer. The error associated with the measurements was  $\pm 5\%$ . The MSA in the pregnant leach solution (PLS) was recovered by vacuum distillation using a standard set-up equipped with an Adixen pump (Pascal 2015SD) and a manometer (TPG 201 Pfeiffer Vacuum). The mineralogy of the solid materials was determined by powder X-ray diffraction (XRD) analysis using a Bruker D2 Phaser diffractometer. Diffractograms were recorded in the measurement range of  $10 - 80^\circ 2\theta$  using  $\text{CuK}_\alpha$  radiation and

applying an acceleration voltage of 45 kV, a current of 30 mA, a step size of  $0.020^\circ$  and a counting time of 2.5 s per step. The raw data were processed with the X'pert HighScore Plus PANalytical software. The carbon and hydrogen content in the solid materials was measured in triplicate using an elemental CHN analyzer (FLASH2000, Thermo Scientific). The structural changes in distilled MSA were studied with Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR). FTIR spectra were recorded in attenuated total reflectance (ATR) mode on a Bruker Vertex 70 spectrometer equipped with a Bruker Platinum ATR module with a diamond crystal. For  $^1\text{H}$  NMR spectroscopy, the samples were dissolved in deuterated water and the spectra were recorded on Bruker Avance 400 spectrometer operating at 400 MHz. The scalability of the leaching at optimized conditions was studied using a customized 1 L jacketed laboratory reactor, linked to an automatic filtration unit (LabKit 36167) constructed by HiTec Zang GmbH, Germany.

### Methodology

The jarosite sludge (as received) was dried in an oven at  $110^\circ\text{C}$  for 24 h. The dried material was crushed and milled using a vibratory ring mill for 30 s at 1000 rpm. The moisture content (MC%) of the final residue (after initial drying and milling) was determined on the basis of its mass loss after drying again in an oven at  $110^\circ\text{C}$  for 48 h, according to equation (1):

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

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 initial leaching experiments were carried out by adding jarosite and MSA in a 4 mL glass vial and stirring on a heating plate. The following leaching conditions were applied: a liquid-to-solid ratio (L/S) of  $10 \text{ mL g}^{-1}$ , a temperature of  $60^\circ\text{C}$ , a contact time of 2 h and a stirring speed of 600 rpm. The scalability of the leaching system was tested using two different set ups. The first one used a 500 mL round bottom flask which was fixed on a customized aluminum heating block and then stirred on a heating plate. The second one used the 1 L batch reactor.

During leaching, the solids in the vials turned from green to grey. The vials containing the PLS and solids were immediately centrifuged (5300 rpm, 30 min) after leaching. Two solid phases (dark green and white) and one liquid phase were distinctly separated after centrifugation due to difference in their density. The PLS was pipetted out from vial and the finer particles suspended in the PLS were further separated by a syringe filter made of a polyester membrane (Chromafil PET,  $0.45 \mu\text{m}$  pore size). The MSA in the PLS was recovered by vacuum distillation and the reusability of the distilled MSA in leaching jarosite was tested using the same set-up as in the leaching experiments described above.

The metal concentration in the PLS was measured using TXRF. The samples were 50 times diluted with ethanol to minimize the matrix effects and a known amount of a  $1000 \text{ mg L}^{-1}$  praseodymium internal standard was added for

quantification. The sample preparation and the measurement procedure were carried out following the recommendation by Regadio et al.<sup>28</sup> The *leaching efficiency*  $E_L$  (%) was calculated according to equation (2). Precipitated metals are not taken into account in the *leaching efficiency*.

$$E_L(\%) = \frac{c_M \times v_{LIX}}{m_1 \times c_1} \times 100 \quad (2)$$

where  $c_M$  is the metal concentration in the PLS after leaching ( $\text{mg L}^{-1}$ ),  $v_{LIX}$  is the volume of leaching agent used for leaching (L),  $m_1$  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 ( $\text{mg kg}^{-1}$ ).

Two solid phases (color: dark grey and white) were present after leaching and they were clearly separated by centrifugation due to difference in their densities. The two solids were physically separated by scooping the white solid from the top using a spatula. The white solid was water soluble and therefore, it was dissolved in water and elemental analysis was performed using TXRF. The samples for TXRF analysis were prepared by diluting the solution of the white solid with a solution of 5 vol% Triton X-100 in water.<sup>28</sup> For XRD measurements, the solids were dried to remove traces of MSA in a vacuum oven at 130 °C and a pressure of <1 mbar for 24 h. A detailed investigation of the solids phases showed that the grey solid correspond to the leaching residue and the white solid to a precipitate. The results are discussed more in detail later in the article. The *precipitation efficiency*  $E_P$  (%) was calculated according to equations (3):

$$E_P(\%) = \frac{c_M \times v_{AQ}}{m_1 \times c_1} \times 100 \quad (3)$$

where  $c_M$  is the concentration of metals in water after dissolving the white precipitate ( $\text{mg L}^{-1}$ ),  $v_{AQ}$  is the volume of water used for dissolving the white precipitate (L),  $m_1$  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 ( $\text{mg kg}^{-1}$ ).

The *selectivity*  $S$  towards lead or zinc over iron was calculated for the solid jarosite and for the PLS according to equation (4):

$$S = \frac{c_M}{c_{Fe}} \quad (4)$$

where  $c_M$  is the concentration of lead or zinc ( $\text{mg kg}^{-1}$  or  $\text{mg L}^{-1}$ ) and  $c_{Fe}$  is the concentration of iron ( $\text{mg kg}^{-1}$  or  $\text{mg L}^{-1}$ ). 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 value of  $S$  (less than 1) is unwanted as it means that the concentration of the desired metals is lower than that of iron.

The *recovery rate*  $R_R$  (%) of the MSA was defined as the amount of MSA recovered after vacuum distillation with respect to the total MSA initially used for leaching (equation 5).

$$R_R(\%) = \frac{V_F}{V_i} \times 100 \quad (5)$$

where  $v_i$  is the volume of the MSA initially used for leaching jarosite (L) and  $v_f$  is the final volume of MSA recovered after

leaching and vacuum distillation (L).

The concentration of sulfate in the white precipitate was determined by gravimetric analysis. The white precipitate was first dissolved in a 6 M HCl solution and then an excess of  $\text{BaCl}_2$  0.5 M standard aqueous solution was added. The solution was stirred for 30 min at 60 °C. The solution turned cloudy due to the formation of  $\text{BaSO}_4$  precipitate, which was separated by centrifugation. Excess amount of the standard  $\text{BaCl}_2$  solution was added again to the centrifuged solution without the precipitate, and stirred for another 30 min to check for any remaining sulfate. The  $\text{BaSO}_4$  precipitate was washed three times with water and dried in an oven at 100 °C for 12 h. The amount of sulfate in the original precipitate was determined from the amount of  $\text{BaSO}_4$  precipitated.

The solubility studies were carried by adding a variable mass of pure metals and metal oxides to a glass vial containing 2 mL of pure MSA. Then the vial was stirred and heated on a heating plate at a temperature of 60 °C, for a contact time of 2 h and at a stirring speed of 600 rpm.

## Results and discussion

### Characterization of jarosite

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  $\mu\text{m}$ , although 90% of the particles were smaller than 1.95  $\mu\text{m}$ . The elemental composition of the residue is shown in the Table 1. The main metal phases were natrojarosite ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), anglesite ( $\text{PbSO}_4$ ) and sphalerite ( $\text{ZnS}$ ).

Table 1: Elemental composition of milled jarosite residue<sup>22</sup>

Metal	[g/kg]
$\text{S}^0 + \text{S}^{2-}$	188
S as $\text{SO}_4^{2-}$	92
Fe	174
Pb	40
Zn	24
Ca	25
Na	18
Al	5.7
Mg	3
K	2.5
Si	1.5
Cu	0.9
Other*	2.44

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

### Effect of the MSA concentration

The leaching of lead, zinc and iron from jarosite was studied as a function of the MSA concentration. All three metals were affected differently by the increasing MSA concentration (Figure 1). The decrease in the leaching efficiency of zinc at 50 vol% MSA is most likely because the optimal leaching of zinc requires a high activity of water. The leaching efficiency of lead

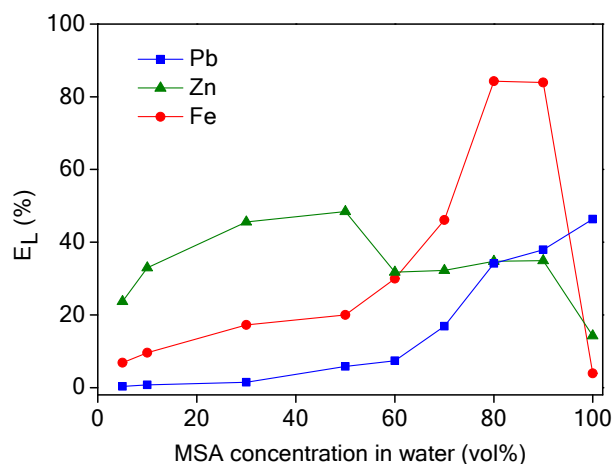


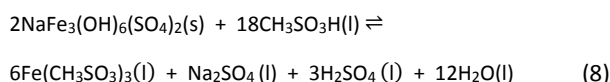
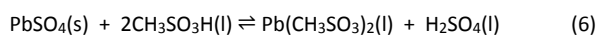
Figure 1: Effect of the MSA concentration on the leaching efficiency EL (%) of Pb (■), Zn (▲) and Fe (●) from jarosite. Leaching parameters: L/S ratio 10 mL g<sup>-1</sup>, contact time 2 h, 60 °C, stirring speed 600 rpm.

and iron increased exponentially with increasing MSA concentration, which is likely due to the higher concentration of MSA acting as a strong acid. However, between 90 and 100 vol% MSA, the leaching efficiency of iron and zinc drastically decreased. This could be explained by the poor solubility of their corresponding methanesulfonate salts in pure MSA, due to the weak solvating properties of the concentrated MSA solution towards these metal cations. The high leaching efficiency of lead at 100 vol% MSA, in contrast to that of zinc and iron, indicates a higher solubility of lead(II) in pure MSA acid than zinc(II) and iron(III). The metal concentrations are listed in Table S1†. The most optimal concentration of MSA for the leaching of jarosite was determined to be at 100 vol% MSA because the highest dissolution of lead was achieved at that concentration and the co-dissolution of iron was suppressed. The selectivity *S* towards lead and zinc over iron (Pb/Fe or Zn/Fe ratio) in the PLS increased when the MSA concentration was increased (Figure S1†). Iron is the main component in jarosite with a concentration higher than lead ( $S = 0.24$ ) and zinc ( $S = 0.14$ ). After leaching with pure MSA, the lead concentration in the PLS surpassed the iron concentration ( $S > 2.66$ ). Furthermore, although Zn ( $S \approx 0.49$ ) was 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  $S \approx 0.49$ .

At MSA concentrations of more than 90 vol%, the formation of a white precipitate was observed (Figure 2). This white precipitate could be separated from the pregnant leach solution (PLS) and the residue by centrifugation and appeared to be soluble in water. To get more insight into the formation of the white precipitate, the leaching efficiency and precipitation efficiency of lead, zinc and iron were studied in more detail at MSA concentrations above 90 vol% (Figure 3). Elemental analysis by TXRF showed that the white precipitate is composed of iron and zinc, without the presence of any lead. Upon increasing the MSA concentration above 90 vol%, the leaching efficiency of iron and zinc decreased gradually, while their precipitating efficiencies of the white precipitate increased

gradually (Figure 3). This might be caused by the low solubility of iron and zinc in pure MSA and shows that these metals require a distinct amount of water to remain in solution. The strongly acidic MSA solution reacts with the iron and zinc minerals in the jarosite, forming well-solvated iron and zinc methanesulfonate in the solution containing distinct amounts of water. In the case of water-lean MSA solutions or pure MSA, the iron and zinc precipitate due to the low solubility of their methanesulfonate salts in pure MSA solution. The high concentration of lead in the PLS and its absence in the precipitate confirms a higher solubility of lead(II) methanesulfonate in pure MSA. The role of water in leaching jarosite is minimal and most likely limited to solvation; water does not act as a proton donor. The fact that water is a weak proton donor together with the high stability of the minerals in the jarosite residue (jarosite, anglesite and sphalerite), makes reactivity of the water towards them low.

The leaching of lead, zinc and iron by MSA can be expressed by equations (6), (7) and (8):<sup>16-18</sup>



#### Leaching jarosite with mineral acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl)

Jarosite was leached with solutions of different concentrations of common mineral acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) in water to compare their leaching results with those of MSA. The leaching results (Figure 4, Table S2†) showed comparable trends to those of MSA (Figure 1, 3). The leaching efficiencies of lead, zinc and iron initially increased due to higher amount of acids available to react with the metal-containing minerals, and sufficient water molecules to keep the metals dissolved. When the concentration of acid was further increased and thus the concentration of water correspondingly decreased, some metals precipitated due to their low solubility in water-lean acid solutions. This explains the decrease in the leaching efficiency of iron and lead after leaching with concentrated nitric acid (14.6 mol L<sup>-1</sup>), and that of lead, zinc and iron when sulfuric acid concentration was higher than 4 mol L<sup>-1</sup>. A white precipitate was formed during leaching at these concentrations (Figure S2†). This is an indication of the low solubility of some metal salts at

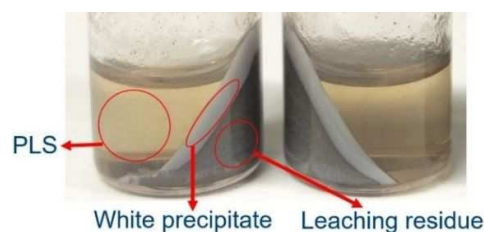


Figure 2: One liquid (PLS) and two solid phases (leaching residue and white precipitate) after leaching of jarosite by pure MSA. Leaching parameters: L/S ratio 10 mL g<sup>-1</sup>, contact time 2 h, 60 °C, stirring speed 600 rpm.

high acid concentration and low water content. The leaching efficiency of the metals did not decrease with concentrated hydrochloric acid (12.2 mol L<sup>-1</sup>) and that is most likely because there is still a sufficient amount of water available to dissolve the metal chloro complexes. MSA showed superior results compared to the investigated mineral acids in selective leaching of lead and zinc from iron-rich jarosite residue. The leaching with HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> resulted in poor selectivity towards lead and zinc due to high co-dissolution of iron in the PLS. During the MSA leaching of lead and iron from jarosite, sulfuric acid and water was released as a by-product (Equations 6 and 8). Sulfuric acid has high reactivity towards iron and zinc, but it has a negative impact on lead leaching due to the low solubility of lead sulfate. On the other hand, the water molecules will increase the solubility of iron and zinc in the PLS, and therefore, it would reduce the selectivity towards lead and zinc. Nevertheless, the influence of the by-products on the leaching would be minimal since their concentration in the PLS is very low (H<sub>2</sub>SO<sub>4</sub> ≈ 0.05 mol L<sup>-1</sup>, H<sub>2</sub>O ≈ 0.2 mol L<sup>-1</sup>).

#### Effect of liquid-to-solid ratio and temperature

Pure MSA was selected as the most suitable leaching agent for further optimization studies because it resulted in maximum leaching of lead with minimum co-dissolution of iron in the PLS. The effect of the liquid-to-solid (L/S) ratio and the temperature on the leaching of jarosite with MSA was studied by varying the L/S ratio from 15 to 40 mL g<sup>-1</sup> and the temperature from 60 to

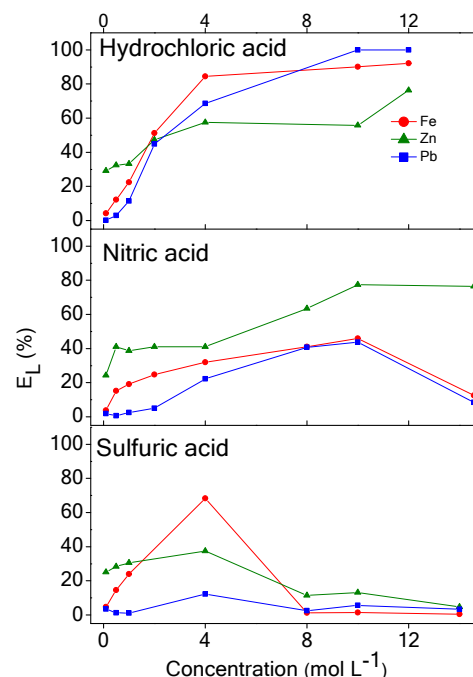


Figure 4: Effect of the mineral acid (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) concentration on the leaching efficiency  $E_L$  (%) of Pb (■), Zn (▲) and Fe (●) from jarosite. Leaching parameters: L/S ratio 10 mL g<sup>-1</sup>, contact time 2 h, 60 °C, stirring speed 600 rpm.

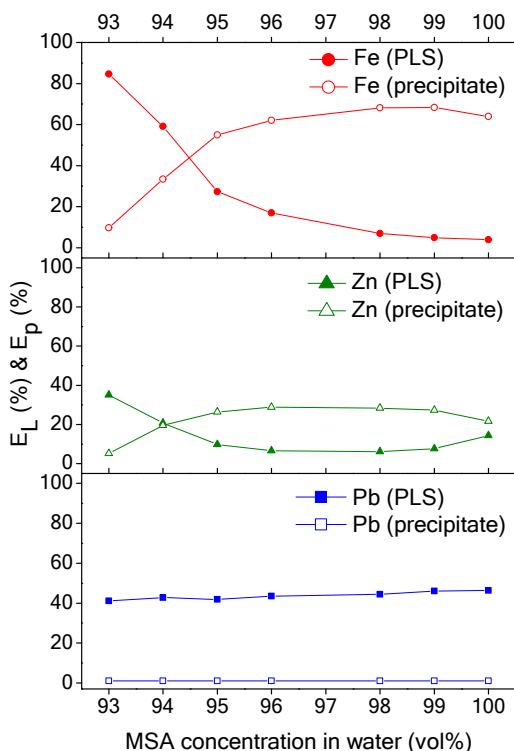


Figure 3: Effect of MSA concentration (90–100 vol%) on the leaching efficiency  $E_L$  (%) and precipitating efficiency  $E_p$  (%) of Pb (■), Zn (▲) and Fe (●) from jarosite. Leaching parameters: L/S ratio 10 mL g<sup>-1</sup>, contact time 2 h, 60 °C, stirring speed 600 rpm.

160 °C (Figure 5, Table S3<sup>†</sup>). Increasing the L/S ratio and the temperature significantly increased the leaching efficiency of lead, which indicates that both parameters have a strong influence on the leaching of lead from the residue. The increase in the leaching efficiency of lead was especially large when the L/S ratio was increased from 15 to 20 mL g<sup>-1</sup>. The influence of L/S ratio is much smaller for the leaching of zinc and iron, which is likely due to the low solubility of the methanesulfonate salts of iron and zinc in pure MSA. Increasing the temperature increased the leaching efficiency of zinc and iron, likely because the maximum solubility is positively correlated to the temperature. It is especially influential for leaching zinc as the leaching efficiency reached >70% at 160 °C. However, when the PLS was cooled overnight from 160 °C to room temperature, part of the dissolved zinc and iron precipitated. The high temperature during leaching resulted in oversaturation of zinc and iron in pure MSA and therefore, these metals partially precipitated when the PLS was cooled.

Although 160 °C resulted in more zinc leaching (~72%), it also resulted in more iron leaching (~19%) compared to leaching at lower temperature (Figure 5). Additionally, the partial precipitation of zinc and iron upon cooling down of the PLS from 160 °C to ambient temperature further complicates the process for downstream processing. Therefore, leaching at a L/S ratio of 20 mL g<sup>-1</sup> and a temperature of 130 °C was chosen to be the most suitable conditions for further investigation. At these conditions, while the leaching efficiency of lead is 100%, the leaching efficiency of zinc is still high at 50% and that of iron is low at 9%, resulting in a good selectivity towards zinc ( $S = 0.74$ ) and lead ( $S = 2.50$ ).

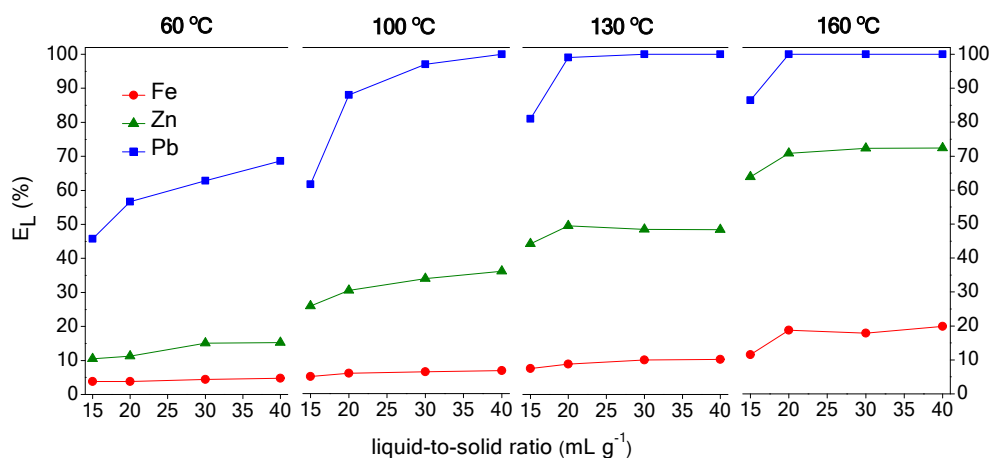


Figure 5: Effect of liquid-to-solid ratio and temperature on the leaching efficiency  $E_L$  (%) of Pb (■), Zn (▲) and Fe (●) from jarosite by pure MSA. Leaching parameters: contact time 2 h, stirring speed 600 rpm.

### Effect of leaching time

The dissolution was faster for lead and iron than for zinc (Figure 6). The leaching efficiency of lead was already 85% after 5 min and then it increased slowly to 100% after 120 min. In the case of zinc, the leaching efficiency after 5 min is 28% and it increased to 56% after 360 min. The leaching efficiency of iron was 5% after 0.5 min and then it reached a maximum of 9% after 120 min. Although the leaching efficiency of zinc was higher with longer leaching times (> 2 h), there was a partial precipitation of zinc and iron when the pregnant leach solution (PLS) was cooled down overnight. The optimum leaching time was kept at 2 h since the leaching efficiency of lead reached its peak of 100% and there was no partial precipitation of zinc and iron when the PLS was cooled down. The metal concentrations in the PLS are shown in Table S4†.

### Recovery of MSA by vacuum distillation

To allow the recyclability of the leaching agent, the unreacted MSA in the PLS was recovered by vacuum distillation at a pressure of 0.04 mbar and a vapor temperature of 110 °C. The reduced pressure during distillation was necessary because MSA decomposes (>225 °C) into sulfur dioxide and methanol before boiling at normal atmospheric pressure.<sup>29</sup> Due to the decrease in volume of the solvent, the dissolved metal salts in the PLS precipitated during distillation. The recovery rate of the MSA after leaching and distillation was about 88±2 vol.%, which means that 12±2 vol.% of MSA was not recovered and thus not available for reuse. It must be noted that about 8 vol.% of the total MSA loss is on account of the metal methanesulfonate precipitates and the MSA from the precipitate could be recovered by electrowinning.<sup>1</sup> The mineral phases of the metals in the precipitates are discussed further in this article. The reusability of the distilled MSA was tested by applying it again to leaching of a fresh jarosite sample. The process of leaching and distillation was repeated up to three cycles and the leaching results were compared to that of fresh MSA (Figure 7, Table S5†). The metal concentrations in the reused MSA were rather similar to the results of the fresh MSA, indicating that the

distilled MSA could be reused successfully. The leaching efficiency of iron slightly increased with the increasing number of cycles and the leaching efficiency of lead slightly dropped after the third cycle, but these are close to the error margins of the experiment. The distilled MSA was studied with <sup>1</sup>H NMR and FTIR to link the minor difference in the leaching efficiency with possible structural and compositional changes in MSA after each cycle. However, the FTIR and <sup>1</sup>H NMR spectra do not show any difference between the fresh MSA and distilled MSA (Figure 8a,b). The concentration of the impurities was most likely too low to be detected by FTIR and <sup>1</sup>H NMR. The minor difference in leaching efficiency might be due to the formation of a small amount of water and methanesulfonic anhydride impurities during distillation.<sup>30</sup> The presence of water as an impurity could explain the increase in the leaching efficiency of iron since water helps to solvate more iron in the MSA solution. In that case, any formed water and methanesulfonic anhydride impurities can be

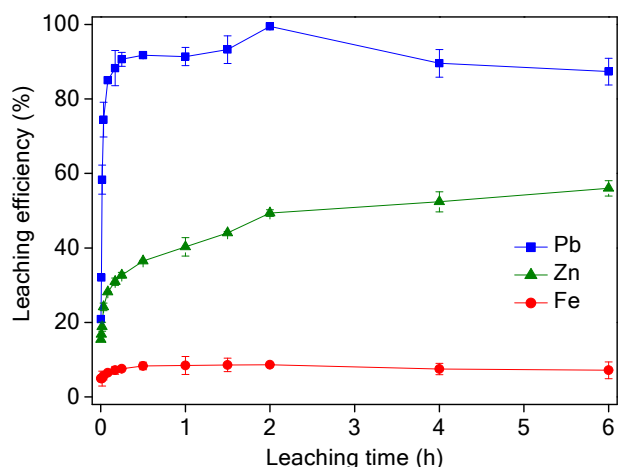


Figure 6: Effect of the leaching time on the leaching efficiency  $E_L$  (%) of Pb (■), Zn (▲) and Fe (●) from jarosite by pure MSA. Leaching parameters: L/S ratio 20 mL g<sup>-1</sup>, 130 °C, stirring speed 600 rpm.

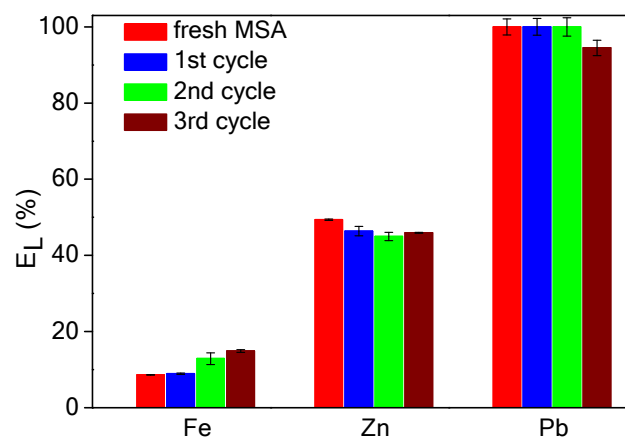


Figure 7: Comparative leaching efficiencies of lead, zinc and iron from jarosite by fresh MSA and vacuum-distilled MSA. Leaching parameters: L/S ratio 20 mL g<sup>-1</sup>, contact time 2 h, 130 °C, stirring speed 600 rpm.

removed from MSA by equilibrating it with methanesulfonic anhydride for 4 to 6 h at 70 °C and then distilling it under reduced pressure (boiling point = 165 °C at 2 mm Hg).<sup>31</sup>

#### Solubility studies and characterization of the residues

The difference in solubility of iron, zinc and lead methanesulfonates in pure MSA, was confirmed by studying the dissolution of the elemental form (metallic Fe, Zn and Pb powder) and the oxide forms of iron(III), zinc(II) and lead(II) in pure MSA under the leaching conditions of 60 °C, 2 h, 600 rpm. Access amount of the metal powder and the oxides were leached in a constant volume of pure MSA and the concentration of the metals in the MSA was determined analytically and compared with jarosite leaching at the same conditions (Table 2). Less amount of iron and zinc were leached from the oxides of iron(III) and zinc(II) compared to their corresponding elemental forms and jarosite, which indicates that the oxides are harder to dissolve in pure MSA. High concentration of lead was leached from both lead(II) oxide and elemental lead and it remain dissolved in the pure MSA, which shows its high solubility in pure MSA, and much higher than that of iron and zinc. This is in agreement with the higher solubility of lead compared to iron and zinc when leaching jarosite. Similarly as during the leaching of jarosite, a white precipitate was formed in the experiments with lead(II) oxide and elemental iron, zinc and lead. Most likely, this is because the maximum solubility of the methanesulfonate salts in MSA was exceeded. Unlike iron and zinc, lead was not precipitated from jarosite because it did not reach the maximum solubility in the PLS. It must be stressed that the white precipitate already formed during the leaching at elevated temperatures and not as a result of the cooling of the PLS.

Three solid materials were produced as an output from leaching jarosite using pure MSA, namely, the leaching residue, the white precipitate and the distillation residue (Figure S3†). The main mineralogical composition of the leaching residue and distillation residue were analyzed by powder XRD and compared with that of jarosite (Figure 9). XRD measurement

Table 2: Solubility of iron, zinc and lead methanesulfonates in pure MSA, from metal oxide, elemental metal and comparison with the leaching of the metals from jarosite using MSA<sup>§</sup>

Concentration (mg L <sup>-1</sup> )	Metal oxide	Elemental metal	Jarosite
Fe	160	3000	767
Zn	470	3524	373
Pb	50100	75668	2038

<sup>§</sup>Leaching parameters: 60 °C, 2 h, 600 rpm.

was not carried out on the white precipitate because it was hygroscopic. The leaching residue consisted mainly of elemental sulfur and zinc sulfide, which were already present in the jarosite residue. The jarosite mineral and lead sulfate were not present in the leaching residue as they were fully leached. The residue can be sent back to the zinc hydrometallurgical plant and added to their zinc sulfide ore for re-leaching. The distillation residue was mainly composed of lead(II) sulfate (PbSO<sub>4</sub>) and zinc oxide sulfate (2ZnO·3ZnSO<sub>4</sub>). This was expected as the PLS contained a significant concentration of sulfate due to the dissolution of jarosite. When MSA was distilled under vacuum, the sulfates precipitated with the metal ions. This lead

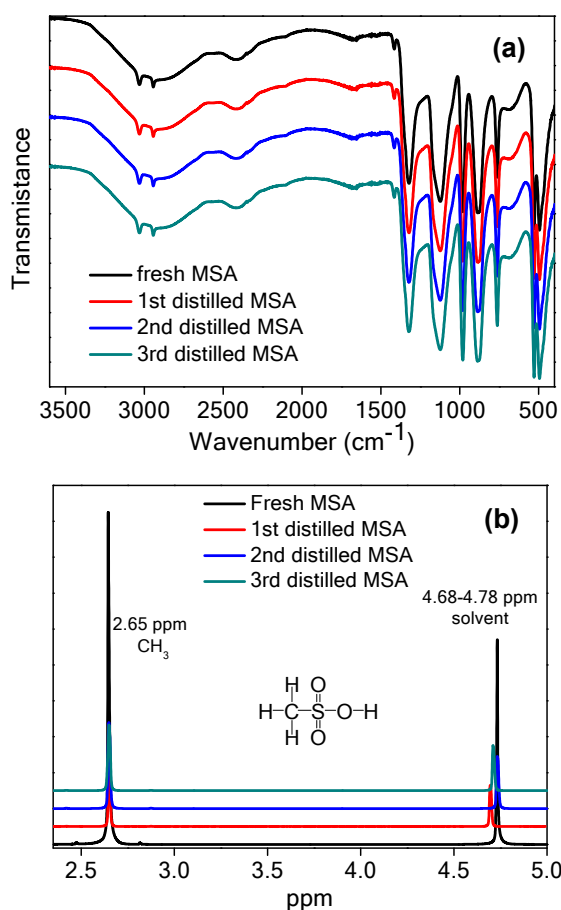


Figure 8: (a) FTIR and (b) <sup>1</sup>H NMR spectra of fresh MSA and distilled MSA in D<sub>2</sub>O.



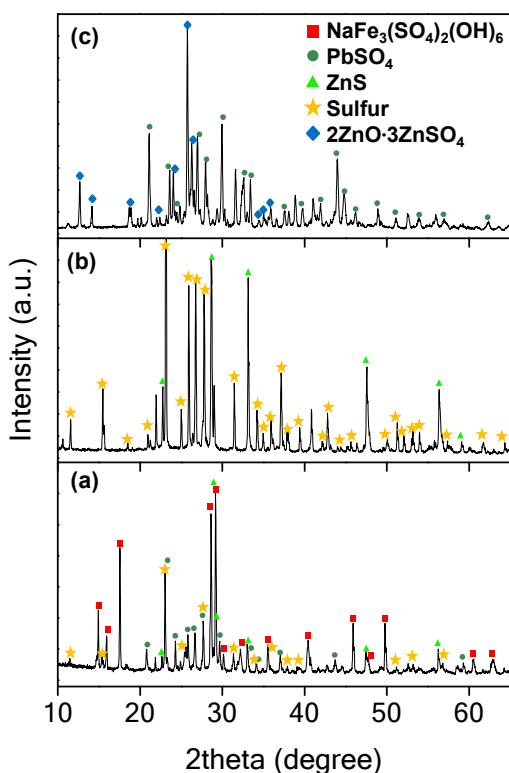


Figure 9: XRD pattern of a) jarosite, b) leaching residue and the c) distillation residue.

and zinc-rich precipitates can be of interest for secondary lead and zinc producers.

CHN analysis was carried out on the three solid outputs from the MSA leaching of jarosite, as well as on the synthetic white precipitates formed during the leaching of metallic iron, zinc and iron in pure MSA were indeed the corresponding metal methanesulfonates salts. Furthermore, the composition of the white precipitates formed during MSA leaching of jarosite corresponded well to the theoretical composition of the and lead in pure MSA, as described earlier in the text. The carbon and hydrogen content of the precipitates and the residues were compared with theoretical values of metal methanesulfonate salts (Table 3). CHN analysis confirmed that the precipitates formed during the leaching of metallic lead, zinc methanesulfonate salts of iron(II), iron(III) and zinc(II). The presence of iron(II) methanesulfonate can be ruled out based on the color of the material: iron(II) methanesulfonate is known to be yellow, whereas the precipitate formed during leaching was white.<sup>32</sup> Since jarosite contains large amounts of sulfate, it is likely that the white precipitate also contains metal sulfate salts. In order to determine the concentration of sulfate in the material, a gravimetric analysis was performed. The precipitate was dissolved in acidic aqueous solution and a standard solution of 0.5 M BaCl<sub>2</sub> was added to it. The amount of sulfate was determined from the amount of BaSO<sub>4</sub> precipitated. The analysis result confirmed that the sulfur in sulfate form in the white precipitate was only 0.83 wt.%. This indicates that there was barely any metal sulfate salts in the white precipitates formed during the MSA leaching of jarosite. Therefore, it can be

concluded that the white precipitate most likely consists of zinc(II) and iron(III) methanesulfonate.

It was calculated that about 8 mol% of the MSA used for leaching was lost in the white precipitate as metal methanesulfonate salts. Gernon et al. described a process to recover pure alkanesulfonic acid (e.g., MSA) from corresponding metal alkanesulfonate salts by electrowinning using an anion-exchange membrane divided cell.<sup>1</sup> Therefore, the MSA in the white precipitate can be recovered by electrowinning and it can be reused in leaching jarosite.

### Upscaling

The MSA leaching of jarosite at optimal conditions was tested on a larger scale (Figure 10, Table S6†). First, the leaching was performed in a 500 mL round-bottom flask with 10 g jarosite and 200 mL of MSA, which corresponds to 100 times upscaling compared to the screening experiments described above. Next, the leaching was tested in a 1 L temperature-controlled leaching reactor (Figure 11) with overhead stirring and automatic filtration starting from 25 g of jarosite and 500 mL of MSA, which corresponds to 250 times upscaling compared to the screening experiments. The results show that the leaching efficiency of lead, zinc and iron using the two larger set-ups corresponds well to the results of the initial small-scale

Table 3: Percentage of C and H, in the precipitate and residues from MSA leaching of jarosite and metallic iron, zinc and lead.

Source	Fraction	C (wt. %)	H (wt. %)
Jarosite	Leaching residue	0.14	0.49
	Distillation residue	0.34	1.02
	White precipitate	9.88	3.04
Elemental metals	Fe precipitate	9.82	3.6
	Zn precipitate	9.46	3.45
	Pb precipitate	5.91	1.62
Theoretical values	Fe(CH <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	9.75	2.44
	Fe(CH <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>	10.55	2.64
	Zn(CH <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	9.39	2.35
	Pb(CH <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	6.04	1.51

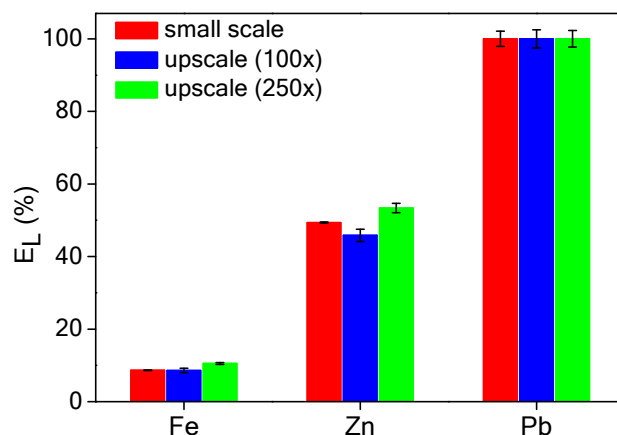


Figure 10: Comparative leaching efficiencies of lead, zinc and iron from jarosite by pure MSA at small scale (red) and at a larger scale in a roundbottom flask (blue) and in leaching reactor (green). Leaching parameters: L/S ratio 20 mL g<sup>-1</sup>, contact time 2 h, 130 °C, stirring speed 600 rpm.

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experiments (Figure 10). Hence, the MSA leaching of jarosite is stable and shows potential for upscaling to a larger scale. Finally, a conceptual flowsheet of the leaching of jarosite by MSA and subsequent recovery of the MSA by vacuum distillation is shown in Figure 12.

### Conclusion

Methanesulfonic acid (MSA) is a promising leaching agent for recovering metals from iron-rich jarosite residue. MSA reacts readily with lead, zinc and iron present in the jarosite due to its high acid strength. However, iron and zinc have a low solubility in pure MSA, resulting in a precipitation of the two metals (90% Fe, 14% Zn) as their methanesulfonate salts. The presence of  $\geq 10$  vol% of water in the MSA solution avoided these precipitate formations, as the high hydration energy of the metal ions kept them well-solvated in the aqueous MSA solution. Lead, on the contrary, has a significantly higher solubility in pure MSA than iron and zinc. As a result, lead did not precipitate along with iron and zinc. This difference in solubility of the metals in pure MSA resulted in solid-liquid separation of lead and zinc from iron. The pregnant leach solution (PLS) obtained after carrying out the optimized leaching procedure contained 100% of the lead, 50% of the zinc and 9% of the iron from the original jarosite residue. The leaching residue contained only zinc since both lead and iron were fully leached either in the PLS or the precipitate. A conceptual flowsheet was designed, which was tested in a 1L leaching reactor. The MSA in the PLS was recovered by vacuum distillation and successfully reused up to three cycles, resulting in a minimization of the consumption of chemicals by the process.

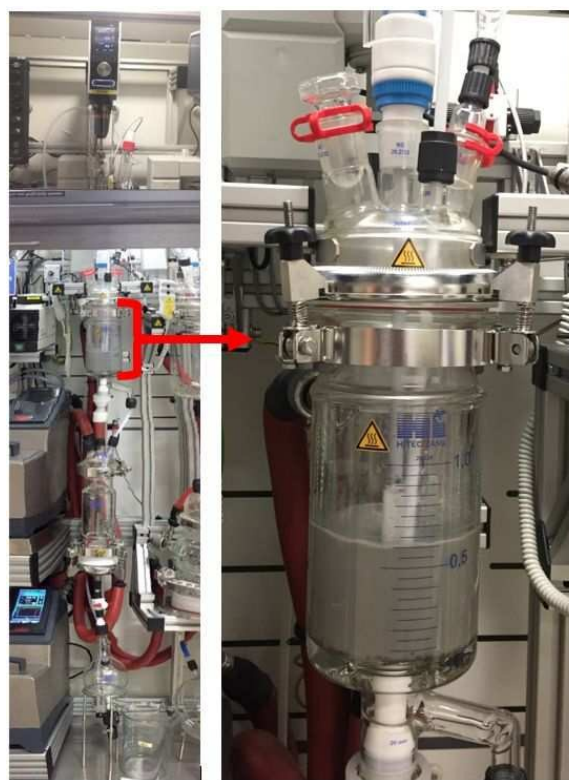


Figure 11: 1 L temperature-controlled leaching reactor used for upscaling MSA leaching of jarosite.

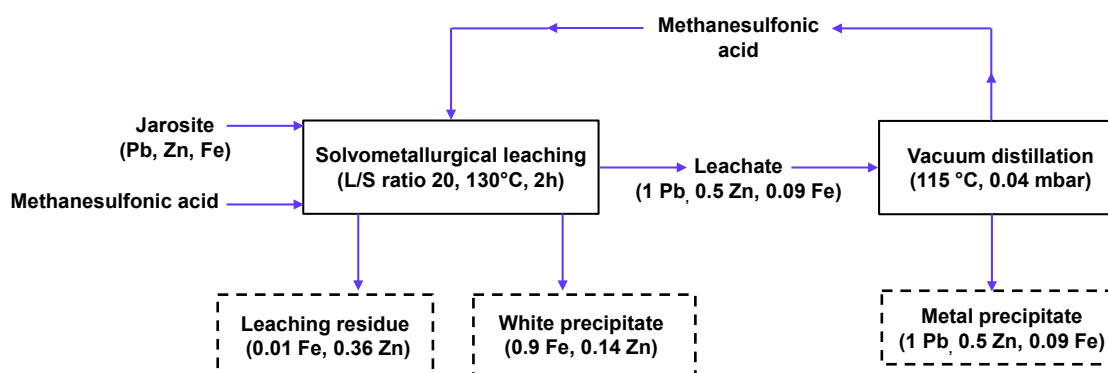


Figure 12: Flow chart for the selective leaching of lead and zinc from jarosite by pure MSA. The numbers denote the ratio of extracted metal to the metals in the initial jarosite sample.

## Supporting Information

Electronic Supplementary Information (ESI) available: a plot of selectivity towards lead and zinc as a function of the MSA concentration (Figure S1), the concentration of the metals leached as analyzed for the different experiments (Table S1–6), an image of the vials containing PLS, leaching residue and precipitate after leaching jarosite with mineral acids (Figure S2), an image of all the solid materials related to this study (Figure S2).

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## Conflict of interest

There are no conflicts to declare.

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