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CLOSING THE MATERIALS CYCLE IN PYROMETALLURGICAL PRODUCTION OF LEAD FROM WASTE FRACTIONS: HYDROMETALLURGICAL PURIFICATION OF IRON CONTAINING WASTE IN VIEW OF RECYCLING

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Abstract

Pyrometallurgical recycling of lead from spent batteries entails secondary waste fractions generated in the blast furnace as iron stone and lead slags. For further purification of both fractions, hydrometallurgical processing is proposed. This paper focuses on purification of iron stone, in view of recovering metals (mainly lead) and of producing decontaminated iron stone fit for further recycling. The results demonstrate that iron stone is mainly composed of iron and lead; copper, zinc and antimony are also of importance. Leaching tests were carried out at pH 1 to 14. Iron leaching can be avoided when the pH is above 6 for residue from soft lead production (i.e. lead with low Sb content); for the fraction obtained from hard lead production (high Sb content), a pH above 13 is needed. Most other compounds (Na, K, Ca, Mn, Zn, Se, Mg) were leached efficiently; the challenges were Cr and Sb (although not critical since present in low concentrations), and Pb and Cu. A challenge, however, was in the variability of composition and extraction results, complicating the assessment of hydrometallurgical processing. In general, the yield of Pb was too low, and the loss of Fe was too large. Extraction with sulphuric acid, sequential extraction, addition of K₂CrO₄ and addition of FeCl₂ were explored to increase the leaching of Pb and Cu. None of these measures allowed a sufficient separation. However, the addition of FeCl₂ might improve the separation efficiency in the nitric acid extraction. Thus, it can be concluded that hydrometallurgical purification of iron stone is possible for a wide range of compounds but Cr, Sb, Pb and Cu may present problems, if present.

Key words: hydrometallurgical separation, iron recycling, leaching, lead production, solid waste

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1. Introduction

During the last decades, recycling of materials has steadily gained importance. Metals in particular are more and more recycled (Negrea et al., 2017), in view of economic profit, environmental awareness, and depletion of naturally occurring metals from mining (Liu et al., 2009). Currently around 75% of

materials from used cars are already recycled, with the metal fractions mainly redirected to companies using these as secondary material. It is generally accepted that recycling of materials will be essential in the future (Durr, 2006). Ever increasing demands related to environmental impact of products during their entire lifetime will force to consider waste products as possible sources of materials and energy.

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Closing the materials cycle is the ultimate goal of production; however, this requires advanced separation technologies to purify valuable components from waste fractions. These separation techniques can be mechanical, but a full recycle of all components requires a further treatment using physico-chemical and chemical separation methods (Srogi, 2008). Metallurgical processes are central to metal processing, and typically produce a wide variety of slags. These are possible sources of metals in other processes and could theoretically be fully recycled, on condition that an economically viable and technically feasible separation method can be found. This is particularly important for high-value metals that can be recycled from waste batteries. Fernandes et al. (2012) developed a hydrometallurgical route to recover nickel, cobalt and cadmium based on leaching of spent Ni-Cd batteries with hydrochloric acid, and achieved recovery of Co(II) and Cd(II) by solvent extraction; Ni(II) was isolated from the raffinate as oxalate. Mechanical pretreatment by crushing is important in this process, as was demonstrated by Huang et al. (2011). This may eventually lead to the design of a full-scale plant for recycling as proposed by Ruffino et al. (2011).

Recovery of Li from spent batteries has also attracted much interest. Granata et al. (2012) considered recycling of Li batteries with simultaneous recovery of cobalt, nickel and manganese by chemical leaching. Sun and Qiu followed a similar approach to recover Li and Co, by using vacuum pyrolysis, oxalate leaching and precipitation (Sun and Qiu, 2012). Pranolo et al. (2010) proposed the use of a mixed system of organic extractants and studied Ionquest 801 and Acorga M5640 for separation and purification of Co and Li. Recycling has a clear environmental benefit, as was demonstrated by Dewulf et al. (2010). They made a detailed analysis of a lithium mixed metal oxide battery recycling scenario, where cobalt and nickel are recovered and re-introduced into the battery production chain, and compared this scenario with production from non-recycled sources. They conclude that the recycling scenario results in a saving of 51.3% in natural resources, not only because of decreased mineral ore dependency but also because of reduced fossil resource (45.3% reduction) and nuclear energy demand (57.2%).

Less attention has been paid to recycling of lead batteries. Lead, among other heavy metals, is considered a threat for public health (Moutsatsou et al., 2006). It accumulates in the human body; known effects are the inhibition of enzymes and severe damage to the liver, brains and central nerve system (Stojakovic et al., 2017; Sadeghi et al., 2017). Worldwide consumption of lead crossed six million tonnes in 2006 (Kreusch et al., 2007). In 1998, 63% of lead production in the USA originated from recycling. Brasil has a yearly production of 15 million car batteries, from which 150,000 tonnes of lead are recycled. Europe produces ca. 2 million tonnes, of which 70% comes from recycling (Lassin

et al., 2007). The fraction that is recycled has increased steadily from ca. 52% in 1994. Batteries are the main source of recycled lead. Thus, particularly for lead containing batteries, recycling is of crucial importance; Sullivan and Gaines (2012) found that on a per kilogram or per watt-hour capacity basis, lead-acid batteries have the lowest cradle-to-gate production energy, and fewest carbon dioxide and criteria pollutant emissions of all batteries considered in their study. Car batteries, the most important source of lead, are composed of 25-30% lead from the electrodes, and 35-45% lead sulphate from the pasty electrolyte. The remainder is 10-15% sulphuric acid, 4-8% polypropylene from the frame, and 10% other materials. This composition makes pyrometallurgical purification in the non-ferrous industry highly attractive.

However, recycling also yields a side production of 200,000 tonnes toxic and unstable slags, and 280,000 tonnes of sludge, mainly coming from neutralisation of sulphuric acid present in batteries. Therefore, even recycling of lead does not close the materials cycle. Slags and sludge have to be disposed of, which is expensive. Smaniotto et al. (2009) studied lead-acid batteries slags composed of mainly iron (ca. 60%) and lead (ca. 6%), and developed an extraction method based on EDTA as a complexing agent with fluoride as additive to mask the iron ions.

The purpose of this work is to study lead recycling from spent batteries. Recycling spent batteries is an activity that currently grows steadily, because of its potential for resource recycling and environmental protection. Many recycling processes are based on pyrometallurgical processing, which leaves a waste fraction that is difficult to process, but may be further treated with a hydrometallurgical approach. This paper describes the challenges encountered in hydrometallurgical purification of iron stone, a waste fraction rich in iron that is produced in the blast furnace during pyrometallurgic recovery of lead from waste batteries. The objective is to further recycle lead (and other metals), and to obtain a stripped iron containing material with sufficient purity to recycle as a source of iron.

2. Methods and materials

2.1. Process description

Fig. 1 describes the recycling process for lead batteries, which was the source material for further processing. In a first step, car batteries are broken and the sulphuric acid is caught in a basin. Other lead sources may be added; the battery frames are not removed since they have a caloric value. The mixture is brought to a blast furnace and melted at a temperature of 1200-1300°C. Cokes are added, which produce heat and reducing CO-gas, and increase the permeability of the blast furnace feed so that CO diffuses more easily. With the addition of cokes, the melting point of iron decreases from 1500°C to 1100°C.

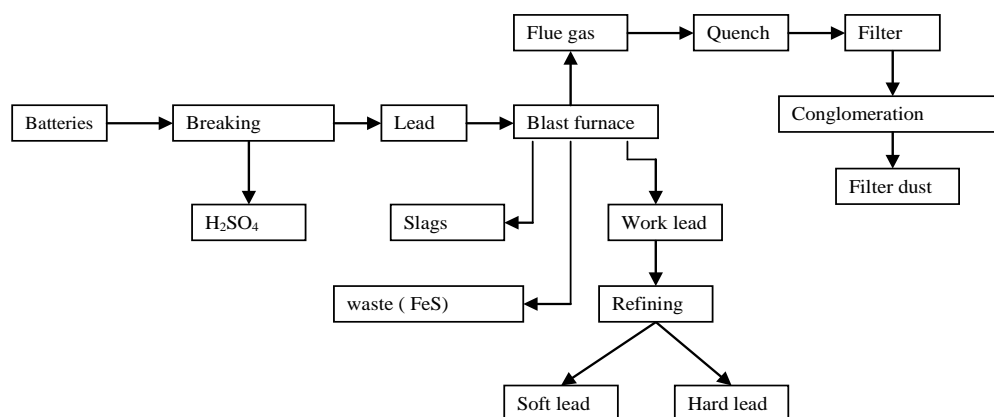


Fig. 1. Pyrometallurgical recycling of lead, a possible flowchart

The blast furnace should be smaller than for iron and rectangular, to keep the incineration zones close to one another. In this way, the production of CO is kept relatively low, which is necessary to avoid reduction of FeO to Fe. This is needed in a blast furnace for iron production, but not for lead production where iron occurs as an impurity. CO reduces PbO to Pb, and PbSO₄ to PbS. Further reduction of PbS to Pb is accomplished by adding metallic iron; Fe is oxidized to FeS in this reaction. The flue gases are further oxidized at 1050°C; remaining lead forms an inorganic precipitate that can be easily filtered. Two types of slags are produced: soft lead with a low Sb content, and hard lead with a high Sb content.

The slag volume is ca. 70 kg/ton lead. In addition, the blast furnace produces ca. 150 kg iron stone per ton lead. This is mainly pyrite but contains significant impurities of lead, copper, antimony, etc. Iron stone is a waste fraction, but after purification, the iron may be used in the ferrous industry, while other metals (mainly lead and copper) might be recycled internally.

2.2. Materials

The iron stone waste was received from a company that produces lead from waste batteries. The material consisted of bricks of up to 10 cm diameter down to powder smaller than 250 µm. The first batch was a sample of 10 kg, whereas the following nine batches were taken on a weekly basis. Two samples were taken per week: one from the soft lead production cycle and one from the hard lead production cycle. All samples were dry-milled to particle size < 1 mm and stored in a closed container awaiting investigation.

2.3. Characterization methods

The total concentration of metal and metalloid constituents in the solid materials was determined in three-fold by digesting 0.1 g of dry particle-size reduced sample with concentrated HNO₃, HClO₄ and HF consecutively (Van Herreweghe et al., 2002).

This method is denoted as the 'three acids' method. HNO₃ is used to dissolve the parts that dissolve the easiest, e.g., oxides and hydroxides. At the same time all metallic compounds are oxidized and dissolved (even copper, which is difficult to oxidize). HClO₄ oxidizes and hydrolyzes all organic matter that HNO₃ would not dissolve (HClO₄ is a stronger oxidant). HF dissolves silicates, which normally do not dissolve in acid environment, but are released by the formation of volatile SiF₄ compounds. If not all material is dissolved, a second cycle is carried out. Subsequently, the resulting liquid sample was diluted with MilliQ water and analysed. Determination of elements was carried out using Atomic Absorption Spectroscopy (AAS) of the type AAnalyst 100 (Perkin-Elmer), and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) of type X-Series I (Thermo Electron). Determination of anions was carried out using Ion Chromatography (IC), type ICS-2000 (Dionex).

The buffering capacity of iron oxide was determined by adding hydrochloric acid to a given amount of solid material (in gram dry matter), and measuring the pH change as a function of the amount of acid added.

The amount of amorphous iron oxides, also called hydrous ferric oxides, was determined by the extraction with ascorbate according to Ferdelman's method (Ferdelman, 1988) based on a weak reductant with the procedure proposed by Kostka and Luther (1994). In addition, an extraction with dithionite at pH 4.8 was used to determine the sum of amorphous and crystalline iron; dithionite reduces all fractions (Kostka and Luther, 1994). Mineralogy was determined using a Philips PW1130/90 X-ray diffractometer (XRD) with Co lamp.

2.4. Leaching tests

Extractions were carried out with distilled water brought to a chosen pH, kept constant using pH adjustment with a type 686 Titroprocessor (Metrohm AG). Concentrated nitric acid was used to maintain pH except for some specific experiments where concentrated sulphuric acid was used. The

liquid-to-solid ratio (L/S) was kept at 10. A distinction was made between time extraction (leaching solution not replaced, duration of 7 days) and sequential extraction (leaching solution daily replaced, duration of 6 to 7 days). In some experiments solid FeCl₂ or K₂Cr₂O₇ solution were added to the leachant; FeCl₂ was used to suppress the leaching of iron, since it was attempted to keep iron leaching low enough, whereas K₂Cr₂O₇ was specifically used to enhance the leaching of copper.

3. Results and discussion

3.1. Characterization of iron stone

The average composition of iron stone, derived from 10 batches of soft lead and hard lead production each, is given in Table 1. It can be seen

that the matrix is mainly composed of iron and lead; copper, zinc and antimony are also of importance. The other compounds constitute only 1.5% of the total metal composition. Thus, treatment of iron stone should focus on a high selectivity of iron vs. lead, with the separation from iron of copper, zinc and antimony as a second priority. A leaching procedure should be found allowing to dissolve lead (and copper, zinc and antimony), but not iron. In addition, the separation procedure should be flexible enough to account for variability in the composition of iron stone.

Table 1 shows besides the average values also the standard deviations for all metal constituents found in iron stone. Table 2 gives the variability of leaching tests with water at the pH dictated by the solid sample (iron stone only from soft lead production).

Table 1. Total concentrations and standard deviations of metal constituents in iron stone (n = 10 averages of triplicates)

	<i>Soft lead production</i>		<i>Hard lead production</i>	
	<i>Average concentration (g/kg DM)</i>	<i>St. Dev.</i>	<i>Average concentration (g/kg DM)</i>	<i>St. Dev.</i>
Na	0.94	0.37	1.09	0.32
Mg	0.13	0.24	0.22	0.10
Al	0.60	0.46	0.75	0.94
K	0.43	0.32	0.42	0.13
Ca	1.40	0.79	1.78	2.12
Cr	0.52	0.25	0.35	0.22
Fe	578	130	562	79
Mn	1.53	0.31	1.32	0.51
Co	0.12	0.03	0.13	0.07
Ni	1.73	0.53	1.29	0.74
Cu	13.73	4.61	9.19	2.40
Zn	6.17	2.93	4.76	1.83
As	1.95	1.18	2.29	2.03
Se	0.16	0.12	0.14	0.06
Sn	1.99	0.97	1.33	0.67
Sb	2.67	2.10	4.96	4.86
Ba	0.80	1.35	0.41	0.57
Pb	197	126	125	67

Table 2. Variability of extractions at pH 11.3 +/- 0.7 represented as average concentrations and standard deviation (24 h extraction, n = 10 averages of triplicates) for iron stone obtained from soft lead production

	<i>Average concentration (mg/kg DM)</i>	<i>St. Dev.</i>
Na	365	164
Mg	0.25	0.17
Al	2.92	1.65
K	57.9	26.3
Ca	28.7	39.2
Cr	< 0.1	-
Fe	3.01	2.56
Mn	< 0.1	-
Co	< 0.1	-
Ni	< 0.1	-
Cu	< 0.1	-
Zn	2.19	1.79
As	< 0.1	-
Se	< 0.1	-
Sn	< 0.1	-
Sb	0.73	1.64
Ba	11.9	11.6
Pb	470	99.5
pH range	10.6 - 12.0	

In both variability tests, the standard deviations are very high; this would not have a large influence on the trace components, but is of particular influence when the separation between iron and lead is considered. Therefore, the process conditions should be such that a good separation can be obtained for a wide range of concentrations. From Table 2, it appears that at the alkaline pH dictated by the sample the Pb/Fe separation factor (w/w) is high, ca. 156. However, only less than 0.3% of the Pb is extracted.

Because of the higher lead content in the iron stone from the soft lead production, it was decided to focus on this type of material. Experiments were performed on samples taken from one single batch. Relevant properties of this batch are given in Table 3. Except for the lead concentration which is lower than usual, this batch appears to exhibit average characteristics.

Table 3. Properties of the iron stone batch (soft lead production) used for further study

Element	Total concentration (g/kg DM)
Fe	560
Pb	95.1
Cu	15.4
Zn	6.7
Sb	1.0
Extraction property (L/S=10, 24h, n=3)	Average value
pH	11.9
Amorphicity and crystallinity	Percentage of total Fe (%)
Fe present in Fe _x O _y (amorphous + crystalline)	16.7
Fe present in amorphous Fe _x O _y	3.0

The mineralogical composition of the chosen batch is given in Fig. 2. Iron proved to occur mainly in the sulphide form (FeS, troilite). Magnetite (Fe₃O₄) is also present. Lead occurs mainly as Pb₂SiO₄. The presence of galena (PbS) would be expected based on the high S content in this type of material, but could not be detected.

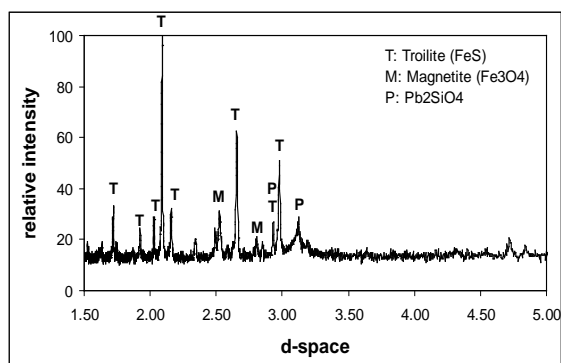


Fig. 2. XRD spectrum for iron stone obtained during production of soft lead

Amorphicity was determined on the basis of extractions with ascorbate and dithionite. The results are shown in Table 2. It appears that the main fraction of iron oxide is crystalline. A crystalline structure is more stable and is therefore more difficult to extract. In addition, the result from the dithionite extraction shows that only one sixth of the Fe is present as iron oxide. This confirms the XRD result, where Fe was detected mostly as troilite.

3.2. Leaching of iron stone

The pH is the most important variable when aqueous extractions are considered. The optimal pH was determined by extracting during 24 h at pH values ranging from 1 to 14. Fig. 3a-c shows leaching of iron and lead from iron stone obtained from soft lead production. If iron leaching is to be avoided, the pH should be above 6. In the pH range 6-14, the highest amount of extracted Pb is obtained at pH 6. At this pH, about 30 g Pb/kg DM (~30% of total Pb) and 1 g Fe/kg DM (~0.2% of total Fe) is extracted. Although the separation factor (Pb/Fe (w/w) = 30) is much lower than the one obtained at alkaline pH in the leaching experiment with water (see previous paragraph), in absolute amounts extraction at this pH recovers about 15 times more Pb. Negligible amounts of Cu, Zn and Sb are extracted in this pH range, suggesting other conditions are needed to remove these components.

Reaching pH 6 in alkaline residues is often not an easy task with respect to the amount of acid needed and the difficulty in maintaining the exact pH during extraction. This appeared to be not an issue with the studied material. Fig. 3d shows the acid buffering capacity of the iron stone. The addition of a small amount of acid readily decreases the pH from ca. 12 to about 6. At pH 6 and lower the material fortunately is buffered so that this pH is fairly easily maintained throughout the extraction experiments. From the industrial point of view, an extraction procedure at pH 6 would therefore imply the addition of low amounts of acid and good pH controllability.

Extraction of iron stone as a function of time at pH 6 is given in Fig. 4 for Fe, Pb, Cu, Zn and Sb.

From Fig. 4a it is clear that iron exhibits a lower extraction efficiency than Pb and even Zn. After a period of 7 days, 25% of lead and 14% of zinc can be extracted, which is more than iron (12%), but a recalculation to absolute quantities yields 65 g Fe/kg DM compared to 23 g Pb/kg DM and less than 1 g Zn/kg DM in the leachate. Cu and Sb are almost not extracted (less than 1 mg/kg DM each). Thus, with a Pb/Fe separation factor (w/w) of 0.35, the separation is clearly insufficient. This is mainly due to the unexpectedly high leaching concentration of Fe. Compared to the amount of Fe leached after one day in the pH variation test (0.2% or 1 g Fe/kg DM, Fig. 3a), about 50 times more Fe is leached after one day in the time-dependent extraction test (Fig. 4a-b).

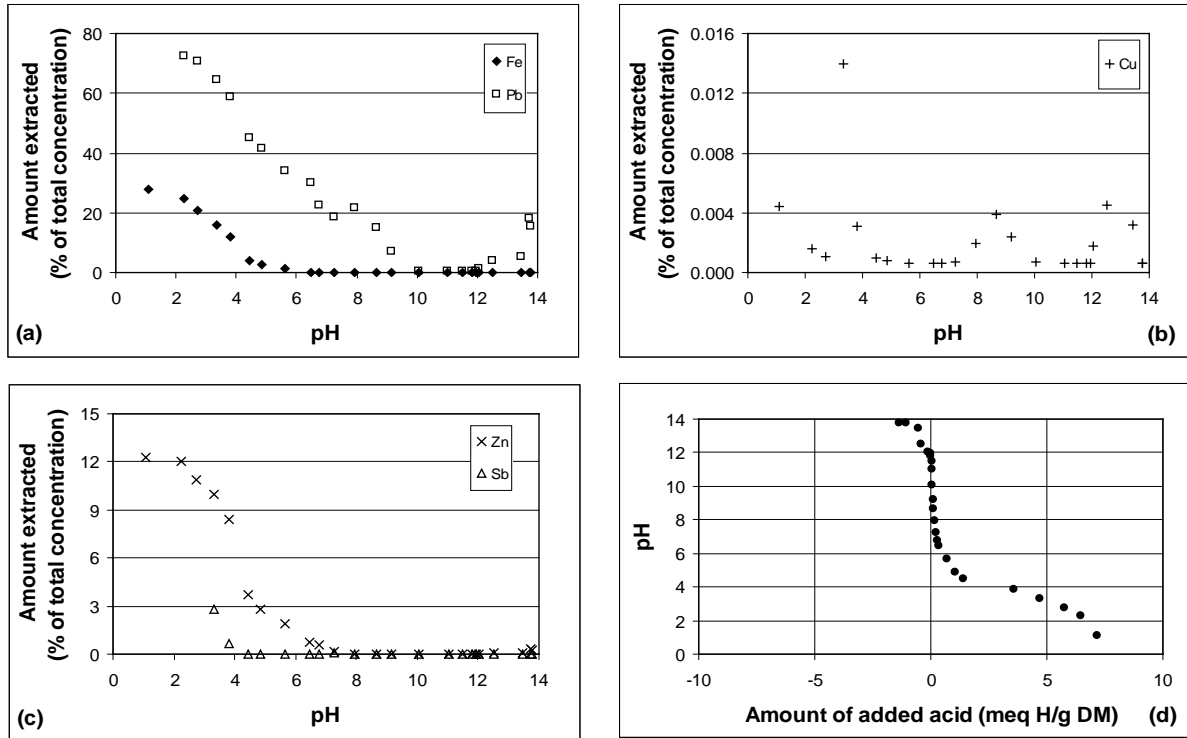


Fig. 3. Extraction profiles as a function of pH (a-c) for iron, lead, copper, zinc and antimony, and acid buffering capacity of the iron stone (d)

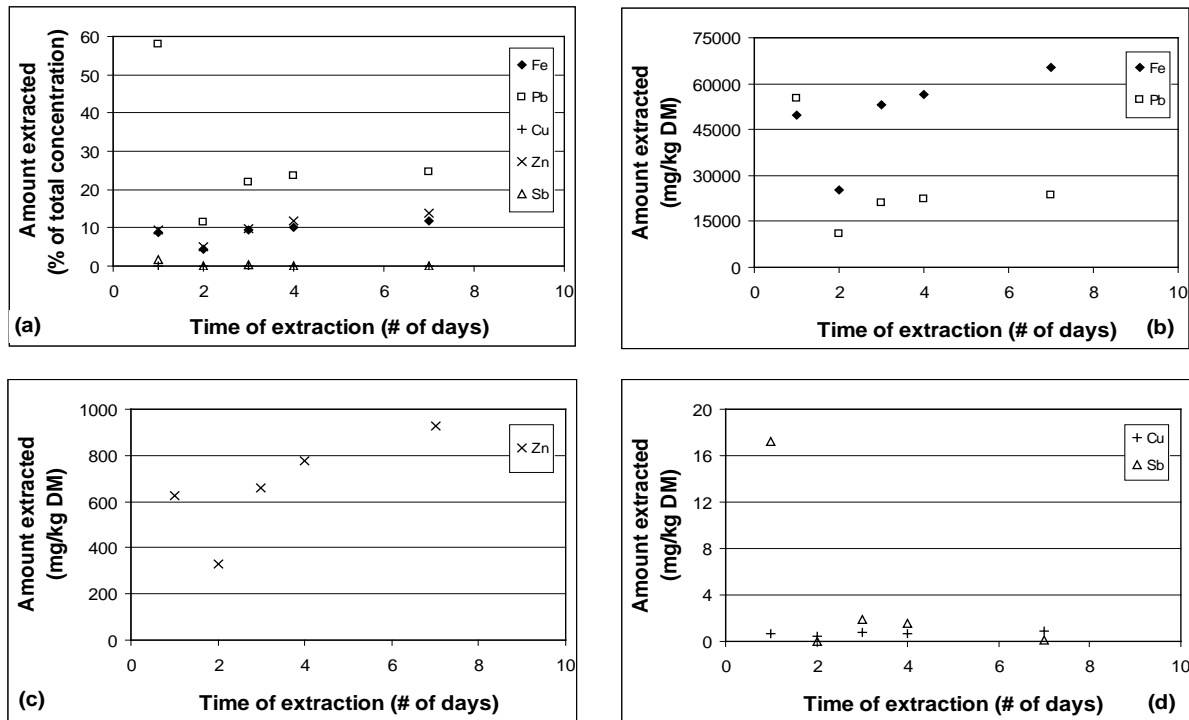


Fig. 4. Extraction of iron from iron stone as a function of time at pH 6, compared to lead, copper, zinc and antimony

Poor reproducibility of the samples is presumed to be the major cause. It can also be seen that the metal concentrations in the leachate fluctuate significantly during extractions, due to non-equilibrium conditions. For Pb, almost 60% appears to be extracted after one day. However, this result

was twice as high as the value at pH 6 in Fig. 3a and was also not attained anymore in subsequent extraction experiments on the same batch. The value therefore needs to be considered as optimistic. Still, a sequential extraction procedure with renewals of the extraction liquid appears promising as it would take

advantage of the high extraction efficiency after one day.

As expected from Fig. 3b-c, extracted amounts of Cu, Zn and Sb are shown in Fig. 4c-d to be lower than the amount of Fe (in relative terms for Cu and Sb, in absolute terms for all three constituents). They are thus less efficiently extracted than Fe at pH 6.

Sequential extraction corresponds to the cascade approach that is well known in chemical engineering (Seader and Henley, 2005), and may lead to both an increase in leaching efficiency and an increase in separation. Results are shown in Fig. 5.

In relative terms it appears that Pb is much more extracted than Fe, whereas the extraction of Cu, Zn and Sb is comparable to or slightly smaller than that of Fe. In absolute terms there is a clear preference for the extraction of Pb: 34.5 g Pb/kg DM is extracted after 7 days compared to only 9.2 g Fe/kg DM. Zn (310 mg/kg DM), Cu (70 mg/kg DM) and Sb (20 mg/kg DM) are extracted scarcely. The absolute values for iron and lead yield a Pb/Fe separation factor (w/w) of 3.75 which is considerably better than what was obtained after 7 days of leaching without leachant renewal. At the same time, only a 50% improvement of absolute extracted quantities was achieved for Pb. However, it must be noted that the amount of extracted Pb after one day in the sequential extraction procedure (Fig. 5c) was about 3 times lower than the one obtained after one day in the extraction procedure without leachant renewal (Fig. 4b) and about 2 times lower than the one obtained in the one-day pH-variation procedure at pH 6 (Fig. 3a). Sample representativity, even within the same batch, appears to be a huge issue. It is assumed that the results from the sequential

extraction procedure are an illustration of the worst-case scenario: at least 30 g Pb/kg DM can be recovered by extracting at pH 6 with at least 3 times less Fe ending up in the leachate.

The sequential extraction results show that maximum extraction is obtained after 4 days (i.e. 3 leachant renewals) with for Pb ca. 1.7 times more extracted than after the first renewal. Using an L/S ratio of 10, however, this implies that 40 m³ of extracted liquid is produced for every ton of iron stone. Lowering the L/S to acceptable values without decreasing extraction efficiency is a clear priority from the industrial point of view. Further experiments with varying L/S should therefore be performed.

3.3. Improvement of separation performance during extraction

The previous extractions were all performed with nitric acid to obtain the desired pH value of 6. Nitric acid is interesting from a scientific point of view since it may easily form complexes that facilitate leaching. Nevertheless, it is not practical in this case; extraction with sulphuric acid is a much more logical approach in view of industrial application, because of the availability of concentrated sulphuric acid from the recycling process. Therefore several experiments were performed with sulphuric acid instead of nitric acid. Other acids may be used; Trezena de Araujo and Araujo do Nascimento (2010) suggest the use of citric acid and NTA for soils from battery recycling sites containing lead. However, this is less interesting from the point of view of process integration.

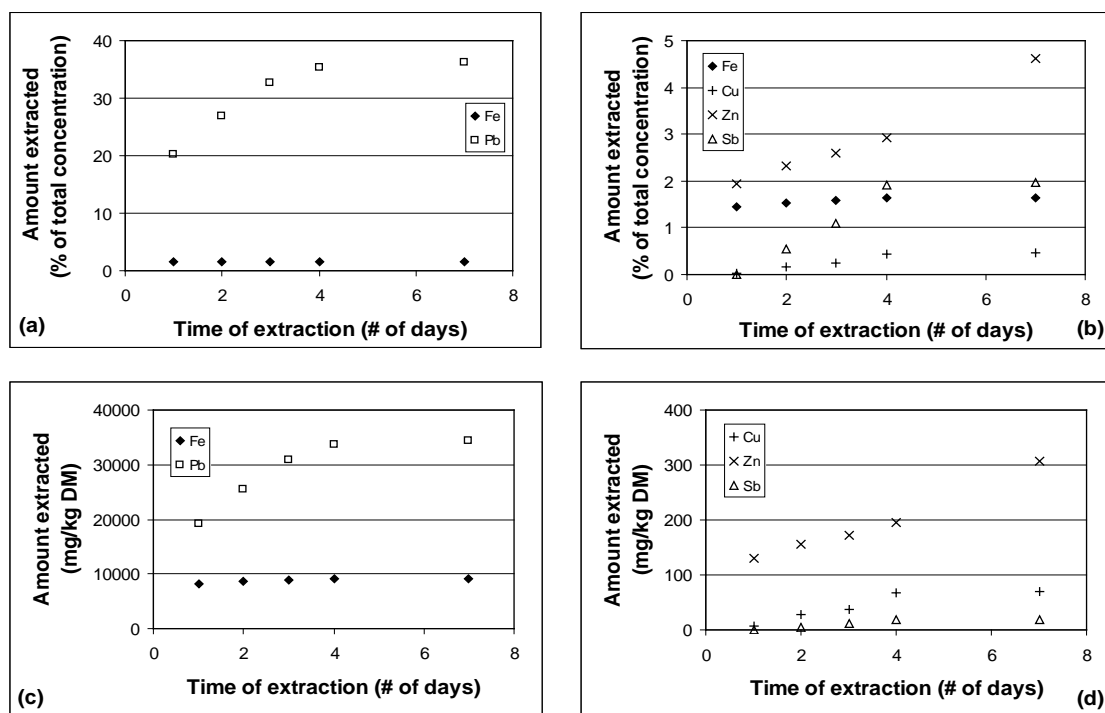


Fig. 5. Sequential extraction results at pH 6 for iron, lead, copper and antimony from iron stone

Extraction for 24 h was compared between obtaining pH 6 with nitric and sulphuric acid (Table 4). A decreased efficiency for Fe was obtained with sulphuric acid, which is positive. However, the extraction efficiency decreased drastically for Pb as well. The extraction of Zn and Sb also worsened by shifting to sulphuric acid as extracting agent, whereas the extraction of Cu remained negligible.

When sequential extraction was performed with sulphuric acid instead of nitric acid, the previous results were confirmed (Fig. 6). After 6 days, relative extracted amounts were 2.9% for Fe (compared to 1.6% with nitric acid after 7 days, Fig. 5), 0.3% for Pb (17.5% with nitric acid), 2.1% for zinc (17.7% with nitric acid), 0.07% for antimony (0.74% with nitric acid) and 0.02% for copper (0.51% with nitric acid).

Two methods were explored to increase this insufficient extraction of Pb, Cu, Zn and Sb compared to Fe when performing the extraction procedure with sulphuric acid: addition of FeCl₂ and addition of K₂CrO₄. It was shown in the literature (Altundogan et al., 2004; Tampouris et al., 2001) that copper removal can be enhanced by using complexing agents such as chlorides. Tampouris et al. (2001) used hydrogen chloride to extract copper from soils, and obtained 90-99% efficiency. It was also observed that lead, zinc and cadmium leaching increased as well.

The required amount of FeCl₂ to be added to the extraction leachant was calculated based on the amount of Fe that was extracted in the one-day pH-variation experiment at pH 6 (i.e. 1 g extracted Fe/kg DM, corresponding to 2.26 g FeCl₂/kg DM). This indeed resulted in a decrease of Fe extraction from 0.5 to 0.1% (Table 5), which can be explained by a shift in the precipitation reactions of Fe towards the solid phase, resulting in a net suppression of Fe

extraction. However, extraction results of Pb and other metals remained below the detection limit. The result was therefore deemed insufficient to obtain a satisfactory separation between Fe and Pb. The addition of FeCl₂ in an extraction procedure with nitric acid could be investigated to further improve the achieved results described in the previous paragraph.

Dichromate solutions are used to leach copper from metallurgical slags (Altundogan et al., 2004); K₂CrO₄ is a strong oxidant and was observed to suppress Co, Fe and Zn leaching while promoting Cu leaching. The mechanism involves adsorption phenomena on minerals containing iron, such as fayalite (Fe₂SiO₄) and magnetite (Fe₃O₄). On these minerals, Cr₂O₇²⁻ and HCrO₄⁻ adsorb, which shields the surface from reactions with H⁺. Sulphidic copper minerals do not adsorb dichromate and therefore dissolve more easily. An additional explanation for the decreased leaching of iron is the formation of insoluble iron-chromate complexes in mild acidic conditions (Olazabal et al., 1997). The formation of insoluble iron-chromate compounds (e.g., KFe₃(CrO₄)₂(OH)₆ and KFe(CrO₄)₂.2H₂O) was also observed in strong acidic conditions and high chromate concentrations (Baron and Palmer, 2002).

Table 6 summarizes the extraction of copper and other metals at pH 0 and 6, with and without addition of K₂Cr₂O₇. It was observed that at pH 0 Cu, Zn and Sb extraction improved drastically, whereas Pb extraction did not improve. However, at this pH Fe removal is too high. At pH 6 on the other hand, the effect of K₂Cr₂O₇ addition proved to be negligible, except for an increase of Fe extraction with a factor of more than 20. The obtained results do not warrant further investigation of the addition of dichromate solution in an extraction procedure with nitric acid.

Table 4. Extraction (in % of total concentration) from iron stone using HNO₃ versus H₂SO₄ (pH 6, 24 h)

	Na	K	Ca	Fe	Mn	Ni	Cu	Zn	Sb	Pb
<i>pH 6 H₂SO₄</i>	5.2	9.7	3.3	0.5	1.0	1.1	0.0	0.1	0.0	0.0
<i>pH 6 HNO₃</i>	17.4	83.9	102.5	8.9	24.6	27.0	0.0	9.4	1.7	58.0

Table 5. Effect of the addition of FeCl₂ (at pH 6) and the addition of K₂Cr₂O₇ (at pH 0 and pH 6) on extracted amounts (in % of total concentration) from iron stone (using H₂SO₄, extraction time 24 h)

	Na	Mg	Ca	Fe	Mn	Ni	Cu	Zn	Sb	Pb
<i>pH 6, no FeCl₂</i>	5.21	0.74	3.35	0.49	1.04	1.12	0.00	0.10	0.01	0.04
<i>pH 6, FeCl₂</i>	9.93	1.65	1.85	0.11	0.95	0.06	0.00	0.02	0.01	0.02

Table 6. Effect of the addition of K₂Cr₂O₇ (at pH 0 and pH 6) on extracted amounts (in % of total concentration) from iron stone (using H₂SO₄, extraction time 24 h)

	Na	Mg	Ca	Fe	Mn	Ni	Cu	Zn	Sn	Sb	Pb
<i>pH 0, no K₂Cr₂O₇</i>	18.3	89.3	56.3	44.7	82.0	6.2	0.0061	2.4	0.0	0.2	0.0
<i>pH 0, 0.3 M K₂Cr₂O₇</i>	46.1	89.1	86.5	39.6	31.6	34.4	77.7	105.9	9.7	21.3	0.0
<i>pH 6, no K₂Cr₂O₇</i>	5.2	0.7	3.3	0.5	1.0	1.1	0.000	0.1	0.0	0.0	0.0
<i>pH 6, 0.3M K₂Cr₂O₇</i>	26.2	14.8	10.9	11.7	0.0	0.1	0.001	0.0	0.0	0.2	0.0

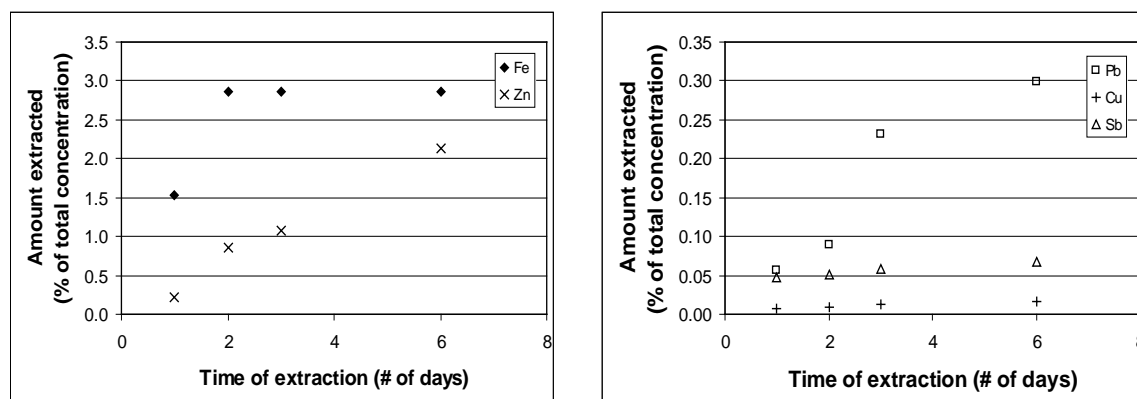


Fig. 6. Sequential extraction results at pH 6 with sulphuric acid for iron, lead, copper, zinc and antimony

4. Conclusions

Total recycling of iron stone obtained during production of lead requires the removal of metal contaminants of which Pb was present in the largest concentration, leaving a pure Fe matrix. This can be carried out with aqueous extractions at the appropriate pH, which was pH 6 for the material studied. Due to the limited acid buffering capacity of the material above pH 6 and the high acid buffering capacity below pH 6, addition of acid to perform extraction at pH 6 would not cause large problems with respect to financial cost and pH controllability.

A major issue appears to be the variability of composition and extraction results, even within the same batch of iron stone. This variability hinders adequate assessment of the extraction efficiencies. A separation was obtained between Fe and Pb, but this was considered to be insufficient in absolute quantities: the yield of Pb was too low, and the loss of Fe was too large. The separation of other metals such as Cu, Zn and Sb from Fe was even less efficient. As a consequence, this work demonstrates that hydrometallurgical treatment is a challenge when high purity is required starting from a very complex material; however, depending on the objectives, it can be a viable pathway as part of a more integrated separation system.

A viable industrial application would take advantage of the sulphuric acid that is available from the recycling process of batteries. However, it was concluded that the use of sulphuric acid instead of nitric acid to perform the acid extraction worsened results, even after modification with the addition of FeCl₂ or K₂Cr₂O₇. Thus, the addition of FeCl₂ might improve the separation efficiency when combined with nitric acid extraction.

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