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Effect of ultrasound on leaching of lead from landfilled metallurgical residues

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ABSTRACT

The potential of ultrasound as a process intensification technique in the extraction of lead from a landfilled metallurgical residues is explored. The silent or non-sonicated process makes use of acidic sodium chloride as the leachate with lead leaching in the range of 45% if a three-stage process is followed. The mixture was sonicated in a batch setup manufactured in-house. The yield obtained in silent conditions at the end of 240 minutes was already obtained within 30 minutes with ultrasound, which by itself was an improvement of 8 times. The yield of the process as a whole was improved by 19-26%. The reason for this improvement was investigated with respect to the reaction kinetics The physical effect of ultrasound on the particle size was also studied by laser diffraction analysis. Finally, the improvement when using ultrasound in a multi-stage process was studied and it was shown that yields being obtained at the end of the 3rd stage in silent conditions is already obtained in the second stage when using ultrasound with 20% more selectivity.

1 INTRODUCTION

Hydrometallurgy is an important and widely used technique in the separation of metals from ores to waste streams. It involves leaching of the required material from a solid feed, followed by concentration by solvent extraction and then precipitation. All these operations involve mass transfer between heterogeneous phases, which can be limiting unless accompanied by good mixing and separation. For this work our focus is on the leaching step, which involves mass transfer over a solid-liquid interface. Many factors such as temperature, solvent selectivity, the particle size, which determine the access of the solvent to the required metal, and the tightness of the bond of the required material with the surrounding materials determine the effectiveness of the separation process. Leaching can sometimes be a slow process as sufficient time has to be given for a proper penetration of the liquid into the solid material for sufficient and effective leaching of the required materials. It is a worthwhile approach to apply process intensification here for enhanced separation in a shorter time. The technique of interest for us is ultrasound because it is known to improve mass transfer and mixing.

Ultrasound applied in a liquid phase can cause vibrating cavitation bubbles which can improve the local micro-mixing of the liquids near the solid surfaces to bring in fresh solvent near the solid surface [1–3]. The cavitation bubbles present near a solid surface can collapse asymmetrically, causing surface erosion and jetting [1]. The surface erosion or the pitting produced can expose new metal-rich surface to the solvent, hence reducing the time it would otherwise require the solvent to penetrate through the material. The micro-jets can also improve the transport rates near the surface [2,4–7]. Therefore, theoretically ultrasound looks like a useful approach and its application has indeed been proven effective in leaching of different starting materials, ranging from ores to waste streams. Some examples of improvements of metal extraction from ores are: Xue et al., 2010 [8] saw an 6.7 % increasement in the leaching rate of nickel from nickel sulphide ore by using ultrasound; Avvaru et al., 2008 [9] saw a 42% increment in leaching of uranium from its ore at lower nitric acid concentration than without ultrasound; and Rao et al., 2007 [10] saw improved ammonia leaching of copper from lean grade copper oxide ore. From waste streams some examples include: Brunelli & Dabalà, 2015 [11] saw a 41% to 55% increase in the recovery of zinc from electric arc furnace dust; Turan et al., 2019 [12] saw a two times improvement of copper recovery from blended copper slag from a flash and converter furnace; and Xie et al., 2009 [13] showed improved metal recovery from treatment of printed circuit board waste sludge. In addition to improving leaching performance it can also be used to improve selectivity. Zhang et al., 2013 [5] showed that by changing the pH and applying ultrasound, the solvent became more selective to copper and chromium in a system consisting of iron and the said compunds.

The focus of our work is on lead extraction from landfilled metallurgical residues that originated from the pyro-metallurgical recycling of old lead batteries and other lead wastes. The work was carried out with two objectives, one was to identify and remove any valuable metals that may be present in the landfill and the second was to remove any lead present from an environmental point of view. The focus of this paper is on the second objective. Without ultrasound, the most common approach to extraction of lead is by making use of acids or chelating agents or a combination of both. The most commonly used complexing agents with lead are EDTA (ethylene diamine tetra acetic acid), which forms $(PbEDTA)^{2-}$ complexes [14–16], or chlorides like NaCl which forms a lead chloride complex [14,15,17,18]. Since EDTA is an expensive and temperature-sensitive solvent [19], NaCl acidified by sulphuric acid is preferred owing to its success in extracting lead from similar starting materials [14,17,18]. Ultrasound has not yet been studied extensively for the purpose of extracting lead from landfill. However, an interesting work in this context is the work by Zhang et al., 2015 [4] who studied the effects of leaching antimony and lead from an oxidizing slag using the acidic sodium chloride solution. They showed a reduction in leaching time by a factor of three with ultrasound. The author also looked at the effect of particle size and the influence of temperature, which showed improved leaching rates with smaller particle size and increased temperatures. In addition, Kim et al., 2016 [20] has also stressed the importance of using mechanical stirring with ultrasound for leaching operation as he observed that ultrasound removes the metals that are strongly bonded to the feed but mechanical stirring increases the macroscopic contact between the soil and the extracting liquid.

The main aim of this work is to investigate as to how ultrasound can be used to improve the rate of lead dissolution with good selectivity from the landfilled material and to study the mechanism of this improvement, in particular if the effect of ultrasound is a chemical or physical phenomenon or a combination of both. For this purpose the kinetics of the rate of extraction are explored and the effect of ultrasound on the particle size is studied with a laser diffraction meter. In addition, the effect using ultrasound at varying stirrer speed is also studied to identify the most feasible option with respect to energy supplied. Finally, a multistage operation with ultrasound is attempted and compared to normal operation (or silent operation, as it is going to be known throughout this paper) .

2 MATERIALS AND METHODS

2.1 FEED ORIGIN AND PRE-PROCESSING

The source for the feed as mentioned before is the landfilled slag and matte from a lead recycling process. There were two sites and both were characterised electromagnetically as shown in Figure 1. The bulk electrical conductivity of the subsoil was measured up to the depth of 12 meters using 2 coil separations, 10 and 20 meters (EM34, Geonics Limited). The electrical conductivity of the subsoil is influenced mainly by the grain size distribution, density, mineralogy, water saturation and electrical conductivity of the ground water. The result of the electromagnetic survey is a map with the spacial distribution of the bulk conductivity putting forward the heterogeneity of the landfill. Based on these readings nine locations were selected and bore holes were drilled up to depth of 6 m (Figure 2). The 9 bore samples were characterized based on soil properties into 58 fractions and XRF (Axios, Malvern-Panalytical) was performed on each of these fractions to understand the elemental concentrations at different conductivity regions with depth.

Figure 1: *The site layout and electromagnetic readings*

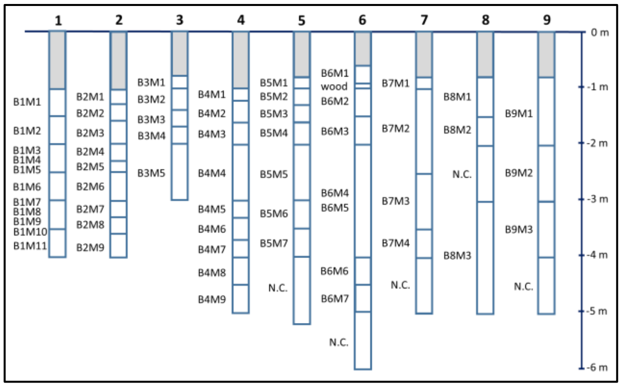

Figure 2: *Bore hole depths and sample segregation depths*

For the purpose of this work an average sample was generated by mixing half of the mass of each of the 58 samples, as the intent is to excavate and process the landfill area as a whole. The average sample generated was then separated in different size fractions to understand their characteristics and to assess whether processing an individual fraction was more economically feasible. In terms of pre-processing, the samples were initially screened for any organic matter, then size-separated by dry sieving and dried at 105°C for 24 h. They were crushed to required sizes if needed primarily with a jaw crusher (especially for fractions > 4 mm) and then with a ball mill. The separated fractions were then characterized with XRF and the results obtained are shown in Table 1.

Table 1: *The weight fractions of the different size fraction present in the landfill & elemental percentages from the XRF of the different size fractions (DL – Detection Limit). The DL for Na in ICP-OS used 100 ppb.*

Size	Weight%	Al	Ca	Cu	Fe	K	Mg	Na	O	Pb	S	Sb	Si	Zn	Others
> 50 mm	12.3	4.34	10.9	0.28	15	0.4	1.31	3.7	38.9	1.25	2.16	2.14	17.3	0.7	1.64
50 mm	29.2	3.03	7.47	0.45	18.8	0.59	0.64	<DL	40	2.1	5.66	2.68	16.1	0.77	1.69
10 mm	18.7	2.84	6.73	0.36	20.9	0.59	0.63	<DL	38.6	3.19	5.04	3.33	15.5	0.75	1.64
4 mm	8.8	2.33	4.07	0.27	15.4	0.61	0.34	<DL	43.3	2.45	4.49	1.5	23.8	0.43	0.98
2 mm	30.0	2.74	6.16	0.41	20.3	0.55	0.54	<DL	39	4.04	4.95	2.81	16.5	0.73	1.4
0.5 mm	0.5	2.28	2.87	0.2	12.3	0.73	0.27	<DL	45.3	2.06	4.2	1.13	27.4	0.37	0.86

The elemental analysis of the fractions indicates lead concentration between 2 and 4% for all fractions, except for the > 50 mm fraction where there is a lower amount of lead and a high amount of calcium. This is the fraction which was seen to be the least degraded over time, almost resembling the original slag material physically. The XRF revealed that the 2 mm fraction (Table 1) has the highest amount of lead at 4.04% in comparison to the 2.20 % on average (determined by taking the average over the initial 58 samples) from the landfill as a whole. This 2 mm fraction was selected for the reminder of the work owing to its largest presence in lead content and quantity. The XRD (X-Ray Diffraction) [D2 Phaser, Bruker] of the fraction revealed that the lead was present in the form of either metallic lead or lead oxide.

2.2 LEACHING PROCESS

The leaching agent considered here is an acidified sodium chloride solution which has been reported in literature to have quite an effective rate of extraction as a result of the formation of soluble lead chloride complex [14,15,17,18,21]. Based on literature, a 4 mol/L sodium chloride solution is used at a ratio of 1:20 with the acid which here is 1 mol/L H_2SO_4. The 2 mm material is utilized as such without size reduction. The solid to liquid ratios (varied between 1:2 to 1:10) and reaction times (studied up to 4 hrs) are decided upon based on preliminary experiments. The remaining parameters are discussed with each individual experiments in the following sections. All experiments were repeated 3 times and the standard deviation was evaluated. The leachate is separated from the solid residue by filtration through a 0.45 µm CHROMAFIL®Xtra PET-45/25 microfilter and analysed with an ICP-OES (PerkinElmer Optima 8300 Optical Emission Spectrometer). For the analysis of solid phases, XRF is used to determine the elemental concentrations and XRD for identifying the mineralogical states of the elements present.

2.3 EXPERIMENTAL SETUP

The preliminary experiments were performed in a 90 ml batch reactor with an overhead stirrer operating at 250 rpm. The ultrasonic batch reactor setup consists of a 200 ml jacketed glass reactor, with an open bottom. An ultrasonic transducer (Ultrasonics world MPI-7850D-20-40-60 H) with a glass plate glued on top acts as the bottom of the reactor. These two pieces are held together with a Teflon ring in between by two metallic rings: one placed on top of the reactor and one at the bottom of the transducer, with the help of three threaded rods. The batch reactor is fitted with an 45° inclined three-bladed PTFE impeller from BOLA, whose rotation speed could be controlled from 50-1000 rpm. The required ultrasonic parameters are set with a Picotest G5100A waveform generator and the signal generated is amplified with a E&I FR200 power amplifier and then fed to the transducer.

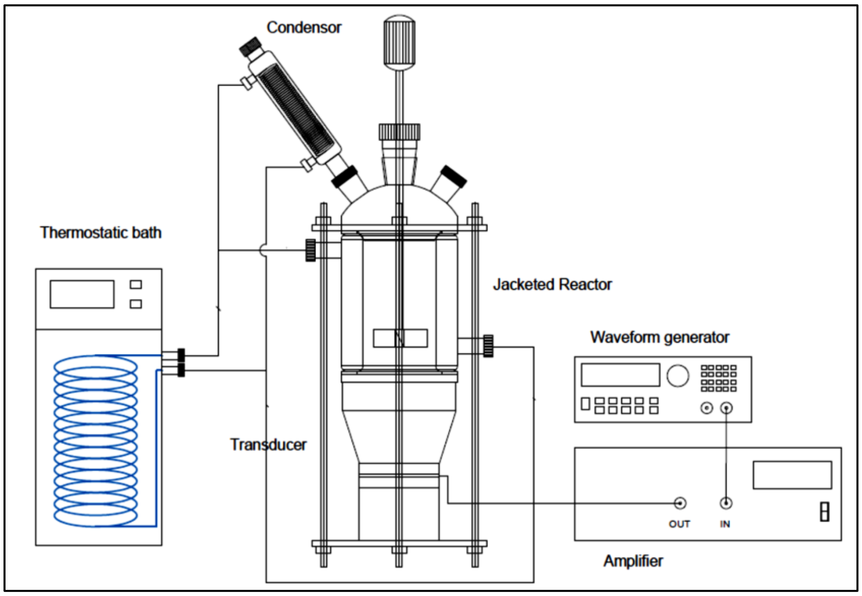

Figure 3: *Ultrasonic batch reactor setup.*

A condenser was fitted to the batch reactor solely as a safety precaution, such that any vapour formed could be recycled back to the reactor. The reactor temperature was controlled using a LAUDA ECO silver RE415 thermostat.

3 RESULTS & DISCUSSION

3.1 PRELIMINARY BATCH EXPERIMENT

The initial experiments were performed in the 90 ml reactor and solid to liquid ratios of 1:10, 1:6 and 1:2 were examined for an effective processes. The ratios were obtained by keeping the solid material constant at 6 g and adding the required amount of the solution as per the ratio required. The experiment was performed with the temperature being maintained at 25°C and the leaching solution consisting of 1 mol/L sulphuric acid and 4 mol/L sodium chloride at a ratio of 1:20. Elements with significant dissolution (> 20 mg/l) were tracked along with the pH and the results obtained are shown in Figure 4.

Primarily looking at the progress of the reaction itself in terms of the dissolution of the elements, it can be seen that the reaction attains maximum leaching after 30 min. This is also represented by the change in pH which stabilizes at the same time. The increase in pH is due to the fact that the solid material added is inherently basic with a pH above 7.5. The pH also increased with increasing solid to liquid ratio. Lead is clearly extracted more with increasing solid content. This does not mean that the extraction efficiency increases with the increasing solid content, it actual remains similar in the range of 30% . The increase corresponds to the extraction capability of the leaching solvent used, so that it can handle even 5 times increase in solid brought about by the 1:2 in comparison to the 1:10 solid to liquid ratios. Additionally, looking at both calcium and iron the dissolution trend is similar to lead such that it is maximized at around 30 min, but they are both affected little by the changing quantity of solid. The little interaction of both Fe and Ca is due to their indifference to the presence of NaCl but they do react in the presence of the little sulphuric acid introduced into to the system which is also consumed for the formation of the Lead complex with the sodium chloride [14,17]. This is advantageous in the sense that increasing the solid content increases also the selectivity of lead.

An important conclusion from these results is that leaching has the capacity to extract more lead but that it is hindered, because otherwise lead would have had constant dissolution concentration values for the different pulp densities, as is the case for calcium and iron. This behaviour points to a mass transfer limitation and ultrasound will be utilized in the following experiments to identify the validity of this hypothesis with the aim to improve the extraction efficiency.

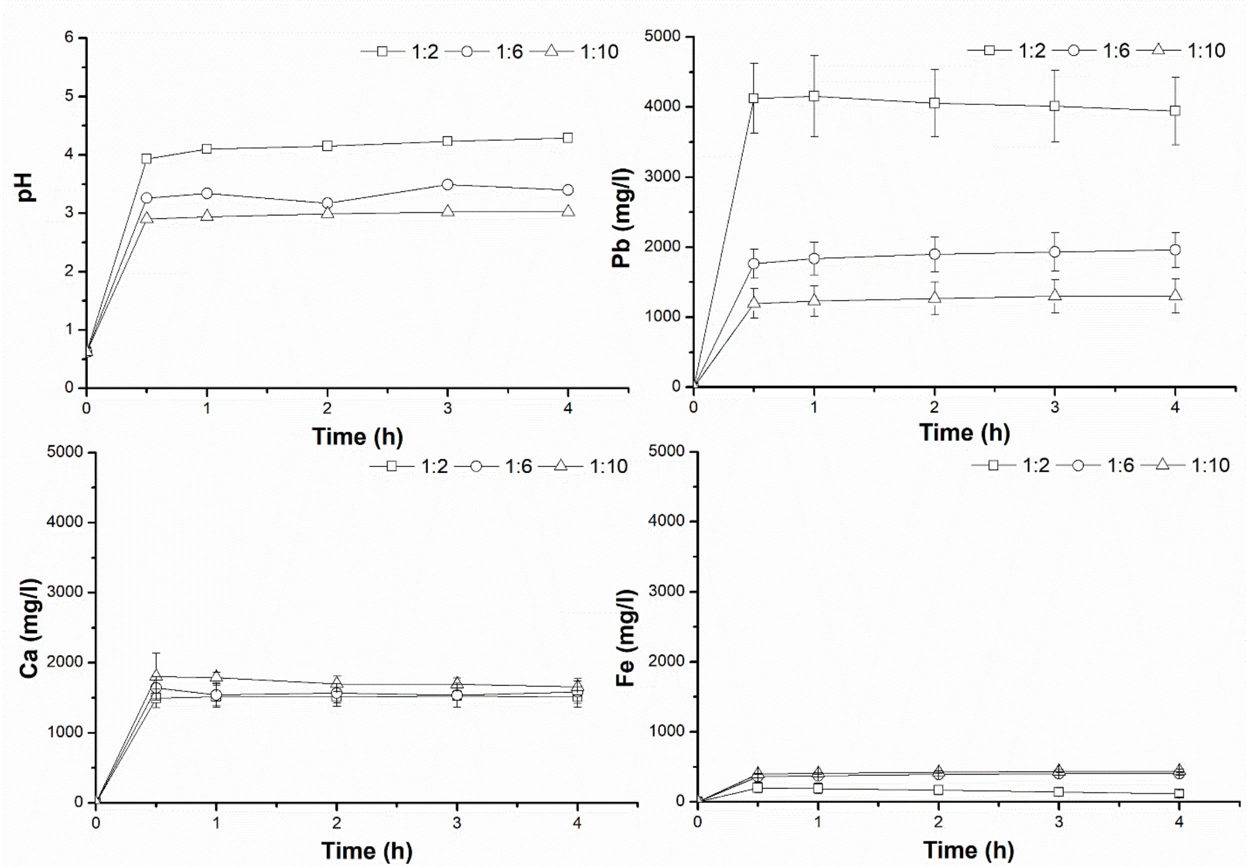

***Figure 4:** Dissolution of metals and the evolution of the solution pH with time for solid:liquid ratios 1:10, 1:6 and 1:2. [t = 4h, T = 25° C, Stirrer speed = 250 rpm, leaching solution = 1:20 (1 mol/L H2SO4 : 4 mol/L NaCl)].(Error bars are based on 3 replicates. If error bars are not visible they are smaller than the symbols representing the average data values)*

3.2 EFFECT OF ULTRASOUND

3.2.1 Ultrasound assisted leaching

In accordance with what was observed in the preliminary experiment, the following parameters were used to perform the experiment with ultrasound. The starting material was utilized at a solid to liquid ratio of 1:2. Another important change is that the batch reactor utilized in the preliminary studies was only 90 ml whereas the one utilized with the ultrasound was about 200 ml, which realizes a four times increase in volume (20 ml to 80 ml leaching solvent). This also gave an opportunity to identify the scalability of the system and its governing parameters. The same ratio of 1:20 of 1 mol/L sulphuric acid to 4 mol/L sodium chloride salt solution was used. The stirrer speed was increased to 300 rpm to compensate for the increase in volume. Since there were changes compared to the preliminary experiments mainly in terms of volume, initially silent experiments without ultrasound were performed followed by sonication experiments at a frequency of 40 kHz, amplitude of 590m.V and a net input electrical power of 20 W. Even though the transducer used is a multi-frequency type, the 40 kHz had the highest and most stable electrical input of 20 W. For the other frequencies, the powers where fluctuating frequently and hence were not considered for this study. Similar to the previous experiment, the dissolution rates of metals with significant dissolution concentration were followed with time and plotted in Figure 5.

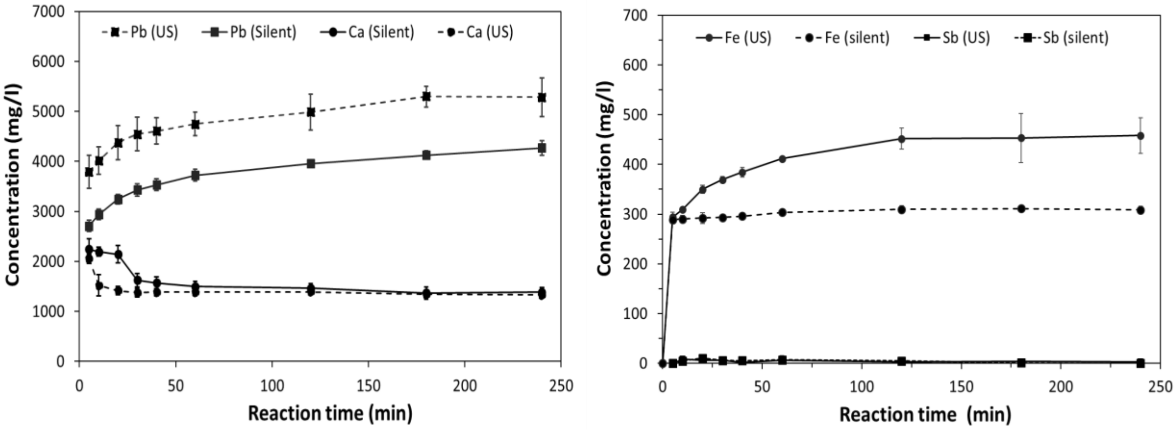

***Figure 5**: Dissolution of lead(Pb), iron(Fe), calcium (ca) and antimony (Sb) with and without ultrasound.. [t= 4h, P_{US} = 20W, Freq = 40 kHz, T = 25°C, Stirrer speed = 300 rpm, leaching solution = 1:20 H_2SO_4: NaCl, solid:Liquid ratio = 1:2]. (Error bars are based on 3 replicates. If error bars are not visible they are smaller than the symbols representing the average data values)*

The effect of scale up is quite evident just following dissolution rates of lead in the silent experiment. The plateau concentration observed in the preliminary experiment after 30 min of leaching is only reached after close to 4 h of leaching without ultrasound. This can also be an indication of the lack of mixing by the stirrer as only a minor increment of 50 rpm was done for a 4 times larger batch scale. The original intent for the 300 rpm was to attain a stirrer speed at which all the solids are in motion without dead zones and this was confirmed by visual inspection. There is an influence of the stirrer speed on the dissolution rates and this was observed in Figure 8 with sonication. There were no significant differences for the trends of calcium and iron, which as indicated before might be at their dissolution capacities. An interesting effect observed for the scaled-up batch reactor was with respect to calcium which showed a decrease in leaching with time. This would mean a precipitation of the calcium owing to the dissolution concentrations reaching its solubility limits. This is a further advantage, as the decrease in the concentration of calcium in the solution increases the lead selectivity. We also looked at whether antimony could be extracted as it was reported to be effectively extracted with the sodium chloride solution[14]. Since no significant change was observed in silent condition it was studied whether it was improved by the addition of ultrasound. There was a very small increase but nothing that was substantial enough to be explored further.

Looking at the sonication results (Figure 5) in comparison with the silent experiment, there is a clear influence of the ultrasound on the process. For the lead dissolution rate the use of ultrasound seems to be positive. Within 20 min of sonication the maximum value of the silent experiment reached after 4 h is already attained. The general progression of the dissolution rate is also augmented by an increase in the region of 1000 mg/l throughout the process. This brings about an improvement of almost 19-26% by sonication throughout the process. This increment is believed to be caused by the improved mass transfer because of either the surface cleaning effect of the cavitation bubble on the solid particles or breakage of the material due to increased attrition by the cavitation effects. The exact cause is explored further in the following section. For calcium, we observed a similar decreasing trend with time as with the silent experiment, but sonication seems to be speeding up this effect which is again an advantage from the selectivity perspective. The dissolution rate of iron seems to be affected similarly to lead with a maximum increment of about 100 mg/l which plateaus off in about 2 h. This is again not a significant effect as the amount of lead dissolved is more than 10 times that of iron.

3.2.2 Kinetics Analysis

To better understand the kinetics of the process the method described in the work of Nedwed and Clifford, 2000 [15] is used. They mention that , if the mass transfer coefficient stays constant, the kinetics of a mass-transfer-controlled reaction should follow a first-order reaction. For this reason, the kinetic data obtained during the ultrasound-assisted and silent leaching experiments are plotted in Figure 6 as if they would follow a first-order reaction, for which the rate equation $\ln(c_{(t)}/c_0) = -k.t$ applies, where k is the rate constant, $c_{(t)}$ and c_0 are the concentrations of lead at time t and in the feed, respectively. Figure 6 indicates identical trends for both silent and sonicated processes that a straight line cannot be plotted with the data. This means that not one single reaction controls the reaction but rather multiple lead dissolution principles, which was also observed by Nedwed and Clifford, 2000 [15] and Gasser et al., 1996 [22].

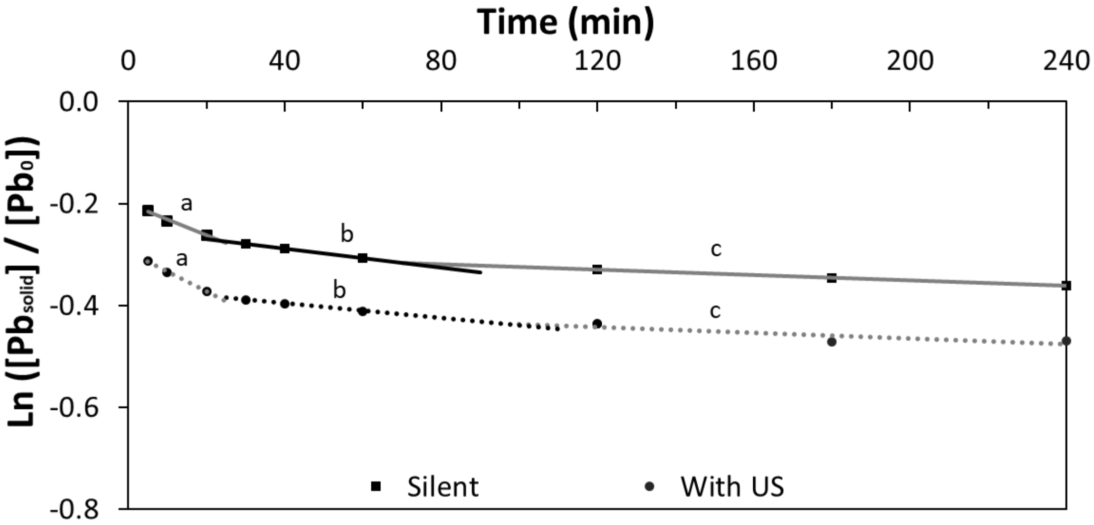

Figure 6: *First order reactions describing the lead leaching behaviour in silent and ultrasound-assisted leaching reactions. The data that are used for this graph are the experiments shown in Figure 5.*

The difference in the dissolution rates as seen in Figure 5 is observed to a similar degree of difference between the silent and sonicated curves in Figure 6. As the reaction starts, presumably in the first five minutes, the unbound lead is dissolved in the liquid (this line is not drawn in Figure 6). The second rate-controlling mechanism (line a) occurs from 5 min until 20 min. In this period, the most accessible lead compounds are probably leached out, such as the compounds present at the solid surface. Subsequently, from a reaction time of 20 min until 1 h (line b), a third process controls the leaching reaction, and after an hour, the slowest step is reached as well (line c). During the latter two time periods, the reaction rates decrease presumably because the lead becomes less accessible as the reaction proceeds [15]. An additional interesting observation is that the slope (k) of the three reaction zones are quite similar for the silent and ultrasonic conditions, as is shown in Table 2. This indicates that the same phenomena are controlling the reactions and that the cavitation effects do not influence the rate of the reactions that are taking place after the first five minutes. Furthermore, this table also shows that the kinetics of the reactions are first order, since the coefficients of determination (R^2) are very close to one. The only exception is line c for the ultrasound experiments, which can be explained by the very large standard deviation of the data at 120 min.

Table 2. *Slope and R^2 values for the three lines found in the kinetic study of the lead leaching for silent and sonicated conditions.*

	Line a		**Line b**		**Line c**	
	Slope (-k)	**R^2**	**Slope (-k)**	**R^2**	**Slope (-k)**	**R^2**
Silent	-0.0032	0.99	-0.0009	0.99	-0.0003	0.99
Sonicated	-0.0039	0.99	-0.0007	0.99	-0.0003	0.72

Figure 5 also shows that the difference in lead solubility between the two experiments is caused in the first five minutes. After these first 5 min the distinction between the dissolved lead concentrations for both experiments stays constant during the remaining reaction time. This is also observed in Figure 6; if the first point would be connected to zero, the gradient for the ultrasonic curve would be higher than that of the silent conditions, meaning that this reaction occurs faster in the sonicated reactor. This effect can be caused by the creation of more easily accessible lead particles due to cavitation effects, for instance by abrasion of the surface of the particles or by fractionation. It is, however, peculiar that the further steps in the lead leaching process are not affected by the addition of ultrasound, while Figure 5 shows that the iron dissolution behaviour is enhanced up till 2 h. The same lead leaching trends are observed by Zhang et al. [4] during sonication. The results for iron leaching imply that after five minutes, the cavitation effects still influence the system, but cannot enhance the lead leaching reactions. This can presumably be caused by the fact that lead is more tightly bound than iron in the particles. The positive implication of this observation is that the ultrasonic energy does not need to be applied during the entire reaction time, leading to lower energy consumption. Moreover, by limiting the ultrasonic effects to shorter periods, the selectivity of the process towards lead could be increased.

The study of the reaction kinetics leads to the belief that the enhancement of the lead dissolution by ultrasound does not seem to be a result of a chemical effect but rather a physical one. This is to say that there can be changes to the particle size due to attrition and surface effects by ultrasound. It is further explored in the following section by analysing the effect on the particle size with and without ultrasound.

3.2.3 Particle size analysis

To examine what exactly happens to the solid particles sizes during sonication, a laser diffraction test is performed on the starting material and on the residue of the leaching process with and without ultrasound. Figure 7 shows the volume distribution of the different particles. The volume distribution is used as it was the best representation of the obtained results.

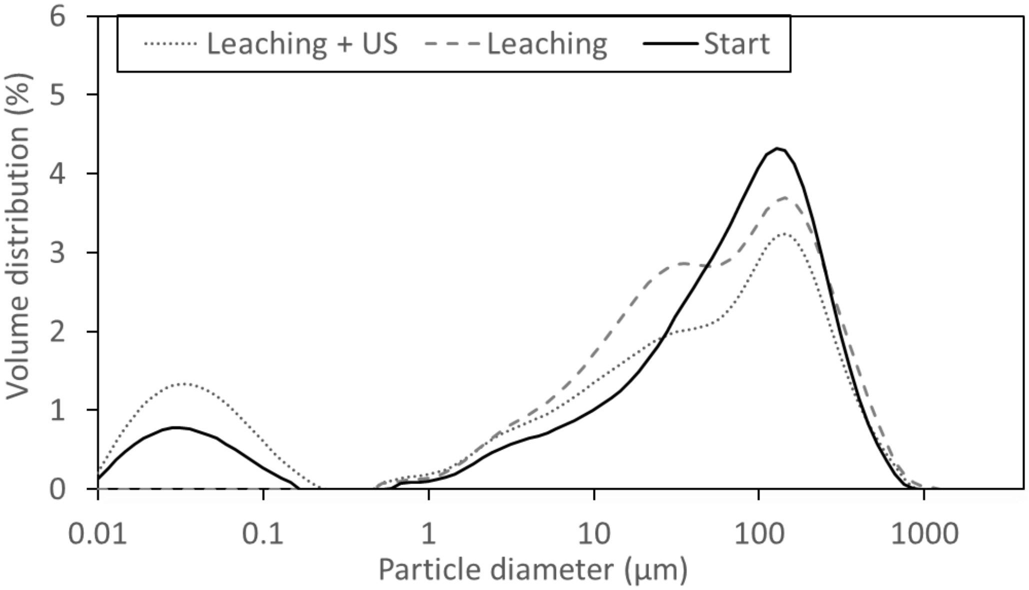

***Figure 7**: Volume distribution of the particle sizes of the 2mm un-milled starting material (Start) and the material after 2 h of leaching without (Leaching) and with ultrasonic assistance (Leaching +US).*

Both for the starting material and the residue of the ultrasonically-assisted leaching process, a peak is observed at very low particle diameters. A major difference between the starting material and the leached residue is that the latter is filtered (0.45µm) after the leaching process but the former is not and interestingly a small peak is not observed for the non-sonicated process. The lack of fines in the non-sonicated leaching process may be because of the loss from the filtration process or formation of strongly bonded agglomerates. The fines peak with the ultrasound indicates a much finer composition with the use of ultrasound presumably due to attrition of material which may have been loosely agglomerated during the filtration process and shaken loose during the laser diffraction experiment. The presence of fines in the sonicated material makes the lack of fines peak in silent operation due to filtration loss unlikely .However, it can still be observed that during the leaching process, the particle size is reduced and is more distributed , which can be caused by the reaction and the stirring operations. By introducing ultrasound, the large particle size peak is decreased even more, indicating a larger interfacial area available for mass transfer, which could be the reason for the better yield with ultrasound.

The introduction of ultrasonic energy shows great potential for concentrating lead in the leachate. By introducing 20 W of ultrasonic power, lead concentration increases with 24% until 40% and also selectivity towards antimony, calcium and sulphur is increased. The lead recovery process is thus improved with ultrasound.

3.2.4 Stirrer speed with ultrasound

Since the ultrasonic energy is added to the stirring power, the total energy imparted to the reactor volume is increased. This section discusses the stirrer speed required for the ultrasound-assisted process. The difference in energy consumption between the experiments without and with introduction of ultrasound, is the energy added by the transducer, since the stirrer speed is kept constant at 300 rpm. This implies that the higher recovery of lead obtained comes at a price of higher energy consumption. This observation raises the question if less energy could be imparted to the reactor volume, by decreasing the stirrer speed and how this affects lead recovery. Figure 8 shows the results of decreasing the stirrer speed down to 50 rpm, when the other parameters are kept similar to the previous ultrasound experiment with the solid to liquid ratio kept at 1:2.

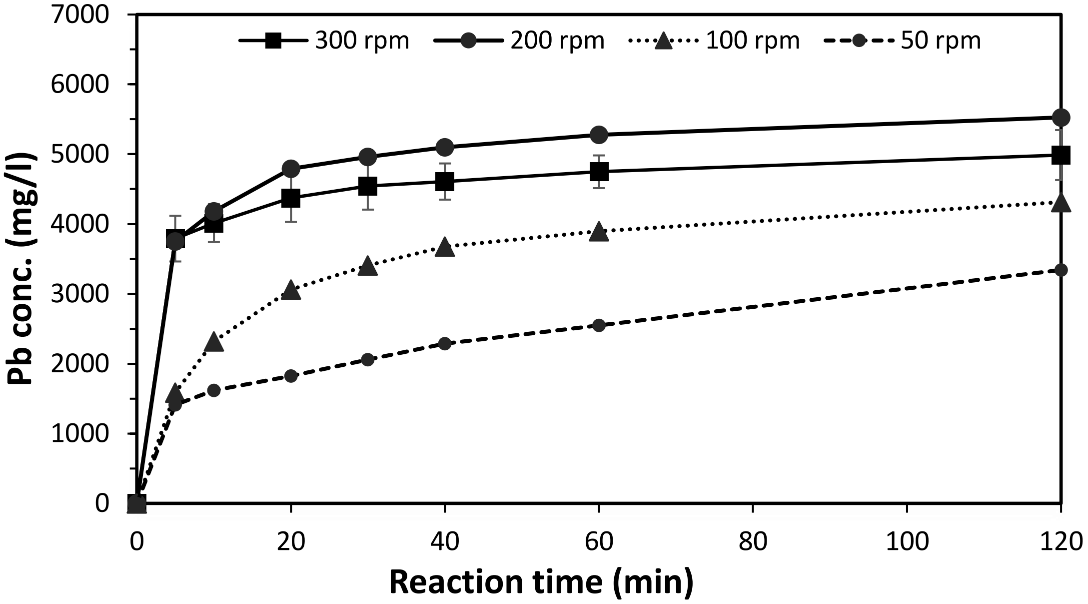

Figure 8: *The effect of varying the stirrer speed on the lead concentration in the ultrasound-assisted leaching process. [t= 2 h, P_{US} = 20 W, Freq = 40kHz T = 25°C, leaching solution = 1:20 H_2SO_4: NaCl, solid:liquid ratio = 1:2]. (Error bars are based on 3 replicates. If error bars are not visible they are smaller than the symbols representing the average data values)*

Figure 8 indicates that a stirrer speed of 200 rpm seems to be most interesting for recovering lead, even more than the stirrer speed of 300 rpm. This stirrier speed not only increases the lead concentration in the leachate, but also decreases the mixing energy consumed. Stirring the mixture can namely disturb the formation of standing ultrasound waves, leading to less effective cavitation and thus in this case, lower lead concentrations. However, macroscopic mixing still needs to be sufficient as well. When the stirrer speed decreases down to 100 or 50 rpm, the concentration of lead decreases significantly. This is caused by insufficient macroscopic mixing at these lower stirrer speeds, leading to decreased mass transfer. This aspect could also be physically observed during the experiments, since the solid material mainly deposited at the bottom of the reactor and was not brought into suspension. From Figure 8 the observation thus follows that at stirrer speeds between 200 and 300 rpm, the optimal combination of macroscopic and microscopic mass transfer effects is obtained.

Finally, during the discussion of all the previous parameters on the lead leaching process, only the absolute concentrations of lead and other compounds in the leachate are considered. However, it is very useful to examine the relative amount of lead recovered, compared to the concentration in the starting material. The following section treats this aspect and discusses how ultrasound would affect a multi-stage operation.

3.3 MULTI-STAGE LEACHING WITH SONICATION

In the experiments performed only percentage extractions of 30 % without ultrasound and 35 % with ultrasound has been obtained.. To further extract lead a three-stage process was attempted with the starting material and the solid residues obtained after each stage being treated with fresh solvent, which in this case is the 1:20 ratio of 1 mol/L sulphuric acid and 4 M sodium chloride. The solid to liquid ratio and temperature was maintained at 1:2 and 25°C, respectively. Each stage was given a reaction time of two hours to ensure completion. After each stage the residue was filtered with a 0.45 µm filter paper and then utilized for the next stage. The ultrasonic experiments were performed similarly to the silent experiments but at frequency of at a frequency of 40 kHz, amplitude of 590m.V and a net input power of 20 W. The results obtained per stage with and without ultrasound are plotted in terms of the cumulative percentage extraction in Figure 9.

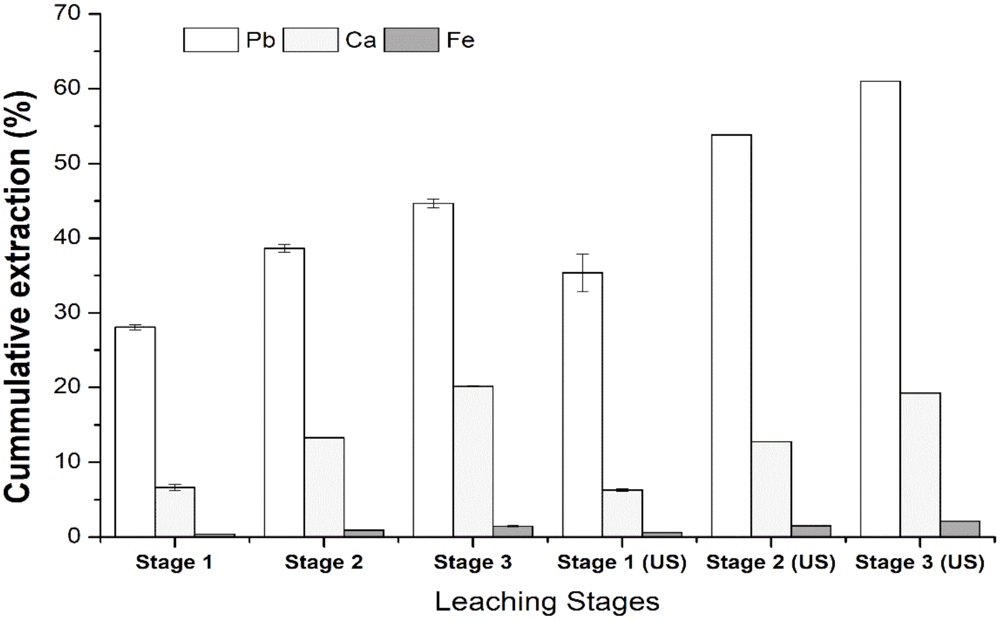

***Figure 9**: The cumulative extraction of lead (Pb), calcium (Ca) and iron (Fe) over three leaching stages with and without ultrasound. [t= 2 h, P_{US} = 20 W, T = 25°C, leaching solution = 1:20 H_2SO_4: NaCl, PD = 1:2]. (Error bars are based on 3 replicates. If error bars are not visible they are smaller than the symbols representing the average data values)*

The results indicates that after three stages, a cumulative lead recovery of, respectively, 45 % and 61 % for the processes without and with ultrasound are obtained. The incremental increase in recovery logically decreases with every stage, since the starting concentration becomes lower, reducing the driving force for the reaction. Moreover, as firstly the most loosely-bound lead is extracted, the material that is left contains more strongly-bound metals or lead compounds that are harder to reach by the liquid. This second aspect can be overcome by ultrasound, as observed in Figure 5.

As the process is repeated, more side products can be recovered as well. Figure 9 also shows the leached concentrations of calcium and iron during the three-stage process. Both iron and calcium concentrations stay relatively constant in comparison to the silent process throughout the three-stage process increasing the selectivity for the lead throughout the stages by the use of ultrasound. The selectivity was calculated as ratio of the desired product formed to the undesired product formed (in moles). It was calculated to be between 0.43 and 0.091 in the silent stages, but in sonicated they were found to be between 0.56 and 0.11 which is an improvement of almost 20% on average.

4 CONCLUSION

The effect of process intensification by ultrasound on the recovery of lead from landfilled slag material in an acidic saline leaching process was explored. The initial experiments to identify the optimal parameters at silent conditions were performed on a smaller scale and then scaled up two times and studied with and without ultrasound. On scale up the reaction time was increased from 30 to 240 minutes. Ultrasound was shown to have a positive effect on the recovery of lead as the time taken to obtain the same yield in the silent condition at the end of 240 min was obtained with ultrasound within 30 min. This is an 8 times reduction of the reaction time. For the process as a whole the dissolution of lead was improved by 19-26%. There was a negative effect by ultrasound on the dissolution of calcium which further improved the selectivity of lead in the process.

The analysis of the kinetics for silent and sonicated conditions was subsequently performed by mapping the data to a first-order reaction. This led to the conclusion that the rate of lead dissolution depends on three first-order mechanisms during the period of four hours. The longer the residence time, the slower the extraction occurred, caused by lead bonds that were presumably harder to reach by the solution. The interesting observation during this experiment was the fact that the main difference between the lead solubility in the silent and sonicated conditions was achieved in the first five minutes. After this period, the difference between the two conditions stayed similar. This implies that the ultrasonic energy does not need to be added to the system during the entire reaction time, but a pre-treatment step could be sufficient. The particle size experiment indicated that the use of ultrasound decreased the particle size with larger amount of fines being created. This can open up new surfaces and allow better mass transfer, and hence lead to better dissolution of the lead.

As ultrasound adds additional energy to the system the effect of lowering the stirrer speed was also studied. By changing the speed from 300 rpm to 200 rpm while maintaining the ultrasonic power at 20 W, the lead recovery increased. Decreasing the stirrer speed even more caused insufficient macroscopic mixing, causing tremendously lower lead recoveries. The optimal stirrer speed is thus certainly a parameter that has to be examined for the scale-up, as it both affects the transmission of standing ultrasonic waves and the energy consumption to a great extent. Finally, applying a three-stage ultrasonic process to the starting material improved the lead recovery from 35% to 61%. Compared to the three-stage process under silent conditions, the potential of intensifying the lead leaching process with ultrasonic energy is certainly proved.

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6 BIBLIOGRAPHY

[1] K.S. Suslick, G.J. Price, Application of Ultrasound to Materials Chemistry, Annu. Rev. Mater. Sci. 29 (1999) 295–326.

[2] G. Cravotto, E.C. Gaudino, P. Cintas, On the mechanochemical activation by ultrasound., Chem. Soc. Rev. 42 (2013) 7521–34. doi:10.1039/c2cs35456j.

[3] D. Fernandez Rivas, P. Cintas, H.J.G.E. Gardeniers, Merging microfluidics and sonochemistry: towards greener and more efficient micro-sono-reactors., Chem. Commun. (Camb). 48 (2012) 10935–47. doi:10.1039/c2cc33920j.

[4] R.L. Zhang, X.F. Zhang, S.Z. Tang, A.D. Huang, Ultrasound-assisted HCl-NaCl leaching of lead-rich and antimony-rich oxidizing slag., Ultrason. Sonochem. 27 (2015) 187–91. doi:10.1016/j.ultsonch.2015.05.020.

[5] P. Zhang, Y. Ma, F. Xie, Impacts of ultrasound on selective leaching recovery of heavy metals from metal-containing waste sludge, J. Mater. Cycles Waste Manag. 15 (2013) 530–538. doi:10.1007/s10163-013-0131-z.

[6] J. Ma, Y. Zhang, Y. Qin, Z. Wu, T. Wang, C. Wang, The leaching kinetics of K-feldspar in sulfuric acid with the aid of ultrasound, Ultrason. Sonochem. 35 (2017) 304–312. doi:10.1016/j.ultsonch.2016.10.006.

[7] T.J. Mason, A. Tiehm, Advances in Sonochemistry, Volume 6, 1st ed., JAI Press, 2001.

[8] J. XUE, X. LU, Y. DU, W. MAO, Y. WANG, J. LI, Ultrasonic-assisted Oxidation Leaching of Nickel Sulfide Concentrate, Chinese J. Chem. Eng. 18 (2010) 948–953. doi:10.1016/S1004-9541(09)60152-X.

[9] B. Avvaru, S.B. Roy, Y. Ladola, S. Chowdhury, K.N. Hareendran, A.B. Pandit, Sono-chemical leaching of uranium, Chem. Eng. Process. Process Intensif. 47 (2008) 2107–2113. doi:10.1016/J.CEP.2007.10.021.

[10] K.S. Rao, K.L. Narayana, K.M. SWAMY, J.S. Murty, Influence of ultrasound in ammoniacal leaching of a copper oxide ore, Metall. Mater. Trans. B. 28 (2007) 721–723. doi:10.1007/s11663-997-0046-y.

[11] K. Brunelli, M. Dabalà, Ultrasound effects on zinc recovery from EAF dust by sulfuric acid leaching, Int. J. Miner. Metall. Mater. 22 (2015) 353–362. doi:10.1007/s12613-015-1080-4.

[12] M.D. Turan, Z.A. Sari, A. Demiraslan, Ultrasound-Assisted Leaching and Kinetic Study of Blended

Copper Slag, Metall. Mater. Trans. B. (2019). doi:10.1007/s11663-019-01597-x.

[13] F. Xie, H. Li, Y. Ma, C. Li, T. Cai, Z. Huang, G. Yuan, The ultrasonically assisted metals recovery treatment of printed circuit board waste sludge by leaching separation, J. Hazard. Mater. 170 (2009) 430–435. doi:10.1016/J.JHAZMAT.2009.04.077.

[14] S. Lafond, J.F. Blais, R. Martel, G. Mercier, Chemical leaching of antimony and other metals from small arms shooting range soil, Water. Air. Soil Pollut. 224 (2013). doi:10.1007/s11270-012-1371-6.

[15] T. Nedwed, D.A. Clifford, Feasibility of extracting lead from lead battery recycling site soil using high-concentration chloride solutions, Environ. Prog. 19 (2000) 197–206. doi:10.1002/ep.670190312.

[16] A. Smaniotto, A. Antunes, I. do N. Filho, L.D. Venquiaruto, D. de Oliveira, A. Mossi, M. Di Luccio, H. Treichel, R. Dallago, Qualitative lead extraction from recycled lead–acid batteries slag, J. Hazard. Mater. 172 (2009) 1677–1680. doi:10.1016/J.JHAZMAT.2009.07.026.

[17] K. Guemiza, G. Mercier, J.F. Blais, Pilot-scale counter-current acid leaching process for Cu, Pb, Sb, and Zn from small-arms shooting range soil, J. Soils Sediments. 14 (2014) 1359–1369. doi:10.1007/s11368-014-0880-x.

[18] C.A. Johnson, H. Moench, P. Wersin, P. Kugler, C. Wenger, Solubility of antimony and other elements in samples taken from shooting ranges., J. Environ. Qual. 34 (2005) 248–254. doi:10.2134/jeq2005.0248.

[19] F. Forte, L. Horckmans, K. Broos, E. Kim, F. Kukurugya, K. Binnemans, recovery of lead from iron-rich secondary lead smelter residues †, (2017) 49999–50005. doi:10.1039/c7ra09150h.

[20] S. Kim, W. Lee, Y. Son, Ultrasonic and mechanical soil washing processes for the remediation of heavy-metal-contaminated soil, in: Jpn. J. Appl. Phys., Elsevier B.V., 2016: pp. 640–645. doi:10.7567/JJAP.55.07KE04.

[21] J.E. Dutrizac, The leaching of sulphide minerals in chloride media, Hydrometallurgy. 29 (1992) 1–45. doi:10.1016/0304-386X(92)90004-J.

[22] U.G. Gasser, W.J. Walker, R.A. Dahlgren, R.S. Borch, R.G. Burau, Lead release from smelter and mine waste impacted materials under simulated gastric conditions and relation to speciation, Environ. Sci. Technol. 30 (1996) 761–769. doi:10.1021/es940737m.