CHALMERS

Hydrometallurgical treatment of spent alkaline and zinc-carbon batteries

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Abstract

Battery recycling processes for alkaline and zinc-carbon batteries need to be developed to meet the increasing amounts of waste that are not being recycled and sent to landfills. A crucial step in hydrometallurgical treatment, which is one of the main processes for the recycling of these types of batteries, is leaching. The purpose in this project was to investigate the leaching process and to determine the optimal conditions. Leaching experiments with sulphuric acid were carried out with different temperature, acid concentration, time and solid to liquid ratio. Based on the results, the optimal conditions have been discussed, with emphasis on how the conditions would be suitable in an industrial process. It was found that a solid to liquid ratio of 1:20 was showing the optimal values of leaching efficiency, accompanied by 120 min leaching time, 0.5 M sulphuric acid and a temperature at 60 °C.

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1. Introduction

Batteries contain plastic components and metallic species, and the disposal of batteries is of great importance (Sayilgan et al., 2009, Salgado et al., 2003). Most spent household batteries nowadays are landfilled, even though the valuable metals they contain can be recycled (Bernardes et al., 2004). There is a need for development of battery recycling processes, primarily due to environmental concerns and cost of disposal (Veloso, et al., 2005). It is also of interest to recycle batteries due to the value of metals as a secondary raw material (Michelis et al., 2007). The consumption of batteries is increasing (de Souza et al., 2001), followed by more battery waste, which entails a need for a greater landfilling area. To avoid the great amounts of waste, recycling of the batteries could be a solution.

The majority of used household batteries such as zinc-carbon and alkaline batteries are at present collected and landfilled, but research and development of processes to improve the recycling are being performed (Bernardes et al., 2004). The Industrial Materials Recycling research group at Chalmers University of Technology aims at strengthening their competence in recycling of primary consumer batteries. In an ongoing project the purpose is to develop recycling processes for alkaline and zinc-carbon batteries. An aspect of their work entails investigating hydrometallurgical routes with emphasis on leaching and separation of metals.

This project will focus on the leaching in a hydrometallurgical route for recycling of alkaline and zinc-carbon batteries. The optimal conditions for the leaching process will be determined by studying different parameters; time, temperature, acid, acid concentration and solid to liquid ratio. The leachate will be investigated to consider its suitability for precipitation or electrowinning. The study will not cover the removal of impurities.

2. Theory

2.1 Alkaline and Zinc Carbon batteries

The alkaline and zinc-carbon batteries are single-use primary cell batteries used for household purposes, for instance in radios, watches and other consumer products. Alkaline and zinc-carbon batteries generally consist of an external case, which is typically made of plastic and steel. The inside of battery contains an anode, a cathode, an electrolyte and separators (Bernardes et al., 2004).

A zinc-carbon battery has a cathode made of a carbon rod which is in contact with carbon and MnO_2, while an alkaline battery has a similar cathode, except there is a steel case instead of a carbon rod. The anode in a zinc-carbon battery consists of a zinc case and the anode of an alkaline battery is a brass rod with powdered zinc (Bernardes et al., 2004). Alkaline batteries contain potassium hydroxide solution as an electrolyte, which gives higher reactivity and better capacity than zinc-carbon batteries (de Souza et al., 2001). Zinc and manganese represent the greatest percentage of metals in alkaline and zinc-carbon batteries. Therefore, it is manganese and zinc that are of interest when it comes to the recycling of the batteries.

The overall reaction for the discharge of the batteries is (Vincent, 1997):

$$Zn + 2MnO_2 \rightarrow Mn_2O_3 + ZnO \tag{1}$$

The general composition of zinc and manganese in alkaline and zinc-carbon batteries has been described in several articles:

Table 1. General composition of zinc and manganese in different batteries.

Battery	Alkaline (wt. %)		Zinc-carbon (wt. %)	Mixture (wt. %)
Manganese	31.10	36.53	26.3	33.59
Zinc	19.56	17.05	28.3	15.46
Reference	Salgado et al. 2003	Veloso et al. 2005	Peng et al. 2008	De Michelis et al. 2007

The recycling of these batteries is divided into two main processes: pyrometallurgical and hydrometallurgical treatment (Veloso et al., 2005). Pyrometallurgical treatment includes high temperature treatment to volatize the metals (Salgado et al., 2003). Even though the pyrometallurgical technique is the most frequently employed, hydrometallurgical processes are more environmental friendly and have lower energy consumption (De Michelis et al. 2007). Hydrometallurgical treatment is described in detail below.
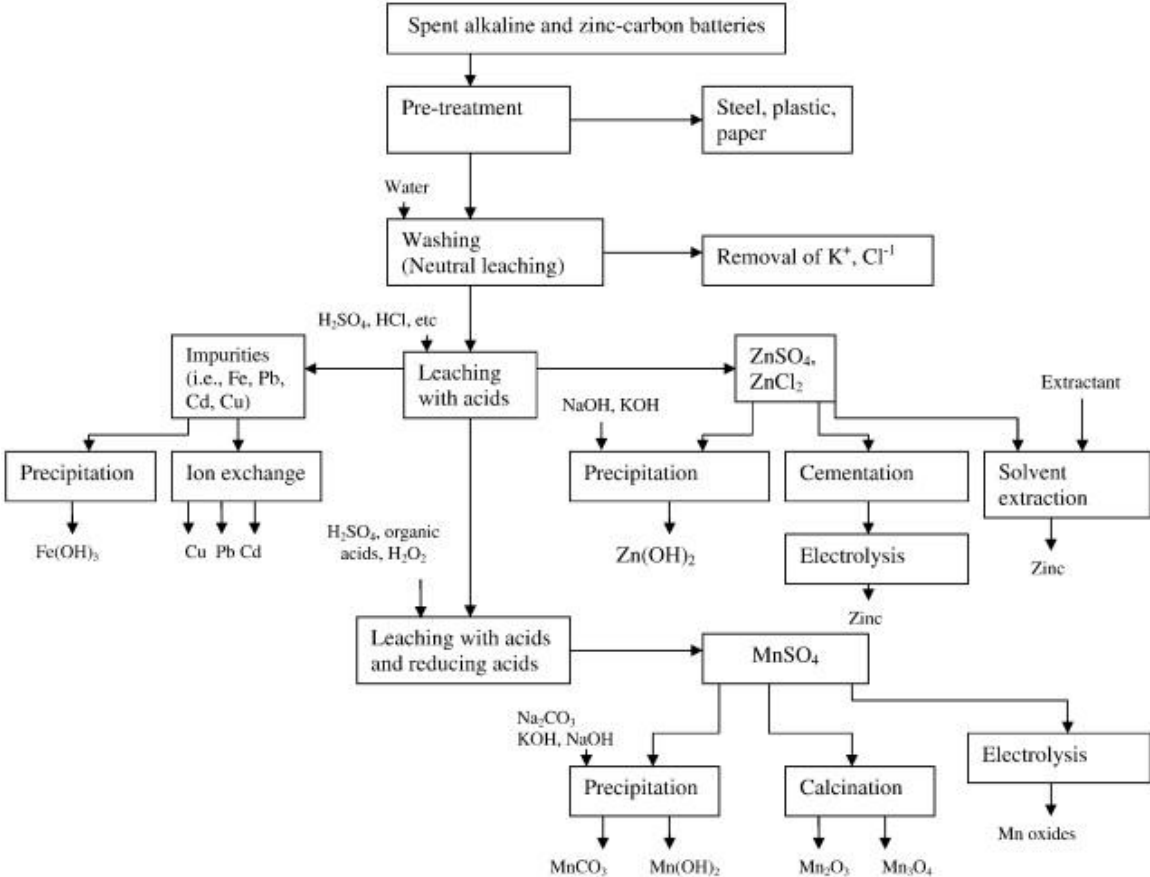
2.2 Hydrometallurgical treatment

Fig. 1. A schematic picture of the general routes in hydrometallurgical treatment (Sayilgan, 2009).

When spent batteries have been collected, they are sorted, often by magnetic separation. Certain battery types contain mercury, and therefore it is important to recycle different batteries in different ways. Alkaline and zinc-carbon batteries do not contain added mercury (Pistoia et al. 2001).

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Once sorted, the batteries are grinded, the case is removed and the remaining part of the battery is shredded down to a fine powder (Pistoia et al. 2001), as represented by the step labelled pre-treatment in Fig. 1. This step is followed by leaching and lastly the metals are recovered, by for example precipitation or electrolysis.

2.2.1 Leaching

Leaching is a process aimed at extracting a solute from a solid with the aid of a suitable solvent. In hydrometallurgical treatment of batteries, the goal is to recover metals by leaching. This is typically performed using an acid. Commonly used acids include sulphuric acid, hydrochloric acid or organic acids. However water could also be used in a process called natural leaching (Veloso et al., 2005).

The most probable reactions for manganese and zinc dissolved with sulphuric acid are the following (de Souza et al. 2001):

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \qquad\qquad (2)$$

$$Mn_2O_3 + H_2SO_4 \rightarrow MnSO_4 + MnO_2 + H_2O \qquad\qquad (3)$$
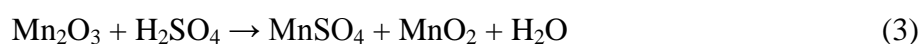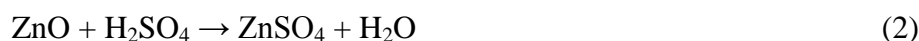
Reaction (1) shows that after the battery has been discharged, the manganese oxide product is Mn_2O_3. However, Mn_3O_4 could also present in the spent battery and leached with sulphuric acid as presented below (de Souza et al. 2001):

$$Mn_3O_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + MnO_2 + 2H_2O \qquad\qquad (4)$$

2.4 Current processes for hydrometallurgical treatment of alkaline and zinc-carbon batteries

There are established hydrometallurgical processes for efficient recovery of metals, even though there is no universally established technique. In a review of technologies for battery recycling, Sayilgan et al. discusses, among others, the REVABAT process that uses treatment with sulphuric acid and recovery of the salt or oxide products of zinc and manganese. Further the BATENUS process is described as a process for recycling batteries with techniques such as liquid-liquid extraction, ion exchange and electrodeposition (Sayilgan et al. 2009).

3. Materials and method

This section describes the material used in the project and the experimental procedure.

3.1 Material

A powder containing spent alkaline and zinc-carbon batteries, was obtained from a landfill in Gothenburg that is managed by Renova, which is a recycling company. Renova process their collected batteries by crushing and magnetic separation. The non-magnetic fraction is then landfilled.

3.2 Preparation of samples from the batteries

Two samples were prepared, one for analysis of the powder and one sample for leaching. To gain representative samples, the quartation technique was used: a heap of the landfill battery powder was divided into four parts, two parts were excluded and the remaining two mixed into one heap. This procedure was repeated until 100 g of powder was acquired. Finally, the powder was grinded with IKA M20 universal mill into a more homogeneous sample. Grinding time for the sample for analysis was 2 minutes and for the leaching sample 45 seconds.

3.3 Leaching with different temperature and acid concentration

Sulphuric acid with three different concentrations, 0.5, 1 and 2 M, were prepared. The leaching experiment was carried out in a 100 mL beaker with magnetic stirring. 50 mL of sulphuric acid was added to the beaker. From the prepared sample of battery powder,   1.0 g was added at t=0 min. The temperature was held at 20, 40 or 60 degrees.

After 5 min the first sample was taken using a syringe with an attached filter. The sampling continued at 10, 15, 45, 60 and 120 min. The volume of each sample was 1 mL. The same set of conditions (acid concentration and temperature) was replicated three timed for each experiment. The table below shows the various combinations of conditions for the experiments.

Table 2. Leaching with different parameters. Focus on the effect of temperature on the leaching.

Acid concentration (M)	Temperature (°C)			Leaching time and sampling (min)	Solid to liquid ratio (g:mL)
0.5	20	40	60	5, 10, 15, 45, 60, 120	1:50
1	20	40	60	5, 10, 15, 45, 60, 120	1:50
2	20	40	60	5, 10, 15, 45, 60, 120	1:50

3.4 Leaching with different temperature, acid concentration and solid to liquid ratio.

Leaching with focus on the solid to liquid ratio was carried out according to the same procedure described above. Instead of solid to liquid ratio 1:50, solid to liquid ratio 1:10 and 1:20 were investigated. The acid concentration 0.5 and 1 M was used and the sampling was done after 5, 15, 60 and 120 minutes. Each experiment was triplicated.

Table 3. Leaching with focus on the parameter solid to liquid ratio.

Acid concentration (M)	Temperature (°C)			Leaching time and sampling (min)	Solid to liquid ratio (g:mL)
0.5	20	40	60	5, 15, 60, 120	1:20
1	20	40	60	5, 15, 60, 120	1:20
0.5	20	40	60	5, 15, 60, 120	1:10
1	20	40	60	5, 15, 60, 120	1:10

3.5 Analysis of liquid samples from leaching

Standard solutions, for a calibration curve, containing 0 ppm, 1ppm, 5 ppm, 10 ppm, 20 ppm and 40 ppm were prepared from solutions of the following metals; Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb and Zn. For a standard solution with a concentration of 40 ppm, 2 mL of each metal solution was added and then diluted to 50 mL with hydrochloric acid. To gain lower concentrations, the 40 ppm solution was diluted.

3.5.1 Samples dissolved for analysis

From the samples prepared for analysis, four samples of 0.2 g of powder were dissolved in 30 mL each of aqua regia (3:1 volume ratio of $HCl:HNO_3$) and stirred with heat over night. The samples were filtered and the remaining solutions were diluted 100 times with hydrochloric acid and then analysed in Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES).

3.5.2 Samples from leaching

After the last sampling at 120 minutes, the remaining solution was filtered and the filter was collected. The samples from the first leaching (paragraph 3.3) were diluted 100 times and samples from the second leaching (paragraph 3.4) 200 times with hydrochloric acid prior to ICP-OES analysis.

4. Results and discussion

4.1 Results from analysis

From the ICP results the metal composition of the samples was given and the leaching efficiency could be calculated by first processing the results from the samples prepared solely for analysis. The results and discussion will mostly focus on the leaching of zinc and manganese, but other metals were investigated as well, to determine whether they had been leached from the solution. As stated in the introduction, this project will not cover the removal of impurities and therefore the results from the leaching of these will not be discussed further.

The percentage of metals was calculated with formula 1 (appendix).

Table 4. Metal content in the battery powder.

Metal	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Sample 4 (%)	Average percentage in sample (%)
Cd	0.011	0.0084	0.0082	0.0073	0.0086
Cr	0.0088	0.0054	0.0062	0.0065	0.0068
Cu	0.030	0.027	0.020	0.027	0.027
Fe	1	0.82	0.85	0.92	0.93
Hg	0.0	0.0	0.0	0.0	0.0
K	4	3.8	3.9	3.89	3.96
Mn	31	31	30.9	31	30.9
Ni	0.20	0.12	0.19	0.22	0.20
Zn	24	23.8	23.9	24.3	24

In table 1 on page 4, the general percentage of Zn and Mn varies from 15.46-28.3 % Zn and 26.3-36.53 Mn. The results from this work in table 4 (24.02 % Zn and 30.88% Mn), are similar to the values in table 1.

The amount of metals in each sample contained prior to leaching was calculated by multiplying the weight with the percentage of metals in the battery powder in table 4. Later the leaching efficiency could be calculated using formula 2 (appendix).

4.2 The optimal conditions for leaching

From the generated leaching efficiency values, it is possible to discuss what the optimal combination of acid concentration, temperature and solid to liquid ratio is. To define the meaning of the term optimal conditions, it is important to state that optimal conditions are not the same as the conditions which gives the highest leaching efficiency. For an industrial application it will be optimal to use conditions with as low temperature, acid concentration and solid to liquid ratio as possible. Higher temperatures require more energy and more concentrated chemicals, which increase the costs. A high solid to liquid ratio entails higher amount of chemicals for the leaching process.

Conditions with lower temperature may give similar leaching efficiencies as those with higher temperatures, and in such cases it will be more suitable to use the lower temperature. Firstly, the influence of temperature will be discussed in order to understand the effect of kinetics on the leaching.

4.2.1 Temperature

The temperature influence on the leaching of zinc and manganese at different acid concentrations shows that the highest leaching efficiency is reached at 60 °C. In the leaching of zinc similar leaching efficiencies are also noted at 40 °C and 20 °C (figure 2, 3 and 4 on page 12). At 40 °C, the behaviour is varying for different acid concentrations, which makes it hard to draw conclusions from these results. However, the leaching of manganese (figure 5, 6 and 7 on page 13) indicates a significant difference between 20 and 60 °C.

In the graphs for leaching of manganese, the highest leaching efficiency values could be noted around 45%. This relatively low value could be explained by the partial dissolution of manganese oxide with sulphuric acid (reaction 3 and 4, page 6). Manganese oxide cannot be leached 100% with only sulphuric acid.
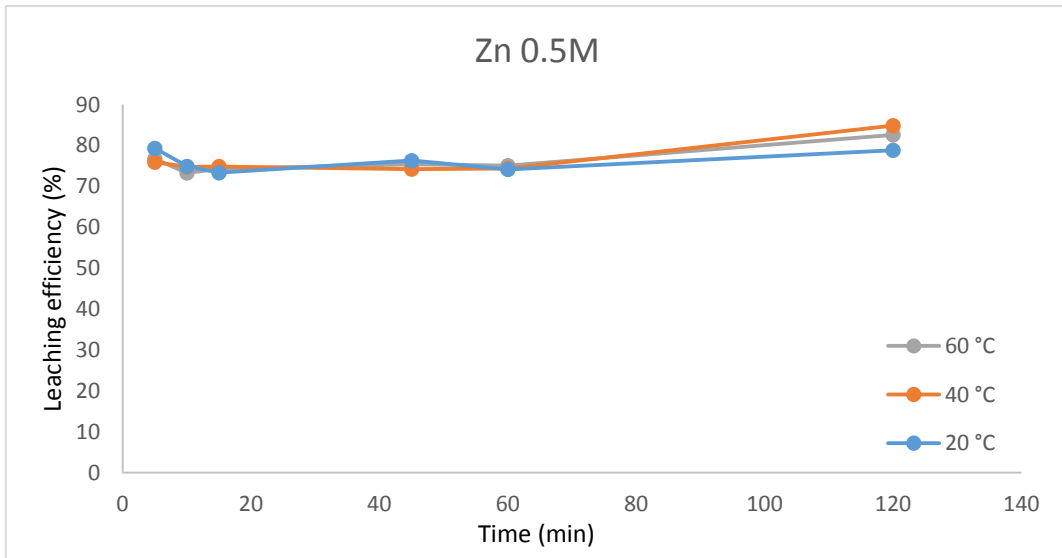
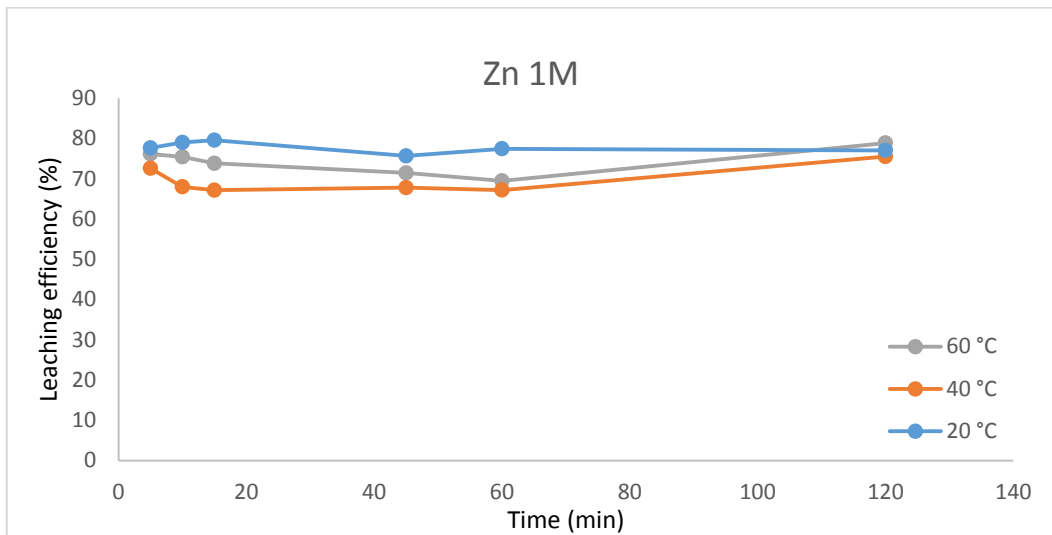**Fig. 2.** Leaching efficiency of zinc for different temperatures with 0.5 M sulphuric acid.

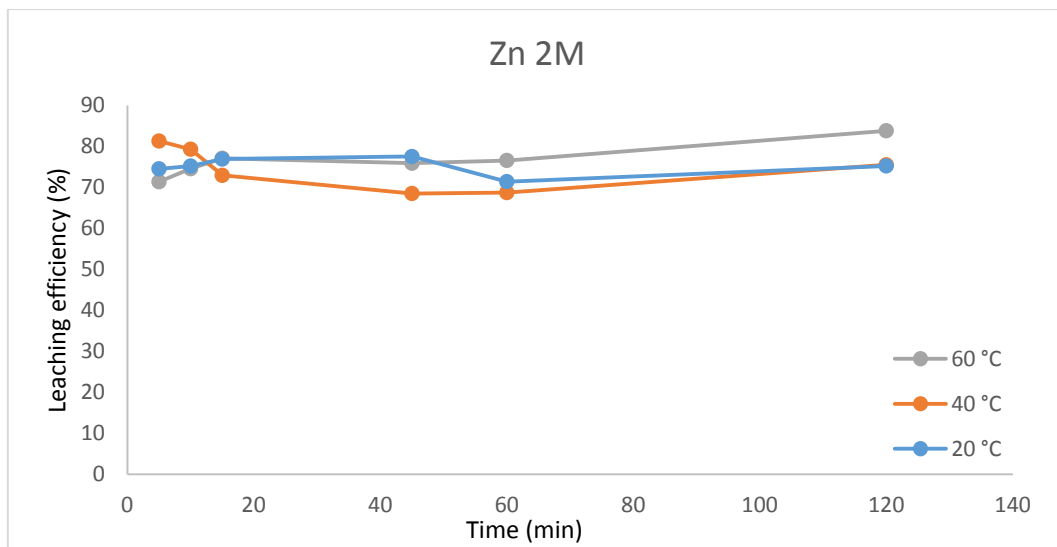**Fig. 3.** Leaching efficiency of zinc for different temperatures with 1 M sulphuric acid.

Fig. 4. Leaching efficiency of zinc for different temperatures with 2 M sulphuric acid.
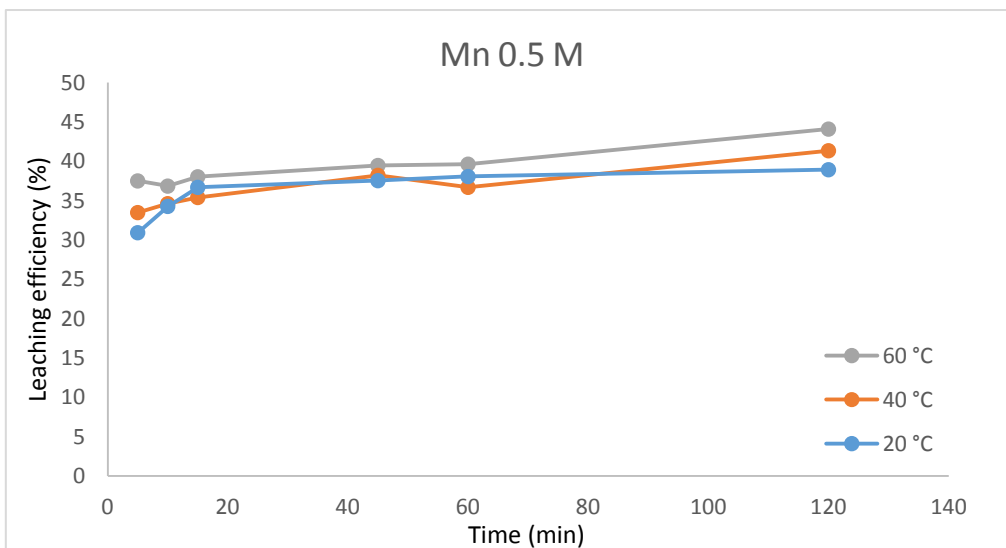
Fig. 5. Leaching efficiency of manganese for different temperatures with 0.5 M sulphuric acid.
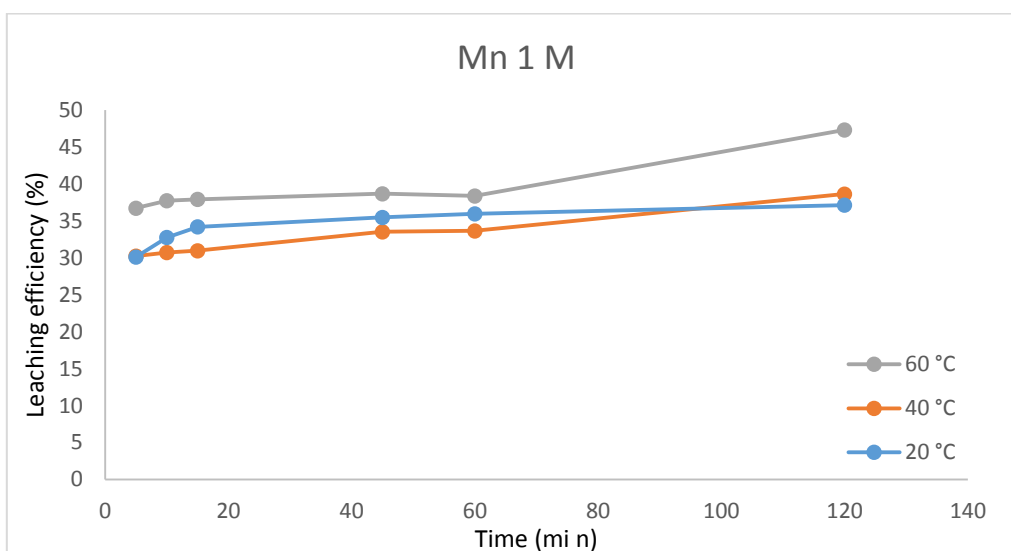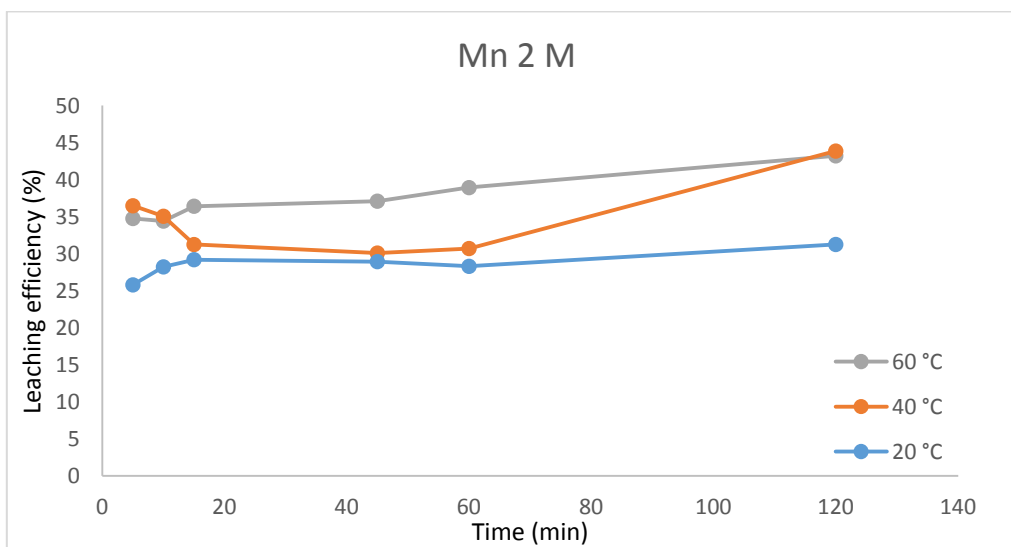

Fig. 6. Leaching efficiency of manganese for different temperatures with 1 M sulphuric acid.

Fig. 7. Leaching efficiency of manganese for different temperatures with 2 M sulphuric acid.

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4.2.2 Acid concentration

In the first leaching the acid concentration was investigated at 0.5, 1 and 2 M sulphuric acid. No significant difference between the concentrations could be observed (see figure 8, 9 and 10), therefore the investigated acid concentrations did not seem to affect the leaching.
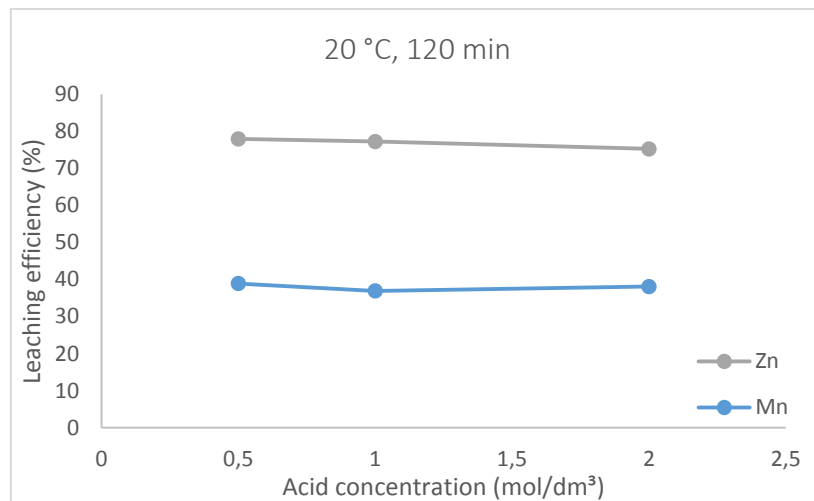
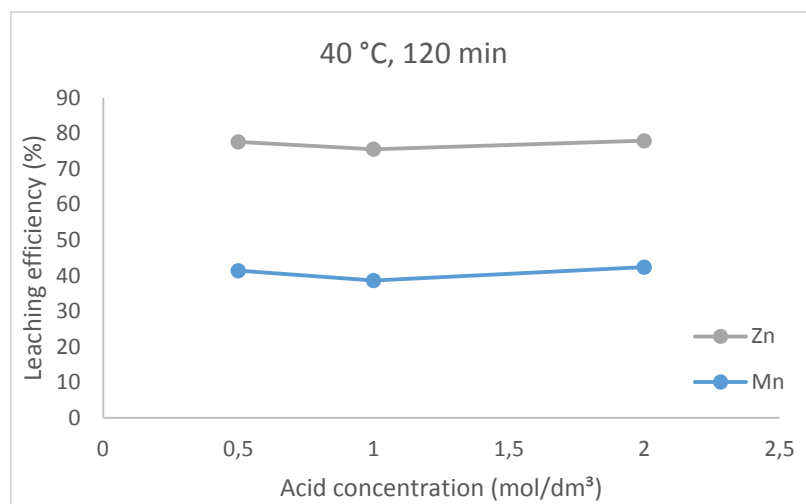**Fig. 8.** The influence of acid concentration on the leaching efficiency for 20 °C, 120 min.

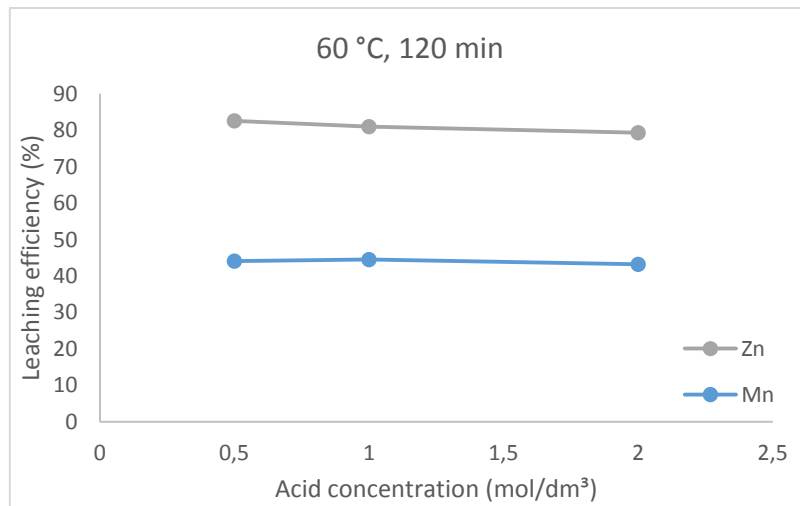**Fig. 9.** The influence of acid concentration on the leaching efficiency for 40 °C, 120 min.

Fig. 10. The influence of acid concentration on the leaching efficiency for 60 °C, 120 min.

4.2.3 Solid to liquid ratio

In the second leaching the aim was to find the optimal solid to liquid ratio, because the optimal acid concentration and temperature had already been investigated in the first leaching. The plots show (figure 11-16) that 1:20 and 1:50 clearly generates the highest leaching efficiency. No significant difference between 1:20 and 1:50 could be observed.
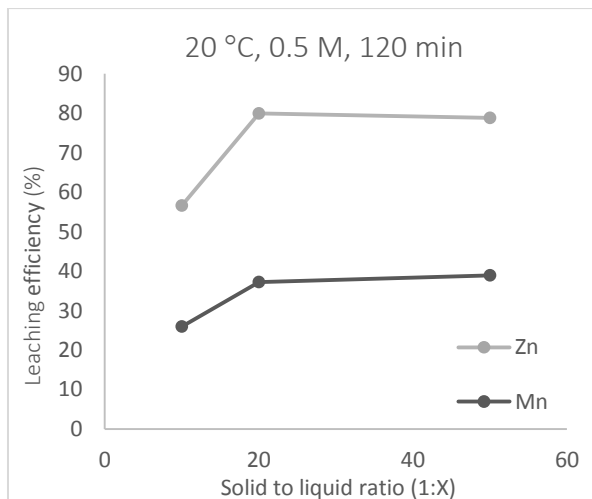

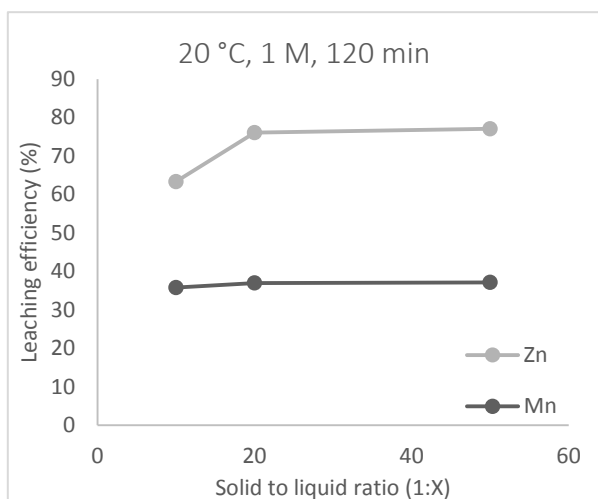**Fig. 11.** Behavior of solid to liquid ratio at 20 °C, 0.5 M.

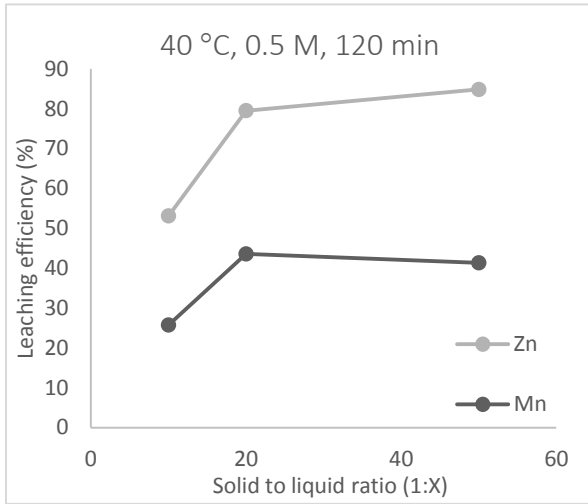**Fig. 12.** Behavior of solid to liquid ratio at 20 °C, 1 M.

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Fig. 13. Behavior of solid to liquid ratio at 40 °C, 0.5 M.
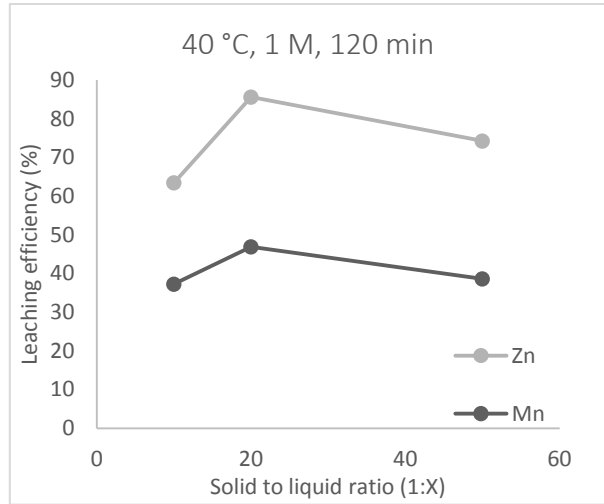

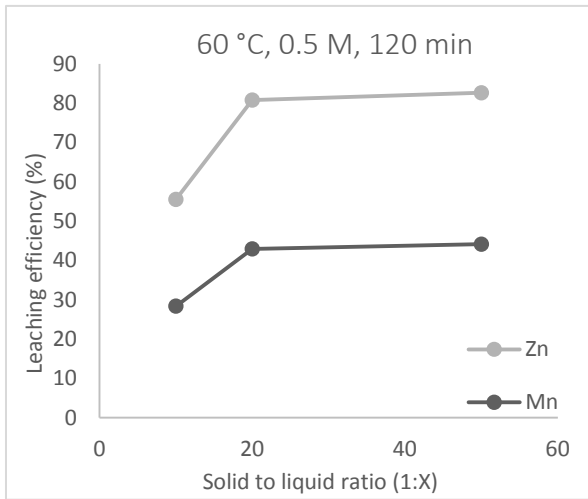**Fig. 14.** Behavior of solid to liquid ratio at 40 °C, 1 M.

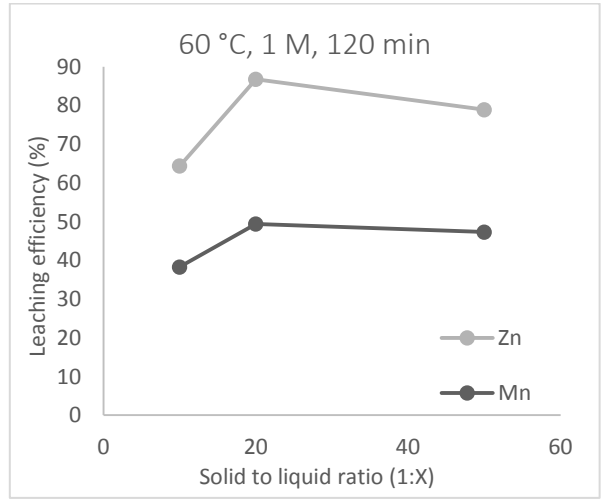**Fig. 15.** Behavior of solid to liquid ratio at 60 °C, 0.5 M.

Fig. 16. Behavior of solid to liquid ratio at 60 °C, 1 M.

4.2.4 Time

Even though the results do not perfectly exhibit the expected behaviour – increasing leaching efficiency with time – the results at 120 min gave the highest values in almost all cases.

5. Conclusion

The purpose of this study was to investigate the leaching process in a hydrometallurgical route for the recovery of zinc and manganese. It has been fulfilled by determining the optimal parameters for leaching; time, temperature, acid concentration and solid to liquid ratio.

By calculating the leaching efficiency for each experiment, the optimal conditions could be set. Three solid to liquid ratios were investigated: 1:10, 1:20 and 1:50. 1:20 generated same leaching efficiency as 1:50 and was therefore determined to be the optimal condition. The acid concentrations did not show any difference in leaching efficiencies, and therefore the lowest possible was chosen. The effect of temperature gave varying results, leaving data difficult to interpret. However the highest leaching efficiencies were obtained at 60 °C, and in the leaching of manganese a significant difference between 20 and 60 °C could be observed. The optimal temperature was decided to 60 °C. The optimal choice for time condition was set at 120 min, because the highest leaching efficiencies were obtained at this time. To sum it up, 120 min, 60°C, solid to liquid ratio 1:20 and 0.5 M sulphuric acid compose the optimal conditions for the investigated leaching process. Due to time limit, no extended investigation of the precipitation or electrowinning process was carried out. However, the product from a trial based on the Newmont process had a purity of 99.5% and 50% of manganese was precipitated. The precipitation study needs further investigation in order to determine the suitability of the produced leachate.

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Appendix

Calculations

<u>Formula 1 – Percentage in sample</u>

To be able to calculate the leaching efficiency, the percentage of metals in the original sample has to be known. The value in the formula below is the value from the ICP analysis. 5000 is dilution factor and 200000 stands for the weight before analysis in µg.

$$Percentage\ in\ sample = (value \cdot 5000)/200000) \cdot 100$$

<u>Formula 2 – Leaching efficiency</u>

The value is the measured value from the analysis of the leached samples. The dilution factor is the factor the sample is diluted with for the ICP analysis. Volume is the volume of the experiment at the sampling time (example: for 5 min, there is 50 mL in the experiment with 1:50 solid to liquid ratio, at 10 min there is 49 mL and so on.).

Step 1:

$$Amount\ in\ sample = value \cdot volume \cdot dilution\ factor$$

Step 2:

$$\left(\frac{Amount\ in\ sample}{Amount\ of\ original\ sample}\right) \cdot 100 = Leaching\ effiency\ (\%)$$

Method of analysis

<u>Inductively coupled plasma</u>

Inductively coupled plasma (ICP) is a tool used for elemental chemical analysis. The plasma has the ability to atomize, excite and ionize an element. Therefore ICP is suitable for analysis of metal elements in the spent batteries investigated in this project.