Integration of physical operations in the hydrometallurgical processing of spent Zn-MnO$_2$ batteries

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Abstract

The recycling of spent Zn-MnO$_2$ batteries by hydrometallurgy involves the leaching of material previously treated by physical processing to allow the liberation of electrode particles and the separation of unwanted scrap. The integration of these physical operations with leaching is therefore crucial for the optimization of the process, allowing achieving high recovery yields of zinc and manganese and minimizing reactants consumption and iron contamination. In this paper, several options involving physical processing and leaching with sulphuric acid are presented and discussed. After batteries shredding and disaggregation, the separation of steel scrap was performed by sieving or magnetic separation, and the remaining solids were treated by leaching. These options were compared, in terms of metals recovery and contamination, with the alternative of direct leaching of all the shredded fractions without physical treatment. The separation of the steel scrap by sieving or magnetic separation allowed the removal from the circuit of 37 or 49% of iron, respectively, with losses of 15 or 6% of zinc and 2 or 4% of manganese. Therefore more than 50% of iron remained in the process, which was attributed to the presence of iron oxides formed by the corrosion of the battery cases. In the leaching operation, zinc dissolution was very effective (yields above 97%) while manganese is strongly depended from the process option, being its leaching proportional to the presence of scrap (yields of 80%, 56% and 43%, respectively in direct leaching, sieving / leaching and magnetic separation / leaching). These results showed that iron plays an important role in the reductive leaching of manganese species (III or IV), and so the presence of steel scrap in leaching, besides disadvantages concerning solutions contamination, contributes positively for the leaching efficiency.

1 Introduction

Recycling of spent batteries is the most appropriate option for management of these potential hazardous waste. Besides environmental advantages, recycling also allows some economic compensation through the recovery of the contained metals. Zn-MnO$_2$ batteries can represent more

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than 70% of the domestic spent batteries flow being therefore important to be considered in the management of this type of residues.

The treatment of spent $Zn-MnO_2$ batteries can be performed in dedicated processes or, in certain cases, using existing facilities such as the Waelz process or the Imperial Smelting Process. In dedicated processes [1], two main alternatives are possible, namely the thermal treatment (pyrometallurgy) [2,3] or the aqueous processing (hydrometallurgy) [1,4,5]. Thermal processes are usually based on zinc volatilization producing zinc in metallic or oxide forms while iron and manganese can be recovered as Fe-Mn alloys or mixed scrap for further treatment. These processes can in addition allow recovering some organics by pyrolysis technology. The hydrometallurgical approach, as presented in Figure 1, is based on dissolution of metal phases (essentially zinc and manganese oxides) in aqueous media, usually using mineral acids as leachants. The solutions are further treated for purification, metals separation and recovery. The hydrometallurgical option is more versatile considering the final metal species produced, allowing easily to adequate the process according with the market needs. After extraction, zinc can be obtained as metal by electrowinning or as sulfate by crystallization, while manganese can also be produced as sulfate salt or precipitated as hydroxide/carbonate.
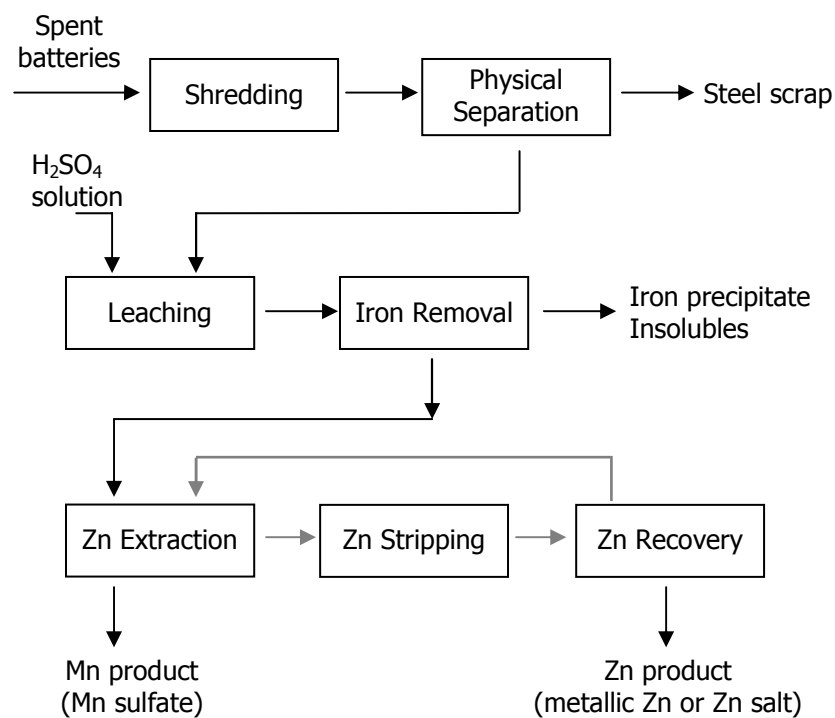

Figure 1 – General diagram of processing spent $Zn-MnO_2$ batteries by hydrometallurgy.

In this paper, a research work on the recovery of metals from spent $Zn-MnO_2$ batteries (alkaline and saline types) is presented. A chemical process by hydrometallurgy is being envisaged, involving leaching of batteries in sulfuric acid solutions [6,7]. To optimize the chemical treatment, the integration with the previous physical operations is mandatory. These operations can include shredding [8-10] and separation of scrap (mainly steel from battery cases) by physical methods. The relationship between physical and chemical steps has several issues: (1) the separation of steel allows

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to obtain a fraction more concentrated in the electrode material (Zn and Mn) reducing costs of its further treatment; (2) iron is an important contaminant of leach solutions and can affect negatively zinc separation and recovery; (3) iron and other scrap components can also have some positive effects in the chemical treatment.

In order to investigate the above indicated aspects, a research experimental program was carried out, which included several process options, combining physical separation and leaching trials, being the results obtained here presented and discussed.

2 Process options

As referred, the research involved the evaluation of several options of physical processing and its integration with leaching. Basically it was intended to compare the performance of direct leaching of shredded batteries with the alternative of previously separate most of the iron present in the scrap by physical methods and to perform the leaching in a fraction rich in the metals of interest (zinc and manganese). Three options were considered as illustrated in Figure 2: the first (DL) corresponded to the reference situation in which all the shredded batteries were leached; the second one (SL), after shredding operation the solids were disaggregated using a low-impact hammer mill to allow the liberation of stuck electrode particles in the coarse materials and then steel scrap was removed by sieving (at 1.4 mm aperture), being only the fines leached; the third option (ML) corresponded to the separation of magnetic materials (steel scrap) by magnetic separation and therefore only the non-ferrous fraction was leached. The behavior of the system was compared in terms of metals recovered (Zn and Mn) in the leach liquor, the iron contamination in the leachate and the losses of zinc and manganese in the solids removed by physical methods.

1 ... Initial spent batteries
2 ... Solids after Size reduction and disaggregation
3 ... Solids rejected in physical processing
4 ... Solids recovered and fed to leaching
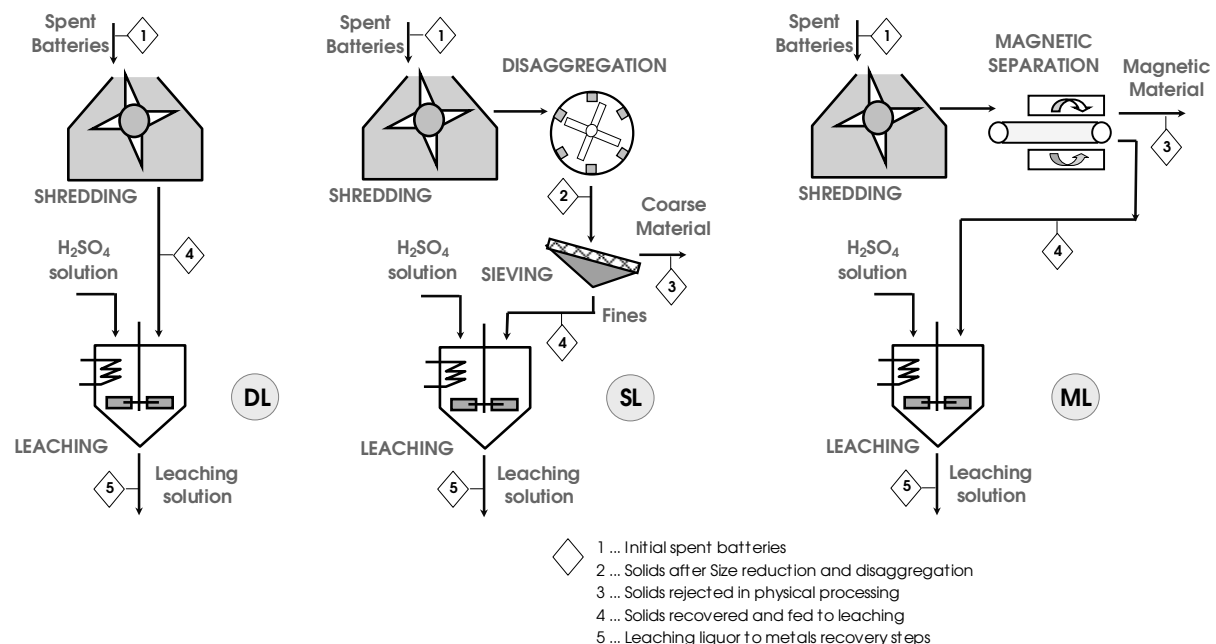5 ... Leaching liquor to metals recovery steps

Figure 2 – Process options considered for the integration of physical operations with chemical treatment by leaching: DL = direct leaching; SL = sieving - leaching; ML = magnetic separation – leaching.

3 Experimental

The spent batteries used in the experimental studies were collected in a collection point. The sample used was composed by mixing alkaline and saline type batteries in a proportion similar to the market. The several sizes and shapes were also utilized according with market distribution. Average composition of the sample used in this research is presented in Table 1.

Batteries were shredded in two steps, the first with a grab shredder (Erdwich EWZ 200) and the second one with a cutting mill (Retsch SM2000), using in both cases a bottom discharge grid of 6 mm. Particle size characterization was proceeded by sieving with DIN sieve series with a vibrating shaker (Retsch AS-200). Concerning physical separation steps, magnetic separation was performed with a lab belt magnetic separator (Permroll MS), and the disaggregation of solids was carried out with a lab low-impact hammer mill (IKA MF 10).

Leaching experiments were carried out in mechanically stirred reactors (1 L capacity) with temperature control. Samples of leachates were collected periodically and analyzed to evaluate the leaching yields along the reaction time. In the end of each experiment, the solution was filtered and the remaining solids washed with water, dried and analyzed. Elemental chemical analysis of solutions was performed by atomic absorption spectrometry (AAS, Thermo Elemental 969AA). Solid samples were previously solubilized with $HCl/HNO_3/HF$ mixtures in a microwave digester (CEM 2000) and the resulting solutions were therefore analyzed by AAS.

Table 1- Chemical composition of $Zn-MnO_2$ spent batteries used in this work.

	Zn	Mn	Fe
Elemental Composition (%)	20	24	23
Common compounds found	ZnO; $Zn_5(OH)_8Cl_2 \cdot H_2O$	MnO_2; $MnO.Mn_2O_3$; $ZnO.Mn_2O_3$; MnOOH	Steel
Other species	Graphite, plastic/rubber insulators, copper wires, metal/carbon collectors, polymer separator, impregnated electrolytes (KOH, $ZnCl_2$, NH_4Cl), paper/plastic and ink (from labels).		

4 Results and Discussion

4.1 Physical Processing

Spent batteries were shredded in two steps resulting particles with an average size diameter (d_{50}) of 0.85 mm. Size distribution is presented in Figure 3. The distribution is relatively wide being the characteristic diameters d_{10} and d_{90}, 0.09 and 2.4 mm respectively. The solids obtained in the shredding operation were sorted and used in the subsequent experimental tests.

After shredding, the separation processes used involved sieving (after disaggregation) in option SL and magnetic separation in option ML. These operations allowed separating a Fe-rich fraction, to be rejected, from the electrode-rich fraction for further treatment by hydrometallurgy. Results obtained are sumarized in Table 2, including the elemental composition in each fraction and the metals recovery, which was calculated from composition and weight distribution.
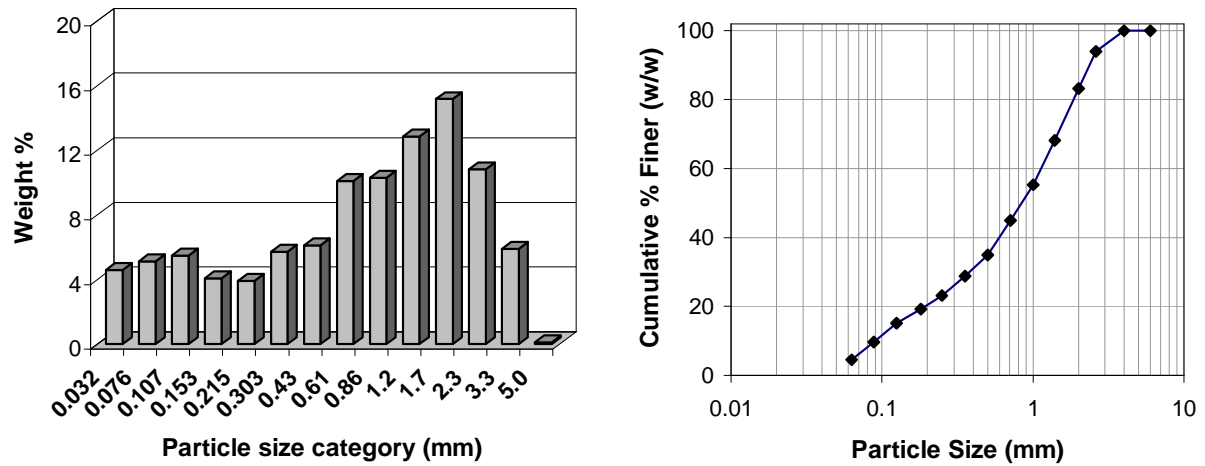
Figure 3 – Particle size distribution and cumulative curve of shredded batteries.

Table 2 – Results of the physical processing tests: composition of fractions and distribution of each metal by the separated fractions.

Fraction	Option	Composition (% w/w)			Metals distribution by fraction (% w/w)		
		Zn	Mn	Fe	Zn	Mn	Fe
Initial		20	24	23	100	100	100
Rejected fraction	DL	-	-	-	-	-	-
	SL	20	3.4	59	14.5	2.3	37
	ML	8.6	7.0	80	5.8	3.8	49
Recovered fraction	DL	20	24	23	100	100	100
	SL	20	28	17	85.5	97.7	63
	ML	22	28	13	94.2	96.2	51

In the process SL, only 37% of iron was removed from the circuit by sieving the coarse fraction above 1.4 mm, being the remaining iron contaminating the fines. Concerning zinc, about 15% were lost in the gross fraction, probably aggregated to the large scrap fragments. Manganese lost was substantially lower (2%) because it is present as a fine powder together with graphite particles. When magnetic separation is used (process option ML) only about 50% of iron was removed. This can be explained by the presence of a large quantity of oxidized steel due to corrosion of battery cases. Zinc loss in this case was only 6% while manganese was near 4%. The physical processing allowed decreasing iron content in the solids to be processed by leaching, from the initial value of 23% to 17 or 13% (respectively in SL and ML cases) and to increase manganese grade from 24% to 28%. Zinc content was not substantially changed.

4.2 Leaching studies

The following investigations were carried out in order to evaluate the leaching behavior for the several options. Leaching was carried out with 0.7 M sulfuric acid solutions, at 90ºC and using a liquid/solid ratio of L/S=14 L/kg. According to previous studies, these conditions allow to obtain a

final leach liquor with a pH value near to 1.5, which is considered adequate to proceed with solution purification through iron precipitation.

Figure 4 shows the leaching yields of zinc and manganese as a function of time. Zinc dissolution was accomplished in few minutes (100% yield in less than 1/2 h) whatever the process option used, due to the high reactivity of zinc oxide in acid media. Manganese behavior was quite different, being the leaching yields substantially lower than for zinc and depended from the process option. Direct leaching allowed higher manganese recoveries (up to 80% after 3 hours of reaction), being considerably lower in the cases where the scrap was partially removed (SL and ML). This behavior seems to indicate that iron (Fe^o) from the steel scrap plays a role in the leaching of manganese, probably acting as reductant of manganese species of higher oxidation state (III or IV). When metallic iron was not practically present (option ML) manganese leaching was depressed. In the case of option SL, some iron particles present in the fines are expected to be found and so the leaching curve of manganese lied between the other two curves.
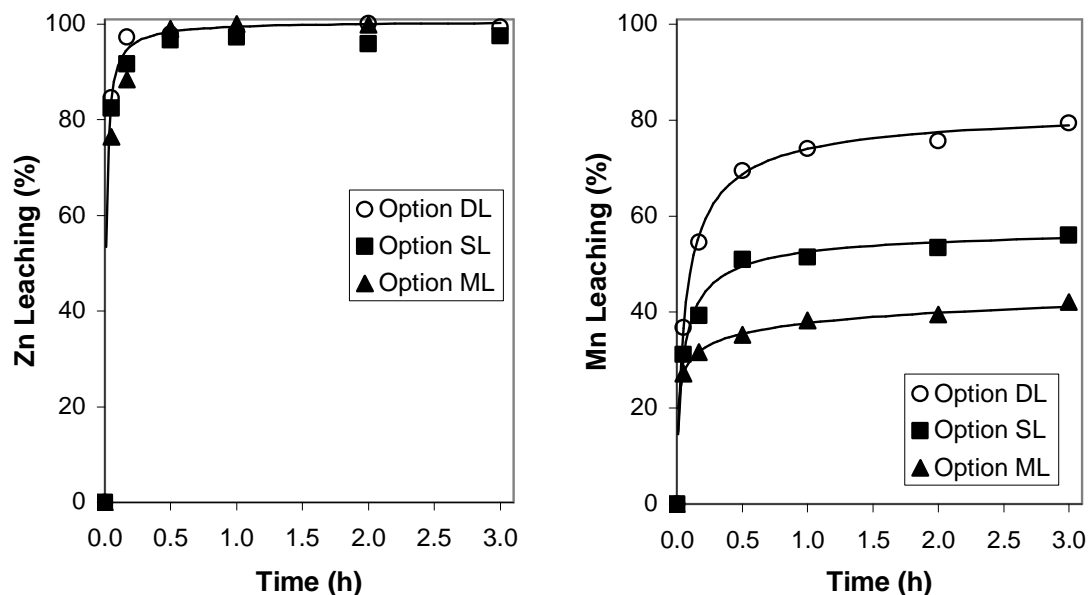

Figure 4 – Leaching yields of Zn and Mn as a function of time, for the several options tested. Leaching conditions: T=90ºC; [H$_2$SO$_4$]=0.7 M; L/S=14 L/kg.

Iron contamination in leach liquors is another important parameter for process evaluation. Figure 5a shows the Fe solution concentrations, in g/L, achieved in each condition, as a function of time. In the first hour of reaction, iron dissolution is higher when direct leaching is used (up to 7 g/L Fe), since the initial iron content of the solids is also higher in this case. When physical separation was performed iron contamination of liquors was lower, mainly in the option corresponding to magnetic separation (about 3 g/L and 6 g/L for options ML and SL, respectively, for the same reaction time). The behavior of iron in solution changed significantly after 1 hour, being observed a strong decreasing in concentration until 2.6 g/L Fe in option DL. This can be explained by the precipitation of iron due to acid consumption (pH reached 1.6 after 1 hour). In the other cases, the resulting pH values were always lower (1.2-1.3) and mostly of the iron solubilized remained in solution. The final metal concentrations achieved (Figure 5b) were relatively similar in case of zinc (14-16 g/L Zn) but quite

different for manganese (from 8 to 14 g/L Mn depending from the process option). Final iron concentrations found ranged from 2.6 g/L for option DL to 5.3 g/L for option SL. To maximize Zn and Mn recovery and minimizing Fe contamination, direct leaching seems to be more adequate.
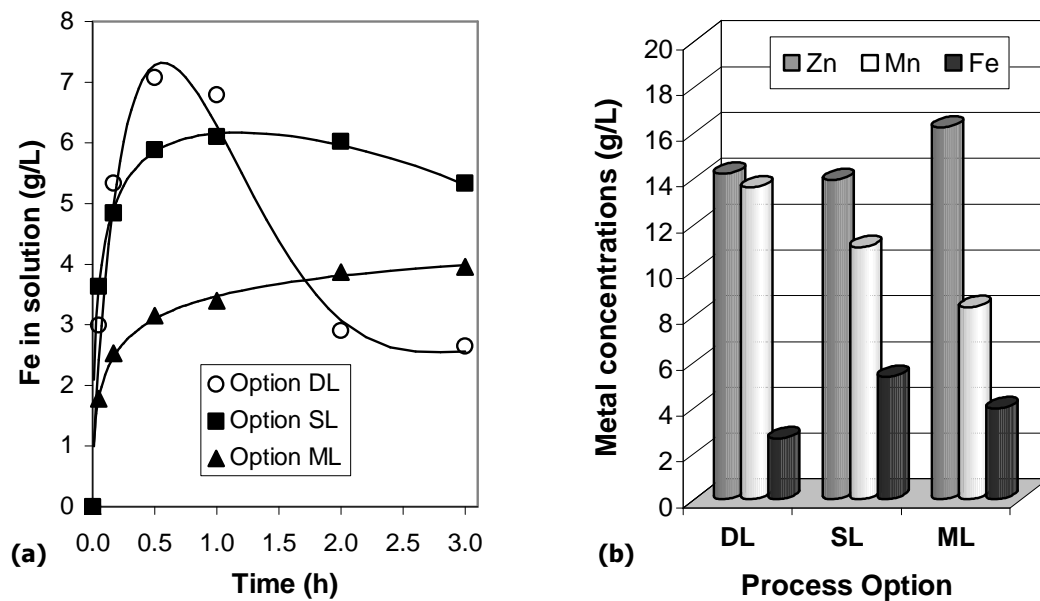

Figure 5 – Iron contamination of leach solutions for the several options tested: (a) Evolution of iron concentration as a function of time; (b) Comparison of Zn, Mn and Fe concentrations after 3h of reaction. Leaching conditions: T=90ºC; $[H_2SO_4]$=0.7 M; L/S=14 L/kg.

4.3 Overall yields and discussion of options

Based on the experimental results obtained in physical processing and leaching, the overall mass balances for each metal were carried out in order to evaluate the recoveries and losses attained in the three process options tested. Table 3 shows the results of the calculations made.

Zinc recoveries are generally higher. In option DL, only 1.3% of zinc was not recovered by leaching. In options SL and ML, zinc losses were mainly found in the physical separation steps (15% and 5.8%, respectively in rejected coarse and magnetic fractions). Manganese losses were substantially higher. Maximum recovery (80%) was achieved in process option DL. When physical separation steps were used, the recoveries decreased, but losses were not atributed to those steps. In fact, 43 or 55% of manganese were lost in the leaching (in options SL and ML, respectively) in the form of unreacted species. Therefore overall recoveries of Mn were strongly affected being only 55 or 41% for those options. Concerning iron, physical separation allowed removing 37 or 49% (in options SL and ML, respectively), and in the leaching an amount of iron remained insoluble and the other part precipitated after being dissolved.

Table 3 - Overall weigh distribution of metals in the process (in %) and evaluation of recoveries and losses, for the three options tested.

		Option DL Direct Leaching	Option SL Sieving - Leaching	Option ML Magn. Separ. - Leaching
ZINC				
Loss	Physic. proc.	0	15	5.8
	Leaching	1.3	2	0.7
	Total	1.3	17	6.5
Recovered (in solution)		98.7	83	93.5
MANGANESE				
Loss	Physic. proc.	0	2	4
	Leaching	20	43	55
	Total	20	45	59
Recovered (in solution)		80	55	41
IRON				
Removed	Physic. proc.	0	37	49
	Leaching	84	35	29
	Total	84	72	78
In solution		16	28	22

Results obtained indicated that the physical steps, envisaging the advantage of removal part of steel scrap, are responsible by substantial losses of zinc and also some manganese, since electrode particles containing these two metals were found fixed in the scrap fragments. Moreover the absence or iron in the leaching operation decreased the efficiency of manganese reactions. From these results it seems that, in the conditions tested, the direct leaching of the shredded batteries can allow to achieve higher recovery of metals.

5 Conclusions

In this paper, a laboratory study of metals recovery from $Zn-MnO_2$ spent batteries by physical processing and acid leaching is presented. The integration of physical steps, such as sieving or magnetic separation, with chemical processing by leaching was evaluated and subsequently the metals recovery was assessed. Magnetic separation of ferrous scrap allowed removing about half of the iron while sieving out the coarse fraction removed only 37% of iron. Large amounts or iron were not efficiently removed because was present as oxide. Losses of zinc in those fractions were 6% and 15% respectively, while manganese losses were less than 4%. Zinc recovery by leaching was almost complete while manganese leaching strongly depended from the previous steps, being as higher as more steel scrap was present in the leaching operation. Overall manganese recovery varied from 41% (in option including magnetic separation) to 80% (in option of direct leaching of shredded materials).

Acknowledgements

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