MultiScience - XXX. microCAD International Multidisciplinary Scientific Conference
University of Miskolc, Hungary 21-22 April 2016, ISBN 978-963-358-113-1

PROCESSING OF SECONDARY RAW MATERIALS BY HYDROMETALLURGICAL METHODS FOR THE RECOVERY OF ZINC

Noémi László[1], Tamás Kékesi[2]
[1]PhD student, [2]Professor,
Institute of Chemical Metallurgy, University of Miskolc, Hungary;
[1] metlnoe5@uni-miskolc.hu, [2]kekesi@uni-miskolc.hu

ABSTRACT

The main purpose of this research was to find a suitable, economical and simple way to recover mainly zinc from waste Zn-Mn batteries. The most feasible way can be leaching the soluble zinc content in diluted sulphuric acid after a proper physical separation of the raw material. The leachate however contains an equally high concentration of manganese, and the residual iron content – not removed by magnetic separation – goes also into solution. Other significant impurities may be copper, nickel and cadmium, by experience. Electrolytic deposition of technically pure zinc is made possible by an efficient hydrolytic separation of iron at the end of the leaching step, followed by the oxidative precipitation of the manganese content. The practically neutral and pure zinc-sulphate solution can be utilized advantageously for electrowinning zinc. The procedure is still hardly economical, which shortcoming can be improved by the admixing of the easily available centrally stored electric arc furnace dust, containing comparable amounts of zinc, but very low concentration of other soluble metals. Experimental results have proved the viability of this combined processing, although complete recovery of the zinc content is not achieved from the added dust, which results in a basically zinc-ferrite type residue. It can be however recycled to ferrous metallurgy together with the manganese dioxide precipitate and the carbon-iron hydroxide – manganese dioxide containing residue from the battery waste leaching step. The other large scale source of secondary zinc is the electric arc furnace (EAF) dust, which is produced and stored at high quantities in a centralized manner. It is an interesting proposition to improve the availability of zinc by introducing the less soluble, but more accessible and less complex EAF dust into the processing scheme of the better leachable but more complex and less available Zn-Mn battery waste.
The latter material represented a collected amount of 164 000 tons in 2003 in Europe consisting of ~30% Zn-carbon and ~60% Zn-Mn varieties [1].

1. INTRODUCTION

There are large quantities of waste materials generated by the high scale industrial activity and communal consumption. These materials can be considered as valuable secondary resources of metals. On the other hand, they also represent environmental or health hazards. Therefore, processing, with the general aim of extracting the metallic values, is more and more often indispensable. As the primary resources of zinc are becoming rather scanty and zinc consumption is dynamically increasing especially by the scale of zinc coating is applied to steel products, zinc containing secondary raw materials are becoming increasingly important.

A preferred secondary source of zinc can be the waste material generated by the discarded and more or less efficiently collected Zn-Mn type primary portable batteries constituting more than 90% of the total mass of global battery waste. Another incentive of processing this waste is the 2006/66/EU directive of the European Union, which requires at

DOI: 10.26649/musci.2016.014

least 45% efficiency of collecting and 50% rate of processing in the EU [2]. This is especially imperative because of the heavy metal components also shown in Table 1. Although the main components of the collected primary battery scrap may be represented by the reagents and the products in the general reaction scheme taking place in the battery during use:

$$Zn + 2MnO_2 \rightarrow MnO / Mn_2O_3 / MnO(OH) + Zn(OH)Cl / Zn(NH_3)_2Cl_2 / ZnO \qquad (1)$$

More than half of the total weight of the examined raw material is made up of substances in eq. (1). The rest is mostly of carbon and iron accompanied by some potassium hydroxide and plastics [3].

Table 1 Composition of the major Zn-Mn type battery scrap

Type	**Zn**	**MnO_2**	**Fe**	**Cu**	**C**	**$ZnCl_2$**	**KOH**	**Plastics**
Zinc chloride	22	25	17	-	8	20	-	8
Alkaline	17	35	22	3	4	-	15	5

A simple way of extracting the zinc content from the very complex battery scrap would be adding it to steelmaking charges to recover zinc as its oxide from the flue dust. However a hydrometallurgical approach may offer the selective recovery of the zinc value. Hydrometallurgical processing is usually based on the main step of leaching applying diluted (~ 10 %) sulphuric acid at different temperatures [3]. This is the most straightforward reagent, available at low costs and requiring no special construction materials for the reactors. The application of room temperature may also alleviate investment costs, although the rate of the main dissolution processes must be carefully tested for practical use. Despite the practical advantages, only laboratory or pilot scale operations are known for a complex processing of the battery waste at present.

The partially reduced portion of manganese oxide and the oxidized portion of zinc can be easily dissolved in dilute acids leaving the remaining MnO_2 fraction behind in the solid residue. Iron can be removed preliminary by magnetic separation, but any remaining part of it entering into the acid solution can be precipitated in the ferric hydroxide form by a controlled neutralization under oxidizing conditions and the filtered solution containing Zn and Mn sulphate can be processed in different ways. During the process of zinc extraction it is also important to separate the numerous accompanying metals, which is best achieved by aqueous techniques.

A complex process of purifying the zinc sulphate solution has been devised and tested on a laboratory scale [3, 4]. The removal of manganese is most efficient by oxidative precipitation applying sodium hypochlorite as the reagent and sodium hydroxide to control the pH of the solution. With careful neutralization, some other major impurities could also be removed, and cementation with Zn powder could remove the dangerous trace elements of higher electrode potential. This complex solution purification is illustrated by Fig. 1.

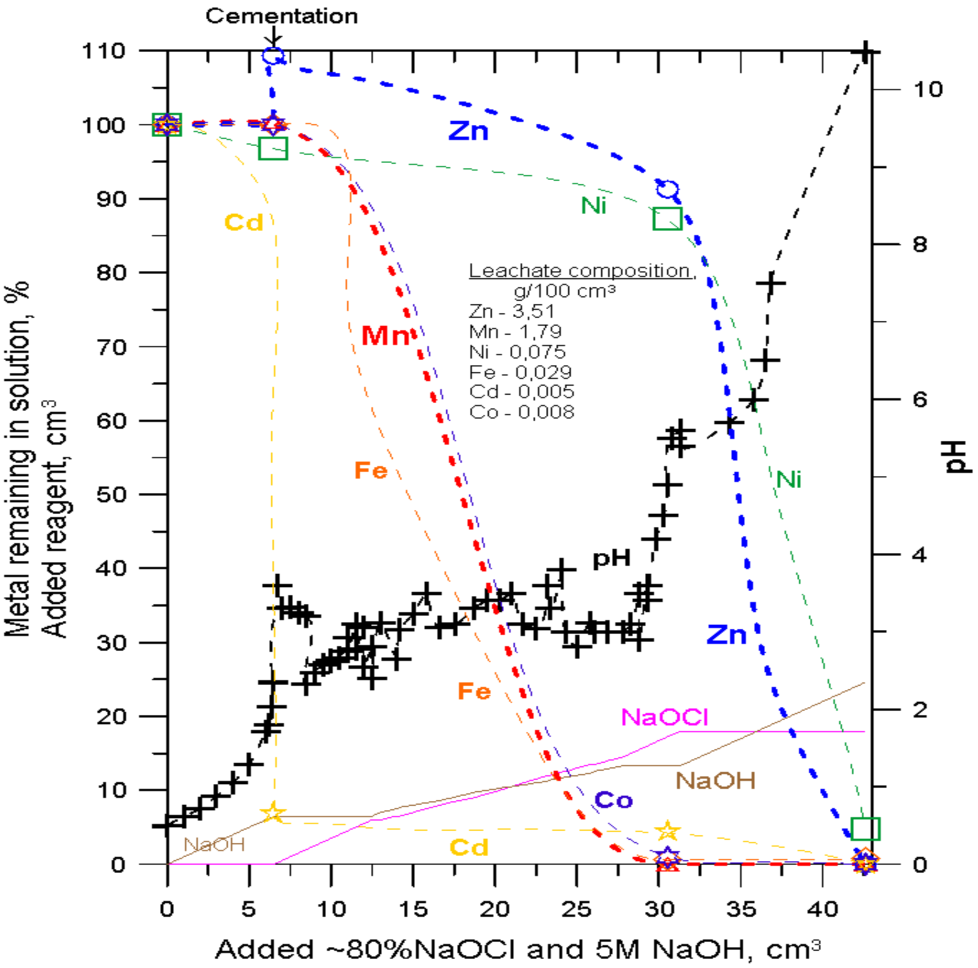

Fig. 1. Separation of metals dissolved from the Zn-Mnox battery scrap raw material by oxidative precipitation [3].

Iron is in the Fe(III) state and it is seen precipitated mostly by hydrolysis as the pH is gradually increased. Oxidative precipitation of the large amount of manganese from the solution is shown to be perfect before the increased pH would start an intensive hydrolytic precipitation of zinc. The purified solution is ready for zinc electrodeposition. One great difficulty of zinc recovery by hydrometallurgy is its strongly negative electrode potential, which makes the cathodic deposition of zinc not quite straightforward [6,7]. Therefore, it is necessary to investigate the suitable conditions for an efficient electrolysis, to reach acceptable current efficiencies, deposit structures and purity of the product [3]. Although the standard electrode potential of zinc is rather negative, as shown in Table 2, the high value of the hydrogen overpotential on this metal makes it possible to be deposited from solution of even lower than neutral pH. Nevertheless, acid concentration in the electrolyte should be kept to the minimum which still assures the stability of dissolved species. As the overall anodic reaction:

$$2H_2O - 4e^- = \tfrac{1}{2}O_2 + 4H^+ \qquad (2)$$

liberates equivalent amounts of hydrogen ions while zinc is deposited at the cathode, the control of acid concentration is a technical necessity during a continuous operation. In order to minimize hydrogen evolution, Zn-concentration should also be kept above a certain level, which can be determined by specific experiments.

In practice some hydrogen evolution may also be tolerated at the cathode, thereby the overall reaction would also include it when zinc is electrowinning from the purified solution produced by the processing of the Zn-containing waste materials:

$$ZnSO_4 + (1+x)H_2O = Zn + ½(1+x)O_2 + xH_2 + H_2SO_4 \qquad (3)$$

The excessive drop of zinc concentration would also incur the danger of more impurity co-deposition. There are some impurities with higher standard electrode potential and with lower hydrogen overpotentials than those of zinc, respectively [5].

Table 2 The main electrochemical characteristics of some selected elements

Hydrogen overpotential (at 25 ^oC and 1mol/dm^3 H^+ concentration)			
	Current density, A/m^2		
Deposited metal, (Std. electrode potential of metal deposition))	**10**	**50**	**100**
Cu(II) (+0.345 V)	0.479	0.548	0.584
Cd(II) (-0.40 V)	0.981	1.086	1.134
Fe(II) (-0.44 V)	0.4036	0.5024	0.5571
Zn(II) (-0.76 V)	0.716	0.726	0.746

Copper can be considered as the most dangerous impurity in terms of co-deposition with zinc because of its high electrode potential and relatively low hydrogen overpotential. Therefore, its preliminary removal from the solution by cementation with zinc powder is of great importance for aiming at high purity zinc produced at the cathode. Another harmful effect may be the reduced hydrogen overpotential if copper is deposited at the surface. A lesser danger is caused by cadmium because electrode potential is lower than that of copper and the relevant hydrogen overpotential is higher. Due to the smaller difference in the standard electrode potentials, its removal by Zn cementation can be less efficient than that of copper. However Fig. 1 shows, that even cadmium is almost entirely removed from the solution by this step.

The effects of the initial Zn concentration and the current density in zinc electrowinning are illustrated by Fig. 2. These results refer to originally neutral $ZnSO_4$ solutions in the first and in the second hours of electrolysis. The current density is expressed from the set current and the original surface area of the cathode. It is seen that the solutions of higher than 50 g/dm^3 initial Zn concentrations yielded higher than 90% current efficiencies in the first hour in the 200 – 1000 A/m^2 current density range. Continued electrolysis in the second hour could produce this efficiency only with solutions of higher than 75 g/dm^3 initial Zn concentration and only at the lowest examined (200 A/m^2) current density [6]. The decrease in the Zn concentration in the cell of 300 cm^3 volume equipped with a cathode of 12 cm^2 effective surface [6], should correspond to only ~4.7 g/dm^3 in an hour with 1000 A/m^2 current density and 95% current efficiency. Still, current efficiencies declined in the second hour even in the solution still containing close to 100 g/dm^3 Zn. As the current efficiency was found close to 100% with solutions of higher Zn concentration than 50 g/dm^3 in the first hour of the electrolysis, the drop of the current efficiencies in the second hour of electrolysis can be attributed primarily to the accumulation of the generated hydrogen ions.

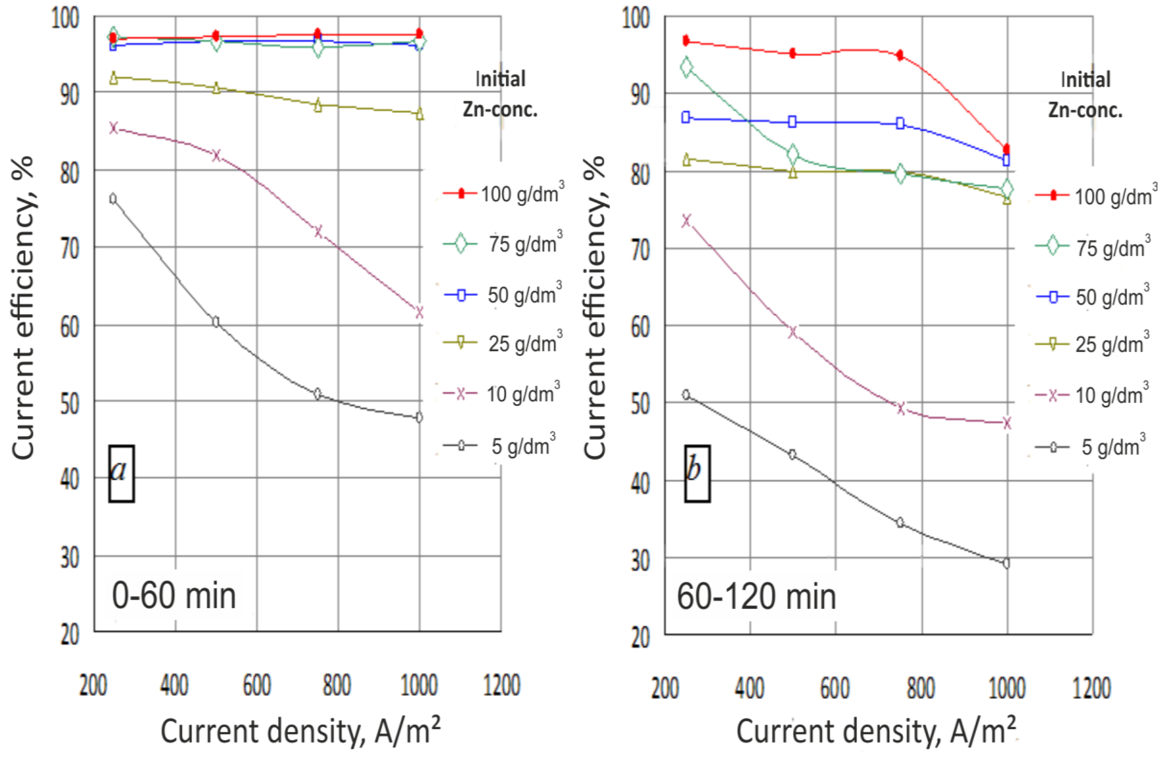

Fig. 2 Average current efficiencies in the first (*a*) and the second (*b*) hours of electrolysis runs at different current densities in solutions of different initial Zn concentration [6].

Acid interfered with the cathodic deposition of zinc even more seriously if the initial solution contained less than 25 g/dm^3 zinc, especially at higher than 200 A/m^2 current densities. These results point at the practical difficulties of Zn electrowinning, if it needs to be included in a hydrometallurgical process of zinc recovery.

Hydrometallurgical processing of the Zn-Mn battery waste also results in a leaching residue and some precipitates of solution purification. These solid by-products - after proper washing and drying, or eventually pelletized – should be fed into ferrous metallurgy, where the residual carbon and the precipitated iron and manganese is utilized.

Because of the high proportion of zinc coated steel scrap returning to steel furnaces, the zinc content is high (20-30%) in the EAF dusts [7], similarly to the battery waste. However, the EAF dust contains only a part of the Zn content in the easily soluble ZnO form, and the rest is in the more refractory ferrites [8]. Thus the efficiency of zinc recovery can be more limited [9], nevertheless it can improve the economy of the process treating both raw materials at the same time. Further difficulty may be introduced by a different composition of the accompanying soluble metals. It may contain higher concentrations of lead, because of the inclusion of painted structural objects and incidentally, high density scrap of different origin and chromium from alloyed constituents, as shown specifically for the dust from a Hungarian steel plant in Table 3.

Table 3 Elemental composition of the EAF dust examined

Comp.	**Fe**	**Zn**	**Pb**	**Cd**	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Sn**	**Ba**
Conc., %	67,16	25.1	7.1	0.043	0.001	0.309	0.231	0.005	0.025	0.004	0.018

Therefore, the possibility of the combined treatment of these two common secondary zinc materials requires the investigation of dissolution characteristics. The undissolved residue of the EAF dust may contain mostly zinc ferrites which can be recycled – together with the precipitated solids form the solution purification steps – to steel making, if proper washing and pelletisation can be applied. Both raw materials contain water soluble salt or alkali components, which should be removed as much as possible before the acid leaching step. This has been proved possible in the case of the Zn-Mnox type alkaline battery scrap [3], but it may require special attention for the EAF dust.

2. EXPERIMENTAL RESULTS AND DISCUSSION

In order to assess the applicability of EAF dust to improve the economy of zinc recovery of mixed secondary raw materials, we have carried out leaching tests with water – to remove alkaline elements and soluble salts – and with 10% H_2SO_4 solution to leach zinc beside the accompanying metals. The effect of H_2O and H_2SO_4 leaching on Zn recovery is illustrated by Fig. 3*a* and 3*b* for three different solid/liquid (s/l) ratios.

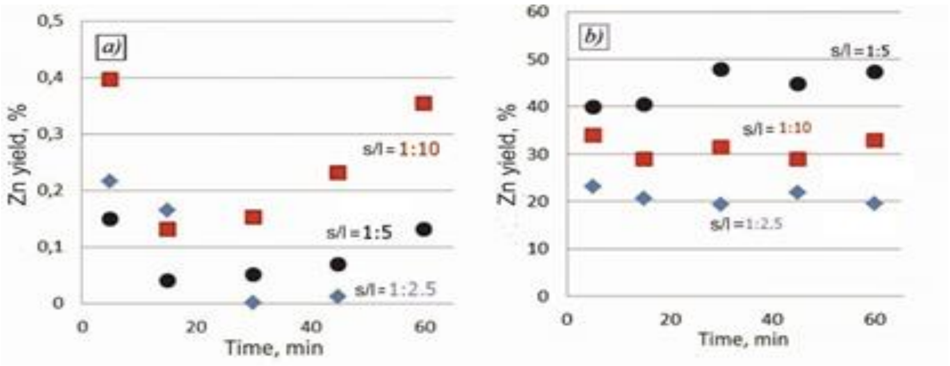

Fig 3. Extraction efficiency of Zinc with water (*a*) and H_2SO_4 leaching of EAF dust as a function of time with different solid/liquid ratios.

Less than 0.5 % of the total zinc content is extracted – lost - by water leaching even with the highest relative liquid amount (1:10 s/l ratio). Decrease of the extraction rate is observed after the first sample, which can be explained by the change of pH in the quasi-neutral solution as a result of dissolved alkalis. The extraction efficiency of zinc in H_2SO_4 leaching reaches practically significant levels, however, it is still lower than in the case of the Zn-Mn dry battery waste [3]. This can be attributed to the high temperature conditions of dust generation in steel making, causing a large part of the zinc content to be transformed into more refractory ferrite compounds.

Although Mn is not contained at as high levels as in the battery scrap, there are some other metals accompanying zinc in the EAF dust. Generally, the most important ones are Fe, Mn, Cu and Cd, whose leaching is illustrated by Fig. 4. Iron, as the main accompanying metal of the dust, poses the greater threat to pure zinc extraction, although Fig. 4*a* suggests that at the lowest liquid ratio (1:2.5) the amount of extracted Fe is negligible. This is caused by ZnO consuming the relatively low amount of the sulphuric acid in the solvent, resulting in an early neutralisation of the solution. It also points at the possible high efficiency of subsequent solution purification by neutralisation. The Fe concentration reached its maximum value of 500 mg/dm^3 in the $ZnSO_4$ solution with the 1:5 s/l ratio. The 1:10 s/l ratio did not increase the Fe concentration. In fact, the concentration was found exactly half of that with the 1:5 s/l ration, indicating that all the soluble iron was removed and the difference in the concentration was caused by the double volume applied.

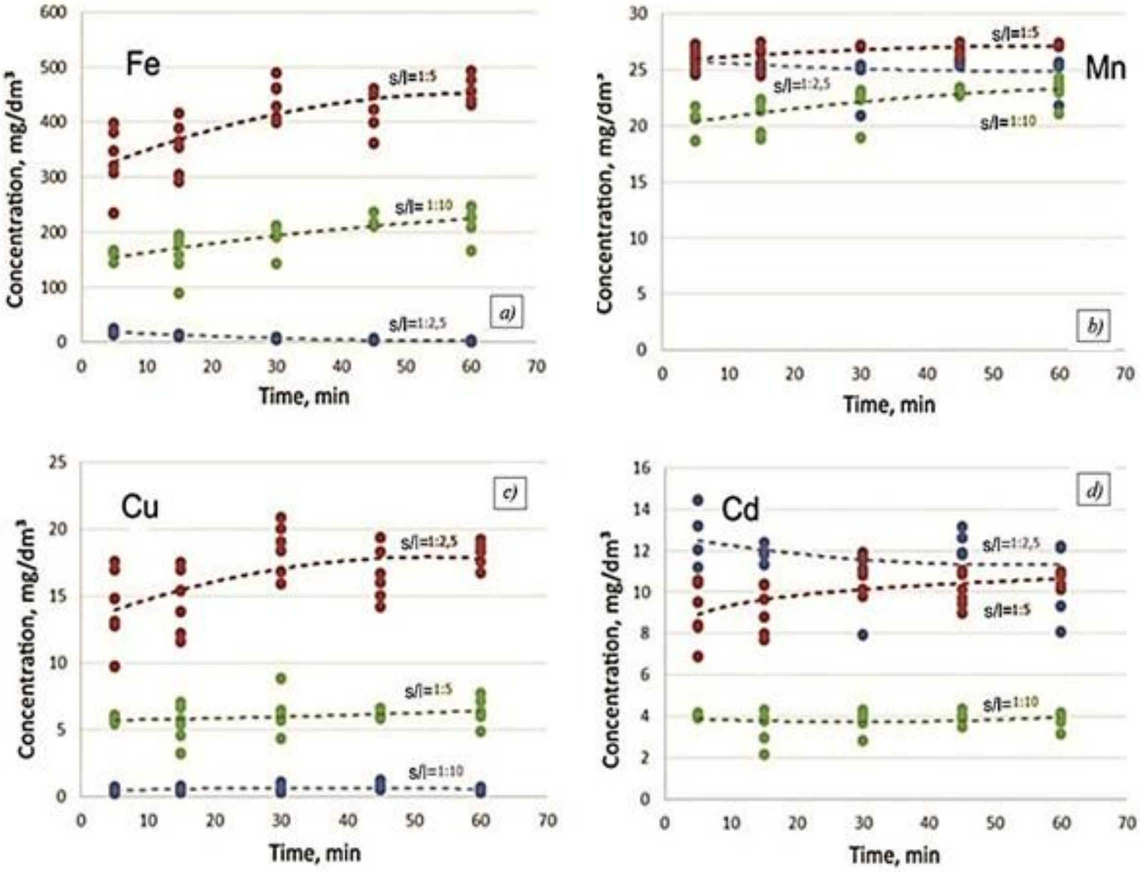

Fig 4. The extracted amount of the elements Fe, Cu, Cd and Mn in the case of different s/l ratios as a function of time

Fig 4*b* shows that the higher solution volume does not cause a decrease in the concentration of Mn, which may be caused by the lower solubility of the manganese content of the dust. The relatively low Mn content of the $ZnSO_4$ solutions arising from the EAF dust does not endanger the purity of Zn, because of the low Mn^{2+}/Mn standard electrode potential.

The behaviour of copper, as shown in Fig 4*c*, is similar to that of iron however, owing to the composition of the raw material the concentration is one order of magnitude lower in the solution. This low Cu content still poses a great danger to the purity of the cathode zinc because of its highly positive standard electrode potential.

The differences in the concentration of Cd on Fig 4*d*, are mainly resulted from the variation of the volume. It suggests virtually complete dissolution even with the lowest ratio of the solution phase. Although Cd has as low standard electrode potential as iron and its concentration is low, it still poses some danger to the purity of the Zn because of the polarization of the cathode, which means it should also be removed before the electrolysis.

Leaching the EAF dust can be directly carried out because of its suitable granular structure, and it causes lower Mn content in the $ZnSO_4$ solution by multiple orders of magnitude compared to those obtained from the Zn-Mn dry battery wastes [3, moreover, Cu and Cd are also present in the solutions of the battery scrap at significantly higher levels. This means that admixing EAF dust to a battery scrap raw material does not affect harmfully the recovery process of Zinc. A higher ratio of the dry battery waste is only beneficial because of the higher Zn extraction efficiency compared to using dust. Co-processing EAF dusts can relieve the economic difficulties of dry battery waste treatment. However the separation, washing and cleaning of the higher amount of solid residues caused by the inert components of the EAF dust may be a disadvantage. On the other hand, the high C, Mn and Fe content of the dry battery scrap residue, together with the undissolved part of the EAF dust can be recycled to ferrous processing.

CONCLUSIONS

Hydrometallurgy is the perspective method of recovering valuable metals, also promoted by environmental regulations. During the hydrometallurgical processing of dry battery wastes, separating zinc and manganese is can be carried out with the oxidative precipitation of manganese, while other elements can be eliminated by hydrolysis or cementation. Zinc can be extracted from the neutralized solution, however, the concentration of remaining elements affect the obtained purity. The hydrometallurgical processing of EAF dust may be included for economic benefits. This secondary raw material is available in great amounts and suitable granulometry as a side-product of EAF steel making. In case of water leaching, which removes alkali elements and soluble salts, the removal rate of zinc is less, than 0.5%. Experiments with 10% H_2SO_4 solutions show that the highest zinc yield in leaching can be achieved with a 1:5 solid/liquid ratio. Compared to the dry battery wastes this means a lower efficiency, but the available amount and the ability to be processed with hydrometallurgical methods of this material are considerable points in combined processing. Admixing EAF dust causes less Mn, Cu and Cd impurities entering the solution, but the solid residue mass increases. It requires washing and cleaning, however it can be recycled to ferrous metallurgy with advantage. Thus a combined processing of the two secondary raw materials may offer improved economy for zinc recovery.

REFERENCES

[1] Eurpoean Portable Battery Assosiation 2008, http:// www.rpbaeuropa.net

[2] European Union, 2008, http://europa.eu.int

[3] Kékesi, T., Matejka, G., Török, T.: Recovery of Zinc from Zn-Mn Secondary Raw Materials by Hydrometallurgical and Hydro-Electrometallurgical Methods, Kammel’s Quo vadis Hydrometallurgy- 6, International Scientific Conf. Herlany, Slovakia, 04-07 June, 2012, 75-85.

[4] Kuniczky, Z et. al.: Processing of Spent Zinc-Carbon and Alkaline Portable Batteries, proc. Conference Recycling of Spent Portable Batteries and Accumulators, 21-24. April, 2009, Sklené Teplice, Slovakia, 96-103.

[5] Horváth, Z.: A cin kohászata, Akadémia Kiadó, Budapest, 1961, p. 345-346.

[6] László, N., Kékesi, T.: A cink elektrolitikus kinyerésének hatásfoka, a kinyert fémtisztasága az áramsűrűség és a szulfáttartalmú oldat összetétele függvényében, Anyagok világa 1, 2015, 12-23.

[7] Zsadányi, N., Kékesi, T., Rőczei, I., Becze, L.: Ívkemence szállóporának előkészítése zsugorító berendezéssel a cink- és a vastartalom hasznosítására. BKL Kohászat, 135, 8-10, 2002, 241-247.

[8] Koleszár, P., Márkus, R.: Acélműi szállóporok ásványtani, geokémiai jellemzői, IV. Kárpát-medencei Környezettudományi Konferencia, 2008, 178-184.

[9] Antrekowitsch, J., Antrekowitsch, H.: Hydrometallurgically recovering zinc from electric arc furnace dusts JOM, 53, 12 (2001) 26-28.