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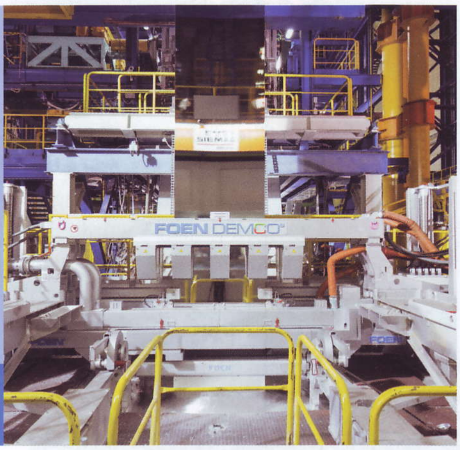

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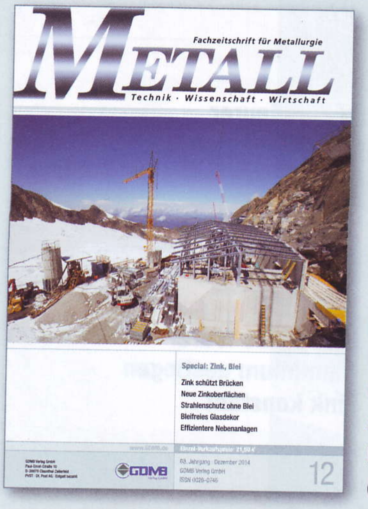

TITELSEITE

Einsatz von verzinktem Stahl in großer Höhe: Mitte August sind die Beton- und Stahlkonstruktion der Gletscherjet 4 Bergstation zu gut 60 % fertiggestellt (siehe Bericht S. 505).
(Foto: Kitzsteinhorn)

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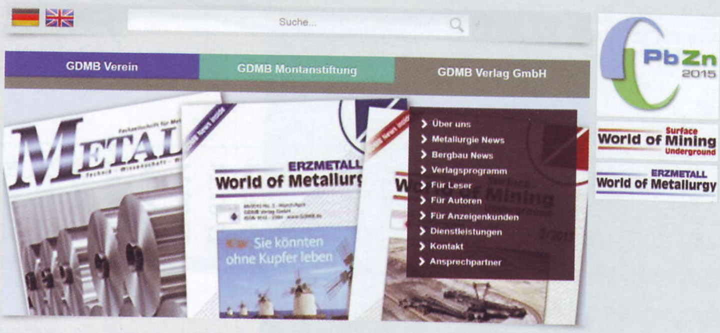

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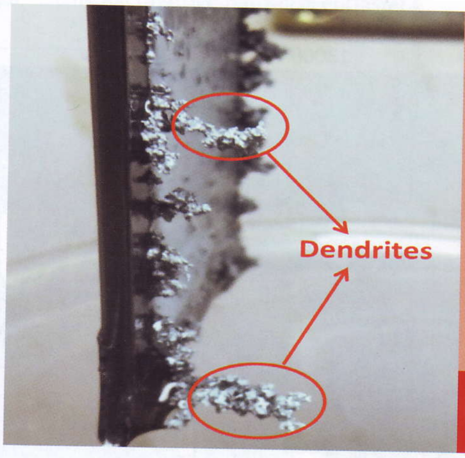

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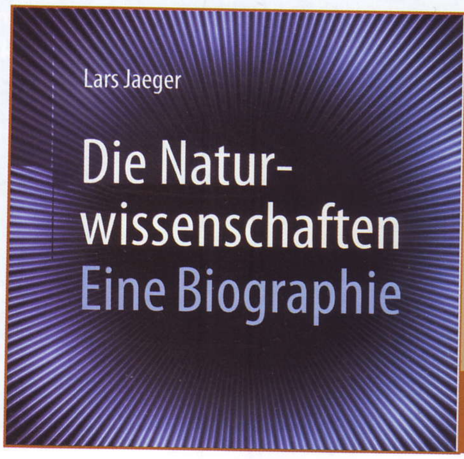

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Hydrometallurgical Treatment of EAF Steelmaking Dust

Maruskinova, G. (1); Kukurugya, F. (1); Parilak, L. (2); Havlik, T. (1); Kobialkova, I. (1)

This work deals with the recycling of electric arc furnace (EAF) steelmaking dust containing heavy metals by hydrometallurgical method. Studied dust was obtained from Železiarne Podbrezová a. s., Slovakia. Hydrometallurgical treatment of EAF dust in order to obtain usable components and to minimize the amount of hazardous waste is composed of several steps. The most important step is leaching. As leaching agent solutions of H_2SO_4 were used. The work is evaluating the effect of acid concentration, temperature and solid to liquid ratio (S:L) on zinc recovery. Subsequently, the refining processes of leachate, refining and removal of iron, copper, lead and other impurities were studied. The final step of the hydrometallurgical process was represented by electrowinning, whose output was zinc of purity of 99.99 %. As the previous experiments, the electrowinning experiments were carried out first on synthetic solutions and then the real solutions coming from leaching of electric arc furnace dust was used for the experiments.

Dust, coming from the production and processing of iron and steel, belongs to wastes with a high percentage of iron. Despite their high iron content they can not be directly recycled in metallurgy production. This is due to the presence of heavy metals, especially zinc, lead and cadmium, which are unacceptable in technological process.

Even landfilling of these secondary raw materials is constrained by the presence of heavy non - ferrous metals. This is a reason why the dust is classified into the category of hazardous waste [1]. Steelmaking dust has a very heterogeneous chemical and mineralogical composition and anisotropic properties.

For this reason, it is very important to determine the chemical and mineralogical composition of dust before the actual processing [2]. Table 1 represents chemical composition of dust from electric arc furnace from 905 meltings in the period from February 2010 to June 2010. For the experiments a sample obtained from Železiarne Podbrezová a. s. with an average composition listed in Table 1 was used.

By X-ray diffraction phase analysis the phase composition of the sample was determined, Fig. 1.

Although recycling of EAF dust is increasing in industrialized countries like the U.S. and Japan, we can not say that there is a perfect technology for the treatment of this type of waste. Economically effective technology of recycling steelmaking dust requires high quantities of dust to be processed at the 10,000 – 100,000 t/year what it is practically impossible to achieve in Slovakia [3]. On the other hand, there are good reasons for the effective recycling of steelmaking dust, mostly:

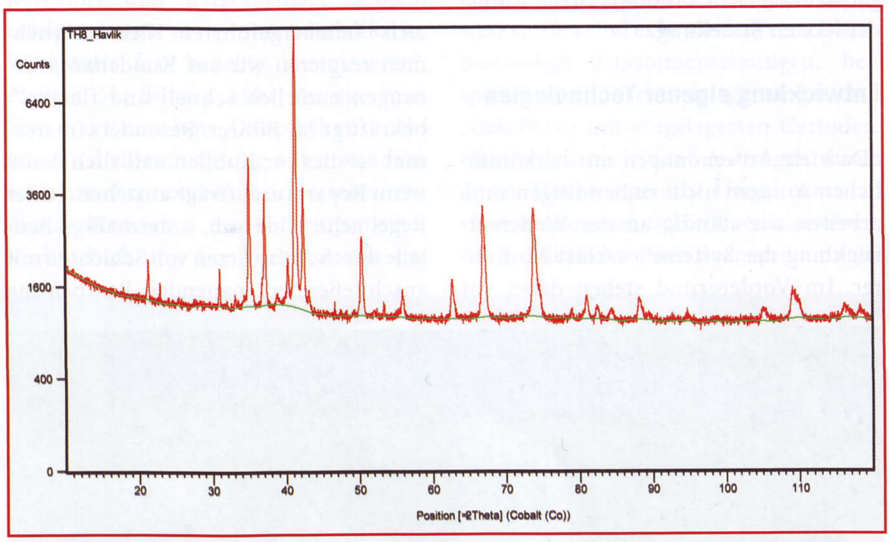
- obtain rich Fe concentrate suitable as an input material into the production of pig iron and/or steel – the current price of iron ore is 100 USD/t
- obtain zinc as a commercial product - the current price of metallic zinc is 2015 USD/t
- reduction of the quantity of hazardous waste and/or its conversion to non - hazardous waste [4, 5, 6]

Experimental

After initial analysis and definition of sample of EAF steelmaking dust, hydro-

Elements	Zn	Fe	Mn	Pb	Ca	Si	Cl	K	Mg	S	C
Content [%]	23.87	30.13	1.55	2.20	3.79	1.28	2.37	1.30	1.08	0.72	1.18

Tab. 1: Chemical composition of the sample



Ref. Code	Score	Compound Name	Chemical Formula
01-089-1012	67	Zinc Iron Oxide	$ZnFe_2O_4$
01-089-7102	62	Zinc Oxide	ZnO
01-075-1609	28	Iron Oxide	Fe_3O_4
01-088-0867	21	Magnesium Aluminum Iron Oxide	$(MgAl_{0.74}Fe_{1.26})O_4$
00-046-0291	20	Calcium Iron Oxide	$Ca_{0.15}Fe_{2.85}O_4$
01-075-0306	17	Sodium Chloride	NaCl
01-089-8936	17	Silicon Oxide	SiO_2
00-026-1077	19	Carbon	C
96-900-6723	10	Lime	$Ca_{4.00}O_{4.00}$

Fig. 1: Results of X-ray diffraction phase analysis of EAF steelmaking dust

metallurgical method comprising of leaching, precipitation, cementation and electrowinning of Zn, with the aim to obtain pure metallic zinc or other commercially marketable zinc compounds, was chosen.

Two-stage leaching of steelmaking dust

Based on the published results of previous experiments two-stage leaching was chosen. In the first stage dilute sulfuric acid was chosen as a leaching agent. The aim of this step was to get as much zinc as possible into the solution, while iron is staying in leaching residue. In the first step the concentration of 0.25 M H_2SO_4 was determined as the minimum concentration needed for leaching zinc without iron passing into the solution (20 µg/ml).

Aim of the second step of leaching was to leach zinc, which is present in the dust in the ferritic form as $ZnFe_2O_4$. Therefore, in the second stage of leaching a more concentrated solution of 2 M sulfuric acid was used. The yield of zinc increased to 80 %. In this case a large amount of iron passed into the solution and therefore it was necessary to precipitate the iron from the solution [3].

Precipitation of iron from the solution after two-stage leaching

In principle, there are a many options to precipitate iron from a solution. This work is focused on the precipitation of iron as goethite or jarosite. Experimental results confirmed the real possibility of using jarosites and goethites precipitation, to achieve concentration of Fe in the solution after precipitation below 1 µg/ml, which represents up to 99.98 % Fe removal efficiency from the solution. Similarly to remove the lead from real solutions with 96.5 % efficiency was managed.

The next step was to optimize the process of iron precipitation from the solution after leaching. The aim of this step was to verify the effect of the oxidizing agent as H_2O_2 and flocculant agents ($CuSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$) on the amount of removed iron and the sedimentation rate of the resulting precipitate. With a use of oxidative agent a lower residual concentration of Fe in the solution was achieved. The use of flocculants, also in real solutions, pointed out their positive effect on sedimentation rate, but this effect was not as pronounced as in the case of synthetic solutions.

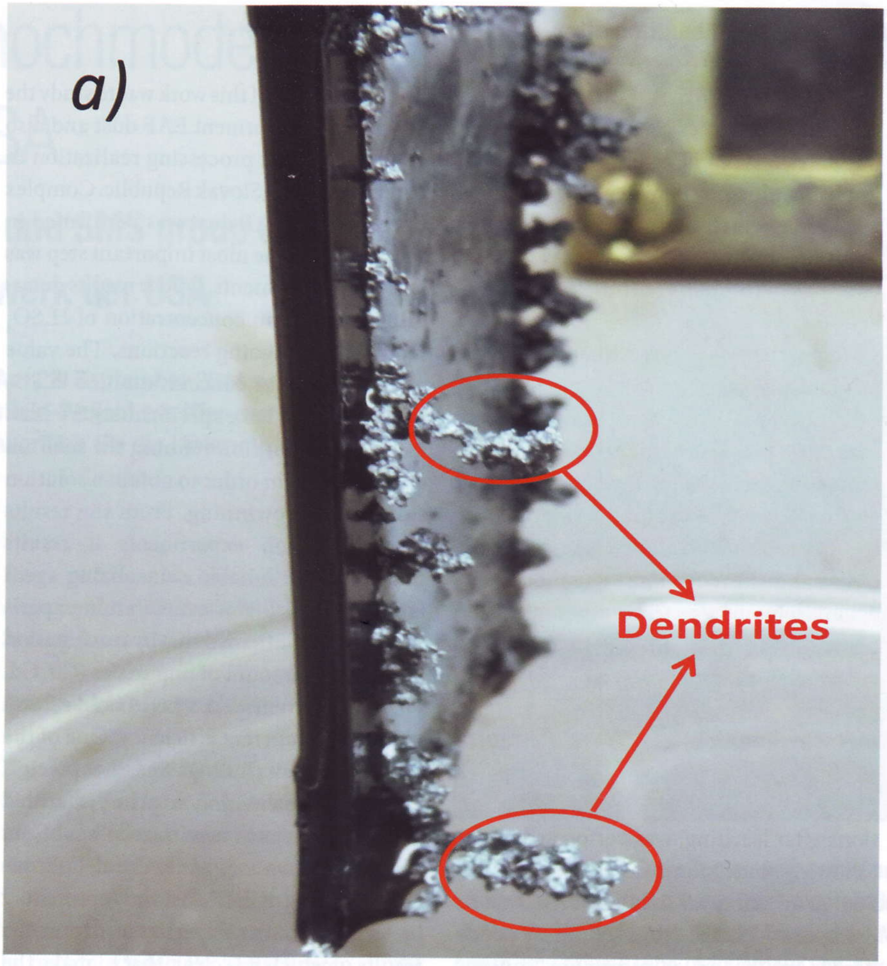


Fig. 2a): Zn cathode with dendritic deposit

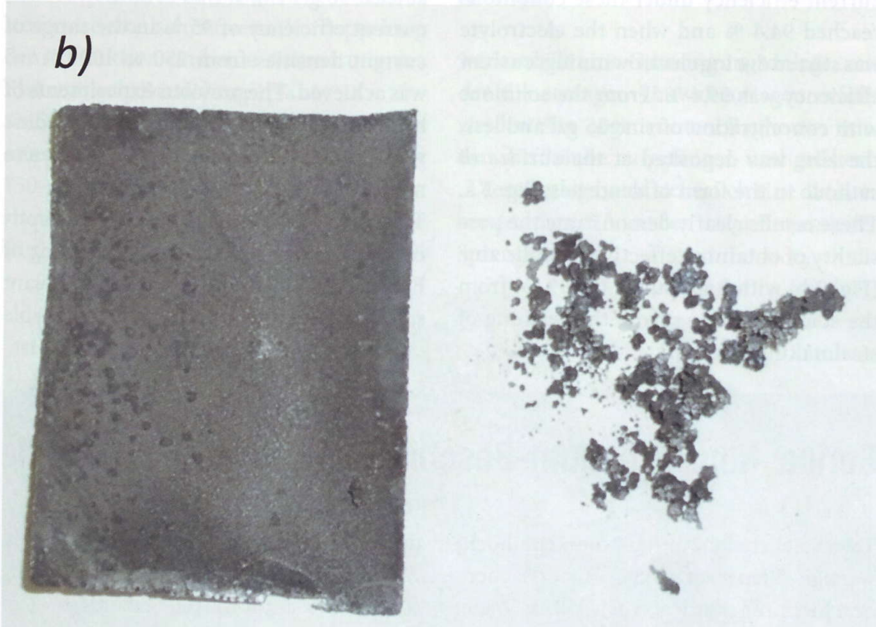


Fig. 2b): electrolytic zinc

The most significant finding in the optimization of iron precipitation from solutions was determining the most suitable neutralizing agent as $CaCO_3$. The biggest advantages of $CaCO_3$ are: faster sedimentation of final precipitate, lower price and lower residual concentrations of Fe.

Cementation of solution after leaching

Cementation experiments were carried out on two types of solutions after leaching using zinc powder. The first type was a solution, which has not undergone previous precipitation of iron. In case of second type of solution the iron was removed before cementation.
The experiments showed that in order to minimize losses of zinc, it is important to carry out these two steps separately. In case that these processes are carried out at the same time there is a physical absorption of zinc to Fe precipitate and the loss of Zn in the process is much higher.
Optimal conditions of cementation process are the follows: temperature 50 ° C or higher, pH = 4 – 5 and cementation time 60 minutes or more [4].

Electrowinning of zinc from solution

Electrowinning of zinc from real solutions after leaching, was performed under following conditions: current density of 500 A/m^2, time of 2 hours 25 minutes, using the Al cathode and an inert anode based on Ti and at minimum concentration of Zn in a solution of 50 g/l. The current efficiency under these conditions reached 94.4 % and when the electrolyte was stirred during electrowinning, current efficiency was 99.4 %. From the solutions with concentration of zinc 25 g/l and less, the zinc was deposited at the surface of cathode in the form of dendrites, Fig. 2 a. These results clearly demonstrate the possibility of obtaining effective metallic zinc (Fig. 2 b) with high purity (99.99 %) from the solution coming from the leaching of steelmaking dust [4].

Conclusions

The main object of this work was to study the possibility of treatment EAF dust and also its technical and processing realization in conditions of the Slovak Republic. Complex processing of EAF dust was performed in several steps. The most important step was leaching experiments, whose results determined minimum concentration of H_2SO_4 required for ongoing reactions. The value of the minimum concentration of H_2SO_4 was 0.25 M. Other experiments were realized with focused on refining the solution after leaching in order to obtain a solution suitable electrowinning. From the results of precipitation experiments it results that the most suitable neutralizing agent is $CaCO_3$. Results of cementation experiments have confirmed that by cementation a very small amount of impurities (Cu, Cd, Pb, ...) can be removed, which could cause a reduction of current efficiency. One of the most important findings was, that precipitation and cementation must be performed in separate steps to minimize losses of Zn. The last step in a complex hydrometallurgical processing of EAF dust was represented by electrowinning experiments, from the results of which it is clear, that to make the process effective, electrolyte must contain at least 50 g/l Zn. If this condition is met, current efficiency of 95 % in the range of current densities from 250 to 1000 A/m^2 was achieved. The previous experiments of hydrometallurgical processing of EAF dust were performed in order to obtain zinc as a metal, or as a commercial product.
The aim of the next stage of research is optimize the hydrometallurgical processing of EAF dust, design and build a pilot plant scale leaching line, which would be capable of processing the required amount of dust.

Acknowledgement

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Serica: Neue Premium-Beschichtung für Außenhautteile von Fahrzeugen

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