Kinetics and mechanism of thermal zinc-ferrite phase decomposition

Dr.-Ing. Srećko Stopić, Prof. Dr.-Ing. Bernd Friedrich

RWTH University Aachen, IME Process Metallurgy and Metal Recycling
Intzestrasse 3, 52056 Aachen, Germany

Abstract

The by-product from neutral leach of EAF-dust (as well as of primary ores) contains large percentages of an insoluble Zinc-iron-intermetallic phase (ferrite). This material (secondary “concentrate”) unfortunately counts as waste for disposal, since former used “Imperial Smelting Furnaces” have disappeared in West-Europe and the sulfur-content hinders applications in Waelz processes. Because of high contents of valuable metals like Pb, Zn and Ag as well as due to environmental issues caused by the presence of Cd, As, and other heavy metals in this material its landfilling is not sustainable. This study focuses on a simple heat treatment of the “iron-zinc concentrate”. The special focus of the investigation is given on the fundamental understanding of the mechanism and kinetics of the process. It is based on the thermal decomposition of the zinc ferrite phase at elevated temperatures in nitrogen in order to obtain ZnO and hematite, suitable for conventional leaching process. The parameters for the process were determined in laboratory tubular furnace. The experimental achievable chemical efficiency and the kinetics of this process step are assisted by computer models. Finally it will be shown by neutral leach treatment that the thermal decomposition of this solid residue based on ZnO is technically feasible to recover high Zn-contents without hot acid leaching and jarosite production.

1 Background and Concept

Since dumping of zinc-containing steel mill dusts is no longer acceptable from the environmental and economical point, a lot of investigations have been done to find appropriate processes that make recycling of these dusts economically and technically possible [1]. While hydrometallurgical process routes up to date did not reach production scale, pyrometallurgy, especially carbothermic reduction has become the most important treatment route. But even the Waelz process - categorized as Best Available Technology - has various disadvantages that motivates searching for an alternative process. During the production of steel from scrap in electric arc furnaces a considerable degree of dust is produced and recovered in gas cleaning units. In recent years the contents of Zn, Pb, Cd, Cr, and other metals has caused the material to be widely regarded as a toxic waste which is unsuitable for the disposal at landfill. For the same reason the direct use of this waste for iron or steel production is not applicable. Besides the Waelz-technology a number of hydrometallurgical processes have been developed in order to treat these dusts from steel plant [2-12]. The EZINEX® process for example is based on a neutral chloride electrolyte to produce zinc from zinc oxide containing materials, in pilot scale proven for the direct treatment of an electric arc furnace dust. INDUTEC® is a thermal process, based on an induction furnace volatilizes zinc and other heavy metals with high energy input. The combination of the above mentioned processes opens opportunities for the treatment of zinc bearing materials, but still many drawbacks like the presence of chlorides, fluorides and metallic impurities, are not overcome up to now successfully. An "Iron-zinc concentrate" as the major waste from secondary dust processing as well as from primary ore treatment is formed in the neutral leaching step (Fig. 1).

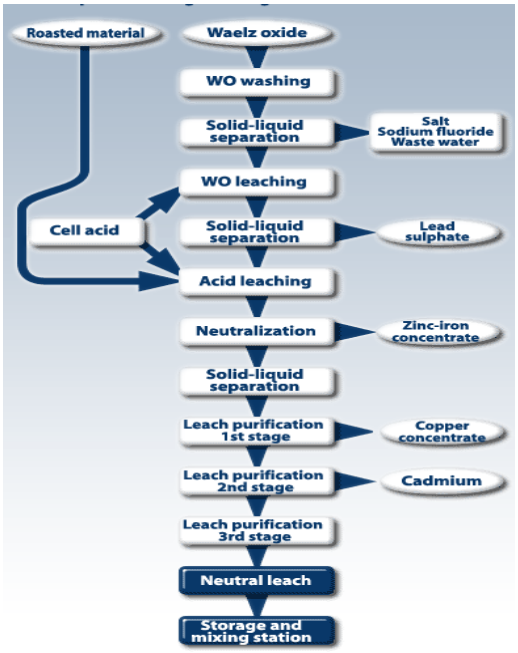


Fig. 1: Flow Chart of the former leaching process at Ruhr-Zink GmbH, Datteln/Germany

The mineralogical analysis of EAF-dust shows that iron is present mostly as hematite Fe_2O_3, magnetite Fe_3O_4 and franklinite $ZnFe_2O_4$. Zinc can be found mostly as ZnO and franklinite $ZnFe_2O_4$, sometimes in complex ferrite forms like $(ZnMnFe)_2O_4$. The nature of the zinc presence determines the efficiency of the EAF dust treatment. Similar phases are formed also in the primary ore route whilst roasting the Zn-Fe-S ore concentrates. ZnO in principle is easily to process by pyro- and for the hydrometallurgical methods, but the ferrite form can be considered as refractory. Moreover, it is almost impossible to predict the nature as well as the content of this zinc compound. Additionally the presence of other heavy metals occurring in the dust and ores causes even more complications. Fig. 2 shows, that under the prevailing process conditions (T=1150°C) the phase $ZnO \cdot Fe_2O_3$ (zinc ferrite) is stable and such insoluble. Using higher temperatures and lower pressures this formation should be prevented, but the existing industrial equipments have no possibility to meet these requirements. Due to the fact that unsoluble zinc-ferrite can not be completely avoided, the solids ("iron-zinc concentrate") separated from the zinc-bearing solution by sedimentation and filtration contains significant Zn-concentrations.

This effect was proven very often by different researchers [4-13]. Cruells et al. [7] leached EAF dust using sulphuric acid solution (0.1 – 2.0M) within the temperature range of 18 - 61 ^{o}C. The sample contained 22 % Zn and 3 % Pb. Previous mentioned results reveal that for the zinc species the reaction rate is virtually independent of the sulphuric acid concentration in the range investigated, whereas for the iron species the reaction rate is a function of the acid concentration. The achieved zinc efficiency amounts to around 90 %, whereas the iron efficiency is within the range 20 - 50 % depending on acid concentration and the temperature. The total leaching time was one hour.

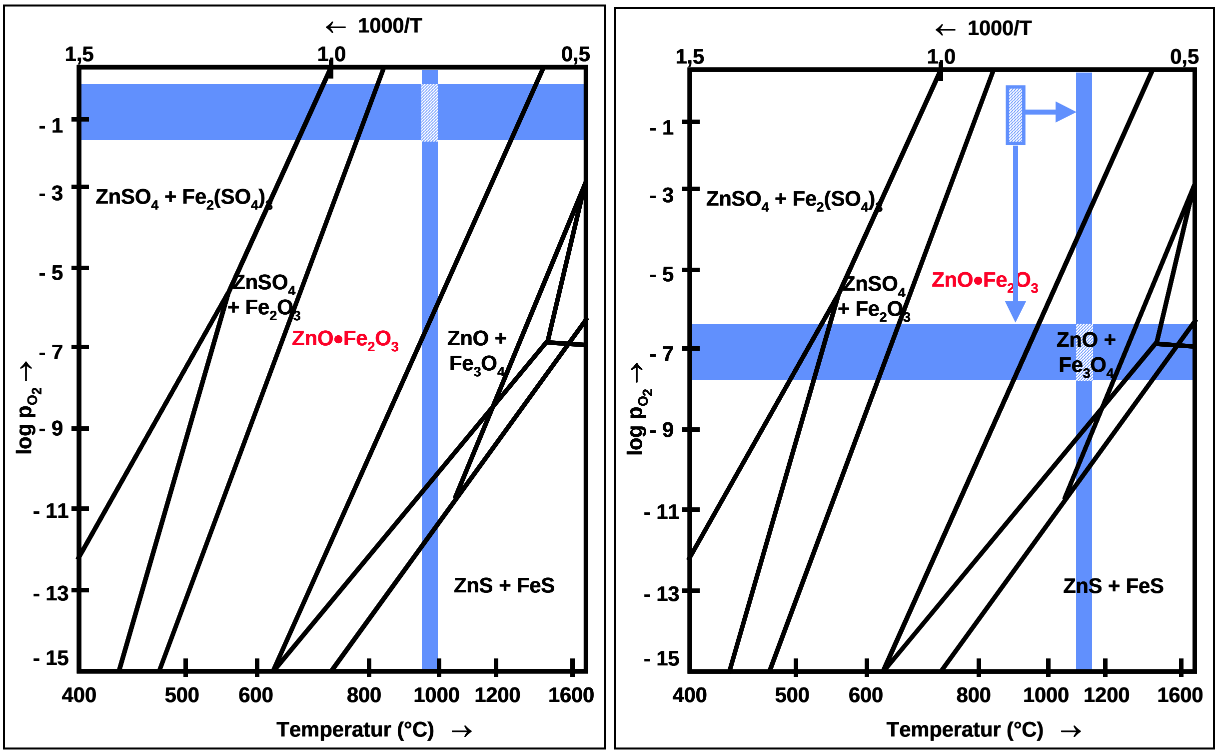


Fig. 2: System Zn-S-O regarding to iron (left real conditions, on the right a desired regime)

Püllenberg [13] has investigated the neutral leaching of partially decomposed iron-zinc concentrate. He has concluded that the previous thermal decomposition of zinc-ferrite between 600°C and 800°C in a weakly reductive atmosphere (up to 10 % of CO) leads to the formation of three products: ZnO, CO_2 and Fe_3O_4.

$$3\ ZnFe_2O_4 + CO = 3\ ZnO + 2\ Fe_3O_4 + CO_2 \qquad (1)$$

The formed ZnO was reduced with gaseous CO to elemental zinc:

$$ZnO + CO = Zn + CO_2 \qquad (2)$$

During the neutral leaching of an obtained product after thermal treatment it is proven that recovery of zinc has a high efficiency.

Based on the previous research work [13, 14] an alternative process is proposed in this study. The concept aims on the thermal decomposition in nitrogen avoiding the energy intensive steps of ZnO-reduction and Zn-evaporation, shown in Fig. 2.

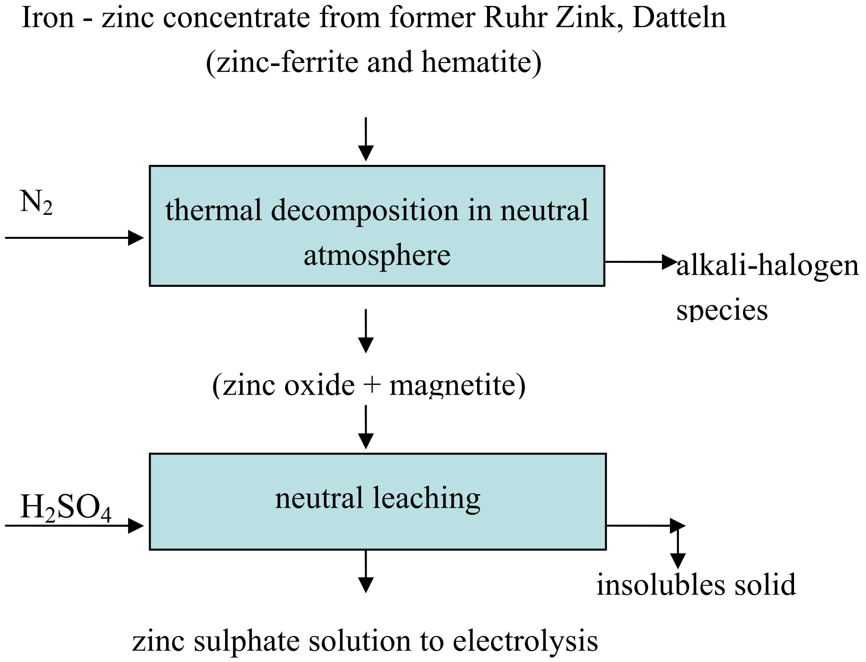


Fig. 3: Proposed new process for treatment of zinc-ferrite containing materials

The research is characterized by exploring the kinetics of zinc- ferrite phase transformation to magnetite and zinc oxide using differential thermal and thermogravimetric analysis of an initial FeZn concentrate. The decomposition yield (efficiency) of a lab-scale furnace treatment will be determined based on the solid phase structure as well as using atmospheric leaching results. The main factors are the furnace atmosphere, temperatures and solid/liquid ratio on the dissolution of Zn, Pb, and Fe when sulphuric acid as leaching agent was used.

2. Experimental

2.1. Material Characterization

2.1.1. Chemical and mineralogical composition

The Zn-ferrite bearing material was obtained by former company Ruhr-Zink, Datteln, Germany with a humidity of 23%. The mineralogical composition is shown in Fig. 4. The chemical composition was determined by ICP method to dry sample.

[%]: 18.6 Zn, 19.8 Fe, 6.7 Pb, 0.6 Cu, 0.2 Cd, 0.2 As, 10.9 Al, 7.3 S, 2.4 Ca, 2.1 Si
[ppm]: 121 Ge, 558 Ag.

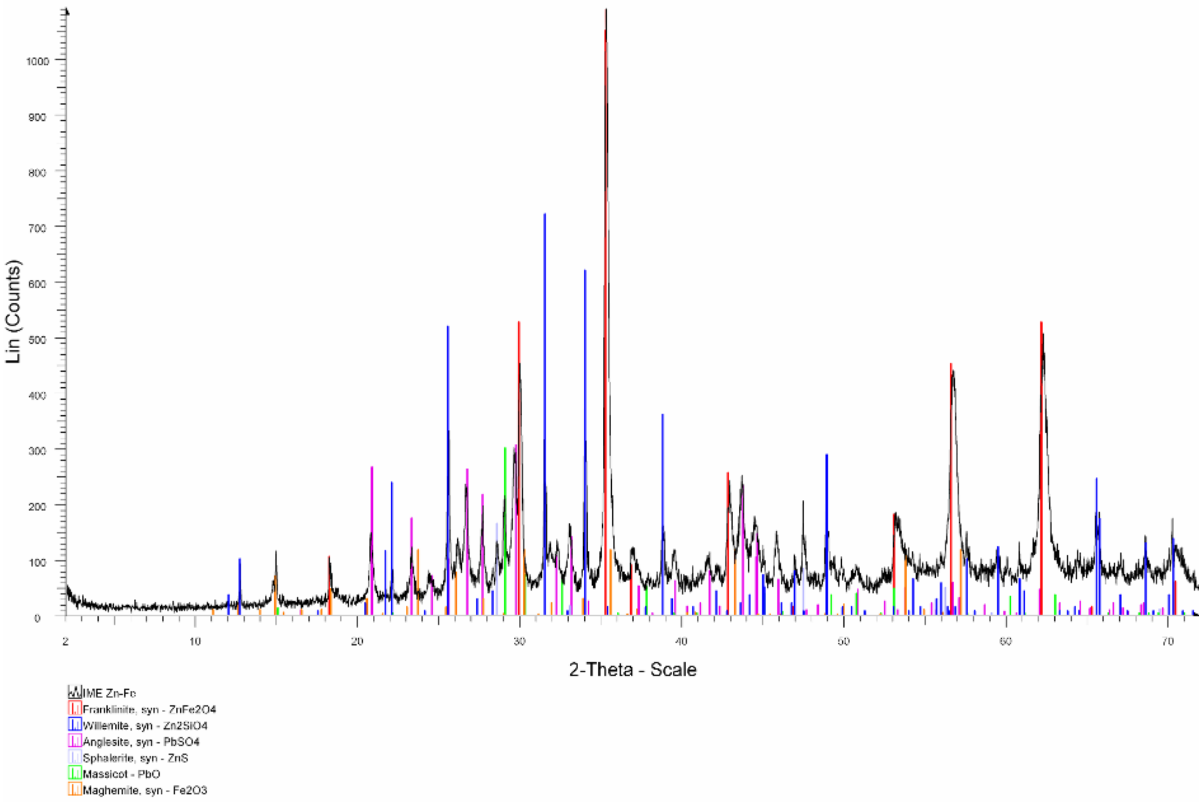
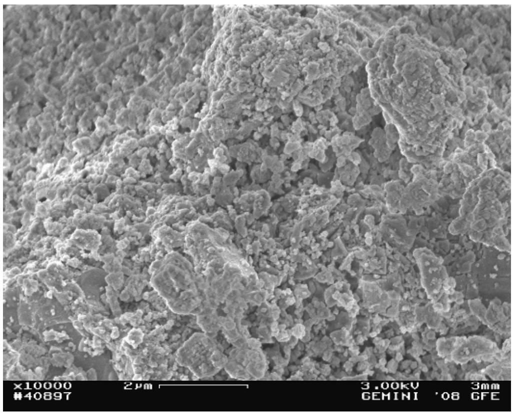


Figure 4: Mineralogical composition of “iron-zinc concentrate” (leach residue of former “Ruhrzink”)

The most present compounds in iron-zinc concentrate shown at Fig. 4 contain $ZnFe_2O_4$ (equal to $ZnO{\cdot}Fe_2O_3$), Zn_2SiO_4, $PbSO_4$, ZnS, PbS, Fe_2O_3. Additional SEM and EDS analysis show that the particles of FeZn concentrate are agglomerated and irregular shapes results (Fig. 5 and 6).



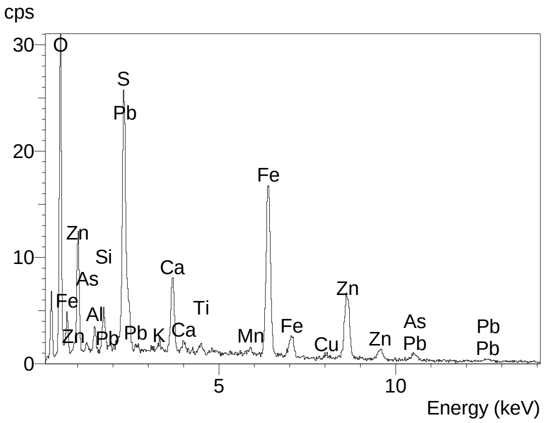


Figure 5: SEM analysis of FeZn residue

Figure 6: EDS analysis of FeZn residue

2.1.2. Thermal analysis

Based on the idea presented in Fig. 3 the following decomposition reactions might expected in a neutral atmosphere:

$$3\ ZnO\cdot Fe_2O_3 = 3\ ZnO + 2\ Fe_3O_4 + \tfrac{1}{2}\ O_2 \qquad (3)$$

$$Zn_2SiO_4 = 2\ ZnO + SiO_2 \qquad (4)$$

$$PbSO_4 = PbO + SO_2 + \tfrac{1}{2}\ O_2 \qquad (5)$$

$$2ZnS + 3O_2 = 2\ ZnO + 2SO_2 \qquad (6)$$

$$3Fe_2O_3 = 2\ Fe_3O_4 + \tfrac{1}{2}\ O_2 \qquad (7)$$

According to Eq. (3) the theoretical mass loss from the sample of zinc iron ferrite ($ZnO\cdot Fe_2O_3$) in form of oxygen amounts to 2.2 %. Concerning to the thermal decomposition of iron zinc concentrate in nitrogen DTA and TGA experiments at heating rates of 5 K/min, 20 K/min, and 40 K/min up to 1200°C were performed in order to determine the real mass loss and temperature range for transformation. The effects detected are summarized in Table 1. The activation energy of the thermal decomposition of the different compounds be calculated using equation (8) from these values.

$$\ln\left(\frac{\alpha_2 \cdot T_1^2}{\alpha_1 \cdot T_2^2}\right) = \frac{E}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (8)$$

T_1 and T_2: temperatures of transformations at corresponding heating rates: α_1 and α_2.

The DTA/TG analyses show thermal effects, which can be related to decomposition phases:

phase 1: 27 - 417 °C
phase 2: 402 - 885 °C
phase 3: 600 - 960 °C
phase 4: 1011 – 1120 °C

According to table 1 the first three decomposition steps are diffusion controlled due to their activation energies (kJ/mol) of 1.2, 4.1, 17.1, respectively. Effect No. 4 may be attributed to the decomposition of zinc ferrite and seems to be a chemical controlled process (an activation energy E_A amounts:166.9 kJ/mol). The maximal mass lost amounted 25 %.

Table 1: Graphically determinated thermal effects/phases with their corresponding weight loss values taken from DTA and TGA curves for thermal decomposition of “iron-zinc concentrate”

Heating rate α (°C/min)	Mass loss in Ar-atmosphere (%)	T_{min} (°C)	T_{max} (°C)
5	5.85	27	402
	4.48	402	600
	6.95	600	1011
	7.34	1011	1189
20	5.67	31	417
	7.81	417	885

	1.1	885	960
	6.83	960	1120
40	6.34	30	427
	7.43	427	884
	7.32	884	1200

Using formula (8) the calculated values of the activation energies are shown in the Table 2:

Table 2: Calculated values of the activation energies for each decomposition phase of Zink-Ferrite containing leach residue

T_1 (°C)	T_2 (°C)	E_a ($kJmol^{-1}$)
27	417	1.2
402	885	4.1
600	960	17.3
1011	1120	166.9

2.2. Thermal Decomposition

The experimental methodology comprises a pyrometallurgical treatment followed by a leaching of the obtained solid residue. Pyrometallurgical treatment is performed in a tubular furnace in order to prepare a solid residue for the following leaching step.

2.2.1. Experimental Methodology - Tubular Furnace

In order to partially decompose the Fe-Zn concentrate into zinc-phases amenable for leaching a thermal decomposition step was carried out in a laboratory tubular furnace (Figure 7).

Figure 7: Tubular furnace

In the first step only 1 g of leach residue was loaded into the reactor. The nitrogen flow through the reactor was amounted 1l/min.. The furnace was heated up to the desired temperature within 40 minutes and kept at this temperature for one hour. Then the power was turned off, the heating hood removed and the sample forced to cool as fast as possible to room temperature (approx. 5 minutes).

The material was removed from the reactor and weighed. The experiments were performed at 1150°C in nitrogen atmosphere (according to Fig. 2, log PO_2= -7).

2.2.2. Results and Discussion

An appearance of the material that was thermally decomposed at 1150°C in a pure N_2 atmosphere (Figs. 8, 9), suggests that no smelting nor iron formation has taken place in the furnace treatment.

Figure 8: Solid residue after a thermal treatment in nitrogen atmosphere

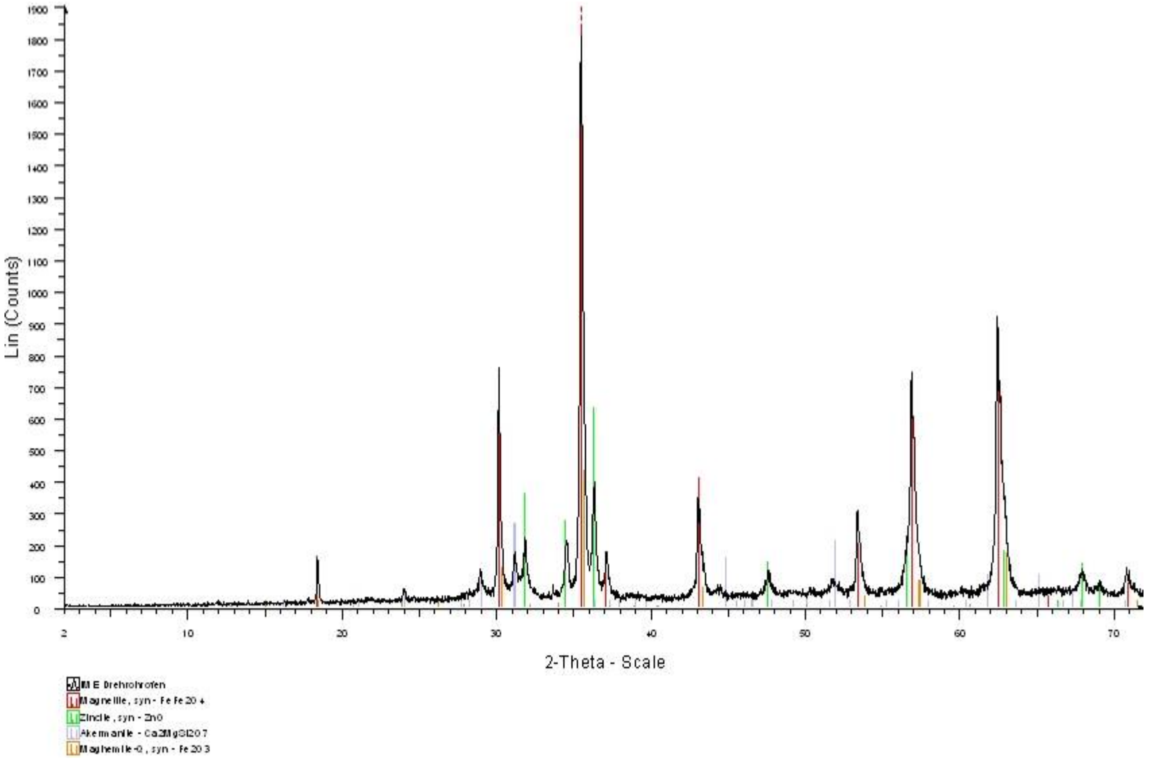


Figure 9: Phase analysis of the Zink-Ferrite containing sample after thermal decomposition in nitrogen atmosphere at 1150°

The obtained phase mix after neutral decomposition contains predominantly ZnO, Fe_3O_4, Fe_2O_3, $Ca_2MgSi_2O_7$, the chemical analysis (in %) of 25.2 Zn, 22.5 Fe, 7.55 Al, 1.37 Al showed that our research idea was correct. The mechanism of formation of ZnO from Zinc-ferrite should be explained in our next publication using an additional SEM and EDS analysis of samples taken in each 15 minutes during the thermal decomposition.

2.3. Validation of the ZnO liberation yield via leaching

2.3.1. Experimental Methodology

Leaching experiments were performed in a neutral regime in order to reach a selective dissolution of zinc. Original samples of Fe-Zn concentrate and those subjected to thermal decomposition are pulverized and screened to produce samples less than 90µm in size for leaching. Leaching tests are performed in a glass beaker at atmospheric pressure with 500 ml of acid on samples weighing 50 g. The solution was agitated with a turbine stirrer. Temperature and pH values are recorded during each test at 20 minute intervals, with samples being taken simultaneously for chemical analysis. The presence of aluminium, zinc, iron and lead is investigated

Figure 10. Experimental setup employed for laboratory scale leaching

2.3.2. Leaching Results

According to the mentioned results by Püllenberg [13] a pH- Value in a neutral regime provides good conditions for a high selectivity for Zinc against Fe. Therefore the experiments were performed at the temperature of 60°C and pH-value of 4.3. The obtained results have shown at Figure 11.

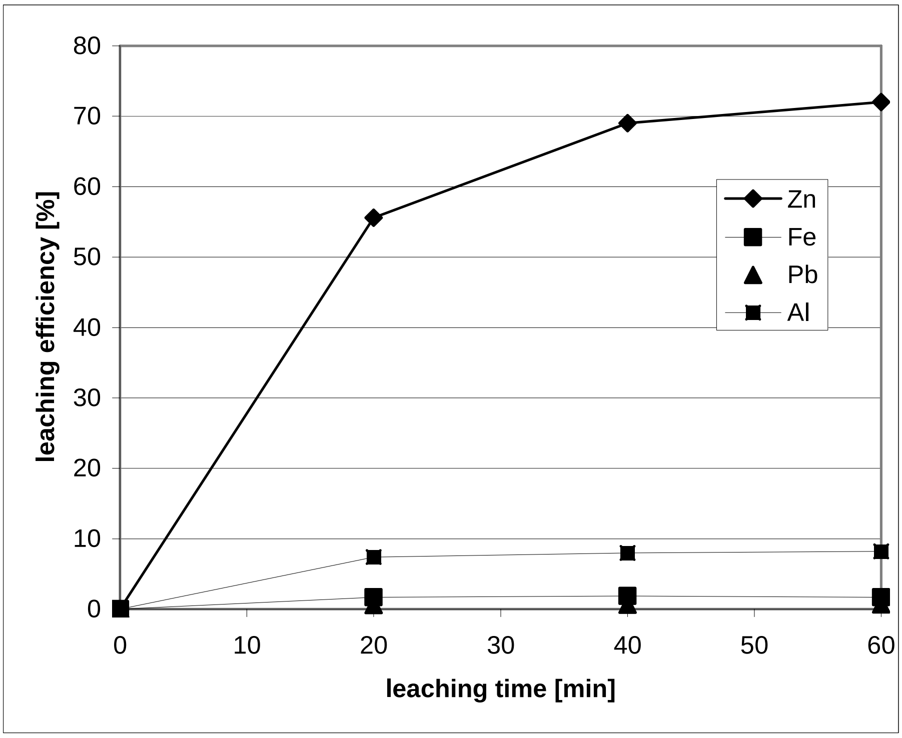


Fig. 11: Leaching results of previous decomposed FeZn concentrate at 60°C for 1hour

The leaching trials performed at 60°C between pH 3.6 and 4.3 confirmed the liberation of leachable ZnO by thermal decomposition at 1150°C in nitrogen atmosphere and reached high selectivity. At 60 °C the leaching efficiency of zinc reached after 60 min. approximately 72 % still with an rising tendency by time, showing only a small dissolution values for Al, Fe, Pb compared to zinc. As reported by Püllenberg the leaching efficiency amounted approx. 95 % for Zn and 8 % for Fe in three hour for pH=4.5 at 60°C, what suggest a higher leaching time in order to reach maximal zinc dissolution.

2.3.3. Kinetic analysis of leaching reactions

The acid leaching of solid residue after thermal treatment in a tubular furnace is a heterogeneous solid-liquid reaction. Kinetics of the reaction with sulphuric acid under an atmospheric pressure was studied at 60°C in order to determine the limiting stage of the process, as well as the corresponding constant. The solid residue was treated a hole even though it is composed by pseudo-spherical particles with a fairly wide size distribution. The acid attacks of homogenous spherical particles with a radius r_o is considered initially, under an acid concentration of C (per one) and a mass of solid residue denominated X has reacted with respect to the total mass (zinc dissolved) at the time t (min) leaching. The possible controlling stages are chemical reaction (Equation 9), diffusion in fluid layer (Equation 10); and diffusion in solid layer (Equation 11).

$$1-(1-X)^{1/3} = K_q \cdot t \qquad (9)$$

$$(1-(1-X)^{1/3})^2 = K_{df} \cdot t \qquad (10)$$

$$1-2/3\cdot X-(1-X)^{2/3}=K_{ds}\cdot t$$
(11)

where: X- extraction yield; K_q, K_{df}, K_{ds} rate constants; and t reaction time.

The testing of mathematical models is shown at Figure 12 and 13:

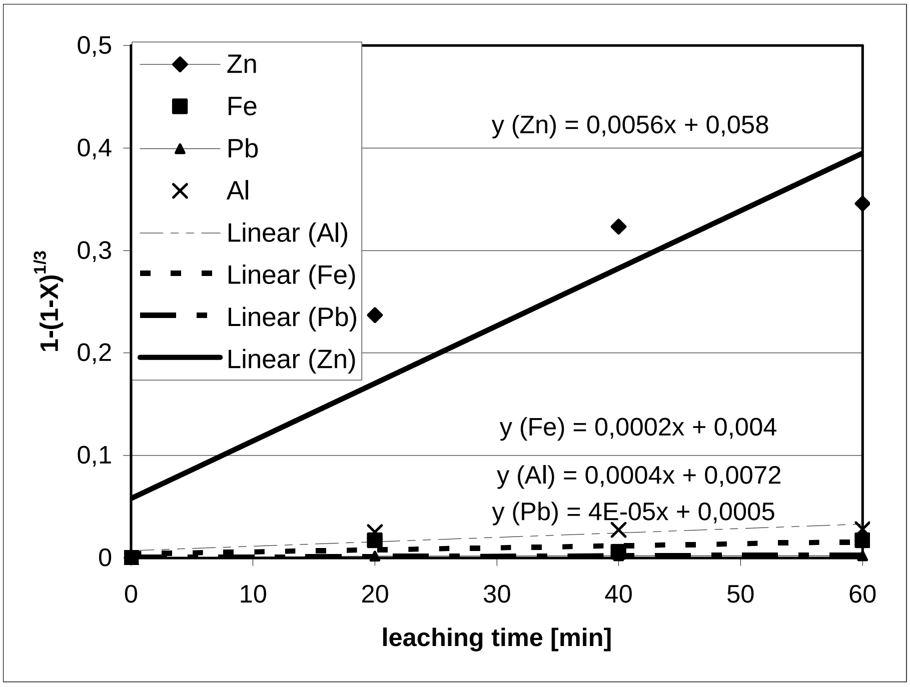


Figure 12: Testing of chosen kinetics models

As shown at Fig. 12 the dissolution of Fe, Al and Pb at 60°C should be described using an equation (9), what is not case for the zinc. The possible controlling stage for dissolution of these metals is a chemical reaction with sulphuric acid. An increase of temperature might intensify a dissolution of Pb, Fe and Zn. In order to determine the limiting step of zinc dissolution the models (10) and (11) were tested. Using the Equation (11) offers a good agreement with obtained results in contrast to results obtained via Eq. 10. Diffusion in a solid layer is a limiting step for zinc dissolution. Generally, a dissolution process of Zn, Fe, Al, and Pb should be presented by next equations:

y (Zn) = 0.016 + 0.086 (12)

y (Fe)= 0.0002 x+ 0.04 (13)

y (Al)= 0.0004 x + 0.0072 (14)

y (Pb)= 0.00004 x + 0.0005 (15)

The rate constant for Zn-dissolution at 60°C amounts 0.016, what is higher in comparison to values for Fe, Al and Pb dissolution (0.0002, 0004, 0.00004).

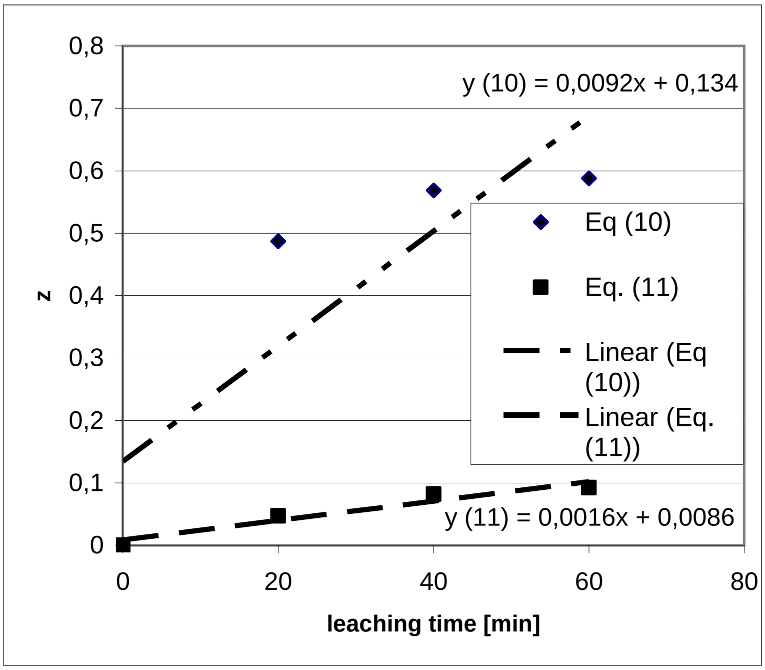


Figure 13. Testing of kinetics models for zinc dissolution (z represents a calculated value for left side of Eqs. 10 and 11)

3 Assessment and Conclusions

Mechanism and kinetics of thermal decomposition of iron zinc concentrate was the main subject of this study. Differential thermal analysis have shown decomposition phases at 27 - 417°C, at 402-885,at 600-960°C and at 1011-1120°C. The first three decomposition steps are diffusion controlled with the following activation energies of 1.2, 4.1, resp. 17.1 kJ/mol. The important decomposition of zinc ferrite as the forth step is described by a chemical control process with an activation energy of 166.9 kJ/mol.

The essential target of experiment part was to liberate zinc oxide from zinc-ferrite, an unsoluble part of the leaching residue from hydrometallurgical processes. Phase analyses of the untreated as well as decomposed material confirmed the presence of ZnO and Fe_3O_4 after decomposition and gave a first confirmation, that ZnO could be separated from the intermetallic phase as a leachable phase avoiding reduction and evaporation. The thermal decomposition of FeZn “concentrate” was performed at 1150°C in a tubular furnace under nitrogen gas atmosphere. The obtained chemical composition of 25.2% Zn, 22.5% Fe, 7.55% Pb, 1,7% Al has proven that the zinc is not evaporated. The XRD analysis of the samples after thermal decomposition shows predominantly ZnO, Fe_3O_4, Fe_2O_3, $Ca_2MgSi_2O_7$.

Simple leaching tests at 60°C and at atmospheric pressure were sufficient to confirm the liberated ZnO in the decomposed “concentrate”. At pH-values of 4.3- all impurities including iron stayed in the leach residue. The leaching efficiency of Zn reached values higher than 72 % within 60 min and even higher yields can be expected after longer times. This is a significant improvement compared to the untreated residue and proves the proposed treatment of Zn-Fe-intermetallics material.

Testing of kinetics models shown that the dissolution of Fe, Pb and Al at 60°C was controlled by a chemical reaction with a sulphuric acid, that is a limiting step. Under same conditions the dissolution of zinc is controlled by a diffusion a solid layer.

4 Acknowledgments

We like to thank Deutsche Forschungsgemeinschaft DFG in Bonn for financial support of the project FR 1713/13-1: "Kinetics and mechanism of thermal zinc-ferrite decomposition".

5 References

[1] Antrekowitsch, J. & Antrekowitsch, H. (2003): Dezinking of steel scrap, Proceeding of European Metallurgical Conference EMC 2003, Hanover, 449-463.

[2] Olper, M. & Maccagni, M. (2005): Zn Production from Zn bearing secondary materials: the combined Indutec®/Ezinex® Process, Proceeding of European Metallurgical Conference EMC 2005, Dresden, 491-500.

[3] Olper, M. & Maccagni, M. (2003): Primary zinc production by direct pressure leaching/EZINEX E.W.: a conceptual study, Proceeding of European Metallurgical Conference EMC 2003, Hanover, 523-532.

[4]. McElroy R.O. & Murray W. (1996): Developments in the Terra Gaia process for the treatment of EAF dust., Iron Control and Disposal, J. E. Dutrizac and G. B. Harris eds., Canadian Inst. of Min., Met., and Petroleum, Montreal, Canada, 39-44

[5] McElroy R.O. & McClaren M (1994).: Processing of electric arc furnace dust via chloride hydrometallurgy, Proc. Hydrometallurgy '94, IMM, Chapman & Hall, 993 - 1010

[6] Barrera-Godinez J. A. (1992): Effect of ultrasound on acidified brine leaching of double-kiln treated EAF dust, Minerals Engineering, Vancouver, 55-61.

[7]. Cruells M., Roca A., Nunez, C. (1992): Electric arc furnace flue dusts: Characterisation and leaching with sulphuric acid, Hydrometallurgy, 213-231

[8] Dreissinger D.B., Peters E., Morgan G. (1990): The hydrometallurgical treatment of carbon steel electric arc dust by the UBC-Chaparral process, Hydrometallurgy, 25, 137-1529.

[9] Barrett E.C., Nenniger E.-H., Dziewinski J. (1992): A hydrometallurgical process to treat carbon steel electric arc furnace dust, Hydrometallurgy, 30, 59-68

[10] Jandová J., Dvorak P., Vu H (2002): Recovery of magnetite and zinc from steelmaking dust by H_2SO_4 leaching, Recycling and Waste Treatment in Mineral and Metal Processing, June 2002, Lulea Sweden, 251-259

[11] Jha M. C., Duyvesteyn W. P.-C. (1985): A two-stage leaching process for selective recovery of zinc from steel plant dusts, Proc. Recycling and Secondary Recovery of Metals, P.R. Taylor, H.Y. Sohn and N. Jarret eds., Met. Soc. AIME, 143-157

[12] Lupi C., Pilone D., Cavallini M. (1996): Hydrometallurgical Processing of EAF Steelmaking Fumes, Proc. Extraction and Processing for the Treatment and Minimization of Wastes, V. Ramachandran, C.C. Nesbitt eds., TMS, 1996, 711-718

[12] Lupi C., Pilone D., Cavallini M. (1996): Hydrometallurgical Processing of EAF Steelmaking Fumes, Proc. Extraction and Processing for the Treatment and Minimization of Wastes, V. Ramachandran, C.C. Nesbitt eds., TMS, 1996, 711-718

[13] Püllenberg, R. (1981): Hydrometallurgische Verarbeitung eisenreicher Zinkkonzentrate nach thermischer Teilreduktion des Röstgutes, Doctoral Thesis, RWTH Aachen University, 88.

[14] Havlik, T., Stopic, S., Friedrich, B. (2005): “Pressure leaching of EAF dust with sulphuric acid, Erzmetall, 57, 2, 113-120.