

Zinc Stripping from Steelwork Dust

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Recycling is extremely important for steelmaking. In developed countries, about 60% of steel is manufactured from scrap. The scrap contains 0.5% of zinc in average, and this percentage steadily increases. During the steelmaking process both in basic oxygen furnaces (BOF) and in electric arc furnaces (EAF), all volatile zinc is released and forms airborne particles of dust. About 20 kg of dust is produced per 1 t of steel. A conservative estimate is that 10 Mt of the dust is produced yearly throughout the world. It contains about 1.5 Mt of zinc, which is still mostly dumped as a dangerous waste. This paper present a method of zinc recycling employing gaseous hydrogen chloride at 900 °C.

1. Introduction

During recycling of steel scrap in converters or electric arc furnaces, exhaust gas contains small particles which are collected in baghouse. These dust consists partly of entrained drops of metal and slag, however it contains also volatile metals, that are fumed from the steel melt, oxidized, and subsequently captured as airborne particles. Solely in the Czech Republic, every year about 100,000 t of this dust are deposited as a waste material. In last decades recycling of zinc plated pieces stays more and more important and therefore, the dust contains considerable percentage of zinc ferrite, $ZnFe_2O_4$, in mineralogical form of franklinite. This compound with a spinel structure is very stable. Dust landfilling needs some pretreatment and is quite expensive. Therefore, separation of Zn and Fe represents a great challenge not only from the view of metal production, but more as a prevention of environmental damage by huge dumps of dangerous material. Generally, there are two principal ways (Liebman 2000, Rao 2006) applied in industry:

Pyrometallurgy treatment is based on reductive heating of the dust at temperatures 1200-1400 °C. Under such conditions, zinc metal is formed, volatilized, and immediately oxidized and condensed as ZnO free of iron, which is captured in baghouses. Solid iron oxides free of Zn, Pb, Cd etc. can be returned to iron metallurgy. Rotary drum countercurrent kilns (Serbent et al.1079, recently e.g. Ezinex 2010) are applied for the process.

Hydrometallurgy treatment employs dissolution of the dust in concentrated acids or bases, followed by precipitation of iron compounds by hydrolysis at modified pH value. Appropriate insoluble iron compounds are haematite (Fe_2O_3), goethite ($FeOOH$), and in

special cases jarosite ($\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) (Riveros and Dutrizac 1997, Langová et al. 2007, Gupta 2003).

Both the pyrometallurgy and hydrometallurgy processes have been originally developed for treatment of rich zinc and lead ores, frequently used in of non-ferrous metals under the conditions when iron is minor constituent in the solution. In such cases the processes are evidently viable. For separation of smaller percentage of the volatile metals from high percentage of iron in materials like steelmaking dust, they are rather expensive. Nevertheless, several industrial scale pyrometallurgy plants are running in US and in EU (Fruehan 2000, Liebman 2000, Ezinex 2010). The hydrometallurgy treatment is technically feasible, however main difficulty lies in the facts, that vast volumes of the liquids and chemicals are required for iron precipitation and following filtration of fine particles of the precipitate is painful. It brings also a high level of hazard during manipulation with dissolved harmful heavy metals.

Recently appeared another option of zinc separation using gaseous hydrogen chloride generated by combustion of waste PVC. Laboratory results (Lee and Song 2007) give basic reasoning of the process, however there have also been reported pilot scale units (Tailoka and Fray 1997, Tee and Fray 2005). In our research we have concentrate ourselves to other option: recovery of zinc by pure HCl (Cieslar and Wichterle 2009, Cieslar 2009) or by HCl generated by pyrolysis of PVC under reduction atmosphere (Wichterlova 2009). In this paper we are presenting conclusions of recent investigation of the reactions of gaseous hydrogen chloride with metallurgy dust at higher temperatures.

2. Chloride metallurgy of steelmaking dust

2.1 Steelmaking dust

Dust under investigation was collected in Door thickener under backhouses in exhaust gas line of the tandem furnaces (TP) in Arcelor Mittal Steel Ostrava plants. As a reference material, SF (i.e. commercial synthetic ferrite manufactured by EPCOS Šumperk) has been applied.

Table 1: Elementary composition of the dust (mass percent)

Element	typical values	TP sample investigated	synthetic ferrite (SF)	method
Fe	45-55	48.7	50.3	photometry
Zn	8-16	14.5	28.0	photometry
Pb	<2	1.8		AAS
Cd	<0.05	0.02		AAS

Table 2: Particle size [μm] (Laser granulometry)

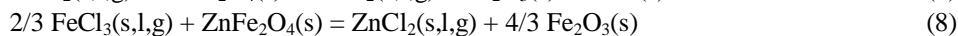
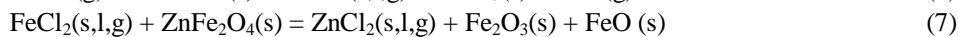
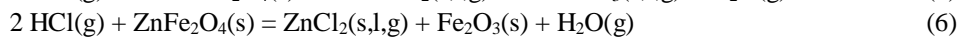
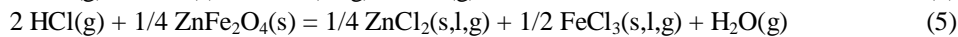
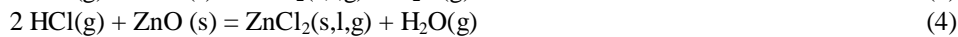
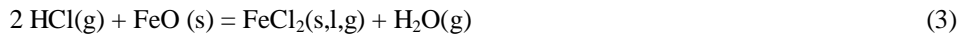
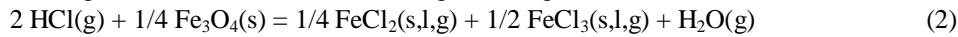
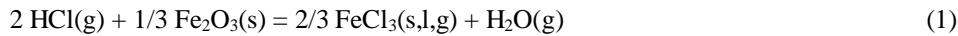
Dust	minimum	median	maximum
TP sample	0.35	3.1	120
SF	1,2	125	350

Table 3: Mineralogy phases of the TP dust (mass percent)

	chemical composition	mass %	mass % Zn
Haematite	Fe ₂ O ₃	3.2	
Magnetite	Fe ₃ O ₄	35.6	
Wuestite	FeO	3.2	
Franklinite	ZnFe ₂ O ₄	36.6	9.9
Grafitite	C	4.4	
Zinkite	ZnO	5.6	4.5
amorphous	-	11.4	

2.2 Thermodynamics analysis of reactions

Our research is oriented to attacking of the dust by gaseous hydrogen chloride at high temperatures employing suitable equilibrium conditions for the reactions



Gibbs energy of particular reactions plotted in Figure 1 were calculated on the basis of energy of formation of particular compounds taken from NIST WebBook and from Perry's tables.

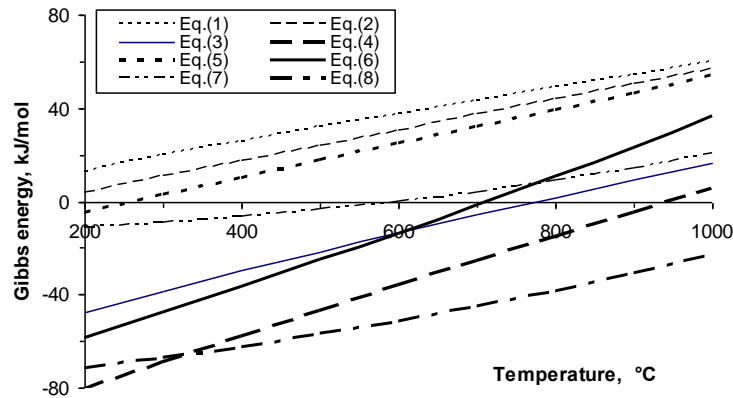


Figure 1: Gibbs energy for the reactions (1)-(8) as a function of temperature.

Evidently, iron chlorides are unstable at temperatures higher than 300°C. Zinc chloride is generally chemically stable up to 700 °C, however at higher temperatures it leaves the reaction space as gas (its boiling point is 756 °C) which affects the equilibrium. Therefore, higher temperatures are suitable to separate ZnCl₂ vapors from the solid

residuum of iron oxides. Similar results were obtained by Lee and Song (2007) or Pickles (2009).

3. Experimental

To investigate the reactions of metallurgy dust with gaseous HCl, a simple vertical quartz tubular reactor (diameter 30 mm) was manufactured (Cieslar, 2009). Solid bed (10 g) of dust was used throughout the experiments. After heating of the tube with sample in an electric oven to the desired temperature under nitrogen atmosphere, hydrogen chloride started to be fed slowly (superficial velocity 0.75 mm/s) to the reactor by a peristaltic pump. For this purpose HCl was generated by the reaction of NH_4Cl with H_2SO_4 and stored in a soft PVC bag. After the experiment, water soluble product collected from the reactor and from the condenser flask were analyzed.

4. Results

The most interesting results can be interpreted as conversion of particular metals. The conversion is understood here as a percentage of particular metals transformed to the water soluble form.

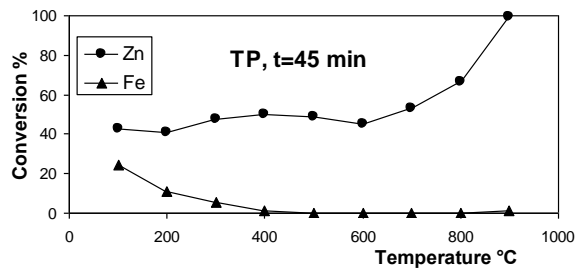


Figure 2: Conversion of metallurgy dust TP sample as a function of temperature.

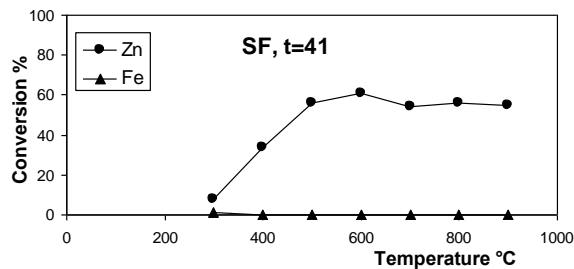


Figure 3: Conversion of synthetic ferrite SF sample as a function of temperature.

As apparent from Figures 2-3, at lower temperatures is the conversion of TP nearly constant. Essentially, mainly the zinkite is attacked. Lower conversion of SF is caused by larger grain of this material and mass transfer may control the reaction. It has been

proven by the results shown in Figures 4-6 with both materials at different time of contact. Evidently the TP sample reacts faster.

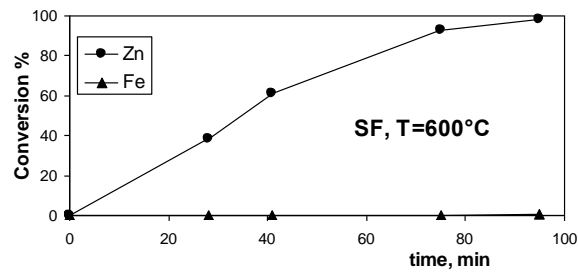


Figure 4: Conversion of synthetic ferrite SF sample as a function of time. $T=600^{\circ}\text{C}$.

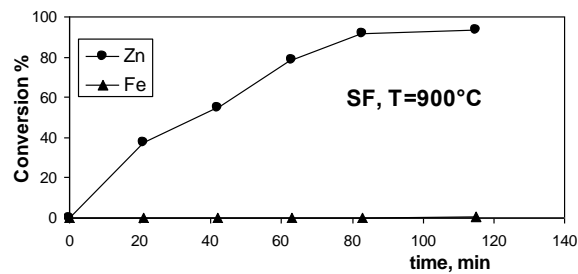


Figure 5: Conversion of synthetic ferrite SF sample as a function of time. $T=900^{\circ}\text{C}$.

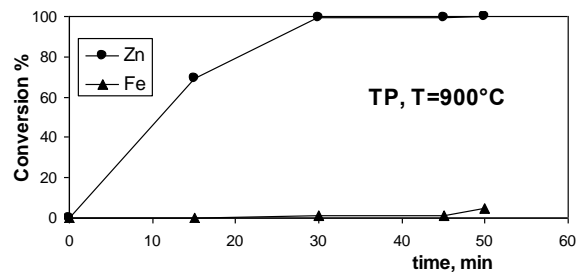


Figure 6: Conversion of metallurgy dust TP sample as a function of time. $T=900^{\circ}\text{C}$.

5. Conclusions

Treatment of steelworking dust with gaseous hydrogen chloride at 900°C enables zinc to be removed practically completely as ZnCl_2 . Time of the reaction should be well adjusted because after zinc removal, Fe is attacked again. It is promising way for employment of large deposits of dangerous waste material for recycling of iron and zinc.

Acknowledgments

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