

PROCESSES FOR STEELMAKING DUST TREATMENT

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ABSTRACT

Waste recycling belongs to important industrial activities resulting from economic and environmental reasons. According to statute, iron and steelmaking dust and sludge from gas cleaning are classified as a hazardous waste. In this study the hydrometallurgical processing of the basic oxygen furnace sludge is investigated on a laboratory scale. The basic oxygen furnace sludge samples containing heavy metals are leached in the sulphuric acid solutions under atmospheric pressure and temperatures up to 80°C. The aim of this study is to find conditions when maximum content of iron remains in a solid residue.

INTRODUCTION

At present, the European Union steel production is based on the blast furnace/ basic-oxygen route (approx. 65%) and the electric arc furnace (EAF) route (approx. 35%). World crude steel production significantly increased in 2006 compared to 1992 as shown in Fig. 1. Basic oxygen furnaces produce steel from molten iron (from the blast furnace) and ferrous scrap metal.

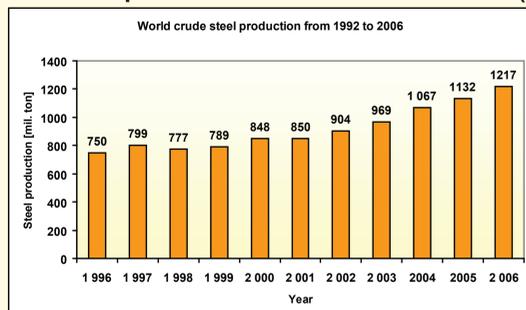


Figure 1. World crude steel production 1992 - 2006.

The proportion of scrap in the charge in a BOF is limited to less than 30%, whereas that in an EAF can be as much as 100%. This scrap contains high level of zinc and other heavy metals. This is due to the fact that in the last years this element has been used progressively in the galvanizing process of the steel. When these steel scraps are reused, the contained zinc is evaporated during the melting (boiling point of zinc is 907°C), passing nearly all to the dust and sludge, remaining very low amount in the steel and in the slag.

Steelmaking dust and sludge are waste oxide materials, whose major components are iron oxides. They also contain zinc, lead, cadmium and other minor element oxides in small amounts.

There are a several alternatives of steelmaking dust and sludge pre-treatment (Fig. 2): pyrometallurgical, hydrometallurgical, and eventually combined. Each of existing methods has their specifics, advantageous as well as disadvantageous and significantly depends on mineralogical and chemical composition of just processed dust and sludge. In general, it still doesn't exist effective and economic advantageous method for treatment these wastes.

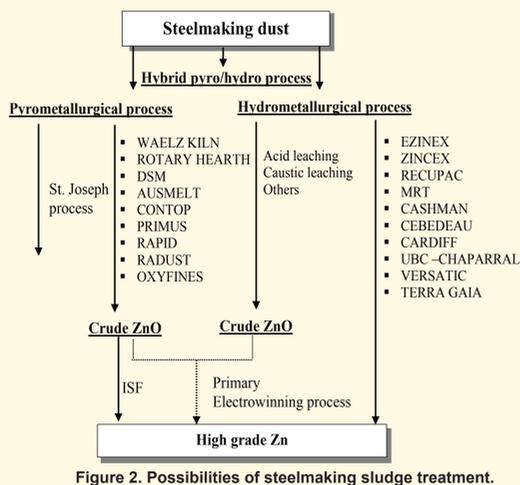


Figure 2. Possibilities of steelmaking sludge treatment.

MATERIALS AND METHODS

The basic oxygen furnace sludge sample was used in these experiments (Table 1). Chemical analysis was performed by Atomic Absorption Spectrometry (AAS) method after decomposition by alkaline fusion. Total loss of ignition was 12.49%. The sludge sample was dried at 80 – 100°C, crushed and screened before use.

Table 1. Chemical analysis of basic oxygen furnace sludge [%].

Element	Cl	Fe	Zn	Pb	Sb	Sn	Cu	Ca	Mg
Content [wt.%]	7.09	47.67	2.74	0.18	0.31	0.2	0.1	6.8	0.55

Element	Cr	Ni	Ag	Co	Si	Mn	Loss of ignition
Content [wt.%]	0.01	0.09	0.06	0.02	0.61	0.49	12.49

The sample of basic oxygen furnace sludge is also examined by an X-ray diffraction qualitative phase analysis. The results are shown in Figure 3, from which the presence of compounds such as Magnetite Fe₃O₄, Wustit FeO, Calcite CaCO₃, Graphite C, metallic Fe can be inferred. Other phases, which, on the basis of the chemical analysis, could be present, (Table 1), are probably below the detection limit.

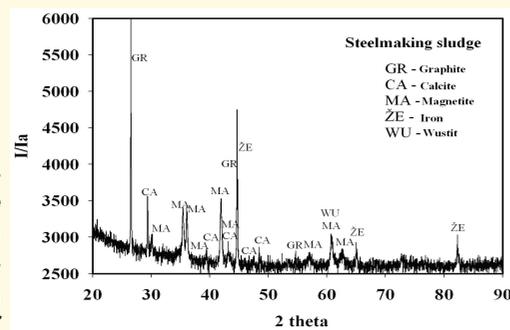


Figure 3. XRD pattern of the steelmaking sludge sample.

Experimental set - up

The leaching experiments were performed in the apparatus, of which a scheme is given in Figure 4. A glass reactor of 800 ml, which was placed in a water thermostat, was used for the leaching. This allowed keeping the desired temperature of the leaching automatically. Leaching tests were performed with a solution 400 ml of 0.1, 0.2, 0.4, 1.0, 2.0 and 3.0 M H₂SO₄ at the temperatures 20, 40, 60 and 80°C. In each of experiment were used revolutions of the glass stirrer equal to 300 min⁻¹. The sample weights for the leaching experiments were 40, 30 and 20 g with a liquid to solid ratio equal to 10, 15 and 30. The liquid samples for chemical analysis were taken to according to a fixed- schedule after 2, 15, 30, 45 and 60 minutes. Then, the samples were filtered for purpose of their separation from residual of the solid phase.

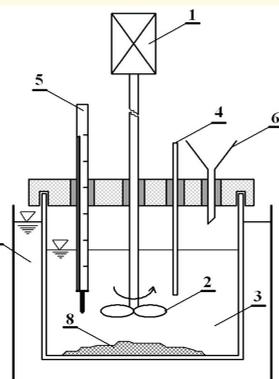
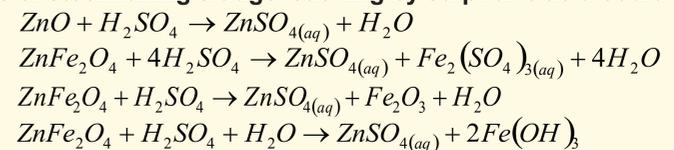


Figure 4. Schematic view of the leaching apparatus 1 - stirrer engine; 2 - propeller; 3 - pulp; 4 - sampler; 5 - thermometer; 6 - feeder; 7 - water thermostat; 8 - BOF sample

The chemical analysis, carried out in order to determine Zn and Fe, was made by means of AAS Variant Spectrometer AA 20+. All results were recalculated because of the change of the pulp volume due to the sampling and evaporation.

RESULTS AND DISCUSSION

The basic reactions of steelmaking sludge leaching by sulphuric acid could be described by following equations:



Reaction (2) is thermodynamically preferable to Eqs. (3) and (4) within the temperature range used in experiments. Zinc and iron behaviour during leaching (at different pH and potential values) is obvious from the E- pH diagrams of the system Fe - S - Zn - H₂O at 25°C and 100°C are shown in Figure 5,6.

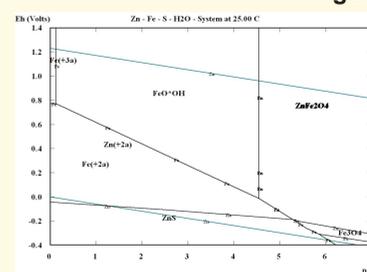


Figure 5. E - pH diagram of the system Fe - S - Zn - H₂O at 25°C

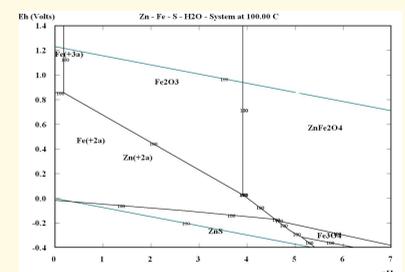


Figure 6. E - pH diagram of the system Fe - S - Zn - H₂O at 100°C

Leaching results

It follows from the kinetic study that the process is faster at higher temperatures. Figure 7 shows the leaching kinetic curves of zinc by using various sample charges at the temperature 80°C and 1 M concentration of H₂SO₄. Zinc extraction efficiency was not influenced by using various L:S ratio.

Figure 8 shows dependency of pH values on leaching time. There is still sufficient amount of free acid in the leaching system at higher L:S ration so zinc and iron are dissolved in the solution and form stable ions. At low values of L:S ration acid is consumed and pH increases to values at which iron hydrolytically precipitates and forms oxides, hydroxides or oxysulphates.

Figure 9 shows the kinetic curves of zinc leaching from BOF sludge depending on sulphuric acid concentration at the temperature 80°C and L:S ratio equal to 20. The leaching process was very fast and practically immediately after the beginning all amount of zinc from BOF sludge is transferred into the solution under the given conditions. However, at low acid concentration the amount of extracted zinc slightly decreases with time. That is probably related to the effort of the system to achieve the dynamical equilibrium. According to the thermodynamic study, the iron precipitates as FeO.OH at low pH values. Zinc probably co- precipitates with iron and some part is adsorbed on the surface of the iron precipitate. The decrease of the zinc concentration in solution during the experiment could be explained by this mechanism. The zinc extractions increased with increasing acid concentration (0.1 – 1M).

Figure 9 shows that there are significant differences in zinc extraction efficiency depending on used acid concentrations. After 2 minutes of leaching the zinc extraction efficiency about 15% was reached by using 0.1 M sulphuric acid. Therefore weak acid is not suitable for BOF sludge leaching. The maximum zinc extraction efficiency (about 80%) was achieved by using 1 M sulphuric acid.

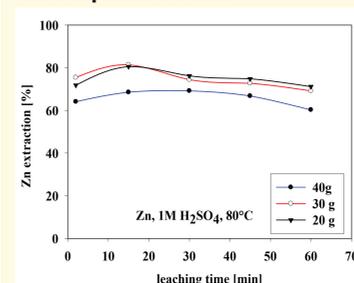


Figure 7. Leaching kinetic curves of zinc by using various sample charges at a temperature 80°C, 1 M H₂SO₄ and L:S=20

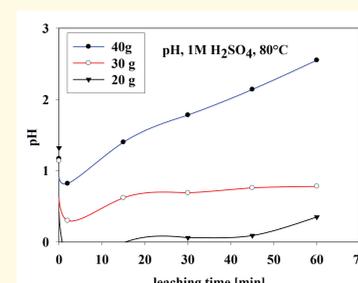


Figure 8. Dependency of pH values on leaching time

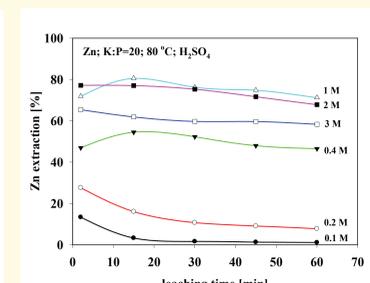


Figure 9. Extraction of zinc with sulphuric acid at a temperature 80°C and L:S=20

CONCLUSION

- It was found that by acid leaching can be extracted 80% of zinc from BOF sludge.
- The leaching process is very fast and practically immediately after the beginning all amount of zinc from BOF sludge is transferred into the solution under the given conditions.
- The best leaching conditions were 1 M H₂SO₄ at 80°C and L:S ratio 20.
- However, the chemical a mineralogical composition of each of steelmaking sludge is individual. So, it is necessary to study the processing conditions for each one of them.

ACKNOWLEDGE

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