

HYDROMETALLURGICAL BASE METALS EXTRACTION FROM STEELWORKS FLUE DUST

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ABSTRACT

The production of steel in electric arc furnace (EAF) generates a by-product called EAF dusts. These steelmaking flue dusts are classified in most industrialized countries as hazardous residues because the heavy metals contained in them, tend to leach under slightly acidic rainfall conditions. However, and at the same time they contain zinc species which can be use as a source to obtain valuable by-products. The present investigation shows results on the processing of a steelwork flue dust using oxidative leaching processes that release in the bulk chlorine gas in charge of dissolving the base metals, copper and zinc in particular. The leachate-bearing copper and zinc ionic species, and other metal species, such as iron, out of the aforementioned oxidative processes, is treated for producing quite important chemicals, such as copper chloride, starting point for producing copper oxi-chloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, a very used fungicide in agriculture, zinc sulphate (ZnSO_4), from where zinc oxide can be produced, and goethite (FeOOH) quite used in the ceramic, paint, cosmetic and pharmaceutical industrial sectors.

KEYWORDS: electric arc furnace; base metals; steelworks flue dust.

1. INTRODUCTION

In 2008, more than 1.33 billion tons of steel were produced worldwide. The main producers were: China (31.6 %)- EIJ-27 (74.9 %), Japan (8.9 %), USA (6.9 %) and Russia (5.2%). In Slovakia, almost 4.5 million tons of steel were produced in the same year; 7.8 % of this amount was produced in electric arc furnaces (EAF) [1]. During the steel production in EAF, around 15 to 20 kg of dust per 1 ton of produced steel is generated as a byproduct [2].

Due to the high content of heavy non-ferrous metals, mainly Zn, Pb, Cd, Cr and others, these dusts are classified as hazardous waste according to US EPA (United States Environmental Protection Agency) [3]. On the other hand, due to the high content of iron and zinc, this material can be considered as a suitable secondary raw material for obtaining these metals. Metal contents in EAF dust from various sources are shown in Table 1.

2. EXPERIMENTAL

2.1. Physical Characterization

The particle size analysis was accomplished, and according to the results of Table I, it was found that around 54% of the sample had particle size equal to/or smaller than 200 mesh. Due to this granulation that material was more likely to be leached/digested, in a stirred tank reactor, since that digestion is more favoured due to a larger surface area for its acid digestion to take place.

Table I. Particle size analysis of the steelworks flue dust.

Tyler series (mesh)	Opening (mm)	Retained Weight (g)	Accumulated Retained Weight (g)	Accumulated Retained Weight (%)	Passing Retained Weight (%)
80	0.177	11	11	11.00	89.00
100	0.149	8.7	19.7	19.70	80.30
150	0.105	11.9	31.6	31.60	68.40
200	0.074	13.9	45.5	45.50	54.50
270	0.053	11.6	57.1	57.10	42.90
325	0.044	3.5	60.6	60.60	39.40
>325	-0.044	39.4	100	100.00	0.00

2.2. Chemical Characterization

The metal contents out of the sample under study were quantified by atomic absorption spectrometry (AAS) after its acid digestion. The equipment used was a spectrometer brand VARIAN model AA.

In accordance with the technique of Flame Atomic Absorption Spectrometry (air/C₂H₂), the copper and zinc contents, present in the steelworks dusts used, were 28.30% and 47.50 %, respectively. However, it is possible to observe the presence of other metals in smaller contents (Table II).

Table II. Metal contents in the steelworks flue dust used.

Chemical analysis	
Cu	28.30%
Zn	47.50%
Pb	1.20%
Fe	0.30%

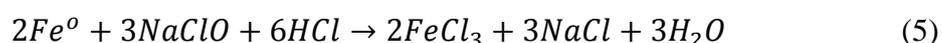
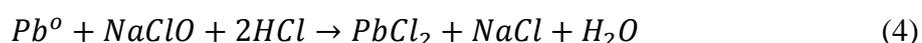
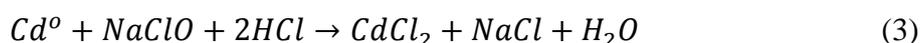
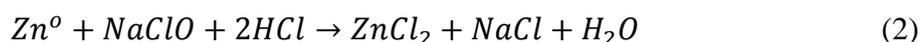
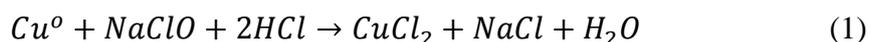
2.3. Technological Routes

The acid route is based on dissolution of metallic particles in hydrochloric acid with periodic addition of sodium hypochlorite (NaClO), an oxidizing agent that releases chlorine gas when in contact with acidic solution.

Once getting the analytical results for the composition of the steelworks flue dust, a sample of this material was placed in the oven, for 3h under 50°C. Approximately 50g of the particulate material were introduced into a 500mL reactor, for further addition of the chemicals so as to digest that residue.

The tests were carried out considering three experimental conditions levels, where the acidic solutions used in the dissolution tests contained hydrochloric acid (HCl) 40%, 50% and 60% v/v, derived from diluting the 37% v/v with a density of 1.18g/cm³, while maintaining a solid/liquid ratio of 1:10, with the periodic addition of sodium hypochlorite (NaClO) to 15% w/v, as oxidizing agent, directly in the bulk of the solid suspension, under mechanical stirring at 500 rpm taking sample of the liquid phase for analysis every hour past.

The equations, as follows, show how the metals dissolution reactions take place when in contact with sodium hypochlorite solution in hydrochloric acid.



The remaining residue, after running the hydrochloric acid leaching for 6 hours, were digested and the aqueous phase analyzed by flame Atomic Absorption Spectrometry (air/C₂H₂) for evaluating the content of the remaining metals of interest (Copper, Zinc and Iron) that might have remained insoluble so as to work out the metal extraction efficiencies. Therefore, the Figure 1 highlights the metal extraction in the tests accomplished under the following experimental conditions: 60% HCl and 70ml of NaClO (98.85% Cu, 95.00% Zn and 72.86% Fe), 50% HCl and 100ml of NaClO (98.66% Cu, 94.97% Zn, and 71.90% Fe), 40% HCl and 150ml of NaClO (98.68% Cu, 95.18% Zn and 72.26). The analyzes of the liquid samples taken at the end of the dissolution process presented concentrations of, approximately, 23g.L⁻¹ in copper and 45 g.L⁻¹ in zinc in more effective tests; while the iron concentrations were close to 250mg.L⁻¹.

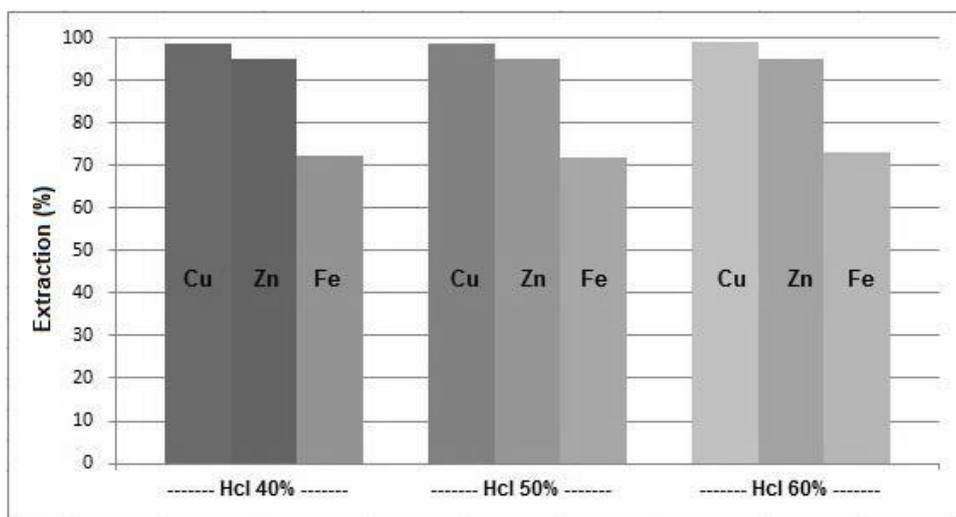
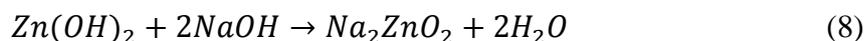


Figure 1. Extraction of copper, zinc and iron in the 6 hours leaching tests.

After dissolving the residue under study, the lead is also oxidized, but as the medium is hydrochloric acid, during the dissolution of metals $PbCl_2$ is generated, which is insoluble in aqueous medium. The first operation is, therefore, the filtration of this precipitate for separating it from the liquid phase that contains Cu^{2+} , Zn^{2+} and Fe^{3+} ions. However, the excess of Cl^- ions may encourage the formation of soluble lead complexes, as shown in equations 6 and 7, which decompose by dilution with water, with the consequent separation of lead chloride.



The remaining solution has its pH raised (for the range of 5.5 to 6.5), by adding 1M NaOH solution, when copper oxi-chloride ($3Cu(OH)_2 \cdot CuCl_2$) and some other metallic impurities (such as iron and cadmium in their respective hydroxides) are precipitated, which are further separated from the aqueous phase by filtration. From given leachate bleach copper oxi-chloride was obtained by precipitation at different pH values. It is worth noting that the zinc content in the inorganic salt obtained may be reduced by alkaline washing it, where the zinc in the form of hydroxide ($Zn(OH)_2$) is solubilised producing sodium zincate (Na_2ZnO_2), as shown in equation 8.



The remaining solution, after filtrating the copper oxi-chloride, undergoes an elevation of pH up to 8.5, by adding of 1M sodium hydroxide (NaOH) solution, when moment occurs the precipitation of zinc as hydroxide ($Zn(OH)_2$), which is separated from the aqueous phase by filtration. The chemical analyzes of such zinc salt obtained showed the following contents: 51.2% of Zn, 2.0g/kg of Cu and 189mg/kg of iron.

Looking for alternatives to the production of other inorganic salts, a thermo-gravimetric analysis was carried out on a zinc hydroxide sample, obtained from the steelworks dust, making it possible to establish the temperature of $270^\circ C$ as the most indicated for obtaining of zinc oxide (ZnO), from the mass loss, depending on the application of an increasing gradient of temperature, as can be seen in Figure 2. This Figure shows the thermal transformations, which were then refuted by X-ray diffraction of Figure 2. The zinc oxide obtained can be used in various industrial applications such as rubber vulcanization, cosmetics, zinc phosphate, medicines, ceramic structures, and polymers

and, still, the starting point for the production of zinc sulphate, as shown in equation 9, to be used as a source of zinc as micro-nutrient.

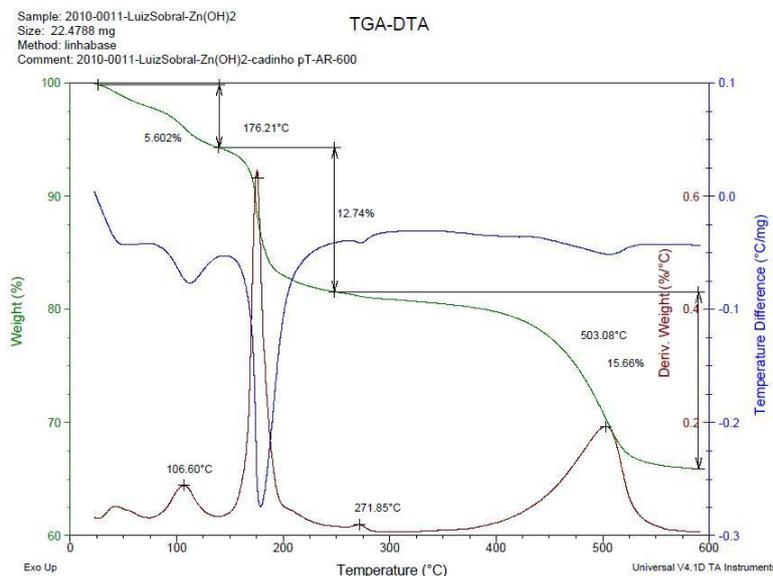
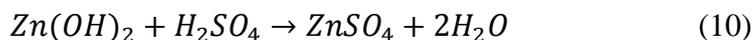


Figure 2. Thermo-gravimetric analysis of zinc hydroxide.

In addition, after obtaining the zinc hydroxide, it is further dried, and transformed into zinc sulphate reacting it with sulphuric acid solution, as shown in equation 10, as follows:



3. CONCLUSIONS

The production of inorganic salts of copper and zinc from the dissolution of a steelworks dust is a very attractive process.

The hydrochloric acid leaching of steelworks flue dust, adding sodium hypochlorite, presented promising results regarding the extraction efficiencies of metals, where it was possible to obtain the dissolution of 98.0% copper and 95.0% for the zinc present in the samples used in 6 hours tests.

4. REFERENCES

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