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Study of Zinc Leaching of EAF Flue Dust Using Sodium Hydroxide

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Abstract

During the production of steel from Electric Arc Furnace (EAF), large amount of by-product called EAF flue dust is generated. The major proportion of flue dust is comprised of Zn (41.5 % wt.). Different phases identified by XRD analysis are zincite, franklinite and magnetite with zincite being dominant. In this study, we have performed flue dust treatment using sodium hydroxide as leaching medium. Different concentrations of alkali were used to optimize maximum recovery of Zn. XRF and wet chemical methods were used to characterize the dust samples both before and after leaching. The optimum alkali concentration for selective leaching of Zn was found to be 4 M with a Zn recovery of 90 %.

Keywords: EAF dust; Leaching; Sustainable environment; Zn recovery.

Introduction

In steel-making plant, the production of Electric Arc Furnace (EAF) dust is 1–2 % of total steel obtained that contains a considerable amount of hazardous metallic wastes [1, 2]. This dust is classified as a hazardous waste class I, code K061 by the Environmental Protection Agency (EPA). The most hazardous metals according to EPA classification are lead, cadmium and chromium (VI), whereas Zn, due to its comparatively large amount present is the most valuable component [1,3–7]. Zn sulphide and Zn carbonate are the main source of Zn production however it is partly produced from various complexes and wastes such as Zn ash, Zn dross, EAF dusts, scraps and slags by pyrometallurgical, hydrometallurgical or their combination processes [8][9].

The flue dust is either directly thrown to landfill without any pretreatment to remove hazardous components or added into the air as pollutant. In addition, it has been observed that this flue dust is rich in valuable metals such as Zn and Fe which may be recovered using standard recovery procedure [10]. The department of mineral resources of Pakistan reported that this dust consisted of 25–50 wt.% Zn, 10–40 wt.% Fe, which is around 225–500 MT of Zn and around 90–400 MT of Fe. The major processes to dispose this dust are chemical stabilization, vitrification, pyrometallurgy and hydrometallurgy. Hydrometallurgy is widely used for Zn recovery due to economic and environmental benefits [11–13].

In Pakistan several types of Zn containing waste materials are available. These include EAF flue dust, Zn scrap and spent dry cell batteries. Among them, the major proportion of Zn is found in EAF flue dust. The contents of Zn, Fe and Pb in EAF dust according to global perspective are shown in Fig. 1 [18-24]. It is noted that the highest percentage of Zn is available in Pakistani EAF flue dust, which is mainly due to the use of 100 % automotive galvanized scrap. As these metals are present in the form of metal oxides and are harmful to the environment, therefore it is strictly prohibited as per the guidelines of EPA to dispose-off the flue dust either in the air or as landfills without treatment. Hence to meet economic benefits and environmental constrains, it is necessary to recover valuable metals from the flue dust.

Until now, extensive research efforts have been conducted to optimize kinetic parameters of hydrometallurgical method leading to maximized Zn recovery. The primary work focused on utilization of the leaching reagent such as sulfuric acid [2,14–21]; hydrochloric acid [22,23]; nitric and citric acids [12]; and sodium hydroxide [1,3,9,11,24–26]. All the leaching agents showed different affinity towards different metals, Zn being the most attractive. Sulfuric acid is widely used leaching medium for both Zn and Fe; although it requires electrowinning step for the purification of Zn, whereas sodium hydroxide selectively removes Zn at low concentrations thus avoiding need of electrowinning [3].

In this paper, hydrometallurgical technique using alkaline leaching from an EAF dust is investigated, aiming at maximum recovery of Zn. Sodium hydroxide was chosen as leaching agent as it is effective in the dissolution of Zn, lead and other toxic heavy metals without significant dissolution of Fe, thus reducing the hazardous character of solid residue.

Materials and Methods

Chemical composition of the sample was determined by wet chemical method (WCM). Trace elements were analyzed as pressed pellet through Axios^{max}, WD-XRF spectrometer of 3KW X-ray tube. The pressed pellets were prepared at 6:1 (sample: binder) with the help of Omnian standard application of PANalytical origin. For mineralogical phase identification, the EAF dust sample was examined by X-ray diffractometer (Model JDX-3532, JEOL Ltd., Tokyo, Japan) using CuKa radiation of wavelength, $\lambda = 1.5418$ A°. Fig. 2 shows the diffraction patterns of the dust.

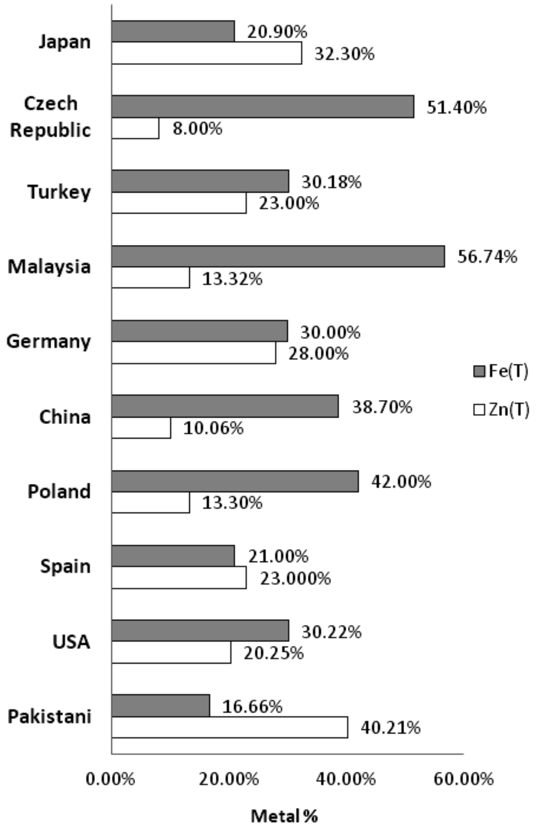

Figure 1. **Comparison of global EAF dust composition**

A small unit was developed to leach out metals from their metal oxide present in EAF Dust. The unit comprised of a glass vessel of 0.5 L covered with a polycarbonate disk of same size as of the beaker. The disk consisted of two openings, one for mechanical agitator having adjustable revolutions and second for thermometer. The temperature was maintained using Isomantle having thermostat for temperature control. To study kinetics, leaching experiments were performed with solution of 400 ml of different alkali concentrations (2, 4, 6 and 8 M NaOH) at 90 ^{0}C. The sample weight was taken as 8 g, measured on analytical weight balance. A solution with alkali-to-EAF dust ratio (ml/g) of 50 was used.

The liquid samples were filtered on ash free filter paper and inserted into vial bottles revealing clear solutions. Residue left on the filter paper weighed, dried in oven at around 110 °C. The elementary analysis of residual samples were carried out in order to determine elements composition using PANalytical XRF spectrophotometer.

Results and Discussion

Characterization of samples

The chemical composition of EAF flue dust depends on types of steel, quality of scraps being processed, operating conditions, recycling of dust, efficiency of de-dusting plant to capture the dust and molten metal to slag thermodynamic reactions. Chemical composition of dust samples was provided in Table 1, which shows that it is rich in valuable metals including Zn 41.446 %, Fe 15.471 % and Pb 2.03 %. In addition, Na, K and Ca are also present around 1 % each, that can be easily leached out by ion exchange technique [14]. Heavy metals like Pb & Cd as well as halides of Cl are also found. They all are beyond the range of disposable landfills as per EPA, USA. (Recommended safe limits for EAF flue dust are Cd: 0.19, Pb: 0.37 mg/L).

Table 1. **Chemical composition by wet chemical & XRF spectrometer.**

Comp	Mg	K	Ca	Cr	Mn	Fe	Cu	Zn	Pb
%	0.694	1.019	0.914	0.260	0.905	15.471	0.226	41.446	2.03

Leaching reaction

The reactions of main species occurring in the sample and their stoichiometry can be stated as follows:

$ZnO + 2NaOH \rightarrow Na_2ZnO_2\,(aq) + H_2O(l)$ (1)
$ZnFe_2O_4 + 2NaOH \rightarrow Na_2ZnO_2\,(aq) + Fe_2O_3(s) + H_2O(l)$ (2)
$PbO + 2NaOH \rightarrow Na_2PbO_2\,(aq) + H_2O(1)$ (3)
$FeO + 4NaOH \rightarrow Na_4FeO_3\,(aq) + 2H_2O(1)$ (4)
$Fe_2O_3 + 6NaOH \rightarrow 2Na_3FeO_3\,(aq) + 3H_2O(1)$ (5)
$Fe_3O_4 + 14NaOH \rightarrow Na_4FeO_3\,(aq) + 2Na_5FeO_4\,(aq) + 7H_2O(1)$ (6)

X-ray diffraction pattern

For the identification of all possible phases, X-ray diffraction of the EAF dust have been performed. Fig. 2 shows the XRD patterns of untreated EAF dust as well as alkali treated EAF dust with concentrations of 2M, 4M, 6M and 8M. The dominant phases identified by XRD analysis are zincite, franklinite and magnetite. In EAF dust, Zn is found in the forms of Zn oxide (zincite–ZnO) and Zn ferrite (franklinite–$ZnFe_2O_4$), whereas Fe is mainly in the form of franklinite and magnetite (Fe_3O_4). Zn oxide has four distinct peaks with 2θ of 31.77°, 34.42°, 36.24° and 47.57°. The graph shows that $ZnFe_2O_4$ and Fe_3O_4 have the same diffraction patterns. Phases with low fractions such as quartz, $CaFe_2O_5$, etc. have also been identified with suppressed peaks in the background. Peak of ZnO phase was found decreasing with increase in alkali concentration.

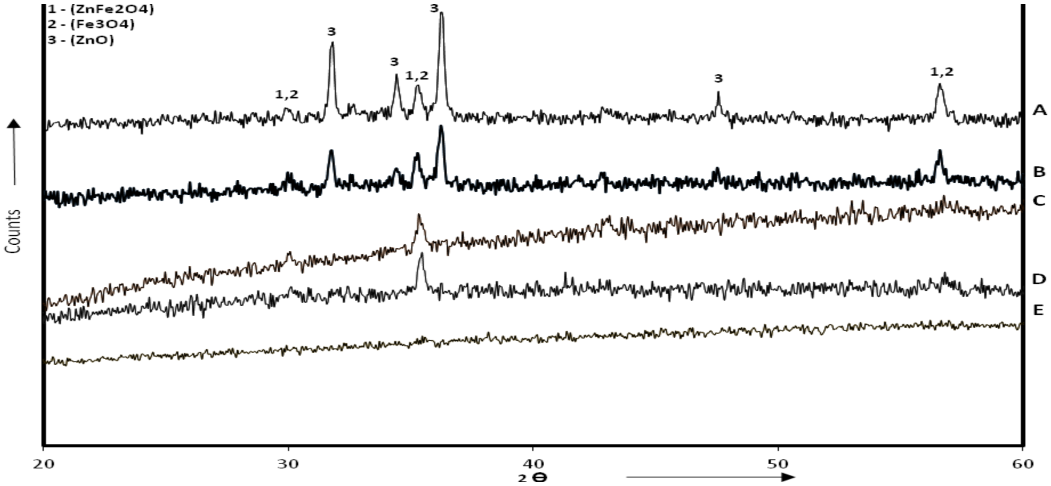

Figure 2. **X-ray diffraction analysis of EAF dust sample. (A) untreated dust (B) 2 M alkali treated (C) 4 M alkali treated (D) 6 M alkali treated (E) 8 M alkali treated**

Effect of alkali concentration on metal recovery

The effect of alkali concentrations was investigated at 120 minutes by keeping other conditions constant as liquid-to-solid ratio of 50 ml/g and temperature 90 ºC in the concentration range of 2 - 8 M. The results obtained are shown in Fig. 3. From these tests, it could be deduced that the recovery of Zn, Fe and Cr are functions of alkali concentrations; increase in concentration of alkali increases the leaching of Zn preferentially. However, when concentration increases beyond 4 M, it has only little effect on the leaching (Fig. 3). Thus, a concentration of 4 M NaOH should be sufficient for selective extraction of Zn. The highest Zn recovery obtained was 98 % at 8 M concentration of alkali. In case of Fe and Cr, percent recovery vary linearly with concentration in increasing order and the highest recovery obtained were 90 % and 92 % respectively at 8 M concentration of caustic soda which is lesser than that of Zn.

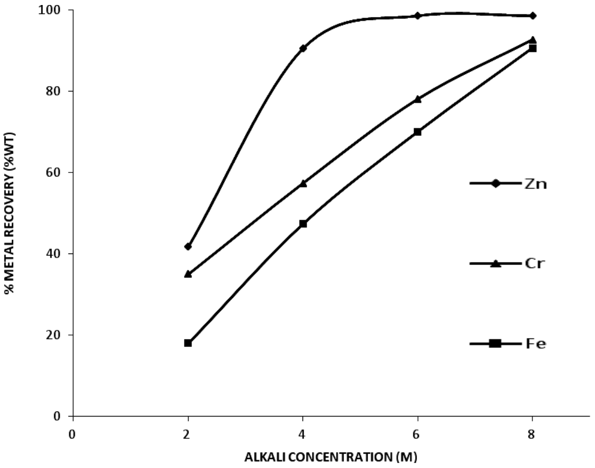

Figure 3. **Recovery % of different metals vs. concentrations (at 2h leaching time, 300 rpm and 90ºC)**

Effect of alkali concentration on metal composition

The effect of concentration was investigated for metals left in the residue after completion of leaching. From (Fig. 4) it could be deduced that at 90°C, as the concentration of alkali increases, composition of Zn and Fe decreases in the residue thus increasing the recovery. This confirms that at 8 M concentration, highest % of Zn is leached. The dissolution of Zn is very high, for all concentrations in comparison to other metals, tending to a maximum value of Zn extraction. From 2 M to 4 M, almost 85 % Zn and 45 % of Fe was reduced, while from 4 M to 8 M the reduction in Zn and Fe are 82 % and 80 % respectively; therefore 4 M is best for selective leaching of Zn.

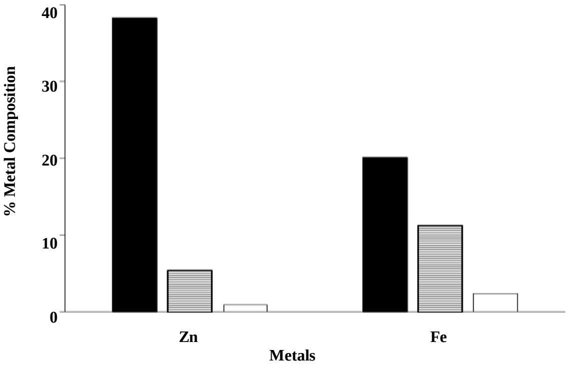

Figure 4. **Metal composition % in residue with respect to concentrations 2M, 4M, 8M at 2h leaching time, 300 rpm and 90ºC**

Comparison of metal composition

Table 2 shows the composition of metals before and after the leaching of EAF dust with alkaline solution at 6 M and 90°C. It confirms that Zn has maximum extraction efficiency in comparison to other metals as it is 80 % reduced while Fe and Pb are reduced to 28 % and 66 % respectively.

Table 2. **The chemical composition of the zinc extraction residue before and after alkali leaching when treated at a concentration of 6 M.**

Sample	Zn %	Fe %	Pb %
Before Leaching	41.45	15.47	2.03
After Leaching	8.11	11.24	0.68

Conclusion

Based on results achieved in the laboratory study, it was found that major portion of Zn present in an EAF dust is zincite, with some portion of Zn ferrite and Fe oxide as confirmed by X-ray diffraction analysis. The characterization of as received EAF dust sample was carried out which revealed the following composition: 41.446 % Zn, 15.471 % Fe and 2.03 % Pb. It was deduced through experimentation that the concentration of 4 M is the optimum for selective leaching of Zn from EAF dust using alkaline solution. It was also observed that the highest Zn recovery was 98 % after leaching for 2 h with 8 M NaOH solution with other heavy metals such as chromium and Fe. The investigation of the residue using XRF showed that the impurities such as Ca, Mg and K were in negligible level, which was further confirmed by XRD results due to the suppressed peaks. In addition, presence of low Fe content in the solution obtained after leaching eliminates the need for the electrowinning process for Zn separation.

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