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LEACHING CHARACTERISTICS OF EAF AND AOD STAINLESS STEEL PRODUCTION DUSTS

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Abstract. In this paper sulfuric acid leaching of four different stainless steel production flue dusts is studied. The main objective is to study and compare the valuable metal Zn, Cr, Ni, Fe, Mo dissolution present in the EAF 1&2 (electric arc furnace) and AOD 1&2 (argon oxygen decarburization converter) dusts. The effect of sulfuric acid concentration, temperature and liquid-to-solid ratio are tested for maximum and selective Zn leaching into solution for recycling purposes. Leaching tests were done in 0.1 M, 0.5 M and 1.5 M sulfuric acid, at temperatures of 30ºC, 60ºC and 90ºC with liquid-to-solid ratios L:S = 10 and 20 under 1 bar pressure for 120 minutes. Maximum Zn dissolution yield was achieved with 1.5M, 90ºC, L:S = 10 where the Zn dissolution yield varied from 65% to almost 100%, depending on the dust type (AOD, EAF) and production line (1 or 2). At the same time Cr was leached 7 – 17%, Ni 37 – 48%, Fe 48 – 89% and Mo 82 – 100%. The best zinc selectivity vs. Cr, Ni, Fe, Mo was achieved with 0.5 M, 30ºC and L:S 10. The Zn dissolution varied between 33 – 72%, Cr 2 – 4%, Ni 6 – 9%, Fe 2 – 9% and Mo 1 – 55%. Higher temperature and acid concentration resulted in faster dissolution of metals. AOD dust in both lines 1 and 2 has better valuable metal recycling possibilities than EAF dust due to better maximum Zn dissolution and better selective dissolution of Zn vs. Cr, Ni, Fe, Mo.

keywords: stainless steel dust leaching, EAF, electric arc furnace AOD, argon oxygen decarburization converter, hydrometallurgy, recycling

1. Introduction

Various amounts of wide range metal containing dusts are generated in separate parts of stainless steel process. In electric arc furnace (EAF), for example, about 1-2% of the charge is turned into dust (Steinlechner and Antrekowitsch, 2010; Tsakiridis and Oustadakis, 2010). Both the EAF and AOD dusts contains various amounts of chromium, nickel, iron, zinc and other heavy metal oxides and the weight percent of these elements usually varies from batch to batch basis (Nyirenda, 1991; Machado and Brehm, 2006; Tsakiridis and Oustadakis, 2010). Due to stricter environmental regulation laws and high price of stainless alloying elements, the valuable segment (Cr, Ni, Mo) of the stainless steel dusts are in the interest to be recycled back to

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process, and the rest, small part of the harmful materials that are now landfilled, to be neutralized or minimized.

Today, most part of the carbon steel and stainless steel dusts are treated in separate plants mainly by pyrometallurgical methods to recover majority of the valuable materials (Zn, Cr, Ni, Mo) for re-use. However, some part of the flue dusts are still stored as landfill, mainly in developing countries (Nasmyth and Cooper, 2010; Ruetten 2010; Steinlechner and Antrekowitsch, 2010).

Hydrometallurgical methods instead of pyrometallurgical ones can offer energy savings and lower CO_2 emissions. Still, many hydrometallurgical processes have been investigated in the past three decades but virtually none of them have passed to wider industrial scale use. The main problem in steel dust leaching is the low yield and separability of zinc. Usually over 50% of Zn in the dusts exists in zinc ferrite structure $ZnFe_2O_4$ (franklinite) which makes the selective leaching of Zn without Fe difficult, whereas ZnO (zincite) phase does not cause problems and dissolves easily (LeClerc et al., 2003; Havlik et al., 2005; Havlik et al., 2006; Langová and Matýsek, 2010). Depending on its current price, the recovery method and amount in the dust, zinc is a valuable material resource for recycling to primary zinc production but a major impurity if recycled back to stainless steel process with Cr, Ni, Mo and Fe. Zinc is a volatile component which recirculates and adds up in the furnace and ventilation system (Nyirenda, 1991). In hydrometallurgical research, Zn - Fe separation and zinc recovery especially from carbon steel dusts, mainly from EAF dusts, has been the most researched topic. However, very few research projects have been focused on other types of dusts, i.e. AOD dust, or in general, on stainless steel dusts to recover Cr, Ni, Mo and Fe. Thus, a developed method to recover these valuable elements by hydrometallurgical means is relatively unknown. This might be due to the fact that stainless steel dust recycling by pyrometallurgical methods is well established and the value and concentration of the recovered elements has been sufficiently high to offset the high-energy consumption, the generation of worthless residues to landfill and high CO2 emissions (Nyirenda, 1991; Tsakiridis and Oustadakis, 2010).

There are numerous reports of EAF carbon steel dust leaching and treatment experiments in atmospheric pressure with sulfuric acid but the results vary greatly depending on the dust composition and leaching conditions (Nyirenda, 1991; Cruells et al., 1992; Strobos and Friend, 2004; Havlik et al., 2005; Shawabkeh, 2010; Tsakiridis and Oustadakis, 2010). Hydrochloric acid is found to be a quite effective lixiviant for the steel dusts zinc ferrite spinel (Baik and Fray, 2000). Jha et al. (2001) have done a review of different hydrometallurgical dust treatment processes for zinc recovery from industrial wastes. Havlik et al. (2004), Nyirenda (1991) and Zunkel (2001) discuss generally hydrometallurgical methods and problems encountered in carbon steel (EAF) dust treatment. For example, it is known fact that Cl and F are detrimental elements with very small ppm level amounts in the liquid phase if considering recycling zinc back to Zn primary metallurgy. The same problems and methods apply to some extent also in stainless steel dust treatment, for example leaching harmful Zn as an impurity from the recyclable solids (Cr, Ni, Mo, Fe) and waste liquid management.

The main focus of the present work is on four stainless steel production dusts (EAF 1&2 and AOD 1&2) and the dissolution characteristics of Zn, Cr, Ni, Mo and Fe with sulfuric acid. The main objective at this first stage is to i) maximize zinc extraction into solution for recovery and ii) selectively leach maximum amount of zinc leaving the valuable elements Cr, Ni, Fe, Mo in the solid residue for further treatment and possible recycling back to stainless process.

2. Experimental

Four stainless steel production dust materials, from EAF 1&2 furnace and AOD 1&2 converter, were used for the leaching experiments. These dusts were collected from bag house filter containers behind each furnace or converter. These dusts are a mixture of different production batches, so each dust is a representative sample of an average dust composition.

The chemical composition of received stainless steel production dusts is presented in Table 1. The chemical analysis was done by a standardized method with molten sodium peroxide and atomic emission spectrometry (ICP-AES) for the most typical metals and earth alkaline metals in the dust. The main elements are Fe, Zn, Cr, Ca, Ni and Mn. Calcium is present due to its presence in fluxes and slag.

The chemical and mineralogical composition of dust depends on the batch feed material and the operating parameters of furnace or converter during production. In carbon steel EAF dusts, the zinc amount is typically from 15 to 35 wt.%, or even up to 40%, which is generally much higher than in dusts generated in stainless steel production (Havlik et al., 2004, 2006) (Table 1.)

Table 1. Chemical composition of received dust material from stainless steel production

Sample	wt-%	Zn	Fe	Cr	Ni	Mo	Mn	Mg	Ca	K	Pb	Cd	Cu	Al	S
EAF1		8	23	10	1.5	0.02	3	2	10	1.3	0.6	0.1	0.3	0.9	0.5
EAF2		6	20	10	2.6	0.1	3	1	13	1.4	1	0.3	0.5	1	0.4
AOD1		10	33	10	0.7	0.03	3	1.3	5	0.9	0.1	0	0.2	0.1	0.1
AOD2		5	26	10	2.9	1.3	3	2.5	15	0.8	0.5	0	0.3	0.2	0.2

Leaching experiments were done in a 1000 cm^3 glass reactor in a temperature controlled water bath with a cap that had sealable holes for dust material feed, thermometer, stirrer (300 rpm) and a condenser for water evaporation (Fig. 1). Total volume of 600 cm^3, 0.1 M, 0.5 M and 1.5 M sulfuric acid was used for the leaching experiments. The dust sample weight was 60 g and 30 g for liquid-to-solid ratios of 10 and 20, respectively. The temperature was 30ºC, 60ºC and 90ºC and the liquid samples for chemical analysis were taken and after 10, 20, 60 and 120 minutes.

The samples (10 cm^3) were filtered and sealed before sending them to multi-element ICP-AES analysis.

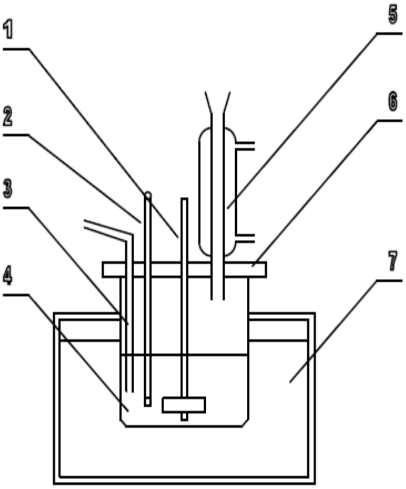


Fig. 1. Schematic picture of the leaching reactor. 1-stirrer, 2-thermometer, 3-sample off take, 4-glass reactor, 5-vapour cooler, 6-reactor cover, 7-temperature controlled water bath

3. Results and discussion

High acid concentration 1.5 M and high temperature 90 ºC results in faster leaching and higher yield of elements into solution versus 0.5 M and 30ºC (Fig.2) for all tested dust materials. With 0.1 M acid concentration the total dissolution was even lower or the elements did not dissolve at all.

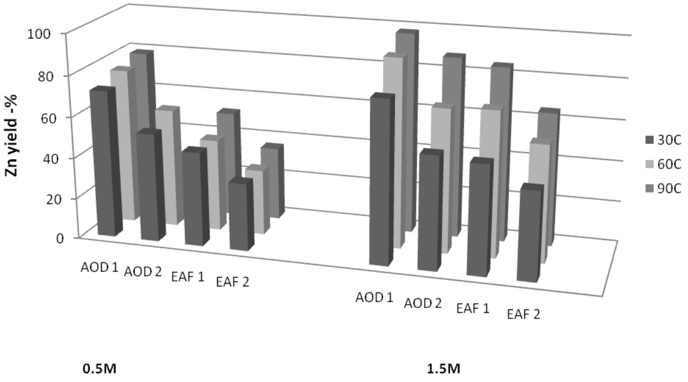
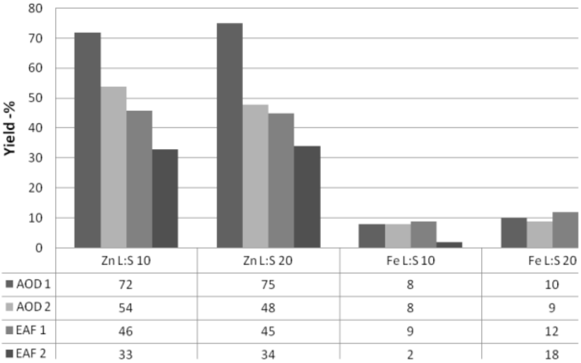


Fig. 2. The effect of temperature and acid concentration (in mol/dm^3) on Zn dissolution (L:S=10, 120 min)

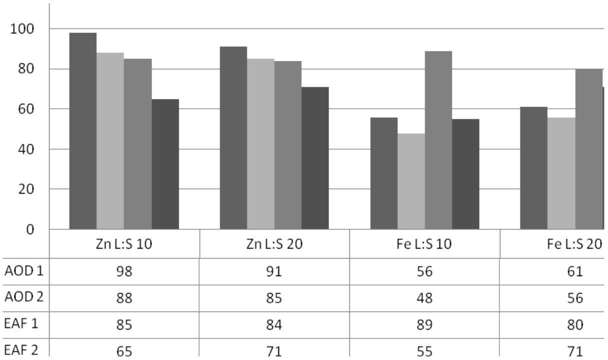
The temperature and acid concentration effect trend is clear, except for 0.5 M, 90ºC AOD 2 dust where Zn probably started to precipitate. Thermodynamically certain elements dissolution depends on pH and Eh, so the pH increase in AOD 2 dust has probably reached Zn precipitation pH limit.

Between L:S 10 or L:S 20 liquid-to-solid ratios we did not notice a clear trend for Zn dissolution (Fig. 3). This could be due to the fact that with both L:S 10 and L:S 20 ratios there were enough free acid left and pH remained sufficiently low for Zn dissolution during the experiment. However, for Fe, it seems that with L:S 20 Fe dissolves somewhat faster and results in slightly higher yield than L:S 10. Exception is 0.5 M, L:S 10, 30ºC EAF 2 dust where acid-alkaline reactions seem to increase the system's pH into an area where Fe starts to precipitate (Fig. 3). This effect is not seen at 1.5 M, 90ºC (Fig. 4). Fe precipitation is a beneficial effect where zinc selectivity into solution is an objective



	Zn L:S 10	Zn L:S 20	Fe L:S 10	Fe L:S 20
■ AOD 1	72	75	8	10
■ AOD 2	54	48	8	9
■ EAF 1	46	45	9	12
■ EAF 2	33	34	2	18

Fig. 3.The effect of liquid-to-solid ratio on Zn and Fe yields, 0.5 M, 30ºC, 120 min

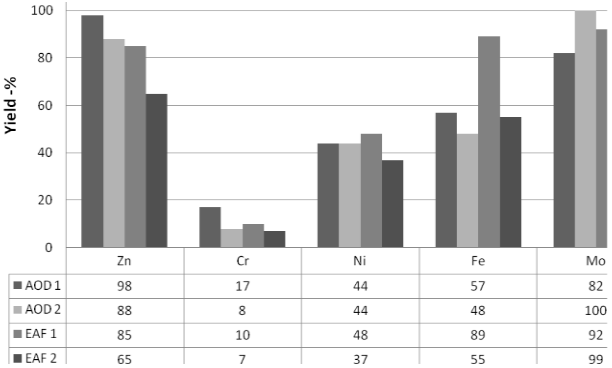


	Zn L:S 10	Zn L:S 20	Fe L:S 10	Fe L:S 20
AOD 1	98	91	56	61
AOD 2	88	85	48	56
EAF 1	85	84	89	80
EAF 2	65	71	55	71

Fig. 4.The effect of liquid-to-solid ratio on Zn and Fe yield -%, 1.5 M, 30ºC, 120 min

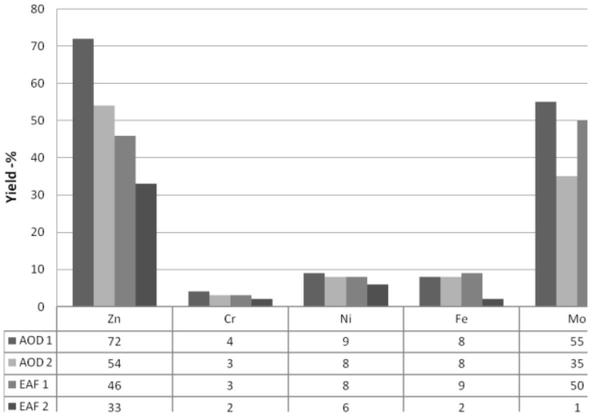
For all dusts, maximum Zn dissolution yield was achieved with 1.5M, 90ºC, and L:S = 10 where the Zn dissolution yield varied from 65% to almost 100%. At the same time: Cr was leached 7 – 17%, Ni 37 – 48%, Fe 48 – 89% and Mo 82 – 100% (Fig. 5.). The best zinc selectivity vs. Cr, Ni, Fe, Mo was achieved with 0.5 M, 30ºC, and L:S 10. Zinc dissolution varied between 33 – 72%, Cr 2 – 4%, Ni 6 – 9%, Fe 2 – 9% and Mo 1 – 55% (Fig. 6.).

A large variation of the yield results is probably due to chemical and mineralogical differences between the original dusts. Additionally, another important factor to affect the yield is to control the dissolution and precipitation reactions by careful pH control.



	Zn	Cr	Ni	Fe	Mo
■ AOD 1	98	17	44	57	82
■ AOD 2	88	8	44	48	100
■ EAF 1	85	10	48	89	92
■ EAF 2	65	7	37	55	99

Fig. 5. Maximum extraction yields for Zn, 1.5 M, 90ºC, L:S 10, 120 min



	Zn	Cr	Ni	Fe	Mo
■ AOD 1	72	4	9	8	55
■ AOD 2	54	3	8	8	35
■ EAF 1	46	3	8	9	50
■ EAF 2	33	2	6	2	1

Fig. 6. Best selectivity (Zn vs. Cr, Ni, Fe, Mo, 0.5 M, L:S 10, 120 min)

4. Conclusions

Sulfuric acid leaching of different stainless steel production flue dusts was studied. The main objective was to study valuable metals (Zn, Cr, Ni, Fe, Mo) dissolution yields for the dusts. The effect of sulfuric acid concentration, temperature and liquid-to-solid ratio were tested for maximum and selective Zn extraction into solution. The aim was to maximize zinc extraction for recovery and selectively leach maximum amount of zinc leaving the valuable elements Cr, Ni, Fe, Mo in the solid residue for further treatment.

Higher temperature and acid concentration resulted in faster dissolution and increased yield. Used L:S ratio and chemical composition of a dust has a presumable effect on pH and, by that, on dissolution of a certain element. The AOD dust in both sample lines 1&2 had better maximum and selectivity results for Zn. The differences in leaching results were presumably from variations in chemical and mineralogical composition between the dusts. Nonetheless, experiments for more efficient selectivity with minimal amount of Fe and as high amount of Zn as possible in liquid phase are still needed for better valuable element (Zn, Cr, Ni, Fe, Mo) recycling possibilities. Understanding chemical and mineralogical effect on leaching is equally important.

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