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ALKALINE LEACHING OF ZINC FROM STAINLESS STEEL ELECTRIC ARC FURNACE DUSTS

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Abstract: Stainless steel production generates dust and sludge that are considered as a harmful waste. These dusts contain also valuable metals but extraction and recovery of valuables is difficult due their complex composition. Zinc is the most troublesome element in the dust and it hinders direct recycling of dust back into furnaces. In this paper two different stainless steel electric arc furnace dusts (EAF1 and EAF2) from Outokumpu Stainless (Tornio, Finland), were leached using NaOH solutions. The purpose was to selectively leach out zinc from the dusts and to find factors that affected most dissolution of zinc. From all leaching factors temperature, agitation speed and NaOH concentration were found to be statistically strongly significant, whereas a liquid-to-solid ratio and bubbling gas were only somehow significant. Two experiments from the test series gave clearly higher zinc extraction, that is around 60% for EAF1 and 30% for EAF2. For those experiments, a strong 8 M NaOH solution with the high temperature and agitation speed was used but bubbling gas and liquid-to-solid ratio changed. Zinc was leached selectively and practically no iron, chromium and nickel dissolved.

Keywords: *electric arc furnace dust, EAF, stainless steel, zinc, leaching, sodium hydroxide*

Introduction

Stainless steel production generates large quantities of various solid wastes in form of dust and sludge. During production of stainless steel, between 30 and 70 kg of dust and fine waste is generated per mega gram of steel produced (Denton, 2005). Their disposal or possible re-use has been a serious concern for an industry as in most industrial countries stainless steel dusts are considered as a harmful waste. On the other hand, the stainless steel dusts contain valuable metals such as alloying elements like chromium, nickel and molybdenum, and zinc from recycling of galvanized scrap. From economic and environmental point of view, it is desirable to recover the valuables and utilize these wastes (Majuste, 2009). Direct recycling of dust back to stainless steel production is however hindered, mainly because of zinc content of the

dust. Zinc vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as oxide or ferrite. Zinc content in the stainless steel dusts is found to vary from 1.0 to 16.4 wt% (Nyirenda, 1992; Atkinson, 2001; Leclerc, 2002; Laforest, 2006).

A number of pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations (Xia, 1999; Youcai, 2000; Jha, 2000; Orhan, 2005; Havlik, 2006; Rao, 2006b) but only few of them have reached commercialization. Today, the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. However, the drawbacks with pyrometallurgical processes are: high energy consumption, production of a raw zinc oxide with low commercial value, and need of relatively large tonnage of dust to be economically competitive (Nakamura, 2005; Oustadakis, 2010; Rao, 2006b). Hydrometallurgical processes are considered to be suitable for on-site treatment as they can fit on small scale and thus offer interesting alternative (Nakamura, 2008).

Principally, two most studied leaching methods for treating carbon steel dusts are sulfuric acid (H_2SO_4) and caustic soda (NaOH) leaching. The benefit with acid solutions is that they are very accessible and cheap, but the drawbacks are that also iron contained in the dust dissolves and high alkalinity of many dusts consumes a lot of acid for pH adjustment (Palencia, 1999). The major advantage of alkaline leaching is selective solubility of zinc compared to iron compounds, and thus a relatively clean and iron-free solution is obtained, and the complicated iron removal process is avoided. So far, the major obstruction in hydrometallurgical extraction of zinc has been the presence of zinc ferrite (ZnFe_2O_4) in the dust, which is insoluble in many solutions (Havlik, 2006). Usually 30–70% of zinc is in a ferrite form (Leclerc, 2002), but to enhance the zinc recovery, a low temperature roasting step prior to alkaline leaching can be used to convert zinc ferrite into soluble zinc oxide (Xia, 1999).

Dusts from stainless steel production contain many elements making metal extraction very complex and difficult. The stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S (Ma, 2006). However, chemical compositions and crystalline phases present in the dusts vary considerably depending on the steel grade produced, raw materials used, and operation conditions and procedures (Rao, 2006a). The composition of stainless steel dusts differs substantially from unalloyed steel dusts and typically the stainless steel flue dusts are richer in alloying elements such as chromium, nickel and manganese, but lower in zinc and lead. The previous studies on the hydrometallurgical methods have concentrated on leaching of carbon steel dusts, and for this purpose both acid and alkaline leaching-based laboratory and pilot set-ups have been constructed. Only few studies of acidic leaching of dusts from stainless steel production are found (Majuste, 2009; Kekki, 2012).

In this paper two different stainless steel electric arc furnace dusts (EAF1 and EAF2) from Outokumpu Stainless (Tornio, Finland) were leached using NaOH solutions. The purpose was to selectively leach out zinc from the dusts and to find factors that affected most on dissolution of zinc. Also possible interactions of the studied leaching factors were observed. Alkaline leaching was chosen because of its selectiveness in leaching of zinc when compared to iron compounds.

Materials and methods

Electric arc furnace dust samples (EAF1 and EAF2) from stainless steel production were received from Outokumpu Tornio Works for the leaching experiments. The EAF1 represents dust from line 1 and the EAF2 from line 2. Line 1 uses molten ferrochrome, whereas in line 2 ferrochrome is melted with scrap in EAF. The dusts are a mixture of different production batches, thus represent an average dust composition.

The chemical and mineralogical analyses of dust samples were executed with thw optical microscopy, scanning electron microscopy (SEM), electron probe micro-analyzer (EPMA), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) with molten sodium peroxide or nitro-hydrochloride acid leaching pre-treatment. The dust samples were also subjected in a particle size analysis by a scanning-foto-sedimentograf. The results from the chemical and mineralogical analyses are given in Tables 1 and 2. The

Table 1. The chemical composition of the dust samples

	Fe	Cr	Zn	Ca	Mn	Ni	Pb	Mg ^a	K ^a	Si ^b
EAF1	19.75 ±1.64	8.07 ±3.03	7.27 ±0.54	10.35 ±0.46	2.47 ±0.45	1.28 ±0.14	0.54 ±0.05	2.59 ±0.15	1.32 ±0.04	4.25
EAF2	16.39 ±1.84	8.10 ±2.95	5.20 ±0.58	13.48 ±0.72	2.14 ±0.40	2.14 ±0.23	0.97 ±0.05	1.24 ±0.17	1.35 ±0.01	4.11
Minor amounts 0 - < 1 % in both dusts	Al, B, Ba, C, Cd, Co, Cu, F, Mo, Na, P, S, Sr, V									

^a calculation is based on three analyses, ^b found only in one analysis

Table 2. The main phases identified in dust samples from XRD analysis (Kukurugya, 2013)

EAF1	EAF2
FeCr ₂ O ₄	FeCr ₂ O ₄
ZnFe ₂ O ₄	ZnFe ₂ O ₄
Ni _{0.25} Fe _{0.75} Fe ₂ O ₄	NiFe ₂ O ₄
ZnO	CaO
CaO	CaCO ₃
	MnO ₂

main components in the dusts are iron, zinc, chromium and calcium. Zinc was found to be present as zincite (ZnO) and as franklinite (ZnFe_2O_4) in both dusts. The microstructure of dusts consists of larger particles and grains surrounded by finer fraction. The particle size for both dusts was around 1–50 μm . Larger particles often consist of several phases and some phases were encapsulated inside of particles. A part of zinc was found in a concentrate into a fine fraction.

The leaching tests were performed using a 2^{5-2} fractional factorial design with two replicates, where the high and low levels of factor were used (Montgomery, 2009). In this method several factors are changed simultaneously in order to find out the most important factors and the possible interactions of the factors. The studied factors were temperature, NaOH concentration, liquid-solid ratio (cm^3/g), stirring rate and oxygen or nitrogen gas bubbling. The extreme values of factors range were chosen to be certain that the factors will have clear effect. The used temperatures were 25 and 95 $^\circ\text{C}$, and concentrations of NaOH solutions were 2 and 8M. The chosen liquid-to-solid ratios (cm^3/g) were 5 and 30. A stirring rate was adjusted to 100 or 400 rpm, and more oxidative or less oxidative conditions were adjusted using oxygen or nitrogen gas bubbling.

Table 3. Factorial (2^{5-2}) test series used in the leaching experiments

N ^o	NaOH,M	L/S ratio	Temp., $^\circ\text{C}$	Bubbling with	Agitation, rpm
1	2	5	25	O_2	400
2	8	5	25	N_2	100
3	2	30	25	N_2	400
4	8	30	25	O_2	100
5	2	5	95	O_2	100
6	8	5	95	N_2	400
7	2	30	95	N_2	100
8	8	30	95	O_2	400

The experimental setup for the leaching test consisted of a thermobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The cover of the glass reactor provided through holes for a mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was added to the structure at higher temperatures. The NaOH solutions were prepared from technical grade grains and distilled water, and a volume of 800 cm^3 was set into reactor. Oxygen or nitrogen gas was fed into the reactor for 1 hour and after that 26.67 g or 160 g of dust was charged and the stirring rate was adjusted. A liquid sample was taken off and filtered in the chosen time intervals of 5, 10, 15, 20, 25, 30, 60 and 120 minutes for EAF1 dust, and 5, 15, 30, 60 and 120 minutes for EAF2 dust. The stirring was stopped 30 seconds before each sampling. After filtering the leach samples were analysed for the

amount of leached Zn with a Perkin Elmer 372 AAS device. A part of the samples after 120 min of leaching was analyzed more precisely with a multi-element ICP-AES analysis in order to investigate which other elements leached with zinc.

Results and discussion

The main response under investigation was the percentage of zinc extraction from EAF1 and EAF2 dusts in the leach liquor. The leaching curves of zinc from the 2^{5-2} fractional factorial experiments are shown in Figs. 2 and 3. From the shape of the leaching curves it can be observed that dissolution of zinc is fast, occurring in a few minutes, and then increased only slightly. The maximum amount of leachable zinc in one experiment was usually achieved at the end of the test, which was 120 min of leaching. In a few experiments the plateau was achieved earlier, and then amount of leached zinc decreased that may indicate that part of zinc was precipitated back.

Under the present experimental conditions, zinc extraction varied from 14 to 61% for EAF1 dust. Generally, extraction was lower for EAF2 dust and varied from 8 to 33%. The difference in zinc extraction was arisen most likely from the mineralogical differences of dusts. In addition to zinc oxide, zinc ferrite was also identified in both dusts. Zinc ferrite is difficult to dissolve in alkaline solutions and zinc extraction is dependent on the amount of zinc in ferrite from.

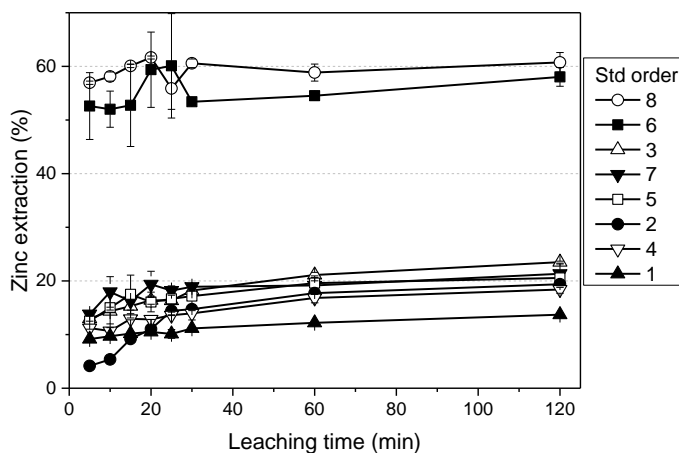


Fig. 1. Leaching curves of zinc dissolution from EAF1 dust according to results from 2^{5-2} fractional factorial design

As can be clearly seen from Figs. 1 and 2 that zinc extraction is higher under two leaching conditions. In both, strong 8 M NaOH solution with high temperature and stirring rate was used, but bubbling gas and liquid-to-solid ratio changed. Almost equivalent zinc extraction was achieved under these two leaching conditions. From

EAF1 dust around 60% of zinc and from EAF2 dust slightly over 30% of zinc was dissolved.

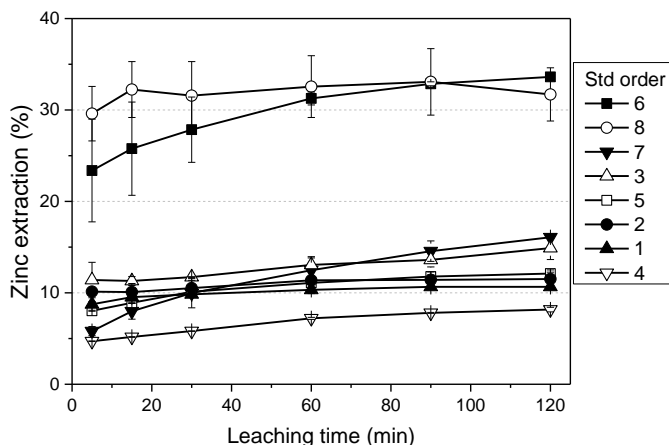


Fig. 2. Leaching curves of zinc dissolution from EAF2 dust according to results from 2^{5-2} fractional factorial design

To study the effect and possible interaction of the leaching factors on zinc dissolution, the results were analyzed using the Minitab 16 software. Figure 3 shows the pareto charts of the standardized effects of the studied factors after 120 min leaching. Mainly, the same trends can be observed for both dusts. Temperature, NaOH concentration and agitation speed were statistically strongly significant factors of zinc dissolution in both dusts. The liquid-to-solid ratio (L/S) and bubbling gas were only somewhat significant for the EAF1 dust and for the EAF2 dust the L/S ratio was even insignificant. The response was positive for all of the studied quantitative factors and

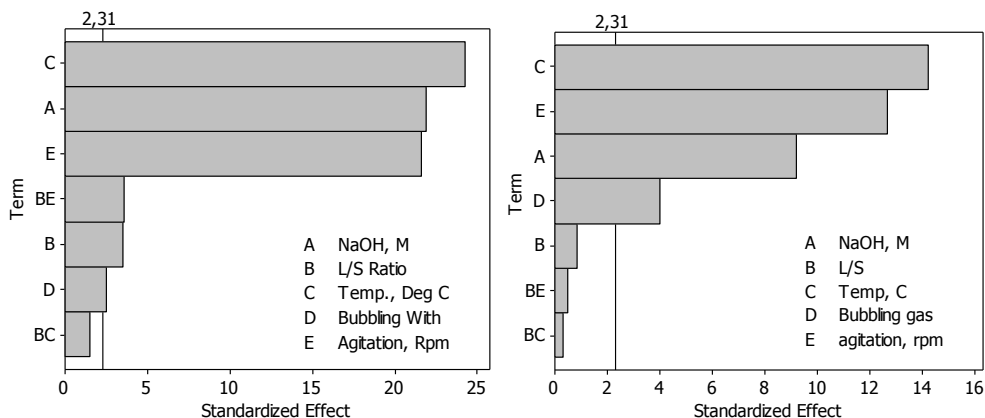


Fig. 3. Pareto chart of standardized effects of studied factors (response is Zn extraction %, alpha = 0.05) for EAF1 (left) and EAF2 (right) dusts

dissolution of zinc was enhanced with increasing level of the factors. Gas bubbling was a qualitative factor and oxygen gas bubbling had a negative response versus dissolution of zinc was enhanced with nitrogen gas bubbling.

Figures 4 and 5 show the interaction charts of the studied leaching factors (determined from extractions after 120 min leaching). The interaction between the factors occurs when the effect that one factor has on the output is dependent on the level of another factor, and the response is different at the low level of the second factor than at the high level of the second factor. For both EAF1 and EAF2 dusts two-factor interactions were found between NaOH concentration and temperature, NaOH concentration and agitation, liquid-to-solid ratio and bubbling gas, and between temperature and agitation. Three of these four interactions were between the factors that stood out with stronger effect on zinc dissolution. The interactions with NaOH

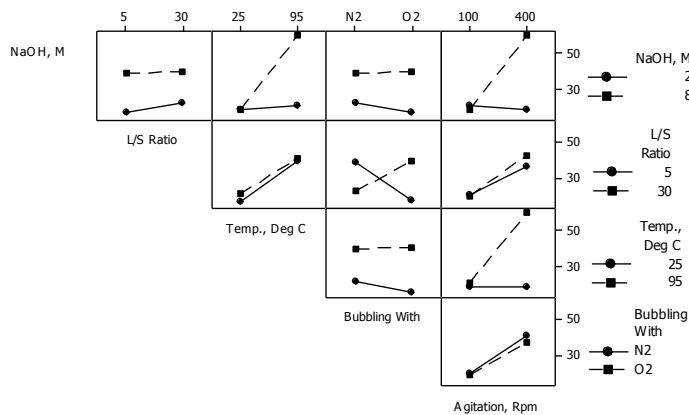


Fig. 4. Interactions of studied factors for EAF1 dust

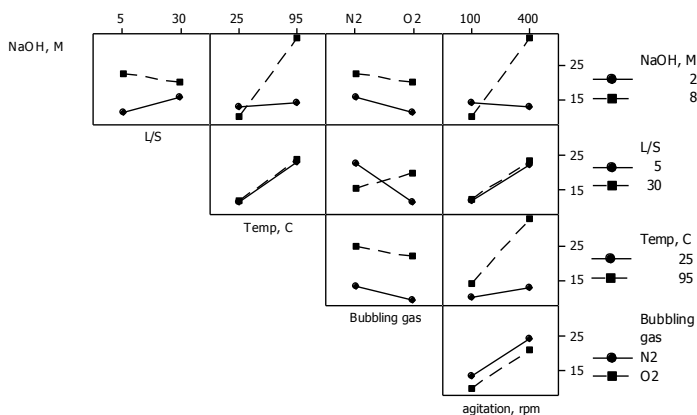


Fig. 5. Interactions of studied factors for EAF2 dust

concentration, stirring rate and temperature are explained by high viscosity of strong NaOH solution. Strong agitation and high temperature enhanced the extraction/dissolution of zinc in strong viscous NaOH solution. The reason for interaction between liquid-to-ratio and bubbling gas is unclear. Bubbling with oxygen reduced zinc extraction with high amount of solid but enhanced it when the amount of solid was low. In the EAF2 dust, the interaction between NaOH concentration and liquid-to-solid ratio was also found. Zinc extraction was slightly increased in low NaOH concentrations but slightly decreased in strong NaOH solution, when small amount of solid was used, but this interaction was not so obvious.

It should be noted that the 2^{5-2} fractional factorial design used in this leaching experiments is a resolution III design, when the main effects are confounded with two-factor interactions. The resolution describes the ability to separate the main effects and interactions from one to another. To increase the resolution and eliminate the confounding between the main effects and two-factor interactions a full fold-over design, in which the signs of all the factors are reversed, can be run and combine to the design used in this study. This would provide clearer basis for optimization of leaching conditions.

The results from the ICP-AES analyses are presented in Table 4. The results showed that zinc was leached selectively. Practically no iron (usually $<1.5 \text{ mg/dm}^3$) and nickel ($< 0.1\text{--}0.21 \text{ mg/dm}^3$) was dissolved. The leaching conditions had only minor effect on dissolution of chromium and less than 3% of chromium was leached from both dusts. In some samples from the EAF2 dust the amount of lead and cadmium was a bit higher, however only 9% of lead and 1% of cadmium was leached. Also the leaching recovery of molybdenum was higher for the EAF2 dust (40 – 60%). As iron and of the valuable alloying elements chromium and nickel remained in the leach residue, for recovering the valuables, the residue could be recycled back into furnaces if the amount of zinc can be lowered to a sufficient level.

Table 4. Amount of certain elements in leachate after 120 min leaching

	Amount in leachate (mg/dm^3)							
	Zn	Fe	Cr	Ni	Mo	Ca	Pb	Cd
EAF1	169 - 8690	< 1.5	43- 277	<0.1 - 0.21	4 - 32	< 5 - 7	3 - 62	< 0.25
EAF2	145 - 3234	<1.5 - 15.5	47 - 446	≤ 0.11	18.3 - 263	<5 - 14.6	<2.5 - 188	<0.25 - 6.51

Conclusions

Dusts formed in stainless steel production are considered as a harmful waste in most industrial countries. At the same time these dusts are also a source of valuable metals but their extraction and recovery is difficult due to their complex composition. The most troublesome element in the dust is zinc, which vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge, usually as oxide or ferrite. In this study two electric arc dusts (EAF1 and EAF2) from stainless steel

production were leached in NaOH solutions aiming to selectively leach out zinc from the dusts, and to find the effect of various leaching factors on dissolution of zinc/find factors that affected most on zinc dissolution.

The results from (2^{5-2}) fractional factorial tests showed that all studied factors (NaOH concentration, temperature, agitation, solid-to-liquid ratio, and oxygen/nitrogen gas bubbling) had statistically significant effect on zinc dissolution, except the solid-to-liquid ratio for the EAF2 dust. However, an increase in the NaOH concentration, temperature and agitation improved zinc extraction preferentially. Two-factor interactions were found between those three factors and also between liquid-to-solid and bubbling gas.

From all the experiments performed in this work, two of them gave higher zinc extraction. In both, strong 8 M NaOH solution with high temperature and stirring rate was used, but bubbling gas and liquid-to-solid ratio changed. Almost equivalent zinc extraction achieved under these two leaching conditions was around 60% for the EAF1 dust and over 30% for the EAF2 dust. The difference in zinc extraction between the dusts arose from the mineralogical differences and is dependent on the amount of zinc in ferrite form.

This study showed that alkaline leaching of zinc from stainless steel EAF dusts using NaOH solutions is selective and practically no iron, chromium and nickel were dissolved. However, the dissolution of zinc is limited due to the presence of zinc ferrites that remains the main problem to be solved. When considering the possibility to recycle dust back to the process, the amount of zinc should be low to effectively recycle dust back to the process. The leaching process can be used in zinc removal if zinc ferrites are decomposed prior to leaching, for example by roasting.

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