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ALKALINE LEACHING OF ZINC FROM ARGON OXYGEN DECARBONIZATION DUST FROM STAINLESS STEEL PRODUCTION

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Abstract: Stainless steel production generates solid wastes such as dust and sludge that are considered as harmful in most industrial countries. Today dusts are recycled in separate treatment plants as these dusts contain valuable metals such as alloying elements. A direct recycling of dust back to steel production is hindered due to the presence of elements, especially zinc, that cause operational difficulties in the stainless steel making process. In this paper two different stainless steel converter argon oxygen decarbonization dusts (AOD1 and AOD2), from Outokumpu Stainless (Tornio, Finland), were leached using NaOH solutions. The purpose was to selectively leach zinc out from the dusts and to find factors that affected most dissolution of zinc. The dust samples were leached under atmospheric pressure and the factors tested were temperature, sodium hydroxide concentration, liquid to solid ratio (L/S), stirring rate and oxygen or nitrogen gas bubbling. All the studied factors had statistically significant effect on the dissolution of zinc. The maximum zinc extraction was achieved at 95°C, with 8M NaOH solution, stirring rate of 400 rpm and L/S ratio of 30 and was around 80% for AOD1 dust and around 50% for AOD2 dust. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. Zinc was leached selectively. Among alloying elements only molybdenum was leached and practically no iron, chromium and nickel were dissolved.

Key words: *AOD dust, stainless steel, zinc, leaching, sodium hydroxide*

Introduction

Stainless steel production generates quantities of various solid wastes in form of dust and sludge. During the production of stainless steel, between 30 and 70 kg of dust and fine waste is generated per ton (megagram) of steel produced (Denton, 2005). In most industrial countries stainless steel dusts are considered as harmful waste, on the other hand, these dusts also contain valuable metals such as alloying elements and zinc. From economic and environmental point of view it is desirable to recover the valuables and utilize these wastes (Majuste, 2009). However, a direct recycling of dust back

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to stainless steel production is hindered because they contain considerable amounts of elements, especially zinc, that cause operational difficulties in the steel making process (Palencia, 1999). Zinc vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite and its content in stainless steel dusts is in the range of 1.0–16.4 wt% (Atkinson, 2001; Leclerc, 2002; Nyirenda, 1992).

Various pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations (Jha, 2000; Orhan, 2005; Rao, 2006; Xia, 1999; Youcai, 2000) but only few of them have reached commercialization. Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants to recover metals. There are still significant problems associated with treating this material and the developed processes have not been entirely satisfying (Xia, 1999). The drawbacks with pyrometallurgical processes are the high consumption of energy and a need of relatively large tonnage of dust to be economically competitive. Hydrometallurgical processes are considered suitable for an on-site treatment (Nakamura, 2007) as they can fit on small scale (Dutra, 2006), but the major obstruction in the hydrometallurgical extraction of zinc is the ferrite form of zinc. Zinc ferrite ($ZnFe_2O_4$) is insoluble in many solutions (Xia, 2000) and usually 30–70% of zinc is in ferrite form (Leclerc, 2002).

Metal extraction from the dusts is difficult due to their complex composition. 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, the 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, 2006). Finding a suitable process is complicated as each dust is unique. Hydrometallurgical processes can offer an interesting alternative for zinc recycling if iron dissolution can be controlled. The major advantage of alkaline leaching is its selectiveness in leaching zinc compared to iron compounds. Thus, a relatively clean and iron-free solution is obtained and the complicated iron removal processes are avoided.

Previous studies on hydrometallurgical methods have concentrated on the leaching of zinc from carbon steel dusts and mainly from the electric arc furnace (EAF) dusts. In this paper two different argon oxygen decarbonization converter dusts (AOD1 and AOD2) from stainless steel production (Outokumpu Stainless Oy Tornio, Finland) were leached using NaOH solutions. The target was to selectively leach zinc out of stainless steel making dusts and to minimize the zinc content in the dust. This would provide an opportunity to effectively recycle the dust back to the steel making process and to recover zinc from the dust.

Experimental

Argon oxygen decarburization converter dust samples (AOD1 and AOD2) from stainless steel production were received from Outokumpu Tornio Works for the leaching experiments. AOD1 represents dust from line 1 and AOD2 from line 2. On line 1 ferrochrome is fed as melt into AOD converter whereas on line 2 solid ferrochrome is melted along with the charge. The dusts are a mixture of different production batches thus representing an average dust composition.

The chemical and mineralogical analysis of dust samples was done with 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 results of the chemical analyses are presented in Table 1. The main components in the dusts are iron, zinc, chromium and calcium. The zinc content is on average 9.762% for AOD1 and 4.650% for AOD2. The identified phases in the AOD1 and AOD2 dusts, according to qualitative phase analysis, are presented in Table 2. Zinc was found to be present as zincite (ZnO) in AOD1 as franklinite ($ZnFe_2O_4$) and zincite in AOD2. In the AOD2 dust, there were phases that contained a significant amount of molybdenum.

Table 1. The chemical composition of dust samples (in %)

	Fe	Cr	Zn	Ca	Mn	Mg	Ni	Pb	Si	Mo
AOD1	26.9–37.8	4.39–18.56	8.96–10.8	4.74–5.56	0.95–2.87	0–1.38	0.4–0.72	0.08–0.1	0–0.89	0–0.075
AOD2	13.8–26.4	2.18–13.39	3.52–5.91	13.08–17.2	0.9–3.4	0–2.53	1.88–2.92	0.39–0.56	0–2.76	0–1.4
Minor amounts 0–< 1% in both dusts	Al, B, Ba, C, Cd, Co, Cu, F, K, Na, P, S, Sr, V									

Table 2. The identified phases according to qualitative phase analysis

Element	AOD1	AOD2
Fe, Cr, Mg	$FeCr_2O_4$ (chromite), $MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite), $(NiFe)Fe_2O_4$ (trevorite), $MgFe_2O_4$ (magnesioferrite), Fe_2O_3 (maghemite)	$MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite), $FeCr_2O_4$ (chromite), $ZnFe_2O_4$ (franklinite), $(NiFe)Fe_2O_4$ (trevorite), Fe_2O_3 (maghemite), $(FeMg)(CrFe)_2O_4$ (donathite)
Zn	ZnO (zincite)	$ZnFe_2O_4$ (franklinite), ZnO (zincite)
Ni	NiO (bunsenite), $(NiFe)Fe_2O_4$ (trevorite)	$(NiFe)Fe_2O_4$ (trevorite)
Ca	CaO (lime)	CaO (lime), $CaCO_3$ (calcite)
Si	$(NH_4)_2SiF_6$ (cryptohalite)	$(NH_4)_2SiF_6$ (cryptohalite)
Mn		KMn_8O_{16} (cryptomelane)
Mo		MoO_2 (tugarinovite)

The microstructure of the dusts consists of bigger particles and grains surrounded by finer fraction. Also agglomeration of finer fraction was noticed. The particle size analysis of dust samples was done with laser diffraction (Beckman Coulter) and by Scanning-Foto-Sedimentograf. All particles measured by Scanning-Foto-Sedimentograf were under 47 µm for both AOD1 and AOD2 dusts with smallest particles under 1 µm. Analyses by laser diffraction showed that all particles were less than 4 µm for AOD1 dust and 20 µm for AOD2 dust. Larger particles consist of several phases and some phases were encapsulated inside of particles. For the finer fraction no encapsulation phenomenon was found. Zinc occurred mainly in the fine fraction in which the maximum ZnO content is around 14% in both AOD1 and AOD2 dusts.

The leaching experiments were carried out in the apparatus shown in Figure 1. The experimental setup for the leaching test consisted of a termobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The cover of the glass reactor provided through holes for mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was added to the structure at higher temperatures.

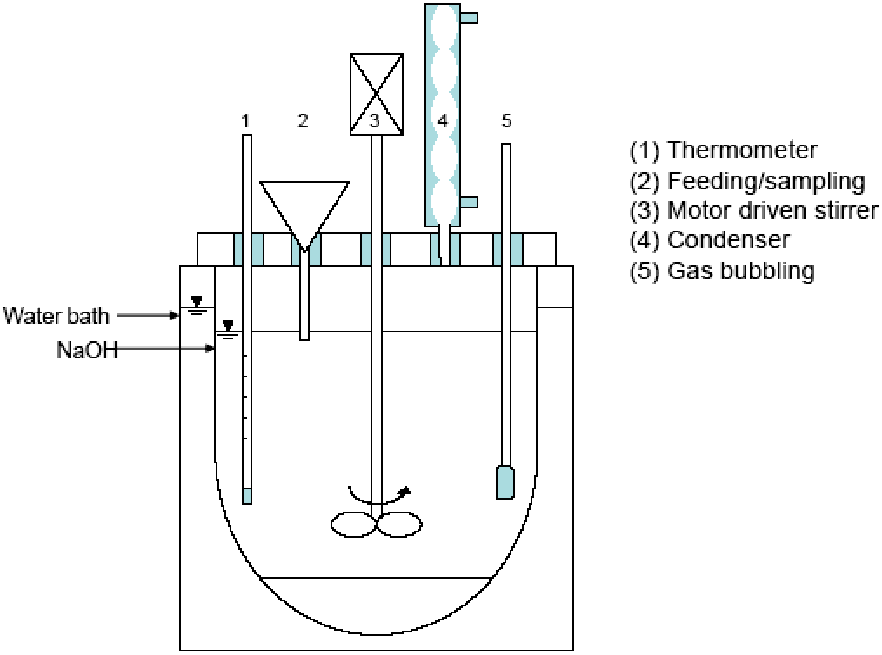

Fig. 1. Leaching reactor in water bath

Volume of 800 cm^3 of NaOH solution (prepared by technical grade grains and distilled water) was set into the reactor, which was put in a water bath in order to control the temperature in the reactor. For adjusting the oxidative or reductive conditions, oxygen or nitrogen gas was fed into the reactor for 1 hour and after that the dust was charged and 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 AOD1 dust and 5, 15, 30, 60 and 120 minutes for AOD2 dust. The stirring was stopped 30 seconds before each sampling.

The leaching tests were done using factorial test series (Table 3) with two replicates where a high and a low level of a factor were used. The studied factors were temperature, NaOH concentration, liquid-solid ratio (cm^3/g), stirring rate and oxygen or nitrogen gas bubbling. In the experiments temperature of 25°C or 95°C and NaOH concentrations of 2 M and 8 M were used. The chosen liquid/solid (cm^3/g) ratios were 5 and 30 and for this 160 g or 26.67 g of dust was added to the reactor. The stirring rate was adjusted to 100 or 400 rpm and the oxidative or reductive conditions were adjusted using oxygen or nitrogen gas bubbling.

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

Std Order	NaOH (M)	L/S Ratio	Temp. Deg 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

After filtering the leach samples were analysed for the amount of leached Zn, with the Perkin Elmer 372 AAS device. The standard solutions were prepared by using an Atomic Absorption Standard zinc 1000 µg/cm^3 Baker 6827 solution. Part of the samples after 120 min of leaching was analyzed more precisely with multi-element ICP-AES analysis in order to investigate that the unwanted iron and other elements were not leached.

Results and discussion

The main response under investigation was the percentage of zinc extraction from the AOD1 and AOD2 dusts in the leach liquor. The leaching curves of zinc are presented in Figs 2 and 3. Figure 2 shows the leaching curves of the four experimental conditions with best zinc recovery. In Fig. 3 the four leaching conditions of lower zinc extractions are shown. From the shape of the leaching curves can be observed that the dissolution of zinc is fast (in the both high and low recoveries of zinc) and occurs in a few minutes. Usually, the maximum recovery was achieved at the longest leaching time (120 min), however, in some experiments the maximum yield of zinc was achieved earlier and then it decreased, which may indicate that part of zinc was precipitated back.

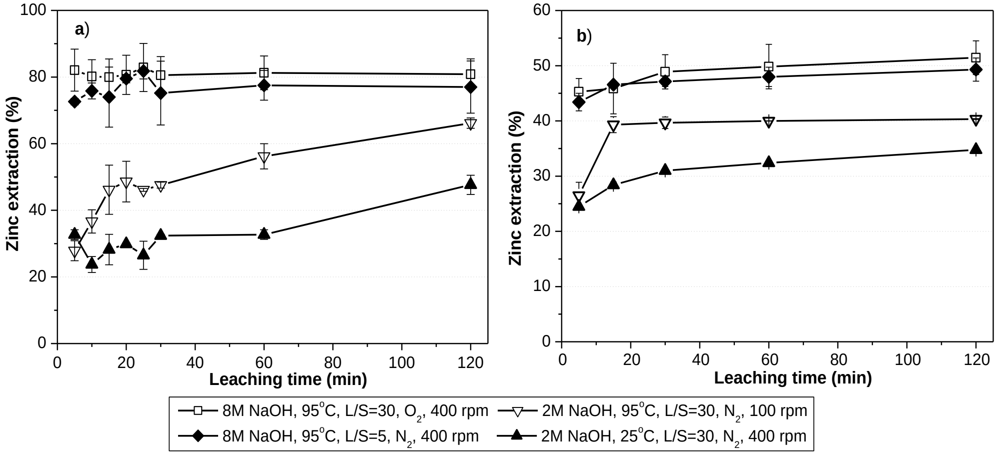

Fig. 2. The four leaching conditions that gave better zinc extractions for a) AOD1 and b) AOD2 dust

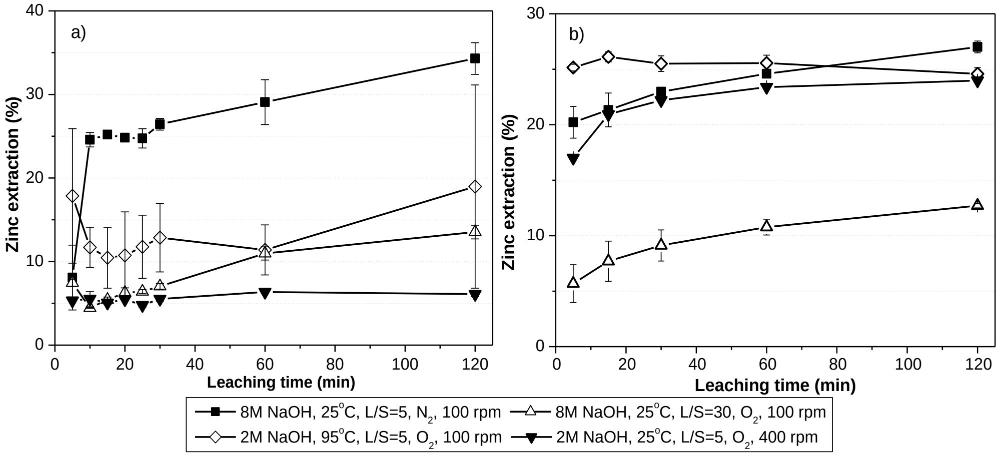

Fig. 3. The four leaching conditions that gave poorer zinc extractions for a) AOD1 and b) AOD2 dust

Under the present experimental conditions, zinc extraction varied from 6% to around 80% for the AOD1 dust. The extractions were on the average lower for AOD2 dust and varied from 13% to around 50%. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. In the AOD2 dust zinc was found to be present also in ferrite form that is difficult to dissolve in alkaline solutions.

For both dusts the maximum value of extracted zinc was obtained by using 8 M NaOH solution and stirring rate of 400 rpm at the temperature of 95°C. The liquid-solid ratio was 30 and oxygen bubbling was used. According to the results the dissolution of zinc was greater when high temperature and stirring rate, strong NaOH solution and lower liquid-solid ratio were used.

To study the effects and possible interactions of the leaching factors on zinc dissolution, the analysis was done using the Minitab 16 software. Figure 4 represents the normal plot of the standardized effects of the studied factors after 120 min leaching.

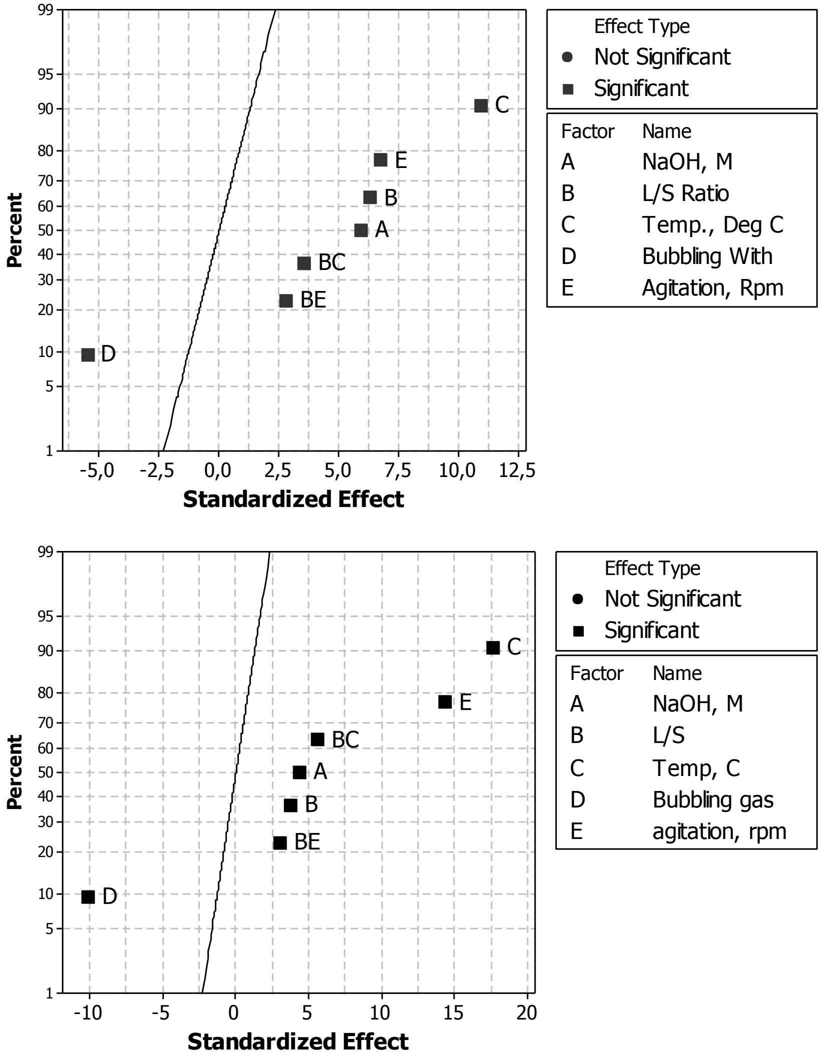

Fig. 4. Normal plot of the standardized effects of studied factors (response is Zn extraction %, alpha = 0.05). Above: AOD1 dust. Below: AOD2 dust

Mainly, the same trends can be observed for both dusts. All leaching factors studied in this work had statistically significant effect on the dissolution of zinc. Temperature affected the zinc extraction preferentially in both dusts and the other factors were nearly equally significant for the AOD1 dust. For AOD2 dust, temperature, agitation and bubbling gas were more significant factors when NaOH concentration and L/S ratio were less significant. For both dusts, temperature, NaOH concentration, stirring rate and liquid-solid ratio had a positive response on zinc dissolution and increasing values of these factors increased the dissolution of zinc. Oxygen bubbling had a negative response and the dissolution of zinc was enhanced with nitrogen gas bubbling although the highest zinc extraction was achieved under conditions in which oxygen bubbling was used.

The interactions of all factors were not easy to observe, nevertheless, two-factor interactions were found between NaOH concentration and other studied factors in both dusts (Fig. 5). The interactions with NaOH concentration, stirring rate and temperature are explained by the high viscosity of strong NaOH solution. The increase of temperature and/or stirring rate enhanced the extraction of zinc in strong viscous NaOH solution. Also a strong 8 M NaOH solution is needed for leaching zinc when the amount of solids was larger. The reason for interaction between NaOH concentration and bubbling gas is unclear. It is possible that there is not significant electrochemical dissolution, where the oxidant could have an effect. To find out the possible interactions between the other factors more experiments are needed.

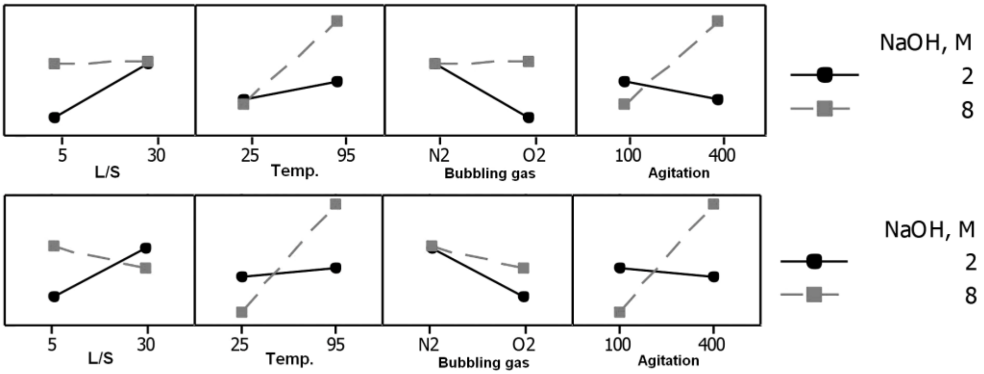

Fig. 5. Two-factor interactions between NaOH concentration and other studied factors after 120 min of leaching. Above: AOD1 dust. Below: AOD2 dust

Some of the samples after 120 min of leaching were analyzed with ICP-AES in order to investigate that iron and other elements such as alloying elements were not leached. The results for iron, chromium, nickel and molybdenum are presented in Table 4. Practically no iron (< 1.5 mg/dm^3) or nickel (< 0.1 mg/dm^3) was dissolved. Chromium was dissolved less than 4% at most. Solubility of molybdenum in strong NaOH solutions differed from the other alloying elements. Molybdenum dissolved well and its amount (mg/dm^3) was almost the same as zinc in the leachates from the AOD2 dust. In couple of samples it was even slightly higher. In the AOD1 dust the amount of Mo was low compared to the AOD2 dust and thus also its amount (mg/dm^3) was low in relation to zinc in the leachate from the AOD1 dust.

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
AOD1	394–14950	< 1.5	27–484	< 0.1	3–56	< 5–21	< 2.5–24	< 0.25
AOD2	194–3722	< 1.5	< 1–258	< 0.1- 0.11	193–2834	< 5–10	< 2.5–61	< 0.25

Conclusions

Two different AOD dust samples from stainless production, delivered from Outokumpu Stainless (Tornio, Finland), were leached in NaOH solution using different leaching conditions. The purpose was to selectively leach zinc out from the dusts and to find factors that affected most on dissolution of zinc. The leaching experiments were done using factorial (2^{5-2}) test series and the studied factors were NaOH concentration, temperature, solid-to-liquid ratio, stirring rate and oxygen or nitrogen gas bubbling. All factors had statistically significant effect on the dissolution of zinc in both dusts and the effect of temperature was emphasized. All factors had positive response except oxygen gas bubbling, that had negative response. In both dusts the maximum zinc extraction was achieved at 95°C, with 8M NaOH solution, stirring rate of 400 rpm and L/S ratio of 30. Maximum zinc extraction was 80% from the AOD1 dust and 50% from the AOD2 dust. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. In the AOD2 dust zinc was found to be present also in ferrite. The experiments showed that leaching of zinc using NaOH solutions is selective, among alloying elements only molybdenum was leached and practically no iron, chromium and nickel were dissolved.

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