

THERMAL TREATMENT OF STAINLESS STEEL DUSTS FOR LEACHING

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Received: 29.03.2013

Accepted: 20.05.2013

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Abstract

Many pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steelmaking dusts. The dusts contain metals and compounds that can harm the processes and one of these elements is zinc that is present in the flue dusts as zincite ZnO and franklinite ZnFe₂O₄. The effect of alkaline roasting on the dissolution of stainless steel flue dusts in acid and alkaline leaching was studied. The extraction of zinc from EAF dust was not significantly improved in alkaline leach (40 – 50 %) but there was indication of better extraction in acid leach (over 90 %). No improvement in extraction from AOD dust was seen either in alkaline (max. 58 %) or acid leach (max. 72 %). The acid leach of synthetic ferrite resulted in less than 32 % Zn recovery, and this must be studied further to find out the effect of franklinite in the dusts.

Keywords: processing, recycling, stainless steel dust, roasting, leaching

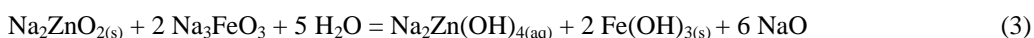
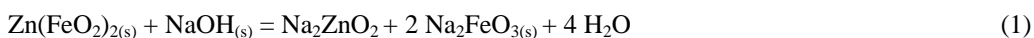
1 Introduction

Stainless steel production produces flue dusts in ferrochrome production, in furnaces used for melting and in decarburization. A number of pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steelmaking dusts in primary operations [1, 2]. The Waelz kiln processing remains the dominant treatment technology with 80 to 85 % of the electric arc furnace (EAF) dust in the US and up to 76 % worldwide treated in Waelz kilns [3]. Autoclave oxidation using sulphuric acid [4] and hydrochloric acid have shown good results [5]. Direct recycling of dust back to steel production is usually not possible because they contain metals and compounds that can harm the primary processes if the materials are not pre-treated [6]. One of the troublesome elements is zinc. Zinc is present in the flue dusts as zincite ZnO and franklinite ZnFe₂O₄. Zinc ferrites can be very difficult to chemically decompose so that zinc can be recovered [7]. Pyrometallurgical processes, such as roasting, can be used to break down the zinc ferrites. The aim of hybrid processes is to decompose zinc ferrites by pyrometallurgical process and then recover the non-ferrous metals by hydrometallurgical techniques [8].

By roasting with caustic soda (NaOH) or sodium carbonate (Na₂CO₃) zinc ferrites can be decomposed and leaching of zinc could be improved [9]. One of the most promising of the combined treatments of roasting and leaching is to convert ferrite into a soluble sodium zincate form, typically Na₂Zn(OH)₄. Both NaOH and Na₂CO₃ become liquids at temperatures used in roasting [10]. Fusing synthetic zinc ferrite with NaOH pellets at 318 – 450 °C for 1 h resulted in 70 – 82 % zinc extraction and extraction increased over 90 % when the zinc ferrite was hydrolysed with water or dilute NaOH solution prior to the fusion step [9]. In caustic roasting of

synthetic zinc ferrite at 350 – 450 °C for 30.60 minutes most of zinc ferrite was decomposed and converted into soluble sodium zincate and relatively insoluble hematite[8]. Conversion of zinc ferrite with Na₂CO₃ has to be done at 850 – 950 °C. The benefits are that lower additions and lower cost of Na₂CO₃ [10, 11]. Addition of CaCO₃ or MnCO₃ in roasting of EAF dust with Na₂CO₃ has increased iron and zinc dissolution [3]. It has also been reported that the hydrophobic behaviour and handling of NaOH causes difficulties, but sintering of calcine product with Na₂CO₃ requires additional crushing step [10].

Using caustic roasting has been proven to improve dissolution also for EAF dust and the trend of using hydrolysis prior to roasting was same for both synthetic ferrite and EAF dust. EAF dust samples (25 % Zn, 1.8 % Pb, 33 % Fe) were leached in caustic soda solution and using caustic roasting pre – treatments the amount of extracted zinc increased from 38 % to 80 % when roasting at 350 °C for 1 hour was used before leaching and hydrolysis before roasting increased the leaching of zinc to 95 % [9]. The chemical reactions in the fusion (1), (2) and leaching (3) are [9].



In this paper we have studied the effect of roasting stainless steel flue dust with sodium hydroxide and potassium hydroxide on the dissolution of the dusts in acid and alkaline leaching. Previous experiments have shown that both in alkaline and acid leaching recovery of zinc depends on dust mineralogy [12-14] and the aim was to test different procedure to break down zinc ferrite and increase zinc recovery.

2 Experimental materials and methods

Flue dusts from Outokumpu Tornio Steelworks in Finland were used as test materials. The dust samples were taken from electric arc furnace (EAF) and argon-oxygen decarburization converter (AOD) baghouses from production line 2 that uses solid ferrochrome. The flue dust samples were washed with water and analyses of washed and dried dusts are given in **Table 1**.

Table 1 Chemical composition of washed dust samples from stainless steel production in wt-%

Sample	Zn	Fe	Cr	Ni	Mo	Mn	Mg	Ca	K	Pb	Cd	Cu	Al	S
EAF2	5.8	18.2	8.9	2.2	0.1	2.7	1.5	12.3	0.8	0.9	0.2	0.5	0.8	0.4
AOD2	4.8	22.3	8.1	2.3	1.1	3.0	2.6	14.4	0.2	0.5	0.0	0.4	0.2	0.1

Synthetic zinc ferrite was prepared from analytically pure oxides mixed in a stoichiometric ratio (81.4 g ZnO and 159.7 g Fe₂O₃) using a Turbula Shaker-Mixer from Glen Mills. The mixed powder was compacted with pressure of 10 – 15 kN to produce homogeneous pellets with a weight of about 5 grams. The pellets were placed into a Lenton UAF 16/10 chamber furnace on top of a refractory brick. The furnace was then slowly heated to 1373 K in air. The reaction time was 72 hours. The zinc ferrite metal ratio was 39.5 % Zn, 59.5 % Fe and 1 % Si and based on XRD analysis it contained franklinite ZnFe₂O₄ but maybe also magnetite (Fe₃O₄) or maghemite (γ – Fe₂O₃). Some silicon was found in EPMA analysis, possibly in the form of willemite Zn₂SiO₄.

For the thermal roasting a Scandiaovnen AS Type K4 oven was used. The temperature could be adjusted electronically with accuracy of 1 °C. The roasting tests were carried out in a ceramic crucible. The crucible was positioned in AISI 316 stainless steel reactor that was closed hermetically. The inner capacity of the reactor was about 100 cm³. A 30 cm long pipe was welded to it so that the hot air inside could leave the reactor through the pipe and the wall of the oven, **Fig. 1**.

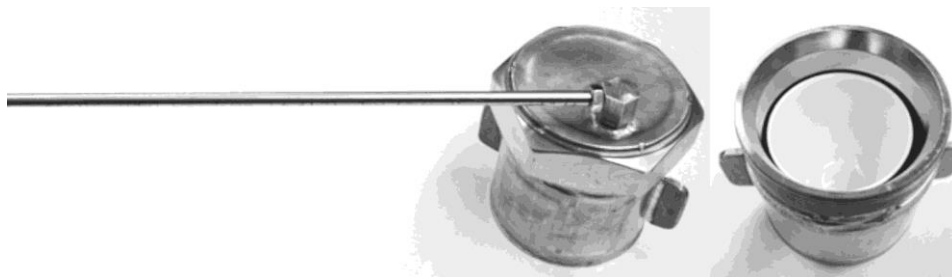


Fig. 1 Stainless steel reactor with lid and pipe on the left and ceramic crucible on the right

The roasting temperatures were 350 – 660°C. Samples were prepared by mixing dust and NaOH or KOH powder. The melting point of NaOH is 318 °C and that of KOH is 406°C and KOH was used to prevent sintering of the batch. In some tests aluminium or iron powder was added to improve heat conductivity within the charge. The treatment time was 1 or 2 hours. In some tests the batch remained in powdery form, but in some tests it melted as a solid piece and was crushed for leaching experiments. Leaching tests of treated dust samples were done at 60 °C using 2 M NaOH, 2 M KOH and 1.5 M H₂SO₄ solution. The leaching test duration was 3 to 8 hours and only the final sample was analyzed for dissolved metals using Inductively Coupled Atomic Emission Spectrometry (ICP – AES).

Synthetic ferrite was crushed before thermal treatment and leaching tests. Different compounds were used as additives in thermal treatment to break down the ferrite. The thermal treatments were done with sodium hydroxide and sodium carbonate to convert ferrite to soluble sodium compounds, sulfur compounds to convert ferrite to sulfates, potassium nitrate to produce soluble salts, and carbon to reduce oxide from ferrite. Thermal treatment temperatures were 350 to 450 °C for sodium hydroxide, sulfur compounds except sodium sulfite, and nitrate and 830 °C for carbon, sodium carbonate and sodium sulfite. Thermal treatment times were 2 – 3 hours. The leaching tests were done for 3 hours in 1.5M H₂SO₄ at 65 °C.

3 Results

The dissolution of stainless steel production dusts is rapid and reactions reach a steady state usually in less than 30 minutes [12-15]. In leaching tests with strong alkali solutions the aim has been selective leaching of zinc. In acid leaching tests the aim has been either selective leaching of zinc with minimum leaching of other metals or total leaching of zinc. The maximum zinc recovery in leaching with 2 M NaOH has been determined previously to be 30 % for EAF2 and 30 – 40 % for AOD2 dust [15]. Maximum zinc recovery in leaching with 1.5 M H₂SO₄ has been determined in previous tests to be 65 % for EAF2 and 71 – 88 % for AOD2 dust [12, 13]. AOD dusts has been found to have better valuable metal recycling possibilities than EAF dusts due to better Zn yields and selectivity compared with Cr, Ni, Fe, Mo [12].

Leaching test results for EAF2 sample are shown in **Table 2**. All these leaching tests were done at 60 °C for 3 hours. Thermal treatment with NaOH at 350 °C has increased zinc selectivity in

NaOH leaching from 30 % to 50 %. The same effect was seen in treatment with KOH and aluminium powder at 500 °C followed by KOH leaching. There was a clear improvement in zinc recovery, but the zinc extraction was still too low. A strong effect was seen in treatment with KOH followed by strong acid leach. The zinc recovery increased to 91 %. For EAF2 dust the alkaline leach recoveries were not significantly improved but for acid leach the result is promising.

Table 2 Zinc recoveries from EAF2 dust after thermal treatments

EAF2 [g]	KOH [g]	NaOH [g]	Other [g]	Temperature [°C]	Time [h]	Leaching conditions	Zn recovery [%]
10		9		350	1	2M NaOH	51
1	1			350	2	2M NaOH	39
1	1			450	1	2M NaOH	40
1	1			450	1	2M KOH	42
1	1			500	1	2M KOH	35
1	1.2		0.1 Al	500	1	2M KOH	51
1	1			500	1	1.5MH ₂ SO ₄	91

Table 3 Zinc recoveries from AOD2 dust after thermal treatments

AOD2 [g]	KOH [g]	NaOH [g]	Other [g]	Temperature [°C]	Time [h]	Leaching conditions	Zn recovery [%]
10		10		350	1	2M NaOH	58
10			1 Al	350	1	2M NaOH	53
10		10	0.5 Al	350	1	2M NaOH	49
1	1			400	1	2M NaOH	48
1	1			450	1	2M NaOH	33
1	1			450	1	2M KOH	50
1	1			500	1	2M KOH	45
1	1.2		0.1 Al	500	1	2M KOH	43
1	1			500	1	1.5MH ₂ SO ₄	72
1	1		0.1 Al	500	1	1.5MH ₂ SO ₄	27
2	2		1 Al	500	1	1.5MH ₂ SO ₄	60
1			0.164Al	660	1	2M KOH	16
1	1		0.164Al	660	1	2M KOH	36
1	1		0.164Al	660	1	1.5MH ₂ SO ₄	74
1	1		0.164Al	660	1	1.5MH ₂ SO ₄ , 8 h	67
1	1			660	1	1.5MH ₂ SO ₄ , 4 h	69
1	1			660	2	1.5MH ₂ SO ₄ , 4 h	64
1	1		0.45 Fe	660	2	1.5MH ₂ SO ₄ , 4 h	72
1	1		0.2 FeCr	660	2	1.5MH ₂ SO ₄	67

Leaching test results for AOD2 sample are shown in **Table 3**. Most of these leaching tests were done at 60 °C for 3 hours, but longer times test were used in some acid leaching tests. Thermal treatment with NaOH at 350 °C has increased zinc selectivity in NaOH leaching to almost 60 %. Generally, treatment with KOH, with or without aluminium powder, followed by alkaline leaching increased zinc recovery but not enough. There is a trend that increasing thermal treatment temperature can lower zinc recovery, and this may be related to sintering of the sample. Thermal treatment with KOH, with or without metal powder, did not increase zinc recovery in acid leach. Zinc recoveries in acid leach tests were even lower than what has previously been determined without thermal treatment.

The results from leaching tests with synthetic ferrite are shown in **Table 4**. In all tests the amount of ferrite was 1 g. Leaching conditions were 1.5M H₂SO₄ at 65°C and leaching time was usually 3 hours. Zinc recoveries from synthetic ferrite were very low in some cases. Untreated ferrite did not react in aqua regia at room temperature. This was surprising as hot acid leach is done in zinc production to dissolve ferrite formed during roasting of zinc sulfide. Alkaline roasting improved zinc recovery, but further tests with higher alkali to ferrite weight ratio must be done.

Table 4 Zinc recoveries from synthetic ferrite after thermal treatments. Leaching conditions were 1.5M H₂SO₄ at 65 °C

ZnFe ₂ O ₄ [g]	Additive [g]	Temperature/Time [°C] / hour	Zn recovery [%]
1.00	0.33 NaOH	350 / 2	18.9
1.00	0.66NaOH	450 / 2	31.5
1.00	0.66 S	450 / 2	12.8
1.00	1.00 KNO ₃	450 / 2	18.1
1.00	0.66S	450 / 2	1.2
1.00	1.00 (NH ₄)S ₂ O ₈	450 / 2	24.1
1.00	0.20C	830 / 2.66	5.9
1.00	0.43 Na ₂ CO ₃	830 / 2.66	11.3 (20 h test)
1.00	0.43 Na ₂ CO ₃	830 / 2.66	27.3
1.00	0.43 Na ₂ CO ₃	830 / 2.66	23.3
1.00	1.56 Na ₂ SO ₃	830 / 2.66	31.7

4 Discussion

The zinc recoveries from EAF and AOD stainless steel dust were not improved to the target level over 95 % extraction. There was just one test, where significant improvement was seen, and that was for EAF dust after leaching in strong acid. The extraction of zinc from EAF dust was 40 – 50 % in alkaline leach but over 90 % in acid leach. No improvement in extraction from AOD dust was seen either in alkaline (max. 58%) or acid leach (max. 72 %). In the work of Xia and Pickles tests with unalloyed steel EAF dusts have given zinc recoveries of 32 – 59 % in 5 M NaOH leaching and 71.7 – 80.4 % in 5 M H₂SO₄ leaching [8]. Both in alkaline and acidic solutions it was difficult to decompose the zinc ferrite. In several tests zinc recovery was better in acidic media than in alkaline media. Our results show same tendencies and same levels of zinc extraction.

In the work of Xia and Pickles [8] roasting with NaOH at 350 – 450 °C resulted in better zinc recovery. Very selective and complete zinc recovery was achieved in 4 M NaOH leaching at 90 °C after roasting of 30 minutes at weight ratio 1 – 1.5 NaOH/ZnFe₂O₄ and over 95 % zinc recovery from EAF dust was achieved when the weight ratio in roasting was above 3 to 4 [8]. Our roasting tests were done with smaller amount of alkali, which can partially explain the low zinc extraction. However, in analysis of stainless steel flue dusts several glassy phases have been seen and they surround dust particles. It is possible that these phases have not been broken to release the other compounds for dissolution.

5 Conclusions

Roasting with alkaline compounds was done to increase zinc extraction from stainless steel production dusts. The extraction was improved for EAF dust but not for AOD dust. The

extraction of zinc from EAF dust was not significantly improved in alkaline leach (40 – 50 %) but there was indication of better extraction in acid leach (over 90 %). Zinc extraction from AOD dust was max.58% in alkaline and max. 72 % in acid leach.

The difficulties in zinc recovery are due to zinc ferrite in the dust. Leaching tests with synthetic zinc ferrite showed rather low zinc recoveries. The acid leach of synthetic ferrite resulted in less than 32% Zn recovery, and this must be studied further to find out the low zinc recovery is really caused by franklinite in the dusts.

References

- [1] G. Orhan: Hydrometallurgy, Vol. 78, 2005, p. 236-245
- [2] M. K. Jha, V. Kumar, R. J. Singh: Resources Conservation & Recycling, Vol. 33, 2000, 2001, p. 1-22
- [3] P. C. Holloway, T. H. Etsell: Journal of Minerals & Materials Characterization & Engineering, Vol. 7, 2007, p. 1-26
- [4] T. Havlik, B. Friedrich, S. Stopić: World of Metallurgy – ERZMETALL, Vol. 57, 2004, No. 2, p. 113-120
- [5] S. Langová, J. Leško, D. Matýsek: Hydrometallurgy, Vol. 95, 2009, p. 178-182
- [6] I. Palencia, R. Romero, N. Iglesias, F. Carranza: JOM, Vol. 51, 1999, p. 28-32
- [7] S. R. Youcai Z.: Minerals Engineering, Vol. 13, 2000, No. 13, p. 1417-1421
- [8] D. K. Xia, C. A. Pickles: Canadian Metallurgical Quarterly, Vol. 38, 1999, No. 3, p. 175-186
- [9] S. R. Youcai Z.: Journal of Hazardous Material, Vol. B80, 2000, p. 223-240
- [10] P. C. Holloway, T. H. Etsell, A. L. Murland: Metallurgical and Materials Transactions B, Vol. 38, 2007, No. 5, p. 781-791
- [11] A. Kekki, J. Aromaa, O. Forsén: *Leaching behavior of five different stainless steel production dusts in sulphuric acid*, In: Kammel's Quo Vadis Hydrometallurgy 6, Herlany, Kosice, Technical University of Kosice, 2012, p. 86-92
- [12] A. Kekki, J. Aromaa, O. Forsén: Physicochemical Problems of Mineral Processing, Vol. 48, 2012, No. 2, p. 599-606
- [13] A. Stefanova, J. Aromaa, O. Forsén: *Alkaline leaching of stainless steel production dusts*, In: Kammel's Quo Vadis Hydrometallurgy 6, Herlany, Kosice, Technical University of Kosice, 2012, p. 208-215
- [14] A. Stefanova, J. Aromaa, O. Forsén: Physicochemical Problems of Mineral Processing, Vol. 48, 2013, No. 1, p. 37-46

Acknowledgements

This work has been done in the METDUST project of the ELEMET research program funded by FIMECC Oy. The financial support of TEKES, Outokumpu Stainless Oyj and OutotecOyj is gratefully acknowledged.