Dissolution Behavior of Fluorine from AOD Slag after Treatments for Volume Stabilization

Qixing Yang^{1, a}, Anjun Xu^{2, b}, Fredrik Engström^{3, c}, Fenglan Han^{4, d}, Peng Xue^{5, e},
Dongfeng He^{6, f}, and Bo Björkman^{7, g}

^{1, 3, 7}MiMeR - Minerals and Metallurgical Research Laboratory, Luleå University of Technology,
SE-971 87, Luleå, Sweden

^{2, 5, 6}Department of Ferrous Metallurgy, School of Metallurgical and Ecological Engineering,
University of Science and Technology Beijing, USTB, 100083 China

⁴School of Material Science & Engineering, Beifang University of Nationality, Yinchuan, Ningxia
750021, China

^aqixing.yang@ltu.se, ^banjunxu@126.com, ^cfredrik.i.engstrom@ltu.se, ^d625477897@qq.com,
^exuepengustb@163.com, ^fhdfcn@163.com, ^gBo.Bjorkman@ltu.se

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Abstract. AOD slag samples from steel works of Outokumpu Stainless Company were used to study F-dissolution relating to treatments for volume stabilization. Results from the slag tests and sample characterizations indicate that the slag re-melting with or without reduction and granulation with either water or gas have rather small effects on F leaching, as well as formation of different C₂S polymorphs. The chemical composition and cooling condition are the two important parameters to control F leaching from slag samples. These two parameters should be combined together in an optimum way by the steel industry to treat slags for F-immobilization.

Introduction

At a steel plant of Outokumpu Stainless Company, there is an AOD (Argon Oxygen Decarburization) converter of 100-ton capacity used to refine steel melt from an EAF (Electric Arc Furnace) for production of stainless steel. After the refining, slag around 10 tons is tapped out from the converter. A natural cooling of the tapped AOD slag often leads to a slag disintegration or dusting. Fines from the slag disintegration are often difficult to handle or use as materials for construction [1]. It is thus important to prevent the slag dusting in order to facilitate slag handling and utilization.

The disintegration of AOD slag is related mainly to the formation of γ phase of dicalcium silicate, γ -Ca₂SiO₄, abbreviated as γ -C₂S [1]. Several authors of the present article from the Minerals and Metallurgical Research Laboratory, Luleå University of Technology, LTU, have carried out research work together with the steel company in order to prevent the γ -C₂S-driven slag dusting. Samples of the AOD slag were modified by different cooling techniques [2] and stabilizing agents [3]. Due to the modifications, the AOD slag samples gained the volume stability and mechanical properties required for its utilization as materials for construction [2, 3].

J. Savolainen et al. have made efforts to manufacture environmentally sound and CE-marked construction materials using different types of stainless steel slag from Outokumpu Stainless Company [4]. The authors found that a fast cooling of some AOD slag samples via gas granulation has led to a higher fluorine leaching.

Fluorite can be used as a slag forming agent in other steelmaking processes, such as hot metal pretreatment, secondary steel refining and the production of high alloyed steels. The slags from these processes can contain some amounts of CaF₂. A potential fluorine contamination to the ground water may occur, when these slags are utilized as road construction or landfill materials [5-7].

Ryo INOUE et al [5] reported that dicalcium silicate, C₂S, could dissolve up to 6 mass% of F and identified C₂S as a main F-containing mineral in hot metal pretreatment and BOF slags. The dissolved

fluorine from the hot metal pretreatment and secondary refining slags can be immobilized via an incorporation of F into precipitated hydrates such as $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ compounds [6, 7].

The C_2S forms when values of CaO/SiO_2 for slags exceed 1.4 [1]. For the AOD slag, the values are often close to 2 and the C_2S is a predominant slag mineral, which can form solid solution with CaF_2 [5]. Thus the C_2S in the AOD slag may associate with both the $\gamma\text{-C}_2\text{S}$ -driven slag dusting and the F leaching.

J. Savolainen et al. performed plant slag granulation trials for a better control of F leaching from AOD slag [4]. Early work on the AOD slag carried out by some of the present authors aimed mainly at the dusting prevention [2, 3]. The present work is thus undertaken to investigate dissolution behavior of F from AOD slag treated for dusting prevention and by the plant slag granulation.

Laboratory slag tests are performed using slag samples from the early studies [2, 3] and the plant tests [4]. Results obtained are discussed together with data from early work [2-4], as well as related literature information [5-7]. The stainless steel industry may be able to use these results for slag treatments, thus producing some slag products with high volume stability and minimum F-dissolution for use in construction to save valuable natural resources.

Experimental

Plant Gas Granulation Tests of AOD Slag. A granulation facility placed in slag yard at one of the steel works of Outokumpu Stainless Company was used for gas granulation tests of the AOD slag [4, 8]. Liquid slag in the pot from the AOD shop was taken by slag dippers of 2-3 meters long and poured into the facility for granulation using either air or N_2 gas with flow rate of 4-5 Nm^3/min . Slag granules weighing about 10 kg were obtained from each of the tests. The slag solidified inside the slag dippers was taken as reference samples.

Slag Tests Performed by the Minerals and Metallurgical Research Laboratory at LTU. Samples from 3 of the gas granulation tests at the steel work of Outokumpu Stainless Company were supplied to LTU for laboratory slag tests with internal sample code AT1, AT2 and AT3. Two AOD slag samples taken from slag yard were supplied by another steel work of the Company for the tests by LTU. The slag sample coded as MA3 has been used for early tests of water granulation [2]. Another sample with code AM4 was crushed and sieved to obtain a sample with size of -0.85 mm, which was melted together with stabilizers containing B and P elements for crystal chemical stabilization of high temperature C_2S polymorphs [3].

The tests at LTU consisted of slag re-melting and treatments with different methods. There was some reduction of slag while it was contained in graphite crucibles for the re-melting. The reduction was avoided by using MgO crucibles to hold the samples.

The graphite/ MgO crucible and an outer refractory crucible formed a crucible system that was inserted in the induction coil, which was connected to a power generator of 60 kW and 3 kHz. The temperature increased from around 20°C to 1600°C with heating rates of 3.6-5°C/minute and heating periods often more than 7 hours to re-melt slag samples in MgO crucibles. After maintaining the temperature of 1600°C for 10-30 minutes, the furnace power was switched off and each of the slag samples left in MgO crucible to cool to room temperature in the closed furnace. The in-furnace cooling took about 5 hours, giving slow cooled slag samples. Some other details about the slag re-melting can be found in [2, 3].

Fig. 1A shows the system for water granulation of AOD slag sample MA3. For re-melting the sample using graphite crucible, the heating time was around 1 hour. Shortly after the slag melting, a crucible holder was used to grasp the outer refractory crucible for placing the crucible system (3 in Fig. 1) above the slag granulation system. The liquid slag (4 in Fig. 1) about 1550°C was tapped through the granulation device (2 in Fig. 1) and hit by water jets to generate slag granules, which fell down into the water tank (1 in Fig.1). Other details about the granulation system can be found in [2].

Fig. 1B shows the granulation system for AOD slag sample MA4. The furnace (5 in Fig. 1) was tilted to pour the liquid slag of 1700°C out of the graphite crucible. An injector (6 in Fig. 1) under the furnace started to inject air of pressure 3 bars into the granulation box (7 in Fig. 1). Slag granules (8 in Fig. 1) generated by air jet, after flying briefly, fell to and cooled on the box base.

Fig. 1 – A. System for water granulation of the re-melt/reduced and re-melt AOD slag sample MA3, B. System for air granulation of re-melt/reduced AOD slag sample AM4; in the figure: 1. Water tank, 2. Granulation Device, 3. Crucible system for slag melting and tapping, 4. Liquid slag for granulation, 5. Induction furnace tilted to pour liquid slag out of the graphite crucible, 6. Air injector, 7. Granulation box, 8. Slag granules flying in the box

Slag samples were analyzed by the analytical laboratory of Outokumpu Stainless Company using XRF method. Leaching tests were performed with SS EN 12457-2 for slag samples from laboratory tests and with SS EN 12457-3 for slag samples from the plant trails of gas granulation [4].

Experimental results and discussion

Oxide contents in slag samples from laboratory tests and plant trails are listed in Table 1. Table 2 presents results of F leaching from MA3 and MA4 samples before and after laboratory tests. The original sample MA3-0 leached F of 89 mg/kg. The upper XRD pattern in Fig. 2 shows that phase 4 or $\text{Ca}_3\text{Al}_2\text{O}_6$, with rather high peaks, is one of the major phases in the sample MA3-3. This phase may contribute to decreasing F-leaching from MA3-3 to the very low value, 0.001 mg/kg, Table 2, as the phase can form F-containing hydrate $\text{Ca}_3\text{Al}_2(\text{H}, \text{F})_{12}$ [5, 6]. By the slow cooling in crucible a higher amount of $\text{Ca}_3\text{Al}_2\text{O}_6$ can form to decrease F dissolved from MA3-3 sample.

There are rather large decreases in heights of peaks for the $\text{Ca}_3\text{Al}_2\text{O}_6$ phase near 2θ of 48° in the lower XRD pattern of Fig. 2, indicating a limited formation of the mineral in MA3-1. The sample MA3-1 and MA3-2 were from the granulation and the liquid slag was quickly cooled by water jets, leaving little or no time for $\text{Ca}_3\text{Al}_2\text{O}_6$ to precipitate or solidify out of the liquid slag to the amount necessary for F-stabilization. Thus a high amount of F, 215 and 255 mg/kg, was dissolved, respectively, from MA3-1 and MA3-2 samples, Table 2.

The original MA4 sample leached 18.6 mg/kg of F. After re-melted together with 0.5% Dehybor and in-furnace cooled [3], F leaching from sample MA4-1 increased somewhat to 37 mg/kg. However, F leaching from MA4-2 increased sharply to 152 mg/kg, after it was granulated by air. Though F content is 2.4% in MA4-2, lower than F content of 3.37% in MA4-1, Table 1.

Table 1 Contents [weight %] of analyzed oxides in the AOD slag samples, $B_2 = \text{CaO/SiO}_2$

	F	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	MnO	TiO ₂	B ₂
MA3-0	2.40	25.2	53.0	6.0	5.2	1.50	0.5	0.43	2.1
MA3-1	2.40	26.2	55.9	9.1	6.4	0.70	0.8	1.08	2.13
MA3-2	2.20	22	49.5	7.6	5.8	1.50	0.7	0.75	2.25
MA3-3	2.30	26.1	53.3	6.4	5.6	0.40	0.9	0.88	2.04
MA4-0	2.05	30.8	57.7	1.6	4.8	0.45	0.8	0.37	1.87
MA4-1	3.37	30.8	54.5	2.2	5.9	0.9	1.2	0.66	1.77
MA4-2	2.40	30.1	49.1	2.4	5.6	0.2	0.9	0.59	1.63
AT1	0.44	26.8	34.5	8.5	14.5	0.5	1.4	2.42	1.29
AT2	3.13	27.8	50.3	1.1	8.5	0.3	0.3	0.5	1.81
AT3	1.52	28.3	47.4	4.3	9	0.3	0.6	0.6	1.68

Table 2 F leaching from slag samples MA3 [2] and MA4 [3] tested at LTU

Sample	Laboratory treatments for the samples	F leaching, [mg/kg]
MA3-0	Original MA3 sample	89
MA3-1	MA3 with reduction/re-melting and water granulation	215
MA3-2	MA3 with re-melting and water granulation	255
MA3-3	MA3 with reduction/re-melting and cooling in crucible	0.001
MA4-0	MA4 after metal separation with size <0.85mm	18.6
MA4-1	MA4 re-melted with 0.5% Dehybor	37
MA4-2	MA4 after reduction/re-melting and air granulation with size <1.7mm	152

Fig. 2 - XRD patterns of sample MA3-3, upper pattern, and MA3-1, the lower pattern

The 3 reference samples from the plant trails leached F of 80-111 mg/kg, which were lower by 80-160 mg/kg than the samples from the gas granulation, Table 3. SEM and EDS analyses of a sample from granules AT3 in Fig. 3 show two nearly round crystals with spectrum 1 and 2, which have Ca/Si

value 1.76 and low contents of Al, Cr and Mn, see the table below the SEM micrograph of Fig. 3. The matrix zones with spectrum 3-5 have higher contents of Al, Cr, Mn and Mg, but lower Ca/Si values of 1.6-1.67.

The minerals in matrix zones may be formed at lower temperature. While in contact with water, the matrix minerals, with weaker structures and larger specific surface areas, may dissolve higher amounts of their internal substances, including F element. The two round crystals with less specific surface area and stronger structures can be more resistant to the leaching.

Table 3 F leaching from slag samples AT1, AT2 and AT3 from the plant gas granulation [4] and laboratory tests of re-melting and in-furnace cooling

Test sample	F leaching from slag samples after treatments, [mg/kg]		
	Plant trails of gas granulation		Laboratory tests of granule re-melting and in-furnace cooling
	Reference	Granules	
AT1	80.6	263	9.5
AT2	110	191	151
AT3	111	251	208

	F	Mg	Al	Si	Ca	Cr	Mn	O	Ca/Si
Spectrum 1		1.8		14.8	25.9	0.08	0.08	57.4	1.75
Spectrum 2		1.4		14.9	26.2	0.08		57.5	1.76
Spectrum 3	2.18	6.2	2.7	12.1	19.4	0.58	0.28	56.1	1.61
Spectrum 4	3.2	5.0	1.5	13.1	21.0	0.15	0.18	55.6	1.60
Spectrum 5	4.35	6.0	2.6	11.7	19.5	0.36	0.29	54.7	1.67

Fig. 3 SEM micrograph and point analyses, in [atom%], by EDS of a sample from granules AT3

The crystals with Ca/Si value near 2 may be C_2S particles, which can dissolve up to 6% of F [5]. However, F element was not detected in the C_2S crystals, rather, was concentrating in the matrix minerals with contents of 2.18-4.35%, which may be one of the reasons for the higher F leaching from the granule samples from the plant trails. More studies may be needed to clarify influences of cooling and other factors on F-enrichment in the matrix.

A sample from AT1, the granules from the plant trails with F leaching of 263 mg/kg, after laboratory treatments of re-melting and in-furnace cooling, leached much less F of 9.5 mg/kg. Whereas, for samples of granules AT2 and AT3 with the same laboratory treatment, F leaching decreased moderately by only around 40 mg/kg, Table 3. The different results for the 3 granule samples treated in the same way may be related to differences in oxide contents.

For granules AT1 the B_2 (CaO/SiO_2) value is 1.29, the lowest, and contents of Al_2O_3 of 8.5% and MgO of 14.5% are the highest as compared with AT2 and AT3, Table 1. These will result in different temperature levels for slag solidification under the same cooling condition. With a lower temperature level there may be a longer time for some mineral phases to precipitate from the liquid slag. The re-melted granules AT1 may have a longer solidification time, which, together with its higher Al_2O_3 content, may facilitate the $Ca_3Al_2O_6$ formation and, hence, a sharp decrease in the F leaching. Besides, F content is 0.44% in granules AT1, lower than the two granules with F contents of 1.52-3.13%, which may make the laboratory treatment more effective to decrease F leaching from AT1 granules.

The granules AT2 and AT3 may be solidified faster with their high B_2 values, 1.81 and 1.68, respectively, leaving short time for the $Ca_3Al_2O_6$ to precipitate. With lower Al_2O_3 contents of 1.1% and 4.3%, Table 1, Al_2O_3 available for the $Ca_3Al_2O_6$ to form were also limited. Thus, the amounts of $Ca_3Al_2O_6$ formed may not be sufficient for a high degree of F-immobilization. Consequently, the decreases in F leaching for the re-melted granules AT2 and AT3 are quite moderate.

The results in Tables 1-3 demonstrate that the re-melting and granulation conditions have rather small effects on F leaching, as well as the phase transformation of C_2S in the slag. The leaching of F may be controlled mainly by the chemical composition of the slag samples and cooling condition for the treatments. These factors should be adjusted together in an optimum way to treat a slag for its F immobilization.

It is also recommended to decrease amounts of CaF_2 containing materials for slag forming. Some researchers have successfully replaced fluoride with some new F-free catalyzers for MgO reduction in Pidgeon process [9]. Some similar efforts may also be made to develop new techniques of F-free slag forming for the steel industry to manufacture high quality steel and slag products, thereby protecting the environment and saving valuable natural resources.

Summary

Samples of AOD slag after tapping and gas granulation at steel works of Outokumpu Stainless Company were tested using laboratory equipment to study F-dissolution relating to treatments of the slag samples for volume stabilization, achieving the following results:

1. The AOD slag samples cooled slowly in plant trails or in laboratory furnaces leached moderate amounts of fluorine. The F leaching was enhanced to 150-260 mg/kg from slag samples with high speed cooling via water and gas granulation.
2. XRD detected $Ca_3Al_2O_6$ as a major phase in a slag sample with in-furnace cooling. The phase immobilized fluorine effectively, leading to a very low F leaching of 0.001 mg/kg. However, a fast cooling by water granulation limited extent of $Ca_3Al_2O_6$ formation, resulting in higher amounts of F leaching from the slag samples.
3. SEM and EDS studies of granules from a plant granulation trail show round crystals containing no F element. F element was observed mainly in the matrix zones, ranging 2.18-4.35%. The gas granulation may lead to an F-enrichment in matrix minerals with weaker

structures and larger specific surface areas. The matrix may easily dissolve, releasing F from the granules.

4. While being treated by re-melting and in-furnace cooling after the granulation, the granule samples with lower CaO/SiO_2 values and higher Al_2O_3 contents may gain longer time for formation of $\text{Ca}_3\text{Al}_2\text{O}_6$ phase, giving a higher degree of F-immobilization.
5. Results from the present study indicate that the slag re-melting with or without reduction and granulation with either water or gas have very limited effects on F leaching, as well as the formation of different C_2S polymorphs. The chemical composition and cooling condition are the two important parameters to control F leaching from slag samples. These two parameters should be combined together in an optimum way to treat the slag for F-immobilization.

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