MODIFICATION STUDY OF A STEEL SLAG TO PREVENT THE SLAG DISINTEGRATION AFTER METAL RECOVERY AND TO ENHANCE SLAG UTILIZATION

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ABSTRACT

A slag sample was produced during laboratory reduction tests of a steel slag for metal recovery. The reduction of the metal oxides changed slag basicity (CaO/SiO_2) to about 1.6 and led to the formation of γ-phase of dicalcium silicate, γ-Ca_2SiO_4, which resulted in disintegration of the slag sample.

A modification study of the slag sample after reduction was performed. The study aimed at acquiring data and fundamental information for choosing environmentally friendly and cost effective methods for preventing slag disintegration in order to increase slag utilization. Effects of some additives, containing SiO_2 or P_2O_5, on the formation of the γ-Ca_2SiO_4 were examined via slag melting tests. The slag was also modified by fast cooling, via air granulation using a laboratory granulation system. In these modification tests, a laboratory induction furnace was used to melt the samples at approximately 1700°C. Samples obtained before and after the modification tests were characterized.

The study results showed that γ-Ca_2SiO_4 and fines did not appear by adding MCP-F or a product from iron ore processing to increase P_2O_5 content in the reduced slag from a very low level, 0.07%, to around 0.3% or higher. A sand addition of 5.12% in the reduced slag could decrease slag CaO/SiO_2 value to 1.34, which prevented Ca_2SiO_4 formation and slag disintegration. The reduced slag was cooled quickly via air granulation, which prevented formations of γ-Ca_2SiO_4 in slag granules.

Based on results from the melting tests and other literature, fundamental aspects regarding slag modification and treatment are discussed, along with utilization of the slag after the oxide reduction and modification.

INTRODUCTION

Slag generated from steelmaking processes contains compounds formed mainly by CaO, SiO_2 and MgO, as well as some metal oxides. Full utilization of steelmaking slag is very important in a modern, sustainable society. Several case studies on the full utilization of slag have been published [1, 2]. Results from the studies indicate that it is possible to first reduce metal oxides in slag for metal recovery and then to treat non-metallic phases left from the reduction to produce cement or fertilizer. Refining the metal from reduction may also be necessary if the metal is to be used as raw material in steel production.

Recently, the present authors conducted laboratory experiments to reduce a steel slag for metal recovery as a part of research work for full utilization of the slag. Different types of reducing agents have been used, obtaining metal and slag phases with different compositions. A slag sample produced during some of the reduction tests, with basicity (CaO/SiO_2) around 1.6, disintegrated during cooling. The disintegration of the sample was rather similar to the disintegration occurring in the slag tapped from some heats of an AOD (Argon Oxygen Decarburization) converter.

Values of CaO/SiO_2 for the AOD slag are often close to 2.0 and γ-phase of dicalcium silicate, γ- Ca_2SiO_4, forms in the temperature range of 400-500°C, inducing a volume expansion of nearly 12%. The volume expansion disintegrates the AOD slag [3]. Some authors have reported γ-Ca_2SiO_4 formation in slag with CaO/SiO_2 values exceeding 1.4 [4]. The disintegration of the slag sample of CaO/SiO_2 around 1.6 experienced in the reduction study could therefore be attributed to the γ-Ca_2SiO_4 formation.

Slag disintegration generates fines, which are often difficult to handle and to use as aggregates in road construction [3, 4]. A modification study of the slag sample after reduction was thus performed by the present authors. The aim of the study was to acquire data and fundamental information for choosing eco-friendly and cost effective methods to prevent slag disintegration, via adjustment of the mineral composition of the slag. This study and other related work may together lead to suggestions for a full utilization of the steelmaking slag.

Samples of the reduced slag were melted along with some additives. The slag sample was also melted for cooling rapidly by air using a laboratory granulation system. Both the reduced slag and samples from the modification tests were characterized. Results from these tests are presented and discussed in this article.

METHODOLOGY

Sampling of Slag Fines after Reduction of Oxides in the Steelmaking Slag

Samples of the steelmaking slag and reducing agents were mixed together and contained in either MgO or graphite crucibles for the reduction experiments. A laboratory induction furnace was used to heat and melt the samples. The induction heating stopped after the furnace temperature reached the level of 1700ºC for about 15 minutes with the reduced slag left in the furnace to cool slowly.

The reduced slag disintegrated during cooling and the crucibles were broken due to the volume expansion of the slag inside, as seen in Figure 1. Samples were collected from the slag fines for characterization and for use in the modification tests.

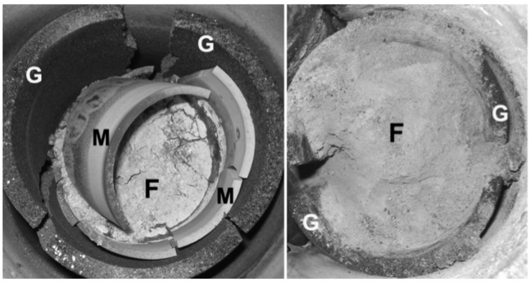

Figure 1: Reduced steelmaking slag disintegrated during cooling inside furnace and the slag volume expansion broke either both MgO and graphite crucibles (left) or graphite crucible (right), in the picture: F - Slag fines, G - Graphite crucible, M - MgO crucible.

Modification Tests – Melting of Slag Sample with Additives

Chemical compositions of additives used in modification test are presented in Table 1. MCP-F is a feed grade mono-calcium phosphate, with 47.2% P_2O_5 for crystal chemical stabilization of volume stable Ca_2SiO_4 polymorphs. The Low-P product originated from the iron ore processing and was provided by LKAB in Sweden. Besides P_2O_5, the by-product contains around 20% Fe oxides, which could decrease melting point of the slag. The sand, with 99% SiO_2, could be added to decrease slag basicity, i.e. ratio of CaO to SiO_2, and, hence, to prevent formation of Ca_2SiO_4.

Table 1: Chemical compositions of additives, in weight %, for modification of reduced slag

	CaO	SiO_2	MgO	FeO	Fe_2O_3	P_2O_5
MCP-F (BOLIFOR)	44.8	0.9	3.6			47.2
Low-P product	18.9	6.1	2.9	14.6	6.7	9.0
Sand	0.15	99.0	0.5		0.08	

Table 2: Additives used to modify the reduced slag in melting tests (sum of weight percents for an additive and reduced slag equalling 100%)

Additive	Sand	Low-P product		MCP-F			
Weight %	5.12	1.96	3.85	0.79	1.19	1.57	1.96

A crucible system was placed in the induction furnace for tests to modify the reduced steelmaking slag. The system was formed by an inner MgO crucible, a middle graphite crucible and an outer crucible made of high Al_2O_3 refractory. Carbon and metal particles in the reduced slag were removed before the tests. The additives, with weight percent values listed in Table 2, and reduced slag (30-150 g) were mixed together and contained in MgO crucibles. The graphite crucible served as an induction heating element to heat the slag/additive to 1700°C with a heating rate of 4.2°C/minute. After maintaining the temperature at around 1700°C for 10 minutes, the furnace power was switched off and the slag/additive left to cool inside the crucible system.

The cooling of the melted slag/additive lasted for about 6 hours. The MgO crucibles were then removed from the system for inspection. A modification of the reduced slag by the additives was considered to be successful if there was neither fine generation nor breakage of the MgO crucible resulting from slag volume expansion. Other details regarding the crucible system and furnace operation can be found in [3].

Modification Test – Melting of Slag Sample for Air Granulation

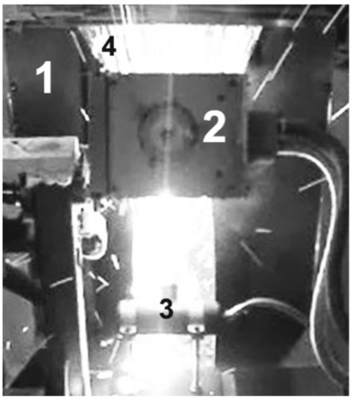

Figure 2: Air granulation of reduced slag, in picture: 1. granulation box 2. induction furnace tilted to pour liquid slag out of the graphite crucible 3. injector 4. slag granules flying in the box

A granulation box (*1* in Figure 2) made of steel plates was placed in front of the induction furnace to receive slag granules. A graphite crucible was used to melt the reduced slag, weighing about 1.0 kg. While the slag temperature was rising to the level of 1700ºC, an injector (*3* in Figure 2) under the furnace started to inject air with a pressure of 5 bars into the granulation box. The furnace (*2* in Figure 2) was then tilted to pour the liquid slag out of the graphite crucible. The air jet impinged on the slag stream, generating slag granules (*4* in Figure 2). The granules, after flying inside the box briefly, fell to the box base. The granulation proceeded for about 1 minute. The slag granules cooled on the box base were subsequently collected for sieving and characterization.

Thermodynamic Calculations of Phase Formation during Heating of Reduced Slag

Thermodynamic calculations were conducted using Factsage 5.5 [5], in order to predict major phases formed in the reduced slag in a temperature range of 200-2000°C and at a pressure of 1 atmosphere. Compound database FS53base and FToxid53base were used together with solution database FToxid53soln. FS53base was suppressed contra FToxid53base to exclude duplications in the data set. Other databases, such as FToxid-slag, FToxid-MeO and FToxid-spinel, were also adopted in the calculations.

RESULTS AND DISCUSSION

Properties of the Reduced Steelmaking Slag

Element mapping, Figure 3, reveals that the slag fines from the reduction consisted of mainly CaO and SiO_2, as well as some oxides containing Mg and Al. Metal particles containing Fe and Mn were also detected in the fines, refer to the mapping of Fe and Mn.

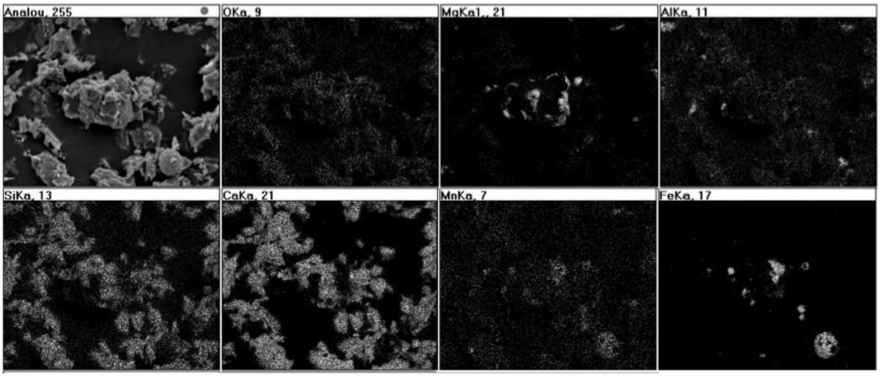

Figure 3: SEM micrographs of fines from the slag reduction and element mapping

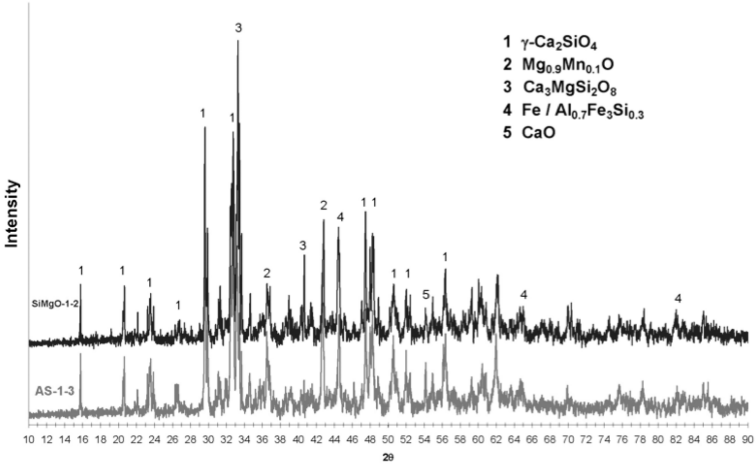

Figure 4: XRD patterns of samples from slag reduction (AS-1-3 – sample contained in graphite crucible, SiMgO-1-2 - sample contained in MgO crucible)

XRD patterns of two samples from the reduction tests are shown in Figure 4. There is a metal phase (phase 4, Fe/$Al_{0.7}Fe_3Si_{0.3}$) formed by the reduction. Both γ-Ca_2SiO_4 (phase 1) and merwinite ($Ca_3MgSi_2O_8$) (phase 3) exist as major phases in the samples. An early study has shown that decreasing P_2O_5 content in slag to 0.12% could cause a complete transformation of β-Ca_2SiO_4 to γ-Ca_2SiO_4 [2]. The reduced slag in the present study contains P_2O_5 of 0.07%, as seen in Table 3. With the P_2O_5 content lower than 0.12%, the β-γ phase transformation then occurred, leading to the slag disintegration shown in Figure 1.

Table 3: Chemical composition of reduced slag after metal separation, weight %

CaO	SiO_2	MnO	P_2O_5	Al_2O_3	MgO	CaO/SiO_2
51.32	32.74	0.11	0.07	2.87	11.82	1.57

Phase distribution calculated by Factsage 5.5 for the reduced slag is plotted in Figure 5. Based on results shown in Figures 4 and 5, it is estimated that contents of γ-Ca_2SiO_4 and $Ca_3MgSi_2O_8$ may reach 30% and 60%, respectively, in the reduced slag cooled in crucibles or with a low cooling rate.

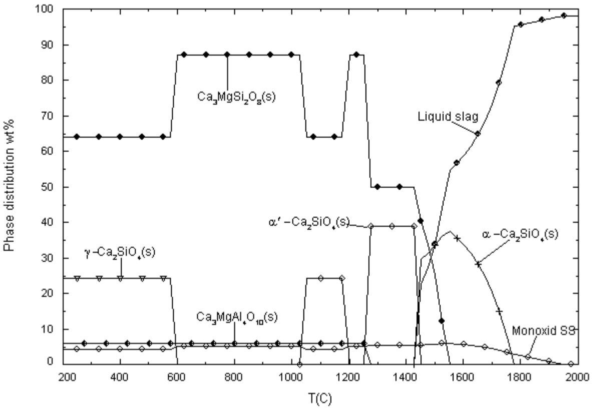

Figure 5: Phase distribution, wt%, during cooling of the reduced slag calculated by Factsage 5.5

Properties of Slag Samples from the Modification Tests

No MgO crucibles were broken due to slag volume expansion and fines were not found in the slag retrieved from the crucibles in the modification tests using sand and MCP-F, as indicated by the slag pieces shown in Figure 6. Data of chemical composition of slag samples from the tests are listed in Table 4. By adding 5.12% sand, the value of CaO/SiO_2 decreases to 1.34, a value lower than 1.4, making it impossible for Ca_2SiO_4 to form [4].

XRD analyses indicate that α'-Ca_2SiO_4 is the only Ca_2SiO_4 polymorph in the sample with 0.86% P_2O_5 (phase 2 in upper pattern in Figure 7). α'-Ca_2SiO_4 can be stabilized by P_2O_5 of higher amounts. With a lower P_2O_5 contents, in range of 0.46-0.69% (Table 4), α'-Ca_2SiO_4 may transform partially to β-Ca_2SiO_4 and both α'- and β-Ca_2SiO_4 may be present in the samples. γ-Ca_2SiO_4 was thus not formed due to the stabilization of β- and α'-Ca_2SiO_4 by P_2O_5 in the added MCP-F.

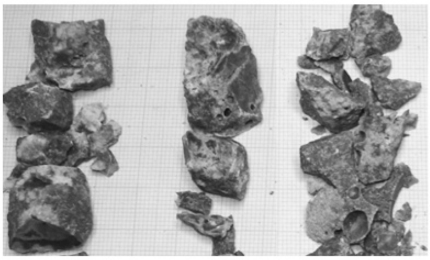

Figure 6: Samples of modified slag retrieved from MgO crucibles, sample on the left: modified with sand of 5.12% and with CaO/SiO2 value of 1.34, sample in the middle: modified with MCP-F of 0.79% and containing 0.46% P2O5, sample on the right: modified with MCP-F of 1.57% and containing 0.86% P2O5

Table 4: Chemical composition of slag samples from modification tests, in weight %

Additive	**Sand**	**Low-P product**		**MCP-F**			
Adding for modification, in wt %	5.12	1.96	3.85	0.79	1.19	1.57	1.96
In modified sample							
SiO_2	35.16	32.2	30.4	31.85	32.0	31.79	31.71
P_2O_5	0.05	0.22	0.32	0.46	0.69	0.86	1.13

Al_2O_3	2.75	2.96	6.2	3.0	2.81	2.90	2.74
MgO	13.75	12.76	13.3	13.16	12.44	12.49	13.23
CaO/SiO_2	1.34	1.55	1.55	1.59	1.59	1.60	1.58

MgO crucibles were not damaged by the slag volume expansion while the slag was melted together with Low-P product. Some slag parts in the central zone were grey/white colour (the left picture in Figure 8) and were found with a weaker structure as compared with the slag near the crucible wall. This is different from the slag modified by the Low-P product of 3.85 % (the right picture in Figure 8). The difference observed in Figure 8 reveals that a small amount of γ-Ca_2SiO_4 survived in the slag with addition of Low-P product of 1.96%.

It has been shown earlier that a partial slag powdering and crucible damaging occurred with the addition of Low-P product of 1.96% in the AOD slag with a CaO/SiO_2 value of 1.75 [3]. Based on these results, it is estimated that adding Low-P product of 4% to increase P_2O_5 content to higher than 0.3% (Table 4) is necessary to eliminate γ-Ca_2SiO_4 in the reduced slag.

Chemical composition of slag granules is quite similar to the composition of reduced slag, Table 3. About 90% granules are with sizes grater than 850 µm, determined by a sieving. A part of the bigger granules with sizes 850-1180 µm are seen in Figure 9. These granules were mostly spherical and had a colour quite different from the grey/white colour of the slag fines seen in Figure 1.

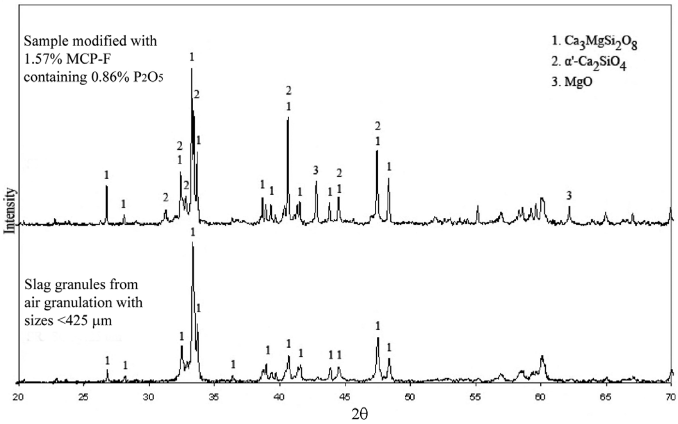

Figure 7: XRD patterns of sample modified with 1.57% MCP-F and sample of granules <425 µm from air granulation

Figure 8: Samples of solidified slag retrieved from MgO crucibles after modification with Low-P product of 1.96% (left) and 3.85% (right)

Granules of sizes < 425 μm are also with similar color and shape as the bigger granules shown in Figure 9. Ca_2SiO_4 is not found and merwinite ($Ca_3MgSi_2O_8$), a volumetrically stable phase (phase 1 in the lower XRD pattern in Figure 7), formed predominantly in the smaller granules (<425 μm). The XRD analyses in Figure 4 and Figure 7 (lower XRD pattern), as well as the colour difference between the granules and slag fines (Figures 9 and 1), implies that γ-Ca_2SiO_4 formation in the slag was prevented by a fast cooling via the air granulation.

CaO and $Mg_{0.9}$ $Mn_{0.1}O$ appeared in the reduced slag, Figure 4. MgO was detected in the sample modified with MCP-F of 1.57%, upper XRD pattern in Figure 7. The free CaO and MgO may react with water forming hydroxides, which leads also to volume expansion and disintegration for the slag [6]. There was, however, neither free CaO nor free MgO detected in the granules of sizes < 425 μm, see lower XRD pattern in Figure 7. Physical properties, the color and shape, of the smaller granules (< 425 μm) are rather similar to the properties of the bigger granules. The similar properties lead to an inference that not only γ-Ca_2SiO_4 but also free CaO and MgO have been prevented largely from surviving in the slag via the air granulation.

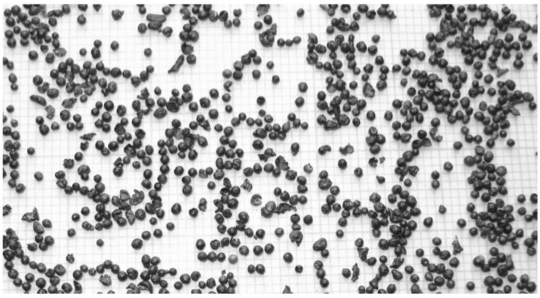

Figure 9: Granules with sizes 850-1180 μm from air granulation of the reduced slag

Discussion on Slag Reduction, Modification and Utilization

The melting point of the slag after reduction is rather high. Special efforts may thus be needed to select additives for the slag modification and to mix and melt an additive in the liquid slag in an industrial-scale operation. Products containing P_2O_5 should be added to the slag after the separation of metal and slag. The sand may be added early during reduction to decrease the slag melting point, facilitating both the slag reduction and modification. The slag modified by P_2O_5 products or sand and cooled slowly as in the present study may be preferably used as aggregates in road construction.

The granules of size < 425 μm may be cooled by a higher rate than the granules with larger sizes. However, the fast cooling generated no glass phase (see lower XRD pattern in Figure 7) but only merwinite ($Ca_3MgSi_2O_8$), a volume stable phase with rather low hydraulic activity. For using as a hydraulic binder, values of CaO/SiO_2 for the reduced slag should be adjusted in a greater extent than in the present study, followed by granulation with water or air [1].

Slag fines with values of CaO/SiO_2 ranging 2.3-2.6, MgO contents greater than 5% and low contents of Fe, Mn and Cr oxides may be suitable to use as Ca-Mg fertilisers, which saves also grinning cost [2]. The reduced slag meets all the requirements, except for the lower CaO/SiO_2 value, 1.57, see Table 3.

In later studies, slag reduction and modification may be considered together and carried out in optimum ways, by which the slag from the treatments can fulfil the requirements of Ca-Mg fertilisers. Different reducing agents may be used to control values of CaO/SiO_2 within the range of 2.3-2.6. One type of the agent may be CaC_2 that generates CO and CaO by reacting with metal oxides. The additional CaO from the CaC_2 reduction may then prevent values of CaO/SiO_2 from decreasing to lower than 2.3.

CONCLUSIONS

A reduced steelmaking slag disintegrated during cooling. The present modification study of the slag was thus undertaken, from which the following results were obtained:

- A sand addition of 5.12% in the reduced slag has decreased slag CaO/SiO_2 value from 1.57 to 1.34, which prevented Ca_2SiO_4 formation and slag disintegration.
- The reduced slag was also modified by adding MCP-F or a product from iron ore processing. These additions increased P_2O_5 content in the slag from a very low level, 0.07%, to the range of 0.22-1.13%. Fines and γ-Ca_2SiO_4 did not appear in the slag as P_2O_5 contents were increased to higher than 0.3%.
- An air granulation of the reduced slag generated spherical granules with a colour quite different from the grey/white colour of the slag fines. Formation of γ-Ca_2SiO_4 was effectively suppressed by the granulation.

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