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MODIFICATION OF MOLTEN STEELMAKING SLAG FOR CEMENT APPLICATION

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Introduction

Brazil has produced around 32 millions of tons of crude steel for the last 10 years and there is no expectation of growth. On the other hand, the construction industry has growth more than 5 %/y. This scenario predicts a lack of blast furnace (BF) slag for cement industry in Brazil in a near future. Steelmaking slag could be an alternative as cement mineral admixture, partially substituting the BF slag. A pyrometallurgical process has been investigated to promote chemical composition modification of molten steelmaking slag in order to make it more appropriate for cement manufacturing.

Effect of cooling rate and chemical composition on slags crystallization

The crystallization of steelmaking slag and chemically modified steelmaking slags has been investigated in an experimental apparatus constituted by a ceramic mold fixed over a copper plate cooled by water, where approximately 1 kg of each molten slag was poured. Slag cooling curves were obtained by thermocouples installed in distinct heights of mold.

Table 1 shows the chemical compositions, determined by X-ray fluorescence (XRF), of four slags evaluated in this system (lab scale). Two slags were supplied by an Iron and Steelmaking company in Brazil; a steelmaking slag (SS) and a blast furnace slag (BF); while others two slags (SS-M1 and SS-M2) were produced by chemical modification of molten SS slag performed through the adding of by-products from metallurgical and civil construction industries in Brazil. The SS slag as well as modified slags were

re-melted and processed in MgO crucibles, while the BF slag was re-melted in graphite crucible.

The chemical compositions of another three modified slags are shown in same table. These three slags were produced in a metallurgical reactor[1] (pilot scale) by adding modifiers agents into 300 kg of molten SS slag. Two samples of the same slag (SS-M3) were produced, one naturally cooled in the same reactor where the modification process took place (SS-M3a) and the other, cooled by steel balls (SS-M3b), using the same technique developed and patented by company Paul Wurth, which has authorized IPT, based on a cooperation agreement, to perform tests using such cooling conditions .

Three samples of slag SS-M4 were obtained, a first one naturally cooled in the modifying reactor (SS-M4a), a second one cooled by steel balls (SS-M4b) and a third one cooled by water quenching (SS-M4c). The slag SS-M5 was cooled only by steel balls.

Table 1: Chemical compositions of slags (XRF).

	Lab Scale (1kg)				Pilot Scale (300) kg		
	BF	SS	SS-M1	SS-M2	SS-M3	SS-M4	SS-M5
Fe_2O_3 (%)[***]	-	13,6	4,4	0,6	6,0	2,0	3,1
FeO (%)[*]	0,2	18,3	7,3	2,4	7,2	7,6	13,2
Fe^0 (%)[**]	-	0,2	0,3	<0,1	0,9	0,3	0,1
CaO (%)	41,5	38,1	38,5	33,1	37,9	37,3	34,5
S (%)	0,7	0,1	<0,1	0,1	0,1	<0,1	0,1
SiO_2 (%)	33,1	9,9	27,5	30,2	27,6	32,2	21,6
Al_2O_3 (%)	10,5	1,7	2,6	11,5	2,1	4,8	10,7
MgO (%)	7,2	8,6	10,6	13,2	10,8	9,8	10,4
TiO_2 (%)	0,6	0,3	0,3	0,2	0,3	0,2	0,3
MnO (%)	0,6	4,4	4,5	2,1	4,4	3,1	3,8
P_2O_5 (%)	0,0	1,3	1,5	0,4	1,2	0,8	1,1

(*) FeO: ASTM E 246-10 - Determination of Iron by Dichromate Titrimetry. (**) Fe^0: XU, Z et al: Journal of Minerals & Materials Characterization & Engineering, v. 2, n° 1, p. 65-70, 2003. (***) Fe^{3+} (%) = Fe_t FRX (%) − Fe^{2+} (%) - Fe^0.

As shown in table 1, the slag modifying process resulted in partial reduction of iron oxides and increasing of SiO_2 and, in some cases, increasing of Al_2O_3 content as well.

Results and discussion

Table 2 shows the mineralogical phases of slag samples, determined by X-ray diffraction (XRD), adopting Rietveld methodology for quantification.

As shown in table 2, only at 2 mm from the chilled plate was observed a high quantity of amorphous in BF slag. Already at 5 mm from the mold bottom, the amount of amorphous dropped to 5.3 %.

Table 2: Mineralogical phases (%) of slag samples determined by XRD (Rietveld).

| | Lab Scale (1 kg) | | | | | | | | | | | | Pilot Scale (300 kg) | | | | | |
| | BF | | | SS | | | SS-M1 | | | SS-M2 | | | SS-M3 | | SS-M4 | | | SS-M5 |
Distante from chilled plate	2 mm	5 mm	30 mm	1 mm	3 mm	5 mm	1 mm	5 mm	30 mm	2 mm	6 mm	30 mm	a	b	a	b	c	b
Larnite (%)				31,2	37,1	35,6							4,0	5,7	4,6			12,1
Brownmillerite (%)				24,1	26,0	38,7							3,4	3,8				
RO (%)				26,3	33,8	21,5	6,5	5,8	7,3				3,2	7,8				16,5
Lime (%)				3,8	3,2	4,2												
Merwinite (%)	4,6	19,4	2,2	2,1			69,0	65,7	68,9	3,3	6,5	2,4	29,6	47,2	10,9	34,9	37,2	37,4
Monticellite (%)											25,6	29,7	30,0	11,1	55,7	42,8		
Melilite (%)		3,3	95,7															
Akermanite (%)		72,0								4,9	54,0	55,1	6,6		17,9	10,9		
Gehlenite (%)											13,9	12,3				9,5		32,1
Amorphous (%)	94,6	5,3	0,1	11,8	-	-	24,5	28,5	23,8	91,2	-	0,5	22,3	23,0	-	11,5	62,8	1,9

a. Natural cooling in the reactor adopted for slag modifying, b. Cooling by steel balls, c. Cooling by water quenching. Contents < 2% no showed, excepting amorphous. MgO as periclase was not detected by XRD.

Based on a heat transferring model, validated by experimental cooling curves of BF slag, it was possible to estimate the average cooling rates between 900 and 1400 °C at 2 and 5 mm from the chilled plate. These rates were estimated as 3.9 °C/s and 2.6 °C, respectively. Therefore, adopting cooling rates faster than 4 °C/s it would be possible to predict more than 95 % of amorphous phase in BF slag. The cooling rates for glassy/crystalline transition found in this paper are much lower than those determined by Kashiwaya et al.[2], however, they are relatively close to the rates found by Gan et al.[3] in BF slags, between 0 5 and 1 °C/s. Discrepancies can be caused by differences among chemical compositions of slag samples, which can affect the beginning of crystallization. For example, the alumina content of BF slag adopted by Gan et al. (17 6 wt.%) is much higher than the alumina content of BF slag used in present work (10 5 wt.%), and it has been mentioned that alumina contributes to the stabilization of amorphous phase in slags[4]. Other reason for such differences can be related to the DSC technique adopted by Gan et al. to evaluate the slag crystallization, which could not have enough sensitivity to detect, by thermal effect, the formation of small crystals during the slag cooling down.

In the region where the slag is mostly crystalline, from 5 mm from the chilled plate, crystalline phases found were mainly akermanite, merwinite and melilite (solid solution between gehlenite and akermanite), which are typically found in BF slags cooled slowly[2]. Simulation of BF slag cooling under equilibrium conditions using FactSage™ shows mostly melilite and some merwinite, phases also found in the BF slag sample evaluated in present work.

As shown in table 2, the steelmaking slag (SS) is mostly crystalline, even in a height close to the chilled plate, where it was detected only 11.8 % of amorphous phase, indicating how it is difficult to stabilize a glassy phase in a steelmaking slag, even under fast cooling, since this type of slag has high basicity and high iron oxides contents, which can act as nuclei for crystallization[5]. The crystalline phases are those typically found in steelmaking slags[6-8]: brownmillerite, larnite, RO phase (solid solution among FeO, MnO, MgO and CaO) and lime. It is also observed an increasing of brownmillerite under slower cooling, since the calcium ferrite, or the calcium ferrite with some iron substituted by aluminum (brownmillerite – $Ca_2(Al,Fe)_2O_5$), is one of the last phases to crystallize, as observed by Gautier et al.[7], increasing the chance of Fe to be substituted by other elements, such as Al. Lime content, determined by XRD (between 3.2 and 4.2 %), can be considered too high in order to prevent soundness.

In the modified slag SS-M1 was observed a higher content of amorphous phase, approximately 25 %, which did not change with the distance from the mold bottom. The tendency of amorphous phase stabilization can be caused by a lower basicity of modified slag[9], B (% CaO/% SiO_2)= 1.4, compared to the steelmaking slag (B = 3.8). Furthermore, it can be observed a significant reduction of RO phase, partially caused by iron oxides reduction, due to the presence of modifying agents, and partially caused by transferring of MgO from RO phase to the merwinite. Besides the MgO stabilization as merwinite, it was observed the elimination of free lime of steelmaking slag.

As shown in table 1, the basicity and Fe^{2+} and Fe^{3+} contents in slag SS-M2 were additionally reduced when compared to slag SS-M1. In addition, the alumina content increased to 11.5 %.

Due to this deeper modification, there was stabilization of the glassy phase, mainly in the region close to the chilled plate, where 91 % of amorphous phase was detected. This behavior is similar to the BF slag. Moreover, high alumina contributes to glassy structure[4]. In addition, RO phase was eliminated and MgO was stabilized in phases with lower CaO/SiO_2 ratio than merwinite ($3CaO.MgO.2SiO_2$), such as monticellite ($CaO.MgO.SiO_2$) and akermanite ($2CaO.MgO.2SiO_2$). Merwinite was dominant in slag SS-M1, which showed higher basicity. Furthermore, gehlenite was formed in slag SS-M2, since this slag has high alumina content, compound which is also present in BF slag cooled slowly, but forming solid solution with akermanite (melilite).

The modified slag SS-M3 is a reproduction of slag SS-M1, however in a larger scale (300 kg). Two samples of this slag (SS-M3) were obtained, one sample was naturally cooled in the same reactor where the modification process took place (SS-M3a) and

the other sample was cooled by steel balls (SS-M3b). The results show no significant differences among crystalline phases formed in slags SS-M1 and SS-M3, since in both cases there was a considerable reduction of RO phase compared to the steelmaking slag without any modification (SS), besides the presence of MgO in stabilized crystalline phases, such as merwinite, akermanite and monticellite. In addition, the amount of amorphous phase is about the same observed in slag SS-M1 and unaffected by cooling conditions as well.

The slag SS-M4 was modified aiming to achieve lower basicity than slag SS-M3 and, at same time, a further reduction of iron oxides. In that case, distinctly from slag SS-M3, it was observed the effect of cooling conditions on the glassy phase formation, since it was achieved 62.8 % of amorphous phase under water quenching (SS-M4c), 11.5 % by steel balls cooling (SS-M4b) and any glassy phase was detected under natural cooling (SS-M4a). As observed in slag SS-M3, MgO was stabilized as monticellite, akermanite and merwinite. The simulation carried out in FactSage™ is consistent with experimental results, predicting even a decreasing of merwinite phase and an increasing of monticellite phase under slowly cooling (natural cooling), behavior also observed in slag SS-M3.

The stabilization of slag SS-M4 is demonstrated by the soundness test (ISO EN 196-3) carried out in a mixture between 75 % of ordinary cement and 25 % of slag SS-M4a or SS-M4b, which did not show any volume soundness under cold or hot water. Furthermore, in the autoclave test (ASTM C 151), the same mixture resulted in an expansion of about 10 times lower (0.04 %) than that determined in a cement sample produced by mixing 75 % of ordinary cement and 25 % of steelmaking slag without any modification (SS) (0.44 %).

The slag SS-M5, modified with the purpose of a partial reduction of iron oxides (Fe^{2+} and Fe^{3+}) and an increasing of Al_2O_3 content, showed 16.8 % of RO phase, value higher than those observed in slags SS-M3 and SS-M4. However, it showed higher amount of larnite than previous slags, which is recognized as a compound with hydraulic activity. In addition, this slag showed MgO stabilized as merwinite and also the presence of gehlenite, phase which must contain most of alumina of the slag.

This slag, such as SS-M4, when used as cement admixture, in proportion of 25 % of slag and 75 % of ordinary cement, did not show expansion under cold or hot water test (soundness test), and showed as well, a low volume soundness (0.07 %) in the autoclave test, demonstrating an appropriate stabilization.

The cement produced with this mixture generated an accumulated heat of 314 J/g in 72 h, while the same mixture based on BF slag resulted in 299 J/g. The compressive

strength in ages 3, 7 and 28 days were 29.9 MPa; 37.7 MPa and 41 MPa, respectively. These values are higher than minimum specified strengths, according to standard NBR 11578 (similar to EN 197-1), which reports 10 MPa, 20 MPa and 32 MPa, in the same ages.

Conclusions

- Only under cooling rates higher than 4 °C/s was possible to achieve more than 95 % of glassy phase in blast furnace slag.
- The crystalline fraction of blast furnace slag showed phases: akermanite, merwinite and melilite, which are typically found in blast furnace slags cooled under slow rates.
- The steelmaking slag was mostly crystalline, even under fast cooling, showing phases typically found in this type of slag: brownmillerite, larnite, RO phase and lime. It also showed an increasing of brownmillerite under slower cooling, since the calcium ferrite or brownmillerite is one of the last phases to crystallize.
- Higher silica and alumina and lower iron oxides in modified slags contributed to the glassy phase formation under fast cooling. Furthermore, the amount of RO phase decreased as consequence of iron oxides reduction as well as MgO stabilization in calcium and magnesium silicates (merwinite, monticellite and arkemanite).
- The stabilization of modified slags was demonstrated by soundness test carried out under cold and hot water, which did not show any expansion, or by low expansion (0.04 and 0.07%) observed in tests carried out in autoclave (ASTM C 151) with cement samples produced by a mixture between 75 % of ordinary cement and 25 % of modified slags.
- The cement produced with this mixture generated an accumulated heat of 314 J/g in 72 h, while the same mixture based on BF slag resulted in 299 J/g. The compressive strength in ages 3, 7 and 28 days were 29.9 MPa; 37.7 MPa and 41 MPa, respectively, values higher than minimum specified in the same ages according to standard NBR 11578.

Acknowledgements

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