Role of Surface Phenomena on Converter Slag Composition

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ABSTRACT: *For beneficiation of converter slag, the role of surface phenomena on slag composition was studied. This work includes some experimental data, which were measured for basic oxygen steel (BOS) slag in Isfahan Steel Plant. All data were collected on site in the plant. The results support the idea that surface activity plays a major role in converter slag formation. It was also a new finding that Mg and S are strongly surface active in melt of converter slag. These findings contribute to better understanding of the slag composition. The ultimate aim of this work is to develop a novel practice, "molten flotation" for separating valuable constituents of converter slag.*

KEY WORDS: *Converter slag, Surface activity, Molten flotation.*

INTRODUCTION

BOS Slag

The basic oxygen steel making (BOS) process manufactures a substantial amount of the total steel produced in the world. Different steel producers adopt practices that create very different slag paths before reaching the "end-point" slag composition. Therefore, slags encountered in BOS can vary greatly and depend on the nature of the blowing (top, bottom or combined) and by the method, form, and timing of lime and dolomite addition. As those reported by van Hoorn et al [1] and Normanton [2] BOS slags contain appreciable amounts of the following oxides:

CaO, SiO_2, FeO, Fe_2O_3, MnO, and MgO and minor amounts of P_2O_5, Al_2O_3, K_2O and Cr_2O_3.

The Isfahan Steel Plant (ISP), which is located in the central part of Iran, currently produces 130 kgs slags per ton of crude steel in addition to about 2.5×10^6 tons of tack piles of BOS slag. A typical analysis of BOS slag in Isfahan steel plant has been shown in table1 [3].

V_2O_5, TiO_2 and MnO are valuable components of the converter slag, because the percentages of them in the slag are comparable to those of the ores currently exploited. Although the utilization of slags as a resource has progressed, the quantity generated is high. Therefore, the finding new methods of utilization is vital, as environmental protection of air, water and land is inevitable. We here by report a new approach towards overcoming the problem i.e., the use of molten flotation for fractionation of converter slag.

Molten flotation

Some separation methods depend on surface activity anong which the most popular is flotation. Foaming is a key parameter in the flotation process. Recently, S.M.Jung and R.J.Fruehan [4] studied the foaming characteristics of BOF slags. Schulze [5] has described various aspects of physico-chemical elementary processing in flotation. Although flotation, foam and bubble fractionations are currently used in many industries, all of them are working at ambient

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temperature. Thus a novel practice would be if hot or "molten flotation" can be employed to concentrate or dilute in a mixture like converter slag. To apply this novel technique, it is necessary to show that surface activity plays a role in slag formation. Thus the research was focussed on beneficiation of converter slag by molten flotation technique.

Theoretical background

A surface-active solute can only be called so with respect to a particular solvent. The surface activity of a solute is not primarily due to its amphipathic molecular structure but to its weak interaction with the solvent. Decreasing the surface tension is a simple indicator for surface - active agents. A tendency toward phase separation is a general indicator of surface activity. Not surprisingly, therefore, the surface activity displayed by solutions or mixtures can be related to the phase diagram. As slag is the product of a propensity toward phase change in molten iron, and has the general behaviour of surface-active materials.

Bodnar et al [6] determined the variation of surface tension brought about by alumina additions to two parents slags (Fe_xO-SiO_2), which contained 32% and 35% SiO_2, respectively. In both instances, an increase in alumina produced an increase in surface tension.

Equilibrium data given by Ban-Ya and Shim [7] for melts at 1400 ^oC in contact with Fe show that Fe^{3+} content decreases at higher concentrations of TiO_2. Larson and Chipman [8] observed similar behaviour for melts at 1550 ^oC. Since increase in TiO_2 content leads to a decrease in surface tension coupled which a concomitant decrease in the Fe^{3+} concentration; TiO_2 must be surface active in melts. Recently, S.M.Jung and R.J. Fruehan [4] showed that as the content of TiO_2 in BOF slag increases, the experimentally measured foam index increases. Foam index is defined as V_f/Q_g where V_f is the volume of the foam at steady state and Q_g is the gas flow rate. This Finding emphasise that TiO_2 must be a surfactant that it is able to decreases the surface tension of BOF slag.

Din-Fen et al. [9] showed that as the P_2O_5 content increases, the surface tension (Fe_xO-P_2O_5) melts is progressively reduced to about 330 mN/m, which is lower than any value found in the FeO-Fe_2O_3 system. This, coupled with the findings of Tromel and Schwerdtfeger [11], that Fe_2O_3 content decreases with increased amounts of P_2O_5 in the melt, indicates that P_2O_5 is strongly surface active in Fe_xO. They concluded that P_2O_5 was more surfaces active in Fe_xO than either Fe_2O_3 or SiO_2. The results given by Mills and keene [10] also show marked decrease in surface tension of the melt as the P_2O_5 level is increased.

As flotation process depends on surface and interfacial tensions, it is important to demonstrate that surface activity plays a role in converter slag formation in order to have molten flotation. This is the main concept in the following experimental design.

EXPERIMENTAL

Materials

Converter slag, a by-product of Isfahan steel plant (ISP), was used in this research.

Analytical Methods

All the experimental work and analysis in this project were carried out in the central laboratory of Isfahan Steel Plant. The concentrations were measured by XRF 8410 made by ARL Swiss. By exciting K and L levels, the intensity as KCPS(kilo count per second)is measured and by using a calibration curve, the intensity can be converted into concentration.

All measurements were repeated and the mean values were reported. The acceptable ratio of standard deviation to mean value was less than 6%.

Techniques and Results

Four series of tests were carried out to investigate the effect of surface activity on slag path (composition). They were:

- A sample was collected at the start of tapping of slag and another sample was collected in the final stage of tapping. Columns 1 and 2 in Table 1 show the composition of slag in the start and final stages of tapping of slag into ladle in batch no.350481.
- The slag in the ladle was allowed to become cold naturally, and then samples collected from various heights of ladle. Table 2 shows the analysis of samples that was collected at the top, middle and bottom of ladle.
- 500 kgs chipped limestone were loaded in the normal ladle before tapping of slag into the ladle. We

Table 1: Slag composition at the start (1) and final (2) stages of tapping

Component (%)	1	2
SiO_2	7.00	7.02
T Fe	17.15	
FeO	16.00	15.66
Al_2O_3	0.77	0.71
CaO	56.25	55.86
MgO	1.36	1.61
MnO	4.80	4.86
P_2O_5	2.50	2.20
TiO_2	1.60	1.40
V_2O_5	2.70	2.68
Cr_2O_3	0.03	0.05

hoped the produced CO_2 by thermal dissociation of limestone could enhance flotation in molten slag. After cooling, various samples of slag were collected and analysed (see table 3).

– A modified ladle, with facility for gas injection from the bottom of the wall, was constructed. Nitrogen gas with high pressure was injected into the molten slag during loading the ladle. For better comparison, half of slag discharged into modified ladle with nitrogen injection (set A) and another half of slag discharged into normal ladle (set B). After cooling, various samples were collected both from the modified ladle (A1, A2, A3, A4) and the normal ladle (B1, B2, B3, B4) of the same batch (no.160628). Then the sample compositions were determined (see table 4).

naturally, and then samples collected from various heights of ladle. Table 2 shows the analysis of samples that was collected at the top, middle and bottom of ladle.

RESULTS AND DISCUSSION

Table 1 shows the slag composition at the start and final stages of tapping of slag into ladle. Although there is a little difference between two stages, it is difficult to judge that the difference is due to surface activity or experimental error.

Table 2 shows composition of the slag in various heights of ladle, i.e., top, middle and bottom. Here compositions are measured in intensities. It seems the difference is not due to experimental errors. There is a depletion of Fe on top of sample but P, S, Si and Mn are concentrated at the top of sample. Distribution of Al, Mg, Ti, V and Cr_2O_3 are not normal. K, Na, Pb and Zn seem unaffected.

Table 3 shows analysis of the various samples of slag in the absence or presence of CO_2 which produced by thermal dissociation of chipped $CaCO_3$.Cheking the composition of Ca in different samples reveals that there is few difference in composition of the slag in different point of ladle. This is due to the fact that the quantity of used lime is small in comparison to mass of slag in a ladle.

To expound the results, it is better to see how the lime has affected the distribution of components at the top and the bottom of ladle. This has been done by dividing column 1 (composition at the top) to 2 (composition at the top when lime has been used) and 3 (composition at the bottom) to 4(composition at the bottom when lime has been used) as shown at columns T and L of table 5 respectively.

It is observed that Mg, S, Ti, V and K have the most changes at the top of ladle whereas Mg, Mn, P and S have most changes at the bottom.

To know the extent of promotion of surface activity produced by lime, a new parameter, enhancement factor, *E,* is defined as ratio of composition of the top to of the bottom in presence of lime divided by ratio of composition of the top to of the bottom in absence of lime.

$$E = \frac{sample_2 \,/\, sample_4}{sample_1 \,/\, sample_3} = \frac{L}{T}$$

If the lime has no influence on surface activity, then E must be about unity.

The last column (E) of table 5 shows that most changes have occurred for Mg, S, Ti but changes for P, Mn, V, K, Fe are noticeable.

Real molten flotation was practised by constructing a modified ladle with facility for nitrogen injection. Table 4 includes all data have been obtained in this series of tests.

Columns A1 and B1 show compositions of components at top of ladle with and without nitrogen injection respectively. The differences are normally very low. This indicates that the pressure of injected nitrogen gas was not enough to overcome the high mass of falling slag. Columns A4 and B4 show analyses of the slag at

Table 2: Analysis of samples collected in various height of ladle (as intensities)

Component	Top	Middle	Bottom
Al	1.4705	1.2757	1.3446
Ca	555.7723	587.2995	557.3386
Fe	195.0194	267.4147	270.9527
K	0.2113	0.2295	0.2984
Mg	8.2907	4.7530	6.4535
Na	1.2565	1.2211	1.1974
P	47.8752	41.4386	39.5317
Pb	0.4569	0.4381	0.4394
S	1.5346	1.3255	1.3271
Si	51.0362	38.6626	37.9504
Ti	8.5412	5.1168	6.4846
V	12.9153	8.0660	9.9706
Zn	0.1693	0.1594	0.1672
Mn	54.3752	44.2591	44.1105
Cr_2O_3	1.0014	0.6415	0.7808

Table 3: Analysis of various samples of slag (as intensities) in presence of chipped $CaCO_3$

Component	Sample 1 top of ladle	Sample 2 top of ladle (with lime)	Sample 3 bottom of ladle	Sample 4 bottom of ladle (with lime)	Sample 5 middle of ladle
Al	1.1233	1.1759	1.2791	1.2339	1.4235
Ca	591.6661	582.9243	562.7343	583.1889	545.6871
Fe	245.1381	266.3765	252.4750	232.8224	273.9597
K	0.1502	0.1685	0.1559	0.1474	0.1652
Mg	5.9900	4.6718	4.7803	6.1245	5.5883
Na	1.1593	1.1631	1.1766	1.1631	1.1730
P	38.6965	44.5544	48.2013	42.3353	47.2496
Pb	0.4350	0.4375	0.4380	0.4400	0.4357
S	1.3800	1.7183	1.7408	1.4659	1.6437
Si	34.2515	32.6614	38.1808	37.8562	40.9732
Ti	5.7023	6.5652	6.9514	6.4511	7.0239
V	9.7100	10.9052	11.6078	10.9081	11.9167
Zn	0.1552	0.1564	0.1571	0.1609	0.1543
Mn	40.0461	37.4399	37.7252	42.0231	38.1248
Cr_2O_3	0.7693	0.8062	0.8377	0.8186	0.9671

bottom of ladle with and without nitrogen injection respectively. Results illustrate that there are meaningful differences for SiO_2, TiO_2 and K_2O. The third column in table 6 shows the extension of promotion, E, which is defined in this case, as below:

$$E = \frac{A_1 / A_4}{B_1 / B_4}$$

$$E = \frac{\text{ratio of composition of the top to of the bottom in presence of nitrogen}}{\text{ratio of composition of the top to of the bottom in absence of nitrogen}}$$

Table 4: Analysis of various samples collected at different depth in modified (with nitrogen injection, A) and normal ladle (without nitrogen injection, B).

Component	A1	B1	A2	B2	A3	B3	A4	B4
	Top		10-15 cm depth		middle		bottom	
SiO_2	10.6	10.35	7.82	9.7	12.22	9.4	12.4	6.66
CaO	49.4	49.26	55.62	48.9	49.73	46.7	48.8	52.17
MgO	1.66	1.58	1.53	1.6	1.54	1.67	1.7	1.84
Al_2O_3	1.2	1.12	1.15	1.26	1.27	1.3	1.21	1.22
TiO_2	0.64	0.61	0.74	0.56	0.63	1.4	0.68	1.33
V_2O_5	2.86	2.90	2.31	3.00	2.75	3.5	2.76	2.56
P_2O_5	2.85	2.88	3.00	2.61	3.4	3.6	3.35	2.70
K_2O	0.005	0.006	0.003	0.003	0.005	0.01	0.003	0.009
Na_2O	0.029	0.026	0.021	0.023	0.025	0.032	0.015	0.026
T Fe	18.48	18.58	16.91	20.8	17.45	20.75	18.15	19.19
FeO	0.34	0.34	12.94	16.83	11.56	13.37	15.97	18.64
MnO	4.28	4.31	4.76	4.4	4.19	4.07	4.56	5.36
Cr_2O_3	0.041	0.039	0.037	0.04	0.04	0.045	0.043	0.047

Table 5: Effect of chipped lime on enhancement of surface activity

Component	A	B	E=B/A
Al	0.955	1.037	1.086
Ca	1.015	0.965	0.951
Fe	0.920	1.084	1.178
K	0.890	1.058	1.189
Mg	1.280	0.780	0.609
Na	0.997	1.012	1.015
P	0.868	1.139	1.312
Pb	0.990	0.995	1.005
S	0.800	1.186	1.483
Si	1.049	1.010	0.963
Ti	0.869	1.080	1.423
V	0.890	1.060	1.191
Zn	0.992	0.976	0.984
Mn	1.070	0.898	0.839
Cr_2O_3	0.954	1.023	1.072

It is seen that extension of promotion for SiO_2, TiO_2, K_2O, Na_2O and P_2O_5 is enough far away unity so that the effect of flotation of components can not be ignored.

Flotation of Na_2O and K_2O may be assumed for low density but for heavy components such as SiO_2, TiO_2 and P_2O_5 are surely due to surface phenomena. These findings support the surface activity of those components that have been reported in technical literature [11].

CONCLUSION

The results of this work support the idea that surface phenomena play a major role in converter slag formation. The results endorse the findings of Ban-Ya and Shim [7], Larson and Chipman [8] that TiO_2 must be surface active in the converter melt.

The findings of Din-Fen et al. [9] and Mills and keene[10] coupled with those of Tromel and Schwerdtfger [11] are in agreement with results of this work that P_2O_5 is strongly surface active in the converter slag. Tables 5 and 6 show that the extension of promotion for Al and Al_2O_3 is near to one. It means that alumina is not a surface-active agent and this result is consistent to finding of Bodnar et al.[6] that an increase in alumina produced an increase in surface tension.

Table 6: Effect of nitrogen injection on slag composition

Component	A-1/B-1	A-4/B-4	E
SiO_2	1.020	1.860	0.548
CaO	1.000	0.935	1.070
MgO	1.050	0.924	1.136
Al_2O_3	1.070	0.992	1.079
TiO_2	1.050	0.511	2.055
V_2O_5	0.986	1.040	0.948
P_2O_5	0.990	1.240	0.798
K_2O	0.833	0.330	2.524
Na_2O	1.120	0.577	1.941
T Fe	0.995	0.950	1.047
FeO	1.000	0.857	1.167
MnO	0.990	0.850	1.165
Cr_2O_3	1.050	0.915	1.148

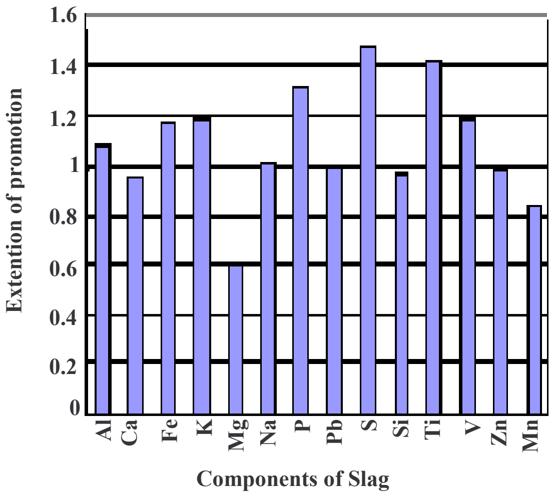

Fig. 1: Effect of Chipped lime on promotion of surface activity of components in slag.

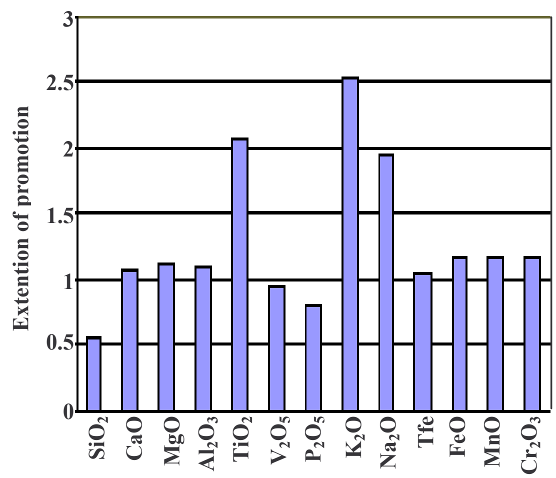

Fig. 2: Effect of nitrogen injection on promotion of surface activity of components in slag.

It is obvious that much more research works should be done to study different aspects of this novel "Moiten flotation" process. In flotation, the production of suitable foam is a prime objective. Thus a knowledge of the factors affecting the surface phenomena would be of considerable value. The kinetics of the flotation process is influenced by different factors. The effect of injected nitrogen pressure and the used other gases such as oxygen or air is among the chief factors should be studied. There are obviously many possible combinations of parameters that can be studied. As all experimental works should be carried out on site, the required expenditures for providing enough data arenaturally very expensive.

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