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Spectroscopic analysis of slags—preliminary observations

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Slags and fluxes used in metallurgical processes are typically made up of oxides (especially silicates), with additions of fluoride and carbonaceous matter. Despite the efforts made towards understanding the role of slags in various processes, little information is available on the structure of these slags. Tools such as X-ray diffraction, spectroscopy, and electron microscopy could be used for this purpose. This paper is based on an ongoing spectroscopic and structural investigation of slags and related materials.

Spectroscopic studies of various commercial slags (predominantly ferrous), ores, glass and related materials, covering a wide range of compositions, have been carried out to understand the structure. The infrared spectra were recorded, predominantly, using FTIR spectrometer (Bruker IFS 66U) spanning 4000 to 100 cm^{-1} using the KBr pellet method. The resolution was typically 4 cm^{-1}. The spectral outputs have been compiled in terms of bands present (corresponding to different bonds) and then compared with the typical bands expected for such bonds. Efforts are in progress to identify the trends with respect to the chemical composition—for example, the effects of SiO_2, Al_2O_3, and non-bridging oxygens.

Data obtained so far indicate some trends such as (i) a shift in the Si-O band (969 to 1099 cm^{-1}) towards a higher wave number with increasing silica content (almost 2 to 92 weight percentage) and (ii) further strong shifts as a function of the alumina content. These are being further investigated structurally and in terms of chemical composition/parameters.

Keywords: slags, silicates, structure, spectroscopic analysis, shifting of bands

Introduction

Slags play an important role in metallurgical processes and are crucial for smelting, refining and casting. Slags and fluxes used in metallurgical processes are typically made up of oxides (especially silicates), with additions of fluoride and carbonaceous matter. The quality as well as productivity of the processes is strongly influenced by the design, selection and performance of fluxes and slags. Behaviour of engineering materials is typically derived from the chemical composition, structure and prior processing. Even though slags are crucial in the said processes, limited efforts have been made toward understanding the structure of slags. Despite the efforts made to understand the role of slags in various processes, little information is available on the structure of these slags. Tools such as X-ray diffraction, spectroscopy, electron microscopy could be used for this purpose. This paper is based on an ongoing spectroscopic and structural investigation of slags and related materials.

Structure of slags

Slags are oxide based materials and the structure and bonding present may be compared with those of oxide ceramics, including glasses. In general, the slags may be treated as silicate glasses and the structure and properties of slags could be interpreted in terms of the degree of polymerization within the silicate network[1]. Theoretical studies are in progress correlating the properties of slags with the structural parameters[2]. Further, it is necessary to obtain data on the structure of slags with tools such as diffraction, spectroscopy and microscopy. The need has been recognized as indicated by published research in spectroscopy, petrology, and related areas[3–9]. Such analysis will also be helpful in understanding slag-like waste materials generated in steel plant operations as well as in formulating ideas about utilization of metallurgical wastes[10]. However, much of the spectroscopic analyses have been confined to synthetic slags produced in the laboratory rather than commercial /industrial slags.

Slag sampling

Industrial slag samples were obtained from metallurgical plants, representing iron ore, iron making slags, steel making slags, continuous casting mould powders, and mill scale. The chemical composition of the samples has been determined by manual procedures such as wet analysis or instrumental procedures such as XRF and ICP. Subsequently, characterization has been done for understanding the structure of slags. Glass was taken for the studies owing to its high silica content, even though it does not play any role in the form of slag. Rice husk ash was considered for its high silica content and also because some products derived from RHA are used during metallurgical processes. The nature of samples taken has been indicated in Table I.

Experimental techniques

X-ray diffraction, chemical analysis and spectroscopy were carried out at other laboratories such as the Indian Institute of Science, Indian Institute of Technology, Central Electro Chemical Research Institute and the Central Glass and

Ceramic Research Institute. The X-ray powder diffraction patterns (as indicated in Table II—for twelve samples) were recorded for slag samples using Philips Analytical X-Ray B.V. The K_{α} Cu radiation (1.54056cm^{-1}) with tube voltage of 40 kV and 30 mA was used as the source. Crystal structure identification was made by comparing the experimentally measured d-values with those cited in the literature. The infrared spectra (as indicated in Table III) of the slags were recorded on an FTIR spectrometer (model: Bruker's IFS 66U) for 4000 to 400 cm^{-1} using KBr pellets method. The resolution used for the measurement was 4 cm^{-1}. The chemical analysis of the sample was done locally by wet analysis and externally by XRF (as in Table IV, for three samples), and ICP. The analysis/characterization for the above and similar samples are in progress, and the preliminary observations are reported in this paper. Figures 1–4 are provided as illustrations of the typical instrumental outputs for characterization by diffraction and spectroscopy.

Table I
Nature of samples taken for structural studies

Sample number	Nature of sample
1, 2	Iron ore
4, 5	Iron-making slag
7, 8, 9	Steel-making slag
11, 12, 13	Refining slag
6, 10	Continuous casting slag
3	Plate glass
14	Rice husk ash

Trends observed in XRD and IR of various samples

- Peaks for iron oxide and alumina were observed in both iron ore samples (1, 2), but peaks for silica is seen only in the case of sample no. 2. In FTIR spectra, the alumina and silica bands are located at the same position, but there is a shift towards a higher wavenumber in the iron oxide band for sample no. 2.
- Silica peaks were present in the diffraction patterns of the iron making slag samples (4, 5), but iron oxide peaks were absent. Peaks corresponding to alumina, calcium carbonate and magnesium oxide were also seen in sample no. 4. The presence of alumina, silica and calcium carbonate could also be confirmed in the corresponding FTIR spectra.
- The XRD pattern for one steelmaking slag (no. 8) indicated an amorphous nature, whereas peaks for a few oxides could be seen in another steelmaking slag (no. 9). Bands corresponding to silica and alumina were observed in the IR spectra of all the three steelmaking slag samples (7, 8, 9). Bands for magnesium oxide, calcium oxide and calcium carbonate were also observed in the three samples.
- The diffraction peak for iron oxide was noticed in only one of the three refining slags (no. 11), whereas, spodumene peaks were observed in two samples (nos. 11 and 13). Peaks for silica, calcium carbonate, magnesium oxide, fluorspar and fluroapatite were seen in sample no. 12 alone. The FTIR spectra of all the refining slag samples (nos. 11, 12, 13) contained the

Table II
X-ray diffraction data for samples
(d values for the cited compounds, if seen, are listed for various samples)

Sl. no.	Ferric oxide	Silica	Magnesium oxide	Calcite	Fluorspar	Alumina	Spinel	Others
1	2.70 2.51 1.69 1.48	-	-	-	-	1.84 2.20 1.45	-	-
2	2.70 2.52 1.69 1.48	3.69 1.36	-	-	-	1.84 2.21 1.45	-	-
4	-	3.73 1.77	1.49	-	-	2.63	-	-
5	-	4.69 3.37 1.79	-		-	-	-	-
6	Only one peak was observed corresponding to silica							
8	No peak							
9	2.8 2.45 1.49	4.33 3.05	2.13 1.49	-	-	2.2 1.93	-	2.63 1.55 Spodumene
10	2.80 2.45 1.49	-	-	-	3.15 1.93 1.64	2.20 1.93	2.48 2.16 1.45	2.7 1.53 Spodumene
11	2.69 2.4 1.69 1.49	-	-	3.028 2.2 2.10	-	-	2.43 11 1.44	2.77 1.55 podumene
12	-	3.73 1.77	1.49	-	3.13 1.94 1.65	2.56 2.02 1.6	2.45 2.12 1.49	2.82 2.76 2.703 Fluroapatite
13	-	-	-		-	2.67 2.05	-	2.81 1.56 Spodumene
14	-	4.43 4.07 3.36	-	-	-	-	-	-

Table III
FTIR data for samples
(Peak values are listed for the cited compounds, if seen, in the spectra)

Sl.No.	SiO_2	CaO	MgO	$CaCO_3$	Al_2O_3	Fe_2O_3
1	1032	-	-	-	469, 544	1096
2	1033	-	-	-	466, 539	1033
3	1018	466	466	-	778	-
4	1019	417, 519	593, 432	1419, 874	607	-
5	1018	-	-	1427	674	-
6	1015	409		1466	535	-
7	1013		723		759, 687	
8	1020	389	-		593	-
9	1018			1466, 839	536	-
10	1038			1466	475	-
11	969		459		792	-
12	1020	490		1467	517	-
13	1017	409			912, 521	-
14	1099	466	466	-	668	-

Table IV
Chemical analysis data (by XRF method)

Sl. no.	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O	F	TiO_2	LOI
2	2.33	0.37	0.27	93.20	0.66	0.48	0.80	trace	trace	1.72
5	33.6	35.27	11.81	1.70	15.5	1.06	0.85	0.05	-	trace
8	24.45	50.48	2.32	4.02	8.43	1.07	0.59	-	0.81	

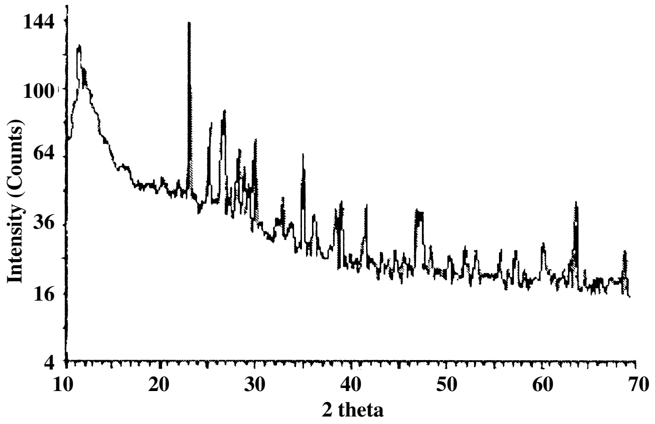

Figure 1. XRD pattern of sample no. 9

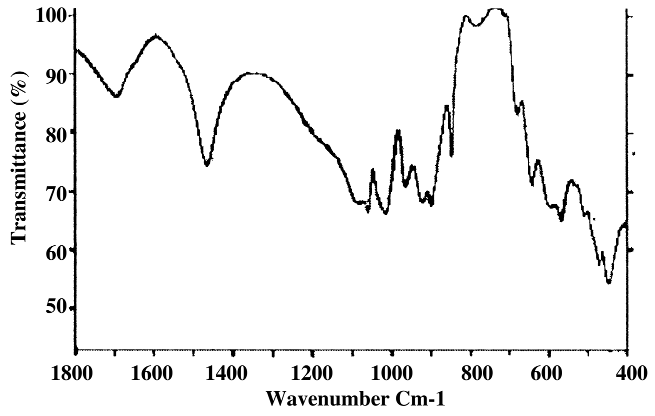

Figure 2. FTIR spectum of sample no. 12

silica and alumina bands. The silica band of sample no. 11 is in the lower wavenumber side and that of the alumina band is in the higher side for sample nos. 12, and 13.

- Sample no. 10 is a fresh mould powder, whereas, sample no. 6 is from the continuous casting mould (melted). Peaks for silica, fluorspar, alumina, spodumene and spinel could be seen in the XRD pattern for sample no. 10, whereas only the peak for silica could be seen in the mould slag sample (no. 6). The IR spectra for the two continuous casting slag samples had some similarities, but there is a wide difference in the silica band values.
- Silica peaks alone were observed in the XRD pattern of the rice husk ash sample (no. 14). A strong band for silica, at a relatively high wavenumber, was observed in the corresponding FTIR spectra.
- Bands for silica, calcium oxide, magnesium oxide and alumina were observed in the spectra for the plate glass sample (no. 3) and the silica band had a relatively low value.

Preliminary inferences

- Samples for which diffractograms were obtained indicated different crystalline peaks, except one steel making slag (no. 8). The spectra indicated bands, in general, along the expected lines (known compounds), except for the bands corresponding to calcium carbonate. The spectra need to be analysed in more detail, given the possible overlapping of bands from different compounds. The bands corresponding to certain critical compounds, such as fluorides, could not be observed within the experimental settings (FTIR) and are yet to be accounted for. The investigation is being continued.

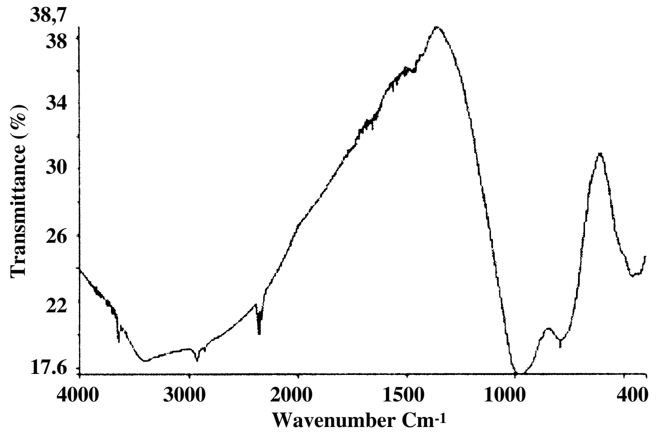

Figure 3. FTIR spectum of sample no. 10

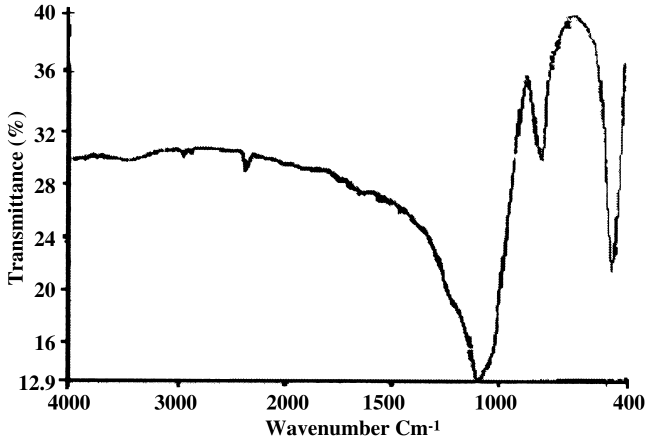

Figure 4. FTIR spectum of sample no. 14

- The presence of) compounds indicated by the diffractograms have similarities as well as differences with the bands indicated by the spectra. This needs to be analysed in more detail.
- The bands corresponding to silica from the various samples were compared in terms of the chemical composition. Indicative values for slag compositions were considered as the XRF analysis is yet to be completed. The samples were arranged along increasing silica content (iron ore, refining slag, steelmaking slag, iron-making slag, casting slag, plate glass and rice husk ash) and the silica peak values were plotted as a function of the silica content (Figure 5). The silica band occurs at 1 099 cm^{-1} for the rice husk ash sample which has high silica content (about 92%).
- Further variations were found in the alumina content (Figure 6). Alumina and silica both influence the extent of polymerization taking place in the slag sample. Further investigation is required to understand the combined effects of alumina and silica on the slag structure (as indicated by the IR spectra).

Concluding remarks

A wide range of slags and related materials has been taken up for structural analysis by diffraction and spectroscopy. The presence of various compounds indicated by the diffractograms and the spectra are along the expected lines. However, the presence of calcium carbonate has been seen in many samples, in contrast to the expectations. Further, information could not be generated on crucial compounds such as fluorides and sulphides.

The bands for silica, in the spectra, are found to increase in proportion to the silica content of these materials. This could be due to the variations in silicate polymerization caused by differences in silica content and non-bridging oxygens. The combined effects of silica and alumina are under investigation. Theoretical studies are in progress relating the extent of polymerization to the shifting of silica bands.

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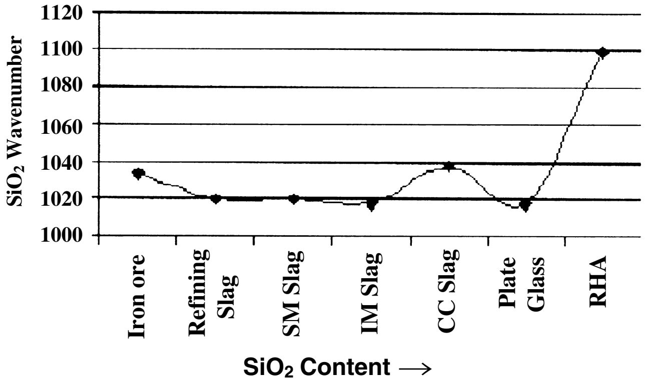

Figure 5. Shift in SiO_2 peaks, in diffetent slags, of (typical) SiO_2 content

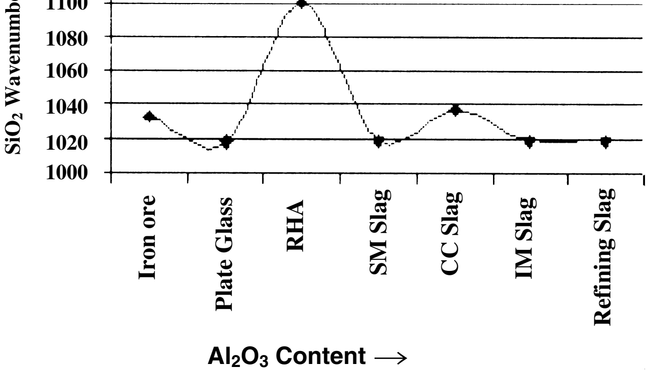

Figure 6. Shift in SiO_2 peaks, in diffetent slags, of (typical) Al_2O_3 content

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