Hyperfine Interact
DOI 10.1007/s10751-012-0699-z

Phase chemical composition of slag from a direct nickel flash furnace and associated slag cleaning furnace

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Abstract During the recovery of base metals from the Bushveld Igneous Complex ores, South Africa, a two-stage process is used to ensure complete recovery of nickel from the ore. A nickel flash smelting furnace is initially used to obtain the valuable metal but the loss of nickel in the slag amounts to about 4 % and thus an electric slag-cleaning furnace has to be subsequently used to reduce the loss of the valuable metal to less than 0.5 % nickel oxide in the slag. The Fe^{2+}/Fe^{3+} ratio and mineralogy in the two different furnaces differ and can be used as a tool to determine the efficiency of the nickel recovered in the two-stage process. By means of XRD, SEM/EDS and Mössbauer spectroscopy the Fe^{2+}/Fe^{3+} ratio and the amount of magnetite was determined in each furnace, which was then used as an indicator of the effectiveness of the whole process.

Keywords Slag · Nickel smelting · Magnetite

1 Introduction

Most of South Africa's nickel is produced as a by-product of platinum mining activities on the Bushveld Igneous Complex. South Africa is about the tenth largest producer of nickel in the world with a production of about 42,000 metric tonnes in 2011 [1]. Slag generated in the direct nickel flash smelting process (DON process) contains approximately 4 % dissolved nickel oxide and has a relatively high ratio of Fe^{2+}/Fe^{3+} because of the oxidizing conditions applied during smelting [2]. To recover

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Published online: 14 November 2012

Table 1 Phase-chemical composition (wt%) of the slag samples determined by powder XRD

	Flash furnace				Electric furnace			
Sample	3	5	7	8	1	2	3	6
Olivine	84	55	89	85	96	99	97	98
Magnetite	16	23	11	15	4	1	3	2
Fayalite	0	23	0	0	0	0	0	0

the nickel oxide from the slag it is transferred to an electric slag-cleaning furnace where NiO is reduced from the slag with a suitable reductant such as coke. Slag from the slag-cleaning furnace contains less than 0.5 % NiO and has a much lower ratio of Fe^{2+}/Fe^{3+} [2]. Because of the relatively high ratio of Fe^{2+}/Fe^{3+} in the flash furnace slag it crystallizes a significant amount of magnetite during cooling. Slag from the electric slag cleaning furnace, on the other hand, hardly crystallizes any magnetite during cooling. The Fe^{2+}/Fe^{3+} ratio and the amount of magnetite, determined with the aid of XRD, SEM and Mössbauer spectroscopy, occurring in the two different furnaces was used as an indicator of the effectiveness of the nickel recovery process.

2 Experimental

2.1 Samples and analytical methods

Water-quenched samples of slag from the DON flash furnace and associated electric slag-cleaning furnace were collected for chemical analysis. Mössbauer spectroscopy, power X-ray diffraction and phase chemical analysis by Scanning Electron Microscope and Energy Dispersive Spectroscopy (SEM/EDS) were performed on the samples. The primary objective of the phase-chemical analysis was to identify the phases in the slag and to establish the dominant mechanism through which pay metals report to the slag. Mössbauer spectroscopy was undertaken to determine the speciation of iron, evaluate the proportion of magnetite and measure the ratio of Fe^{2+} to Fe^{3+} in the slag.

All XRD analyses were conducted with a Panalytical X'pert MPD diffractometer, equipped with a Panalytical X'celerator detector. SEM analyses were performed on the slag samples, using a Jeol, Model 733 with an EDS system from Thermo Noran. All Mössbauer spectra were obtained with the aid of a Halder Mössbauer spectrometer, capable of operating in conventional constant acceleration mode using a proportional counter filled with Xe-gas to 2 atm. The samples were placed between Perspex plates and then irradiated with γ-rays from a 50 mCi $^{57}Co(Rh)$ radioactive source to obtain a room temperature Mössbauer spectrum. The Mössbauer spectrometer was calibrated using α -Fe as the reference.

3 Results

3.1 Powder x-ray diffraction

The phase-chemical composition of the flash furnace and electric furnace slag samples, as determined by powder X-ray diffraction is reported in Table 1. As expected, the flash furnace slag containend much more magnetite than what was

Table 2 Distribution of iron between olivine, glass and magnetite (wt%)

	Flash furnace				Electric furnace			
Sample	3	5	7	8	1	2	4	6
Olivine (Fe^{2+})	49 ± 3	44 ± 3	77 ± 3	75 ± 3	70 ± 3	70 ± 3	70 ± 3	70 ± 3
Glass (Fe^{2+})	10 ± 3	1 ± 1	3 ± 1	4 ± 1	30 ± 10	30 ± 10	30 ± 10	30 ± 10
Magnetite ($Fe^{2+}/Fe^{3+} = 1:2$)	41 ± 3	56 ± 3	20 ± 3	21 ± 2	<dl[a]	<dl	<dl	<dl
Fe^{2+}/Fe^{3+} ratio	2.7	1.7	6.5	6.1	~ 0.02	~ 0.02	~ 0.02	~ 0.02

[a] dl–detection limit

Table 3 Bulk chemical analysis of the flash- and electric furnace slag samples

	Flash furnace				Electric furnace			
Sample	3	5	7	8	1	2	4	6
SiO_2	33.3	24.9	33.4	34.2	33.9	37.4	35.6	34.5
Al_2O_3	1.9	1.4	1.6	1.9	2.0	2.0	2.1	2.0
CaO	1.9	1.8	1.6	1.9	2.0	1.9	2.0	2.0
MgO	9.5	11.5	9.8	9.4	11.8	11.0	10.9	11.5
Fe	36.0	39.7	36.9	35.6	37.7	36.2	37.0	37.0
Cr_2O_3	0.3	0.3	0.34	0.32	0.4	0.4	0.4	0.4
Co	0.1	0.2	0.11	0.13	0.0	<0.02	0.0	<0.02
Cu	0.6	1.3	0.4	0.61	0.2	0.1	0.2	0.2
Ni	2.5	4.3	1.3	2.5	0.2	0.1	0.4	0.2
S	0.1	0.0	0.2	0.1	0.2	0.2	0.1	0.2
Total	86.2	85.4	85.7	86.7	88.4	89.2	88.7	88.1

found for the electric furnace slag. The average distribution of iron (measured by Mössbauer spectroscopy) between olivine (all iron as Fe^{2+}), glass (all iron as Fe^{2+}) and magnetite ($Fe^{2+}/Fe^{3+} = 1:2$) for the flash-and-electric furnace samples is given in Table 2. The Fe^{2+}/Fe^{3+} ratio of the flash furnace slag samples ranges between 1.7 and 6.5, with an average of 4.3. The concentration of magnetite in the electric furnace slag was below the detection limit of Mössbauer spectroscopy (about 3 %, as indicated by the standard deviation)

3.2 Bulk composition

The bulk chemical compositions of the flash- and electric-furnace slag samples are reported in Table 3. From the table it is clear that the flash furnace slag contains much more nickel (as oxide) than the electric furnace slag.

3.3 Mössbauer spectroscopy

Olivine (fayalite) and magnetite were readily identified in the spectra of the slag samples (Table 4). In addition, an amorphous, Fe^{2+}-bearing glass phase was also present in the samples. The magnetite content of the electric furnace slag samples (1, 2, 4 and 6) was below the detection limit confirming that conditions in the electric furnace are much more reducing than in the flash furnace. All the Mössbauer parameters of species observed in the present investigation are consistent with those found in literature [3].

Table 4 Mössbauer parameters of Fe-components in the flash- and electric furnace slag samples

Sample	Component	IS mms^{-1} ($\pm$0.02)	QS mms^{-1} ($\pm$0.02)	H Tesla ($\pm$0.3)	Relative intensity (%)
1	Doublet 1 Fayalite	1.14	2.88		70 ± 3
	Doublet 2 Fe^{2+}	0.91	1.63		30 ± 10
2	Doublet 1 Fayalite	1.15	2.84		70 ± 3
	Doublet 2 Fe^{2+}	1.19	1.70		30 ± 10
3	Doublet 1 Fayalite	1.14	2.88		49 ± 3
	Doublet 2 Fe^{2+}	0.98	1.63		10 ± 3
	Sextet 1 Magnetite	0.40	−0.10	47.0	41 ± 3
4	Doublet 1 Fayalite	1.16	2.88		70 ± 3
	Doublet 2 Fe^{2+}	0.98	1.75		30 ± 10
5	Doublet 1 Fayalite	1.13	2.85		44 ± 3
	Doublet 2 Fe^{2+}	1.00	1.68		1 ± 1?
	Sextet 1 Magnetite	0.29	0.03	48.3	40 ± 2
	Sextet 2 Magnetite	0.65	−0.06	44.7	16 ± 3
6	Doublet 1 Fayalite	1.15	2.85		70 ± 3
	Doublet 2 Fe^{2+}	0.99	1.75		30 ± 10
7	Doublet 1 Fayalite	1.13	2.85		77 ± 3
	Doublet 2 Fe^{2+}	0.97	1.44		3 ± 1
	Sextet 1 Magnetite	0.26	0.10	48.1	14 ± 2
	Sextet 2 Magnetite	0.69	−0.14	44.7	6 ± 3
8	Doublet 1 Fayalite	1.13	2.85		75 ± 3
	Doublet 2 Fe^{2+}	0.94	1.52		4 ± 1
	Sextet 1 Magnetite	0.28	0.12	48.1	12 ± 2
	Sextet 2 Magnetite	0.69	−0.19	44.8	9 ± 3

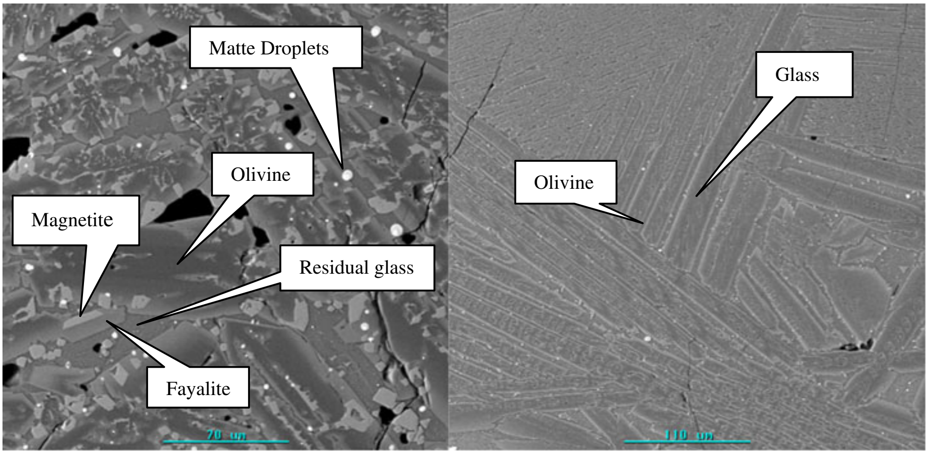

Fig. 1 On the left the backscattered electron image of the flash furnace slag and on the right the backscattered electron image of the electric furnace slag

3.4 Scanning electron microscopy

Scanning electron microscopy of the flash furnace slag samples show a glassy matrix containing olivine, magnetite and fayalite (Fig. 1). Nickel is predominantly present

Table 5 Average compositions of olivine, magnetite, fayalite and residual glass in flash-and electric furnace slag samples

	Al_2O_3	CaO	Cr_2O_3	CuO	FeO	MgO	Na_2O	NiO	SO_3	SiO_2	Total
Flash furnace											
Olivine	0.0	0.0	0.1	0.1	29.3	26.2	0.2	10.6	0.0	35.6	102
Magnetite	2.9	0.4	0.5	0.1	79.4	1.2	0.4	2.2	0.0	1.3*	93
Chrome magnetite	2.5	0.0	9.9	0.1	69.1	4.1	0.5	6.1	0.0	1.2*	100
Glass	4.2	8.3	0.0	0.7	47.6	0.6	0.6	0.5	0.0	36.6	99
Electric furnace											
Olivine	–	0.3	0.6	–	42.4	22.7	0.6	0.5	–	35.1	102
Glass	7.3	6.4	–	0.3	44.8	0.5	0.9	–	1.2	38.5	100

as NiO dissolved in slag. Textural relationships suggest that olivine is the primary liquidus phase. Magnetite crystals are typically found in the iron-enriched rims of the olivine crystals indicating that magnetite crystallisation started when the slag was already saturated with olivine. The electric furnace slag samples comprise a glassy matrix containing quenched olivine crystals (Fig. 1). Olivine is also the primary liquidus phase for the electric furnace slag and very little magnetite is present.

The average compositions of residual glass, olivine, fayalite, magnetite and chrome magnetite in the flash furnace and electric furnace slag are given in Table 5. In the flash furnace samples, nickel is primarily contained in olivine crystals with an average nickel oxide content of 10.6 %. Magnetite and fayalite have and average nickel oxide content of 3.5 % and 2.1 % respectively. The residual glass contains about 0.5 % NiO. In the electric furnace samples, nickel oxide is predominantly present in olivine (about 0.5 % NiO).

4 Discussion

Relatively oxidized slag from the flash furnace contains in the range of 20 to 40 wt% magnetite and about 4 % nickel, dissolved in the slag as nickel oxide. The Fe^{2+}/Fe^{3+} ratio of the slag is in the range of 2 to 6 (the magnetite content and Fe^{2+}/Fe^{3+} ratio will depend on furnace conditions and the rate and conditions under which the slag was cooled).

After reduction in the electric furnace the slag contains less than 0.5 % nickel and less than 3 % magnetite. The magnetite content of the slag is thus a useful indicator of redox conditions and therefore of nickel reduction in the electric furnace.

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