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# **Synopsis**

The effect of ore mineralogy on ferroalloy smelter operation is not sufficiently understood. The ore mineralogy can influence energy and reductant requirements, melting and reaction rates, and effectiveness of prereduction. These are all important factors to consider for furnace design, warranting a deeper study of the effect of ore mineralogy on ferroalloy production processes. This work focuses on smelting furnace mass and energy balances. Furnace mass and energy balances are among the most fundamental calculations done on a regular basis, from the project feasibility stage right through to everyday operations. Whether the energy balance is calculated by a tried and tested spreadsheet calculation, or by applying thermodynamic fundamentals using tools such as FactSage or EMSIM, most engineers simply use a chemical analysis of the raw materials. This ignores the potential effect of the ore's true mineralogical composition and may cause errors, the magnitude of which are not fully understood. In this paper we present the results of mineralogical analyses of South African, Zimbabwean, and Khazakstan chrome ores and compare energy balance results based on standard chemical assays to results based on mineralogical information.

### Keywords

chromite smelting, ore mineralogy, mass balance, energy balance.

# **Background**

Ferroalloy furnace technologies have developed over the years through tried and tested experience. With the technology available today, it is near-sighted to believe that experience will be enough to stay ahead into the future. The companies that control the ferroalloy industry in the future will be those that are able to absorb the most knowledge and draw insights from it to develop better processes.

Most ferrochrome plants take regular ore samples and perform ICP or XRF analyses to determine the chemical composition. These tests measure the contents of various metallic elements, such as Cr, Fe, Si, Mg, and Ca, and report results based on assumed oxidation states. The resulting assays are expressed in terms of Cr<sub>2</sub>O<sub>3</sub>, FeO, SiO<sub>2</sub>, MgO, CaO, and various trace elements. In our experience, most producers, and even authors in the literature, use this assay directly in their calculations (Xu, 2013).

The enthalpy of formation of one ton of chromite (FeCr $_2$ O $_4$ ) is -1458 kJ/mol, but if the

chromite is assumed to be equivalent amounts of FeO and  $Cr_2O_3$ , the enthalpy of formation is only –1393 kJ/mol – a difference of 77.4 kWh/t chromite. These results show that handling ore mineralogy incorrectly has the potential to affect the calculation of the furnace energy requirement. Ex Mente performs numerous furnace mass and energy balance investigations, so it is valuable to us to have insight into the effect of ore mineralogy so that we can make our calculations as accurate as possible. This paper therefore aims to answer the question: To what extent does ore mineralogy influence the furnace mass and energy balance?

# Method

One approach to answer these questions would be direct measurement of the energy required to melt an ore sample, and the reductant required to achieve a specific recovery. Instrumentation for this kind of work is extremely sensitive and it is time-consuming and expensive to obtain accurate results. It was therefore decided to use straightforward ICP-OES and XRD results, and reconcile them as far as possible, and calculate the reductant and energy requirements using Factsage (Bale *et al.* 2009) equilibrium calculations. Each of these methods is described in this section.

# Ore samples

Several samples were used for this work from different orebodies in South Africa, Zimbabwe, and Khazakstan, as shown in Table I. Grab samples of 2–3 kg were obtained and were crushed, milled, and split at UIS Analytical

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Table I					
Ore samples	used in this work				
Sample name	Country of origin	Mine/description			
LG6 A	South Africa	LG6			
LG6 B	South Africa	LG6 run-of-mine (ROM)			
MG4 A	South Africa	MG4			
MG4 B	South Africa	MG4 lumps			
ZIM A	Zimbabwe	Ngezi			
ZIM B	Zimbabwe	Ngezi			
ZIM C	Zimbabwe	Mapanzuri			
Marico	South Africa	Marico			
Khaz	Khazakstan	Unknown			

Services to ensure homogeneity between the samples used for chemical and mineralogical analysis. Since the samples are grab samples they are not necessarily representative of the orebodies.

### Chemical analysis

All samples were dried, and their moisture content determined to ensure that assay results are reported on a dry basis. For determination of elemental composition, samples were first subjected to sodium peroxide ( $Na_2O_2$ ) fusion, followed by dilute hydrochloric acid dissolution. The solutions were then analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES). ICP-OES involves nebulizing a sample of the solution and injecting it into a plasma. The various elements are identified and quantified through their unique optical emission spectra. ICP-OES was used for the analysis of both major and minor elements.

In addition to the elemental analysis, the oxidation states of iron (Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio) were determined by selective dissolution of Fe<sup>3+</sup> with hydrochloric acid, while assuming that Fe<sup>2+</sup> in the chromite will not dissolve. The solution was then analysed by ICP-OES to determine the Fe<sup>3+</sup> concentration. This procedure is proposed here as a new method for determining the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio of chromite ores. This property is typically difficult or impossible to measure by other methods.

In the LECO analysis, carbon and sulphur contents were determined by using a high-frequency combustion instrument with infrared detection. Hydrogen and nitrogen contents were determined using a H/N elemental analyser.

To complete the chemical analysis, the loss on ignition (LOI) was determined. This was done by determining the mass change of a sample while heating it to a temperature of  $1000^{\circ}\text{C}$  for 2 hours, in air. The heating process releases crystal water, water from hydroxide compounds,  $CO_2$  from carbonates, and  $SO_2$  from sulphates. The analysis therefore aims to determine the content of such volatile matter in the sample. LOI tests in an oxidizing atmosphere can return a negative result, indicating a gain on ignition. This can be the result of, for example,  $FeCr_2O_4$  being oxidized to  $Fe_2O_3 + Cr_2O_4$ .

# Mineralogical analysis

The ore mineralogical composition was determined by X-ray powder diffraction (XRD) (Loubser and Verryn, 2008). XRD identifies and quantifies the phases in a sample from their

unique powder diffraction patterns. This technique uses the crystalline structure of the different minerals and is therefore able to distinguish between spinels such as  $FeCr_2O_4$  and  $MgAl_2O_4$  and other oxide phases.

### Reconciliation

The goal of the reconciliation was to convert the chemical and mineralogical assays to calculated mineralogical assays that reflect the same chemical composition as the chemical analysis results, while remaining as close as possible to the measured mineralogical composition. This was done by manually assigning elements to known minerals and equilibrating the remainder of the assay to calculate an approximated chemical composition of multi-component minerals such as spinels.

### Thermodynamic equilibrium

Calculating thermochemical equilibrium is an important part of the reconciliation procedure. FactSage (Bale *et al.*, 2009) contains data based on thousands of experiments and uses rigorous optimization routines to determine the equilibrium state of elements in hundreds of phase structures. The equilibrium state is the state of the lowest Gibbs free energy and therefore the most likely condition that will be reached, given enough time.

Ores are unlikely to be at thermodynamic equilibrium due to the numerous processes that led to their formation and the weathering that changed their structures over the years. It is therefore necessary to manipulate the equilibrium calculations to achieve a representative assay.

FactSage takes account of solid solutions such as spinels and pyroxenes that consist of various constituents. The calculations incorporate the heats of mixing of these various phases, which is more accurate than assuming that  $FeCr_2O_3$  and  $MgCr_2O_3$  are two separate spinels, when in fact they are together in solution.

# Mass and energy balance

A simplified mass and energy balance was calculated for each of the ores. Several assumptions were made to simplify the calculations:

- 1. Pure graphite (C) was used as the reductant to remove the effect of ash and volatile matter from actual reductants.
- 2. No flux was added to any of the calculations. Fluxing design is critical to ensure effective furnace operation, but flux adds complications that might obscure the ore effects that are the focus here.
- 3. The reagents (ore and graphite) were equilibrated at 1700°C. This temperature was used throughout this study to allow for comparison on the same basis.
- 4. A chrome recovery to alloy of 95% was selected for the furnace and the graphite was adjusted to achieve this recovery for each case.

# **Results and discussion**

### Chemical analysis

Table II shows the chemical analysis results for the ore samples. The LG6 A ore has the highest content of  $Cr_2O_3$ , the lowest  $SiO_2$ , and the highest Cr/Fe ratio of the South African ores. The Zimbabwean ores have much higher Cr/Fe ratios.

Table II

Chemical analysis results (in mass %) for the ferrochrome ores under consideration

	LG6 A	LG6 B	MG4 A	MG4 B	ZIM A	ZIM B	ZIM C	Marico	Khaz
Main									
Cr <sub>2</sub> O <sub>3</sub>	43.13	39.77	30.99	29.97	39.62	42.54	34.8	49.708	49.1232
Fe <sub>2</sub> O <sub>3</sub>	0.81	0.96	0.44	0.72	5.44	2.5	2.29	0.71	0.62
FeO	23.29	21.92	21.77	21.64	13.02	14.51	13.16	20.25	11.24
Cr/Fe	1.6	1.5	1.2	1.2	1.9	2.2	2	2.1	3.7
Major gangue									
SiO <sub>2</sub>	3.47	7.97	15.4	15.84	9.52	10.41	14.42	4.03	6.22
$Al_2O_3$	15.53	14.14	14.7	14.88	12.2	11.6	11.1	12.5	8.07
CaO	0.47	0.71	3.13	3.97	0.23	0.22	0.27	0.2	0.2
MgO	10	11.68	10.06	9.74	16.38	15.12	21	10.4	21.1
Minor gangue									
TiO <sub>2</sub>	0.63	0.59	0.83	0.98	0.34	0.39	0.32	0.45	0.15
MnO	0.29	0.29	0.23	0.24	0.26	0.24	0.16	0.2	0.13
$V_2O_5$	0.34	0.3	0.32	0.34	0.19	0.2	0.17	0.63	0.2
Trace									
K <sub>2</sub> O	0.03	0.033	0.034	0.044	0.019	0.024	0.023	0.008	0.035
Zn	0.093	0.084	0.078	0.081	0.089	0.073	0.06	0.1	0.065
Ва	0.003	0.003	0.005	0.003	0.003	0.002	0.001	0.001	0.001
Cu	0.002	0.002	0.003	0.003	0.001	0.002	0.002	0.001	0.002
Ni	0.083	0.081	0.086	0.084	0.127	0.123	0.142	0.062	0.13
Other									
CO <sub>2</sub>	0.121	0.337	0.059	0.029	0.311	0.289	0.326	0.106	0.242
H <sub>2</sub> O	< 0.005	< 0.005	< 0.005	< 0.005	1.591	0.304	0.769	0.954	2.178
N	0	0	0	0	0.059	0.03	0.01	<0.01	<0.01
S	0.003	0.007	0.008	0.003	0.004	0.01	0.007	<0.003	0.024
Moisture	0	0	0	0	0.48	0.34	0.08	0.06	0.06
LOI	-0.42	-0.16	-0.74	-0.44	2.81	2.15	2.79	-0.98	1.98

Table III

XRD analysis results (in mass %) for South African LG6 samples, with and without plagioclase

Mineral	Chemical formula	LG6 A	LG6 A new	LG6 B	LG6 B new
Chromite	FeCr <sub>2</sub> O <sub>4</sub>	23.06	25.65	16.81	19.21
Chromite1	FeCr <sub>2</sub> O <sub>4</sub>	14.38	16.32	22.28	23.39
Magnesiochromite	MgCr <sub>2</sub> O <sub>4</sub>	40.89	40.72	32.56	31.35
Chlorite	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	1.45	1.64	3.37	2.19
Plagioclase	NaAlSi <sub>3</sub> O <sub>8</sub> , CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	13.02		14.75	
Enstatite	MgSiO <sub>3</sub>		8.51		16.35
Vermiculite		6.46	6.75	7.71	7.22
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	0.74	0.40	2.52	0.30

They also tend to have less  ${\rm Al}_2{\rm O}_3$  and higher MgO than South African ores. The South African ores exhibited a gain on ignition; this is likely due to iron being oxidized during the test. The assays all summed to less than 100%, which is typical for chemical analysis results. The Zimbabwean ores were slightly wet, whereas the South African ores contained no moisture. All calculations in this work were done on a dry-ore basis to standardize the calculations.

The H and C results from the LECO analyses were converted to H<sub>2</sub>O and CO<sub>2</sub> respectively. No H was detected in

the South African samples, but the LECO is designed for analysing coals, so it is not optimized for detecting small amounts of H.

# Mineralogical analysis

Table III shows two sets of XRD results for the LG6 A and LG6 B samples, and Table IV shows the results for the remaining ores. Three different spinel phases were detected by XRD; they are named chromite, chromite1, and magnesiochromite by the XRD software.

Table IV
XRD analysis results (in mass %) for other ores

Mineral	Chemical formula	MG4 A	MG4 B	ZIM A	ZIM B	ZIM C	Marico	Khaz
Chromite	FeCr <sub>2</sub> O <sub>4</sub>	40.39	51.83	42.51	61.36	64.29	97.51	87.21
Chromite1	FeCr <sub>2</sub> O <sub>4</sub>			33.50	17.45			
Lizardite	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>			9.79	10.36	11.46		12.79
Chlorite	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>			5.14	3.30	4.19		
Haematite	Fe <sub>2</sub> O <sub>3</sub>			5.60	2.19	0.83		
Goethite	FeO(OH)			3.47	5.35	0.06		
Enstatite	MgSiO <sub>3</sub>	19.37	11.59			13.12		
Diopside	MgCaSi <sub>2</sub> O <sub>6</sub>	1.60	7.93			6.05	2.49	
Plagioclase	NaAlSi <sub>3</sub> O <sub>8</sub> , CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	31.63	21.37					
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	0.00	0.34					
Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	1.37	1.36					
Smectite		1.82	2.71					
Actinolite	Ca <sub>2</sub> Fe <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	3.82	2.87					

The LG6 chemical analysis results showed very little CaO in the ore, and no Na. Therefore, it unlikely that the ore contains as much plagioclase as suggested by the preliminary XRD results in Table III. Plagioclase and enstatite peaks can, however, overlap in the diffractogram. The XRD results were therefore updated to favour enstatite, which is much more likely given the chemical composition of the sample. This illustrates the importance of critically analysing any laboratory results, and of providing the mineralogist with a chemical assay to assist in interpreting XRD results. Chromites of different compositions were detected and the simplified chemical formulae shown in the table do not necessarily reflect the actual composition.

The XRD results show that the LG6 ores contain chlorite and vermiculite. These are both hydrated minerals, but the chemical composition results show that the hydrogen contents of the ores are below the 0.05% detection limit of the LECO. For this reason, the ores were assumed to contain 0.05% water.

# Mineralogical reconciliation

The mineralogical reconciliation was performed to convert the chemical analysis into a calculated mineralogical assay as close as possible to the measured mineralogical composition. The mass and energy balance was then compared using the measured chemical assay and the calculated mineralogical assay. In the reconciliation, the chemical assays were used as the primary source of information, since chemical analyses are fully quantitative and more accurate than XRD analysis. The chemical analysis results were therefore used as the basis, with the XRD results as a guide.

# South African LG and MG ores

The following steps were used to produce a calculated mineralogical assay from the measured chemical and mineralogical assays.

1. The trace elements were removed from the chemical assay to simplify the thermochemical equilibrium calculations. The assay was normalized by proportionally increasing the gangue elements in their oxide forms ( $SiO_2$ , CaO, MgO, and  $Al_2O_3$ ) so that the

- final assay summed to 100%. This allows for trace elements to be substituted by gangue minerals, rather than normalizing the entire assay, which would increase the amounts of iron and chromium above their measured values, causing an over-estimation of chrome production.
- 2. The carbon from the LECO analyses was used to form dolomite, and the required amounts of CaO and MgO were removed from the chemical assay. The amount of dolomite calculated for the MG ores is below the typical XRD detection limit, which is why it was not identified by XRD. Dolomite is the most likely carboncontaining phase, therefore it was assumed that all the carbon is present in dolomite.
- 3. The remaining CaO was used to form plagioclase.
- 4. It was assumed that the ores contain 0.05% water. The LECO test is unable to detect water below this limit. This assumption was made because the XRD results suggest that there are hydrated minerals in the ores. This water was used to make chlorite.
- 5. The remainder of the assay was equilibrated at 25°C to approximate the spinel and orthopyroxene phases. The equilibrium phases allowed in the calculation were restricted to produce the desired result:
  - (i) LG6 A and B
    - (a) Only MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were provided as inputs to the calculation.
    - (b) Three spinel phases were allowed to form because three distinct spinel phases were observed by XRD.
    - (c) MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were allowed to form as individual compounds.
    - (d) A stable gas phase was forced by adding Ar. This was done to improve numerical stability and speed of convergence.
  - (ii) MG4 and MG4
    - (a) Only SiO<sub>2</sub>, MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were provided as inputs to the calculation.
    - (b) One spinel phase was allowed to form because only one spinel phase was detected by XRD.

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Table V
Mineralogical reconciliation results (in mass %) for South African ores

Phase	Chemical composition	LG6 A	LG6 B	MG4 A	MG4 B
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	0.25	0.71	0.12	0.06
Plagioclase (anorthite)	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	2.10	2.61	16.07	20.31
Chlorite	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	0.39	0.39	0.39	0.39
Spinel 1	Mostly MgCr <sub>2</sub> O <sub>4</sub> and FeCr <sub>2</sub> O <sub>4</sub>	58.67	54.10	58.80	54.68
Spinel 2	Mostly FeAl <sub>2</sub> O <sub>4</sub> and MgAl <sub>2</sub> O4	26.54	23.08		
Spinel 3	Fe <sub>3</sub> O <sub>4</sub>	0.13	0.46		
Orthopyroxene	Mostly Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> , some FeMgSi <sub>2</sub> O <sub>6</sub>	0.00	0.00	15.31	12.68
Quartz	SiO <sub>2</sub>	2.66	7.02		
Wustite	FeO	5.36	5.76	7.94	10.32
Periclase	MgO	2.66	4.71		
TiO <sub>2</sub>		0.63	0.59	0.83	0.98
MnO		0.29	0.29	0.23	0.24
V <sub>2</sub> O <sub>5</sub>		0.34	0.30	0.32	0.34
Total		100.00	100.00	100.00	100.00

- (c) MgO, FeO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were allowed to form as individual compounds.
- (d) Orthopyroxene, talc, and clinopyroxene were allowed to form. There was no remaining CaO to form clinopyroxene, or water to form talc.
- (e) A stable gas phase was again forced with Ar.

The results are shown in Table V.

# Zimbabwean ores

The reconciliation for the Zimbabwean ores was similar, but with some changes to reflect the different mineralogical and chemical assay results:

- 1. The gangue portion of the assay was normalized to account for the mass of the trace elements.
- 2. The LECO results suggest that there is a small amount of carbon in the ore. The most likely source of this is dolomite. No dolomite was detected by XRD, but it is likely that it is below the detection limit. The carbon was therefore allocated to the dolomite phase.
- 3. For ZIM A and ZIM B, the XRD results suggest that there is more Fe<sup>3+</sup> (in haematite and goethite), than the chemical results allow for. All the Fe<sup>3+</sup> was set aside for these phases, and divided between goethite and haematite in the ratios suggested by the XRD results. For the ZIM C ore, the haematite and goethite are less than the amount of Fe<sup>3+</sup>. The Fe<sup>3+</sup> required to make up the amounts of goethite and haematite from the XRD results was set aside and the remainder of the Fe<sup>3+</sup> was allocated to the spinel phase.
- 4. Some of the water was already allocated to the goethite phase, as indicated above. The remaining water, from the chemical results, was allocated to the lizardite and chlorite phases in the ratio between the phases suggested by the XRD results.
- 5. The spinels were generated by equilibrating the remaining elements in oxide form at 25°C.

The results for the Zimbabwean ores are shown in Table  $\mbox{VI}$ .

### Other ores

The Marico and Khazakstan ores are similar in that they both have an extremely high content of a single spinel phase. These samples were received at a later stage in the investigation, so there was insufficient time to perform as meticulous a reconciliation as was done for the other ores. Nevertheless, the results are included here for interest's sake. Similar steps were taken to reconcile the mineralogies of these ores.

- 1. The gangue portion of the assay was normalized to account for the mass of the trace elements.
- 2. The chemical assay was then equilibrated with restricted phases:
  - a. One spinel phase was allowed.
  - b. Each of the simple oxides for the available elements was allowed to form to ensure that the mass balance could be calculated.
  - c. For the Marico ore, clinopyroxene (diopside) was allowed, and for the Khazakstan ore lizardite was allowed.
- 3. The elements that did not fit into the spinel or accompanying phases were left as pure substances, as shown in Table VII.

The results for the Marico and Khazakstan ores are shown in Table VII.

# Mass and energy balance

Table VIII show the mass and energy balance results for three cases for each of the ores:

- 1. Assay as given by chemical analysis, with all Fe as FeO
- 2. Assay as given by chemical analysis, with forms of iron as determined by analytical work.
- 3. Mineralogical assay calculated through reconciliation.

# Mass balance

The differences in the mass balance depend solely on the oxidation state of the iron in the ore. A new method is proposed to measure the  $Fe^{2+}/Fe^{3+}$  ratio of chrome ore, but

Table VI Mineralogical reconciliation results (in mass %) for Zimbabwean ores Phase Chemical composition ZIM A ZIM B ZIM C Dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> 0.65 0.61 0.68 Haematite Fe<sub>2</sub>O<sub>3</sub> 3.49 0.78 0.83 Goethite Fe<sub>2</sub>O<sub>3</sub>(H<sub>2</sub>O) 2 17 0.06 1 91 Lizardite Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> 6.92 0.64 4.30 Chlorite  $Mg_5Al_2Si_3O_{10}(OH)_8$ 3.63 0.20 1.57 Spinel 1 MgCr<sub>2</sub>O<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub> 52 95 57.15 47.57 Spinel 2 FeAl<sub>2</sub>O<sub>4</sub>, MgFe<sub>2</sub>O<sub>4</sub> 19 39 19 90 19 43 Orthopyroxene Mostly Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, some FeMgSi<sub>2</sub>O<sub>6</sub> 0.03 0.07 CaO 0.04 Quartz SiO<sub>2</sub> 5.57 10.53 12.42 Periclase MgO 4 41 7 39 12 30 Wüstite FeO 0.11 0.34 TiO<sub>2</sub> 0.39 0.32 MnO 0.26 0.24 0.16 0.19 0.20 V<sub>2</sub>O<sub>5</sub> 0.17 Total 100.00 100.00 100.00

Table VII
Mineralogical reconciliation results (in mass %) for
other ores

Phase	Chemical composition	Marico	Khaz
Haematite	Fe <sub>2</sub> O <sub>3</sub>	0.55	
Lizardite	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>		14.56
Spinel 1	MgCr <sub>2</sub> O <sub>4</sub> , FeCr <sub>2</sub> O <sub>4</sub>	90.15	82.96
Orthopyroxene	Mostly Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> , some FeMgSi <sub>2</sub> O <sub>6</sub>	7.09	
Lime	CaO		0.2
Periclase	MgO		1.7
TiO <sub>2</sub>		0.45	0.15
MnO		0.20	0.13
V <sub>2</sub> O <sub>5</sub>		0.63	0.2

this method requires validation against standard samples to ensure its effectiveness.

The Fe $^{2+}$ /Fe $^{3+}$  ratio directly affects the mass balance because if the iron is more oxidized, more reductant is required to reduce it. There are two reasons to believe that the methods of iron analysis may be underestimating the Fe $^{3+}$  content:

- 1. The XRD results, particularly for the Zimbabwean ores, suggest much higher haematite and goethite than the measured Fe<sup>3+</sup> content accounts for.
- 2. All the equilibrium calculations had 'left-over' FeO that did not 'fit' in the spinel phases. This is obviously an unrealistic result, and is another possible indication that more of the iron might be present as Fe<sup>3+</sup>.

Preliminary calculations using the Zimbabwean ores, which were based more strongly on the XRD results, suggested a much higher Fe<sup>3+</sup> content because of the haematite and goethite measured by XRD. This resulted in carbon requirements as much as 15% higher than calculated when assuming all iron is present as FeO. This result

correlates with industrial experience of higher reductant requirements for Zimbabwean furnaces than South African ones. The reductant requirement results are therefore inconclusive until the ore Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio can be confirmed.

# Energy balance

The difference in iron oxidation states does not have as significant an impact on the energy balance as the difference indicated by the approximated mineralogical assay. This shows that using phases such as spinels to represent the ore has a more significant effect on the energy balance than knowing the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio.

The difference in the energy balance when using a chemical assay and the approximated mineralogical assays developed in this work is in the order of 5%. This means that, provided the calculated mineralogical assay is a more accurate representation of the ore, then using a chemical assay for energy balance calculations results in the smelting energy requirement being underestimated by approximately 5%. In practice, this 5% is being consumed in the furnace, but it is most likely accounted as heat losses rather than due to the theoretical smelting energy requirement of the ore.

# Differences between ores

Any discussion on the differences between the ores analysed in this paper is limited, because the samples used are not necessarily representative of the various orebodies. In addition, different fluxes would be required for the different ores and these have not been considered. It is, however, interesting to draw some preliminary conclusions.

The South African ores tend to have lower smelting energy requirements than the Zimbabwean ores. LG6 A ore has the lowest energy requirement and highest yield of alloy per ton of ore. ZIM B has the lowest energy requirement and highest yield of alloy per ton ore of the Zimbabwean ores.

# **Conclusions and recommendations**

### Mass balance

The amount of reductant required has been shown to be

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Table VIII

# Mass and energy balance results for South African ores

	Fe recovery	Cr recovery	t ore/t alloy	kg C/t alloy	MW/t alloy
LG6 A					
1	99.9%	95.0%	2.018	334.109	2.749
2	99.9%	95.0%	2.018	335.325	2.755
3	99.9%	95.0%	2.018	335.325	2.887
			Increase	0.36%	5.00%
LG6 B					
1	99.8%	95.0%	2.169	334.066	2.906
2	99.8%	95.0%	2.169	335.608	2.914
3	99.8%	95.0%	2.169	335.608	3.048
			Increase	0.46%	4.87%
MG4 A					
1	99.7%	95.0%	2.528	328.072	3.180
2	99.7%	95.0%	2.528	328.875	3.184
3	99.7%	95.0%	2.528	328.875	3.359
			Increase	0.24%	5.65%
MG4 B					
1	99.7%	95.0%	2.567	326.525	3.184
2	99.7%	95.0%	2.567	327.868	3.191
3	99.7%	95.0%	2.567	327.868	3.369
			Increase	0.41%	5.82%

### Mass and energy balance results for Zimbabwean ores

ZII	ИΑ				
1	99.8%	95.0%	2.374	368.710	3.292
2	99.8%	95.0%	2.375	378.344	3.337
3 99.8%		95.0%	2.375	378.344	3.510
			Increase	2.61%	6.64%
ZII	ИΒ				
1	99.8%	95.0%	2.313	352.937	3.192
2	99.8%	95.0%	2.314	357.215	3.213
3	99.8%	95.0%	2.314	357.215	3.347
			Increase	1.21%	4.85%
ZII	ИС				
1	99.7%	95.0%	2.731	361.533	3.563
2	99.7%	95.0%	2.731	366.212	3.585
3	3 99.7% 95.0%		2.731	366.212	3.747
			Increase	1.29%	5.16%

# Mass and energy balance results for other ores

wass and energ			y balance resul	to for other ore.	3
Kh	ıaz				
1	99.8%	95.0%	2.29	394.06	3.43
2	99.8%	95.0%	2.29	395.09	3.44
3	99.8%	95.0%	2.28	396.69	3.59
			Increase	0.67%	4.75%
Ma	rico				
1	99.9%	95.0%	1.93	355.81	2.88
2	99.9%	95.0%	1.93	356.82	2.88
3	99.9%	95.0%	1.93	357.26	2.99
			Increase	0.41%	3.99%

strongly dependent on the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio. A new method was proposed and used to determine the oxidation states of iron. The XRD results and reconciliation suggest that the Fe<sup>3+</sup> contents may be higher than measured by this new method. It is recommended that the method be validated using standard samples of known iron oxidation state to improve its accuracy, and that it be routinely used when analysing ore samples for mass and energy balances.

# **Energy balance**

The energy balance results suggest that the calculated energy requirement is approximately 5% higher when using the approximated mineralogical assays compared to chemical assays. These results are by no means conclusive, because they are also based upon several assumptions, but they have shown that using a mineralogical composition makes a difference in the energy balance. These results should be verified using analytical techniques for measuring the actual energy requirement directly.

With today's strong focus on maximizing energy efficiency, it is critical to obtain as good an understanding of the furnace energy balance as possible. Understanding ore mineralogy is an important part of this. One option for improving this understanding is to smelt ore samples under controlled conditions, measure the actual energy requirement, and compare that to these approximated results. Another is to measure the heat of formation of the ore directly. The feasibility of both these options is speculative at this stage.

These results may not be so critical to operating plants that have long since made accommodations for their energy balances, but they are worthwhile for designers of future furnaces to understand. The analyses performed in this work are not expensive, and the method proposed here can be used to reconcile the analyses and produce more accurate assays for mass and energy balances.

Finally, to answer the initial question: ore mineralogy does influence both mass and energy balance calculations for ferrochrome smelting furnaces. The extent of this influence depends on the specific ore, but it has been shown that both reductant and energy requirement calculations are impacted. Reductant requirement differences are small enough to be within the band of uncertainty due to variations in raw material composition, and sampling and analytical error. Smelting energy requirement differences appear to be more significant, and these could prove to be important when switching between different raw materials, or when doing feasibility and design calculations for new plants.

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