PRE-REDUCTION AND SMELTING CHARACTERISTICS OF KAZAKHSTAN ORE SAMPLES

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ABSTRACT

Chromite samples from bore hole drill cores obtained during the exploration and development of the Voskhod Chrome project in Kazakhstan were studied mineralogically and in laboratory-scale tests to characterise their pre-reduction and smelting behaviour.

The ore was readily reduced using carbon in a TGA furnace to levels of over 70% at 1400°C and well over 80% at temperatures of 1500 deg C in just over 2 hours. Samples were also smelted in an induction furnace at 1750 deg C using limited silica flux additions and reductant to produce a high carbon ferrochrome alloy with chromium contents of around 65 to 70%.

Mineralogy, Mossbauer spectroscopy and Chemical Composition were used to assist with the assessment of the results obtained from the pre-reduction tests. Initial findings suggest that the moderate levels of CaO and the presence of SiO_2 could potentially have a positive impact on the extent of overall pre-reduction attained (90%) whereas high Cr^{3+}/Fe^{3+} and Mg^{2+}/Fe^{2+} ratios appear to result in a somewhat lower overall extent of pre-reduction (80%). These values were obtained at 1500 deg C for 3 hours on the four different chromite samples tested. The average activation energy for reduction of just over 120 kJ/mol is also lower than for typical Southern African chromites at 200 to 300 kJ/mol. This was unexpected but appears to relate to possible non-stoichiometric spinel structures that affect the of the lattice of the chrome spinel.

The potential benefits of pre-reduction include:
1. A significant decrease in the electrical energy requirements for smelting of up to 60%
2. Lower consumption of metallurgical grade coal in the smelter of up to 65%
3. Increased production from existing furnace capacity in existing plants or smaller transformer capacity in new plants.

1 INTRODUCTION

The upward trend in the price of electricity and the constraints on availability in some regions is encouraging the Ferroalloy Industry and Ferrochrome producers in particular to implement pre-heating technology more widely and to consider pre-reduction as an alternative or complementary approach.

The pre-reduction of South African chrome ore has been in operation since 1977 at the Lydenburg Ferrochrome Plant of Xstrata[1]. The Lion Project near Steelpoort South Africa is a joint venture between Merafe and Xstrata and also has a pre-reduction stage based on Xstrata's more advanced Premus pre-reduction technology. The pre-reduction process comprises pelletising using milled chrome fines, coke fines as a reducing agent and bentonite as a binder. Pre-reduction levels of up to 90% of the iron and 50% of the chrome are achieved which reduces electrical energy consumption by up to 40% from around 3.9 down to 2.4 MWh/t. The operation of the SAFs (Submerged Arc Furnaces) has to take the extent of pre-reduction, the residual carbon content and the temperature of the feed into account. Variations can have a significant impact on the furnace operation due to changes in the energy balance and process conditions. The furnace resistance and hence power level at which the furnaces operate are also factors that need to be considered in the control of the process. This is particularly the case with the AC SAF (Submerged Arc Furnace) and only to a very limited extent with the DC arc furnace.

Alternative processes that have been used or have been partly developed include the CDR (Chrome Direct Reduction Process) of originally Krupp in Germany but acquired by Polysius and the RHF (Rotary Hearth Furnace) developed by INMETCO and applied to stainless steel dust recycling and DRI (Direct Reduced Iron). The 'Nugget' project in Minnesota involves the metallisation of iron and its separation into metallic nuggets using high temperatures (around 1500 ºC) and very high level of pre-reduction. Attempts to apply the RHF process to chrome ore pre-reduction carried out in the early late 1980's and 1990's were only partly successful, the main problem being the re-oxidation of the pre-reduced chrome pellets. However Industry in South Africa has favoured the rotary kiln approach to date but the only plants in operation are those of Xstrata/Merafe. The CDR pre-reduction process installed at SAMANCOR's Middleburg Ferrochrome Plant that involved the partial fluxing of the chrome ore fines (not pellets) and the use of oxygen enrichment to attain temperatures of around 1500 ºC ran into problems in particular with refractory wear. There is thus a need to find a reliable improved pre-reduction process to provide a controlled feed to existing and new SAFs as well as to consider the option of smelting pre-reduced and pre-heated feed into DC arc furnaces that have the ability to respond more rapidly to variation in feed characteristics.

Mintek has carried out pre-reduction test work on a bench scale on many South African chrome ores over the years. However it was only recently that pre-reduction and smelting work was carried out on high Cr/Fe ratio ore from Kazakhstan. Oriel Resources based in London commissioned bench-scale characterisation test work on samples of its Voskhod chrome ore produced from mineral processing work that was carried out in 2005 to assist in the design of the beneficiation plant. This paper describes the mineralogical characteristics and thermal behaviour of the Voskhod chrome ore during pre-reduction and smelting. This test work has assisted with the smelting of Voskhod ore at the existing Tikhvin Ferrochrome Plant near St Petersburg, Russia and with the evaluation of a proposed new smelter near the Voskhod mine. The option to pre-reduce the ore and decrease electricity consumption depends on access to a viable technology. However the preliminary assessment of pre-reduction based on the results obtained at Mintek indicates that there could be significant potential benefits. However in the absence of proven off the shelf technology, pre-heating never the less currently offers savings of up to around 20% in electrical energy consumption with lower risks and capital investment.

2 CHEMICAL COMPOSITION

The bulk chemical composition of the chromite concentrates examined were determined by Induction Coupled Plasma Optical Emission Spectrometry (ICP-OES) and are shown in Table 1 together with some typical South African examples for comparison.

3 PRE-REDUCTION

Thermo-gravimetric (TG) tests were conducted to determine the pre-reduction characteristics of the chromite concentrates. The samples were mixed with 120% of the stoichiometric carbon required to reduce chrome (Cr_2O_3) and iron oxides (Fe_2O_3 and FeO) to metallic Cr and Fe, milled to 80% passing 75µm and placed in the TG furnace with a constant supply of inert argon gas. The temperature was then ramped at a rate of 10ºC/min until the target temperature was reached. Constant temperature was then maintained for up to 5 hours. The mass loss of the sample was recorded throughout the test. To ensure reproducibility and allow comparison between each pre-reduction test, a constant mass of chromite (20g) and sample geometry was used per test.

Pre-reduction tests were conducted at 1300ºC, 1400ºC and 1500ºC together with a few additional tests at 1200ºC and 1550ºC using selected concentrates. The typical output of these tests is shown in Figure 1:.

Table 1: Bulk chemical composition of chromite concentrates compared to two South African chromite concentrates. (mass %).

Concentrate	1	2	3	4	SA1[†]	SA2[+]
Cr_2O_3	54.6	61.7	55.4	50.9	48.9	46.4
FeO[§]	9.99	12.0	10.2	9.79	20.2*	25.0
Fe_2O_3[§]	2.78	1.82	2.16	2.72	-	
MgO	18.8	15.5	19.1	21.4	14.6	10.8
Al_2O_3	6.43	7.75	6.54	5.93	10.5	15.1
SiO_2	5.06	0.75	5.75	8.13	4.30	0.61
CaO	<0.07	<0.07	0.21	<0.07	0.26	0.16
TiO_2	0.14	0.15	0.15	0.13	0.24	0.56
V_2O_5	0.09	<0.09	0.21	0.11	0.14	0.32
MnO	0.14	0.15	0.14	0.14	0.25	0.21
NiO	0.14	0.11	0.13	0.15	-	-
Total	98.2	99.9	99.9	99.4	99.4	99.1
Cr/Fe	3.85	3.98	4.02	3.66	2.14	1.63
MgO/Al_2O_3	2.93	2.00	2.92	3.61	1.39	0.72
Fe^{2+}/Fe^{3+}[‡]	3.99	7.33	5.24	4.00		

† *South African chromite – Grass Valley Mine, Potgietersrus.*

\+ *South African chromite – Winterveld Chrome Mines, Steelpoort.*

‡ *Fe^{2+}/Fe^{3+} ratio determined through Mössbauer spectroscopy.*

§ *FeO and Fe_2O_3 calculated from total Fe and Fe^{2+}/Fe^{3+} ratio.*

* *Total Fe expressed as FeO*

The pre-reduction tests were compared based on the degree of reduction obtained during each test, complete reduction being defined as the mass loss associated with the reduction of all chrome (Cr_2O_3) and iron oxides (Fe_2O_3 and FeO) to metal. Reduction and or dissolution of carbon and silicon into the alloy were not taken into account in calculating the degree of reduction.

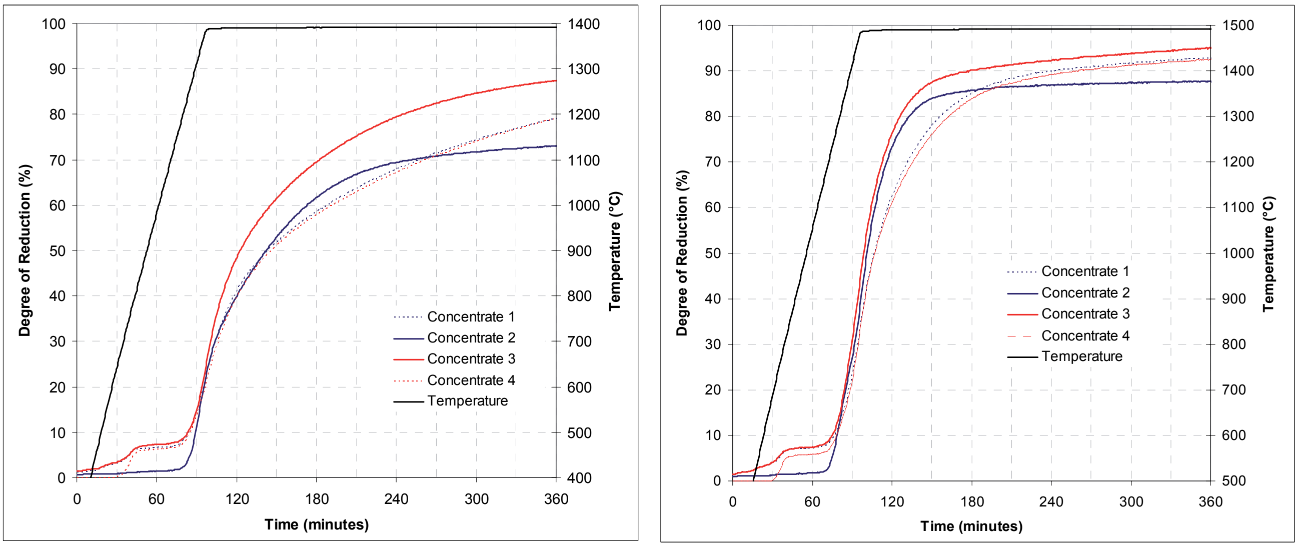

Figure 1: Pre-reduction of chromite samples at 1400 and 1500ºC.

From this data, a reduction rate constant was determined over a period where the rate of mass change appears relatively linear and thus independent of the concentration of reactants. The reduction rate constants were determined in this fashion for all temperatures examined and are given in Table 2:.

Table 2: Reduction rate constants as determined for each pre-reduction temperature. (%.min^{-1}).

Concentrate	1	2	3	4
1200ºC	0.20	0.53	0.24	-
1300ºC	0.49	1.13	0.62	0.54
1400ºC	1.06	1.40	1.35	0.99
1500ºC	1.44	1.82	1.98	1.49
1550ºC	-	-	-	1.46

The reduction rate, as expected, is temperature dependent and was found to conform to the relationship proposed by Arrhenius as shown in equation 1.

$$k(T) = Ae^{-\frac{E}{RT}} \qquad \textbf{(1)}$$

Where

k = conversion rate constant, %.min^{-1}
A = pre-exponential factor
E = activation energy, J.mol-^{1}
R = gas constant = 8.314 J.mol^{-1}K^{-1}
T = absolute temperature, K

Taking the natural logarithm of equation 1, it can be seen that a plot of (ln*k*) versus (1/T) will be a linear relationship the slope of which is proportional to the activation energy as shown in equation 2.

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad \textbf{(2)}$$

A plot of the reduction rate for each of the concentrates as a function of temperature is given in Figure 2: together with data for the reduction of two Southern African chromite samples according to Barcza [2] and Ding[3]. The activation energy (E), thus derived, for each of the chromite concentrates is shown in Table 3:. The mean activation energy for the Kazakhstan concentrates was found to be 122 kJ/mol.

4 SMELTING

Smelting tests were conducted at 1750ºC in an argon atmosphere. The pulverised smelting charges made use of silica as a flux and a petroleum coke as a reductant (Table 4:), and were combined in the ratios given in Table 5:. The smelting charges were contained in graphite crucibles and allowed to react for 30 min at temperature. The use of high purity alumina (Al_2O_3) and magnesia (MgO) crucibles was investigated, but reaction between the slag and these crucibles resulted in significant contamination of the slag with both crucible materials. The cooled products (slag and alloy) were separated and analysed, the compositions of which are shown in Table 6: and Table 7:.

The slags resulting from the smelting tests were typically light in colour and appeared molten with little evidence of entrained alloy. The concentrations of Cr_2O_3 in the resulting slag were consistently below 0.5% and composed almost predominantly of $MgO\text{-}Al_2O_3\text{-}SiO_2$ and the approximate composition of the slags (mean composition of the slags) is projected on the $MgO\text{-}Al_2O_3\text{-}SiO_2$ phase diagram shown in Figure 3:. The approximate composition of the Kazakhstan concentrates are also indicated on the diagram together with a comparison to those of South African concentrate and slag. The low Cr_2O_3 concentration of the slag is undoubtedly a result of the use of graphite crucibles which results in over-reduction, but this was unavoidable if contamination of the slag by ceramic oxide crucibles was to be avoided. During commercial furnace operation, levels of 4 to 5% Cr_2O_3 in slag are expected. It is evident from Figure 3: that the expected liquidus of the Kazak slag is predicted to exceed 1700°C, however successful slag/metal separation was observed at a smelting temperature of 1750°C.

The alloys produced during smelting are dominated by the presence of over 67% Cr and exhibit a high Cr to Fe ratio (generally in the region of 4). The alloys appeared molten for the test temperature exhibiting good collection. To some extent, the carbon values may be excessive and it is possible that partial contamination of the alloy from the crucible material may have occurred. Cr recoveries to the alloy were in excess of 95%.

5 PROCESS FLOWSHEET ENERGY ANALYSIS

The energy requirements of several flowsheet scenarios were evaluated using MINTEK's in-house free energy minimisation modelling software (Pyrosim©). The aim of the simulations was to demonstrate the benefits of preheating and pre-reduction in smelting of Kazakhstan chromite and compare these energy requirements to a typical South African chromite. The flowsheets examined are illustrated in Figure 5: and effectively cover the following generic processes:-

- direct smelting at 1800°C for Kazakhstan chromite and 1750° for South African chromite.
- pre-heating at 900°C.
- sintering at 1300°C for Kazak chromite and 1200°C for South African chromite.
- pellet induration at 1100°C, followed by pre-reduction at 1400°C.
    - pre-reduction was evaluated at 4 levels of overall reduction.

The simulations were further expanded to compare smelting in a submerged arc furnace (SAF) to smelting in a DC arc furnace (DC), the principle difference being the assumed energy losses of the two furnaces.

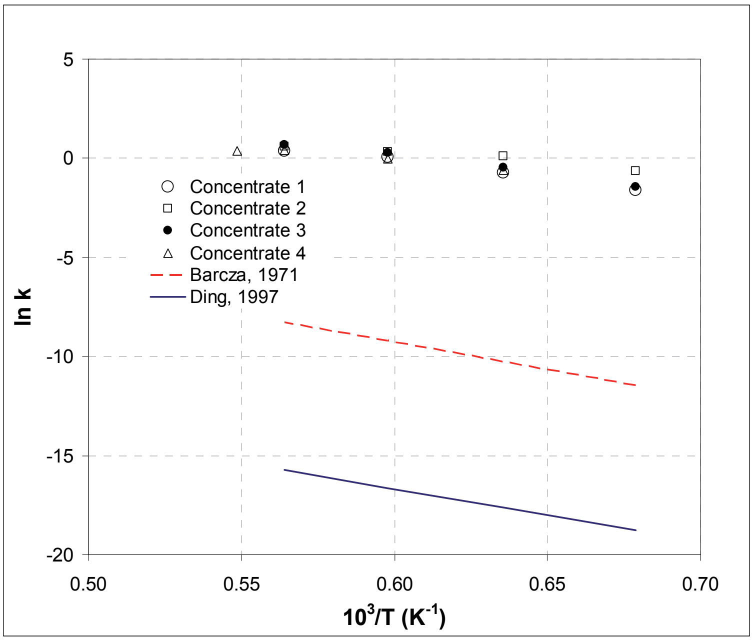

Figure 2: Plot to determine Arrhenius equation constants compared to literature

Table 3: Empirical constants determined for the Arrhenius equation

Chromite	A [1/min]	E [kJ/mol]
Concentrate 1	372	148
Concentrate 2	6.7	86
Concentrate 3	8.7	156
Concentrate 4	12	100
F584, Barcza, 1971	13	228
F524, Barcza, 1971	6.5	186
F588, Barcza, 1971	9.2	197
SA pellets, Ding, 1997	0.005	221

Table 4: Bulk chemical analysis of reductant and silica. (mass %)

	Silica	Coke†
SiO_2	99.5	-
FeO	0.5	-
C	-	98.7
Volatiles	-	0.97
Ash	-	0.33

† Low sulphur petroleum coke

Table 5: Smelting recipes and alloy fall. (mass %)

Concentrate	Chromite	Coke	Silica	Alloy Fall†
1	100	20.33	13.5	49.8
2	100	22.61	14.7	56.0
3	100	20.09	13.0	51.3
4	100	18.92	12.8	46.7

† Alloy fall expressed as a percentage of the chromite mass.

Table 6: Chemical composition of the slags produced in the smelting tests. (mass%).

Concentrate	MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	Ni	Total	MgO/Al_2O_3
1	48	19	33	0.3	0.3	0.1	0.0	100	2.53
2	42	32	23	0.3	0.0	0.2	0.0	98	1.31
3	47	21	32	0.8	0.0	0.1	0.0	101	2.24
4	49	16	34	0.3	0.0	0.1	0.0	99	3.06

Note: TiO_2, V_2O_5, and MnO less than 0.1%

Table 7: Chemical composition of the alloys produced in the smelting tests. (mass %).

Concentrate	Si	Cr	Fe	Ni	C	Total	Cr/Fe
1	4.9	68.4	17.6	0.2	9.5	100.6	3.9
2	4.4	71.9	16.6	0.2	9.2	102.3	4.3
3	5.3	68.5	16.7	0.2	9.3	100.0	4.1
4	6.4	67.1	18.3	0.2	8.4	100.4	3.7

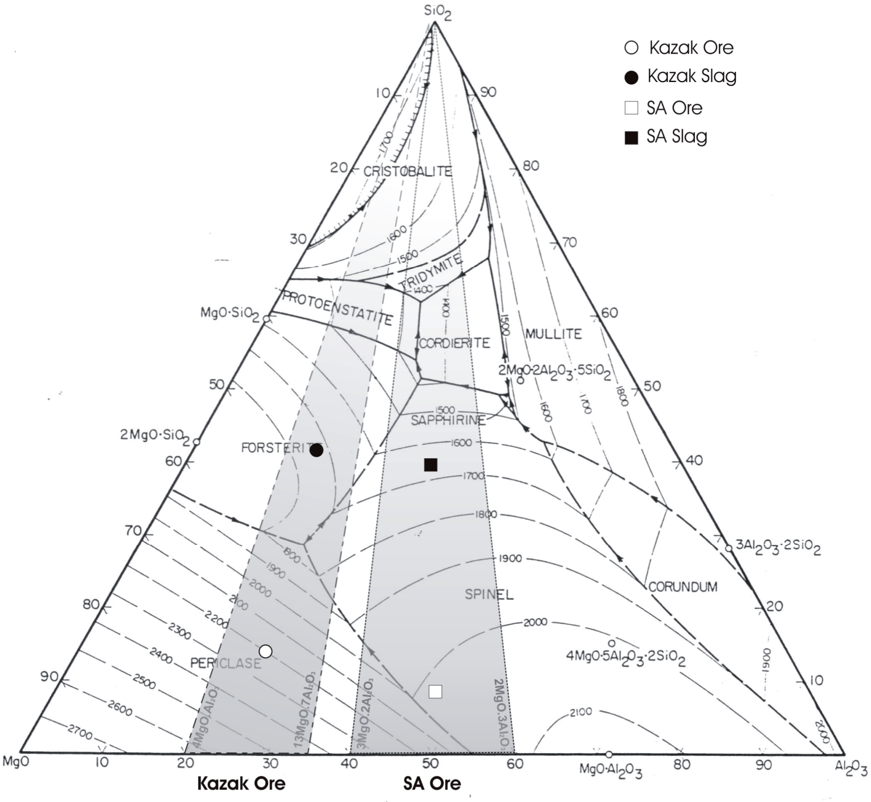

Figure 3: Ore and slag compositions indicated on MgO-Al_2O_3-SiO_2 ternary phase diagram for Kazak and SA chromite ores.

The following assumptions were used for the simulations:

a. The compositions of the feed materials used in the simulations are shown in Table 8:.
b. The material consumption for the various flowsheets is given in Table 9:.
c. The tapping temperature of the alloy is 100ºC below the smelter operating temperature.
d. The furnace off gas temperature of a SAF is 900ºC lower than the operating temperature of the furnace, while the off gas temperature of a DC furnace is 200ºC lower than the operating temperature of the furnace.
e. Reductant and fluxes are fed to the furnace at 25°C, although this may not be practical for a SAF a point of comparison is provided.
f. The temperature of materials transferred from preheating, sintering or pre-reduction units is 800ºC although other temperatures could be contemplated.
g. The furnace availability for a SAF is 95% and that for a DC furnace is 90%.
h. Metallurgical reactions in the SAF and DC furnaces are identical.
i. During pre-reduction simulations FeO is reduced to Fe and Cr_2O_3 to Cr_7C_3.
j. Fossil fuel efficiency of 40% and 50% of ash from fossil fuel enters the smelter.
k. The alloy produced during smelting contains 8% carbon and 2% silicon.
l. The residual slag contains 4% Cr_2O_3 and 1.5% FeO.
m. Four degrees of pre-reduction were simulated namely, 32.5, 65, 77.5 and 90% metallisation as shown in Figure 4:.

The calculated energy requirements for each of the simulated process flowsheets are given in Table 10: (expressed both in MWh/ton of alloy produced and MWh/ton of Cr) and shown in Figure 6:.

Table 8: Composition of materials as used in simulations. (mass %).

	Al_2O_3	Cr_2O_3	MgO	SiO_2	FeO	CaO	C	Volatiles	Total
SA Chromite	13.8	46.0	8.5	1.0	31.0				100
Kazak Chromite	6.1	59.2	17	3.1	15.0				100
Flux	1.3		0.1	97.0	0.5	0.8			100
Coal	0.5		0.3	2.7	0.5	0.3	83.2	12.5	100
Coke Fines	10.6		0.3	20.0	6.9	1.0	52.5	8.5	100
Fossil Fuel	5.4		0.2	10.0	3.6	0.5	55.0	25.0	100

Table 9: Material flowrates assumed for each flowsheet. (mass per unit time).

	Flowsheet	Chromite	Coal	Flux	Coke Fines	Fossil Fuel
SA Chromite	Direct Smelting	100.0	30.9	14.0		
	Preheating	100.0	30.9	14.0		
	Sintering	100.0	30.9	14.0		
	Pre-reduce 33%	100.0	10.6	8.0	28.6	62.5
	Pre-reduce 65%	100.0	10.6	8.0	28.6	103.4
	Pre-reduce 78%	100.0	10.6	8.0	28.6	123.6
	Pre-reduce 90%	100.0	10.6	8.0	28.6	146.5
Kazak Chromite	Direct Smelting	100.0	31.2	7.0		
	Preheating	100.0	31.2	7.0		
	Sintering	100.0	31.2	7.0		
	Pre-reduce 33%	100.0	10.7	6.0	28.6	54.6
	Pre-reduce 65%	100.0	10.7	6.0	28.6	101.2
	Pre-reduce 78%	100.0	10.7	6.0	28.6	126.2
	Pre-reduce 90%	100.0	10.7	6.0	28.6	155.0

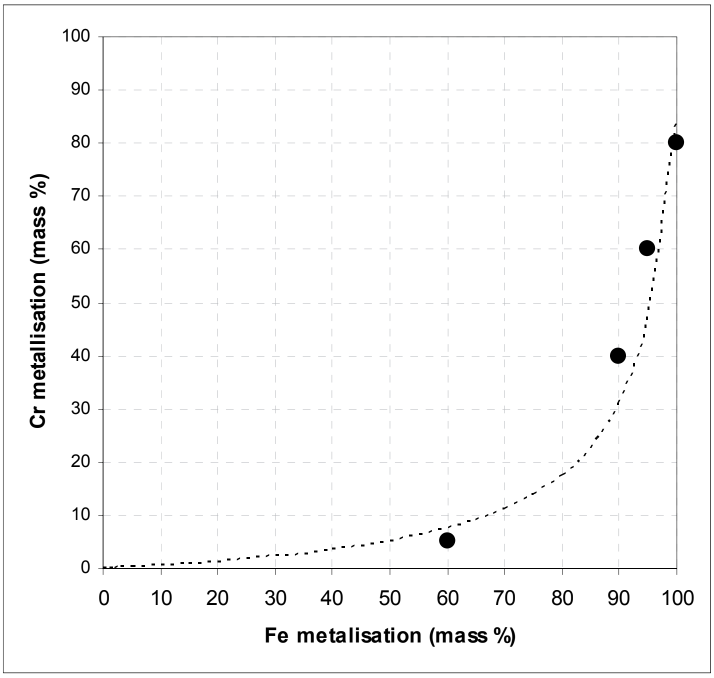

Figure 4: The assumed relationship between Fe and Cr metallization during pre-reduction for both Kazak and SA chromite ores.

6 DISCUSSION

In order to understand the pre-reduction and smelting behaviour of the Kazakhstan chromite and compare it to that of the more well understood and studied South African chromite, it is necessary to consider the geological setting of the two deposits. Generally speaking, a diverse variety of chromite ore fields exist distributed across the globe, the single significant link between all these deposits is the close association of chromite with ultramafic rocks either as

- layered differentiates of gabbroic magmas e.g. the Bushveld Complex, S.A, or
- cumulate and mantle residue units of ophiolite complexes (alpine-type chromitites) e.g. the Main Ore Field of the Kempirsai Massif, Kazakhstan (Voskhod)[4].

Several parameters promote crystallization and influence the composition of these chromite ore fields, including; the geochemical composition of the parent magma, the composition of the country rock with which magma interacts, and the environmental conditions (temperature, pressure and oxygen fugacity). Initial minerals that crystallize from a parent magma are enriched in high-temperature components such as magnesium[4]. The Kazakh chromite ore is considered the result of early stage crystallization of chrome-spinel from a high temperature (~1250°C) magnesium-rich, boninitic melt under high pressure upper mantle conditions (~30km depth)[5] and possesses a high MgO/Al_2O_3 ratio. On the other hand, the South African Bushveld chromite ore is considered to result from the mixing of two magmas, a tholeiitic and boninitic magma[6]. The combined magmas would have had a temperature of ~1150°C and were emplaced 3km below surface under low pressure (1-2 Kbars) crustal conditions[7].

The principal mineral of economic interest in chromitite deposits is the spinel chromite, and the majority of the reduction and smelting behaviour of a chromite concentrate can be attributed the phase chemical composition and stoichiometry of this mineral. In general spinels contain two differing cations, or two different valence states of the same cation, in the ratio 2:1 giving the general crystallographic formula AB_2O_4. The tetrahedrally coordinated sites are labelled A, and octahedrally coordinated sites, B[8]. In the case of chromite, the mineral is dominated by compositions containing the cations Mg, Fe, Cr, Al and minor amounts of Mn and Ti. The major cations substituting into the A site are the divalent cations Mg^{2+}, Fe^{2+} and Mn^{2+} whereas substitution within the B site involves the trivalent cations Al^{3+}, Cr^{3+}, Fe^{3+} . Tetravalent Ti^{4+} can also be substituted into the octahedral B site based on a coupled substitution $2B^{3+} \Leftrightarrow Ti^{4+}+A^{2+}$ mechanism. This gives rise to a range of chromite solid solutions within a magmatic system. Spinel solutions may also contain some degree of non-stoichiometry[9]. Non-stoichiometry is associated with defects in the oxide structure resulting in the ratio of the elements in the ideal formula of the oxide becoming indefinite.

This may result from chemical weathering of the spinel induced by the mechanisms that occur during the alteration of the ore body (chromite ore and proximal ultra-mafic rocks included), leading to diffusion of iron and other divalent elements out of the spinel, with oxidation of the remaining iron to the trivalent state to maintain the charge balance. The resulting ore, in this case, is oxidised and cation deficient.

For the Kazakhstan ore field, the magnesium-rich boninitic magma made available a wealth of magnesium ions and scarcity of aluminium ions during crystallisation resulting in spinels in which Cr^{3+} dominates the octahedral sites of the lattice while Mg^{2+} dominates the tetrahedral sites. These high melting point components would suggest that this spinel is more refractory. By implication, the Bushveld chromites would be judged to be less refractory due to more octahedral sites being occupied by Al^{3+} and Fe^{3+}, and tetrahedral sites by Fe^{2+}. Perhaps more importantly, from an economic aspect, the increased iron concentration of the chromite spinels in the Bushveld results in an ore that has a Cr to Fe ratio that is generally low, (1.6-2.6) compared to that of the Kazakhstan ore (3.6-4.0). Given that the Cr-oxide requires a lower oxygen potential and more energy to reduce than Fe-oxides, the higher chromium content of the Kazak spinel, would tend to indicate that the Kazakhstan spinels are more stable than the iron rich-spinels encountered in the Bushveld. Consequently, it would be expected that a higher activation energy (A.E) for reduction would be required to reduce the Kazakhstan chromite than Bushveld chromites. Test work, however, shows that the average A.E for reduction of Kazakh ore is just over 120 kJ/mol which is significantly lower than for Bushveld chromites at 200-300 kJ/mol[1][3]. This reduction behaviour is atypical to that expected given the chemistries of the chrome-spinels of the two ore types and it is clear that other factors must be considered to explain what is observed.

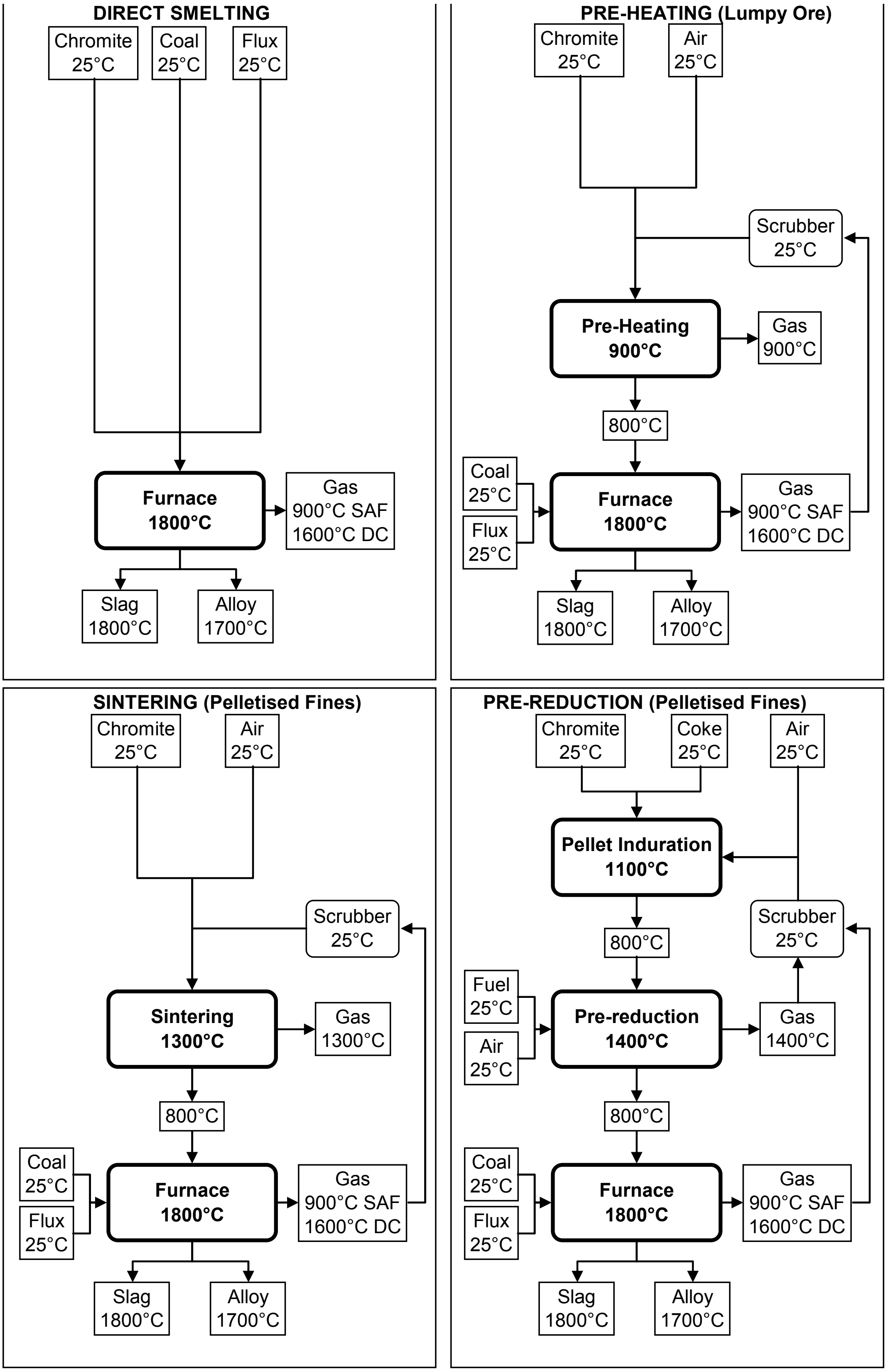

Figure 5: Schematic representation of the various flowsheets evaluated. Unit operating temperatures given are for Kazak chromite. For South African chromite, the furnace is operated at 1750°C with furnace off gas temperatures being 50°C lower than this and the sintering unit is operated at 1200°C.

Table 10: Calculated energy requirements for the various process flowsheet options. (MWh/t).

		Flowsheet	Pre-Heat (Off-gas)	Pre-reduce (Fuel)	Smelt (Electric)	Total	Pre-Heat (Off-gas)	Pre-reduce (Fuel)	Smelt (Electric)	Total
				MWh/t of FeCr alloy				MWh/t of Cr		
SA Chromite	SAF Furnace	Direct Smelting	25°C		3.34	3.34	25°C		6.60	6.60
		Preheating	Transfer temp. 800°C		2.95	2.95	Transfer temp. 800°C		5.82	5.82
		Sintering			2.95	2.95			5.82	5.82
		Pre-reduce 33%		1.61	2.42	4.03		3.31	4.98	8.28
		Pre-reduce 65%		2.64	1.88	4.52		5.49	3.90	9.39
		Pre-reduce 78%		3.15	1.62	4.77		6.58	3.38	9.96
		Pre-reduce 90%		3.71	1.35	5.06		7.81	2.83	10.64
	DC Furnace	Direct Smelting	25°C		4.00	4.00	25°C		7.90	7.90
		Preheating	Transfer temp. 800°C		3.56	3.56	Transfer temp. 800°C		7.03	7.03
		Sintering			3.56	3.56			7.03	7.03
		Pre-reduce 33%		1.61	2.89	4.50		3.31	5.95	9.26
		Pre-reduce 65%		2.64	2.21	4.85		5.49	4.59	10.08
		Pre-reduce 78%		3.15	1.90	5.04		6.58	3.96	10.54
		Pre-reduce 90%		3.71	1.55	5.27		7.81	3.27	11.08
		Flowsheet	Pre-Heat (Off-gas)	Pre-reduce (Fuel)	Smelt (Electric)	Total	Pre-Heat (Off-gas)	Pre-reduce (Fuel)	Smelt (Electric)	Total
				MWh/t of FeCr alloy				MWh/t of Cr		
Kazak Chromite	SAF Furnace	Direct Smelting	25°C		3.72	3.72	25°C		5.32	5.32
		Preheating	Transfer temp. 800°C		3.36	3.36	Transfer temp. 800°C		4.79	4.79
		Sintering			3.30	3.30			4.72	4.72
		Pre-reduce 33%		1.49	2.89	4.39		2.23	4.31	6.53
		Pre-reduce 65%		2.75	2.26	5.00		4.14	3.40	7.55
		Pre-reduce 78%		3.41	1.92	5.33		5.18	2.91	8.08
		Pre-reduce 90%		4.16	1.56	5.72		6.37	2.38	8.75
	DC Furnace	Direct Smelting	25°C		4.47	4.47	25°C		6.38	6.38
		Preheating	Transfer temp. 800°C		4.05	4.05	Transfer temp 800°C		5.79	5.79
		Sintering			4.00	4.00			5.72	5.72
		Pre-reduce 33%		1.49	3.45	4.95		2.23	5.15	7.38
		Pre-reduce 65%		2.75	2.67	5.42		4.14	4.03	8.17
		Pre-reduce 78%		3.41	2.25	5.66		5.18	3.41	8.59
		Pre-reduce 90%		4.16	1.80	5.96		6.37	2.75	9.12

If one reconsiders that the cation ratio (Al_2O_3+Cr_2O_3+Fe_2O_3)/(MgO+FeO) typical of a spinel is expected to be 2:1, it is found that (based on the raw geochemical data) the Kazakh cation ratios range between 2.5-3.0 and those of a typical Bushveld ore between 1.8-2.5. These values would indicate that a greater abundance of trivalent ions are present in the spinel lattice that constitutes the Kazakh ore compared to the more divalent dominated Bushveld ore. The Kazakh ore is therefore deemed naturally more oxidised than the Bushveld ore. Previous workers found that oxidised ore is more readily reduced than unoxidised material and non-stoichiometric chromite is likely to be a more suitable feedstock for the ferro-alloys industry[10]. If the Kazak ore is indeed more oxidised, this could potentially be a plausible explanation for the differences in activation energy between the Cr-rich spinel Kazakh ore and the Fe-rich Bushveld ore.

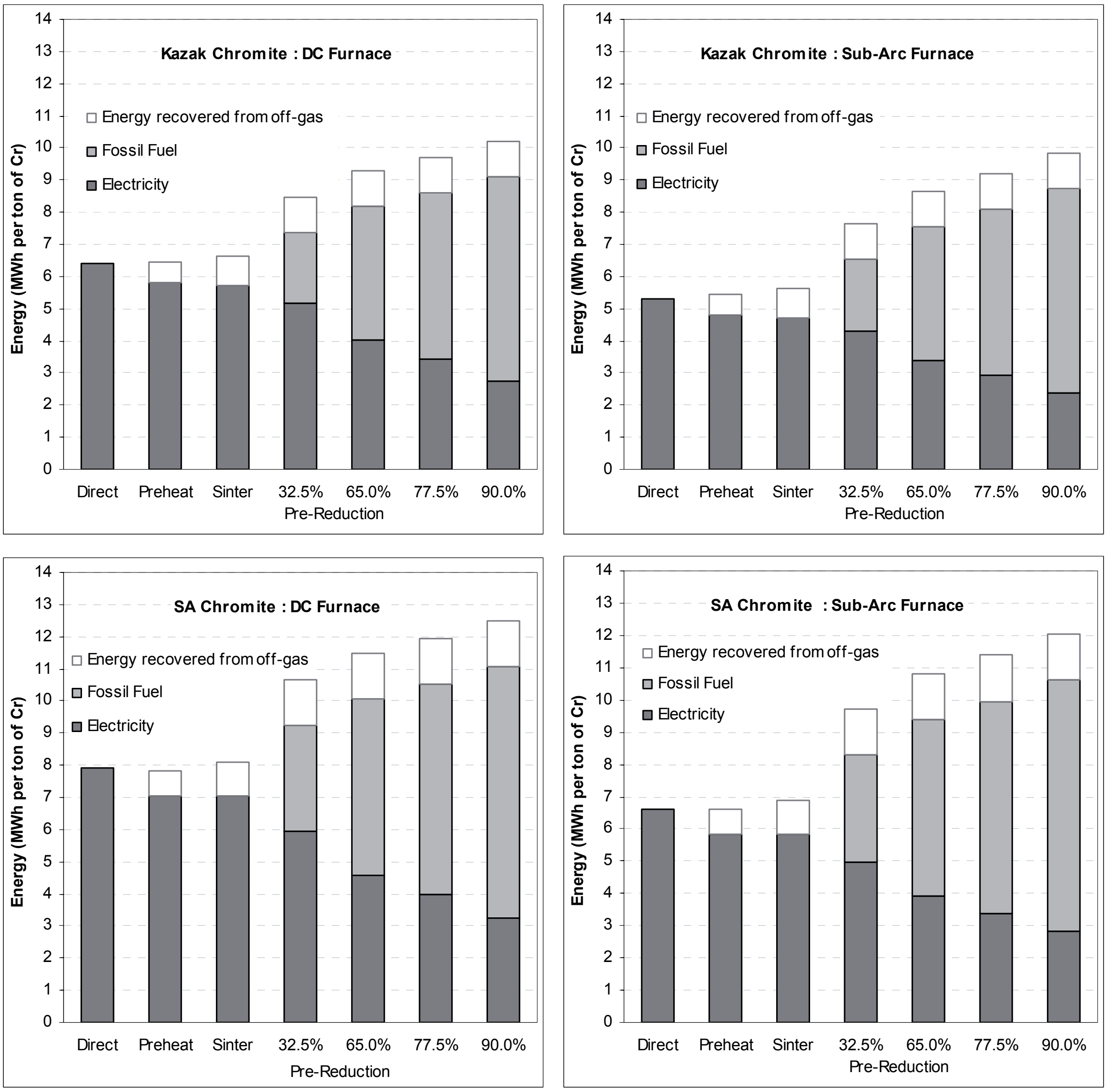

Figure 6: Calculated energy requirements for South African and Kazak chromite for various process flowsheets for a DC or submerged arc furnace operation.

Another important distinction between the Kazak and Bushveld chromites is the difference in the MgO/Al_2O_3 ratio of the ores. The elevated MgO content of the boninitic melt that formed the Kazakh ore resulted in high MgO/Al_2O_3 ratio of the chromites formed, while the tholeiitic component of the magma in genesis of the Bushveld chromite increased the presence of Al_2O_3 available in the chemical system thus lowering the MgO/Al_2O_3 ratio. This has a significant impact on the slag composition during smelting. The slag forming oxides MgO and Al_2O_3 encountered during the smelting of chromite are traditionally fluxed using SiO_2. The approximate compositions of the Kazak and Bushveld chromites in terms of the major slag forming components $MgO\text{-}Al_2O_3\text{-}SiO_2$ are indicated in Figure 3: together with the approximate slag compositions for both assuming a moderate (15%) SiO_2 flux addition. The higher MgO/Al_2O_3 ratio of the Kazakh ore results in a Mg-rich slag with a composition within the primary phase field of forsterite. The Bushveld ore, produces a slag with a composition that lies within the spinel primary phase field. The liquidus temperature of the slag resulting from smelting of Bushveld ore is somewhat (~100°C) lower than that of Kazak, for the same flux addition. More importantly however, is that variations in the MgO/Al_2O_3 ratios, typical of what would be encountered in treating a variety of Bushveld ores, have little effect on the liquidus temperature. The liquidus temperatures of the resulting Kazak slags are however relatively sensitive to differences in the MgO/Al_2O_3 and require a higher flux addition to achieve liquidus temperatures similar to that of the

Bushveld slags. As expected, treating Kazak ores requires a higher smelting temperature or higher flux addition relative to that of the Bushveld, both of which impact on the total energy requirement. The higher MgO/Al_2O_3 ratio of the Kazakhstan chromites does however result in a slag that would be more compatible with a MgO furnace refractory lining as the higher MgO content is more likely to promote the formation of a freeze lining.

In summary, reduction of the relatively Cr-rich Kazakhstan chromite requires a lower activation energy than it's Bushveld equivalent, but has a slag forming oxide component, in particular the MgO/Al_2O_3 ratio, that requires a higher amount of energy to maintain a liquid slag. The Kazakhstan chromite does however offer the advantage of possessing a higher Cr to Fe ratio compared to that of the Bushveld (~4 versus ~2 respectively), which results in a higher grade ferro-chrome alloy. Indeed, smelting tests show that the Kazakhstan chromite is capable of producing an alloy containing over 67% Cr whereas typical values for ferro-chrome produced from Bushveld chromites are more likely to be between 52 and 54%. Combined, these factors make it difficult to judge the energy requirement for smelting the Kazakhstan chromite, which in turn led to the use of simulation software to calculate this energy requirement. In order to ensure the validity of the simulations, South African chromite was included in the calculations, for which a great deal is known about the energy required to smelt.

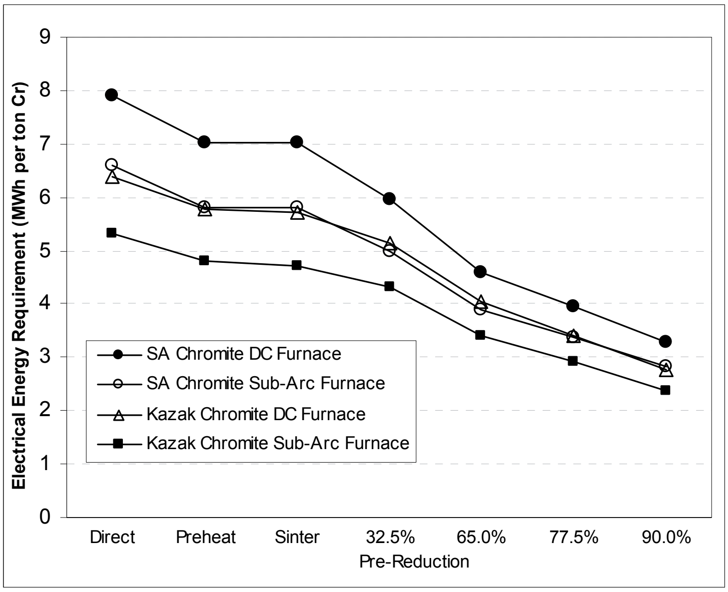

Figure 7: Comparison of the calculated electrical energy requirements for the various process flowsheets.

Of the numerous process flowsheets evaluated, comparison of the direct smelting of South African and Kazakhstan chromites in a submerged arc furnace indicates that 3.34MWh of electrical energy is required per ton of ferro-chrome alloy when smelting South African chromite. This is marginally lower than the 3.72MWh/t required for the Kazakhstan chromite. The Kazakhstan alloy, will contain a higher concentration of chromium and probably realise a higher revenue, it is therefore probably more realistic to compare the energy requirements on the basis of tons of chromium metal produced. In this case the Kazakhstan chromite requires 5.32MWh per ton of chromium produced which is significantly lower than the 6.6MWh required for South African chromites.

Evaluation of pre-heating/sintering and various levels of pre-reduction see a continuous reduction in the amount electrical energy required for smelting culminating in a 60% energy saving (Figure 7:) when smelting highly pre-reduced feed. The overall energy requirement (including fossil fuel) is however increased primarily due to inefficiencies in the utilisation of fossil fuel, which are based on rotary kiln experiences. Improved efficiencies, through the use of rotary hearth or fluid bed pre-reduction units, would significantly impact on the overall energy requirement.
As is expected, DC arc smelting requires more energy than a submerged arc furnace primarily as a result of the higher heat losses from the DC unit. This difference in energy requirement between the

two types of furnace become less significant as increased pre-reduction and pre-heating are applied to the furnace feed. Interestingly, smelting Kazakhstan chromite in a DC furnace requires the same amount of energy as smelting South African chromites in a submerged arc furnace on a MWh per ton of chromium basis with further energy savings being realised if smelting is carried out in a submerged arc furnace.

7 CONCLUSIONS

Kazakhstan chromite samples have been characterised chemically, mineralogically and thermally (pre-reduction and smelting) and compared with South African ores.
The activation energy for reduction of Kazakhstan chromite appears favourable so high levels of both chromium and iron can be expected to be achieved at reasonable temperatures and times in a pre-reduction unit.

Smelting requires the trade off between silica addition and liquidus temperature to be optimised in terms of energy consumption and recovery, but the higher MgO/Al_2O_3 ratio of this deposit will require higher operating temperatures than typically used in the smelting of South African chromites. The resulting slag is however more compatible with a magnesia furnace lining.

The higher MgO/Al_2O_3 ratio of the slag will allow submerged arc furnaces to operate at higher temperatures, which in itself will see a higher degree of chromium reduction in the furnace possibly allowing for higher chromium recoveries if metal entrainment is not an issue i.e. when high proportion of fine ore/concentrate is used.

The use of pre-reduced and pre-heated feed theoretically narrows the difference between the energy consumption between a DC arc and submerged arc furnace. However there is a need for improved pre-reduction technology to the rotary kiln process.

The rotary kiln process has advanced to a larger scale. However the rotary hearth furnace process offers an interesting alternative but has not as yet progressed to successful large-scale operation. The increasing costs of electrical energy and supply considerations in some regions are likely to stimulate further interest in such improved pre-reduction technology both in Kazakhstan, South Africa as well as elsewhere.

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