

# Carbothermic Reduction and Desulphurization of Chromite with Nickel Oxide and Sulphide

W. DRESLER\*, B.C. JENA\*, and A. McLEAN†

\**Laurentian University, Sudbury, Canada*

†*University of Toronto, Toronto, Canada*

Laboratory experiments on the carbothermic reduction of Canadian and Turkish chromite concentrates were conducted in the presence of nickel-containing materials between 1550 and 1650°C. The nickel materials were low-cost nickel oxide sinter 75 and nickel sulphide, all supplied by the International Nickel Corporation (INCO) Ltd, Canada. The chromium-to-nickel ratio was aimed at 2 as generally required for corrosion- and heat-resistant steel. The chromium contents of the extracted high-carbon ferrochromium-nickel alloys ranged between 31 and 48,6 per cent. Sulphur partition ratios of up to 50 were obtained at carbon saturation, and at 1650°C when nickel sulphide was added.

Some desulphurization tests were carried out on ferrochromium-nickel alloys with synthetic slags. Sulphur partition ratios of between 91 and 675 were achieved at basicities spanning 4 to 30.

## Introduction

The production of corrosion- and heat-resistant steels is mainly dependent on the availability of ferrochromium, nickel, and raw steel. Usually, high-carbon ferrochromium and metallic nickel are added to a stainless-steel refining process. In previous work, the authors suggested that cost-intensive nickel or ferronickel could be replaced by low-cost nickel oxide sinter 75, or nickel sulphide, when these materials are charged directly to a chromite reduction process<sup>1,2</sup>. This process generates a high-carbon ferrochromium-nickel alloy that can be utilized as a master alloy for stainless-steel production if the sulphur content is controlled.

The object of the present study was to investigate the optimum amount of nickel sulphide ( $\text{Ni}_3\text{S}_2$ ) that can be added to a carbon-saturated chromite-reduction process operating between 1550 and 1650°C. For this purpose, the partition of sulphur ( $L_s = (\text{S})_{\text{slag}} / [\text{S}]_{\text{alloy}}$ ) between liquid ferrochromium-nickel alloys and reduction slags was studied. Wide ranges of chromium, silicon, and sulphur contents in the alloys and basicities in the slags were covered. The present study also incorporated the determination of sulphur-partition ratios during desulphurization of the alloys with slags based on synthetic calcium and sodium silicate up to high basicities at 1550°C.

## Experimental

Canadian low-grade and Turkish high-grade chromite concentrates were utilized in the laboratory reduction tests. The original chromite ores were upgraded by sedimentation and decantation procedures. For most experiments, low-grade Canadian concentrates with approximately 28 per cent  $\text{Cr}_2\text{O}_3$  and a chromium-to-iron ratio of 1,1 were

utilized with main gangue components of 14,2 per cent  $\text{MgO}$ , 16,3 per cent  $\text{Al}_2\text{O}_3$ , 10,5 per cent  $\text{SiO}_2$ , and 0,4 to 2 per cent  $\text{CaO}$ . The Turkish concentrate had a chromium-to-iron ratio of 4,17 and 59,7 per cent  $\text{Cr}_2\text{O}_3$ , 16,2 per cent  $\text{MgO}$ , 8,5 per cent  $\text{Al}_2\text{O}_3$ , 0,3 per cent  $\text{SiO}_2$ , and 1 per cent  $\text{CaO}$ . The particle size of the concentrate was below 0,21 mm. Flux additions were chemical-grade  $\text{SiO}_2$  and  $\text{CaO}$ . They were used to ensure sufficient fluidity and to control the basicity of the slag. For the reduction tests only, Bell's ratio<sup>3</sup> - B =  $[(\% \text{CaO}) + 0,69 (\% \text{MgO})] / [0,93 (\% \text{SiO}_2) + 0,18 (\% \text{Al}_2\text{O}_3)]$  - was used because it gives a good reflection of the effects of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  on the basicity. For the experiments with low sulphur levels, nickel oxide sinter with 76,2 per cent Ni, <0,01 per cent S, and 0,65 per cent Cu (Tests 1 to 3 in Table I) was added to the burden. Alternatively, nickel was added as nickel sulphide, supplied by the International Nickel Corporation (INCO) Ltd, Canada with approximately 70,4 per cent Ni, 26 per cent S, and 0,58 per cent Cu, to all the other reduction tests. Nickel sulphide is an intermediate product during the processing of pentlandite-containing sulphide ores to metallic nickel. Such ores occur, for example, in the rim of the Sudbury basin and in northern Manitoba.

A typical burden for the Canadian concentrate consisted of

- 150 g of chromite concentrate,
- 28 g of charcoal,
- 16 g of quartzite, and less than
- 13 g of calcium oxide,
- 19 g of nickel sulphide, or
- 17 g of nickel oxide sinter.

Tests 1 to 15 were conducted with chemical-grade charcoal in graphite crucibles. The crucibles, covered with graphite lids, were placed on a pedestal in a 15 kVA

vertical-tube furnace with heating elements of molybdenum disilicide. Experimental temperatures were 1550 and 1650°C. Tests 1 to 3 were conducted under carbon monoxide, and the other tests under ultra-high-purity argon atmospheres. A specific heating and smelting pattern, as shown in Figure 1, was chosen for the chromite reduction. With this heating profile, eruption of the charge by carbon monoxide evolution was avoided.

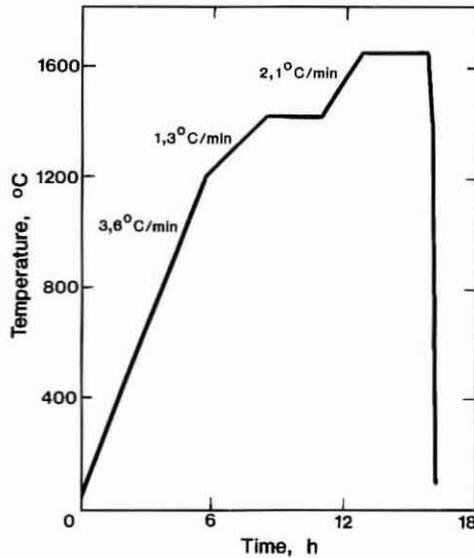


FIGURE 1. Heating and smelting pattern for the experiments

Tests 15 to 21 were desulphurization experiments employing specially prepared master alloys with sulphur contents ranging between 0,2 and 0,7 per cent. The alloys were placed in graphite crucibles together with a desulphurization mixture containing 35 per cent CaO, 35 per cent CaF<sub>2</sub>, and 30 per cent Na<sub>2</sub>CO<sub>3</sub>, or 25 per cent CaO, 25 per cent CaF<sub>2</sub>, 25 per cent Na<sub>2</sub>CO<sub>3</sub>, and 25 per cent Al<sub>2</sub>O<sub>3</sub>. The composition of these mixtures guaranteed a highly fluid slag that allowed good contact with the alloy phase at reaction temperatures of 1550 and 1568°C. The resulting slag-to-metal ratio was very high when compared with that in industrial operations (generally 2,24 for a slag containing 10 per cent SiO<sub>2</sub>). The crucible was covered with a lid that had a 1 mm hole for the escape of gas. The heating pattern was altered to 4 °C/min up to 1060°C and then increased to 6,1°C/min. The reaction time was usually limited to 1,5 hours at the destination temperature.

The sulphur both in the metals and the slags was analysed by use of the combustion-infrared LECO spectrometer. All the other elements and compounds of metals and slags were analysed by induction-coupled plasma spectrometry.

## Results

The analytical results for the alloys and slags obtained in the experiments are listed in Table I. The Cr<sub>2</sub>O<sub>3</sub> and FeO concentrations were found to be around 0,25 and 0,91 per cent at 1650 and 1550°C respectively<sup>4,5</sup>.

TABLE I  
METAL AND SLAG ANALYSES (IN MASS PERCENTAGES) WITH BASICITIES (B) AND TEMPERATURES (T) IN DEGREES CELSIUS

Test	T	Metal					Slag						
		Cr	Cr/Fe	Ni	Si	[S]	(S)	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	(S)/[S]	B*
<i>Smelting reduction tests, Ni source NiO</i>													
1	1650	36,5	1,20	20,2	5,46	0,019	0,52	25,7	11,4	32,0	30,0	27,4	0,83
2	1650	37,6	1,07	17,7	5,18	0,015	0,32	18,4	12,8	22,9	31,7	21,6	0,94
3	1650	50,0	3,94	27,4	4,4	0,014	0,35	38,3	7,2	35,1	19,5	23,3	0,93
<i>Smelting reduction tests, Ni source NiS</i>													
4	1650	36,7	1,06	19,8	6,86	0,10	4,45	20,9	18,5	31,2	20,2	44,5	1,01
5	1650	35,1	1,08	18,5	9,99	0,093	4,60	21,7	23,7	28,3	20,6	49,5	1,29
6	1650	36,7	1,17	17,1	4,21	0,39	5,34	28,4	7,1	32,6	26,4	13,7	0,76
7	1650	44,9	3,78	25,8	7,61	0,116	4,75	26,7	23,3	29,0	14,8	40,9	1,41
8	1650	47,6	3,87	24,9	8,03	0,145	5,85	35,1	10,8	26,3	18,6	40,3	1,26
9	1550	31,0	0,92	18,7	5,37	0,94	3,28	16,6	10,0	32,9	32,8	3,5	0,59
10	1550	37,5	1,09	21,2	1,27	0,91	2,79	19,4	17,5	40,1	20,6	3,1	0,75
11	1550	40,7	1,21	19,0	1,37	0,69	3,44	19,4	18,6	40,1	20,9	5,0	0,78
12	1550	38,2	1,16	19,9	1,97	0,61	3,39	19,9	18,6	40,0	21,9	5,6	0,79
13	1550	38,2	1,08	21,2	3,23	0,23	3,57	20,2	17,6	37,4	20,6	15,5	0,82
14	1550	37,4	1,05	19,7	4,03	0,64	3,23	28,9	3,8	29,0	32,5	5,0	0,72
<i>Desulphurization tests</i>													
15	1568	38,8	1,13	19,5	3,45	0,018	1,64	0,5	65,1	19,3	1,1	91,1	3,4
16	1568	38,8	1,08	19,5	0,9	0,022	2,94	1,9	64,5	16,3	2,8	133,6	4,1
17	1568	44,6	1,44	18,0	trace	0,005	1,70	0,2	51,3	5,7	32,8	340	9,0
18	1550	44,9	1,51	14,2	0,08	0,003	1,79	0,2	70,6	3,8	0,3	600	18,6
19	1550	48,6	1,64	12,7	0,08	0,002	1,35	0,1	69,6	3,0	0,2	675	23,2
20	1550	39,9	1,25	20,7	0,10	0,004	0,94	0,5	75,7	9,1	0,3	235	8,4
21	1550	37,0	1,13	22,0	0,08	0,004	0,87	0,4	74,6	11,1	0,2	215	6,4

\*For Tests 1 to 14, Bell's ratio was applied

For Tests 15 to 21,  $B = [(\%CaO) + (\%MgO)]/[(\%SiO_2)]$  was applied

Tests 1 to 3 were conducted with additions of nickel oxide. The sulphur source for these tests was mainly the chromite concentrates. For these tests, sulphur-partition ratios were found between 21,6 and 27,4 at 1650°C. The tests indicated low sulphur concentrations between 0,014 and 0,019 per cent in the alloy.

Tests 4 to 8 were conducted at 1650°C with nickel sulphide as the nickel source. The basicity was controlled with lime additions so that a wide range (spanning 0,76 to 1,41) of Bell's ratio was covered. These tests indicate that high sulphur amounts of approximately 5 per cent can be absorbed in the slags. The sulphur partition ratios ranged from 13,7 to 49,5, depending on the slag basicity, as shown in Figure 2.

Tests 9 to 14 were conducted at 1550°C, and indicate expected lower partition ratios ranging from 3,1 to 15,5, with high sulphur concentrations of up to 0,94 per cent in the alloy. The sulphur contents in the slags remained close to 3,3 per cent.

Tests 15 to 21 were carried out in order to determine the sulphur partitioning under strong basic conditions, at carbon saturation, and mainly at 1550°C. For the desulphurization experiments, the basicity was expressed as  $B = [(\%CaO) + (\%MgO)] / [(\%SiO_2)]$ . The addition of sodium carbonate increased the oxygen potential at the beginning of the desulphurization process so that significant desilicization occurred in some tests, resulting in relatively low slag basicities for Tests 15 and 16.

All the calcium fluoride present was listed as calcium oxide. Sulphur-partition ratios of 91 to 675 were found, depending on the slag basicity.

The experimental results are shown in Figure 3, demonstrating the effect of basicity as a function of sulphur-partition ratio. The regression line incorporates all the reduction and desulphurization tests at 1550 and 1568°C. The correlation coefficient,  $R^2$ , was 0,972, indicating a satisfactory correlation.

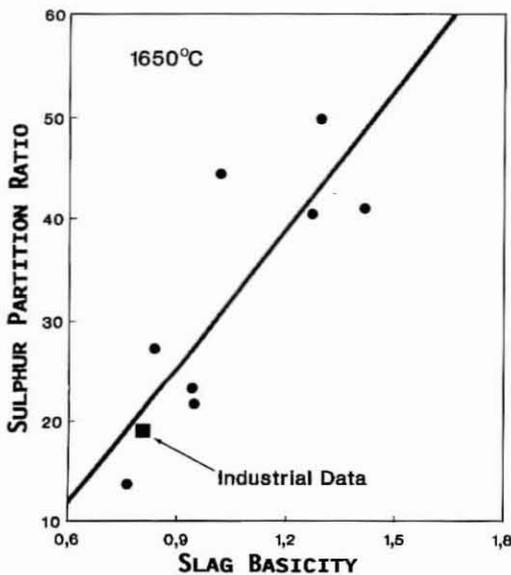


FIGURE 2. Sulphur-partitioning ratio as a function of basicity in the reduction tests

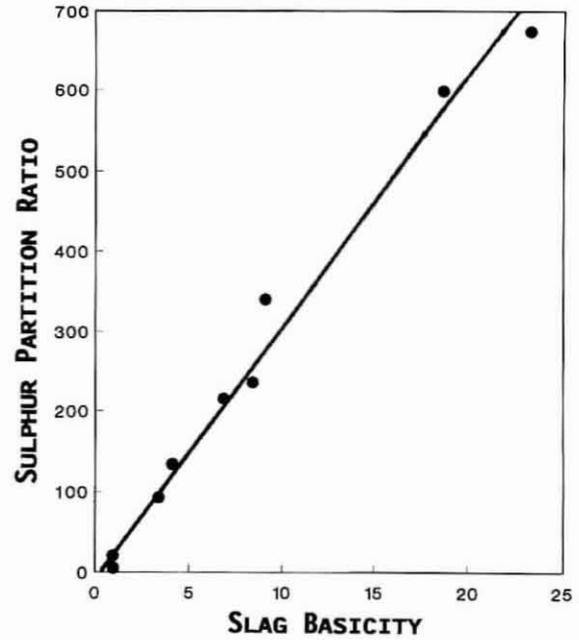
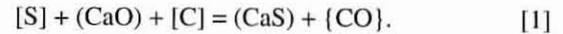


FIGURE 3. Sulphur-partitioning ratio as a function of basicity in the reduction and desulphurization tests at 1550°C

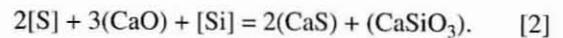
## Discussion

### Sulphur Reaction

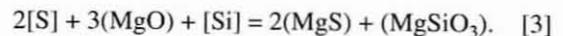
The overall reaction of sulphur between a carbon-saturated alloy and a slag containing liquid lime can be represented by



Since considerable amounts of silicon, ranging between 1,3 and 10 per cent, were formed during the reduction tests, sulphur can be considered to have been transferred from the alloy to the slag with the participation of silicon instead of carbon, forming  $CaSiO_3$  according to reaction [2]:



When lime is deficient in chromite-reduction processes (Test 14), lime is replaced by the less-effective sulphur remover, magnesia, according to reaction [3]:



If silicon is responsible for the removal of sulphur from the alloy, the silicon concentration and the sulphur partition should indicate a significant correlation. This is shown in Figure 4 for the reduction tests at 1550 and 1650°C. Since the silicon formation is strongly favoured by temperature<sup>6</sup>, this simplified approach is adapted to both temperatures. Figure 4 demonstrates a correlation in that increasing silicon contents result in improved sulphur partitions. Unfortunately, a definite scatter of the results is apparent, being expressed with a correlation coefficient of  $R^2 = 0,78$  for all the data points.

The modest correlation of Figure 4 may be due to the conditions adopted in the present experiments. Since the reaction time was generally limited to 2 hours, equilibrium was not attained for the complete system. This is valid, particularly for the silicon and sulphur partitions, where a reaction time of 5 hours has been suggested<sup>5,7-9</sup>. Also, the

slag composition or basicity was not considered in the graph, which also contributed to the irregular distribution of the data points.

Turkdogan *et al.*<sup>6</sup> derived two relationships, equations [4] and [5], that allow the determination of the sulphur partition for blast-furnace conditions at a defined temperature, slag composition, and silicon content in the metal:

$$k_{\text{sis}} = L_s \sqrt{(\% \text{SiO}_2) / [\% \text{Si}] [1/(\% \text{CaO})]} \quad [4]$$

$$\log k_{\text{sis}} = 6327/T - 4,43 + 1,4B. \quad [5]$$

$$B = [(\% \text{CaO}) + (\% \text{MgO})] / [(\% \text{SiO}_2)]. \quad [6]$$

When these equations are applied to the reduction tests conducted at 1650°C (1 to 8), the calculated sulphur-partition ratios are on average 2,4 times larger than the experimental ratios. The same comparison for the tests conducted at 1550°C (9 to 14) leads to a better agreement, the calculated partition ratios being larger by a factor of 1,36 than the experimental ratios. This suggests that carbon-saturated ferrochromium–nickel melts retain sulphur more strongly than do iron melts. This finding may be understood in the light of the difference in the slag composition between ferrochromium and iron reduction slags. While blast-furnace slags are much richer in the stronger basic oxide, CaO (approximately 40 per cent), ferrochromium process slags usually contain less than 18 per cent CaO.

### Sulphide Capacities

The ability of a slag to absorb sulphur is commonly described by the sulphide capacity,  $C_s$ , which is defined according to

$$C_s = (\% \text{S})_{\text{slag}} (P_{\text{O}_2}/P_{\text{S}_2})^{1/2}. \quad [7]$$

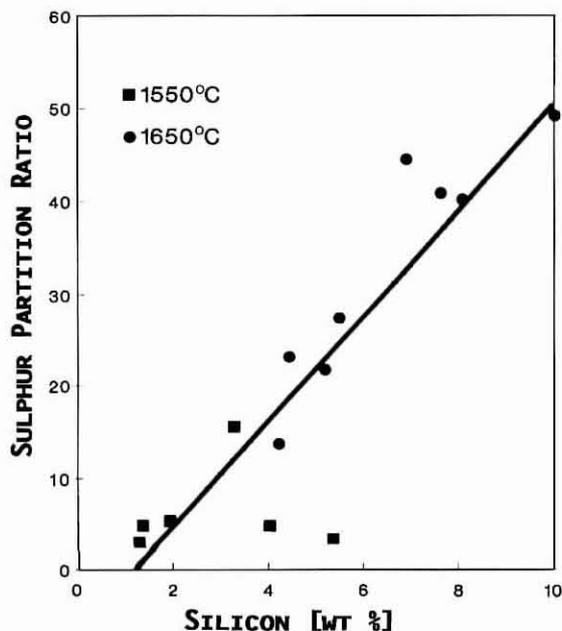


FIGURE 4. The effect of silicon on the sulphur-partitioning ratio in the reduction tests

Sosinsky and Sommerville<sup>10</sup> developed equation [8], which allows the determination of the sulphide capacity for any slag composition at any temperature between 1400 and 1700°C:

$$\log C_s = [(22690 - 54640\Lambda)/T] + 43,6\Lambda - 25,2, \quad [8]$$

where  $\Lambda$  is the optical basicity and can be evaluated from a knowledge of the electronegativity of all the slag components<sup>10</sup>. The sulphide capacities were calculated according to equation [8] for the chromite-reduction tests, only the major slag components – MgO, CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> – being taken into consideration. The data for  $\log C_s$  ranged from –3,35 to –4,0 at 1650°C, and fell well within the normal range for other slags<sup>10</sup>. At 1550°C, the data fell close to –4,35.

An attempt was made to estimate the oxygen potential under the present experimental conditions from equation [7] and the knowledge of the sulphide capacity from equation [8]. The required thermodynamic data for the determination of the partial pressure of sulphur are listed in the Addendum. The oxygen partial pressure was estimated to be  $4 \times 10^{-14}$  atm. at 1650°C. The oxygen pressure would be  $5,9 \times 10^{-16}$  atm. under ideal experimental conditions, with thermodynamic equilibrium attained in an atmosphere of pure carbon monoxide and at a carbon activity of unity. Nevertheless, the considerably low value of  $4 \times 10^{-14}$  atm., apparently attained under the present experimental conditions, is another reason for the relatively high sulphur-partition ratios.

### Prediction of the Sulphur Partition

Katayama *et al.*<sup>8</sup> demonstrated, for iron–chromium alloys containing up to 17,2 per cent Cr, that the logarithm of the sulphur-partition ratio can be described with an expression of the type

$$\log L_s = a \log N_{\text{CrO}} + b[\text{mass}\% \text{Cr}] + c \sum K_i N_i + d/T + e, \quad [9]$$

where  $K_i$  and  $N_i$  are the equivalent coefficient for lime and the molar fraction of the major slag component,  $i$ , respectively.

In the present study, it was found that equation [10] best represents the experimental data:

$$\log L_s = -0,445 \log N_{\text{CrO}} + 0,0088 [\text{mass}\% \text{Cr}] + 2,22 \sum K_i N_i - 680/T - 0,002, \quad [10]$$

with

$$K_i N_i = N_{\text{CaO}} + 0,75 N_{\text{MgO}} - 0,2 N_{\text{Al}_2\text{O}_3} - N_{\text{SiO}_2} \quad [11]$$

The correlation between the experimental ( $\log L_s$ )<sub>exp</sub> and the theoretical ( $\log L_s$ )<sub>theo</sub> sulphur-partition ratios is shown in Figure 5. The correlation coefficient,  $R^2$ , for the data is 0,928.

### Industrial Application

Sulphur concentrations in industrial chromite-reduction slags are usually between 0,2 and 0,35 per cent, with sulphur concentrations of carbon-saturated ferrochromium ( $a_c = 1$ , Raoultian standard state) at the higher end of the range<sup>11</sup>. A carbon-saturated ferrochromium alloy, of charge chrome quality with an average composition of 63,6 per cent Cr, 7,43 per cent C, and 4,9 per cent Si, generally contains<sup>11</sup> between 0,012 and 0,022 per cent S at slag

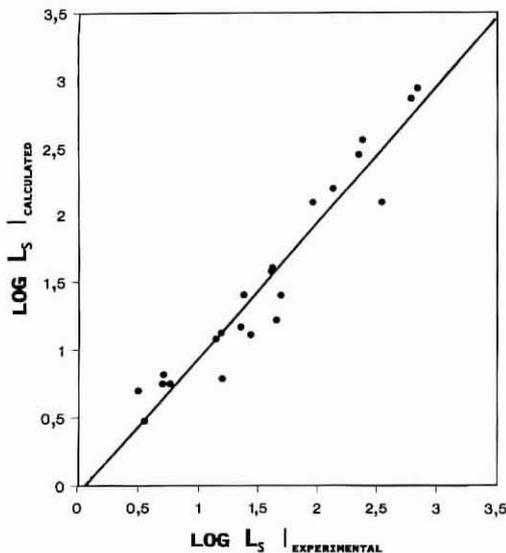


FIGURE 5. Correlation between the logarithms of the calculated and the experimentally determined sulphur-distribution ratios

basicities of approximately 0,8. An average sulphur-partition ratio is then approximately 19, which is in agreement with the experimental results at 1650°C, as shown in Figure 2.

A ferrochromium alloy that is not carbon-saturated, of a '4-6 ferrochrome' quality, can contain<sup>12</sup> between 0,08 and 0,12 per cent S. Such an alloy can have a composition, for example<sup>12</sup>, of 64,5 per cent Cr, 4,4 per cent C, and 0,7 per cent Si. For this particular composition, the Raoultian activity of carbon<sup>4</sup> would be 0,045, indicating that the alloy is strongly under-saturated with carbon, and therefore high sulphur concentrations must be expected. This example demonstrates that it is not unusual in the ferrochromium industry to produce an alloy containing high concentrations of sulphur. The market specification for sulphur in high-carbon ferrochromium (charge chrome and 4-6 ferrochrome qualities) is below 0,05 per cent S. Therefore, desulphurization has to be conducted. The common practice under these conditions is desulphurization with a basic slag that originates from an in-house low-carbon ferrochromium operation.

A comparison of industrial data with the results of tests 4, 7, and 8 indicates similar sulphur contents of approximately 0,12 per cent, although nickel sulphide was used. However, to achieve such a relatively low value in a chromite-reduction process with nickel sulphide in the charge, three conditions have to be satisfied:

- (1) operation has to occur under carbon saturation,
- (2) the operating temperature must be approximately 1650°C, and
- (3) limestone has to be added to ensure a CaO content in the slag of more than 10 per cent.

It is apparent that desulphurization is required if nickel or portions of nickel are replaced with nickel sulphide at a ratio of Cr/Ni = 2. A reduction process with subsequent external desulphurization was proposed based on mass balances and on the results of sulphur-partition ratios found in this study.

In the proposed chromite-reduction process, it was assumed that half of the required nickel is supplied by

technical nickel sulphide and half by nickel oxide sinter 75. This results in a charge of 76 kg of nickel sulphide and 70 kg of nickel oxide per tonne of chromite, with a total of 20,9 kg of sulphur per tonne of chromite in the charge.

This value includes a reasonable allowance for sulphur in the carbonaceous reducing materials and in the chromite concentrate. A sulphur-partition ratio of 15 is certainly a reasonable assumption for a reduction slag with 15 per cent CaO and a temperature of 1650°C at the tap. The ferrochromium-nickel alloy will then contain 0,16 per cent S at a slag-to-metal ratio of 1,3. Subsequent external desulphurization would be conducted with 25 kg of desulphurization mixture per tonne of alloy on the assumption of a modest sulphur-partition ratio of 150. After the treatment, the alloy would contain 0,033 per cent S, which is an acceptable value for the production of stainless steel and satisfies market standards.

## Conclusions

The main results of the laboratory-scale experiments can be summarized as follows.

- (1) Depending on the basicity, temperature, and silicon content of the alloy, sulphur-partition ratios of between 3 and 50 were found in the chromite-reduction tests.
- (2) Desulphurization tests indicated that the sulphur-partition ratios varied from 91 to 675 at a slag basicity ranging from 3,4 to 23,2.
- (3) Sulphide capacities were estimated for the reduction tests, and it was found that  $\log C_s$  was between -3,35 and -4,35.
- (4) A relationship for the estimation of sulphur-partition ratios was determined.
- (5) The sulphur concentration was theoretically estimated for an industrial reduction operation when half of the required nickel was supplied by nickel sulphide. After external desulphurization, the sulphur content was predicted to be 0,033 per cent in the final product, which is a master alloy suitable for the stainless-steel industry.

## Acknowledgments

The financial support provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged. This research is also supported by the Energy, Mines and Resources Canada (CANMET), the Centre for Chemical Process Metallurgy (C-CPM) in Toronto, and the Ministry of Energy and Mines, Manitoba. The authors also thank the International Nickel Corporation (INCO) in Sudbury for analytical support.

## References

1. Dresler, W., and McLean, A. (1990). In: *Ferrous and Non-Ferrous Alloy Processes*, ed. R.A. Bergman, Toronto, Pergamon Press. pp. 177-185.
2. Dresler, W., and McLean, A. (1991). In *Refractory Metals Symposium*, eds. KN.C. Liddell *et al.*, New York, Pergamon Press. pp. 177-197.
3. Venkatadri, A.S., Srinivasan, C.R., and Gupta, S.K. (1989). Prediction of sulphide capacities of blastfurnace slags. *Scan. J. Met.*, vol. 18, no. 2. pp. 89-94.

4. Dresler, W. (1989). In *47th Elec. Fur. Conf. Proc. AIME*, Warrendale, Iron and Steel Society, Inc. pp. 49-55.
5. Dresler, W., and McLean, A. (1992). The extraction of ferrochromium in the presence of nickel from Bird River chromite ores. *Can. Metall. Q.*, accepted for publication.
6. Turkdogan, E.T., Kor, G.J.W., and Fruehan, R.J. (1980). In *The making, shaping and treating of steel*, 10th edn, ed. Association of Iron and Steel Engineers, Pittsburgh, Herbeck and Held. Chap. 13, pp. 450-453.
7. Kawai, Y., Mori, K., and Iguchi, M. (1972). In *Metallurgie der Stahlherstellung*, ed F. Oeters, Berlin, Springer-Verlag. Chap. 4, pp. 198-201.
8. Katayama, H.G., Tsao, T., and Matsushima, N. (1988). Chromium and sulphur distribution between liquid Fe-Cr alloy and calcium aluminate based slag for ladle refining. *Trans. ISIJ*, vol. 28. pp. 186-191.
9. Susaki, K., Maeda, M., and Sano, N. (1990). Sulphide capacity of CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slags. *Metall. Trans. B*, vol. 21B. pp. 121-129.
10. Sosinsky, D.J., and Sommerville, I.D. (1986). The composition and temperature dependence of the sulphide capacity of metallurgical slags. *Metall. Trans. B*, vol. 17. pp. 331-337.
11. Volkert, G. (1971). In *Metallurgie der Ferrolegierungen*, 2nd edn, eds. G. Volkert and K.-D. Frank, Berlin, Springer-Verlag. Chap. B II, p. 326.
12. Archives Elektrowerk Weisweiler GmbH, FRG (1973). Cited with permission of GfE and EWW, Düsseldorf, FRG.
13. Sigworth, G.K., and Elliott, J.F. (1974). The

thermodynamics of liquid dilute iron alloys. *Met. Sci.*, vol. 8. pp. 298-310.

### Addendum: Determination of Sulphur Partial Pressure

The sulphur pressure was estimated from the sulphur concentration in the metal phase by application of the Wagnerian Taylor series expansion with the interaction coefficients as given by Sigworth and Elliott<sup>13</sup>:

$$\log h_s = \log[S] + e_s^s[S] + r_s^s[S]^2 + e_s^c[C] + r_s^c[C]^2 + e_s^{Cr}[Cr] + e_s^{Si}[Si] + r_s^{Si}[Si]^2, \quad [A1]$$

where  $h_s$  is the sulphur activity with respect to the standard state of 1 mass per cent. The interaction coefficients are listed in Table A1. The sulphur pressure can then be determined from equation [A2]:

$$\ln P_{S_2} = -32500/T + 5,639 + 2 \ln h_s. \quad [A2]$$

For the reduction experiments, the sulphur pressures ranged from  $0,09 \times 10^{-6}$  to  $64,7 \times 10^{-6}$  atm.

TABLE A1  
INTERACTION PARAMETERS FOR SULPHUR<sup>13</sup>

System	Parameter	1650°C
Fe-S	$e_S^S = 233/T - 0,153$	-0,0318
	$r_S^S = -0,0009$	-0,0009
Fe-S-C	$e_S^C = 0,11$	0,11
	$r_S^C = 0,0058$	0,0058
Fe-S-Cr	$e_S^{Cr} = -94,2/T + 0,0396$	-0,00936
Fe-S-Ni	$e_S^{Ni} = 0$	0
Fe-S-Si	$e_S^{Si} = 0,063$	0,063
	$r_S^{Si} = 0,0017$	0,0017