COAL BASED DIRECT REDUCTION OF PREOXIDIZED CHROMITE ORE AT HIGH TEMPERATURE

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ABSTRACT

Reduction of preoxidized chromite ore composite pellets using coal reductant is investigated at high temperature (1500 ^{0}C). Chromite ore oxidized in air at 900 ^{0}C for 2h duration is used as base material for carrying out the reduction studies. During preoxidation of chromite ore, the FeO present in chromite spinel oxidizes to Fe_2O_3 (sequioxide) in the form of exholved precipitate on the surface of chromite grains and generates cation vacancies. The preoxidized ore is reduced using coal reductant and fluxes (lime, quartz). The effect reductant coal, fluxes and degree of preoxidation of initial chromite on Fe and Cr metallization is studied. About 80% of iron and 77% of chromium metallization is observed in the reduced product. Clear slag and metal separation is achieved during reduction. It is also observed that preoxidation of chromite ore improves the degree of Fe and Cr metallization during reduction process. The aim of this research is to develop a pre-reduction process using oxidized chromite ore which will help to minimize the energy and coke consumption in ferrochrome production process.

1 INTRODUCTION

The mineral chromite is the only significant ore mineral of chromium. Chromite (with suitably high chromium to iron ratio) is smelted to produce ferrochromium, an alloy of iron and chromium that is a critical raw material in the production of stainless steel. Historically, ferrochromium is produced worldwide mostly in submerged arc furnace (SAF) process. However, the SAF process is highly energy intensive and requires Low Ash Minerals (LAM) coke as a reductant. In past, Outokumpu, Kawasaki, and Krupp investigated various possibilities to improve the SAF process 1). Their developments mainly included pre-reduction and preheating methods in order to improve chromium recoveries and minimize smelting costs. However, most of these pre-reduction techniques can not be used directly for processing MgO rich Indian Chromite ores especially Sukinda chromite ores due to their highly refractory nature 2). Therefore a new process is developed with objective of effective pre-reduction of Sukinda Chromite ores, wherein chromite ore is subjected to oxidation before its reduction 3,4,5). Preoxidation enhanced the reactivity of chromite spinel and thereby increased the degree of reduction. In this paper, the effect of coal reductant, fluxes (lime, quartz) and also the effect of degree of preoxidation on Cr and Fe metallization during reduction is examined with aim to gain a better understanding of the reduction mechanism of preoxidized chromite ores.

1.1 Mineralogy of Chromite Ore

Natural chromite is a mixture of chromium and iron oxide, with varying amounts of magnesium and aluminum with general formula $(Fe^{2+}, Mg)O.[Cr, Al, Fe^{3+}]_2 O_3$. Chromite being the spinel group of mineral can be represented by chemical formula of chrome spinels as AB_2O_4, where A represents divalent cations (i.e. Fe, Mg) in the tetrahedral sites, and B represents trivalent cations (i.e. Cr, Al, Fe) in the octahedral sites. Each unit cell is made up of eight AB_2O_4 units, where the cubic close-packing of 32 oxygen atoms provides 64 tetrahedral and 32 octahedral sites6). The relative proportions of the various cations, oxidation state of iron and mineralogical properties of the ore vary from source to source.

2 EXPERIMENTAL

2.1 Materials Preparation

The chromite ore from Sukinda chromite mines, Orissa, India is studied. The cumulative size analysis and weights retained in different size fractions for chromite ore is given in **Figure 1**. It can be seen from Figure 1 that the d_{80} (80% passing) of the particles in the ore is about 206 μm. The chemical analysis of the ore, reductant coal (anthracite), quartz, flux (lime) and bentonite (as binder) is given **Table 1**. Anthracite coal and the fluxes are used in powdered form having average particle size of about 55μm. The raw materials are mixed at different ratios and agglomerated by using disc pelletizer to form green pellets feed for reduction process.

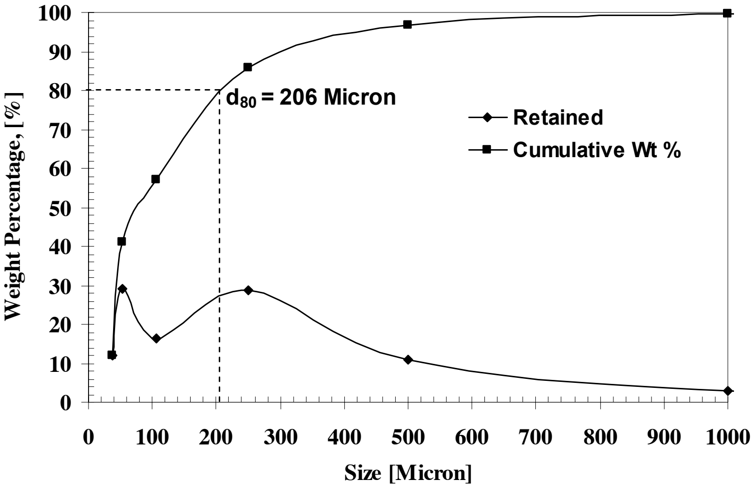


Figure 1: Cumulative size analysis and weights retained in different size fractions for chromite ore

Table 1: Chemical analysis of raw materials for reduction process

Item	**Chemical analysis (wt%)**					
	Fe(t)	**Cr_2O_3**	**CaO**	**MgO**	**SiO_2**	**Al_2O_3**
Chromite Ore	11.5	41.8	0.02	8.8	6.3	12.6
Lime	2.9	-	64.6	0.9	1.9	0.05
Quartz	0.28	-	-	-	99.4	0.4
Bentonite	7.7	-	1.05	1.7	58.0	5.5
	Proximate analysis of coal, wt % (wet basis)					
Anthracite Coal	**FC**		**VM**		Ash	Moisture
	73.5		12.5		10.0	4.0

2.2 Experimental Procedure

A chamber furnace is used to carry out the pre-oxidation of chromite ore. The oxidized chromite ore is prepared by heating the initial chromite ore for 2h isothermally at 900 ^{0}C in a chamber furnace. A constant flow rate of 40 lpm air is purged inside the furnace to maintain oxidized atmosphere during the preoxidation stage. The preoxidized chromite ore is then used in reduction studies.

A horizontal tubular furnace is used to conduct the reduction experiments at 1500 ^{0}C. Throughout the reduction experiments nitrogen gas having 99.0 % purity (rest impurities like oxygen and moisture) purged at rate of 5.0 lpm through the furnace in order to maintain the inert atmosphere within furnace during reduction. A schematic diagram of the horizontal tube furnace used in the reduction studies is shown in Figure 2. The green pellets are produced by agglomeration of pre-oxidized chromite ore, quartz, lime, binder (bentonite) and reducing agent (coal) for carrying out the reduction process. The weighed pellets were placed in the alumina crucible and inserted in the tube furnace at room temperature (25^{0}C). The heating is done such that a constant heat cycle is followed in all the experiments. A typical heating and cooling cycle used in the reduction experiments is shown in Figure 3. A constant holding time of 2.5h at 1500 ^{0}C is maintained in all the reduction experiments. After each experiment, the crucible was taken out of the furnace and the weight of the reduced products is noted and subsequently subjected to chemical analysis.

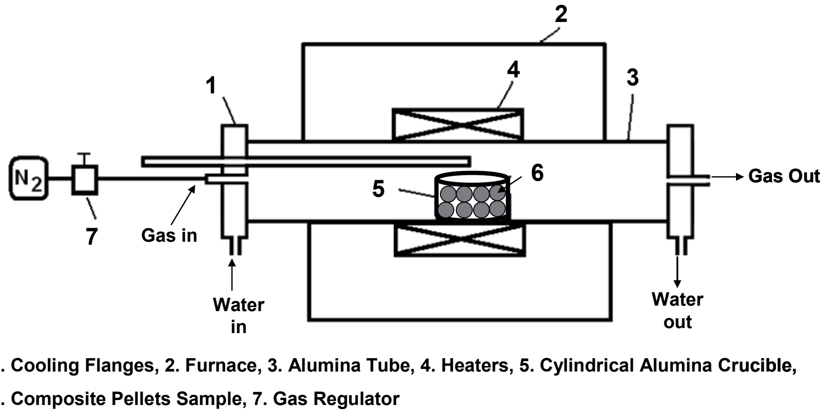


Figure 2: Schematic diagram of horizontal tube furnace operation

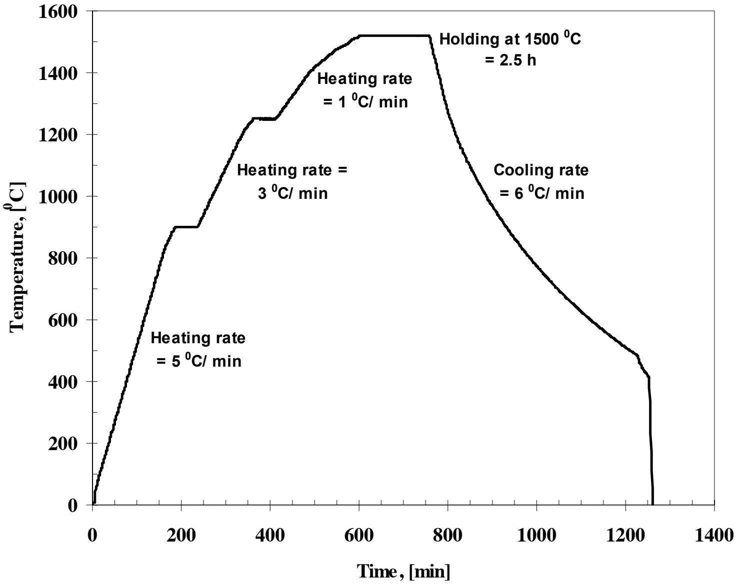


Figure 3: Typical heating and cooling cycle used during reduction experiments

2.3 Estimation of chromium metallization

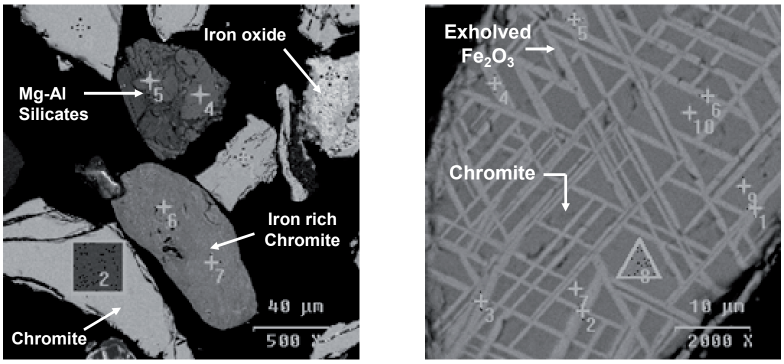
The method for estimation of total chromium analysis in a reduced sample is instituted process. However, for estimation of metallic chromium in a reduced sample is developed in the present study. For this, 0.25g of the finely ground (<100mesh) of the partially reduced chromite sample is taken in a round bottomed flask fitted with a reflux condenser. An acid mixture is prepared by adding 100ml of ortho-phosphoric acid and 400 ml of sulfuric acid to 500 ml of water. 100ml of the acid mixture is added to the sample and the contents are refluxed for 90 minutes. The contents are cooled and filtered through Whatman No. 41 filter paper and the residue washed five times with hot water. The filtrate and the washings are made up to 250ml in a volumetric flask and the chromium concentration is measured by ICP emission spectrometric method.

The method is validated by analyzing a certified reference material of Ferro chrome having a known concentration of metallic chromium. The recovery of metallic chromium is found to be complete. When a pre-oxidized chromite ore sample containing only Cr_2O_3 and no metallic chromium is treated in a similar manner, the chromium content of the solution is found to be less than 0.5%, indicating that only a negligible amount of Cr_2O_3 passes into solution in the treatment process given above and the method given is highly selective for the determination of metallic chromium. The chromium metallization in a reduced chromite sample is obtained as a ratio of metallic chromium to total chromium.

3 RESULTS AND DISCUSSION

3.1 Preoxidation of Chromite Ore

The raw chromite ore is oxidized in air for 2h duration at 900 ^{0}C using the chamber furnace. This pre-oxidized chromite ore is used as base material for the reduction studies. As the iron is present in the form of FeO in Indian chrome spinel, during oxidation reaction, the FeO present in spinel gets oxidized to Fe_2O_3 as exsoluted sequioxide (Fe_2O_3) phase on chromite mineral grain and additional cation vacancies are generated. A representative comparison of the SEM micrograph for raw chromite and pre-oxidized chromite at 900 ^{0}C for 2h duration is shown in Figure 4. It can be seen from Figure 4b that after preoxidation of chromite the sequioxide phase has precipitated on the surface of chromite grain in a typical Widmanstatten pattern. The bright lines are iron rich phases and the matrix is magnesium rich phase. It is observed from these results that iron is precipitating from the matrix on {111} crystallographic planes.



Point	O	Mg	Al	Si	Cr	Fe
1	22.7	11.7	8.4	0.5	46.9	7.7
2	23.3	10.3	7.9	0.6	46.4	10.9
3	21.2	0.0	1.7	2.7	2.4	71.3
4	31.9	10.6	3.5	32.0	0.3	11.3
5	32.2	11.1	1.7	34.1	0.4	12.1
6	26.4	0.5	7.3	3.1	30.9	30.0
7	24.5	0.0	7.7	2.9	37.2	25.8
8	22.7	10.2	7.0	0.7	47.8	10.2

Point	Mg	Cr	Fe
1	7.3	45.9	15.5
2	4.2	47.1	28.8
3	3.3	47.2	20.2
4	2.0	47.8	22.5
5	0.0	46.6	26.1
8	12.5	46.8	9.3
9	12.6	46.7	8.8
10	13.3	47.4	8.6

(a) **(b)**

Figure 4: SEM Micrograph of raw (un-oxidized) chromite-(a) and preoxidized chromite particle-(b)

The pre-oxidation of chromite resulting in a typical Widmanstätten pattern on the surface of chromite grain is in accordance with the established theory of oxidation and precipitation of sesquioxide phase. According to this theory, the preferential crystallographic orientation of Widmanstätten lamellae was along the {111} plane of spinel matrix phase. The {111} planes of spinel and the {0001} planes of sesquioxide have a similar close packing arrangement of oxygen ions, which account for the common orientation of sesquioxide lamellae along the {111} plane of the spinel matrix. Tapered terminals develop at the intersection of two or more lamellae, which are indicative of a diffusion-controlled process. Also, in an oxidizing atmosphere, in addition to the intrinsic driving force for phase transformation, the imposed oxygen chemical potential promotes the diffusion of Fe^{2+} ion from the core of chromite grain towards the solid-gas interface on the surface of the grain. This outward diffusion of Fe^{2+} cations and oxidation to Fe^{3+} cations takes place via following reactions:

$$\frac{1}{2}O_2 \xrightarrow{T} O_o^{2-} + V_{cat}^{n} + 2.h^{\bullet} \qquad [1]$$

$$2Fe^{2+} \xrightarrow{T} 2Fe^{3+} + 2.e^{'} \qquad [2]$$

Where O_o^{2-} represents oxygen anions on the cubic closed packed lattice, V_{cat}^{n} is cation vacancy, $h^{\bullet}$ is hole, and $e^{'}$ is electron. Oxidation of chromite ore results in opening up of the spinel structure. Thus newly formed Fe_2O_3 phase alonwith the additional vacancies generated during oxidation improves the reactivity of chromite ore and helps in the slag formation at lower temperatures during reduction.

3.2 Reduction of Pre-Oxidized Chromite Ore

The preoxidized chromite ore at 900 ^{0}C for 2h duration is used as base material for carrying out the reduction studies. The effect of various reduction process parameters such as reductant coal and fluxes (lime, quartz) on reduction of preoxidized chromite ore is investigated and discussed in the following sections.

3.2.1 Effect of coal addition

Anthracite coal is used as carbon source for reduction process of pre-oxidized chromite ore. The charge composition used consists of 100g preoxidized chromite ore, 15.6g quartz, 5g lime and 1.5g bentonite as binder. The amount of quartz to be used in the reduction experiments is estimated based on the theoretical requirement of silica in order to form the alumino-silicate and magnesio-silicate slag during the reduction. The coal content in the charge was then varied from stiochiometric requirement (18.6g) to 70% excess (31.6g) in order to understand the effect of coal addition on the Cr and Fe metallization in the reduced product. The Cr-metallization is defined as the ratio of Cr recovered in metal to the initial Cr present in the charge. Similarly the Fe-metallization is defined as the ratio of Fe recoverd in metal to initial Fe present in the charge. The effect of variation in coal on the Cr and Fe metallization at 1500 ^{0}C is shown in **Figure 5.** It can be seen from Figure 5 that the Cr-metallization have improved up to 77% with increase in coal from 18.6g to 27.9g (50% excess of stiochiometry) and then decreased with further increase in coal addition. In case of Fe-metallization similar behaviour is observed and maximum Fe-metallization of about 82% is obtained at 27.9g of coal addition. With increase in the carbon (from coal) content beyond certain limit (27.9g) the residual excess carbon increases in the reduced product and results in decreased Cr and Fe metallization. Therefore, the suitable coal mix established from reduction experiments is 27.9 coal for reduction of 100 g preoxidized chromite ore at given flux conditions.

3.2.2 Effect of Lime

In order to understand the effect of lime addition on the reduction of pre-oxidized chromite ore, the charge composition is maintained constant (100g pre-oxidized ore, 27.9g coal, 15.6 quartz, 1.5g bentonite) and the lime addition to charge is varied from 3.0g to 10g. The effect of variation in lime content in the charge on the Cr and Fe metallization is shown in **Figure 6**. It can be seen from Figure 6 that increase in lime from 3.0g to 5.0g have improved the Cr metallization marginally upto 77% and decreased with further addition of lime. Similarly it is observed that the Fe-metallization have increased upto about 80% at 5.0g lime and dropped further to as low as about 60% with increase in lime upto 10g. Increase in CaO content due to lime addition in the charge helps in forming fluid slag at high temperature (1500 ^{0}C) during the reduction and results in proper slag metal separation. However excessive amount of lime (greater than 5.0g) also results in increase in slag volume and high fluidity which may cause loss of metal values to slag. The maximum Cr-metallization of about 77% and Fe-metallization of 82% is achieved at 5.0g lime addition. Therefore, the optimum amount of lime quantity is established at 5.0g per 100 g of pre-oxidized chromite ore.

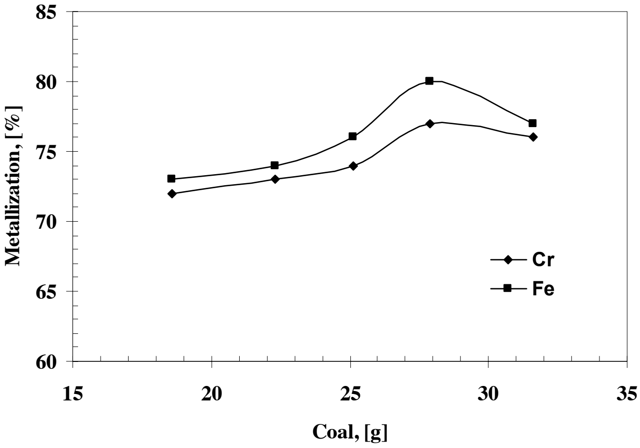


Figure 5: Effect of coal addition on Cr and Fe metallization in reduced product at 1500 ^{0}C

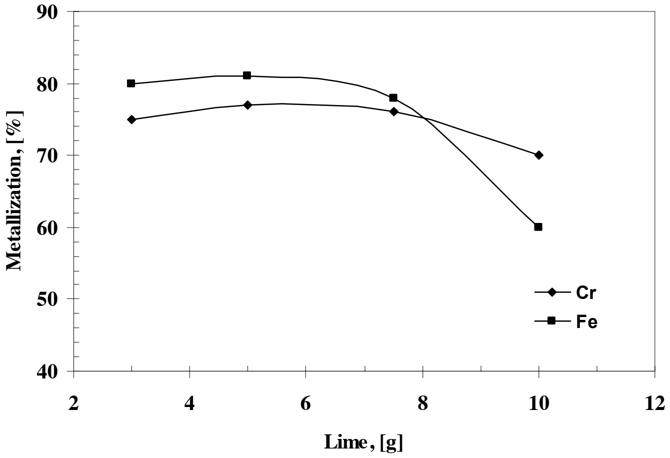


Figure 6: Effect of variation in lime on Cr and Fe metallization in reduced product at 1500 ^{0}C

3.2.3 Effect of Quartz

The effect of quartz (silica) addition on the Cr and Fe metallization is studied by varying the quartz content in close range of 15.6g to 17.2g per 100 g of chromite ore. The minimum required silica is 15.6g for dissolving the alumina and MgO in the chromite spinel to slag and forming the alumino and magnesio silicate slag. Therefore, the silica content is varied upto 10% excess (17.2g) than the minimum theoretical required. The effect of variation in quartz on Cr and Fe metallization in reduction product at 1500 ^{0}C is shown in Figure 7. It can be seen that the maximum Cr and Fe metallization is obtained at 15.6g quartz addition, which was minimum required theoretically. However, with further increase in quartz the metallization have decreased for both Cr and Fe due to increase in slag volume. Based on the experimental results, the optimum amount of charge mix for achieving the maximum Cr and Fe metallization in reduced product at 1500 ^{0}C is established at 100g pre-oxidized chromite, 27.9g anthracite coal, 5.0g lime, 15.6g quartz and 1.5g bentonite as binder. It is also observed that clear slag and metal separation is achieved at optimized flux conditions.

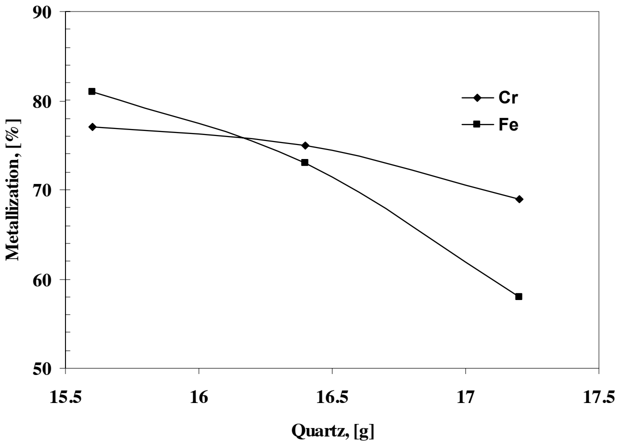


Figure 7: Effect of variation in quartz on Cr and Fe metallization in reduced product at 1500 ^{0}C

3.3 Effect of Degree of Pre-oxidation on Reduction Behaviour

The effect of degree of preoxidation on the reduction behaviour of chromite is investigated by subjecting the raw chromite ore to oxidation at 900 ^{0}C for different duration. For this the raw chromite ore is heated in air atmosphere upto 180 min duration in step of 30 min. These pre-oxidized chromite ore samples heated for different duration were then reduced at 1500 ^{0}C at optimized coal and flux conditions. The variation of Cr and Fe metallization in the reduced product with increase in degree chromite ore oxidation is shown in **Figure 8**.

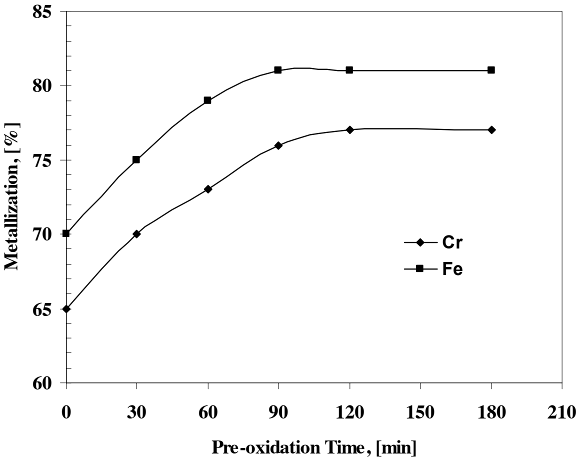


Figure 8: Effect of pre-oxidation time on Cr and Fe metallization in reduced product at 1500 ^{0}C

It can be observed from Figure 8 that, with increase in degree of preoxidation of raw chromite the Cr and Fe metallization in the reduced product have increased upto preoxidation time of 120min and further increase in the preoxidation time did not have significant effect on the respective metallization. It was also observed during reduction experiments that the slag and metal separation was better with increase in the degree of pre-oxidation in raw chromite ore. With increase in the preoxidation degree, the improvement in Cr and Fe metallization is expected since during reduction the sequioxide (Fe_2O_3) phase formed in pre-oxidation stage reduces first to FeO and then this newly formed FeO acts like flux even at low temperatures (1200 ^{0}C) for slag formation. The cation vacancies generated during the preoxidation stage of chromite also results in increasing the reactivity of raw chromite thus resulting in high metallization of Cr and Fe during the reduction. About 77% of Cr and more than 80% of Fe-metallization is observed during reduction of chromite ore oxidized for 120 min duration.

3.4 Quality of reduction products

The slag and metal products obtained during reduction of preoxidized chromite at 1500 ^{0}C and 2.5h reduction time are shown in **Figure 9**. The chemical composition of the metal and slag is given in **Table 2**. It can be seen from Table 2 that, the metal nuggets contain high chromium of about 61%, and iron upto 30%. It was also observed that the metal nugget is easily separable from the associated slag by physical separation techniques.

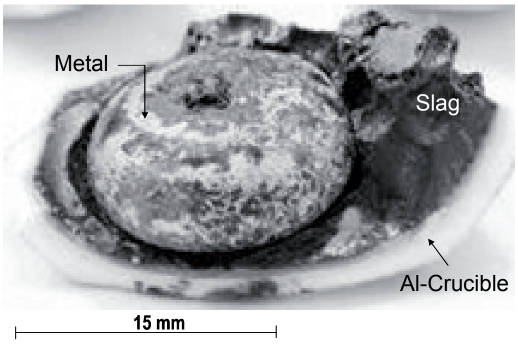


Figure 9: Ferrochrome metal and slag obtained at 1500 ^{0}C and 2.5 h duration reduction time

Table 2: Typical chemical compositions of the metal and slag at 1500 ^{0}C and 2.5 h reduction time

Item	Chemical analysis, wt%					
	Fe (t)	Cr	Si	C	S	P
Metal	28	61	1.0	4.5	0.03	0.15
Slag	wt%					
	Cr_2O_3	SiO_2	Al_2O_3	CaO	Fe(t)	MgO
	26.5	19.9	19.4	5.2	6.1	14.1

4 CONCLUSIONS

The reduction behaviour of preoxidized chromite ore is studied at high temperature (1500 ^{0}C) with objective of development of process for minimizing the coke and energy consumption in the ferrochrome production process. It is observed that the preoxidation of chromite ore results in oxidation of FeO present in chromite spinel to Fe_2O_3 (sequioxide) as exholved precipitate on the surface of chromite grains and generates cation vacancies. The effect of various reduction process parameters such as coal addition and fluxes on the reduction behaviour of pre-oxidized chromite is examined. The optimum amount of charge mix for achieving maximum Cr and Fe metallization is established as 100g pre-oxidized chromite, 27.9g coal, 5.0g lime, 15.6g quartz and 1.5g bentonite as binder. It was seen during reduction experiments that more than 80% of iron and 77% of chromium metallization is obtained by reduction of pre-oxidized chromite ore at 1500 ^{0}C. Clear slag and metal separation is achieved during reduction. It is also found that increase in the degree of preoxidation in chromite ore improves the Cr and Fe metallization during reduction process due to improvement in the reactivity of chromite by preoxidation. The reduced metal obtained in lab reduction experiments is found to contain high chromium of about 61%, and iron upto 30% and the reduction products (slag and metal) were easily separable from each other by physical separation.

5 REFERENCES

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