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Reaction Mechanism and Thermodynamics of Segregation Roasting of Iron Oxide

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Abstract: This paper presents the reduction mechanism of iron recovery from pure ferric oxide by the segregation roasting-magnetic separation process both from the chemical reaction and physical phenomena point of view. In segregation roasting process, coal is used as the reducing agent and calcium chloride as chlorinating agent. Segregation roasting of iron oxide has been studied at different temperatures from 800 to 1000°C varying the chloride and carbon percentages. The same experimental conditions have been adopted to recover iron from mill scale by the process of segregation roasting. By segregation roasting, iron oxide is reduced by a combination of chlorination, volatilization and hydrogen reduction. Elucidation of the reaction mechanism of segregation process is being attempted in this present study. Characterization of the segregated iron particles recovered after magnetic separation both from ferric oxide and mill scale is studied by electron probe microscopy analyzer.

Keywords: Segregation Roasting, Iron Oxide, Alkali Chloride, Thermodynamics, Reaction Mechanism, EPMA, SEM

1. Introduction

The segregation process of copper oxide ore is a technique which was accidentally discovered by Moulden & Tapline in 1923 and it was first reported by M. Rey at the VII International congress of mining and metallurgy in 1935. Since then, many workers have investigated this process with shaft furnace, rotary kiln and other equipment. However, the TORCO process which comprises a fluidized bed roaster and a sealed, vertical tube reactor has been developed recently and it has been proved that this is successful in commercial operation [1]. In the early 1970's companies such as Falconbridge, Hanna Mining, Lurgie, Anglo American, Inco etc., were active in the development of chloride segregation for the recovery of nickel [2]. INCO carried out test research work at a Laboratory and small pilot plant scale on Cu and Ni segregation, but the process was not commercialized for nickel production. Xstrata recently carried out laboratory scale test work on segregation roasting of laterite (Saprolite) ore. This batch testing of 500g total weight resulted in nickel concentrates with 2.1-15% Ni with a recovery between 33-85% [3]. Different authors have also been studied similar laboratory test [4-7]. The process of chloride segregation for nickel recovery has been developed using different equipment, for example the MINPRO-PAMCO mechanical kiln [8-9]. Liu & co-workers [10] has been carried out chloridizing segregation roasting of nickel latterites for the extraction of Ni and Co and concluded that they have achieved Ni as 91.5% and Co as 82.3%. Authors have made an attempt to separate iron from the gangue by the process of segregation roasting in the presence of coke and alkali chloride followed by screening & wet magnetic separation [11]. The Hatch-Ironstone Chloride Segregation is a novel process developed to produce DRI from Oolitic ores available at Ironstones' Clear Hill deposit. HICS process has been demonstrated at laboratory scale and is capable of producing a commercial quality DRI product from Clear Hills Oolitic iron ores containing 90% iron, 0.12% P and 0.3%C [12]. The steelmaking by-products such as dust and mill scale, very rich in iron ($\approx$ 72% Fe), are currently produced in large quantities and represent a potential of almost 5 million tons in the world [13]. The reduced iron powder from these by-products is most widely used material in powder metallurgy industry. The direct reduction process has commonly been used by many companies (such as Hoeganas in Sweden, Kawasaki in Japan and Pyron in US) to obtain metallic iron powder by the reaction of iron oxide (magnetite, hematite ore or mill scale) and reducing gases (CO/H_2) under high temperatures

(>1000°C) [14]. The reduction of iron oxides and various ores containing iron oxides have been studied in the past [15-17]. Their researches are conducted using solid carbon as reducing agents and reducing gas (CO and/or H_2).
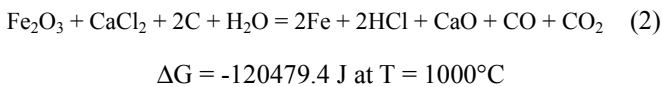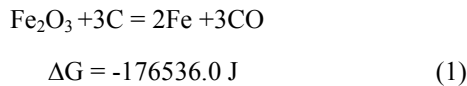
The basic chemistry and thermodynamics plays a vital role in the understanding of chloride segregation process. Magnetic iron powder is produced from the iron oxide and mill scale by the process of segregation roasting-magnetic separation. An attempt is being made to elucidate the reaction mechanism of chloride segregation roasting process of iron oxide.

2. Chemistry & Thermodynamics of the Segregation Process

There is considerable understanding of the basic chemistry and thermodynamics of the segregation process.

The segregation roasting process is a pyrometallurgical process where the ore is calcined and blended with a highly reactive carbon source, e.g., coal and additive to produce metallic iron at temperature 900°C.

The reaction in the chloride segregation process can be described as

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

$$\Delta G = -176536.0 \text{ J} \qquad (1)$$

$$Fe_2O_3 + CaCl_2 + 2C + H_2O = 2Fe + 2HCl + CaO + CO + CO_2 \qquad (2)$$

$$\Delta G = -120479.4 \text{ J at } T = 1000°C$$

This reaction takes place through the use of catalyst, hydrogen chloride, which chlorinates the iron. The main chemical steps of the process:

when iron oxide containing ores are heated with a small amount of halide salt and a reducing agent to a suitable temperature, metallic iron from the' ores migrate to the surface of reducing agent. In this chemical reaction, hydrogen chloride gas is produced, chlorination of oxides and their volatilization take place, and these chloride vapour are reduced to metal with H_2 gas. M. Rey's theory of this process which has been widely accepted can be explained by the following reactions:
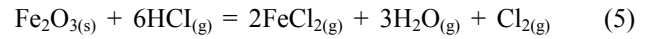
$$CaCl_{2(s)} + H_2O_{(g)} = CaO_{(s)} + 2HCl_{(g)} \qquad (3)$$

$$\Delta G = 4132.4 \text{ J}$$
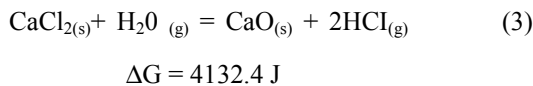
When H_2O is gas steam, then

$$\Delta G = 72636.7 \text{ J}$$

SiO_2 present in the ore reacts with $CaCl_2$ to produce hydrochloric acid.

$$SiO_{2(s)} + CaCl_{2(s)} + H_2O_{(g)} = CaSiO_{3(s)} + 2HCl_{(g)} \qquad (4)$$

$$\Delta G = -90454.2 \text{ J at } T = 1000°C$$
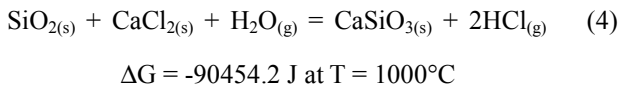
The combined water and silica in the' ore are useful for decomposing halides and the hydrochloric acid formed by the reaction, chloridizes the metallic oxides in the ore.
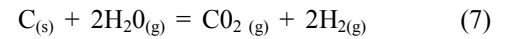
$$Fe_2O_{3(s)} + 6HCl_{(g)} = 2FeCl_{2(g)} + 3H_2O_{(g)} + Cl_{2(g)} \qquad (5)$$

$$\Delta G = 184716.9 \text{ J when } FeCl_2 \text{ is gas}$$

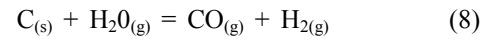$$Fe_2O_{3(s)} + 6HCl_{(g)} = 2FeCl_{3(g)} + 3H_2O_{(g)} \qquad (6)$$

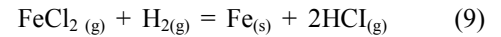$$\Delta G = 125463.1 \text{ J when } FeCl_3 \text{ is gas}$$

The water vapor formed by the chloridizing step produces H_2, CO and CO_2 gases by reacting with the carbon which has been added. The H_2 gas reduces the iron chlorides to metal readily.
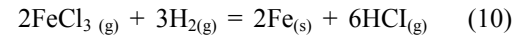
$$C_{(s)} + 2H_2O_{(g)} = CO_{2 (g)} + 2H_{2(g)} \qquad (7)$$

$$\Delta G = -41555.7 \text{ J}$$

$$C_{(s)} + H_2O_{(g)} = CO_{(g)} + H_{2(g)} \qquad (8)$$

$$\Delta G = -46739.9 \text{ J}$$

$$FeCl_{2 (g)} + H_{2(g)} = Fe_{(s)} + 2HCl_{(g)} \qquad (9)$$

$$\Delta G = -8029.4 \text{ J}$$

$$2FeCl_{3 (g)} + 3H_{2(g)} = 2Fe_{(s)} + 6HCl_{(g)} \qquad (10)$$

$$\Delta G = -161779.3 \text{ J}$$

The HCl gas formed by this reaction can be used again for chlorination of metallic oxide in Eqs. (5) and (6). In such segregation process, a smaller amount of the chloridizing agent than the stoichiometric amount is required for converting all oxides to chlorides because it is a regeneration-recycle process. Changing the oxides to chlorides by producing hydrogen chloride using chloridizing agent is a simple chloridizing roasting process. However, if regeneration and recycle of hydrogen chloride gas to the reaction which takes place among metallic oxide, chloridizing agent and reducing agent are considered, this reaction can be said to be a special chloridizing process.

For instance, if Eqs. (6) & (10) are combined; then the reaction is simply reduction of oxides by hydrogen.

$$Fe_2O_{3(s)} + H_{2a (g)} = Fe_{(s)} + H_2O_{(g)} \qquad (11)$$
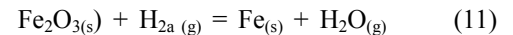
Therefore, direct reduction by H_2 gas is completely inhibited to ensure good segregation. The reaction progresses by the reduction of metallic oxide-chloride-vaporization of chloride-H_2 reduction. These reactions depend on selection of suitable conditions such as temperature range, kinds and amounts of salt, blending method, amount of reducing agent etc.
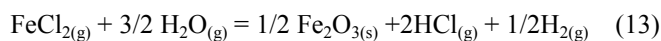
2.1. Role of Additives

Water plays a vital role in segregation process. If excess water is present in the prepared sample, hydrolysis of the chlorides formed by the reaction may take place. On the other hand, if an excess of carbon is present, the amounts of

H_2 and CO gases increase by the water gas reaction,

$$2FeCl_{3(g)} + 3H_2O_{(g)} = Fe_2O_{3(s)} + 6HCl_{(g)} \qquad (12)$$

$$\Delta G = -125463.1 \text{ J at } T = 1000°C$$

$$FeCl_{2(g)} + 3/2\ H_2O_{(g)} = 1/2\ Fe_2O_{3(s)} + 2HCl_{(g)} + 1/2H_{2(g)} \qquad (13)$$
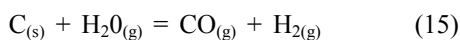
$$\Delta G = 10128.7 \text{ J}$$

It can be seen from the above that there is possibility of hydrolysis of ferrous chloride when the water content is high. Water present in the segregation process is believed to be due to the following:

i.   free moisture and combined water in the ore
ii. moisture due to salt,
iii. water formed by combustion of fuel and
iv. water formed by chlorination of oxide as in Eq. (3).

Now, if water in the ore is removed by calcination, the charge preheated and dehydrated and sealed reactor is used, then water due to (i) and (ii) can be eliminated. Water due to (iii) consumes a large amount of salt and the amount of HCI gas becomes large. As a result of this, hydrolysis of Fe_2O_3 and water gas reaction takes place between the coexisting reducing agent and water vapor as mentioned above in equations (7) and (8). Thus according to equations (7) and (8), the water gas reactions are:

$$C_{(s)} + 2H_2O_{(g)} = CO_{2(g)} + 2H_{2(g)} \qquad (14)$$
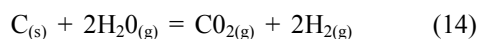
$$\Delta G = -41555.7 \text{ J at } T = 1000°C$$

$$C_{(s)} + H_2O_{(g)} = CO_{(g)} + H_{2(g)} \qquad (15)$$

$$\Delta G = -46739.9 \text{ J at } T = 1000°C$$

The segregation roast involves two interrelated reactions. One is the hydro-chlorination of certain metal compounds which have sufficient volatility to migrate to nearby carbon surfaces. On the carbon surfaces, the second reaction occur which is the reaction of water to reform the hydrogen chloride, with the carbon being oxidized and leaving the reaction site. The exact mechanism of the reaction has not been established but it has been postulated that water reacts with carbon in the well known "water gas" reaction to produce hydrogen which reduces the chloride to metal and regenerates the hydrogen chloride. The carbon monoxide of the water gas reaction may also play a role in reducing metal oxide formed by the hydrolysis of the metal chloride. This results in the carbon with metal chloride on it reacting to become a gas, and leaving behind a metal. The metal that remains is often, but not always, in hollow spheres which are holed. This is because gas is escaped through the hole.

2.2. Effect of Reducing Agent

The segregation reaction of iron oxide in the presence of carbon is simply the following reaction as mentioned in Eq.(1):

$$Fe_2O_{3(s)} + 3C_{(s)} = 2Fe_{(s)} + 3CO_{(g)}$$
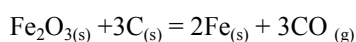
Consequently, the amount of reducing agent required will be more than the stoichiometric requirement. It is clear from the chemical analysis of the segregated particle formed on carbon surface that depending on the temperature, a large amount of iron is formed. It can therefore be assumed that these metals are also reduced by the same mechanism. Moreover, it is necessary to make the amount of reducing agent a little larger than the stoichiometric quantity because a part of it is required for the formation of metal nuclei at the start and subsequent migration of metal on them.

2.3. Influence of Moisture

Water vapor is effective for decomposition of salt and production of HCI gas. Once HCI gas is produced in a reactor heated externally, the combined reactions of Eq. (5) and Eq. (6) take place as long as oxides are present in the system and additional water vapor is not necessary because this is a repeating, regenerating reaction. It has been reported that good yield is obtained when segregation is carried out after pelletizing, drying and preheating the charge with indirect heating.
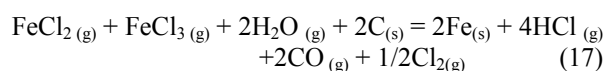
2.4. Amount of Chloridizing Agent

The most important additive in the segregation process is chloridizing agent. When ore is heated in externally heated reactor, the required amount of salt is much less than the stoichiometric amount because of HCI gas formation and HCI gas regeneration cycle. Iron oxides are chloridized easily and consequently, a somewhat larger amount of salt is required. However, it must be noted that HCI gas is supplied by decomposition of $FeCl_2$ and $FeCl_3$ vapors at a high temperature. When segregation experiments are carried out by adding excess salt and with short retention time, un-decomposed salt remains in the calcined product. Moreover, there were cases in which the salt did not decompose but vaporized at a higher temperature and condensed on the colder part of the reaction tube. As indicated above, addition of a very small amount of chloridizing agent is sufficient but chloridizing reaction is promoted with a large addition rate and the proportion of direct reduction becomes small. The segregation results indicate a tendency of growth of precipitated metal and thus increase in yield.

Thus, the reaction mechanism of iron oxide in segregation roasting is the combination of Equation (4) to Equation (10) as mentioned above.

Therefore, the overall reaction of segregation roasting of iron oxide is

$$Fe_2O_{3(s)} + 6HCl_{(g)} = FeCl_{2(g)} + FeCl_{3(g)} + 3H_2O_{(g)} + 1/2Cl_{2(g)} \quad (16)$$

$$\Delta G = 125463.1 \text{ J at } T = 1000°C$$

$$FeCl_{2\ (g)} + FeCl_{3\ (g)} + 2H_2O_{(g)} + 2C_{(s)} = 2Fe_{(s)} + 4HCl_{(g)} + 2CO_{(g)} + 1/2Cl_{2(g)} \qquad (17)$$

$$\Delta G = -175988.1 \text{ J at } T = 1000°C$$

Table 1. *Different constituents obtained at equilibrium at different temperatures using FACTSAGE software.*

| Constituents (mole)	Temperature °C	Gas Phase	Solid PhaseFe (fcc)
$FeCl_3$, $3H_2O$, $2C$	1000	CO, H_2, HCl, $FeCl_2$, H_2O, CO_2	C
$FeCl_3$, $3H_2O$, C	1000	HCl, CO, $FeCl_2$, H_2, CO_2, H_2O	No Iron
$FeCl_2$, H_2O, C	1000	CO, HCl, H_2, $FeCl_2$, CO_2, H_2O, CH_4, $FeCl_3$	Fe (fcc), Fe_3C
$FeCl_2$, $FeCl_3$, $3H_2O$, $2C$	1000	HCl, CO, H_2, $FeCl_2$, H_2O, CO_2	Fe (fcc)
Fe_2O_3, $CaCl_2$, H_2O, $2C$	1000	CO, H_2, CO_2, H_2O, HCl, $FeCl_2$, $CaCl_2$	Fe (fcc), FeO, $CaFe_2O_5$
Fe_2O_3, $CaCl_2$, H_2O, $2C$	800	CO, CO_2, H_2, H_2O, CH_4, HCl	Fe (bcc), FeO, $Ca_2Fe_2O_5$

3. Experimental

Small amount of the sample (mixture of coal, alkali chloride and mill scale) in pellet form of 5mm dia was taken in an Al_2O_3 boat and placed in a quartz tube with both end closed. The boat was weighed before and after the experiment. The quartz tube was heated to raise the temperature to the required temperature for different time in an argon atmosphere. The furnace was allowed to cool and taken out. The boat with sample was weighed, and then, metallic fraction was analyzed for Fe.

4. Results and Discussion

SEM micrographs of mill scale at low and high magnifications are shown in Figures 1& 2.
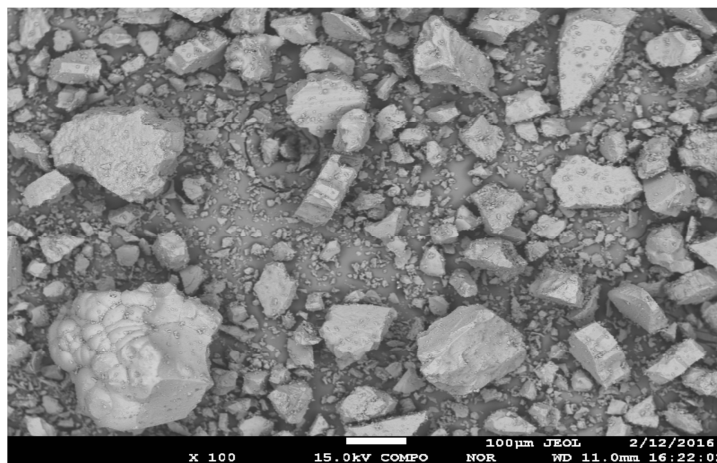
Figure 1. *Shows the micrograph of raw mill scale at low magnification.*
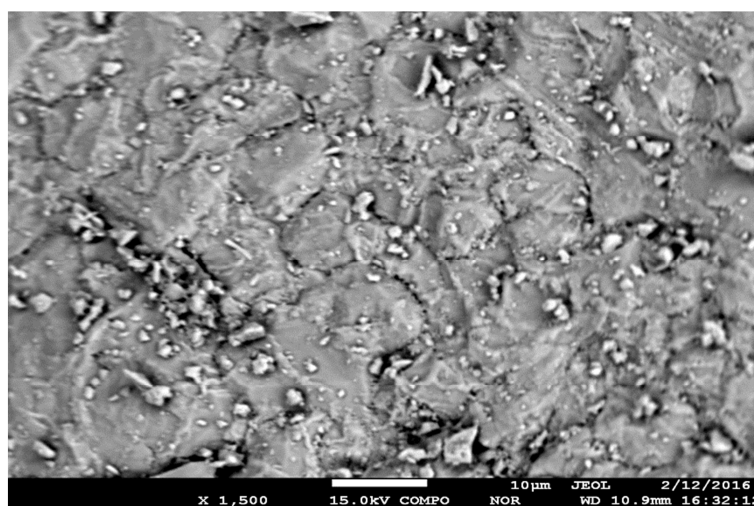
Figure 2. *Represents the micrograph of raw mill scale at high magnification.*

Raw mill scale contains 76% total iron. The main constituents of raw mill scale are Fe_3O_4, FeO, traceable metallic iron, manganese, chromium and phosphorous.

The segregation roasting of mill scale using coal and alkali chloride at 1000°C is carried out in this present work. More than 90% metallic iron is produced. Fig. 3 shows the micrograph of segregated iron particles after magnetic separation determined by EPMA (Electron Probe MicroAnalyser).
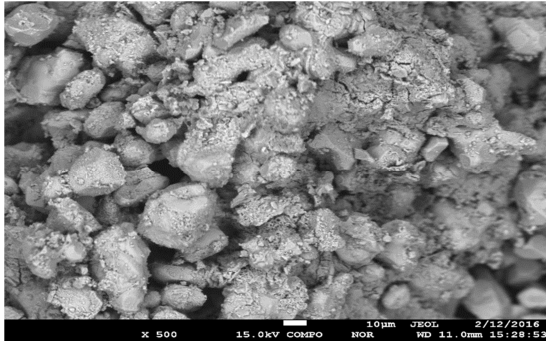
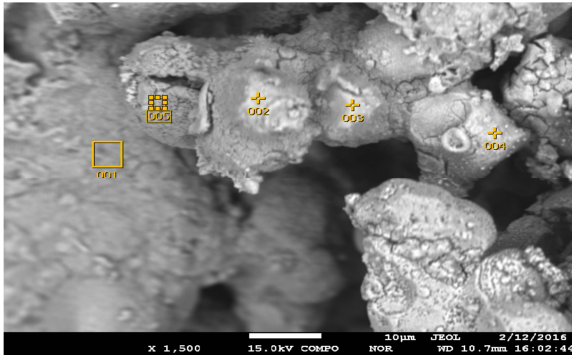*Figure 3. Segregation roasting of mill scale at 1000°C.*

Figure 4. Segregation roasting of mill scale at 1000°C.

In Fig. 3 it seen that the micrograph contains hollow sphere with lot of holes. This is because, on the carbon surfaces, water reacts with carbon in the well known "water gas" reaction to produce hydrogen which reduces the chloride to metal and regenerates hydrogen chloride. The carbon monoxide of the water gas reaction may also play a role in reducing metal oxide formed by the hydrolysis of the metal chloride. This results in the carbon with metal chloride on it reacting to become a gas, and leaving behind a metal. The metal that remains is in hollow spheres which are holed where the gas escaped.

In the segregation roasting, the iron chloride vapor migrates to the carbon surface and gets reduced by hydrogen gas to metal. The segregation roasting indicates a tendency of growth of precipitated metal which is shown in Fig. 4 and thus increases in yield.
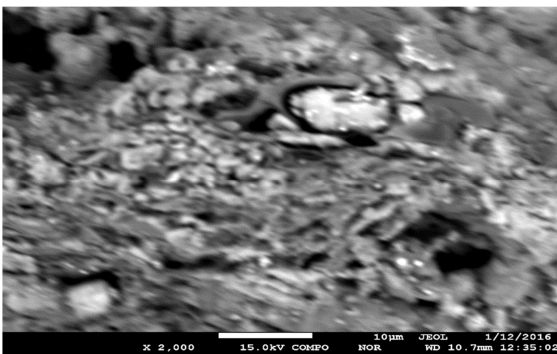

Figure 5. Segregation roasting of pure Ferric Oxide at 1000°C.

Fig. 5 shows the micrograph of very fine segregated

spherical magnetic iron particles produced from pure ferric oxide.

5. Conclusion

Chloridizing segregation process of iron oxide involves the reaction in number of steps. The reaction cycle is initiated with the production of hydrogen chloride by the hydrolysis of alkali chloride in the presence of silica:
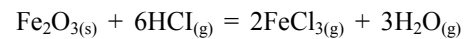
$$SiO_{2(s)} + CaCl_{2(s)} + H_2O_{(g)} = CaSiO_{3(s)} + 2HCl_{(g)}$$
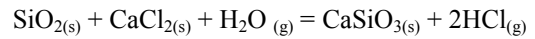
$$\Delta G = -90454.2 \text{ J at T} = 1000°C$$

The above reaction is highly exothermic and produces large amount of hydrogen chloride in the presence of water vapor.

The hydrogen chloride formed by the above reaction, chloridizes the iron oxides in the ore:

$$Fe_2O_{3(s)} + 6HCl_{(g)} = 2FeCl_{2(g)} + 3H_2O_{(g)} + Cl_{2(g)}$$

$$\Delta G = 184716.9 \text{ J when FeCl}_2 \text{ is gas}$$

$$Fe_2O_{3(s)} + 6HCl_{(g)} = 2FeCl_{3(g)} + 3H_2O_{(g)}$$

$$\Delta G = 125463.1 \text{ J when FeCl}_3 \text{ is gas}$$

The reaction is highly endothermic and is relatively slow.

The water vapor formed by the chloridizing step produces H_2, CO and CO_2 gases by reacting with the carbon which has been added. The H_2 gas reduces the iron chlorides to metal readily. Reduction of iron chloride with hydrogen is very rapid and the reaction is highly exothermic.

The HCl gas formed by the reaction

$$FeCl_{2(g)} + FeCl_{3(g)} + 2H_2O_{(g)} + 2C_{(s)} = 2Fe_{(s)} + 4HCl_{(g)} + 2CO_{(g)} + 1/2Cl_{2(g)}$$
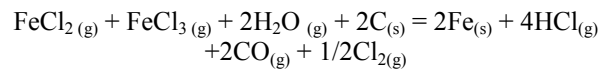
can be used again for chlorination of metallic oxide as in Eq. (5) and (6). In such segregation process, a smaller amount of the chloridizing agent than the stoichiometric amount is required for converting all oxides to chlorides because it is a process of regeneration of HCl and H_2 gases.

The unreacted iron oxide left in the ore may get reduced by hydrogen directly as a result the metal gets precipitated. The growth of the metal is shown in Fig. 4.

$$Fe_2O_{3(s)} + 1/2H_{2(g)} = 2Fe_{(s)} + 3/2 H_2O_{(g)}$$
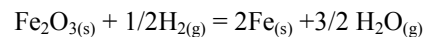
In addition, the different gas phases take place during the reaction involving C, CO, CO_2, H_2, H_2O, Cl_2, HCl, CH_4 and O_2 (see Table 1). The kinetics of these reactions may be influenced, by the type of carbonaceous reagent used, its particle size and by the nature of its surface.

In segregation roasting of ore, first HCl gas is produced and chlorination takes place next. The chlorides formed are volatilized and absorbed on coke and are immediately reduced with H_2. Then, adsorption, reduction and growth progress, on the metal surface. Such a process was reproduced in the above-mentioned experiments. The

segregation mechanism can be explained very well if both chemical reactions and physical phenomena are considered together. That is, iron in the oxide ore is chloridized, and iron is precipitated on the carbon surface by way of mixed, fused salts of chlorides and vaporized gas phase. Then, H_2 reduction takes place on precipitated metal surface, i.e. iron is not reduced directly from oxide but vaporization, chlorination and reduction progress successively and the particles of reduced metal grow and become coarse. The temperature range from 950°C to 1000°C is suitable for segregation of iron ore.

Acknowledgement

References

[1]   M. I. Brittan, 'Kinetics of copper segregation by the TORCCO process', Journal of South African Institute of Minning and Metallurgy, Bebruary 23, 1970, pp. 278-289.

[2]   M. Kawtara, "Segregation roasting of a Saprolitic ore- An Expermental Investigation", TMS, San Diego, California, February 27 March, 2011.

[3]   I. Iwasaki, Nickel segregation, Proceedings of the panel discussion on Nickel segregation, AIME, San Francisco, California, February 23, 1972.

[4]   S. P. Mehrotra and V. Srinvasan, "Extraction of nickel from an Indian Laterite by segregation roasting", Trans. Instn. Min. Metall., 103, May-August 1994, pp. C97-C104.

[5]   J. K. Right, "Nickel Laterite Treatment by Segregation", Pyrometallurgy for complex materials & Wastes, Ed. M Nilmani, The Minerals, Metals & Materials Society, 1994, pp219-232.

[6]   I. Illic, et al., "The study of Chlorination Nickel Oxide by Chlorine and Calcium Chloridein the presence of active additives", Scandivian Journal of Metallurgy, 1997, 26, pp 14-19.

[7]   I. D. Reznik et al., "Mechanism and Technology of Segregation Roasting of oxide Nickel ores with subsequent Calcine Flotation and concentrate Leaching", EPD Congress, TMS, 2004, pp725-737.

[8]   A. S. Ericson, J. Svensson, K. Ishii, "Development of the MINPRO-PAMCO, "Nickel Segregation Process, Journal of Metals, September, 1984, pp 42-46.

[9]   A. S. Ericson, J. Svensson, K. Ishii, "Development of the MINPRO-PAMCO, "Nickel Segregation Process, International Journal of Mineral Processing, 19(1987) pp223-236.

[10] Liu Wan-rong, Li Xin-hai, HU Qi-yang, WANG Zhi-xing, GU Ke-zhuan, Li Jin-hui, Zhang Lian-xin, "Pretreatment study on chloridizing segregation and magnetic separation of low-grade nickel Laterites", Trans. Nonferrous. Met. Soc. China 20,2010, 82-86.

[11] AbdulWahab A. Al-Ajeel and Saly. N. Mandy, "Beneficiation of AL-Hussainyiat Low grade Iron Ore by segregation Roasting", Iraqi Bulletin of Geology and Minning, 2, 2, 2006, pp 103-113.

[12] V. Hermandez, K. Peake, R. Brown, J. Olurin, T. O' Farell, M. Zhou, B. Liu, I. Cameron, 'Process Development of a New DRI Technology for Oolitic Iron Ores".

[13] Bouvard, D. Métallurgie des poudres, Paris, Hermès Science Publications, (2002).

[14] Pineau, A., Kanariand, N., Gaballah, I. Kinetics of Reduction of Iron Oxides by H_2, Part I: Low Temperature Reduction of Hematite, *Thermochimica Acta*, 447 (2006) 89.

[15] Pineau, A., Kanariand, N., Gaballah, I. Kinetics of Reduction of Iron Oxides by H_2, Part II: Low Temperature Reduction of Magnetite, *Thermochimica Acta*, 456 (2007) 75.

[16] El-Geasy, A. A., Nasr, M. I. Influence of Original Structure on the Kinetics and Mechanisms of Carbon Monoxide Reduction of Hematite Compacts. *ISIJ International*, 30 (1990) 417.

[17] O. Benchiheub, S. Mechachti, S. Serrai, M. G. Khalifa, Elaboration of iron powder from mill scale, J. Mater. Environ. Sci., 1, 4, (2010) 267-276.