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 (=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/H₂) under high temperatures.
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 H₂).

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:

\[ \text{Fe}_2\text{O}_3 + 3C = 2\text{Fe} + 3\text{CO} \]
\[ \Delta G = -176536.0 \text{ J} \quad (1) \]

\[ \text{Fe}_2\text{O}_3 + \text{CaCl}_2 + 2\text{C} + \text{H}_2\text{O} = 2\text{Fe} + 2\text{HCl} + \text{CaO} + \text{CO} + \text{CO}_2 \]
\[ \Delta G = -120479.4 \text{ J at } T = 1000^\circ\text{C} \quad (2) \]

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 H₂ gas. M. Rey’s theory of this process which has been widely accepted can be explained by the following reactions:

\[ \text{CaCl}_2(g) + \text{H}_2\text{O}(g) = \text{CaO}(s) + 2\text{HCl}(g) \]
\[ \Delta G = 4132.4 \text{ J} \quad (3) \]

When H₂O is gas steam, then
\[ \Delta G = 72636.7 \text{ J} \]

SiO₂ present in the ore reacts with CaCl₂ to produce hydrochloric acid:

\[ \text{SiO}_2(s) + \text{CaCl}_2(s) + \text{H}_2\text{O}(g) = \text{CaSiO}_3(s) + 2\text{HCl}(g) \]
\[ \Delta G = -90454.2 \text{ J at } T = 1000^\circ\text{C} \quad (4) \]

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.

\[ \text{Fe}_2\text{O}_3(\text{s}) + 6\text{HCl}(g) = 2\text{FeCl}_3(g) + 3\text{H}_2\text{O}(g) + \text{Cl}_2(g) \]
\[ \Delta G = 184716.9 \text{ J when } \text{FeCl}_2 \text{ is gas} \quad (5) \]

\[ \text{Fe}_2\text{O}_3(\text{s}) + 6\text{HCl}(g) = 2\text{FeCl}_3(g) + 3\text{H}_2\text{O}(g) \]
\[ \Delta G = 125463.1 \text{ J when } \text{FeCl}_3 \text{ is gas} \quad (6) \]

The water vapor formed by the chloridizing step produces H₂, CO and CO₂ gases by reacting with the carbon which has been added. The H₂ gas reduces the iron chlorides to metal readily.

\[ \text{C}(s) + 2\text{H}_2\text{O}(g) = \text{CO}_2(g) + 2\text{H}_2(g) \]
\[ \Delta G = -41555.7 \text{ J} \quad (7) \]

\[ \text{C}(s) + \text{H}_2\text{O}(g) = \text{CO}_2(g) + \text{H}_2(g) \]
\[ \Delta G = -46739.9 \text{ J} \quad (8) \]

\[ \text{FeCl}_2(g) + \text{H}_2(g) = \text{Fe}(s) + 2\text{HCl}(g) \]
\[ \Delta G = -8029.4 \text{ J} \quad (9) \]

\[ 2\text{FeCl}_3(g) + 3\text{H}_2(g) = 2\text{Fe}(s) + 6\text{HCl}(g) \]
\[ \Delta G = -161779.3 \text{ J} \quad (10) \]

The HCI 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.

\[ \text{Fe}_2\text{O}_3(s) + \text{H}_2(g) = \text{Fe}(s) + \text{H}_2\text{O}(g) \quad (11) \]

Therefore, direct reduction by H₂ gas is completely inhibited to ensure good segregation. The reaction progresses by the reduction of metallic oxide-chloride-vaporization of chloride-H₂ 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...
H₂ and CO gases increase by the water gas reaction,
\[ 2\text{FeCl}_3(g) + 3\text{H}_2\text{O}(g) = \text{Fe}_2\text{O}_3(s) + 6\text{HCl}(g) \]  
\[ \Delta G = -125463.1 \text{ J at } T = 1000^\circ \text{C} \]
\[ \text{FeCl}_2(g) + 3/2 \text{H}_2\text{O}(g) = 1/2 \text{Fe}_2\text{O}_3(s) + 2\text{HCl}(g) + 1/2\text{H}_2(g) \]  
\[ \Delta G = 10128.7 \text{ J} \]

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:

1. free moisture and combined water in the ore
2. moisture due to salt,
3. water formed by combustion of fuel and
4. 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 HCl gas becomes large. As a result of this, hydrolysis of Fe(iii) consumes a large amount of salt and the amount of HCl gas becomes large. Therefore, the required amount of salt is much less than the stoichiometric amount because of HCl gas formation and HCl gas regeneration cycle. Iron oxides are chloridized easily and consequently, a somewhat larger amount of salt is required. However, it must be noted that HCl gas is supplied by decomposition of FeCl₂ and FeCl₃ vapors at a high temperature. When segregation experiments are carried out by adding excess salt and with short retention time, undecomposed 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
\[ \text{Fe}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Fe}(s) + 3\text{CO}(g) \]  
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 HCl gas. Once HCl 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 HCl gas formation and HCl gas regeneration cycle. Iron oxides are chloridized easily and consequently, a somewhat larger amount of salt is required. However, it must be noted that HCl gas is supplied by decomposition of FeCl₂ and FeCl₃ vapors at a high temperature. When segregation experiments are carried out by adding excess salt and with short retention time, undecomposed salt remains in the calcined product.
Table 1. Different constituents obtained at equilibrium at different temperatures using FACTSAGE software.

<table>
<thead>
<tr>
<th>Constituents (mole)</th>
<th>Temperature °C</th>
<th>Gas Phase</th>
<th>Solid Phase Fe (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₂, 3H₂O, 2C</td>
<td>1000</td>
<td>CO, H₂, HCl, FeCl₂, H₂O, CO₂</td>
<td>C</td>
</tr>
<tr>
<td>FeCl₂, 3H₂O, C</td>
<td>1000</td>
<td>HCl, CO, FeCl₂, H₂, CO₂, H₂O</td>
<td>No Iron</td>
</tr>
<tr>
<td>FeCl₂, H₂O, C</td>
<td>1000</td>
<td>CO, HCl, H₂, FeCl₂, H₂O, CO₂,</td>
<td>Fe (fcc), Fe₃C,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O, CH₄, FeCl₂</td>
<td>Fe (fcc)</td>
</tr>
<tr>
<td>FeCl₂, FeCl₂, 3H₂O, 2C</td>
<td>1000</td>
<td>CO, H₂O, CO₂, H₂O, HCl, FeCl₂, CaCl₂</td>
<td>Fe (fcc), FeO, CaFeO₃</td>
</tr>
<tr>
<td>Fe₂O₃, CaCl₂, H₂O, 2C</td>
<td>1000</td>
<td>CO, H₂O, CO₂, H₂O, HCl, FeCl₂, CaCl₂</td>
<td>Fe (fcc), FeO, CaFeO₃</td>
</tr>
<tr>
<td>Fe₂O₃, CaCl₂, H₂O, 2C</td>
<td>800</td>
<td>CO, CO₂, H₂O, CH₄, HCl</td>
<td>FeO, CaFeO₃</td>
</tr>
</tbody>
</table>

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 Al₂O₃ 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.

Raw mill scale contains 76% total iron. The main constituents of raw mill scale are Fe₂O₃, FeO, traceable metallic iron, manganese, chromium and phosphorus.

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).
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.

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:

\[
\text{SiO}_2(s) + \text{CaCl}_2(s) + \text{H}_2\text{O}(g) = \text{CaSiO}_3(s) + 2\text{HCl}(g)
\]

\[\Delta G = -90454.2 \text{ J at } T = 1000^\circ\text{C}\]

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:

\[
\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(g) = 2\text{FeCl}_2(g) + 3\text{H}_2\text{O}(g) + \text{Cl}_2(g)
\]

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

\[
\text{Fe}_2\text{O}_3(s) + 6\text{HCl}(g) = 2\text{FeCl}_3(g) + 3\text{H}_2\text{O}(g)
\]

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

The reaction is highly endothermic and is relatively slow. The water vapor formed by the chloridizing step produces H₂, CO and CO₂ gases by reacting with the carbon which has been added. The H₂ 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

\[
\text{FeCl}_2(g) + \text{FeCl}_3(g) + 2\text{H}_2\text{O}(g) + 2\text{C}(s) = 2\text{Fe}(s) + 4\text{HCl}(g) + 2\text{CO}(g) + 1/2\text{Cl}_2(g)
\]

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 H₂ 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.

\[
\text{Fe}_2\text{O}_3(s) + 1/2\text{H}_2(g) = 2\text{Fe}(s) + 3/2 \text{H}_2\text{O}(g)
\]

In addition, the different gas phases take place during the reaction involving C, CO, CO₂, H₂, H₂O, Cl₂, HCl, CH₄ and O₂ (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 H₂. 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, \( \text{H}_2 \) 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

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References


