Heat Generation by Oxygen Injection during
Reduction of Iron Ores in the Fluidized State by Hydrogen

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Problems relating to the oxygen injection through the Electrogen Furnace shaft were studied to meet some of the heat requirements during reduction. Reduction was performed mainly in a small silica fluidized bed reactor with Aswan iron ore using pure hydrogen or hydrogen mixed with either steam or oxygen or both. Preliminary work using a tube furnace arrangement was useful in understanding the process and determining the working conditions in the fluidized bed reactor.

The rate of reduction increased with temperature and hydrogen flow rate, but was retarded by the addition of steam and oxygen. However, in case of oxygen addition, the heat generated due to hydrogen-oxygen reaction counteracted the retarding effect.

The rate of the hydrogen-oxygen reaction was found to increase with the O₂ content but was retarded with the increase in the amount of steam present. The latter has a moderating effect on the explosion tendency of the hydrogen-oxygen mixture. This tendency increased with the oxygen content in the gas mixture and under the present experimental conditions no explosions occurred as long as the oxygen content was less than 15% of the hydrogen content. Heat generated was calculated theoretically and determined experimentally.

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I. Introduction

The present work is done in conjunction with an Egyptian project “Electrogen Furnace project”, which aims at the production of iron from its ores through hydrogen reduction(1). Hydrogen can be produced economically from some cheap excess petroleum products and gases in the Middle Eastern countries.

Energy calculations showed that, unlike the blast furnace, it is difficult to deliver all the heat requirements in the furnace shaft by the hot gases. Accordingly, it was decided to imitate the Wiberg process(2) by burning some of the spent gases at the furnace top to preheat the incoming ore.

The shaft consists of a certain number of trays on which the ore is reduced in the fluidized state. In the second bed from the top the gas composition will be about one part of steam and two of hydrogen, and it still has some reducing power. Oxygen will be blown in this bed to react with some hydrogen, thus generating the required amount of heat.

The aim of this work is to investigate the problem of oxygen blowing into a reducing atmosphere of a H₂-H₂O mixture in the presence of partially reduced iron ore to generate heat, avoiding conditions favouring explosions.

The reduction of the ore with pure hydrogen was first studied, and then the effect of mixing of hydrogen with an inert gas was found. Different amounts of steam, oxygen and steam-oxygen mixtures were then injected with hydrogen during the reduction process. The progress of both the reduction of the ore and the reaction between hydrogen and oxygen were followed.

Temperature variation during the process was recorded and thermodynamic calculations were used for evaluating the amounts of heat evolved. Some preliminary experiments were conducted in a tube furnace system to find out the general trends in the process.

II. Theoretical Considerations

The reaction between hydrogen and oxygen is sensitive to catalytic influences(3). Although much has been known about the reaction with respect to the surfaces of some metals and oxides, there are no detailed studies in the presence of iron or iron oxides.

The action of different catalytic surfaces depends upon their adsorption phenomena for gases, and many types of behaviours are met with(4). For some metallic surfaces the combination rate of hydrogen and oxygen is approximately proportional to the hydrogen pressure but independent of oxygen pressure(5). Accordingly, it was concluded that the reaction occurs between gaseous hydrogen and a layer of adsorbed oxygen which fully covers the surface(6).

The reaction between the two gases can take place at a controllable and measurable speed only in certain ranges of temperature, pressure and gas composition. The change in these conditions may increase the speed so greatly that the heat liberated in the system cannot be dissipated away and the gases inflame and explode(8).

The presence or formation of steam inhibits the reaction because of it being preferentially adsorbed on the surface of reaction(3)(7).

(3) C. N. Hinshelwood: The Reaction Between Hydrogen and oxygen, Oxford Univ. Press (1934).

Trans. JIM 1968 Vol.9
As to the reduction of iron ores in the fluidized state, Ezz(8)(9) was the first to study, basically, the factors affecting it. He concluded that the rate of reduction increases with increasing temperature and rate of reducing gas supply. Other workers arrived at similar conclusions(10)(11).

III. Experimental

Reduction experiments were performed on the Egyptian iron ore from Aswan which contains: 64.27% Fe₂O₃, 16.00% SiO₂, 1.12% Mn, 1.10% P, 5.52% Al₂O₃, 4.32% CaO, 1.30% MgO, 0.63% M. C and 6.13% L.O.I. The particle size worked on was -0.5 + 0.25 mm.

The apparatus used for reduction is shown in Fig. 1.

![Fig. 1 The reduction system](image)

It consists of three gas trains; for H₂, N₂ and O₂. A small steam generating unit was adjoined at the end of the hydrogen train just before the reduction tube, whenever required. Hydrogen bubbles through it and H₂O/H₂ is controlled by its temperature. Heating arrangements were done to prevent water condensation before entering the reactor.

The fluidized bed reactor is a silica tube 70 cm long, and 3.5 cm inner diameter with a sintered silica disc fixed at its center. Arrangements to determine the pressure drop through the fluidized bed are provided. While H₂ or the H₂–H₂O mixture enters the reactor from the bottom to induce fluidization, O₂ enters it from the top and is distributed evenly within the fluidized bed. The reactor is externally heated by a tube furnace of which the constant temperature zone extends 5 cm below and above the fluidized bed. The temperature is measured below the fluidized bed and inside it by two Chromel-Alumel thermocouples.

Water vapour coming out of the reactor is collected in anhydrous calcium chloride U-tubes. The exit end of the reactor to the CaCl₂ tubes is heated with an infrared lamp to prevent water condensation.

1. Determination of the minimum fluidizing gas velocity

The minimum fluidizing gas velocity was determined by Leva's formula(12);

$$G_{mf} = \frac{688 D_p^{1.88} \left( \rho_f - \rho_s \right)^{0.94}}{\mu^{0.88}}$$

where

- $G_{mf}$ = fluid mass velocity for the onset of fluidization (Lbs/hr/sq. ft)
- $D_p$ = particle size (inches)
- $\rho_f$ and $\rho_s$ = solid and fluid densities (Lbs/ou. ft)
- $\mu$ = fluid viscosity (centipoise).

The density and viscosity of the fluidizing gas or gas mixture were determined for the working temperatures.

The value given by this formula was used only as an indicative value to know approximately the minimum fluidizing gas velocity. This was determined experimentally for each run by gradually, but quickly, increasing the gas flow rate and plotting the pressure drop through the bed against it. The flow at which the pressure drop becomes constant determines the minimum fluidizing gas velocity. The actual fluidizing gas velocity used is some multiple of this value as will be seen later.

2. The reduction procedure

All runs were conducted on 50 g of ore charges. The temperatures worked at were 400°, 600° and 700°C. After switching on the furnaces nitrogen was allowed to pass through the apparatus until the required temperature in the reactor was attained and fixed to within ±2°C. During the passage of nitrogen the upper and lower thermocouples read exactly the same temperature, but when reactions set in, due to the passage of other gases, the two readings differ; the lower thermocouple represents the actual temperature of the furnace and incoming gas while the upper one reflects the heat changes taking place during the reactions.

In case of passing hydrogen alone the progress of reduction was followed by changing the absorption tubes at the predetermined time intervals and the cumulative percentage reduction-time curves were plotted. When H₂–O₂ mixtures were used the gas coming out from the

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absorption tubes was analysed for its O$_2$ content by the Orsat apparatus. Accordingly, the amounts of water formed due to the reduction and the H$_2$-O$_2$ reaction could be determined, respectively. When steam was introduced into the reactor its amount was deducted from the amount of water collected in the absorption tubes.

IV. Results and Discussion

Some preliminary experiments were carried out using a simple tube furnace arrangement. One gram of the ore was used in each run, the working temperature was fixed at 600°C and the hydrogen flow rate at 0.5 L/min. The ore was placed in a boat at the central part of a horizontal silica tube which replaced the fluidized bed reactor in Fig. 1.

Before studying the effects of additions of steam and oxygen to hydrogen on the reduction process the effect of nitrogen was investigated since it acts only as an inert diluent gas. Fig. 2 shows a retarding effect of the reduction reaction, in addition to the decrease in the partial pressure of the reducing gas.

When oxygen is injected with hydrogen two different reactions take place side by side; the reduction of the ore and the reaction between hydrogen and oxygen. The oxygen flow rates used were 25, 50 and 75 cc/min that correspond to 5, 10 and 15% of the hydrogen flow rate. Fig. 4 shows that the rate of reduction decreases and the deviation from complete reduction increases as the amount of oxygen increases. Oxygen here has a dual effect; as a diluent gas and a water vapour producer. It may also be possible to suggest that the freshly reduced active sites are liable to be reoxidized by adsorbed oxygen which would delay the reduction process. The tendency of hydrogen to react with free or adsorbed oxygen is more than to reduce the oxide.

The rate of the H$_2$-O$_2$ reaction is represented in the curves on the upper part of Fig. 4, from which it is evident that the reaction rate increases with the O$_2$ content of the gas phase, in agreement with previous work. The deviation of the curves with reduction time to a greater reactivity indicates that the catalytic effect of the freshly reduced iron on this reaction is greater than that of the oxide.

1. The explosion phenomena

No explosions were detected in the experiments carried out in the tube furnace arrangement even by the increase of the oxygen flow to 20% of that of hydrogen. Runs were then carried out at 800°C and 1000°C, using

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References:

(13) W. M. McKewan; Trans. AIME, 224 (1962), 387.
(15) M. Udy and C. Lorig; Trans. AIME, 154 (1943), 162.
(16) O. Specht and C. Zapfle; Trans. AIME, 167 (1946), 237.
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an oxygen flow rate of 100 cc/min. Vigorous explosions that took place did not permit further experiments. With 75 cc/min oxygen flow at 800° and 1000°C, a series of very light explosions were noticed at the start of the reaction but ceased with its progress. Below 15% O₂ at same temperatures no explosions occurred. Accordingly, it has been concluded that 15% O₂ of the amount of hydrogen passing gives an approximate safe value for the explosion limit under the present experimental conditions.

The ceasing of explosion by the progress of reaction can be attributed to the formation of water vapour which has a hindering effect on explosions as found before(3)(20).

2. Reduction with hydrogen in the fluidized state

The hydrogen flow rate used in this study is in most cases 4 L/min which equals to double the minimum fluidizing gas flow at 600°C. The reduction curves are shown in Fig. 5. The increase in reduction rate with temperature is natural since the reaction rate is controlled by the gaseous and solid diffusion and the dynamic potential of the reaction; the latter is related to the fundamental driving energy of the reaction, i.e., the free energy. Both factors increase with temperature. It should be noted that reduction is performed on a porous hematite ore which should have no anomalies as to the effect of temperature on its reduction(8)(21).

Beside the effect of temperature, the rate of reduction of iron ores in the fluidized state is mainly controlled by the rate of reducing gas supply because of the intimate contact between gas and ore which makes the water vapour formation appreciable(9)(11). Fig. 6 shows the effect of hydrogen flow rate on the reduction at 600°C using 2, 4 and 6 L/min, and it confirms the findings of previous workers.

3. Reduction with H₂-H₂O mixtures

Fig. 7 shows the effect of steam addition to hydrogen during reduction and it can be seen that with the increase in percentages of water vapour the retarding effect becomes so large as to stop the reduction reaction. This is understandable in terms of the change in free energy of the reaction which depends upon the equilibrium concentrations of the constituent as compared with their actual activities. The activities of the solid phases remain essentially unchanged. The free energy formula can be written as:

\[ \Delta F = RT (\ln K' - \ln K) \]

where \( K' = \frac{(H_2O)}{(H_2)} \) during reduction and \( K = \frac{(H_2O)}{(H_2)} \) at equilibrium.

K is constant for a given temperature and as \( K' \) approaches the value of \( K \) the dynamic potential of the reaction decreases and the reaction should stop when \( K' \) equilibrates \( K \). This is about the case with the addition of 20% water vapour in respect of the reduction stage, FeO (wüstite)→ Fe at 600°C, and thus the reduction rate is very slow. The 30% addition stopped completely the Fe₃O₄→ FeO reduction stage (compare with Fig. 8).

Beside this thermodynamic effect the increase in water vapour content in the ambient gas has a kinetic retarding effect in that it suppresses the diffusion of the gaseous product from the reacting site to the ambient gas, thus increasing its concentration(15)(21)(22). As

\[ \Delta F = RT (\ln K' - \ln K) \]

Fig. 7 Reduction with H₂-H₂O mixtures in fluidized bed at 600°C

Fig. 8 Iron-oxygen-hydrogen equilibrium diagram

(23) J. Lewis: Trans. AIME, 172 (1947), 27.
the concentration of H$_2$O increases at the reacting site its molecules will deprive hydrogen molecules from a larger portion of the reaction interface which decreases the reduction rate $^{(24)}$. McKewan assumed the occurrence of an oxidizing reaction of the active centres by the adsorbed water molecules, thus suppressing the reduction $^{(25)}$.

4. Oxygen injection during reduction with hydrogen

The starting temperature used for this study is 400°C, since the temperature rises excessively during experimentation. The oxygen ratios used are 5, 10 and 15% of the hydrogen flow. The results are shown in Fig. 9, in which the lower part gives the rate of reduction curves while the upper part shows the temperature variation in the bed due to both the reduction and the H$_2$-O$_2$ reaction. The lower curve in the upper part represents the cooling rate of the furnace when turned off.

In contrast with the results obtained in the preliminary study using the simple tube furnace arrangement; the reduction rate here increases with the increasing O$_2$ content in the gaseous mixture. This is due to the increase in the temperature of the reaction system as a result of the conspicuous heat liberation from the H$_2$-O$_2$ reaction. In these experiments the reduction furnace was turned off upon admission of the reducing gas mixture, and then it cooled gradually as indicated by the lower thermocouple.

It could be seen here that the reduction rate at the start of the experiments using H$_2$-O$_2$ mixtures is always higher than that for the experiment using hydrogen alone. This is due to the fact that the reduction temperatures in the former experiments are higher than that in the latter. At the earlier stage of reduction the H$_2$O/H$_2$ ratio in the ambient gas is not so effective in reduction as compared with the case for the intermediate and later stages of reduction since the equilibrium constants for the reduction reaction are high at the earlier stage and decrease with the progress of reduction. Accordingly, the effect of temperature is a decisive factor at the start of reduction. As reduction proceeds the retarding effect of the water vapour fugacity on reduction increases until it remarkably slows down the reduction rate when its value approaches that in the equilibrium state at this stage of reduction. Since there is no such hindering effect when using pure hydrogen, the rate of reduction curve should continue to 100% reduction intercepting the other three curves successively.

The first stage of reduction (Fe$_2$O$_3$-Fe$_3$O$_4$) is exothermic, and considering the heat liberated from the H$_2$-O$_2$ reaction, a steep rise in temperature should be expected at the start as has actually been observed. However, an equilibrium state will be attained between the heat liberated due to the H$_2$-O$_2$ reaction and the heat loss from the system and due to the endothermity of the following reduction reactions. This equilibrium state results in a peak value for the temperature rise, after which the temperature decreases gradually indicating a net heat loss.

When reduction stops, the heat effect in the system will arise only from the H$_2$-O$_2$ reaction, and since this is constant (all oxygen injected reacts with hydrogen as indicated from the exit gas analysis) the curve should become parallel to that giving the cooling rate of the furnace. The vertical distance at any moment between any of the three curves and that giving the cooling rate of the furnace, represents the resultant heat effect in the system.

The heat effect taking place per gram-mole hydrogen is represented in Table (1).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$ cal/g mol H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 O$_2$ + H$_2$ = H$_2$O</td>
<td>-58,600</td>
</tr>
<tr>
<td>3 Fe$_2$O$_3$ + H$_2$ = 2 Fe$_3$O$_4$ + H$_2$O</td>
<td>-2,500</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ + H$_2$ = 3 FeO + H$_2$O</td>
<td>+16,100</td>
</tr>
<tr>
<td>FeO + H$_2$ = Fe + H$_2$O</td>
<td>+4,000</td>
</tr>
</tbody>
</table>


The rise in temperature for the three O$_2$ : H$_2$ ratios used was checked by thermodynamic calculations at 11% reduction, (the end of the Fe$_2$O$_3$-Fe$_3$O$_4$ stage) by considering the amount of Fe$_2$O$_3$ reduced and the amount of oxygen reacted in this period and the specific heats of the materials encountered at the working temperatures. The calculated values were found to be close to the experimental ones; for example, for the 5% oxygen addition the actual rise is 170°C and the theoretically calculated one is 187°C.

5. Reduction in presence of oxygen and steam

The curves shown in Fig. 10 are self-explanatory on the basis of the previous discussion. The decrease in heat generated with the increase in water vapour content is expected since steam is the gaseous product of the \( \text{H}_2-\text{O}_2 \) reaction and thus will suppress the reduction. This was substantiated by the increase in the amount of unreacted oxygen in the exit gas.

In all the experiments conducted in the fluidized state no explosions were detected since the oxygen content was beyond the explosion limit as found in the preliminary study.

V. Conclusions

1. The rate of reduction of Aswan iron ore increases with the increase in temperature and gas flow rate.
2. The reduction is retarded when diluent gases as \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{H}_2\text{O} \) are added to hydrogen; in the latter two cases the retardation is mainly due to the formation or existence of the reduction gaseous product.
3. However, in case of oxygen injection the rise in temperature due to the heat liberated from the \( \text{H}_2-\text{O}_2 \) reaction counteracted and overwhelmed the retarding effect.
4. The rate of the \( \text{H}_2-\text{O}_2 \) reaction increases with the increase in \( \text{O}_2 \) content of the gas but decreases with the increase in \( \text{H}_2\text{O} \) content.
5. The explosion limit, under the present experimental conditions, was found to be about 15\% \( \text{O}_2 \) of the hydrogen volume.