

REACTIONS LEADING TO THE AUTO IGNITION OF DIRECT REDUCED IRON

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INTRODUCTION

Direct reduced iron, DRI, is produced without forming the liquid phase by reducing pellets of a very pure iron ore using a reducing gas obtained by reforming gas or from coal.

The importance of DRI in steelmaking⁽¹⁻⁴⁾ lies in the following considerations.

It may be used as a source of iron units for blast furnaces or cupolas.

It makes a low residual substitute for scrap or coolant.

Its pellet form lends easily to continuous charging and melting procedures with electric arc furnaces.

It is very easy to weigh and handle on belts, in hoppers and chutes.

The composition of DRI is more precisely defined than that of scrap.

The use of DRI will depend to a large extent on its price at the steelmaking site compared with the price, availability and quality of scrap.

Many DRI plants are located in the developing nations that are also oil producers^(5,6) and use DRI production as a means of storing the energy, or value, of the natural gas that frequently must be flared. The DRI produced by the developing nations, with abundant iron ore as well as energy, is likely to be less expensive than that produced in the USA⁽⁵⁾. Therefore, significant importation of DRI from its production site to the steelmaking site is to be expected and transportation represents a significant fraction of the cost of DRI to the steelmaker.

The reactions that occur during storage and transportation lower the degree of metallization of the DRI and are known to be the cause of several incidents that have endangered ships^(7,8).

DRI pellets are very porous, have a very high surface area to volume ratio, are highly reactive chemically and are good thermal insulators. Thus, when corrosion occurs it proceeds rapidly evolving heat that cannot easily be dissipated, consequently the temperature around the reaction site increases. The reactions that occur can also involve the generation of hydrogen gas as a further hazard, the problems being more acute in the case of sea transportation due to the more rapid corrosion reactions in sea water than in rain water.

Clancey⁽⁷⁾ has adequately highlighted the incidence of the hazard at sea where, at the time of his paper, out of 40 voyages, 4 resulted in serious fire hazard. Such incidents are a danger to life and incur heavy costs. The record of ocean transportation of DRI to date is unacceptable to insurers and shippers and calls for an understanding of the problem leading either to a solution or to a means of testing and evaluating batches of DRI to decide whether they are safe to transport or not.

A similar problem arises in the case of storing DRI in piles. Even in the presence of rain, DRI piles outside can be quite safe, however if the pile is moved to a new site, ignition can occur very rapidly. This is apparently due to sealing the moist pellets on the inside of the pile during restacking.

Jensen and Smailer⁽⁸⁾ contend that safe ocean transportation is possible if water can be excluded from the cargo. Clancey⁽⁷⁾ rightly claims this to be impossible because hatches that are removable, i.e. not welded, can never be watertight and are prone to take in water in bad weather when the decks are flooded and hatch covers distort, neither can it be guaranteed that the DRI will not be exposed to water at any time between production and loading. Indeed, it is not yet possible to define how 'dry' a cargo must be to be safe. Even if the ship could be kept dry, a typical porous cargo may contain 1% moisture due to capillary retention of water. That is 60 tons of water in a 6000 ton cargo.

Unless a simple solution to the problem is found, ships may have to be specially modified for transporting DRI. This of course will reduce the flexibility and increase the cost of transportation.

Clancey⁽⁷⁾ prefers the Sidbec technique in which the holds filled with DRI are flushed with carbon dioxide to displace the air. The technique has been shown to be effective over relatively short time voyages, however the holds cannot be 'topped up' en route, unless CO₂-producing equipment is fitted to the ship, which is costly and reduces the choice of ships for DRI transportation.

Nagel⁽⁹⁾ separated the attack of DRI into two processes, corrosion in aqueous media and oxidation in air. Due to the poor thermal

conductivity of the pellets both types of reaction can lead to temperature excursions at the reaction site. Whereas the dry oxidation reaction proceeds slowly at low temperatures, the aqueous reactions proceed more rapidly and were regarded⁽⁹⁾ as the cause of temperature escalation to levels at which high temperature oxidation can proceed sufficiently rapidly to be self sustaining. Although this view is regarded⁽¹⁰⁾ as being too simple, it is quite clear that wet DRI in an oxygenated atmosphere can satisfy all the conditions to become a fire hazard.

Passivation by magnetite and cementite layers has not proved to be effective against aqueous corrosion⁽⁷⁾ and sodium silicate coatings slow down corrosion in fresh water with little effect in salt water. The difficulty of achieving complete surface passivation, together with the probability of subsequent fracture and fines formation exposing new surfaces during handling, reduces the confidence that can be placed in passivation techniques.

Pietsch⁽¹¹⁾ showed that passivating the fresh pellets by exposing them to air reduced their reactivity in dry air but was not effective in stopping aqueous corrosion.

Pietsch⁽¹¹⁾ described techniques to assess the aqueous corrosion reactions and to simulate conditions in a ship's hold, however the techniques were used exclusively to obtain kinetic data with no observation of the micro-structural features, identification of reaction products or derivation of the mechanisms of the reactions.

It appears that reduction conditions cannot be varied economically to have a significant effect on the reactivity of the product^(12,13,14). The only technique that has reduced the reactivity of the pellets has been to press them into briquettes or to work the surface mechanically to reduce porosity and close up the surface pores. The latter technique is claimed to be effective in the Krupp kiln process⁽⁶⁾ and should be effective, initially at least, in reducing the reaction rates under both aqueous and dry conditions. Unfortunately this additional process does not prevent fracturing and fines formation during handling.

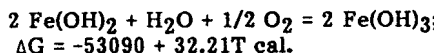
The mechanisms by which rust forms at room temperature have been reviewed by Misawa, Hashimoto and Shimodaira⁽¹⁵⁾ showing that the room temperature rusting of iron is a complex process involving the formation of ferrous hydroxide, Fe(OH)_2 , green complexes and green rusts as intermediate products leading eventually to the oxidized Fe_3O_4 or fully oxidized FeOOH products.

A substantial amount of work has also been carried out on the reactions between iron and water in oxygen-free conditions because of the importance of these reactions commercially in boilers, heat exchangers and central heating systems⁽¹⁶⁾. The final corrosion products are found to be Fe_3O_4 and hydrogen gas formed

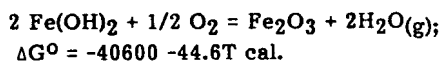
through Fe(OH)_2 as an intermediate product. These reactions, involving the formation of hydrogen from iron and liquid water, are almost all endothermic and therefore do not lead to the generation of high temperatures. On the contrary, the heat to support the reactions must be supplied externally.

The presence of copper metal did not appear to catalyse the reaction producing hydrogen⁽¹⁶⁾, as might have been expected in view of the low hydrogen overpotential on copper compared with that on iron. Temperature apparently also had little effect on the hydrogen evolution rate, as also observed by Brush and Pearl⁽¹⁷⁾, whereas Gallagher⁽¹⁸⁾ found that the reaction rate increased with increasing temperature, although the extent of the increase in reaction rate varied strongly with the source of the iron.

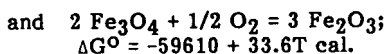
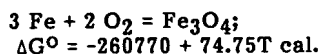
The subject of ferrous metal fires has recently been reviewed by the National Materials Advisory Board⁽¹⁹⁾. In their conclusions they call for the development of a simple test of cargo susceptibility to spontaneous heating. They also present a simplified model to demonstrate the effects of thermal imbalance (i.e. between heat generation and heat loss) in causing temperature excursions. Their model assumes that all of the ferrous hydroxide, Fe(OH)_2 , that forms is converted to ferric hydroxide, Fe(OH)_3 , by oxidation in the aqueous environment by



Since this reaction proceeds in the presence of water, it is limited in temperature to 100°C or the boiling point of a salt solution. An alternative would be to oxidize the Fe(OH)_2 in a gaseous environment as



This reaction is capable of heating beyond 100°C and might therefore be regarded as one of the reactions in the ignition process since the higher the temperature above 100°C that can be reached by this reaction, the more easily and more rapidly the oxidation of iron can proceed according to

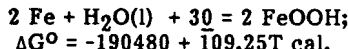
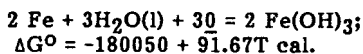


These reactions will also proceed faster if the oxide forms as an open porous oxide rather than as a compact adherent oxide. Thus the morphology of the reaction product is very important, unfortunately little is known about the oxidation of iron in atmospheres of nitrogen, oxygen and water vapor at temperatures between 100°C and 400°C.

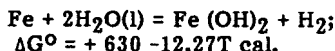
The object of the current work is to establish the detailed mechanism by which ignition of DRI proceeds and to suggest techniques of preventing it and of testing the susceptibility of different batches of DRI to auto ignition. The work described in this paper represents progress made towards these goals.

EXPERIMENTAL AND RESULTS

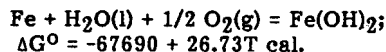
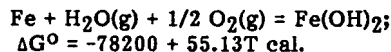
The objectives of this work are to study the kinetic and morphological steps of reactions that form a sequence leading to ignition of direct reduced iron. The reactions to be studied were derived from a preliminary model of the various zones thought to develop within a stack of DRI pellets in the hold of a ship. This is shown in Figure 1 and suggests that the DRI pile sits in water whose depth defines the 'aqueous zone'; water rises by capillary action into the DRI piles to a level which defines the limit of the 'capillary zone'. In both of these zones the iron may react with water to form rust under oxidizing conditions



or endothermically when the oxygen level falls

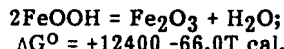
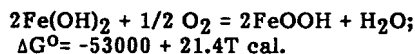
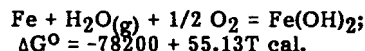


Due to the presence of liquid water that defines the extent of these zones, the temperature rise will be restricted to 100°C but will be sufficient to cause evaporation of water which will condense higher in the DRI pile. This action defines the 'reflux zone' in Figure 1 and further rusting proceeds by reactions such as

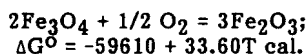
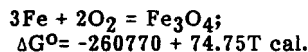


Condensation of water vapor will also supply latent heat and the temperature of this zone is likely to reach up to 100°C thus supplying further water vapor to the next zone called the 'vapor zone' in Figure 1.

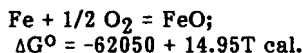
In the vapor zone the reactions involve water vapor but not condensed water. This zone was previously heated by in situ corrosion reactions that proceeded to completion i.e. to exhaust the water initially present, it is also heated by warm nitrogen rising by convection from the lower zones that have been heated by exothermic reactions. Examples of the type of reaction expected to occur in the vapor zone are



These exothermic reactions may lead to temperature escalation such that oxidation reactions may occur such as



and above 570°C



Once these high temperature oxidation reactions are established, they can encourage convective circulation of gases with entrainment of air from the hatches and the situation will be very difficult to reverse.

This starting hypothesis involves three stages:

- (a) Aqueous corrosion reactions provide heat and water vapor while forming $\text{Fe}(\text{OH})_2$, ferrous hydroxide.
- (b) Ferrous hydroxide formed in sufficient quantity will oxidize to produce oxide, oxyhydroxide and heat. This stage, first introduced by Marquis, limits the aqueous reactions with the high temperature oxidation reactions.
- (c) At temperatures well above 100°C reached in (b) iron starts to oxidize directly and ignition is established.

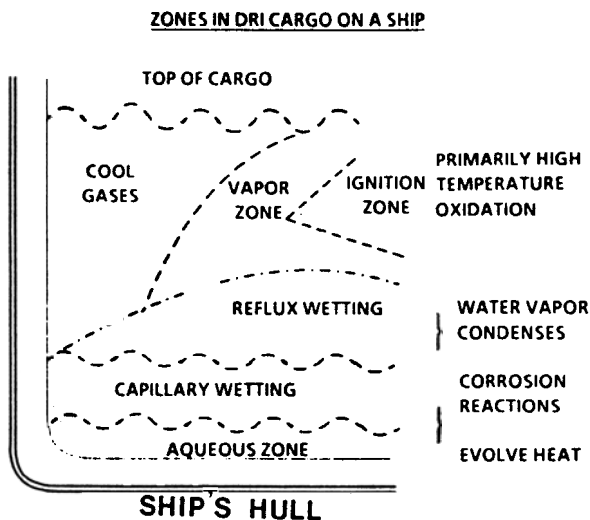


Fig. 1 - Preliminary model of reaction zones in a DRI cargo hold.

This initial hypothesis served as a convenient and very helpful basis on which to plan an experimental program. This was designed to study the kinetics and morphologies of the reactions that occur in the various zones.

Since the DRI pellets are highly porous and give results that are not reproducible it was necessary to use iron foil specimens for the initial experiments, in which the specimens are exposed to water and to water saturated oxygenated gases to represent the aqueous and reflux situations respectively. These experiments were carried out at temperatures up to 90°C and using up to 20% oxygen content in the gas stream. Salt water was used to simulate the environment relevant to ocean transportation.

The apparatus used is shown in Figure 2. A glass or stainless steel baffle is used to prevent the gas bubbles from contacting the specimen. It was found that this precaution led immediately to more uniform and reproducible attack of the iron foil specimens. The reproducibility of the results was improved further by maintaining the gas flow at 100 ml sec⁻¹ which ensured good circulation of salt water without allowing bubbles to entrain and be pulled into the specimen area. The initial results are shown in Figures 3 and 4.

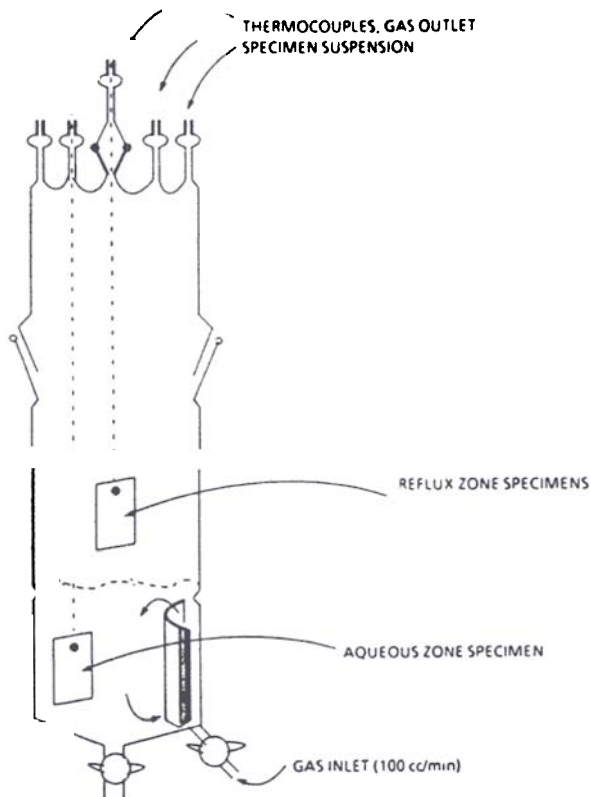


Fig. 2 - Apparatus for specimen exposure.

It was clear from early specimens that two corrosion products were formed. One product adhered strongly to the specimen and could only be removed by cathodic stripping. The second product was produced as a flocculent precipitate at the metal surface.

The results of weighing the specimen before exposure, after exposure with the flocculent precipitate washed away and, finally, after stripping away the adherent precipitate, allow the amounts of iron in the adherent layer and in the precipitate, together with the total amount of iron corroded, to be established. The results are shown in Figures 3 and 4 for different conditions as indicated.

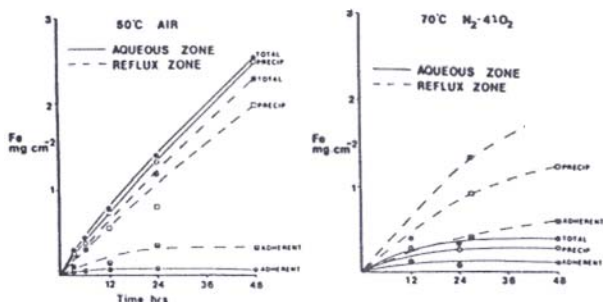


Fig. 3 - Kinetics of reaction between iron and salt water showing amount of iron in precipitate, adherent scale and total iron reacted.

(a) 50°C 20% oxygen (b) 70°C 4% oxygen

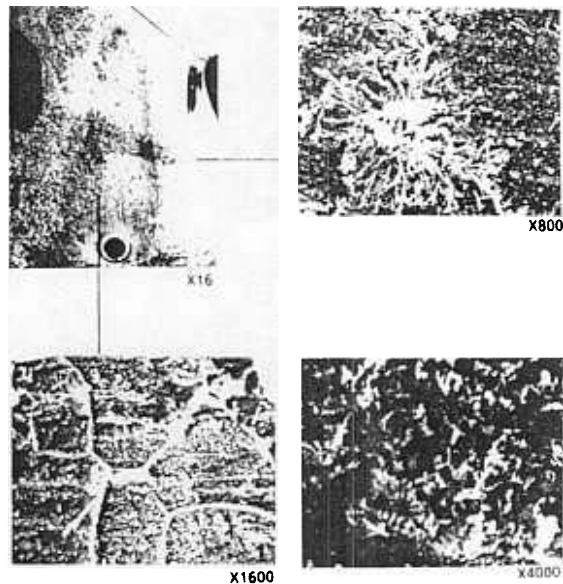


Fig. 4 - Morphologies of precipitate growth and adherent layer formed on specimens exposed at 50°C and 20% oxygen in (a) immersed and (b) reflux situations

This type of experiment was carried out using two specimens immersed in the water bath and two specimens suspended immediately above the water in a zone where the temperature is still maintained close to that of the water bath, water droplets can form on the specimen but the oxygen is available from the gas phase directly instead of having to dissolve and transport through a large mass of water. It was found that, at low oxygen potential, and higher temperatures the reaction rates in this 'reflux' situation could be faster than with immersed specimens.

In both reflux and immersed cases one specimen of the pair exposed was used to establish the weight changes and the other was used to establish morphological features.

X-ray diffraction was used to identify the species present in the corrosion product. It was found that the predominant species were Fe_3O_4 , FeOOH and $\text{Fe}(\text{OH})_3$. Thus, under the conditions examined so far, only the highly oxidized species are found. It should be noted however that color changes on the specimen during initial reaction stages indicate that the initial reaction product is ferrous (green) which changes to brown indicating predominance of the ferric state at later stages. This indicates that the ferrous state may be produced by reactions involving low oxygen potentials which would be expected to exist within a pile of DRI pellets as corrosion reactions exhaust the limited oxygen supply. So far it has not been possible to remove reaction products in the ferrous state from the reactor and to maintain them in that state due to the very rapid oxidation of ferrous iron. This is encouraging in terms of the role that $\text{Fe}(\text{OH})_2$ may play in the overall ignition mechanism.

The results obtained indicated, Figures 3 and 4, that a very thin layer of Fe_3O_4 is formed rapidly during the initial reaction stages. Thereafter, the corrosion product is almost entirely composed of the loose, flocculent, precipitate. Although the Fe_3O_4 layer is observed to cover the surface of the specimen quite uniformly, as seen in the SEM micrographs of Figure 4, it clearly does not markedly influence the rate of the reaction by which the loose precipitate is formed. Thus the mechanism by which the precipitate forms is likely to be represented by Figure 5 which involves a porous Fe_3O_4 adherent layer. In this case, ions of iron migrate predominantly through the network of pores filled with the (salt) water, electrons migrate outwards through the Fe_3O_4 . The reaction products form at the outer Fe_3O_4 /solution surface since here the dissolved oxygen can form hydroxide ions in a cathodic reaction. The ferric hydroxide can thus form by precipitating from solution close to the Fe_3O_4 surface where the hydroxide ions form as observed. The formation of FeOOH requires the involvement of oxygen also, this would be expected to occur most conveniently on the

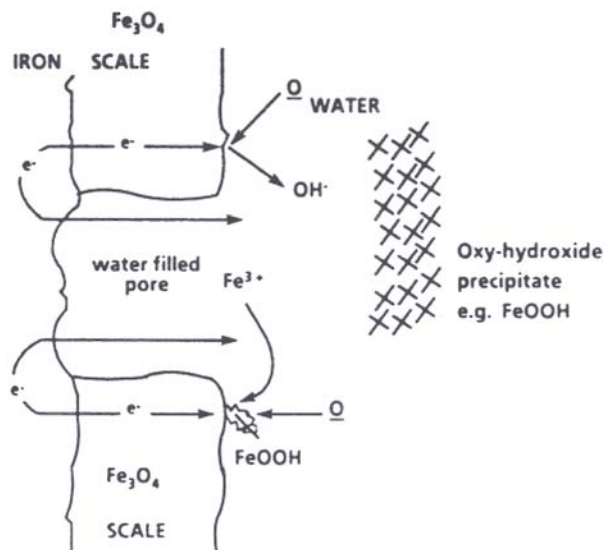
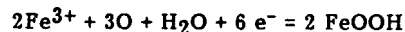
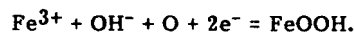


Fig. 5 - Reaction mechanism proposed for the development and formation of the precipitate and adherent scale reaction products formed on iron in aerated salt water.

Fe_3O_4 surface since the oxygen may ionise as well as forming OH^- to allow the FeOOH to form by the reaction



Alternatively, this may be split into reactions such as the independent formation of hydroxide ions and FeOOH formation according to



Examination of the surface of the adherent (Fe_3O_4) layer after washing away the loosely adherent precipitate phase shows, using the SEM, that a 'feathery' phase is growing on top of the Fe_3O_4 . This is shown in Figure 4 and is identified as FeOOH growing according to the mechanism proposed above.

It appears that the porous Fe_3O_4 layer offers little or no resistance to the corrosion reaction. However it ensures that a relatively high oxygen potential exists at the outer surface which interfaces with the aqueous solution. This means that, under the conditions studied, it is most likely that fully oxidized precipitates will form. However, in the real case of DRI pellets and limited oxygen supply, somewhat different circumstances may obtain especially within the pores which are expected to become rapidly starved of oxygen.

Specimens exposed in the reflux zone of the apparatus similarly showed reaction products of an Fe_3O_4 layer and very finely divided FeOOH outgrowths. At higher temper-

atures and lower oxygen potentials the reaction proceeds more rapidly in the reflux situation which gives easy access of the oxygen in the gas stream to the metal surface wetted with condensed water. Under low oxygen potentials, reactions in the aqueous zone, where specimens are submerged, proceed more slowly due to the low concentration of oxygen available in solution for reaction.

The rate at which oxygen is removed from the salt solution during rust formation has been followed using an Orion oxygen cell which allows oxygen in solution to be measured. At the same time any hydrogen evolved was measured either using a gas chromatograph or a gas burette. Typical results are given in Figure 6 for a pile of 12 DRI pellets submerged in 200 ml of salt solution at 25 and 40. It can be seen that the oxygen content is reduced rapidly to a value that remains fairly constant or falls very slowly. Over the same time period hydrogen is evolved continuously, regardless of the oxygen content of the solution, and settles down to a constant rate of evolution. The evolution of hydrogen from a pile of DRI pellets under highly oxidizing conditions is not surprising since the liquid within the pores would rapidly become denuded of oxygen. However, when the experiment was repeated using non porous iron foil specimens, hydrogen evolution was observed from solutions of high oxygen content (7ppm). These observations were made using a gas chromatograph because of the very low rate of gas evolution. These results indicate very

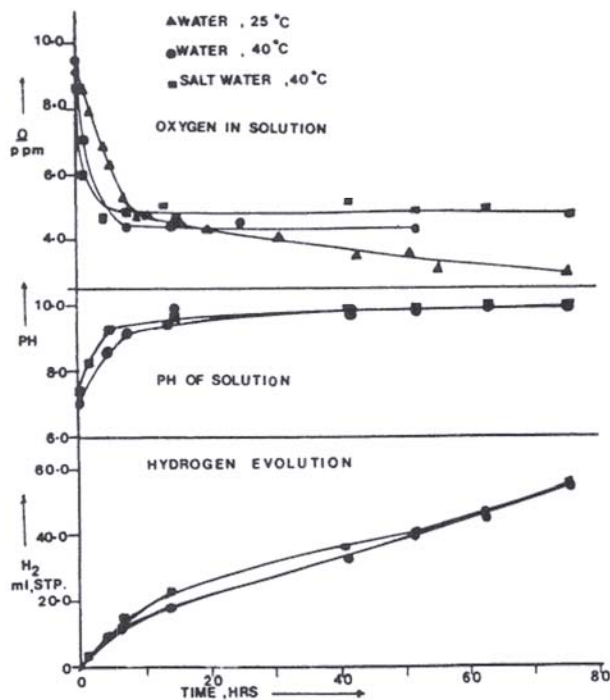
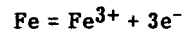
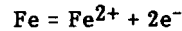


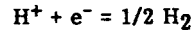
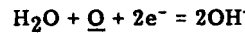
Fig. 6 - Consumption of oxygen and evolution of hydrogen by immersed DRI pellets.

clearly that several cathodic reactions may proceed simultaneously to consume the electron liberated by the anodic reaction that primarily involves the ionisation of iron

Anodic Reactions



Cathodic Reaction



This is important because it indicates that hydrogen is being evolved continuously from the pellets in the aqueous and capillary zones of a DRI pile or cargo.

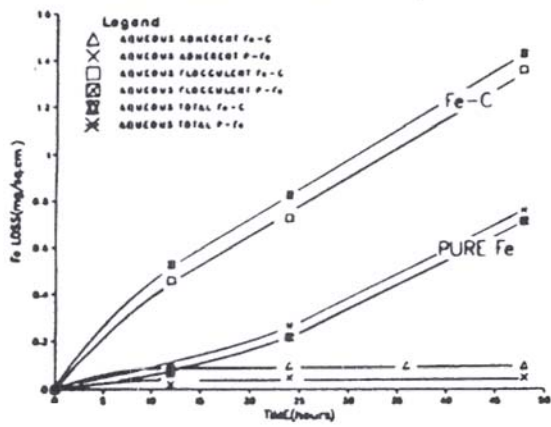
The systems for which kinetics have been studied used pure iron foil whereas the pellets contain substantial concentrations of carbon, depending on manufacture. The effect of carbon on the corrosion reactions was studied briefly using iron foils carburized to 0.8%C throughout. It was found that, at 50°C in the aqueous condition oxygenated with nitrogen 4% oxygen, the carburized foils reacted more rapidly and accelerated the formation of the flocculent FeOOH precipitates. The kinetics of reaction for Fe-C foils are compared with those for pure Fe foils in Figure 7. Figure 8 shows an SEM micrograph of the surface of a corroded carburized specimen and it can be seen that the ferrite phase is preferentially leaving the carbide laths of the original pearlite structure barely attacked. The acceleration of the corrosion reaction is regarded as the result of increased cathodic reaction rates when the pearlite acts as the cathode. This is the first indication that purity is important in the corrosion of DRI but, if the corrosion reactions are to be interpreted by an electrochemical mechanism, the nature of the cathode and, particularly, the value of hydrogen overpotential is regarded as being highly important. The corresponding hydrogen evolution characteristics have not yet been evaluated.

The results that are regarded as significant are that a very finely divided oxidation or corrosion product is formed in the interstitial spaces between the pellets and that hydrogen is produced continuously from the pellets that are constantly in contact with water. The production of hydrogen which was previously regarded simply as an additional hazard is now thought to play a key role in the auto ignition sequence.

Improved Model for Auto Ignition of DRI

The basic mechanisms proposed are shown in Figure 9. It is considered that a very flocculent corrosion product forms wherever the pellets are wetted. In the

COMPARISON OF THE CORROSION OF Fe-C AND PURE Fe FOILS AT 50 C AND 4%O2 UNDER AQUEOUS CONDITIONS



COMPARISON OF THE CORROSION OF Fe-C AND PURE Fe FOILS AT 70 C AND 4%O2 UNDER AQUEOUS CONDITIONS

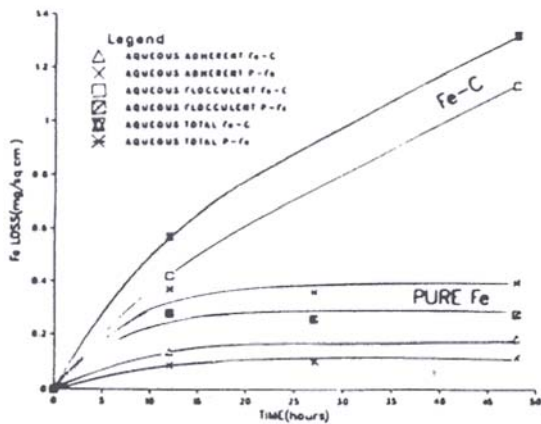


Fig. 7 - Comparison of reaction kinetics between pure iron and iron - 0.8% carbon foils at 50°C and 70°C with 4% oxygen.



Fig. 8 - Surface of corroded Fe - 0.8% C foils showing preferential attack of ferrite leaving Fe₃C laths exposed

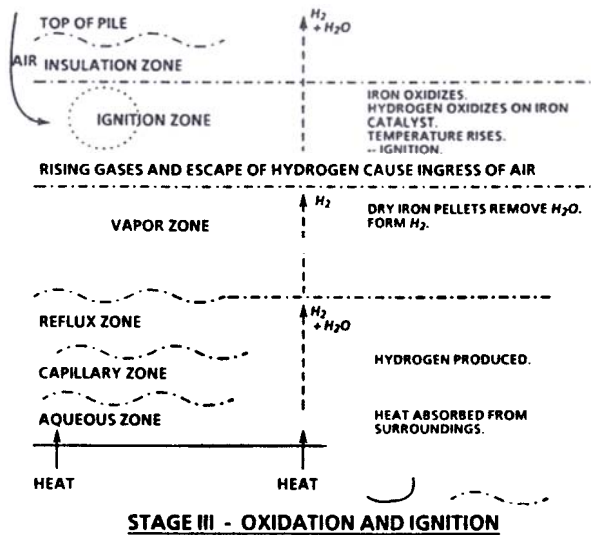
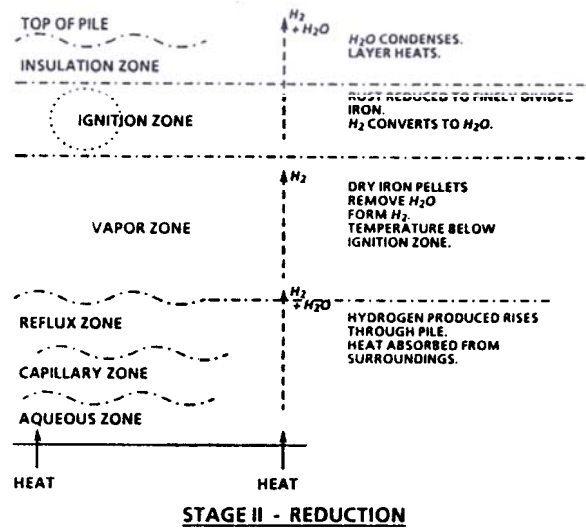
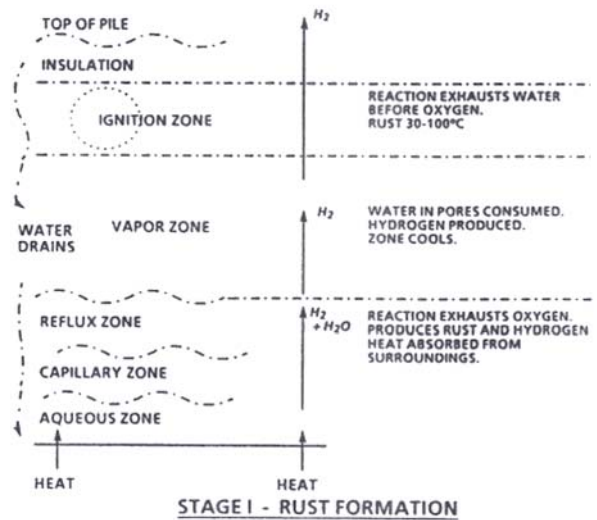
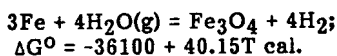
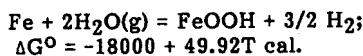


Fig. 9 - Improved model for the autoignition of direct reduced iron.

presence of oxygen the reactions with condensed water are exothermic and wherever they occur local heating will result. Those sites that are dampened by percolation of water will react exothermically so long as the oxygen is present in the gas spaces. The reaction will consume water and these zones will dry out, finishing with a finely divided reaction product somewhat warmer than the rest of the cargo. Such zones are expected to exist in the upper levels of the cargo since excess water will run down through the pile to accumulate at the base.

In contrast, the lower zone of the cargo is permanently immersed in bilge water and, when oxygen is exhausted, continues reacting to produce rust and hydrogen by endothermic reactions which normally would be expected to cool the zone and reduce the rate. However in a ship, with good thermal contact with the sea, the reaction conditions in this zone are more realistically regarded as isothermal, rather than adiabatic, since the presence of the water will ensure good heat conduction in the pellet layer that is water saturated. Under these conditions, a steady rate of hydrogen production is expected to be maintained from the aqueous, capillary and reflux zones.

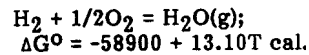
The gases rising from the reflux zone will contain hydrogen, nitrogen and will be saturated with water vapor at the reflux zone temperature. As this gas mixture rises it may react with the dry pellets above it to consume water vapor according to



Both types of reaction remove water vapor and replace it by hydrogen, thus reducing the oxygen potential of the atmosphere as it rises through the pellet stack.

If the rising gas mixture passes through a pellet zone where, previously, the finely divided precipitate was formed exothermically and which now exists at a higher temperature than its surroundings, reduction of the precipitate will proceed and will produce a very finely divided iron product. Such a finely divided metal will be extremely pyrophoric and, as subsequent exposure to oxidizing conditions, will react vigorously leading to rapid temperature increase at this specific site. The temperature increase depends upon the amount of finely divided

iron available to react when rough seas cause air or oxygenated water to be admitted to the DRI hold. The more of the initial corrosion product that is formed and the more of this that is converted to finely divided iron, the more likely is subsequent exposure to oxidizing conditions to lead to temperatures high enough for high temperature oxidation reactions to be sustained. If this occurs then convection currents will bring in air from the outside to oxidize the metal further. At this stage also, in the presence of excess oxygen, the rising hydrogen may burn on the hot metal which now will act as a catalyst for the reaction



For this sequence of reactions to succeed in provoking ignition, an adequate supply of hydrogen of low water vapor content must be supplied to the reduction site for the formation of finely divided iron. Thus, it is necessary to have a column of dry pellets between the top of the reflux zone and the ignition site to modify the H₂O content of the rising gas. Further, this column must be sufficiently long to sustain the removal of H₂O from a quantity of hydrogen large enough to complete reduction of the initial precipitate in the ignition site.

Thus it is seen that the production of hydrogen and its purification are important functions in the ignition sequence and it may be predicted that, if the column of dry pellets is not tall enough, then ignition may not occur. This correlates well with the observations that shallow DRI piles do not ignite readily.

It is anticipated that the hypothetical mechanism given here is close enough to being correct and experiments are in hand to study the vital components of the ignition sequence. Subsequently an apparatus will be built to study the integrated mechanism in order to evolve a test of the tendency of a batch of DRI to ignite. In the most favorable case it may be possible to propose steps that can be taken to minimize, or even prevent, ignition within the economic restrictions of the use of the material.

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