

POLARIZATION MEASUREMENTS ON IRON IN ALKALINE SOLUTIONS AT HIGH PRESSURES AND HIGH TEMPERATURES.

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During the last few years the corrosion research section of the KEMA laboratories has performed electrochemical measurements at high pressures and high temperatures in weakly as well as in strongly alkaline solutions to obtain more information about the reaction mechanism of oxide formation and corrosion in boiler tubes.

For this purpose an autoclave (500 ml volume) had been developed, in which three electrode wires were mounted, electrically isolated from the autoclave by P.T.F.E. gaskets. A chemically pure iron wire was applied as a working electrode; the counter electrode was a platinum one. For reference electrode the Hg/HgSO₄-0.1 n K₂ SO₄ system was chosen.

In the bottom of the autoclave a stainless steel Luggin-Haber capillary was mounted, at the end of which the reference electrode was fixed. The temperature of this electrode did not exceed 60 °C at an autoclave pressure and temperature of respectively 42 atm. and 250 °C. According to Van Ipenburg the potential value of this half cell (+ 720 mV vs SHE) is independent of temperature up to 90 °C. A "Wenking Breitband Potentiostat type 61 R" was employed. The potentiometer of the potentiostat was driven via a gear wheel system by a synchromatic motor, which was controlled by a time switch. During the measurements the potentiometer was moved for a period of 5 minutes every 30 minutes, resulting in a potential change of 50 mV, and the potential was kept constant during the remaining 25 minutes.

Polarization measurements were carried out on iron wires in alkaline solutions starting at cathodic potentials and finishing at anodic values. Some of the polarization curves at 250 °C and 42 atm. have been summarized in Figure 1. The potentials at which current maxima and some other specific current discontinuities occurred have been plotted in a potential-pH diagram, shown in Figure 2.

For a certain electrochemical reaction the slope of the corresponding line in a potential vs pH diagram at a constant iron ion concentration depends upon the ratio of the number of electrons and the number of hydroxyl ions involved in that particular reaction. To establish the electrochemical reactions which might correspond to the lines plotted in Figure 2, an equilibrium diagram was calculated of potential values versus log iron ion concentrations for various possible reactions using the Nernst law. See Figure 3 and Table 1. The reaction having the lowest equilibrium iron ion concentration at a certain potential was assumed to be thermodynamically the most favorable one at the potential concerned. In this way the most probable reactions for the various lines in Figure 2 could be deduced.

In strongly alkaline solutions (pH 11-14), the potential-pH lines in Figure 2 are in our opinion the results of HFeO₂⁻ formation by reaction (20), magnetite development by reaction (25), αFe₂O₃ formation by reaction (12a) and/or (28a), and finally oxygen development by reaction (32), going from low to high potentials. The HFeO₂⁻ ions will be transported via the pores in the magnetite layer and will dissociate at the more alkaline oxide-solution interface. Forming iron anions hydroxyl ions will be consumed, so that the pH value at the oxide-metal interface will decrease. Besides, magnetite development from ferroate anions causes an increase of pH value at the oxide-solution interface. Corrosion exposition tests, applying a constant potential of -800 mV on the working electrode, were carried out in 0.5 n NaOH to study the morphology of the oxide layer formed. The oxide thus formed consisted of a very porous inner layer and a more compact outer layer with many coarse magnetite crystals. The porous inner layer was weakly red polarizing, indicating a mixture of magnetite and hematite. In our opinion, ferrous hydroxide will be partly transferred into magnetite by reaction (11), coupled with a volume decrease of 43%, and the rest will be dissolved, forming ferrite anions (FeO₂⁻) by reaction (23), that will be further oxidized to αFe₂O₃ by reaction (31 a). Dissolution of ferrous hydroxide, transition into magnetite as well as development of hydrogen gas will cause the porosity of the inner oxide layer also frequently found by many scientists in the past.

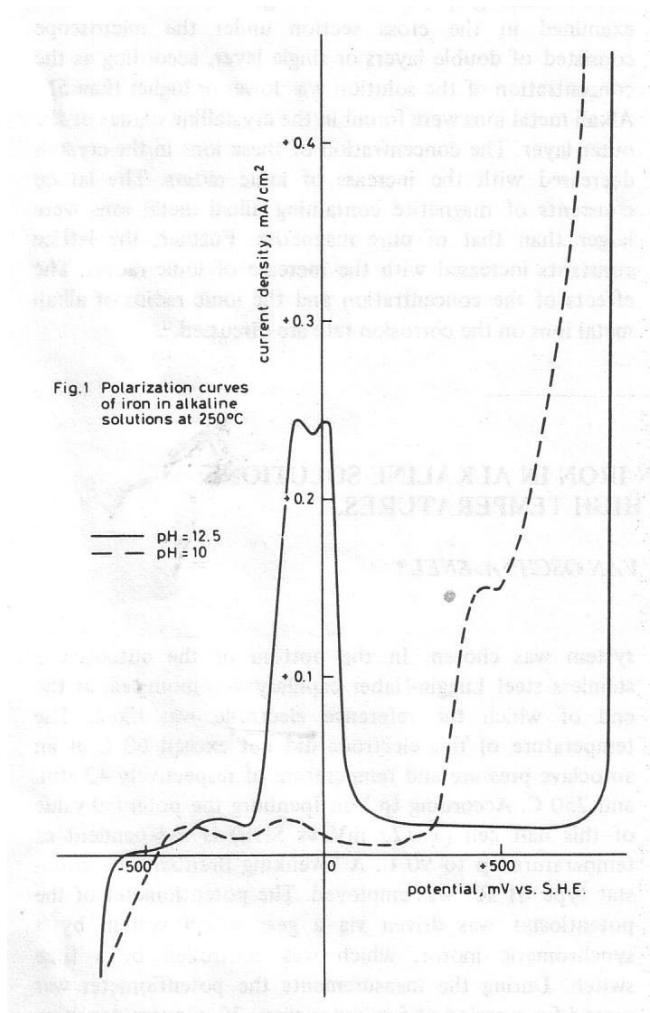


FIGURE 1 - Polarization curves of iron in alkaline solutions at 250 C.

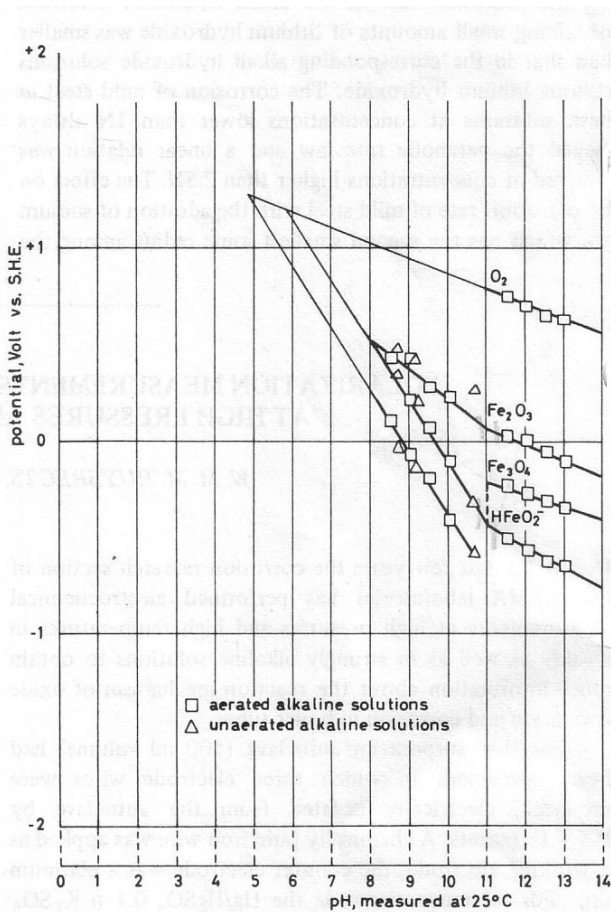


FIGURE 2 - Potential-pH lines of iron, derived from polarization measurements in NaOH solutions at 250 C.

Corrosion exposition tests at higher potentials (-400 mV) resulted in more crystalline oxide layers due to oxidation of FeO_2^{2-} ions by reaction (25). When the solid-state transport of iron in magnetite to the oxide-solution interface is too small, for instance on account of cracks in the oxide parallel to the oxide-solution interface, magnetite will not be developed by reaction (25), but $\alpha\text{Fe}_2\text{O}_3$ platelets will be developed by reaction (30a), which reaction is thermodynamically more favourable at this high potential value (Figure 3). Corrosion exposition applying a constant potential in the area of $\alpha\text{Fe}_2\text{O}_3$ formation showed that this oxide is developed in different modifications, namely a brown more amorphous oxide, beside light grey $\alpha\text{Fe}_2\text{O}_3$ platelets.

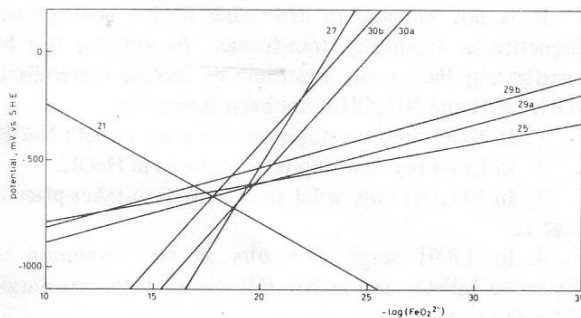


FIGURE 3 - The equilibrium FeO_2^{2-} concentration plotted a function of the potential for various electrochemical reactions in 1n NaOH.

In weakly alkaline solutions, two small current maxima appeared to occur, which are probably due to magnetite formation by reactions (7) and (8). At the first current peak, reaction (7) will dominate and at the second maximum reaction (8) will do. Thermodynamically, the reactions (7) and (8) appeared to be the most favourable ones at those peak current potentials because of the corresponding lowest iron ion concentrations. In 10^{-4} n NaOH solutions the iron ion concentrations at the first and second current maximum were respectively $(\text{Fe}^{2+}) = 3.5 \cdot 10^{-10}$ and $(\text{Fe}^{3+}) = 5 \cdot 10^{-10}$. At higher potentials the current increased slightly and become oscillating (in 10^{-4} n NaOH at + 230 mV), and different small current peaks often occurred pointing to ferrate formation and pitting of the sample by reaction (18). The potentials at which the current starts oscillating are also plotted in Figure 2. X-ray diffraction of wires tested at constant potentials showed formation of magnetite and $\alpha\text{Fe}_2\text{O}_3$, no matter what polarization potential was applied. However, the higher the potential value the more $\alpha\text{Fe}_2\text{O}_3$ was found. At high potentials many small pits were formed.

From the measurements mentioned above we suggest the following corrosion reaction mechanism. Magnetite will be formed by transition of ferrous hydroxide or by direct oxidation of ferrous cations at low corrosion potentials in strongly as well as in weakly alkaline solutions.

In weakly alkaline solutions magnetite is also formed at higher corrosion potentials by oxidation of both ferrous and ferric cations, developing hydrogen gas. Magnetite will dissolve at still higher corrosion potentials, forming ferrate ions coupled with pitting of the iron samples.

TABLE I

$3 \text{Fe}(\text{OH})_2$	$+ 2 \text{OH}^-$	$\rightleftharpoons \text{Fe}_3\text{O}_4$	$+ 4 \text{H}_2\text{O}$	$+ 2 \text{e}$	(11)
2Fe	$+ 6 \text{OH}^-$	$\rightleftharpoons \alpha\text{Fe}_2\text{O}_3$	$+ 3 \text{H}_2\text{O}$	$+ 6 \text{e}$	(12a)
$2 \text{Fe}(\text{OH})_2$	$+ 2 \text{OH}^-$	$\rightleftharpoons \alpha\text{Fe}_2\text{O}_3$	$+ 3 \text{H}_2\text{O}$	$+ 2 \text{e}$	(17)
Fe_3O_4	$+ 16 \text{OH}^-$	$\rightleftharpoons 3 \text{FeO}_4^{2-}$	$+ 8 \text{H}_2\text{O}$	$+ 10 \text{e}$	(18)
Fe	$+ 3 \text{OH}^-$	$\rightleftharpoons \text{HFeO}_2^{2-}$	$+ \text{H}_2\text{O}$	$+ 2 \text{e}$	(20)
Fe	$+ 4 \text{OH}^-$	$\rightleftharpoons \text{FeO}_2^{2-}$	$+ 2 \text{H}_2\text{O}$	$+ 2 \text{e}$	(21)
2Fe	$+ 4 \text{OH}^- + \text{FeO}_2^{2-}$	$\rightleftharpoons \text{Fe}_3\text{O}_4$	$+ 2 \text{H}_2\text{O}$	$+ 6 \text{e}$	(25)
3FeO_2^{2-}	$+ 2 \text{H}_2\text{O}$	$\rightleftharpoons \text{Fe}_3\text{O}_4$	$+ 4 \text{OH}^-$	$+ 2 \text{e}$	(27)
$2 \text{Fe}_3\text{O}_4$	$+ 2 \text{OH}^-$	$\rightleftharpoons 3 \alpha\text{Fe}_2\text{O}_3$	$+ \text{H}_2\text{O}$	$+ 2 \text{e}$	(28a)
Fe	$+ 2 \text{OH}^- + \text{FeO}_2^{2-}$	$\rightleftharpoons \alpha\text{Fe}_2\text{O}_3$	$+ \text{H}_2\text{O}$	$+ 4 \text{e}$	(29a)
		$\rightleftharpoons \gamma\text{Fe}_2\text{O}_3$			(29b)
2FeO_2^{2-}	$+ \text{H}_2\text{O}$	$\rightleftharpoons \alpha\text{Fe}_2\text{O}_3$	$+ 2 \text{OH}^-$	$+ 2 \text{e}$	(30a)
	4OH^-	$\rightleftharpoons \text{O}_2$	$+ 2 \text{H}_2\text{O}$	$+ 4 \text{e}$	(32)

In strongly alkaline solutions, however, the reaction mechanism is probably as follows. The ferrous hydroxide formed that might be transferred into magnetite and perhaps also into hematite by the reactions (11) and (17) respectively, will also dissolve partly, forming ferrate anions (FeO_2^{1-}), which will oxidize together with iron to $\alpha\text{Fe}_2\text{O}_3$ according to reaction (31a). Besides, iron will dissolve forming HFeO_2^{1-} anions, which will be transported in the pores of magnetite to the oxide-solution interface. These anions will dissociate into the ferroate anion FeO_2^{2-} at this interface, where the solution will be more alkaline. When iron can diffuse in the magnetite layer to the oxide-solution interface in a sufficient amount, coarse crystalline magnetite will be developed by reaction (25). However, $\alpha\text{Fe}_2\text{O}_3$ can be formed by reaction (30a) at high corrosion potentials, if the solid state transport of iron in magnetite is too small. At low corrosion potentials, magnetite will always be formed from ferroate oxidation by reaction (27), resulting in coarse magnetite octaeders too.

A double layer, consisting of a porous inner layer and a coarse crystalline outer layer, will be formed when transition of ferrous hydroxide into Fe_3O_4 dominates. A single coarse crystalline magnetite layer will be developed if the oxidation of ferroate ions is the most dominant reaction. In our opinion strange cathodic surfaces do not depolarize the cathodic reaction so much, but they rather create a

large concentration gradient for the iron anions causing too low a concentration on the oxide-solution interface and therefore magnetite formation from ferrous hydroxide dominates, which results in the development of the double layer mentioned before.

From our experiments it is evident, that the corrosion reaction mechanism of iron at high pressures and high temperatures is very complex. So it will be very hard to determine an activation energy with a clear physical meaning for the corrosion of steel under the conditions mentioned, because different reactions can occur at the same time. Some test circumstances such as the presence of cathodic surfaces, stirring of the solution, Cl^{1-} contamination etc. do influence one or more of the electro-chemical reactions and so the overall corrosion process.