

EFFECT OF COPPER AND COPPER OXIDE ON CORROSION OF BOILER STEEL

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ABSTRACT

Electrochemical measurements made on iron and copper have shown that under certain conditions copper and copper oxide promote corrosion in the magnetite coating of boiler pipes.

1. INTRODUCTION

Suspended matter in boiler water is often deposited on the tubes where the heat transfer is high. Relatively large amounts of the deposits. It is difficult to decide whether the copper is produced directly by coprecipitation of iron oxide and copper or by reduction of the copper oxide with simultaneous oxidation of the magnetite film on the tubes (Refs. 1, 2). The deposits have led to a series of tube failures. In an investigation of the problem, polarisation measurements were made on copper and iron and corrosion experiments were carried out on steel in alkaline containing suspended copper and copper oxide.

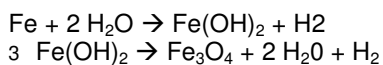
2. ELECTROCHEMICAL EXPERIMENTS

The polarisation experiments were made in an autoclave at 250 and 42 kg/cm² pressure, in alkaline solution. The autoclaves and the methods have already been described (Ref. 3). The polarisation curves at 250 and 42 kg/cm² pressure for chemically pure iron and for copper are shown in **Figures 1-3**.

2.1 Measurements in 0.0001 N NaOH

It can be seen from **Fig. 1** that the polarisation curves for iron show two current density maxima (- 400 and - 100 W) which probably correspond to the oxidation of Fe²⁺ and Fe³⁺ to Fe₃O₄. At +230 W and higher potentials the current density fluctuates so that different, irregular current density maxima were measured. In our opinion, this phenomenon indicates oxidation of Fe₃O₄ to FeO₄²⁻, associated with pitting of the iron sample.

At the rest potential (- 475 mV) iron is oxidised to Fe₃O₄ according to the Schikorr reaction;



Other electrochemical reactions such as the formation of alpha Fe₂O₃ by oxidation of Fe₃O₄ are also thermodynamically possible. No reaction of this type however can be established from the polarisation measurements

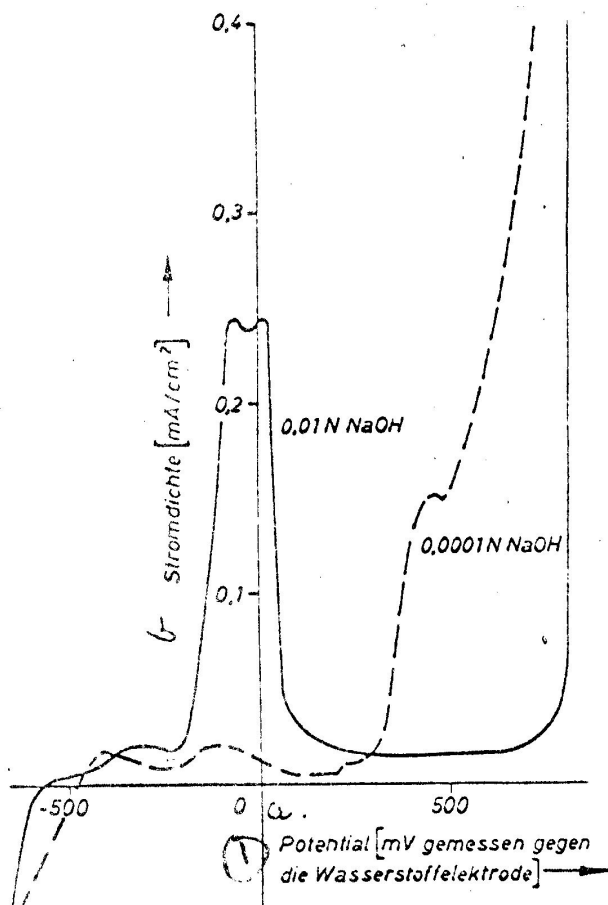


Figure 1: Polarisation curves, measured with iron in $1 \cdot 10^{-4}$ n NaOH and $1 \cdot 10^{-2}$ n NaOH at 250 °C.

The curve for copper (**Fig. 2**) shows two current density maxima which can be attributed to the formation of Cu_2O and CuO . The polarization curve measured from cathodic to anodic show a rest potential of - 240 mV. At this potential the slope of the curve is small which suggests a small corrosion rate for copper. The anodic to cathodic scan shows a relatively high rest potential (+200 mV) at which CuO is converted into Cu_2O which in turn is reduced to copper at a still lower potential.

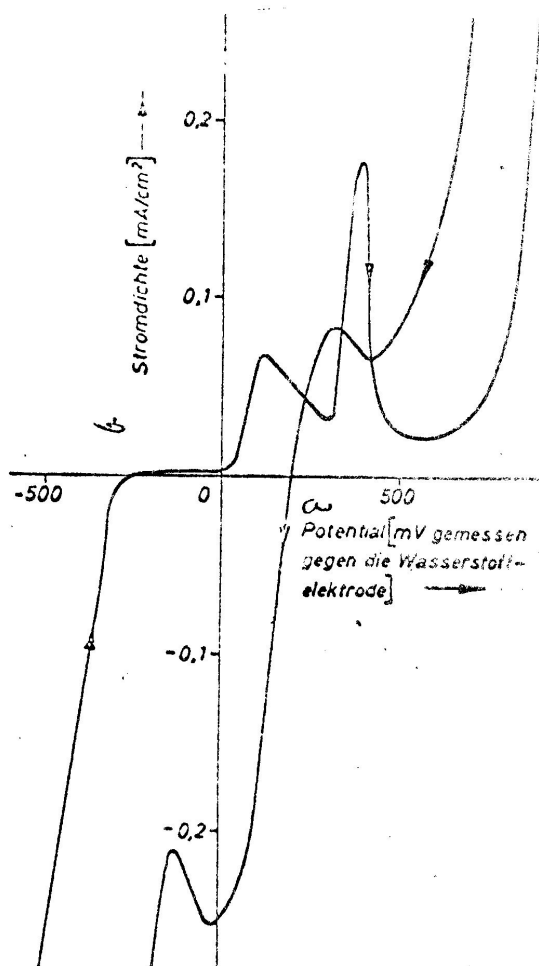


Fig 2. Polarisation curve for copper 0.001 n NaOH at 250 0 C.

The reduction of copper oxide is scarcely retarded by polarization resistance hence this reduction could be involved in the anodic corrosion reaction. The rest potential of iron can therefore be increased by the reduction of copper oxide and ferrous and ferric ions can be very easily oxidized in this way to finely powdered Fe_3O_4 . Further increase of the iron rest potential to the pitting potential by reduction of CuO to Cu_2O must of course be very unfavourable with regard to the tendency to corrosion.

2.2 Measurements in 0.01 N NaOH

The polarisation curve for iron measured in 0.01 N NaOH is also shown in **Figure 1**. There are two current density maxima; -290 mV and about 40 mV.

The latter is split into two maxima at -69 and +20 mV. The first maximum at -290 mV is attributed to the formation of Fe_3O_4 from FeO_2^{2-} ions and the second maximum at -40 mV to the formation of Fe_2O_3 from HFeO_2^- or FeO_2^{2-} ions. The split of the second maximum may be due to the growth of alpha and gamma Fe_2O_3 or of alpha Fe_2O_3 in various modifications. The mechanism however is not yet adequately explained. According to Fig. 1 the Fe_2O_3 formation in any case causes effective passivation. The production of oxygen occurs at +710 mV. At the restpotential Fe_3O_4 is formed both by the Schikorr reaction and by oxidation of FeO_2^{2-} ions.

Fig. 3 shows the polarisation curve for copper in 0.01 N from cathodic to anodic and from anodic to cathodic potentials. It can be concluded from the anodic to cathodic potential curve that the CuO is

very easily reduced at +290 mV to Cu₂O and Cu₂O is equally easily reduced to Cu at -20 mV. Copper oxides must therefore be regarded as very strong oxidising agents under these conditions.

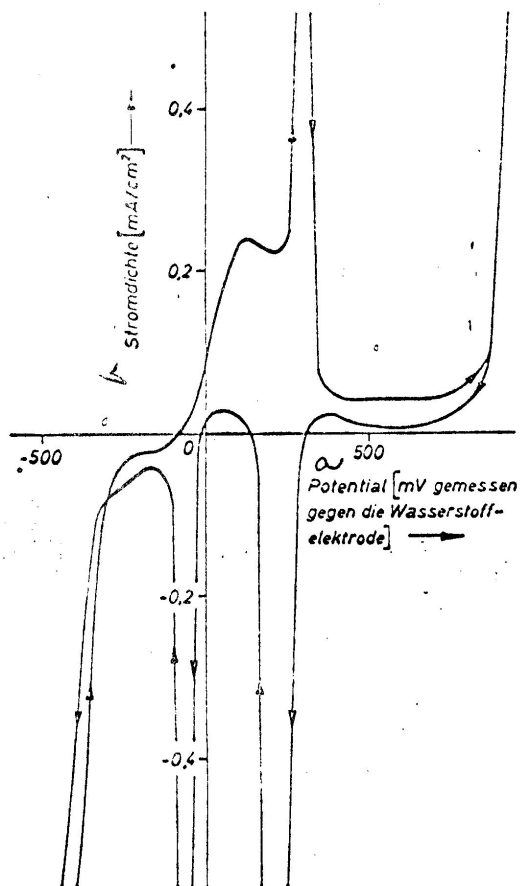


Fig 3. Polarisation curve for copper 0.01 n NaOH at 250 ° C.

The rest potential of iron is increased by the reduction of CuO to Cu₂O in situ at 290 mV so that the iron is passivated under formation of Fe₂O₃.

The reduction of Cu₂O to Cu and hydrogen evolution on copper result in minor increases of the iron rest potential without giving rise of the formation of protective alpha-Fe₂O₃. Whether the rate of corrosion in fact increases depends on the morphology and consistency of the oxide film which is formed.

3. LONG TERM EXPERIMENTS IN ALKALINE SOLUTIONS

It should be possible to obtain a general view of the effect of copper oxide reduction on the morphology of the protective magnetite film and the rate of any corrosion reactions from long term experiments on steel in alkaline solution containing suspended copper and copper oxide. With this in mind long term experiments were carried out on mixtures of powdered Fe₃O₄ and CuO and also on oxidised steel sheet. To avoid galvanic contact of the sample with the walls of the autoclave, the samples and the solution were contained in PTFE capsules.

The experimental conditions are set out in Table 1 and the composition of the steel used is shown in Table 2.

Table 1

Long term experiments with Fe_3O_4 - CuO mixtures in powder form and pre-oxidised steel sheet with copper and copper oxide coats. Temperature: 310 °C Experimental time: two days.

Samples	Solution	Solution	Addition
Tablets of Fe_3O_4 and CuO	0.1	$1 \cdot 10^{-5}$	none
Preoxidised steel sheet	0.1	1.10	suspended CuO
Preoxidised steel sheet	0.1	1.10	suspended Cu
Preoxidised steel sheet	0.1	1.10	none

Table 2 Chemical analysis of the steel sheet.

C	Mn	Si	S	P	Ni
0.16	1.08	0.40	0.025	0.023	0.15

3.1 Results with a mixture of Fe_3O_4 - CuO powders

A mixture of 2 mols Fe_3O_4 and 1 mol CuO was compressed to form tablets and heated to 310 °C in 0.1 N and 0.00001 N NaOH solution. X-ray analysis of the tablets at the end of the experiment showed the copper and red alpha Fe_2O_3 .

Examination under the microscope established that copper was present in different crystalline forms. In 0.1 N NaOH the copper was in the form of platelets. In 0.00001 N NaOH, it had grown in a spherical form. Both forms of copper have also been found in the iron oxide scales in boiler tubes.

3.2 Long term experiments with pre-oxidised steel sheet in alkaline solutions dosed with suspensions of CuO.

To simulate the protective oxide film on tubes in operation, steel sheet was first placed for two days in a 0.5 N NaOH solution so that a passivating magnetite film could be obtained (**Fig. 4**). The oxidized samples were bent at one end and placed in PTFE capsules (**Fig. 5**). On the bent part of the sample 0.5 g of CuO was scattered. The samples were then heated at 310 °C in alkaline solution for two days.

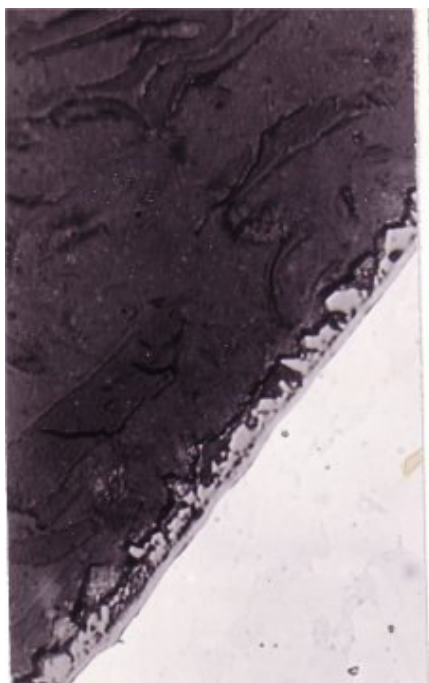


Figure 4: Cross section of boiler steel corroded in 0.5 n NaOH at 310_C for 2 days in order to produce a protective magnetite coat.

3.2.1. Long term experiments in 0.1 n NaOH solution

At the end of the experiments copper and Cu₂O were detected on the pre-oxidised steel samples. In **Fig. 5** (position a) yellow copper and red-violet Cu₂O can be seen on the bent part. Between the red coloured position c. and position a. there is a grey oxide lauer (position b.) The **pos a-c** are photomicrographs of cross sections at the individual positions.

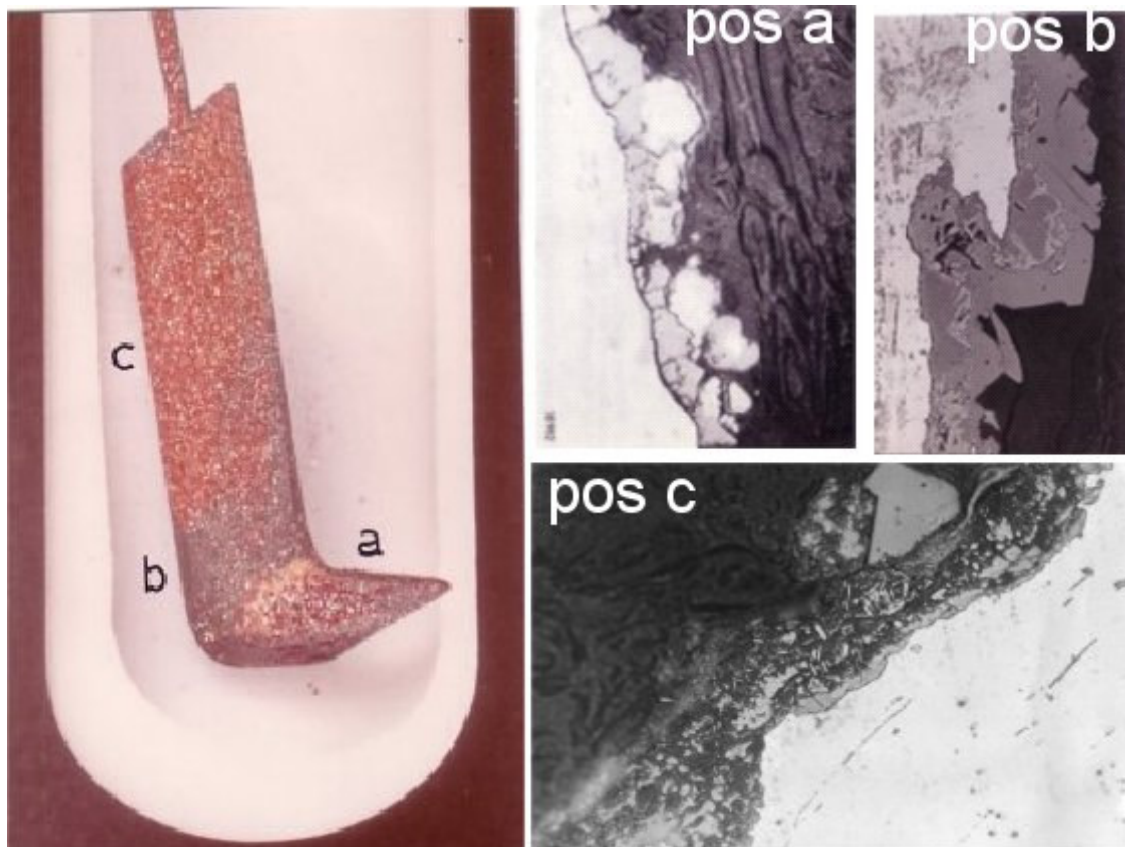


Figure 5: Pre-oxidised steel sample at the end of a long term experiment in 0.1 n NaOH at 310_C with the addition of 0.5 g CuO.

Pos a: Cross section at the copper coated position a.

Pos b: Cross section at the grey position b. above the copper coated zone a.

Pos c: Cross section at the red upper part c.

The grey oxide growth on the original magnetite film (position b.) is shown under the microscope in polarised light to be an optical anisotrope; this is also the case with the needle form of oxide on positions b and c. As the crystal structure Fe₃O₄ and γ Fe₂O₃ are cubic, that is optical isotropes, the anisotrope oxide must be the trigonal α Fe₂O₃.

When the red oxide at position c. (**Fig. 5**) was illuminated by polarized light it shone with red internal reflection, indicating very finely grained α Fe₂O₃.

These phenomena can be explained by a drop in the stress in the oxide surface, produced by reduction of the copper oxide on the bent specimen (position a, **Fig. 5**) which allowed several

oxidation types to be formed. In **Fig. 6** the effect of resistance polarisation on the rest potential of the iron is represented in diagram form.

At position a. where CuO is reduced to Cu₂O a high iron potential prevails so that good passivation associated with the formation of platelet alpha Fe₂O₃ (Ref 3.) results. Because of the high electrical resistance of the magnetite film, the rest potential of iron in the upper part of the sample (position c) must be lower and insufficient for the formation of the platelet form of alpha Fe₂O₃ (**Fig 5 pos c**).

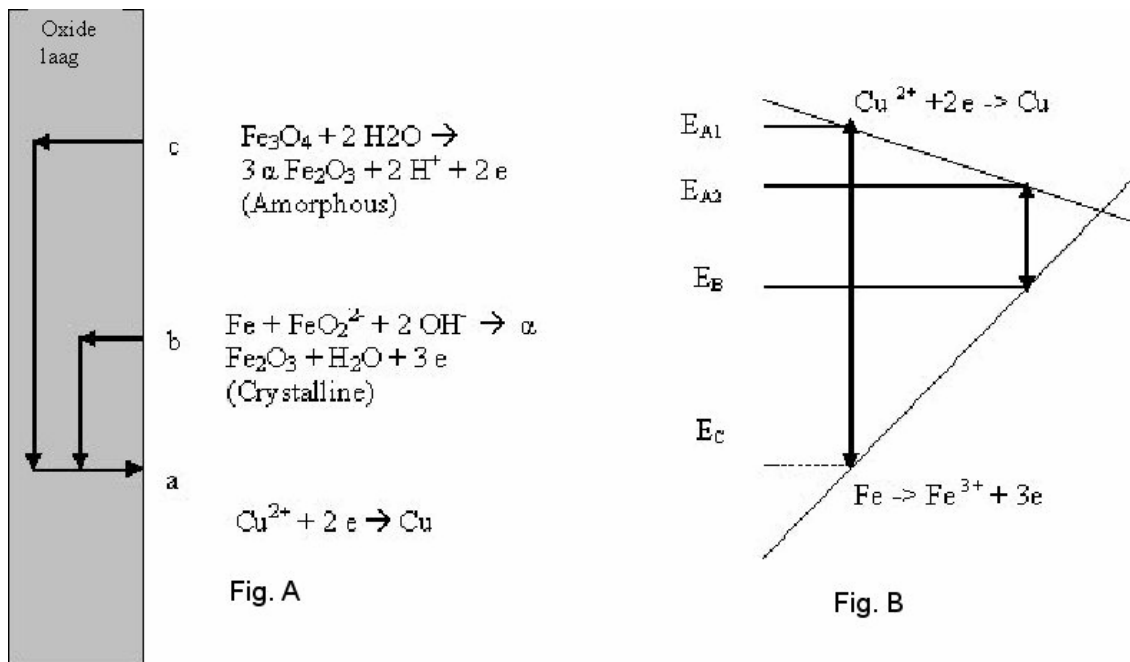


Figure 6: (Fig 9)

Fig A; The electron transport with iron corrosion under the influence of copper oxide reduction.

Fig B; Schematic representation of the influence of resistance polarization on the iron rest potential.

3.2.2. Long term experiments in $1.10^{-5} n NaOH$.

As mentioned before, in alkaline solution Fe₃O₄ is oxidised to fine grained α-Fe₂O₃ by reduction of CuO. The protective magnetite film can therefore be destroyed in this way (**Fig. 7**).

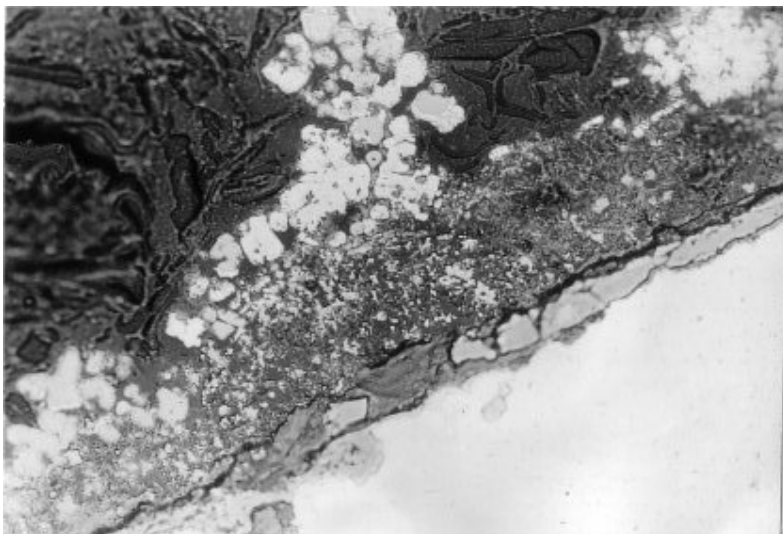


Figure 7: Cross section of a magnetite layer which has been destroyed by reduction of CuO after a long term experiment in $1 \cdot 10^{-5}$ n NaOH . Fine grained α -Fe₂O₃ and copper can be recognized.

It can be concluded from polarisation measurements that the reduction of CuO to Cu₂O sets up a high iron rest potential if the electrical resistance of the magnetite is fairly small. At this high rest potential (+230 mV) Fe₃O₄ should dissolve with formation of FeO₄²⁻ ions and pitting of the steel should occur. This pitting was not however observed in long term experiments in $1 \cdot 10^{-5}$ NaOH solutions.

3.3. Long term experiments on pre-oxidised steel sheet in alkaline solutions with Cu addition

0.5 g copper powder was scattered over the pre-oxidised steel sheet . After heating for two days to 310°C no great difference could be distinguished between the approximately 1.5 µm thick protective oxide film on samples with and without copper (Figs 8 and 9) . The outer surfaces of the Fe₃O₄ film is converted into α -Fe₂O₃ and this has clearly not affected the protective effect of the film.

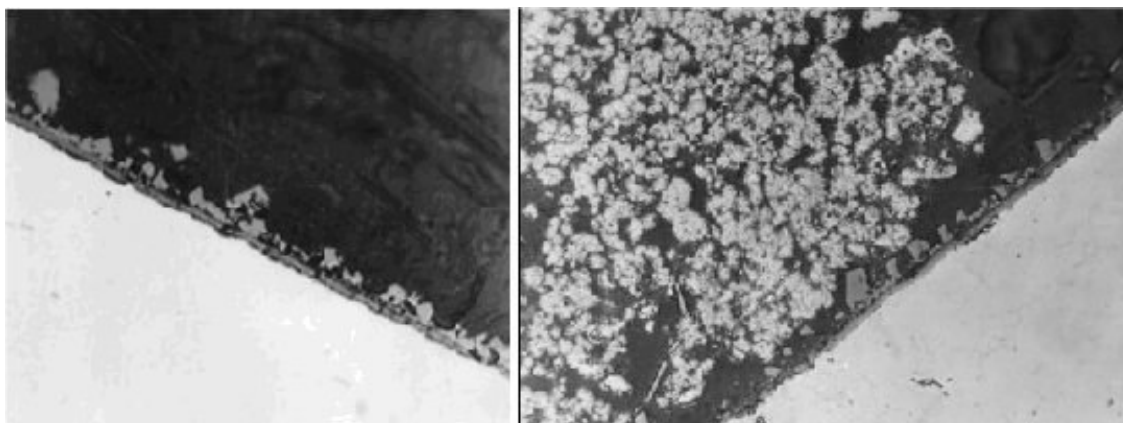


Figure 8
 Left: The oxide layer after a long term experiment in 0.1 n NaOH without copper addition.
 Right: The oxide layer after a long term experiment in 0.1 n NaOH with copper addition. Platelets of α -Fe₂O₃ have grown between the copper particles.

In long term experiments in 0.1 N NaOH solution, however, platelet crystals of α -Fe₂O₃ were formed at the places covered with copper, probably as a result of oxidation of FeO₂²⁻ ions (Ref.3) (Figs 8 right

photo). Copper is therefore to be regarded as a cathodic surface, and the presence of copper on the magnetite film stimulates oxide coating in strongly alkaline solutions (pH value greater than 11).

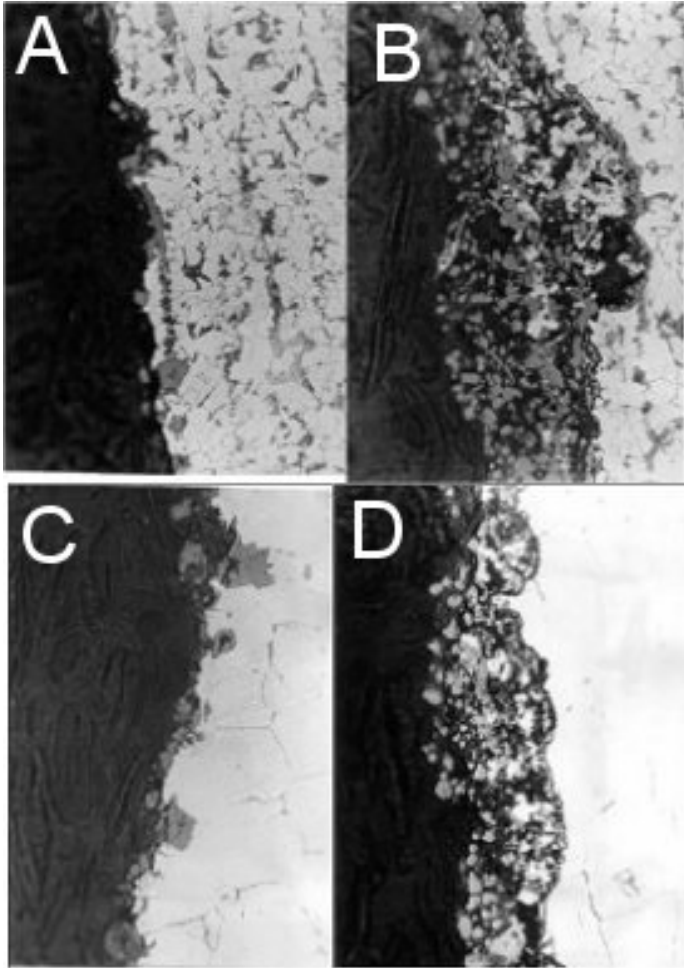


Figure 9: The oxide layer after a long term experiment in $1 \cdot 10^{-5}$ n NaOH with copper addition. A: without copper addition, B: With copper addition.

4. INVESTIGATION OF SOME COPPER CONTAINING OXIDE LAYERS ON SAMPLES TAKEN FROM OPERATION.

An important objective of the investigation was the establishment of the extent of agreement between the results obtained from operation, samples and the laboratory tests. **Figs 10** show photomicrographs of cross sections of oxide layers from boiler tubes.

Where copper was present in the oxide layer, the magnetite layer was cracked in most instances. Layers of this type were found the decarburized as well as on the non-decarburised steel surfaces (**Figs. 10**). The cracking of the protective magnetite coat is therefore not connected with the steel structure. (ferrite-pearlite ratio). Cracked magnetite layers however were also found on the side away from the furnace, although in this position the coating contained only a small amount of copper or none at all. Copper was deposited with iron oxides on the side with high heat transfer. Occasionally pitting was found (**Figs. 11A and 11B**). Metallic copper was precipitated on the bottom of the pits.



*Figure 10:
The oxide layer on an evaporator tube of a 170 kg/cm² absolute pressure boiler after 10500 operating hours..*

Upper: A: unheated side, B: heated side

Below: The oxide layer on a decarburated evaporator tube C: unheated side, D: heated side

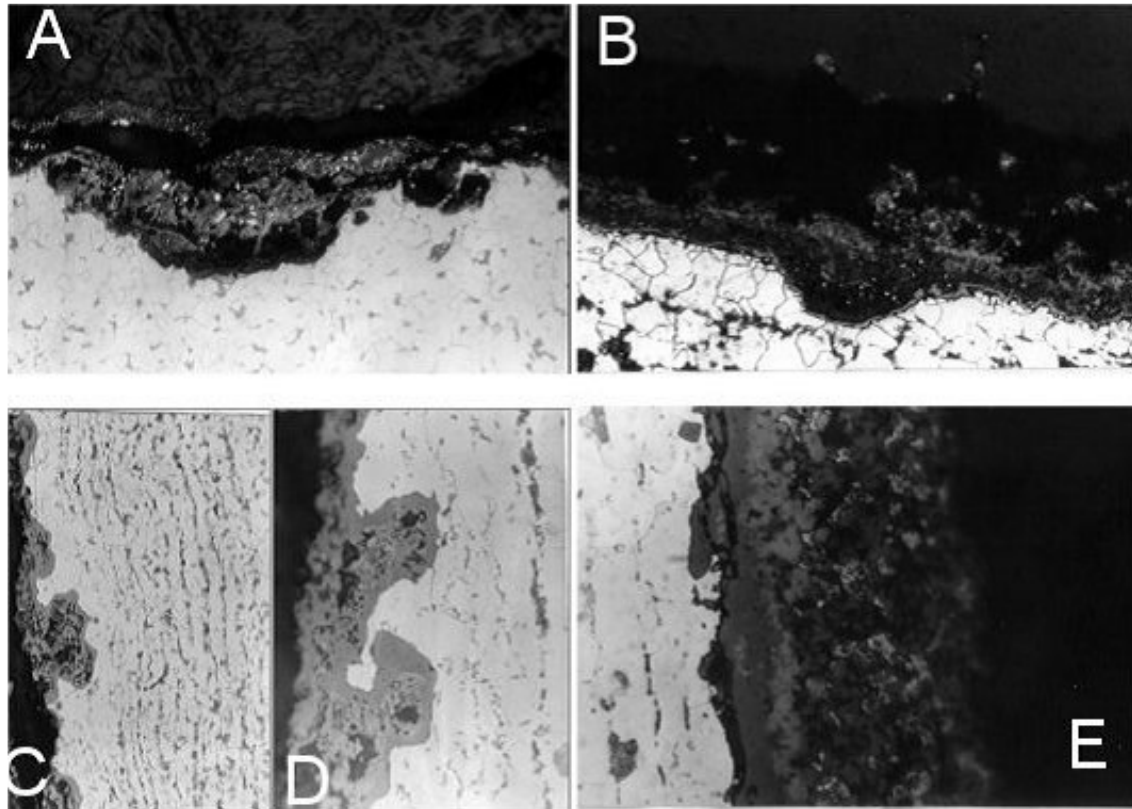


Figure 11:

A: Pitting and copper in the pits of a steam receiver in a 73 kg=cm² absolute pressure boiler (fig 20)

B: Cross-section of an oxide coat on an evaporative tube of a 165 kg=cm² absolute boiler. Under the amorphous copper-rich oxide a protective magnetite coat has grown.

C and D: Homogenous unbroken oxide layers growing on an evaporator tube of a 150 kg=cm² absolute boiler after 58000 operating hours.

C: unheated position, D: heated position.

E: Oxide layer on an evaporative tube of a 130 kg=cm² absolute boiler.

Figures 11C and 11D show an oxide layer from a boiler of the same type as that from which the magnetite layers in **Figs. 10A - D** were taken. There was no copper in the water in these boilers (**Figs. 11C and 11D**). The boiler tubes were not acid cleaned before commissioning. It is worth noting that a homogenous, continuous oxide layer was formed in these circumstances. A new protective coat can form under cracked, copper-coated magnetite layers provided copper oxides are no longer present in the water (**Figs 11B and 11D**).

5. CONCLUSIONS

- 1 Polarisation measurements on iron and copper have shown that copper oxides may affect the corrosion of iron and boiler steel can be derived.
- 2 Corrosion experiments on oxidised steel in galvanic contact with copper and copper oxide confirm the corrosion mechanism suggested by the electrochemical measurements.

- 3 In alkaline solutions parts of the magnetite layer are oxidized as a result of the reduction of copper oxide to copper. In general red α - Fe_2O_3 with a lower protective effect is produced.
- 4 However, in the immediate neighbourhood of areas in which copper oxide is reduced, in strongly alkaline solution, aggregates of platelets of α - Fe_2O_3 are formed which have a protective effect. In weakly alkaline solutions on the other hand, pitting can occur at such points, due to the oxidation of the magnetite to FeO_4^{2-} .
- 5 Metallic copper has, in weakly alkaline solutions, no corrosive effect on the underlying magnetite layer.
- 6 In strongly alkaline solutions (pH greater than 11) FeO_2^{2-} ions are easily oxidized to Fe_2O_3 on copper and thicker coatings can result.
- 7 Since relatively high local concentrations of alkali can occur in boiler tubes even with weak alkali operation, metallic copper cannot be disregarded as an agent which stimulates layer formation.

6. BIBLIOGRAPHY

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