

AN EXAMINATION OF THE PROTECTIVE FILM PRODUCED IN MICROBIOLOGICAL
CORROSION OF STEEL PLATES BY THE SULPHATE-REDUCING ANAEROBE
DESULPHOVIBRIO DESULFURICANS.

by

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1. INTRODUCTION.

On July 7th. 1966 Mr. D. Wakerly (N.P.L.)

forwarded to me three specimens of steel plate from certain microbiological corrosion experiments he was engaged in. The particular set of experiments from which the specimens came were unusual inasmuch as corrosion was not proceeding as rapidly as was expected from the results of previous experiments. The three specimens were:

(a) a fresh steel plate similar to those employed in the corrosion experiments.

(b) a steel plate having suffered 25 weeks immersion in a culture of Desulphovibrio desulfuricans, strain Hildenborough. (N.B. the older nomenclature will be used throughout).

(c) a steel plate after 25 weeks in a culture of D. desulfuricans strain Teddington R.

Specimens (b) and (c) were transported in McCartney bottles, which had been topped up with Medium C. The Medium C used to cover specimen (b) was iron-rich, whereas that with specimen (c) was not. The plates were not removed from their bottles until July 14th.

2. PREPARATION OF SPECIMENS.

Specimens (b) and (c) were extracted from the McCartney bottles and quickly washed in distilled water and subsequently with acetone. During this washing process a little of the blue-black film which covered the specimens fell away, but

most of it was unaffected. The specimens were kept under nitrogen between filter papers in a vacuum dessicator for four days, and whenever the specimens were not being examined they were kept in this way.

After four days the specimens were taken out of the dessicator . They appeared dry and showed no signs of oxidation when examined with a binocular microscope.

All three specimens were cut in half transversely. Three of the halves were mounted vertically in cold setting plastic and polished. The other three halves were kept in the dessicator for surface examination.

3. OPTICAL EXAMINATION.

Macroscopically specimens (b) and (c) appeared to be covered with identical blue-black cohesive films of apparent homogeneity which were not dissimilar to the material known as melnikovite. The wet precipitate still apparent in the media in which specimen (b) was transported appeared similar to the films in all ways except in the matter of consistency.

The surface of the films were examined by reflected light microscopy. No apparent differences were seen between specimens (b) and (c). In both cases the film surfaces were covered with tiny balls of pyrite. These balls consist of a spherical agglomeration of pyrite microcrysts, this type of texture falling under the wider definition of 'framboidal'. (from the french 'framboise' or raspberry). These framboids rarely appeared larger than 150 microns in diameter and it was

suspected that these larger spheres were made up of an accumulation of smaller ones. The framboids are shown in figure 1.

The framboids rested on the surface of the film and could be easily dislodged. The film itself was very irregular in thickness. Other than the pyrite framboids, no other crystalline minerals could be seen or identified. The film was a relatively cohesive and could be flaked off the surface of the steel plate.

Beneath the thick film the surface did not appear to be wholly exposed, and the presence of a second film, much thinner and more firmly attached to the surface, was suspected. The surface of the steel itself had been beautifully etched and the individual crystals of the steel were easily seen. (see fig.2)

The examination of the polished section was made difficult by the great difference in hardness between the steel plate and the film, the steel plate standing proud of the film. Figure 3 shows the relatively smooth edge of the uncorroded steel plate and was included to demonstrate the relative roughness of the edge of the corroded plate (fig.4).

The microscope in figure 4 was focussed on the surface of the edge of the steel plate, and thus the film cannot be seen. It was focussed here to demonstrate another feature of the corroded specimens : the semicircular concentric rings of varying colour and reflectivity that were abundant on the edges of both corroded specimens but totally absent from the noncorroded

specimen. These rings ^ewere always centred on a small group of highly reflecting particles, which were thought to be fragmented steel. Their radii were never greater than 100 microns.

The film itself (fig 5) was on average about 150-200 microns in thickness. The edge of the film was never exposed in the polished section because of the difference in hardness between it and the plate. Figure 5 shows this edge sloping away under the plastic. Surface features, such as pyrite spheres were therefore not seen in polished section. Most of the film demonstrated no textures other than the banding and the blebs associated with those of precipitates of near colloidal sized particles. The optical properties of the film suggested that it was an oxide rather than a sulphide, but there was a possibility that it might have been similar to greigite. In some sections large transparent crystals were seen embedded in the film. These lacked the cleavage normally associated with carbonates and they were thought to be phosphates possibly of iron.

The presence of a second inner film under 10 microns thick is demonstrated in figure 5. As can be seen in the photograph there is apparently little difference in the nature of the two films except that the inner film is slightly the darker.

4. X)-RAY EXAMINATION.

Two samples were taken for x-ray examination: (i) a sample of the film attached to a glass fibre, for examination in a 11cm. camera,

(11) a

smear mount of a sample of the precipitate in the Hildenborough culture bottle for diffractometer examination.

The inadequacies of these methods of sample preparation are obvious and since then other methods of preparation have been developed, the results of which, being pertinent to this discussion, are mentioned below.

The sample of film gave a very strong pattern of a hydrated ferrous orthophosphate and a suspicion of the presence of ferrous hydroxide or 'GREEN RUST 1'.

The smear mount of the precipitate gave a very poor diffractometer trace, with only the stronger lines of lepidocrocite and, possibly, pyrite, being present.

D. E.P.M.A. EXAMINATION.

The polished section of the steel plates was repolished and coated with a carbon film, ready for electron probe microanalysis. These two precautions prevented any chance of the specimen surface being contaminated by atmospheric oxidation.

During a period of five hours machine time, no element other than iron was found. The only exception to this was the discovery of a crystal of iron phosphate embedded in the film on specimen (b).

The film gave iron maxima approaching 75%, (without correction), equivalent to the formula $FeOOH$. On the E.P.M.A. a second, inner, film was not distinguished.

The curious ring structures apparent at the edges of the corroded specimens showed no meaningful variations in

composition relative to the steel plate itself. This probably implies variations below the detection limits of the micro-analyser rather than the total absence of such variations.

6. DISCUSSION.

The results from the electron probe microanalyses show that at least the inner 50 microns of the film coating the corroded specimens is of iron oxide or oxyhydroxide. The x-ray results suggest that this oxide is in the γ -iron oxide/oxyhydroxide series.

The iron precipitate I obtain in my chemically defined medium has been analysed anoxically both wet and dry. The immediate precipitate consists of the basic salts of iron hydroxide, mostly of ferrous hydroxide. These are highly unstable phases and rapidly change, by autoxidation, to a mixture of the green rusts, γ -FeOOH and Fe_3O_4 , the latter pair becoming predominate with time. Dry oxidation of these phases leads to the formation of γ - Fe_2O_3 , before the ultimate formation of haematite.

A knowledge of the form of the original oxyhydroxide is important since it might indicate the expected forms of the sulphide. The spinel structures of magnetite and γ - Fe_2O_3 would be expected to lead, on sulphidation, to the formation of the thiospinel Fe_3S_4 , greigite, which is very magnetic. Likewise, from the γ -series of oxyhydroxides in general, pyrite, rather than marcasite would be expected to be the stable crystalline form.

Thermodynamic considerations show that the iron sulphides

and the ferrous and ferroso-ferric ^xoxides/oxyhydroxides have similar Eh-pH stability fields. The predominance of the oxide or sulphide phases depends on the partial pressure of the sulphur species .

In the media used in these experiments we must therefore assume that when the steel plate was inserted into the culture the partial pressure of the sulphur species present was not high enough to satisfy the iron concentration, and that iron oxyhydroxide was precipitated. Whilst the oxyhydroxide was undergoing its series of topotactic autooxidations, sulphidation of the film started from the outside. The occurrence of pyritespheres on the surface of the film is rather perplexing. That the only evidence of sulphidation is the formation of well-crystalline pyrite on the film surface is suspicious and might well be taken to imply that amorphous sulphide occurs on the outer edge of the film, that is, beneath the plastic surface of the polished section.

With a film present it is very difficult to see how the bacteria could multiply rapidly at the film surface, because of the limited supply of nutrients they would receive in this position. Therefore biological corrosion should be limited to cracks and defects in the film. The weak etching seen all over the surface of the plate is caused mainly by normal chemical corrosion.

The multicoloured concentric hemispheres seen at the

edges of the corroded specimens were first thought to be percussive in origin, possibly due to the polishing technique. However since they were not seen on the noncorroded specimen this leads me to believe that these are real corrosion features. Although variations in chemical composition across these rings were not detectable, it is possible that these features reflect a loss of certain constituents on the preliminary stages of corrosion.

The inner film seemed to be of similar composition to the thicker outer film. Although a drop in iron content was suspected we were unable to demonstrate the significance of this result. If we accept that the inner film is of similar constitution to the thicker film, its increased adherence to the specimen may be explained by the stronger effect of weak forces at the specimen surface. These weak forces, in addition to the electrostatic forces keeping the film as a whole on the specimen would give a more compact and more adherent film of oxyhydroxide on the surface of the specimen.

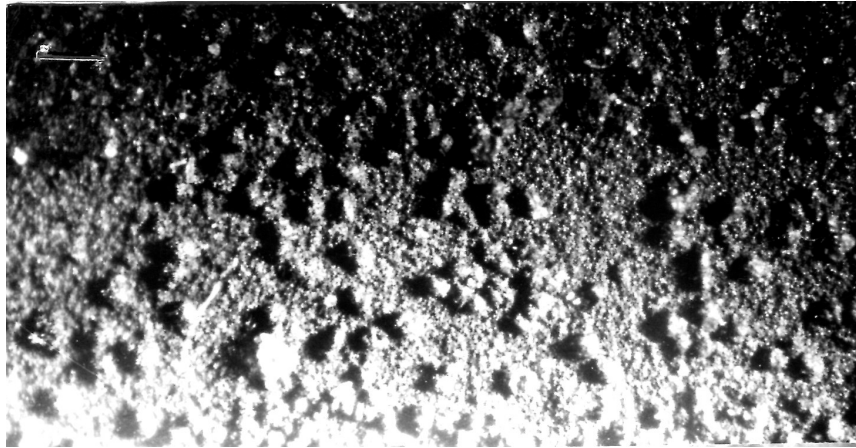


Figure 1



Figure 2