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O T T A W A November 30th, 1943.

R E P O R T
of the
ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1545.

Investigation of the Corrosion of
a Steam Condensate Steel Pipe.

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(Copy No. 10.)

Bureau of Mines
Division of Metallic
Minerals
Ore Dressing
and Metallurgical
Laboratories

CANADA
DEPARTMENT
OF
MINES AND RESOURCES
Mines and Geology Branch

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Origin of Sample and Object of Investigation:

Mr. G. A. Browne, for the General Superintendent, Engineering Division, Department of Pensions and National Health, Ottawa, Ontario, submitted, on November 1st, 1943, a sample of a failed section of two-inch-diameter high pressure return line (installed in 1939) from the Christie Street Hospital, Toronto, Ontario. A portion of the pipe about one inch wide had been "eaten" away to a thickness of about one-third of the remainder. This type of defect was not confined to this length of pipe but was said to have been found in other parts of the line.

Samples of water from the return line and the feed boiler were received. The water in the boiler proper was reported to be controlled to give one grain of hardness, by additions of boiler compound every twenty-four hours.

Since it was felt that the pipe should have had longer than a four year life, request was made for an analysis of it and comments on the defect.

Chemical Analysis:

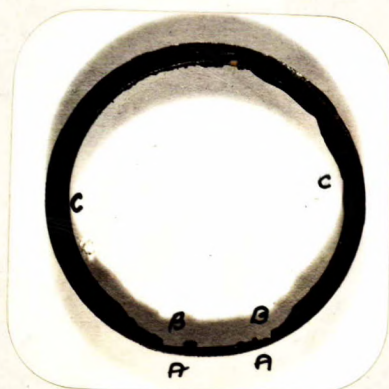
Millings taken from the pipe, after the surface had been ground, were chemically analysed. Results were:

	<u>Uncorroded</u>	<u>Corroded</u>
	<u>Section</u>	<u>Section</u>
	- Per cent -	
Carbon	- 0.09	-
Manganese	- 0.36	-
Silicon	- None detected.	-
Sulphur	- 0.048	0.041
Phosphorus	- 0.097	0.097
Copper	- Trace.	Trace.

Macro-Examination:

Figure 1 is a photograph of a cross-section of the pipe.

Figure 1.



CROSS-SECTION OF PIPE.
(Approximately $\frac{3}{4}$ size).

In the most heavily attacked portion of the pipe, A-A (Figure 1), the surface was covered with a black corrosion constituent. Small projections in this area had a partial coating of red constituent over the black. Through B-B and above to C, the outer constituent is red. The decrease in steel thickness and the reddish colour taper off from the thin area until both are apparently negligible through a plane C-C and above it.

Tests showed the black corrosion constituent to be magnetic.

A macro-etch revealed that the pipe seam was not

(Macro-Examination, cont'd) -

in the area most heavily attacked.

The Vickers hardness (10-kilogram load) of the pipe was 110-122.

Micro-Examination:

A cross-section of the pipe was mounted in bakelite and polished. Two types of corrosion constituents were seen in the pipe below the plane C-C (Figure 1). These are shown, at 250 diameters, in Figure 2. In some places, such as the one pictured, the red constituent (light colour) is both next to the steel (shown white) and on the outer surface. In other places (particularly between A-A) the black constituent is adjacent to the metal. Very little evidence of corrosion or of corrosion products was found on the side of the tube opposite to the heavily attacked portion.

Figure 2.



X250, unetched.

The steel, after etching, was seen to have a ferrite and pearlite structure throughout, with the latter constituent

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(Micro-Examination, cont'd) -

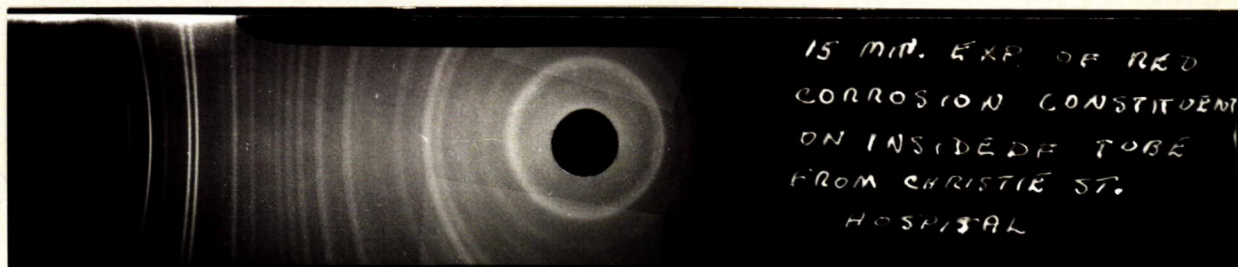
occupying a comparatively small proportion of the field.

X-Ray Diffraction:

The X-ray diffraction technique employing filtered cobalt radiation was used in an attempt to identify the corrosion products.

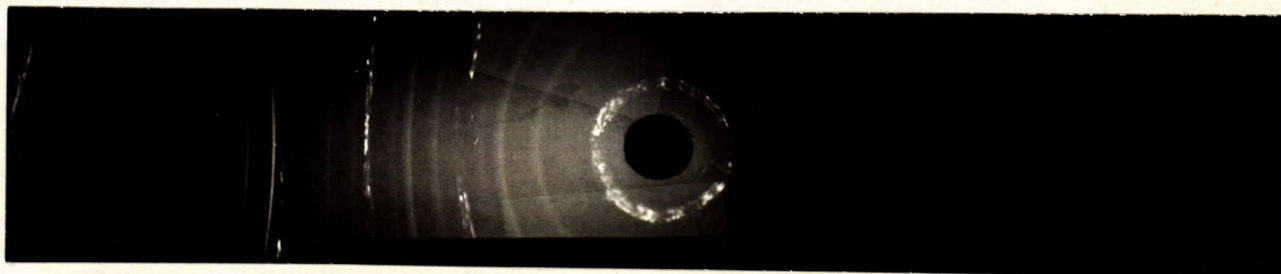
Patterns obtained from the red and black corrosion constituents, the etched deeply-corroded steel, and the prepared Fe_2O_3 (possibly, in a technical sense, $Fe_2O_3 \cdot xH_2O$) are given in Figures 3 to 6 inclusive. Patterns from an etched lightly-corroded section of the pipe and a sample of magnetite (Fe_3O_4) ore (suitable for a comparison test but not for publication, because of interference from impurities or large grains) were also taken.

Figure 3.



RED CORROSION CONSTITUENT.

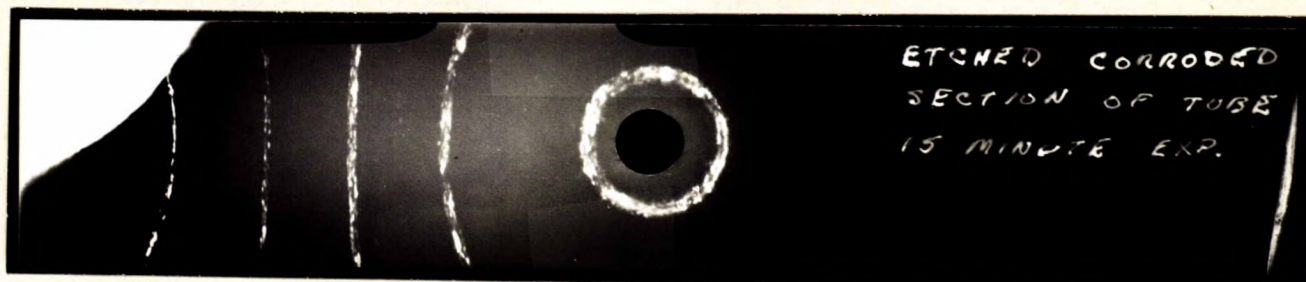
Figure 4.



BLACK CORROSION CONSTITUENT.

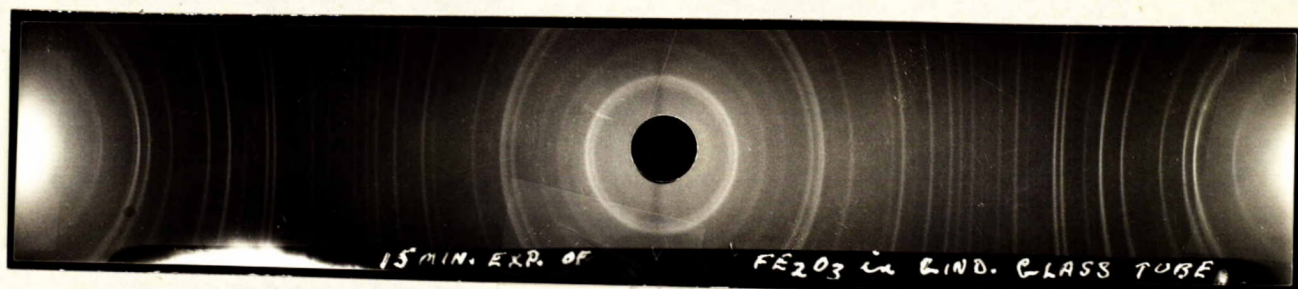
(X-Ray Diffraction, cont'd) -

Figure 5.



MACRO-ETCHED, HEAVILY CORRODED STEEL.

Figure 6.



PREPARED Fe_2O_3 ($\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$).

Water Determinations:

The pH (hydrogen ion concentration) of the steam condensate, determined at room temperature, was 8.4 and that of the feed water was 7.4 (pH of 7, neutral). Because of the conditions of sampling, other determinations were not thought to be worthwhile.

Discussion of Results:

Chemical analysis (low carbon, high phosphorus) showed the steel to be of the low-carbon, Bessemer type. This high-phosphorus Bessemer steel is commonly used in most makes of pipe, because it is considered to lead to better production welding. In so far as corrosion is concerned, the

(Discussion of Results, cont'd) -

high phosphorus should not be a drawback, as the literature indicates that the corrosion resistance of low-carbon steel is not appreciably affected by small variations in the phosphorus content. Discussing this, the following statement is made in the book, "The Metal Iron":⁽¹⁾

"The effect of purity, in comparison of very pure irons with commercial products or in comparison of different grades of commercial products one with another, usually is less important than the effect of external conditions."

Because of the adhering corrosion products the "eating" action is said to be corrosive rather than erosive. The localized nature and gradation of the corrosive attack indicate that the corroded area was at the bottom of the pipe. The returning steam condensate, at most times, is evidently not nearly enough to fill the pipe and thus the corrosive agent or agents were presented for a much longer time to the bottom of the line. This assumption could, of course, be checked by comparing the location and nature of the corroded areas encountered. In so far as the pipe is concerned the localized nature of the attack would support the above contention, especially as the possibility of this being due to a particular length of pipe being defective is ruled out by the fact that similar failures are reported to have occurred in other parts of the line.

The microstructure of the pipe shows that it has been normalized (probably from the forming temperature). X-ray diffraction patterns of macro-etched sections from heavily corroded and relatively uncorroded parts of the tube confirmed the fact that there was no great difference in

(1) "The Metal Iron," by H. E. Cleaves and J. G. Thompson. ALLOYS OF IRON RESEARCH MONOGRAPH; 1935, page 339.

(Discussion of Results, cont'd) -

internal strain and that no severe strain existed in the tube.

Comparison of diffraction patterns (Figures 3 and 6) positively identifies the red corrosion constituent as $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$. The black corrosion product, as indicated both by comparison of diffraction pattern, Figure 4, with one obtained from magnetite ore and by magnetic tests, is predominantly or wholly Fe_3O_4 ($\text{Fe}_3\text{O}_4 \cdot x \text{H}_2\text{O}$).

It would seem, then, from the observations and results described, and from conditions under which the tube is operating, that failure was caused by an oxidation process and that pipe composition (as compared with other pipes of the low-carbon type, i.e., excluding highly alloyed steels) or fabrication was not an important factor. Oxygen and carbon dioxide contents of the steam condensate and related factors (temperature, film quality of corrosion product, pressure, pH, rate of condensate flow, catalysts, and oxidizers) were the deciding factors in the length of life of this pipe. In considering the following discussion of these variables it must be borne in mind that many of the conclusions drawn are influenced by results of tests on materials beyond the control of these Laboratories.

Some oxygen and carbon dioxide, if driven off with the steam in the boiler, would be available for corrosion because they are going off into what is, for some time, a closed system. As a result, when the steam condenses they can go back into solution. The pressure present will influence this to some extent. The condensate then flows through the return line, losing some of the gases in corrosion, into the feed water boiler. Since this is exposed to the atmosphere, more oxygen and carbon dioxide can be dissolved and the cycle repeated. In systems where the feed water tank is not open to the air, gases in the system may be quickly used up and as a consequence

(Discussion of Results, cont'd) -

corrosion is largely proportional to the amount admitted in evaporation replacement water and through leaks.

Although the boiler water is reportedly held to one grain of hardness, positive conclusions with respect to the present corrosion can not be drawn from this fact alone, because the soluble compounds causing the hardness are not known. Also, the composition of the water may vary considerably between additions of boiler compound.

It is realized that an attack by CO_2 would cause a pH increase due to the removal of the acid radical from solution. Also, it is known that a high pH may be lowered at an elevated operating temperature. Nevertheless, it is felt in this case that the pH is sufficiently high (8.4) to rule out the possibility of an acid radical such as CO_2 (carbonic acid) being the cause of the trouble. The alkalinity of the condensate also seems to indicate that solid compounds are carried over from the boiler. Soluble bicarbonates that might exert some effect may be in the condensate, but oxidizers or other compounds that might play an important part are very probably not present.

All evidence points to oxygen as the deciding factor in this corrosion. Even if the condensate did not contain much oxygen, the condensate is flowing steadily and considerable oxygen would be available for corrosion. The rate of flow of the water will be a determining factor, both in this regard and as it tends to influence the constitution of the corrosion product layer. Certain oxygen contents and rates of flow tend to produce the black corrosion constituent instead of the red, the general tendency being for the red oxide to form with higher oxygen contents and higher rates of flow. This will probably be greatly influenced by the pH of the solution, however. There is good reason to believe, from experiments described in

(Discussion of Results, cont'd) -

the literature, that $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ has very much more of a film effect (tendency to interfere with the migration of oxygen to the surface of the steel) than Fe_3O_4 . Oxidation, then, will tend to proceed at a faster rate in areas covered by the black constituent than in those covered by the red. This is in agreement with the observation that the most heavily corroded section of this pipe had a coating of practically pure Fe_3O_4 .

The corrosion rate is approximately doubled for each rise of 20°C .⁽²⁾⁽³⁾ of the corroding solution. Considered in terms of years, then, temperature is an extremely important variable, indeed.

Corrosion, in the present case, is thought to have been unusually rapid because of the cooperative combining of oxygen content, temperature, rate of condensate flow, and the character of the corrosion products. Consideration might be given to some method of feed water de-aeration or to neutralization of oxygen by chemical means. If chemicals are used, the pH of the water must not, of course, be allowed to rise too high because of the danger of pitting or caustic embrittlement in the steam boiler. The removal of oxygen would largely remove the problem as to the oxide formed. Indeed, any marked reduction in oxygen content would be expected to result in considerable improvement and may possibly serve, as well, to change the corrosion product to the more protective red constituent.

A practical expedient would appear to be to rotate the

(2) The Electrochemistry of Corrosion, by C. L. Bulow, in METAL FINISHING, October, 1943, Page 632.

(3) Corrosion of Steel by Dissolved Carbon Dioxide and Oxygen, by G. T. Skaperdas and H. H. Uhlig, in INDUSTRIAL AND ENGINEERING CHEMISTRY, Vol. 34, No. 6, June, 1942, Page 749.

(Discussion of Results, cont'd) -

pipe from time to time (if this does not involve considerable mechanical difficulties). This would assure more uniform corrosion and a consequent increase in pipe life.

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