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EXAMINATION OF TWIN WATER-WALL BOILER TUBE SAMPLE

by

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PHYSICAL METALLURGY DIVISION

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D.E. Parsons* and D.A. Munro**

SUMMARY OF RESULTS

Water-wall tube samples from a New Brunswick Electric Power Commission boiler contained pits on the water-side, having depths of 0.004 in. to 0.010 in. The pits were marked by the presence of hydrated iron oxide corrosion product. The water-side scale contained significant quantities of copper and zinc and was characterized by the presence of non-adherent Fe_3O_4.

Patches of black scale on the inside surface of the tube were identified as Fe_3O_4. The origin of this material, as residual mill scale, or as a product developed by steaming, was not determined, although the latter appeared to be more probable.

The results of the metallurgical examination and the samples were also referred to the Industrial Waters Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys for comment and examination. (See Report MP-Min-637, letters, 3-3-0/GEN/1-2, September 8, 1964 and Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys letter, July 30, 1964). (1,2,3)

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INTRODUCTION

A sample of twin water-wall boiler tube, 11 in. long, taken from the sidewall of #8 Babcock-Wilcox boiler at the Grand Lake Generating Station was forwarded to the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys by Mr. J. R. Dean of the New Brunswick Electric Power Commission.

The covering letter, dated June 24, 1964 (File No. 3-463g. G.L. #8 Boiler) stated that .... "The sample was taken from the sidewall of our #8 Babcock-Wilcox boiler at the Grand Lake Generating Station. This boiler, rated at 500,000 lb/hr, at 1450 psig, has been in service approximately six months. The sample was obtained incidental to installation of a viewing port in the side-wall approximately 15 ft from the bottom of the furnace, and represents the first opportunity of inspecting the water-side of the tubes since pre-operational cleaning.

Our examination of a similar sample, which we had split lengthwise, shows the same reddish-brown oxidation mottling. On polishing a section with a wire brush, we find what appears to be mill scale at certain spots on the water-side not necessarily connected with the mottling.

Pre-operational cleaning consisted of an oil removal boilout with an alkaline solution containing trisodium phosphate and caustic soda, followed by the scale removal stage employing a chelating agent "Vertan 675" supplied by Dowell of Canada. Since coming into service, the boiler has been treated with phosphate, neutralizing amines, and hydrazine. The black deposit of Fe_3O_4 is of course characteristic of hydrazine treatment."

The letter requested the following information:

(1) Whether or not any mill scale remains on the water side of the tube sample.

(2) Comments on the reddish-brown mottling and the extent of pitting under the mottles.

(3) Any other comment on the condition of the tube.

Chemical analysis of drillings from a section of the tube gave the results shown in Table 1.

TABLE 1

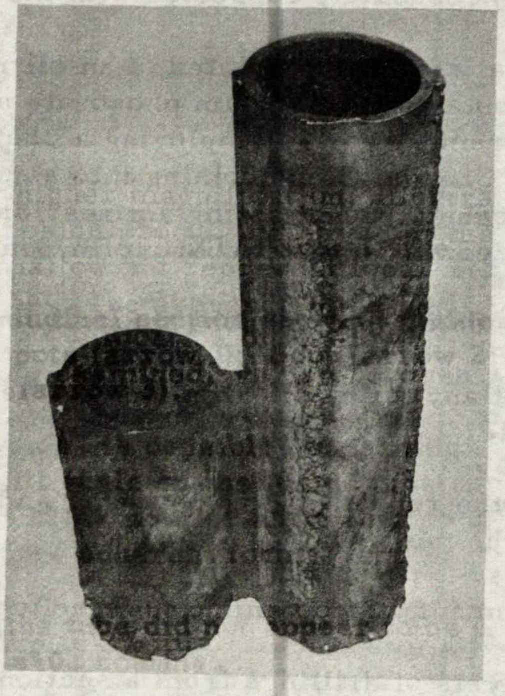
Chemical Composition of Water-Wall Tube (Per Cent)

	C	Mn	Si	S	P	Cr	Mo	Cu*	Ni*	Al*
Tube Sample	0.23	0.54	0.12	0.042	0.033	0.05	0.01	0.03	0.05	0.007
ASTM A210	0.27 max	0.93 max	0.1 min	0.058 max	0.048 max					

* Semi-quantitative spectrographic analysis.

The pipe was of seamless grade and conforms to the chemical requirements for seamless medium carbon steel tubes ASTM-A210. The nickel, copper and molybdenum contents are residual rather than alloying additions.

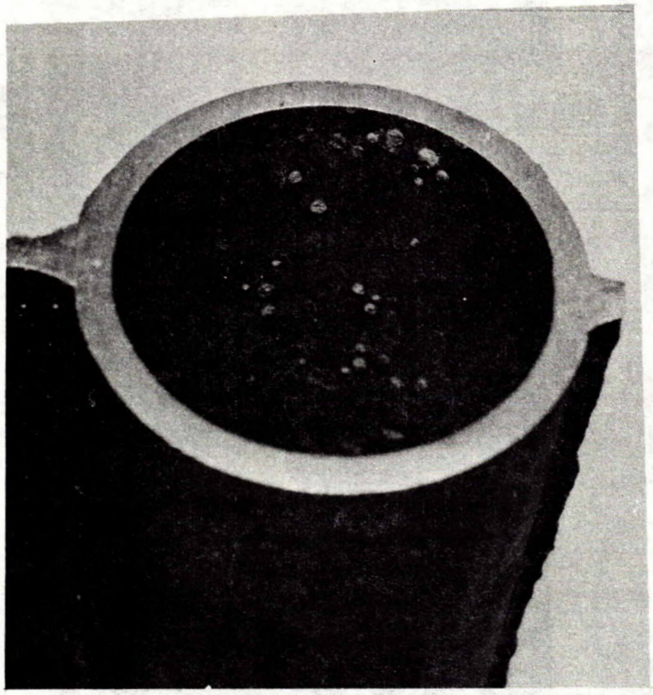
Figure 1 shows the tube in the "as-received" condition. The tubes are viewed from the combustion surface.



X1/4 approximately

Figure 1. Water-wall tube sample, combustion surface. The combustion side and the back (outside) surface of the water-wall sample appeared to be in almost new condition.

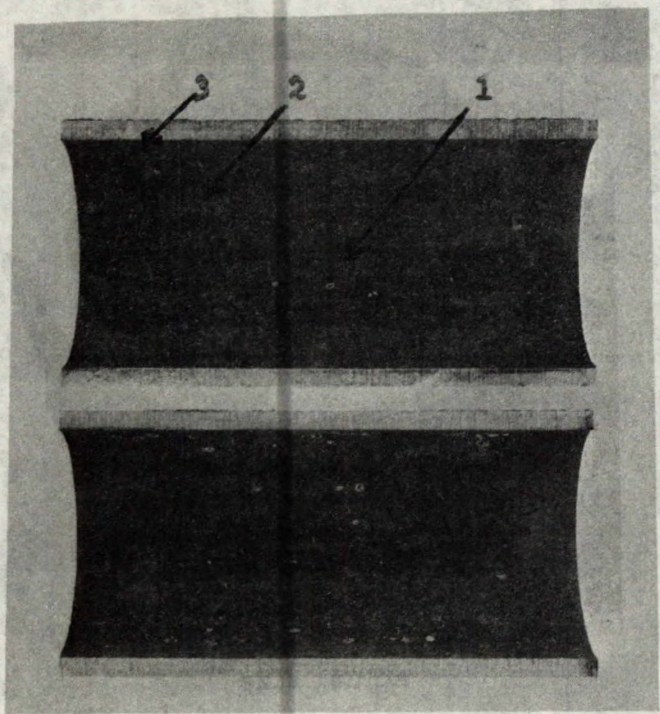
Figure 2 illustrates the appearance of the "red spots" (corrosion product concealing pits).



actual size

Figure 2. "Red spots" on inside tube surface. The clean outer surface of the tube is visible in this photograph.

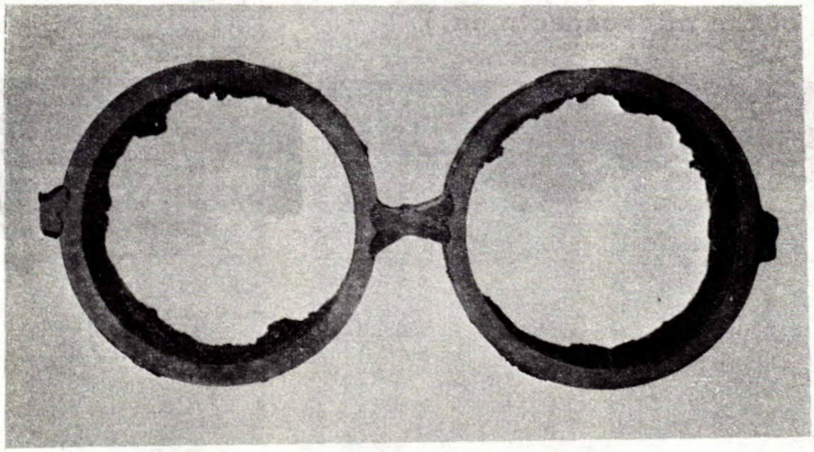
Figure 3 illustrates a split 6 in. length of tube containing red spots (arrow 1), sooty material (arrow 2) and black scale (arrow 3). The latter constituent was suspected of being mill scale that had not been removed by pre-operational cleaning.



X1/2 actual size

Figure 3. Longitudinal section showing inside tube surface. Red spots (arrow 1); Soot (arrow 2); Suspected scale (arrow 3).

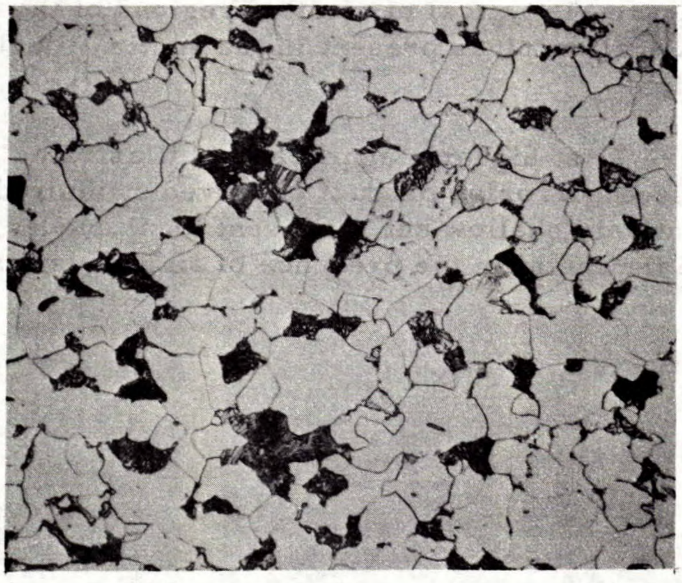
A transverse section through the sample, Figure 4, was deep-etched to determine if the tube was of seamless manufacture.



X1/2 actual size

Figure 4. Deep-etched transverse section. (The tubes were of seamless manufacture).

The transverse microstructure of one of the tubes is illustrated in Figure 5 and consists of ferrite and lamellar pearlite. The ferrite grains are equiaxed and refined. The hardness, measured on the clean (outside) surface of the tube was Rockwell B 68.



etched in 2% nital X500

Figure 5. Microstructure of tube viewed in transverse section. The microstructure appears normal with respect to constituents, cleanness, hardness and grain size for seamless tubing manufactured from killed steel to the requirements of ASTM A-210.

Figure 6 illustrates the appearance of transverse sections taken through "red spots" on the inside water surface of the tube. (The corrosion product has been compressed by the bakelite mould material used for preparation of the microspecimen.).

As-polished X100

Figure 6. Sections through red spots at the surface of the tube. The corrosion product has been compressed by the bakelite (grey) visible at the top of the photomicrographs. The water-side scale, illustrated at the left of this figure, is typical of unpitted regions of the inside surface. A shallow pit is present in the section illustrated at the right.

Figure 7, at higher magnification, illustrates the appearance of the compressed corrosion product observed at the red spots. These pits are relatively shallow but represent local anodes that may continue to penetrate the metal in the presence of an adequate supply of oxygen.

As-polished **X500**

Figure 7. Inside (water surface) of tube. Section taken at red spot. The corrosion product consisted of magnetite and hydrated iron oxide, Fe0 (OH) lepidocrocite. Copper-coloured constituent is visible (arrows) in the corrosion product.

DISCUSSION

Analysis of material scraped from the red spots (pits) showed a significant quantity (2% to 5%) of copper and strong traces of zinc. The corrosion product consisted of FeO (OH) - lepidocrocite (hydrated iron oxide) and Fe_3O_4 - magnetite. The loose black powder and the black patches were identified as magnetite. No decision could be made as to the origin of this constituent, i.e., whether it was residual mill scale (not removed by pre-cleaning) or magnetic iron oxide formed by steaming. Metallographic examination of the surface suggested that the latter was more probable.

The tube appeared to conform to ASTM-A210, medium carbon, seamless, killed steel, in the annealed or normalized condition. The surface hardness, Rockwell B 68, and the microstructure appeared satisfactory for this grade.

The tube wall thickness appeared to be approximately 0.188 in., with a 2.516 in. OD and 2.141 in. ID, approximately. The pits have a depth of 0.004 in. to 0.010 in., the location of each pit being marked by the yellow-red spot of hydrated iron oxide. Reference is made to the previous letter (1) and to a Mineral Processing Division letter and report (2) (3).

CONCLUSIONS

1. Copper and zinc are present with iron oxide on the inside tube surface.

2. The red spots consist of a mixture of hydrated iron oxide and loose magnetite and mark the location of shallow "anodic" pits. The pit depth in the samples examined, varied between 0.004 in. and 0.010 in.

3. No positive conclusion is possible concerning the presence of original (manufacturer's) mill scale on the inside tube surface. Magnetite was detected as a loose black powder and was also detected in occasional black patches in more adherent form.

4. The water side of the tube did not appear to be uniformly coated with an adherent FeO-Fe_3O_4 coating.

REFERENCES

1. Letter - Physical Metallurgy Division - to Mr. J. R. Dean, The New Brunswick Electric Power Commission (July 31, 1964)

2. Letter - Mineral Processing Division - to Mr. J. R. Dean, The New Brunswick Electric Power Commission (Sept. 8, 1964).

3. Mineral Processing Division, Industrial Waters Section Report, MP-MIN-637 (July 7, 1964).

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