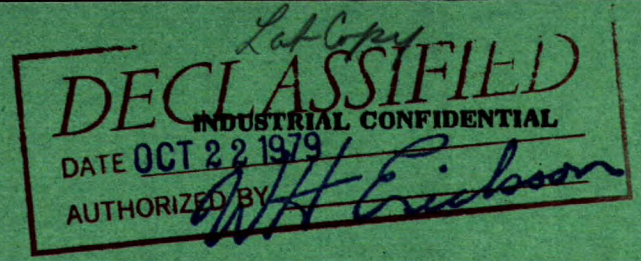


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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 65-29

IR 65-29

**EXAMINATION OF NOVA SCOTIA PULP
LIMITED RECOVERY BOILER TUBE SAMPLE**

FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

by

D. E. PARSONS & D. A. MUNRO

PHYSICAL METALLURGY DIVISION

COPY NO. 14

MAY 12, 1965

Mines Branch Investigation Report IR 65-29

EXAMINATION OF NOVA SCOTIA PULP LIMITED RECOVERY
BOILER TUBE SAMPLE

by

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

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SUMMARY OF RESULTS

Metallurgical examination of a corroded, upper screen tube from an acid sulphite pulp mill recovery boiler showed that the tube was a seamless grade manufactured from rimmed carbon steel. Localized thinning of this tube appeared to result from progressive oxidation of the tube surface and slagging of the oxide in the presence of large quantities of sodium sulphate and sulphur trioxide.

A superheater tube sample was identified as of the 1% Cr, 0.5% Mo grade. This sample was thinned, apparently both by oxidation in the presence of sulphate and by mechanical thinning of the outside wall due to the hot bending operation but appeared to be less affected than the rimmed carbon steel.

Wastage was attributed to lack of oxidation resistance of the tube materials in the presence of sulphur rather than to attack by vanadium pentoxide although 0.10% V was detected in the external tube deposit.

The desirability of separating the boiler function and the sulphite recovery function was discussed. The boiler tubes submitted for examination are typical of those used in boilers designed for combustion of fuels having controlled maximum contents of sulphur and vanadium.

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INTRODUCTION

On October 19th, 1964 two lengths of steel tube, taken from a Nova Scotia Pulp Limited recovery boiler, were submitted to the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys with the request that these samples be examined to obtain information about the mechanism of tube wastage in this type of boiler.

The boiler is a 420 tons per day Foster Wheeler - JMW, Chemical Recovery Unit at Nova Scotia Pulp Limited - Stora Mill, Port Hawkesbury, N.S. The design pressure is 1040 psig, corresponding to final steam temperature of 860°F. A drawing of this unit (Figure 1) was supplied showing the location of the two tube samples submitted for metallurgical examination. This boiler burns red liquor (5.2 pH) from the sodium sulphite (acid) pulp digester. Crude oil or light oil can also be used as a supplementary fuel. Sodium sulphite is recovered from the combustion hearth and process steam is generated.

The letter covering this enquiry, dated October 19, 1964 from Mr. W.F. McKee, General Superintendent stated:-

"I am enclosing a sketch of our unit on which we have marked in red pencil the areas of pronounced thinning.

Under separate cover we are forwarding a section of tube taken from a bend of the upper screen tube section. The scale on the outside of this tube is typical of that found throughout the tube area. However, the thinning, while plainly in evidence, is not nearly as severe as that which we encounter in the bends of the primary and secondary super-heater sections.

The unit we are operating is fired with concentrated waste sulphite liquor (54% solids) and has a pH in the order of 5.2. This is the primary fuel used in this boiler. However, over the past 3 years we have been burning some Venezuelan bunker "C" as an auxiliary fuel. This fuel carries in excess of 250 parts per million (0.025%) vanadium and at the present time is a prime suspect in our corrosion problem.

During the past month we have completely renewed the superheater and screen tube sections and have replaced the bunker oil with a light oil having a vanadium content of 0.05 parts per thousand (0.0005%) as the secondary fuel. We have

at the same time virtually discontinued the use of oil as a fuel in this unit.

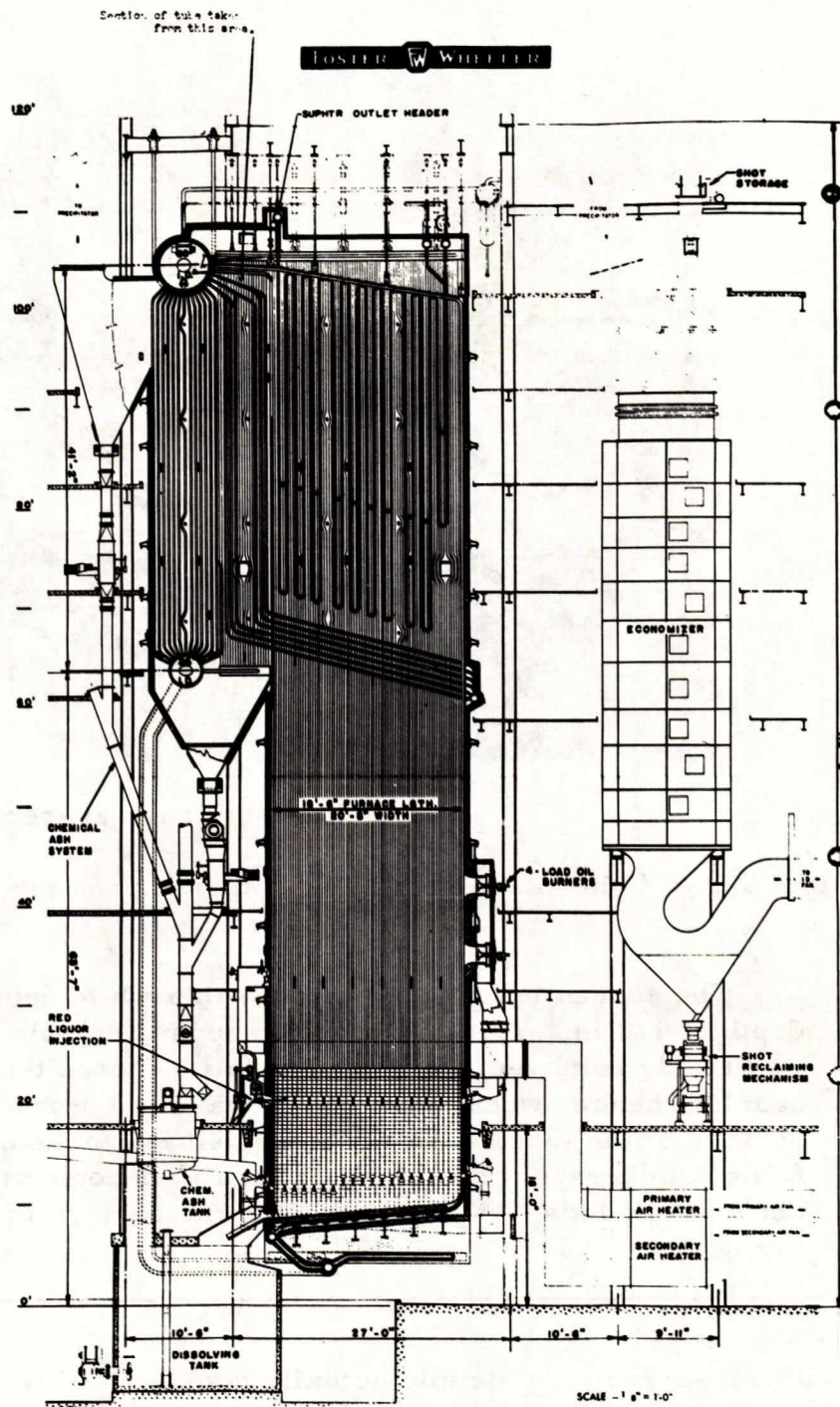
While the cost of repairs to this unit was in excess of \$100,000 this expense is actually of secondary importance when we consider the hazards to life and property that we associate with catastrophic corrosion.

Our investigation into this problem has led us to seek the services of J. T. Donald Company of Canada, Sheppard T. Powell of United States, the Swedish Steam Users Association, the Metallurgy Department of Canadian Industries Limited, the Research Department of British American Oil (our suppliers), as well as the manufacturers of many types of products designed to passivate the vanadium present in bunker "C" fuels.

We feel that the problem is actually of national importance as several disastrous explosions have occurred in recovery units in both Canada and the United States. We are, therefore, soliciting your assistance in this investigation and would be most desirous of receiving information on the subject of tube wastage particularly associated with high pressure units".

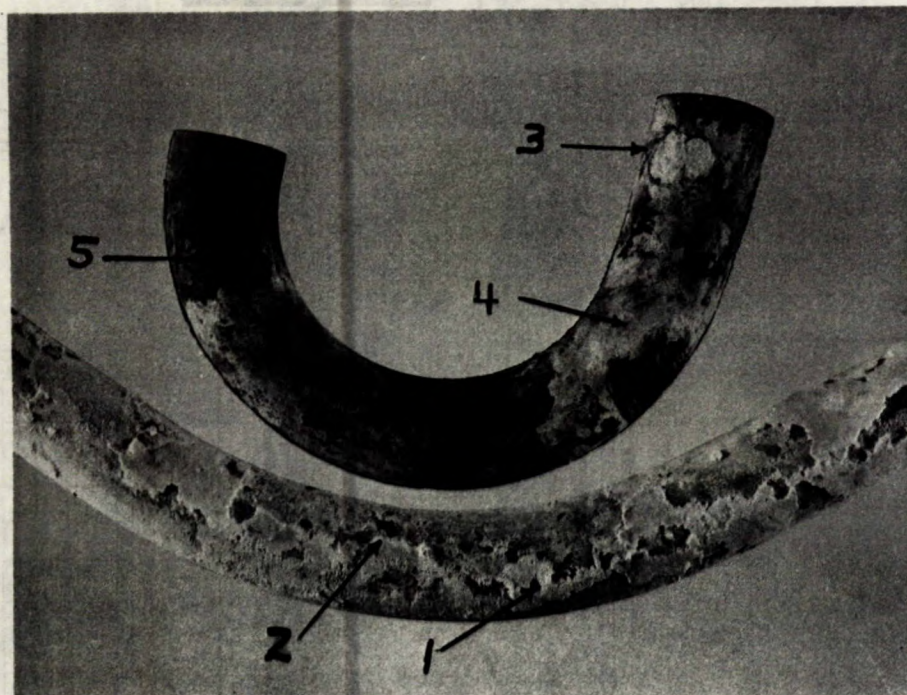
Figure 1 illustrates the boiler and shows the location of the samples submitted for metallurgical examination.

Figure 2 illustrates the appearance of the U-bend and upper screen tube samples submitted for metallurgical examination.



(Sketch. Mat. October 19, 1964.)
420 TONS PER DAY FOSTER WHEELER-JMW CHEMICAL RECOVERY UNIT
FOR NOVA SCOTIA PULP LIMITED - STORA MILL - PORT HAWKESBURY, N.S.
Design Pressure - 1040 psig. Final Steam Temperature - 860°F.

Figure 1 - Chemical recovery boiler - design pressure 1040 psig. Final temperature 860°F - The location of the upper screen tube sample is shown. The U-bend sample was not identified as to exact location.



X 1/4 (half sections, as-received).

Figure 2 - U-bend sample, (top); Upper screen tube sample (bottom)

The screen tube* was coated with a white deposit having a depth of 1/8 in. This thick white deposit (soluble in hot water) was easily removed and tended to fall off when the sample was handled; hence, when received, it was not continuous on the surface of the tube. The white deposit is marked, arrow 1. A black adherent, non-magnetic (scale) deposit was observed between the loose white deposit and the surface of the metal, arrow 2.

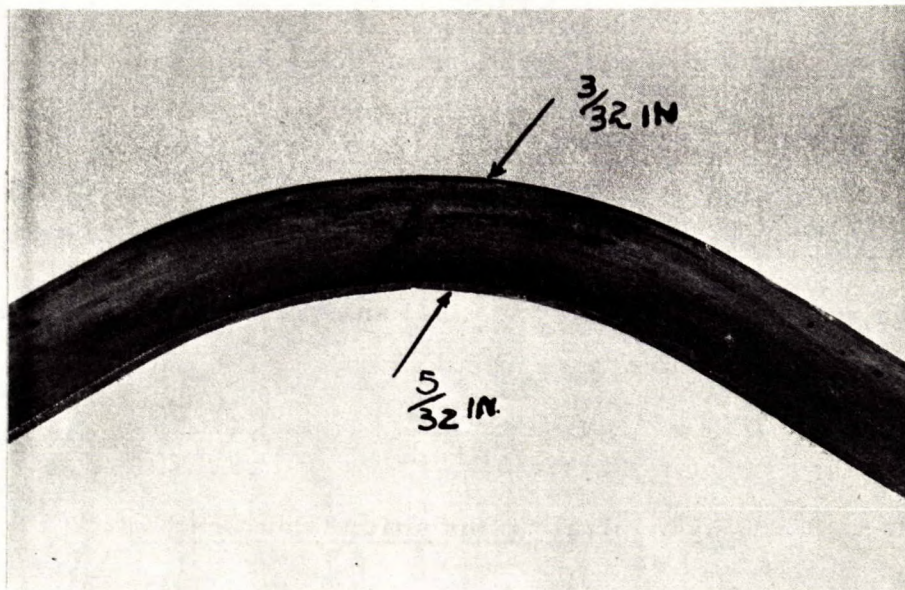
* Note:-

The upper screen tube sample actually consisted of two lengths of tube joined by a circumferential weld (out of the picture at the right). Hence, analysis was made on both tubes described as the long screen tube, (visible) and the short screen tube, (out of picture at right).

The U-bend sample, when received, contained only one patch of thick white deposit, arrow 3, - the remainder of the U-bend surface was coated with areas of thin magnetic scale containing sufficient sulphate compound to vary in colour from black to white, arrow 4. This scale was not continuous and showed evidence of flaking and spalling, arrow 5.

Thinning of the tubes is apparent in samples taken at the outside bend surface. Thinning was due partly to the bending operation and partly to wastage of metal by formation of iron-rich scale between the white deposit and the metal surface.

Figure 3 illustrates the appearance of a longitudinal half-section of bent screen tube viewed from the inside surface. The wall thickness of this sample is shown in Figure 3 and in Table 4.



X 1/4 - (half section)

Figure 3 - Screen tube sample viewed from the inside surface.

The tube wall thickness is shown in inches at the inner and outer surfaces. The inside tube surface is comparatively free from pitting, is smooth and is coated with black, water-side deposit.

EXAMINATION

Metallurgical examination of the tubes was carried out as follows:-

- (1) Chemical Analysis - of drillings from each of the tubes that were girth-welded together to form the bent upper screen tube sample - analysis of drillings from the superheater U-tube sample.
- (2) X-Ray Diffraction Analysis - of white powder and deposit residue from the outside surface of the screen tube and U-tube samples.
- (3) Chemical (wet) Analysis - of deposit removed from the outside surface of the upper screen tube, having particular regard to vanadium and sulphur contents.
- (4) Dimensions and Wall Thickness of Tube Samples
- (5) Metallographic Examination

(1) Chemical Analysis

The results obtained by chemical analysis are listed in Table 1.

TABLE 1

Chemical Composition (Per Cent)

Sample	C	Mn	Si	S	P	Cr	Mo
Screen Tube 1	0.11	0.41	0.01	0.028	0.018	0.05	0.03
Screen Tube 2	0.12	0.41	0.01	0.030	0.017	0.05	0.03
U-Superheater	0.09	0.43	0.28	0.021	0.008	1.01	0.51

The upper screen tubes are carbon steel of rimmed grade, having a chemical composition resembling AISI-1010 and appear to conform to ASTM, A83-grade A, Specification for Seamless Steel and Iron Boiler Tubes.

The U-bend superheater tube sample is manufactured from killed steel containing 1% Cr and 1/2% Mo and appears to conform to ASTM, A200-61T, Seamless Intermediate Alloy-Steel Tubes for Refining Service.

Tube containing 9% Cr and 0.5% Mo; austenitic stainless (Type 316) and carbonized carbon steel tubes are sometimes recommended (1, 2) for similar reducing environments at 860°F. Alloy tube, 60% Cr, 40% Ni is reported to give optimum service.

(2) X-ray Diffraction Analysis

The results obtained by X-ray diffraction analysis of six samples of deposit, removed from the outside screen tube surface, are shown in Table 2. X-ray powder patterns (3), were obtained using 57.3 mm diameter Debye-Scherrer cameras with Fe-filtered Co, K radiation. Representative material from five samples and two differently-coloured materials from the sixth sample were examined. The films were interpreted using the ASTM Powder Diffraction File and available standard patterns. (These materials were not completely identified with respect to all the compounds indicated by the presence of lines in the diffraction patterns).

TABLE 2

Results of X-ray Diffraction Analysis of Powder
Removed from the Outside Screen Tube Surface

Sample	Colour	Identification
Screen Tube, Outer layer of deposit	White	Major:-Sodium sulphate, (thenardite, Na_2SO_4).
" " " " " " " "	"	Small minor: - Unidentified X.
" " " " " " " " Mid layer of deposit	White	Major:-Sodium sulphate.
" " " " " " " "	"	Small minor:- Unidentified X.
" " " " " " " " Inner layer of deposit	White	Major:-Sodium sulphate.
" " " " " " " "	"	Minor:- Unidentified X.
" " " " " " " " Inner layer, next metal	Blade	Major:- Unidentified X (non magnetic)
" " " " " " " "	"	Trace:- Sodium sulphate.
Superheater U - outer layer	White	Major:- Sodium sulphate.
" " " " " " " "	"	Small minor:- Unidentified X.
" " " " " " " " mid layer	Grey	Major:- Magnetite (Fe_3O_4), sodium sulphate.
" " " " " " " "	"	Minor:- Unidentified Y (may include some $NaFe_3(SO_4)_2(OH)_6$)
" " " " " " " " next metal layer	Black	Major:- magnetite - (magnetic)
" " " " " " " "	"	Minor:- hematite, Fe_2O_3 . Very small trace:- Unidentified Z.

The principal phase is sodium sulphate (Na_2SO_4). There is also evidence that oxidation of iron to Fe_2O_3 , Fe_3O_4 and to $\text{Na Fe}_3 (\text{SO}_4) (\text{OH})_6$ has occurred in the superheater sample.

Unidentified constituents X and Y did not match available patterns, hence wet analysis was made to confirm that vanadium was not a major unidentified constituent. The results of wet analysis, of deposit removed from the outer surface and pulverized, are shown in Table 3.

TABLE 3

Chemical Composition of Deposit on Outer Surface
of Screen Tubes

Element	Per Cent
K	7.09
Na	13.4
Fe	12.0
Total S	21.6
*V	0.10

*This vanadium content is considered low in comparison with ash obtained from units used for combustion of high vanadium fuels, however, it is not known whether this element has catalyzed reaction of the Na_2SO_4 and SO_2 .

(4) Dimensions and Wall Thickness of Tube Samples

The apparent, nominal tube dimensions were as listed in Table 4.

TABLE 4

Nominal Dimensions Screen Tube and U Tube

<u>Screen Tube</u>	OD = 2.406
" "	ID = 2.156 in.
" "	apparent, nominal wall thickness "t _s " approximately = 1/8 in. (0.125 in.)
<u>U Tube</u>	OD = 2.344 in.
" "	ID = 1.906 in.
" "	apparent nominal wall thickness "t _u " approximately = 7/32 in. (0.219 in.)

Measurement of the wall thickness (screen tube) showed that this dimension was about 1/8 in. (0.125 in.) on the inside of the bend radius and was about 3/32 in. (0.094 in.) on the outside of the bend. Some of the thinning observed at the outside radius of the bend was due to the hot bending operation, although thinning had apparently been increased by loss of metal due to slag action and oxidation. This relatively uniform thinning was observed at the bend and extending for about 1 ft in each tangent direction at the outside tube radius. The most serious and unpredictable type of thinning was observed in an area 13 in. from the bend where localized thinning of the tube wall (outer tangent surface) had reduced the wall thickness to 5/64 in. (0.078 in.). This serious localized attack appeared to be directly related to process operation, i.e., to slag action, acid attack, oxidation and erosion of the steel surface (4) and was not due to the tube bending operation. Attack or catalysis by vanadium pentoxide may have occurred but at the time of analysis the quantity of vanadium was 0.10% in a ground bulk sample including both the white and black, surface deposits.

Examination of the superheater U-sample (each arm of the U having a length of about 9 in.) showed that the wall thickness of this sample at the inside bend radius was about 7/32 in. (0.219 in.) and at the outside bend was only about 5/32 in. (0.156 in.). There was no evidence of localized pitting in the short length examined so that thinning of this tube appeared to be due, either to the bending operation, or, to the bending operation combined with uniform wastage of steel at the outer bend surface.

METALLOGRAPHY

Metallographic examination showed the microstructure of the screen tube to consist of ferrite and lamellar pearlite. Traces of ferrite rim were visible at the inside surface but were absent at the outside surface, probably due to wastage of metal from the outside surface. The scale on the inside surface was adherent and had accumulated, whereas the appearance of the outer scale was consistent with loss of metal by progressive oxidation followed by spalling or erosion to expose new surface to attack, i.e., continuous wastage of metal.

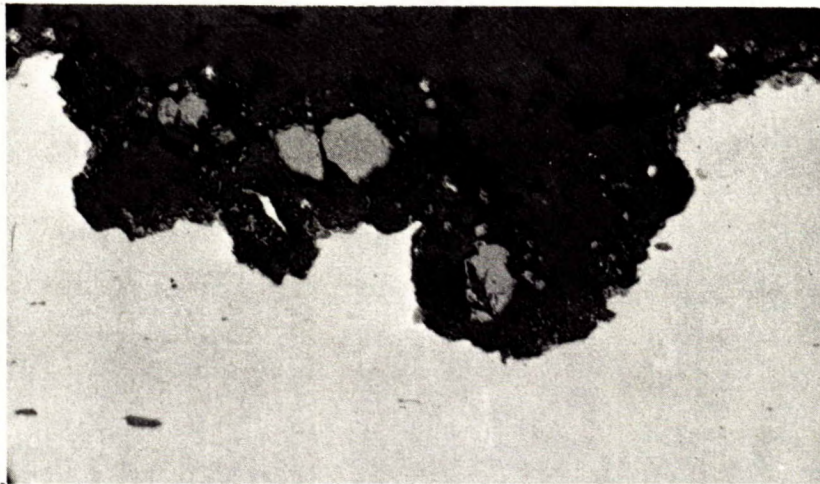
The screen tube microstructure is illustrated in Figure 4. Figures 5 to 7 inclusive illustrate the appearance of scale at the screen tube surface.



X100 - etched 2% nital

Figure 4. Transverse section through screen tube.

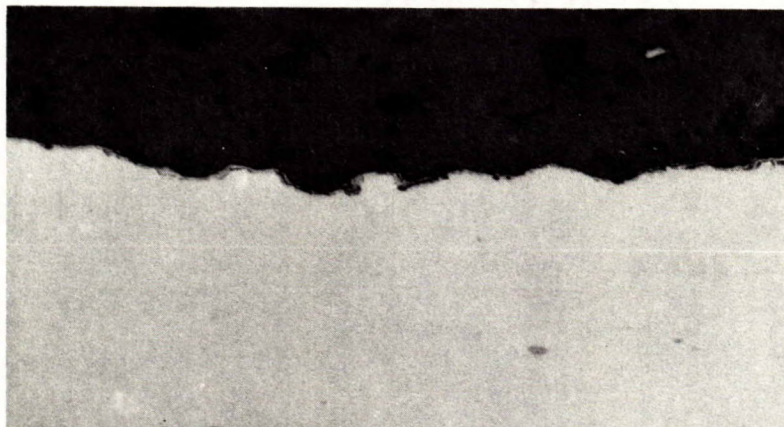
The microstructure consists of ferrite and lamellar pearlite. The grains are equiaxed and have a ferrite grain size of ASTM No. 6.



X 250 - as-polished

Figure 5 - Screen tube transverse section - inside water side of tube.

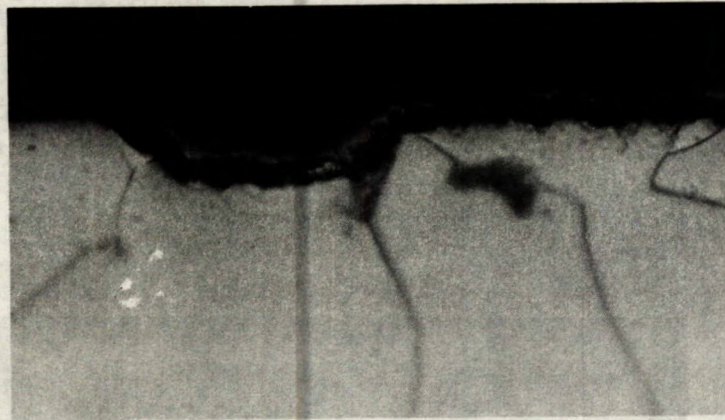
Minor pitting has occurred but the scale appears to have accumulated and to have remained in position. The original ferrite rim, visible at this surface, confirms that metal has not been lost from this surface.



X 250 - as-polished

Figure 6 - Screen tube transverse section - outside (fire) side of tube.

The scale appears to have been removed continuously and progressively, leaving only the layer of subscale as illustrated.

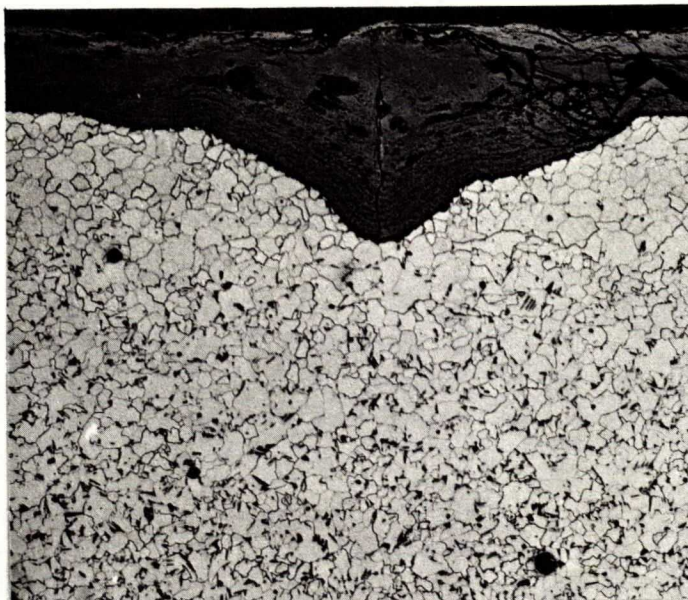


X 1500 - 2% nital etch

Figure 7 - Part of the same area as Figure 6 - outside (fire) side of screen tube.

Illustrates the residual scale and method by which wall thickness is reduced due to progressive oxidation and loss of scale (oxidation, slagging and erosion).

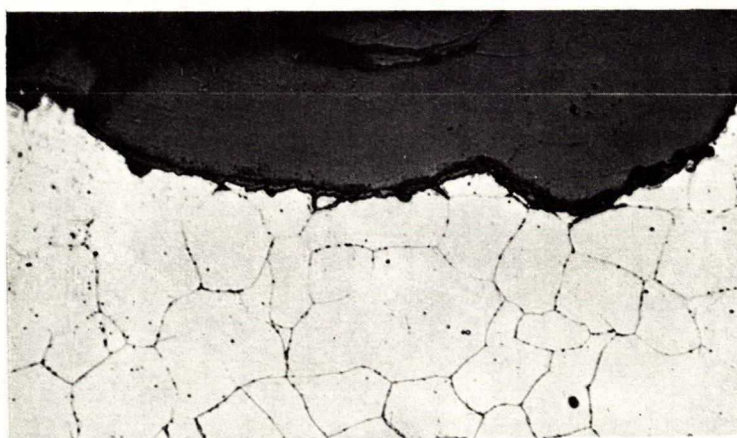
Figures 8 to 10, inclusive, illustrate the microstructure of the 1% Cr 1/2% Mo superheater "U"-tube sample and the appearance of the scale observed on the outside (fire side) of this tube.



X 100 - 2% nital etch

Figure 8 - Superheater U-sample. Transverse section of fire surface.

Progressive oxidation at the surface of the tube, accelerated by the formation of iron-sulphur compounds, is illustrated. The scale-metal interface is illustrated at higher magnification in Figure 9.



X 500 - 2% nital etch

Figure 9 - Same area as Figure 8 at higher magnification.

The metal-scale interface is illustrated. Intergranular attack is also visible.



X 500 -- 2% nital etch

Figure 10 - Superheater U-sample. Transverse section.

The microstructure consists of fine-grained ferrite and slightly divorced pearlite, typical of hot formed seamless 1% Cr 1/2% Mo.

DISCUSSION

The deposit present on the tubes was identified as consisting principally of sodium sulphate and contained only 0.10% V in the bulk sample.

Definite localized thinning was observed in an area (diameter 1-1/2 in.) about 13 in. from the bend in the screen tube where the wall thickness had been reduced from 0.125 in., nominal to 0.078 in. This thinning appeared to be due to progressive oxidation and slagging caused by reaction of sodium sulphate with iron oxide in an SO_2 atmosphere containing a low concentration of sulphur trioxide and with alkali metal deposits on the tubes catalyzing the reaction of SO_2 to form the corresponding sulphate⁽⁴⁾. The presence of any chloride ion would also have accelerated wastage of tubes.

More uniform thinning of the screen tube was also observed for a distance of about 1 ft on either side of the bend. This thinning was believed partly due to the original hot bending operation during fabrication of the boiler but was mainly attributed to FeSO_4 slagging. Thinning at the bends caused a total reduction (slagging and hot bending) from 0.125 in., nominal thickness, to 0.094 in. (The observed pitting, previously mentioned, resulted in wall thickness of 0.078 in., even in regions remote from the bend).

Examination of the U superheater sample showed that the wall thickness of the tube was about 0.219 in., at the inside of the bend and was only 0.156 in., at the outside bend surface. Some of this thinning was probably due to the bending operation but most appeared due to oxidation and intergranular slag attack at the bottom of the U-bend surface. No localized areas of corrosion were observed in the short length examined. It was also observed that, the black scale in direct contact with the metal was strongly magnetic in this U-sample, whereas the black subscale on the super heater tube sample was nonmagnetic. (This subscale was insoluble when the Na_2SO_4 was removed by washing with hot water).

The subject boiler tubes appear to be unmodified commercial types used for combustion of fuels controlled with respect to sulphur and vanadium contents. The tubes used in this boiler, mild steel and 1% Cr - 1/2% Mo - have been specified, having regard to service temperature, operating pressure and heat transfer, but fail to take account of the accelerated surface oxidation caused by reaction of Na_2SO_4 and SO_2 in the presence of alkali oxide and iron oxide. (Under some conditions, 9% Cr - 1/2% Mo and austenitic type 316 tubes have given improved service in high sulphur environments, although failure of type 304 tubes in 18 months has also been reported in unfavourable environments). Some success has been reported in less critical service for the use of calorized or ceramic-coated carbon

steel tubes. Detailed recommendations as to tube materials would probably be available through the boiler manufacturer and from steel tube manufacturers.

Published information (4) indicates that there are numerous uncertainties in predicting the life of materials in the recovery boiler service described. Separation of the (boiler) steam generating plant and of the sulphite recovery process would seem to be the safe solution and might be economic in a comparison including maintenance costs and costs of modification for $\text{SO}_2 - \text{Na}_2\text{O}$ service.

CONCLUSIONS

- (1) Localized thinning (pitting) was observed on the combustion side of the screen tube sample. The wall thickness had been reduced from 0.125 in. to 0.078 in., due to oxidation and loss of metal by slagging in the presence of sodium sulphate, alkali oxides and sulphur dioxide combined with erosion and possible flame impingement. Uniform thinning was also observed at the outside bend surface of both samples.
- (2) Large quantities of sodium sulphate and quantities of oxidation products of iron, Na_2FeS compound, Fe_2O_3 and Fe_3O_4 were observed, indicating corrosive reaction with the surfaces of the carbon steel and 1% Cr - 1/2% Mo steel tubes.
- (3) The vanadium content of the bulk deposit was relatively low at 0.10% suggesting that wastage of tubes is due primarily to oxidation in the presence of Na_2SO_4 and SO_2 rather than to V_2O_5 attack - although the possibility of catalysis by V_2O_5 was present. (The marine location may also allow acceleration of tube wastage if chlorides are present).
- (4) The boiler appeared to be an unmodified commercial boiler designed for the combustion of fuels controlled with respect to sulphur and vanadium contents, whereas, in service, a constant supply of SO_2 , SO_3 alkali-oxides, iron oxide and sodium sulphate is available.

NOTES (1) - (6)

Items (1) to (6) are included as tentative recommendations if these are considered feasible by the boiler manufacturer, the operating company and are acceptable within the insurance and provincial boiler codes.

- (1) If possible separate the two functions - steam generation and sulphite recovery.
- (2) Consult the boiler manufacturer concerning any modification of the boiler which will prevent $\text{SO}_2:\text{SO}_3$ attack in the presence of Na_2SO_4 at 860°F . Use of 9% Cr - 1/2% Mo tubing, of austenitic stainless type 316, possibly of calorized or ceramic coated carbon steel might be considered. (International Nickel Co., Corrosion Laboratories might offer recommendations about use of Inconel tubing in this service).
- (3) Use of vanadium-rich fuel should be avoided since V_2O_5 on the tube surface accelerates FeSO_4 corrosion in the presence of SO_2 .
- (4) The presence of chloride ion in the system could accelerate attack if present. Additions of chlorides in the liquor or water should be avoided.
- (5) Use of excess burner air and control of flame conditions to minimize SO_3 content, gas passage and reaction time might be combined with tube washing to minimize the thickness of Na_2SO_4 deposit. Also, except from the product contamination viewpoint - combustion of MgO (added as $\text{Mg}(\text{OH})_2$ or dolomite has, in some circumstances, assisted in absorbing SO_3 during its passage through the combustion chamber.
- (6) Trial tubes or trial metal strips could be installed for test of the service life of particular materials, especially by weight loss tests of metal strips.

High alloy, 60% chromium, 40% nickel steel tubes* have recently been reported to offer maximum resistance to vanadium pentoxide or sulfate corrosion at elevated temperatures.

*Manufactured by BLAW-KNOX Company, Pittsburgh, Pa.

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3. X-ray Diffraction Analysis of Powder from Tube Samples. Internal Report MS-64-107, Physical Chemistry Section, Mineral Sciences Division, Department of Mines and Technical Surveys by N. F. Bright and J. E. Rowland.
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5. Babcock and Wilcox Tube Company Data. Technical Bulletin 1-A - Summary of Properties, B and W Croloy Stainless Steels. Technical Bulletin 2-A - Corrosion Resistance, 18% Chromium, 8% Nickel Alloy. Technical Bulletin 3-B - Properties and Application of Seamless Tubes of B and W Croloy 18-8 at Elevated Temperatures. Technical Bulletin 14 - B and W Croloy 9, an Economical Alloy for High-Temperature Service - with Corrosion Resistance.

APPENDIX A

Corrosion and Deposits in Boilers and Gas Turbines.
Review - Research Publication. ASME 29 West 39th St., New York
18, N. Y., report of ASME Research Committee on Corrosion and
Deposits from Combustion Gases by Battelle Memorial Institute.
H.W. Nelson, H.H. Krause, E.W. Ungar, A.A. Putnam, C.J.
Slunder, P.D. Miller, J.D. Hummel, B.A. Landry.

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"A comprehensive study of the external corrosion of furnace wall tubes was reported in a series of papers by W.T. Reid and others (23, 23, 24). It is reported in these papers that corrosion was found to occur when the temperature of the tube metal usually did not exceed 700°F, while the maximum temperatures observed were less than 900°F. One type of deposit found in corrosion areas was largely soluble in water, producing an acid reaction, and consisted principally of a solid solution of sodium and potassium sulphates and alkali-metal trisulfates, such as $K_3Fe(SO_4)_3$. These trisulfates were produced in the laboratory by reacting sodium and potassium sulfates with iron oxide in an atmosphere containing a low concentration of sulphur trioxide. However, neither the sulfates nor the iron oxide reacted with SO_3 separately. Thus, it was postulated that alkali-metal oxides were deposited on the tubes where they reacted with SO_3 to form the corresponding sulphates. These in turn reacted with the iron oxide on the tube surface in the presence of SO_3 to form the trisulfates and cause corrosion of the tubes. A preventive measure suggested was to decrease the SO_3 concentration below that necessary to form the alkali-metal sulfates by supplying air to the surface of the tubes, generally through control of the path of the excess air leaving the burner".

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"Shirley (19) found that alkali and alkaline-earth sulfate contaminated with chlorides are highly corrosive - so corrosive that severe corrosion occurred in ash handling in stainless and heat resisting steel components. The corrosion was associated with sulphur absorption from the sulfates rather than from the gaseous products of combustion.

Corrosion of chromium alloy tubing and stainless superheater tubing has been reported in installations using coal having high chlorine content (0.30 to 0.75 percent). In one instance, type 321 tubes operating at a temperature of 1100 - 1125°F had a useful life of only 18 months. In another case, thinning was observed after five years of service. It was observed that wherever corrosion was severe, the inner layer of deposit adhering to the metal surface was high in alkali and sulfate".

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