REMOVAL OF EXTERNAL DEPOSITS ON BOILER TUBES

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The superheater tubes in Port and Starboard boilers of IN Ship were found to have completely clogged by heavy deposits, which on analysis gave mainly vanadium pentoxide and sodium sulphate together with small amounts of other inorganic salts and oxides, carbonaceous and siliceous matter. The cleaning of the deposits was accomplished by alternate spraying with 15–20 per cent hydrogen peroxide and washing with hot water jets. Over the past two years, since the date of cleaning, the IN Ship is operating without any trouble in the boilers.

The superheater tubes and firerow on Port and Starboard boilers of IN Ships were found to be covered with hard deposits which completely clogged the passage of hot combustion gases produced by burning of furnace fuel oil. The ship became inoperative and a need was felt to remove the hard deposits from the boiler tubes.

The deposits were partially removable by mechanical chipping from the easily accessible areas of the front firerow tubes facing the combustion chamber. The residual layers of deposits which remained after mechanical chipping were found to firmly adhere to the surface of tubes and could not be removed by mechanical method. The normal method of removing deposits such as by hot water jet washing could not be successfully employed as the bulk of deposits were inaccessible to water jet.

The boilers used on IN Ship are of the Babcock and Wilcox Main Boiler Type, Whitby class. It is built up of steel tubes consisting of firerow tubes, generator tubes, superheater tubes and economiser tubes. The superheater tubes are made of chrome steel while the other tubes are of mild steel. The clogging of the gaps between the tubes by external deposits prevent heat transfer fully or partially and produce differential heating as well. It was observed that firerow and superheater tubes were heavily covered with deposits. The generator tubes at the back and the economiser tubes on the top were generally free from deposits.

The rate of heat transfer in superheater tubes ($1\frac{1}{4}''$ dia.) is of the order of 43900 BTU/sq ft/hr at the full output of steam power which attains temperature of 750°–850° F and pressure of 500 lb/sq. in. In each of the boilers, there are 279 superheater tubes, each with a bend and 78 firerow tubes of two different cross sections. It is thus clear that even the partial clogging of the boiler tubes can render the ship inoperative.

PRELIMINARY INVESTIGATIONS ON THE DEPOSITS

Chemical nature of the deposits : The deposits were black. Lumps of the deposits collected from the header end superheater tubes, when broken showed yellow materials inside. The deposits were found to be feebly conducting and feebly magnetic. On chemical analysis, neither the Port nor the Starboard boiler deposits showed any presence of iron or its oxides. The deposits on the Port boiler consisted mainly of sodium sulphate and vanadium pentoxide together with small amount of sulphates of magnesium, calcium, and nickel, nickel oxide, silica, organic matter and carbon. The deposits on the starboard boiler showed, in addition, presence of chromium oxide. Fig. 1 shows the condition of rows of superheater tubes at the header end before cleaning. All tubes and intervening gaps are covered with vanadium rich deposits. Fig. 2 shows the condition of the superheater bends before cleaning the deposits. The view is exposed after removing the BW 5 baffle wall tube. The thick deposits are visible on each bend from top to bottom. The analytical data on the two samples, one from the port and the other from the starboard boiler are given in Table 1.

Chemical Disintegration of the Deposits

(*a*) *By water and alkali* : The deposits when boiled with water or dilute caustic soda disintegrated slowly and only partially. In the powdered state, it parted with its soluble salts readily in cold or hot water. It was clear from these experiments that water or dilute caustic soda will not be suitable for removing the deposits.

(*b*) *By hydrogen peroxide* : It was found that the hard deposits could be completely disintegrated at room temperature within a few minutes by 30 per cent hydrogen peroxide.

The reaction is exothermic. On further studies with regard to concentration and time, it was found that 15–20 per cent hydrogen peroxide would be suitable for disintegrating the lumps *in situ*. Lower concentration was rather sluggish in effect and happened to take considerably longer time. Fig. 3 shows the condition of the same superheater tubes after cleaning with hydrogen peroxide. There is no deposit upon any tube after cleaning.

EFFECT OF HYDROGEN PEROXIDE ON BOILER TUBES

Experiments were conducted to determine the extent to which the boiler tubes may be attacked by hydrogen peroxide solution during the cleaning operation. Corrosion experiments

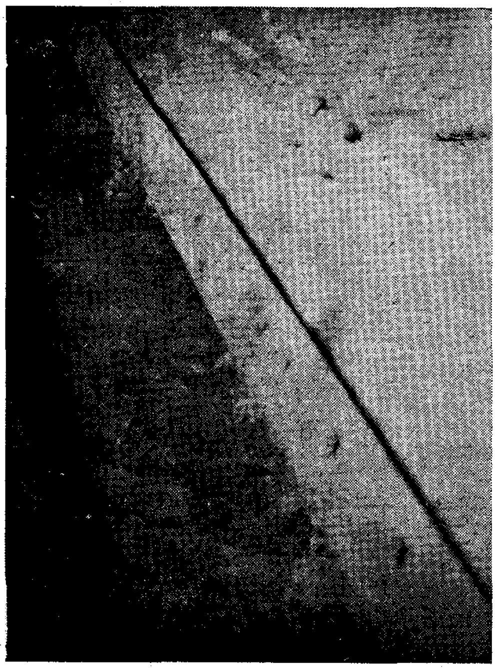

Fig. 1—Plugging of superheater tubes by vanadium rich deposits.

Fig. 2—Return bend of superheater covered with deposits.

TABLE 1

PHYSICO-CHEMICAL PROPERTIES OF THE EXTERNAL DEPOSITS ON BOILER TUBES IN IN SHIP

	Port Boiler Deposit	Starboard Boiler Deposit
Sp. Gr.	2·46	2·55
pH (4% aqueous extract)	2·85	2·90
Loss on heating (per cent)		
(1) 105°C	1·1	Not done
(2) 850°C	7·5	7·0
Constituents (per cent)		
Vanadium pentoxide	36·2	23·9
Sodium sulphate	43·4	42·8
Magnesium sulphate	2·7	3·1
Calcium sulphate	3·7	3·3
Nickel sulphate	1·4	0·8
Nickel oxide	2·0	2·1
Chromium oxide	Nil	2·0
Acid insolubles	2·5	15 (by difference)

TABLE 2

EFFECT OF HYDROGEN PEROXIDE ON SUPERHEATER AND FIREROW TUBES

Type of Boiler Tube	Loss in wt. (mg/sq. dm.) after immersion for 90 hours at room temperature		
	30% H_2O_2	20% H_2O_2	Tap water
Superheater tube	—	49·7	76·3
Firerow tube	99·8	67·6	102·5

Fig. 3—Return bend of superheater after chemical cleaning.

were, therefore, conducted by immersing polished degreased and weighed pieces of superheater and firerow tubes (1″ in length) in 20 per cent hydrogen peroxide for 90 hours at room temperature. Simultaneously, mild steel specimens (2″×1″, 16 BG) polished, degreased and weighed were immersed in tap water for 90 hours. The weight loss determined after derusting in inhibited hydrochloric acid was taken as a measure of attack. The results are given in Table 2. It may be seen that the use of 20 per cent hydrogen peroxide has an inhibitive effect upon the rate of corrosion when compared with ordinary tap water or 30 per cent hydrogen peroxide. The material of superheater tube is found to be more resistant to 20 per cent hydrogen peroxide than firerow tubes. The superheater tubea nd the firerow tubes gave 49·7 and 67·6 mg/sq. dm. loss in 20 per cent hydrogen peroxide respectively against 76·3 and 102·5 mg/sq. dm. loss in tap water during the period of 90 hours immersion at room temperature. The firerow tube suffered 99·8 mg/sq. dm. loss in 30 per cent hydrogen peroxide, indicating that it does not retard corrosion rate.

REMOVAL OF DEPOSITS *IN SITU* FROM PORT AND STARBOARD BOILERS

(*a*) *General aspects*: The application of 15–20% hydrogen peroxide in removing the deposits from the Port and Starboard boilers of IN Ship presented various technical difficulties and a careful planning of the operation had to be made, with the support of FOC WEF, Bombay in close collaboration with the Fleet Engineer Officer and the Commanding Officer of the Ship. The Naval Dockyard rendered help in fabricating some of the accessories required for carrying out the cleaning. The crews of the ship and Fleet Office formed the main source of operating man-power.

In order to gain greater accessibility the BW 5 baffle wall tube of the boiler was removed, thus exposing the return bend of superheater tube for efficient cleaning.

(*b*) *Protection of the refractory materials*: The floor, wall and roof of the combustion chamber of both the boilers required to be protected from the deleterious action of hydrogen peroxide. The walls and roofs were protected by applying ½″ to ¾″ thick cover of mineral jelly.

The floor of the combustion chamber, which is laid with refractory bricks, was covered with PVC sheet.

(*c*) *Collection of wash liquid and debris*: In order to catch the washings and the debris resulting from hydrogen peroxide cleaning, a set of 4 aluminium trays (5′ × 1½′ × ⅓′) was placed side by side on the PVC sheet in the combustion room floor. The dimensions of aluminium tray were such that these could be taken in and out through the manhole of the combustion room. The waste products were removed from the trays by means of buckets at suitable intervals.

(*d*) *Other details*: The removal of deposits on the boiler tube was done by spraying 15-20% hydrogen peroxide solution. A pump with PVC impeller was initially used but as it gave mechanical trouble this was dispensed with. A stirrup pump used in fire-fighting was found to deliver high pressure jet. Therefore this pump was subsequently used in the cleaning operation.

Dilution of hydrogen peroxide was made in PVC buckets, placed inside the boiler room. The diluted hydrogen peroxide (15—20%) was pumped by the stirrup pump directly from the bucket. Long PVC tubings were used for conducting the hydrogen peroxide.

The delivery ends for hydrogen peroxide were of two types namely the stirrup nozzle and long lances. The stirrup nozzle could be used either to give a long straight jet or a fan spray. But its construction was such that it could not be used for forcing the jet deep into the header superheater bends nor it could be applied at top portions of tubes. In such cases, lances 6 ft. and 3 ft. in length, having flattened delivery end with 8 to 10 holes of 1/32″ dia were used. The selection of the lances or the nozzles had also to be made depending on the stubborness of the deposit at a particular site.

Usually 45 minutes spraying of hydrogen peroxide was done. The deposits were allowed to remain in the active condition for about an hour. It was then thoroughly washed with hot water for nearly 2 hours. The water jets were forced through 6 ft. or

3 ft. lances or $\frac{1}{4}''$ dia (1 ft. length) nozzles, as required. The temperature of tap water, which was separately heated on the Weather Deck in Cast Iron taknks by means of hot steam was maintained at 155°–165°F. A pump operating on 440 V AC was used for delivering the hot water under high pressure through the nozzles or the lance. At the end of the day, the boiler deposits were left sprayed with hydrogen peroxide and the next morning, washing with hot water was carried out at the outset.

(e) *Safety measures*: The operators actually engaged in spraying the hydrogen peroxide by going inside the combustion chamber or from any other site were provided with gum boots, rubber gloves, overalls and gas mask. They remained under constant watch and supervision so that on the slightest complaint by anybody of any feeling of giddiness etc, he could be at once removed.

(f) *Period required for cleaning*: In the case of Port boiler, the total hours of spraying with hydrogen peroxide solution consisted of 10 hours whereas it took 14 hours in the case of Starboard boiler. Hot water washings were given for about 40 hours in each boiler.

On the termination of cleaning, the boilers were examined by the representatives of Flag Officer Commanding Western Fleet, Naval Dockyard, IN Ship, and Naval Chemical and Metallurgical Laboratory, Bombay and were found to be in satisfactory conditions IN Ship has since been successfully operating, for over two years.

DISCUSSION

The use of 10% hydrogen peroxide containing 0·1% Kreelon, a trade name of the wetting agent alkyl aryl sulphonate, has been first made by Sewell and Barer[1] in cleaning the vanadium rich superheater deposits[1] in HMCS Ottawa where the high vanadium deposits had been found to have resulted from the use of Venezuelan Oils. Farquharson gave subsequently a detailed account of experience of the Royal Canadian Navy in the slagging of boiler superheaters and their removal[2]. Preliminary experiments at Naval Chemical & Metallurgical Laboratory, Bombay showed that the deposits of IN Ship would take considerably longer time for its removal, with 10 per cent hydrogen peroxide. The concentration was therefore increased to 15-20 per cent. The 20 per cent hydrogen peroxide was invariably used for spraying into the interior and on stubbornly clinging deposits. The deposits contained on an average, 24 to 36 per cent vanadium pentoxide. The vanadium pentoxide percentage was found to depend on sampling. In one of the sample collected from the superheater tubes in the header end, vanadium pentoxide was found to be present in 85 per cent concentration. The core of this lump was deep yellow. Such samples were, however, rare.

The percentage of hydrogen peroxide will require to be chosen depending on nature of the deposit, its thickness and other physical characteristics.

The thermal energy for heating the boiler tubes is derived from the combustion of furnace fuel oil. The depositions of soot on the boiler tubes occur due to incomplete combustion of the fuel and the complex nature of air draft, differential speeds of products of combustion that suffer many changes on their way through the various tube paths. Vanadium is derived from the furnace fuel oil. Vanadium pentoxide is yellow to orange-red in colour and is readily fusible at 650°C but does not volatalise. Vanadium pentoxide along with other carbonaceous product can thus act as binder for the deposits. The sulphates of sodium, calcium and magnesium are likely to be derived mainly from the air used in the combustion, though a part may have come from the fuel. The source of chromium and nickel appears to be the superheater tubes. It is rather strange that no iron or its oxide could be detected in the deposit. Sodium, calcium and magnesium sulphates also contribute towards the cementing of the deposits.

It may be mentioned that one furnace fuel oil sample, examined at the Naval Chemical and Metallurgical Laboratory, contained 15 ppm vanadium though this particular sample has not been burnt in the IN Ship.

CONCLUSION

The cleaning of vanadium rich boiler deposits can be done by hydrogen peroxide *in situ*. Its concentration would require to be determined depending upon the nature of the deposits, whose compositions and physical texture can widely vary and upon the time that can be allowed for the cleaning by the Commanding Officer of the Fleet. Health hazards do exist with the use of hydrogen peroxide spray, even in low concentration and the boiler room should be ventilated with requisite compressed air draft. Gas masks, overalls and gloves made of PVC or neoprene should be used by the operators. Medical aid should be available at hand.

ACKNOWLEDGEMENTS

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