NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
Bench Scale Apparatus for the Study of Slag Formation and Slag Removal

Part 1 - Apparatus and Operation

R. M. Roe
Surface Chemistry Branch
Chemistry Division

A bench scale apparatus for the study of slag formation and slag removal has been developed at this Laboratory. The apparatus consists of a rectangular firebox heated by electrical resistance panels and a collecting tube heated by a glass blower's blast lamp. Temperatures in the firebox approximate very closely those found in shipboard boiler operation.

Synthetic slags of varying compositions are fed into the furnace and deposited on the collecting tube. When the furnace is operated as described, the deposited slag, both before and after removal from the collecting tube, had the appearance of slag from a full size ship's boiler.

INTRODUCTION

The slagging of oil-fired marine boilers has been, and still is, a problem of long standing for the Navy (1-4). Slagging manifests itself in the accumulation of fused inorganic residues on the fireside surfaces of boiler tubes and prevents efficient heat transfer from the hot combustion gases to the boiler tubes.

The main sources of the material forming the fireside deposits are:

1. The sea-water-fuel-oil emulsion that is formed in the fuel bunkers as a result of ballast ing. This is, by far, the greatest source of contaminants.
2. The amount of sulfur in the fuel.
3. The fuel itself, which has concentrated in it the organometallic compounds naturally occurring in the fuel as well as other adventitious material picked up in the course of transportation and refining.
4. Sea salts carried into the firebox by the combustion air.

Other imponderable factors such as boiler firing practice, furnace design, atmospheric dust, and "housekeeping" also contribute.

A lack of understanding of slagging has resulted in a large volume of literature that is concerned with the corrosion resulting from slagging and not with slagging itself. Especially numerous are published articles on the corrosion caused by vanadium and residual fuel-oil ash. Monkman and Grant (5) demonstrated the corrosiveness of mixtures of sodium sulfate and vanadium pentoxide on heat resistant metals; Buckland, Gardiner, and Sanders (6) demonstrated the corrosiveness of synthetic oil ash, containing widely varying amounts of vanadium pentoxide on heat resistant alloys used for gas turbine blades; Brasunas (7) has reported on the catastrophic corrosion resulting from vanadium pentoxide in fuel-oil ash; while Foster, Leipold, and Shevlin (8) have reported on phase studies of sodium oxide and vanadium pentoxide with reference to oil-ash corrosion. Slunder (9) has given an excellent review of oil-ash corrosion.

Boiler slag varies widely in composition, and vanadium is only one of the many elements found in boiler slag. Unfortunately, the emphasis placed on it by investigators in the field would lead one to believe that without vanadium there would be no slagging problem. Sodium sulfate is the chief constituent of boiler slag, varying in amount from 50% to 90% (or higher), the remainder being principally the oxides, vanadates, and/or sulfates of other metals.

A precise analysis would undoubtedly indicate the presence of silicates, sulfides, chlorides, and phosphates as additional minor constituents.

Sulzer (10) in a discussion of the formation of deposits on gas turbine blades states that sodium sulfate deposits are formed by precipitation on
the blade surfaces. The sodium sulfate is formed in the combustion process by the reaction

\[
2 \text{NaCl} + \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl} + 51 \text{kcal/mole.}
\]

Jarvis (11) states that "at flame temperatures the alkalies are vaporized and condense on the superheater tube surfaces where they become converted to the corresponding sulfates and acid sulfates by reaction with \(\text{SO}_2\) and \(\text{O}_2\), or \(\text{SO}_3\). Vanadium in fuel oil is also volatilized and condenses on the relatively cooler surfaces."

Results obtained at this Laboratory in a study of slagging using "Navy Special" fuel oil and miniaturized furnaces, microburners, miniaturized sprayer plates, combustion rigs, etc., demonstrated that such apparatus was difficult to control, time consuming, and decidedly inadequate for the purpose intended. This was confirmed by the results obtained from the small slagging furnace tests at the Naval Boiler and Turbine Laboratory (12) and Engineering Experiment Station (13).

The full scale boiler tests on the Fletcher boiler at the Naval Boiler and Turbine Laboratory (14) demonstrate conclusively how difficult and expensive it is to use a full scale ship's boiler for research purposes.

The following considerations have been used to guide the work reported here:

1. Slagging is the result of deposition of volatilized, molten, and solid compounds on the boiler tubes.
2. Slag is, in essence, a basic glass; in fact, it should be considered a ceramic.

**REQUIREMENTS FOR BENCH SCALE APPARATUS**

A study of the factors involved resulted in the following requirements for a slag-forming device suitable for bench scale study of slag deposition and slag removal.

1. The apparatus should be truly bench scale, i.e., suitable for operation in a chemical hood so that heat and combustion products could be removed with normally available facilities.
2. It should be capable of accelerated slag formation so that an experimentally useful slag could be formed within one working day.
3. It should form slag under conditions of thermal gradient and temperature that simulate boiler operation.
4. The device should include (a) a removable or replaceable collecting unit that can be liquid, steam, or air cooled to simulate tube temperatures, and (b) heated furnace walls to control radiant heat balance within a range simulating boiler conditions.
5. It should include means for introducing slag-forming and slag-removing components of known composition.
6. It should have instrumentation for measuring the temperature of the slag, the furnace wall, and the tube-cooling medium.

Guided by these requirements there evolved a bench scale apparatus which, it is believed, more closely approximates boiler conditions than previous designs.

**DESCRIPTION OF APPARATUS**

The apparatus consists essentially of a rectangular firebox and a collecting tube which passes through the sides of the firebox as illustrated in Fig. 1. The top and side walls of the firebox are heated electrically. Openings at either end of the firebox provide for the introduction of a blast-lamp flame and for the removal of combustion gases. Slag-forming and slag-removing components are fed into the blast flame by a screw conveyor as a powder which passes through a 200-mesh screen.

Three electrical resistance panels (5-1/4 x 12 inches and 500 watts—115 volts ac), comprising the top and sides of the firebox, are mounted on a 3000K firebrick base notched to accommodate the panels, and connected to a Variac supplied with 110/220 volts ac. The two middle rows of resistance wire were removed from the two side panels and a 1/2-inch hole drilled through the center of each panel to accommodate the collecting tube. The front and rear faces of the firebox are made from 3/4-inch Transite blocks—a 2-1/2-inch circular opening in the front block to introduce flame from a blast lamp and a 3-inch circular opening in the rear block for exit of combustion gases and slag particles. The walls and base are held in place by Transite blocks bolted together, fitted with 3000K insulating firebrick, and the joints sealed with asbestos fiber paste. The resistance panels do not have sufficient heating
the deposition of slag with the exception that slag-removal additives are added to the flame and allowed to impinge on the slag previously deposited.

**EXPERIMENTAL PREPARATION**

A typical run is described to illustrate the operation of the furnace.

Previous runs had shown the desirability of studying slag deposition and removal at 1000°C (1832°F). The furnace was accordingly dismantled and the collecting tube from the previous run removed. The furnace was then reassembled and a new collecting tube placed in service.

Synthetic slag was prepared from dry, reagent grade chemicals. Since slags vary widely in composition, the choice of slag components will depend on the purpose of the investigation. The selected materials in the form of oxides or sulfates are placed in a ball mill and milled until they pass through a 200-mesh sieve. It is advisable to mill the chemicals in a dry-air atmosphere. For this run, synthetic slag of the composition shown in Table 1 was used.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>65.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.9</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>20.8</td>
</tr>
<tr>
<td>MnO</td>
<td>2.0</td>
</tr>
<tr>
<td>NiO</td>
<td>2.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.4</td>
</tr>
<tr>
<td>CaO</td>
<td>2.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.1</td>
</tr>
<tr>
<td>MgO</td>
<td>1.4</td>
</tr>
</tbody>
</table>

A blast lamp was positioned in front of the furnace so that the flame tip entered the firebox but did not strike the collecting tube. The heating panels were turned on and the furnace heated to 1000°C as indicated by the optical pyrometer. When the furnace temperature had stabilized (about 30 minutes), synthetic slag was introduced into the blast flame and the molten slag particles allowed to impinge on the collecting tube. Wet steam was passed through the collecting tube continuously from the start of the heating period at about one cubic foot per minute.

Prior to insertion in the furnace the collecting tube was examined for surface imperfections in the area that would be exposed to slagging action. Any such imperfections were noted in order that they might be distinguished from localized corrosion centers. In dismantling the furnace, the firebox walls were removed from the tube rather than drawing the collecting tube through the holes in the panels. Thus, the slagged portion was not marred or damaged.

**FURNACE OPERATION**

Synthetic slag was added by the mechanical feeder at the rate of about 20 grams per hour. The rate of addition is at the discretion of the operator. However, if too rapid, the addition will cool the flame, while if too slow, it will prolong the run unduly.

The greatest portion of the molten slag did not adhere to the collecting tube, but within a few minutes isolated areas of incandescent slag were evident. After an hour the leading surface exhibited a thin coating of slag and at the end of three hours the coating had appreciable thickness. In this particular instance, the temperature of the slag surface was 1025°C (1877°F) as compared with the wall temperatures of 1000°C (1832°F). The slag deposit was thicker on the inlet steam end of the collecting tube, thinning toward the exit end.

After a deposition time of about 3-1/2 hours, the slag was allowed to "bake" on the collecting tube for one hour. A slag-removing agent was then added to the flame in the same manner as in forming the synthetic slag. When the furnace was operated as described, it was possible to form slag and add slag-removing additive in one day.

**RESULTS**

The results obtained by using this procedure are interesting and are indicative of the research potentialities of the apparatus and method. The effect of individual components or the combined effect of mixtures on slag formation or removal is readily demonstrated.

When the furnace was operated as described, the deposited slag, both before and after removal from the collecting tube, had the appearance of
CONCLUSIONS

The apparatus described in this study offers a convenient method for observing slag formation and studying the effect of antislagging additives. This system also lends itself nicely as a means for the study of the corrosive effects of slag on various tube metals.

The pronounced changes in the physical character of the slag when silicates are added to the flame suggests the possibility that, under controlled conditions, silicates could be used for slag removal in full scale boiler operation.

Further study of slagging by the described procedure might demonstrate that a minimum thickness of slag coating is essential to minimize high temperature oxidation and the loss of tube metal due to oxidation and erosion.

ACKNOWLEDGMENTS

The author expresses his appreciation to Mr. V. L. Bigby of BuShips for obtaining samples and for discussion of Fleet problems, to Dr. W. A. Zisman and Dr. C. R. Singleterry for many helpful suggestions and criticisms, and to Mrs. Jeanne Burbank for x-ray analysis.

REFERENCES

1. Hock, F.R., J. Am. Soc. of Naval Engineers 57:508 (1945)
4. Clarke, F.E., J. Am. Soc. of Naval Eng. 65:253 (1953)