considerable effect on the role aluminum plays in the ash-deposition problem.

5 A solid solution of magnesium orthovanadate and magnesium oxide is formed when magnesium is added to the oil in the ratio of 1.5 magnesium to 1 vanadium or higher.

Acknowledgments

The authors appreciate the co-operation of Mr. Bruce Buckland of General Electric Company, Mr. J. O. Collins of Esso Research and Engineering Company, and Dr. W. E. Young of the Westinghouse Research Laboratories, who, together with their associates, offered valuable technical assistance as well as many helpful suggestions.

Acknowledgment is also due Peabody Engineering Corporation for designing and fabricating the miniature burner, Esso Research and Engineering Company for furnishing the residual fuel to close specifications, Bangor Hydroelectric Company for washing the oil at their facilities, and Dow Chemical Company for making x-ray analyses of ash samples.

References

1 Bruce O. Buckland and Donald G. Sanders, “Modified Residual Fuel for Gas Turbines,” ASME Paper No. 54—A-246.

APPENDIX

Additive Data

MgSO₄ solution
Water-soluble salts—MgSO₄·7H₂O
Mg by weight in solution—5 per cent

Mg(OH)₂
Manufacturer—Dow Chemical Company
Oil dispersion of Mg(OH)₂
Particle size—average 0.48 microns,
90 per cent of all particles less than 1.05 microns
Mg(OH)₂ by weight 57 per cent
Viscosity at 25 C 3850 centipoise
Density at 25 C 1.372 gm/cc

MgAl citrate
Laboratory sample
Water-soluble solution of magnesium oxide and aluminum nitrate with citric acid as a sequestering agent
Mg by weight 2.4 per cent
Al by weight 1.6 per cent

Mg HBC
Manufacturer—Continental Oil Company
Colloidal solution of Mg(OH)₂ and MgCO₃
Mg by weight 7.62 per cent
Sulfonate 16 per cent
CO₂ 9.3 per cent
Oil 58 per cent
H₂O 0.2 per cent
Viscosity at 100 F 263 centistokes
Specific gravity 1.068

Al HBC
Manufacturer—Continental Oil Company
Colloidal solution of Al(OH)₃
Al by weight 4.36 per cent
Sulfonate ca. 55 per cent
CO₂ 90 per cent
Oil ca. 50 per cent
H₂O 0.5 per cent
Viscosity at 100 F 4821 centistokes
Specific gravity 0.994

Al(OH)₃
Manufacturer—Dow Chemical Company
Oil dispersion of Al(OH)₃, inversion products
Particle size—average agglomerates 0.60 microns,
95 per cent of agglomerates less than 1.50 microns
Al(OH)₃ by weight 51.0 per cent
H₂O 7.8 per cent
Viscosity at 25 C 5500 centipoise
Specific gravity 1.51 gm/cc

Mg(OH)₂
Manufacturer—Dow Chemical Company
Oil dispersion of Mg(OH)₂
Particle size—average agglomerates 0.28 microns,
95 per cent of particles less than 1.20 microns
Mg(OH)₂ by weight 43.2 per cent
H₂O 18.3 per cent
Viscosity at 25 C 9500 centipoise

Descaling Process

The descaling process consisted of 5-min immersion in molten salt (Virgo) at 475 C (877 F), quenching in cold water, 30-sec immersion in hot water, 30-sec immersion in six-normal hydrochloric acid at 64 C (148 F), water washing, and scrubbing.

DISCUSSION

J. O. Collins

To those of us who are interested in the problems of oil ash corrosion and deposits in boilers and gas turbines, this meeting has been a fruitful one in this field. Both the present excellent paper and the one presented earlier this week by Messrs. Phillips and Wagoner not only have enhanced our knowledge of what can be expected from the use of additives but serve to emphasize the complexity of the mechanisms involved and the need for more fundamental studies.

The authors of the present paper are to be commended for venturing forward into an area of severe operating conditions which has not been investigated before to my knowledge. There is no question in my mind that the supercharged boiler with its combined high gas and metal temperatures together with physical
compactness represents a new high in severity for heavy fuel oil or coal application. If a satisfactory solution can be found in this area, I am sure the same answer will apply to more conventional boilers and probably gas turbines as well. It is hoped that these studies will be pursued further.

Taking a look at the paper as a whole, it appears that magnesium in almost any form is a good high temperature corrosion inhibitor for vanadium even under these most severe conditions, when used in amounts which have been applied elsewhere for this purpose. The authors based this conclusion on static crucible tests in which the metal specimens were imbedded in what I choose to call "equilibrium" ash deposits removed from the operating unit. While I could find no direct statement in the report, I wonder if the authors can assure me that the same low degree of corrosion was found on the superheater elements in the operating unit during the formative stage of the deposits.

The hypotheses advanced by the authors regarding possible mechanisms by which corrosion and deposits occur are certainly thought-provoking and deserve close consideration. The inhibiting properties of magnesium compounds seem to stem from the formation of noncorrosive magnesium vanadates, usually associated with excess magnesium oxide or sulfate. Just where the reaction occurs is a matter of much speculation but of vital importance. If the major reaction occurs on the surface of the metal, then it is quite clear that deposit formation is almost inevitable. We cannot assume that the corrodent and the inhibitor arrive at the tube surface in the proper proportions simultaneously and therefore the reaction must proceed through initial stages in which the sintering and initial melting points of the reaction products are quite low. Under these conditions, adherent deposits which later attain considerable strength at the tube surface can occur.

To avoid such a condition, it would seem that we must look for some additive or operating condition by which the desired reaction can be obtained rapidly in the gas phase in the hope that the final higher fusion point reaction products will be formed before they reach the metal. In this way, more of the solids may be carried past the heat exchange surfaces and, in addition, those which do strike the surfaces by some physical or aerodynamical means may not develop such a strong bond. This leads to a question I would like to ask the authors, namely, whether any free gas samples were withdrawn from in front of the screen or superheater section and the solids contained therein analyzed for comparison with the actual tube deposits? From such data, some idea of the amount of gas phase reaction occurring between additives and corrodents could be obtained.

Other investigators have indicated that deposits formed on hot metal surfaces, except in cases where severe corrosion has occurred, are not too far different in character than the ash found in the oil by the conventional oil ash test method. Since quantitative data were obtained on total ash deposits in the present study, we wonder whether an attempt was made to correlate the amount of these deposits with total ash fed to the unit from the fuel oil. The establishment of this so-called "collection efficiency" of the unit might provide a better basis for comparing the effect on deposits of various ratios of a given additive or different additives than just a comparison of the total deposits, per se.

I was particularly interested in the observations made through the observation ports of the unit describing the way in which deposits tend to form.

To me, this means of studying the mechanism of deposit build-up, possibly supplemented by time elapsing movies to obtain a permanent record, deserves more consideration by all investigators in this field.

Finally, I would like to say that we in Esso Research are very much concerned with the problems of deposits and corrosion from oil ash and are actively engaged in laboratory and field studies of them. These studies include unit operations under isothermal conditions similar to those encountered in gas turbines, current construction of a simulated boiler unit for deposit investigations, and bench scale studies aimed at learning more about high temperature corrosion and deposits and their inhibition.

W. E. Young* and A. E. Hershey*

The authors are to be congratulated on an excellent piece of experimental work, the results of which are another step toward the eventual understanding and solution of the high temperature corrosion and deposition problem. Furthermore, they should be commended for their fortitude in attacking this problem at a temperature level of 2500 to 3000 F. We in the gas turbine industry have found a formidable challenge even at a 1500 F level. It is gratifying to see a test program of this nature carried out at pressures characteristic of operating pressures in supercharged boilers and gas turbines. For some time we have felt that deposits and corrosion occurring in atmospheric test rigs do not reproduce those occurring in gas turbines because of the effect of pressure on the chemical reactions which are taking place. We would suggest that pressure be added to the list of five variables affecting deposit formation and corrosion if only to emphasize its importance.

Our interest in aluminum-magnesium mixtures as additives stemmed from an examination of the periodic table and some elementary chemical reasoning. Metals of group two such as beryllium, magnesium, calcium, zinc, strontium, and barium, are very active, and in fact are second only to the alkali group in basic strength. They should tend to form metal vanadates with the vanadium in the fuel. Metals of the higher groups such as aluminum and boron of group three, silicon of group four, chromium, iron, and many others, are amphoteric and may react in either an acid or basic manner. (Vanadium itself has this property.) In the presence of sufficient excess active metal of the groups one or two, they should form acid radicals and a compound such as magnesium aluminate would result. Essentially these may still be considered mixtures of metal oxides or spinels of high melting point. It is only necessary that the acid radical be more active than the S03 radical formed in the combustion gas stream. Otherwise the active metal sulfate would result. This hypothesis is at least partially verified in the present case where MgO(VO3)2, MgAl2O4, and MgO were identified in a deposit. Excess magnesium in the form of an oxide would be expected from the initial ratio in the fuel of 3 Mg: 2Al: 1V. On the expectation of possible sulfate formation in the lower temperature regions, it would be preferable to have excess aluminum but one would have to assure himself that the vanadate radical was more active than the aluminate, otherwise all the vanadium might not be combined with the available magnesium and free V2O5 rather than Al2O3 would result.

The hypothesis may also explain why it has been found necessary to remove sodium compounds from residual oil before combustion. Sodium is such an active element that it tends to disrupt the reactions just outlined and produces the relatively low melting point sodium vanadates and sulfates. These can be counteracted only physically by large amounts of high melting point material and even then a small amount of low melting point eutectic may remain to cause the mixture to become deposit forming. But once more, referring to activities of the acid radicals, it is possible that for a low vanadium, high sodium oil, an aluminum addition might result in the formation of sodium aluminate NaAlO2, a stable compound, with a melting point of 3000

* Research Engineer, Research Laboratory, Westinghouse Electric Corporation, East Pittsburgh, Pa. Mem. ASME.
* Manager, Development Engineering, Steam Division, Westinghouse Electric Corporation, Lester, Pa. Mem. ASME.
F, rather than sodium sulfate. Thus the necessity of washing a low vanadium fuel might be eliminated but would still be required when sodium and vanadium are both present to prevent the formation of the more stable sodium vanadate. The reaction just outlined will take place only at high temperatures. We have found that furnace heating of a stoichiometric mixture of sodium sulfate and aluminum oxide at 2000 F results in little if any sodium aluminate but that if the mixture is heated with a torch, the reaction proceeds readily. This suggests that, although the gas turbine combustion system might not be depended upon to reach the necessary temperature for reaction, the presently described high temperature furnace may be adequate. Perhaps the authors would consider runs on unwashed low vanadium fuel with and without an aluminum addition for comparative purposes. It should be pointed out that all of the foregoing is based on simple chemical reactions. In practice there are many factors to be considered such as time and the conditions under which the reactions are taking place. The net effect may be that equilibrium is never reached, and the reactions, if they occur at all, may be only partially complete, resulting in a hopelessly complicated mixture of compounds.

One final comment on additive economics is perhaps in order. It was stated, and correctly so, that the use of magnesium aluminum citrate in a full-size installation would be economically prohibitive. This applies to other oil soluble and proprietary additives whose high cost per pound of contained metal makes their use unattractive with highly corrosive fuels where rather large amounts of additive are necessary. However, in some of our newer gas turbine installations, the vanadium content of the fuel has been consistently lower than 100 ppm rather than the 400 ppm figure on which earlier economic studies were based. We are also considering applications where vanadium contents will be in the order of 20 to 50 ppm. And, finally, where machines are sometimes operated at part load it may be possible to cut back on the amount of additive if not to eliminate it entirely during these lower temperature intervals. Thus there appears to be an area, in the case of gas turbine operation at least, where oil soluble additives such as the metallic soaps with their inherent advantages may be economically feasible.

Authors' Closure
The authors appreciate these thoughtful and informative discussions both of which contain excellent suggestions for future experimental work.

In answer to the questions asked by Mr. Collins, the superheater elements are always kept at a temperature low enough to avoid corrosion since replacement of the superheater involves considerable expense. Recently, controlled-temperature test probes were inserted in the gas pass behind the superheater to obtain corrosion data. Initial results have been inconsistent and additional tests and refinement of technique appear to be necessary.

No sampling and analysis of solids contained in the flue gas has been attempted. The so-called “collection efficiency” of the unit does provide a convenient basis for comparing the relative merits of different additives with regard to deposits. However, its use alone can be misleading if its variation with time is not taken into account along with the selective collection efficiency of the different surfaces in the unit.