SUMMARY

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The authors of the preceding papers have discussed in detail some of the techniques that can be brought to bear on identification of water-formed deposits. Many of these instruments are now routine tools in the laboratories of water consultants, boiler manufacturers, and some of the larger public utilities. In many other industrial plants, these same instruments are used in product control and research but have not been applied to the problem of water-formed deposits.

If we are to help ourselves toward a greater understanding of the mechanism of deposit formation, we must not only learn more about deposit composition, but we must also know what to do with this information after we have learned it.

Some interesting examples of interpretation of the results of identification are presented in the paper by Rice. His comments illustrate vividly the value—almost necessity—of phase identification in arriving at the probable cause of a number of deposits. In other cases a complete chemical analysis, including minor elements, may pinpoint the source of a corrosion product.

Anderson has presented a thorough review of emission spectroscopy, flame photometry, and X-ray fluorescence spectroscopy. His conclusions may be summarized as follows:

1. Emission spectroscopy is the most rapid and economical method for qualitative analysis and for determination of most minor and trace elements.

2. X-ray spectroscopy allows a more accurate estimation of major constituents and is particularly valuable in the analysis of corrosion products, many of which give extremely complex optical spectra.

3. The flame photometer, while almost indispensable for analysis for the alkali metals, is also valuable in the determination of the alkaline earths, the ferrous and many of the non-ferrous metallic constituents. The analysis of solutions by this method eliminates many sampling problems. Increased sensitivity for a number of elements has been made possible by development of higher flame temperatures. Simultaneously, however, the spectrum produced becomes more complex, making increased dispersion of the spectrum necessary.

As pointed out by Rice, elemental analysis of a deposit is frequently inadequate to provide the information necessary for correction of the condition which led to its formation. Maddin and Rosene have pointed out some of the many techniques of compound, or phase, identification of deposits.

As in elemental analysis, one or two methods are most generally applicable. The others are used primarily for special investigations or for unusual deposits. X-ray diffraction is probably the best survey technique because it is both qualitative and at least semiquantitative. While the initial cost of a diffractometer is fairly great, the upkeep is relatively small, and it should be considered a

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"must" for any laboratory analyzing a considerable number of deposits.

The petrographic microscope is also an extremely useful tool, as can be shown by the accumulation of much knowledge of the composition, crystal size, and orientation of the phases in a deposit before X-ray techniques were developed to their present status. The microscope continues to be a useful supplement to X-ray diffraction.

Differential thermal analysis and infrared absorption spectroscopy are suggested as possible useful tools in deposit identification. The latter is of special interest in the identification of organic deposits since, generally speaking, organic compounds give sharper absorption bands than do inorganic compounds. Infrared absorption should be of increasing value in the study of the changes that occur in organic treatment chemicals in boilers.

Gulbransen and Copan have presented a new and potentially extremely useful technique in the study of corrosion mechanisms. If, for instance, one wished to determine the effectiveness of an inhibitor or the resistance of a given metal to corrosion, either the test must be of very long duration or more severe than normal operating conditions are required in order to produce differences measurable by most techniques.

Because of its ability to work with such thin films and minute crystals, electron microscopy and diffraction can not only shorten test periods but also tell much about how corrosion processes start. It is certainly hoped that the authors will continue this fine piece of work and, particularly, run tests with water vapor in the absence of oxygen, where magnetic iron oxide is usually the ultimate compound formed. Does this compound form directly from iron and water vapor under certain conditions, or does the alpha-Fe_2O_3 form first, then react further with iron to give Fe_3O_4 ?

Smith is to be commended for a thought-provoking contribution to the knowledge of the composition of the various crystal phases found in water-formed deposits. While all of us who are concerned with the composition of deposits were aware that not all crystal phases are pure, probably not many of us realized how few of the common constituents are of constant chemical composition. Consider, for instance, a corrosion product consisting of magnetic iron oxide and metallic copper. Frequently, if this deposit comes from a boiler where tidewater is used for cooling, 1 to 3 per cent of magnesium oxide is found by chemical or spectrographic analysis, but no evidence of distinct magnesium compounds by X-ray or microscope. However, if one considers the similarity of ionic radii of Mg^{++} and Fe^{++}, it is not difficult to conclude that the magnesium may be substituted for part of the ferrous iron in magnetite. Similarly, we might expect to find sulfate or carbonate in a phosphate sludge without any evidence of anhydrite or calcite. The possible effect of such substitutions on crystal growth and their relation to the physical characteristics of deposits cannot be overlooked.

The manner in which Smith has fitted the analyses to the phase identification, with no information as to the composition of the water or the conditions under which the deposits were found, is a striking example of how much a mineralogist can contribute to our further knowledge of deposits. Let us look for a moment at the individual computations.

In assigning the analysis to the "magnetite," or spinel, phase in samples 677 and 223, he first assumes that the sum of the divalent ions is half the sum of the trivalent ions. Something is amiss in the analysis of 677, for the total is far too high, and one might suspect that the

copper is not all CuO, and did not reach CuO on ignition. If it did, there would probably be a gain on ignition, instead of a loss.

Notice, however, how easy it is to fit a wide variety of atoms into this "spinel" structure. Starting with magnetite as a base, we might expect to find Cu, Ni, Zn, Mn, or Mg partially replacing the Fe^{++} atoms, and Cr or Al for Fe^{+++}. Small amounts of substitution are nearly impossible to detect by X-ray methods, particularly since substitutions in the divalent group are by atoms both larger and smaller than iron.

The "electron probe," mentioned by Smith, would seem to offer many possibilities in solution of the spinel problem because it should be possible to "chemically analyze" a small single crystal and thus determine its composition, instead of requiring a bulk analysis which would not indicate crystal-to-crystal variation.

On studying the analyses and Smith's interpretation on samples 847, 596, and 597, it would seem desirable to have washed these samples free of water-soluble salts after identification before the chemical analyses were made. This would have allowed assignment of the correct amount of alkalies to the complex silicates and eliminated any question as to the possible presence of water-soluble phosphate, as opposed to hydroxyapatite.

Another interesting point brought out by Smith is the variation in composition of analcite. There is generally too much silica for the alumina in a deposit of this sort, and the introduction of a composition approaching $NaAlSi_3O_8 \cdot 1\frac{1}{2} H_2O$ offers a possible explanation for this variation.

From the data and suggestions offered in this paper, I believe much can be learned about the most probable state of combination of most of the chemical analyses in the field of water-formed deposits. It seems probable that fewer, more complete, chemical analyses should be made in order to establish compositional variations in the phases under different conditions of formation, and that instrumental methods could carry most of the routine load.

In summary, it is hoped that the foregoing papers have, at least, pointed the way to a fuller understanding of water-formed deposits and have suggested some methods of attack on the problem. For routine identification, emission and X-ray spectroscopy, X-ray diffraction, and chemical and petrographic microscopy will probably continue to carry much of the load. Undoubtedly, infrared absorption spectroscopy will be increasingly used, especially in identifying organic deposits. The electron probe, differential thermal analysis, electron diffraction, and electron microscopy will become necessary tools of research, and finally, the recent and current work by the mineralogists and geophysicists should help us in fitting our analyses to the mineral phases found.