DISCUSSION

The information obtained as a result of the small-scale, pilot-plant, and full-scale trials would appear to indicate that the hydrazine/oxygen reaction in dilute solutions may not be, as at first considered, a simple homogeneous reaction. The available information suggests that the major event is a surface reaction, either wholly or partially homogeneous in character or that it may even be a heterogeneous reaction. This reaction, that is undoubtedly taking place on the suspended solids or solid surfaces in the boiler circuit, provides one adequate explanation for the anomalous results observed during the experimental and practical work. If this be the case, then merely fixing as a parameter the quantity of hydrazine to be added on the basis of dissolved-oxygen content, the temperature of the feedwater, and the time of reaction, does not necessarily guarantee successful deaeration in any boiler installation. It is also possible to say that in old boiler systems where some form of iron oxide is likely to be present, or in new installations fitted with cast-iron or steel economizers, successful deaeration may be expected.

Such facts, however, do not help the boiler operator who may have the responsibility for the running of a modern high-pressure highly rated boiler installation, in which extreme purity of the boiler make-up feed is an essential factor, and where nonferrous feed heaters may have been installed to reduce the danger of introducing iron compounds into the feed system. Paradoxically, it is in such plants, where it is desirable to keep dissolved solids in the boiler water to a minimum, that the attractive claims of hydrazine deaeration are paramount. The key to a successful and universal use of hydrazine will be a more complete understanding of the kinetics of the hydrazine/oxygen reaction in dilute solutions, a field in which valuable results are expected as a result of the work in progress at Birmingham University. Should this work confirm the essential nature of the surface reaction and in addition establish whether it is a homogeneous or heterogeneous mechanism, then methods will have to be developed for catalyzing the hydrazine/oxygen reaction in the external feed system.

The problem of the decomposition of hydrazine in the boiler has been left to the end as this very much depends upon the degree of reaction between hydrazine and oxygen prior to the water entering the boiler. The pilot-plant experiments at the Admiralty Materials Laboratory have shown that, providing the residual hydrazine content of the boiler water is not greater than 0.2 ppm, little or no decomposition of hydrazine occurs. The point at which thermal decomposition commences varies considerably with the quantity of iron oxide present in the boiler or feedwater system. With an excess of iron oxide present throughout the boiler system, the hydrazine reaction proceeds normally, even when a large excess of hydrazine has been added to the feedwater. The reverse, however, is the case in a clean boiler with little or no iron oxide in the feedwater, all the hydrazine added to the feedwater passing into the boiler where it immediately decomposes to form ammonia and nitrogen.

Whatever degree of efficiency is achieved in the hydrazine/oxygen reaction, it would seem that any practical treatment will require excess hydrazine dosage over the theoretical to cover any unexpected rise in the dissolved-oxygen content of the feedwater. In such cases, it is probable that a proportion of uncombined hydrazine will pass into the boiler and decompose and it therefore appears that one may have to accept the presence of 0.3 to 0.5 ppm of ammonia in the steam and condensate lines. The quantity of ammonia that can be tolerated in the boiler system will greatly affect the degree of accuracy required for the hydrazine addition. The development of suitable injection and metering equipment obviously will be required for this purpose. The presence of ammonia alone is not necessarily harmful, as it is known to provide a convenient method of pH control for boiler feedwater. What must, however, be considered is the effect of this ammonia in conjunction with oxygen and carbon dioxide, and the possible corrosion of nonferrous metals in the system.

CONCLUSIONS

1. While acknowledging that hydrazine hydrate or dihydrazine phosphate provides an ideal chemical method for the deaeration of boiler feedwater, the fact must be faced that their successful reaction with dissolved oxygen is by no means universal.

2. The hydrazine/oxygen reaction in dilute solutions, such as would be the case in boiler feedwater systems, would appear to be a surface reaction. The mechanism of this reaction is not yet fully established but there is some evidence to indicate that it may be heterogeneous. In the light of this knowledge, it appears impossible to predict that hydrazine will work satisfactorily in all types of boiler plants.

3. In view of the possible surface-reaction mechanism, it would seem that to insure complete reaction with the dissolved oxygen, some form of catalyst unit in the feedwater supply will be necessary.

4. The decomposition of excess hydrazine to ammonia in the boiler water is necessarily bound up with the completeness of the hydrazine/oxygen reaction and the degree of reaction occurring at oxide surfaces in the system. Providing the residual hydrazine content of the boiler water does not rise above 0.2 ppm, it is unlikely that the ammonia in the steam will be greater than 0.3 to 0.5 ppm.

5. Owing to the danger of nonferrous-metal corrosion in the presence of excessive amounts of ammonia, it will be necessary to devise accurate metering equipment for the dosage of hydrazine.

ACKNOWLEDGMENTS

The author wishes to thank the British Admiralty for permission to publish the present paper. The views proposed therein are the author’s own responsibility and not necessarily those of the Admiralty.

Thanks are expressed to Dr. Ellis and Mr. Moreland of Birmingham University and to Mr. Wagg of the British Launderers’ Research Association, for their contribution to the theoretical and laboratory work. For the valuable information relating to practical boiler trials, it is desired to thank Mr. Vero of Messrs. Fisons Research Laboratories, Mr. Spencer of Messrs. Whiffen & Son Limited, Mr. Webb of Babcock and Wilcox Limited, Mr. Hamer of the Alkali Division, Imperial Chemical Industries, Limited, and Mr. Howes of the British Electricity Authority.

Discussion

R. C. Adams. We are grateful to the author for reporting to us on British progress in the use and control of hydrazine as an oxygen scavenger. The simple reaction of hydrazine with oxygen to yield completely harmless products is so appealing that it is exasperating to attempt to use hydrazine and then find either no reaction or that the hydrazine decomposes ineffectively. What we all wish to know is how to put hydrazine to work.

Our studies of the subject add little information to that which the author has provided. They show that hydrazine is quite stable in water solution at temperatures up to 175 F. At room temperature hydrazine and oxygen can coexist in solution apparently indefinitely. These experiments in glass show that heat or some other stimulant is required to initiate reaction.

4 Superintendent, Chemical Engineering Laboratory, United States Naval Engineering Experiment Station, Annapolis, Md.

NOTE: The opinions expressed are those of the writer and are not necessarily those of the Engineering Experiment Station or of the Navy Department.
When we come to the more varied systems of feed lines and boilers, the situation is quite different. Here we have a hydrazine which is all too ready to become something else. It will destroy itself in scavenging oxygen, if the oxygen is properly served. But if there is no oxygen, the hydrazine will destroy itself any way, yielding ammonia. Since there are cheaper sources of ammonia for adjustment of condensate pH than that derived from hydrazine, it behooves the operator to channel hydrazine into the job of oxygen scavenging. This is the job for which theoretically it appears to be ideally suited. The means to this end will be found by such studies of reaction conditions and kinetics as the author, his compatriots, and other investigators now are conducting.

Despite the room-temperature stability of hydrazine, it has been suggested for corrosion protection in idle boilers, particularly for protection of superheaters. This would seem to be a good idea because the modern superheater tends to be increasingly inaccessible and difficult to drain or wash out. A protective material which could be drained, or even boiled out, without leaving a solid residue sounds ideal. Preliminary laboratory tests indicate that this is feasible, although fairly high concentrations of hydrazine would be required. We have tried only two concentrations, namely, 30 ppm and 300 ppm. The lower concentration was ineffective but 300 ppm of hydrazine prevented rusting and weight loss of steel coupons during exposure for 30 days.

One minor criticism of an otherwise excellent paper is that such graphs as Fig. 4 through 8, are more convincing if actual data points are shown in addition to the smooth curves. The number of such points and their closeness to the curves support the fact that the curves represent more than inspiration on the part of the investigators.

S. K. Adkins. The author certainly has contributed important data on hydrazine and its reactions as an oxygen scavenger in boiler feedwater. We applaud the work he and his associates have reported and the planned investigation yet to be completed.

As stated in the paper, hydrazine compounds are most exciting, from a practical operating standpoint, to operators of high-pressure, high-temperature, high heat-transfer-release, low make-up steam-generating systems. Since dissolved solids are not increased by its use, it is particularly attractive for use in modern units that use feedwater of high purity in spray-type steam-temperature controls. Also as stated in the paper, it is important to remove or react all oxygen before the feedwater enters the boiler. In view of the strong evidence presented that hydrazine does not always react with a predictable speed, it is important that it be introduced immediately after the deaerator or hot well, when the hot well also incorporates deaeration. Until more is known about accelerating or catalyzing the reaction, this will insure maximum allowable reaction time.

The indicated role of iron or iron oxides in the reaction are extremely interesting. Since surface area of the iron or iron oxides appears to be a major item, it would be very interesting to know if a large surface area of any type, particularly nonmetallic, would have any desirable effect. If so, the possibility of speeding the reaction without the addition of a soluble catalyst might be accomplished and the dissolved-solids advantage of hydrazine compounds retained. With some of the tube failures that have occurred due to excessive iron oxides still vivid in our minds, many will continue to eliminate them whenever possible. In this connection, preliminary indications from one moderate-pressure plant in the United States are that hydrazine may actually assist in reducing the quantity of iron oxides present in the boiler. We may hope, therefore, that advancing knowledge may reveal some equilibrium between iron oxides and hydrazine that will permit removal of oxygen and, at the same time, limit the quantity of iron oxides in the system. Those concerned with the fundamental studies of the iron reaction and its relation to this subject may be interested in a paper by Messrs. Gotthub, Kehman, and Johnson. This paper discussed observations of the ferrous-ferric relationships and the apparent effect on deposition at various points in the system when the oxidation rate could be controlled within rather narrow limits. The actual problem in the plant experiences described was ferrous and ferric-oxide deposits on feed-pump impellers. Some relation may exist between the fundamentals considered by these authors and the observations by the present author.

One important factor of great interest is that of analytical control. It is fully realized that development of analytical-control procedures was not a part of the ambitious program undertaken by the author and his colleagues. It is important, however, that a relatively simple, reliable, analytical method be available if widespread application of hydrazine compounds is to be entirely successful. While the problem of precise microanalytical work is not great in large, well-equipped, high-pressure central stations, a great many plants are neither staffed nor equipped with the precise analyses indicated by the very low residuals mentioned. Fractional parts per million, 0.1 to 0.3 ppm, are shown as maximums allowable before excessive ammonia is introduced by decomposition. We sincerely hope that techniques will be simplified as the general knowledge of hydrazine and its compounds advances.

Another practical aspect that usually concerns operators when a relatively new chemical is introduced is handling and storage. Hydrazine does have some objectionable characteristics which must be recognized, but relatively simple precautions make it no more difficult to handle and store than other treatment chemicals. The ability of the manufacturers to produce several hydrazine compounds, no doubt, will result in further developments to reduce the minor objections that may arise.

The work presented has pointed out some important problems. The challenge is clear, and the apparent advantages of hydrazine will stimulate further research that will solve the difficulties and permit the use of a material that seems particularly helpful as pressures and temperatures in steam operation advance upward.

T. J. Finnegar. Hydrazine has been aggressively promoted during the past year or two as an oxygen scavenger. A certain type of boiler operator is especially receptive to its charms. This is the operator of the high-pressure, high-capacity utility boiler who has reduced his make-up to a small fraction of a percent and who uses very pure water for the purpose. Good boiler-water conditions are achieved with a minute amount of added chemical so that the total solid content is so low that carry-over troubles are minimized and little or no blowdown is required except perhaps during start-ups.

When a boiler of this class has trouble it is generally associated with iron oxide and a little research and much speculation have ensued regarding the origin and effect of this iron oxide and how it can be controlled to form a thin continuous protective film instead of a bulky mass surrounding or overlying actual or potential pits.

Oxygen may be a factor. Grabowski has explained some curious cases of boiler corrosion by the presence of unsuspected oxygen and, in our own experience using an oxygen recorder, we

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1. Director, Technical Service, Boiler Feedwater, National Aluminate Corporation, Chicago, Ill. Mem. ASME.


3. Chemical Engineer, Engineering Department, Niagara Mohawk Power Corporation, Buffalo, N. Y. Mem. ASME.
have found evidence of oxygen on start-ups and low loads, although the full steady-load oxygen content of the water is regularly zero.

The obvious precaution is the use of an oxygen scavenger but the usual scavenger, sodium sulphite, would increase the boiler-water solids and make continuous or at least very frequent blowdown necessary, and it may also decompose to form the objectionable gases, hydrogen sulphide and sulphur dioxide. Consequently, sulphite is not very attractive to those of us who operate with the delicately adjusted water conditions just described, especially since, on the whole, very satisfactory operation is being obtained without it.

However, hydrazine is something different. Here is a material which leaves no solid residue and upon oxidation forms only harmless water and nitrogen. Here is a substance which will permit those who would ordinarily use no scavenger but, knowing that a small amount of oxygen may get into the boiler and perhaps be harmful, would like to obtain the security of such an agent without risking the objectionable effects of sulphite.

Into this paean of joy the author has injected a sour note. He says, if the writer may make a brief paraphrase of his comments, that hydrazine is indeed a reducing agent with the ultimate products nitrogen and water in the presence of oxygen, but before we eagerly accept it as the ideal oxygen scavenger we should consider the mechanism of its oxidation; that is, the chemists should study its chemistry. His investigation of this chemical problem suggests that hydrazine needs a higher oxide of iron than the FeO with which we are so familiar in order to effect its oxidation in water. He suggests that, in the very clean condensate-fed boilers the writer mentions, hydrazine may be of no value.

He did not reach this conclusion by theorizing. He made an experimental study begun in the laboratory, continued through the pilot plant to full-scale boiler operation. He has done what should be done more often in the field of power-station chemistry, has he not? It is appropriate to remind ourselves that this and other papers have been in plants having very efficient deaerating heaters.

The author's conclusions may have to be modified eventually. The physical chemists may not be satisfied with the thermodynamics of his postulated reactions but even if his conclusions are changed completely, he must be commended for his fundamental approach to this highly important problem.

It is important to remind ourselves that this and other papers on water treatment at meetings of the Society are contributed by associations which are concerned with boiler feedwater and other parts of the system. The author's observation that hydrazine did not react completely with oxygen in the feed line of a pilot-plant boiler coincides very closely with results obtained in our laboratory in an experimental boiler unit.

Numerous tests were made in our unit to determine if hydrazine would be effective as an oxygen scavenger at 1500 psi. With about 0.1 ppm of dissolved oxygen in the feedwater, a hydrazine excess of 200 to 300 per cent of theoretical was not sufficient to eliminate oxygen corrosion on the boiler heating surfaces. With higher excesses, oxygen corrosion was prevented but ammonia formation increased to about 0.4 ppm. At 1500 psi the excess hydrazine detected in the boiler water was less than 0.1 ppm, even though the amount in the feedwater was as high as 2 ppm. The amount of residual hydrazine which can be maintained in the boiler water appears to decrease as the pressure increases.

Some recent tests with the same experimental boiler connected to a dissolved-hydrogen recorder indicate that hydrogen is also one of the decomposition products of hydrazine at 1500 psi. The addition of 0.5 ppm of hydrazine to the feedwater caused an increase of 6 ppb (parts per billion) of dissolved hydrogen in the steam. This corresponds to about 10 per cent of the hydrogen added as hydrazine.

This observation may only increase the complexity of the problem, but it may account for slight shifts in hydrogen evolution observed when hydrazine is used in plants which have hydrogen recorders.

V. M. Marcy

Prior to the presentation of this program on the use of hydrazine in boiler-water treatment, it had been presumed that hydrazine completely removed dissolved oxygen from feedwaters. The slowness of reaction between oxygen and hydrazine has been of concern to us for about three years. We are indebted to the author for his data which showed the reaction to be nil in some cases before the feedwater reaches the boiler. Of course, reaction may be hastened when the water reaches boiler temperature and pressure. However, it always should be remembered that when reaction is sluggish, considerable unconsumed oxygen can be volatilized with the steam from the drum.

Lack of published data on the speed or completeness of reaction between oxygen and hydrazine arises largely because of the uncertainties in the determination of dissolved oxygen when minute quantities are involved. Many of the trials run with hydrazine have been in plants having very efficient deaerating heaters. When a feedwater contains less than 0.005 ppm O2, it is difficult to determine with any degree of certainty if hydrazine is or is not effective in removing oxygen.

The author's hypothesis of iron oxide acting as a catalyst for

C. Jacklin.

The author is to be congratulated for his courage in attacking the complex problem of determining the reactions which occur when hydrazine is used as an oxygen scavenger in boiler feedwater. The information he has presented and the results of work in progress should aid materially in clarifying the advantages and limitations of hydrazine for use in boilers.

In the first part of the paper the author mentions that ammonia resulting from the decomposition of excess hydrazine could provide a means of insuring a suitable alkaline pH condition throughout the steam and condensate system. It would reduce the danger of corrosion of iron or steel by aggressive carbonic acid. A word of caution should be inserted here. Ammonia is effective in reducing corrosion of iron and steel in steam and condensate systems, but it has a serious defect. It does not afford protection in zones where initial condensation occurs. Certain volatile alkaline organic materials have the advantage of giving protection in these zones as well as the other parts of the system.

The author's observation that hydrazine did not react completely with oxygen in the feed line of a pilot-plant boiler coincides very closely with results obtained in our laboratory in an experimental boiler unit. Numerous tests were made in our unit to determine if hydrazine would be effective as an oxygen scavenger at 1500 psi. With about 0.1 ppm of dissolved oxygen in the feedwater, a hydrazine excess of 200 to 300 per cent of theoretical was not sufficient to eliminate oxygen corrosion on the boiler heating surfaces. With higher excesses, oxygen corrosion was prevented but ammonia formation increased to about 0.4 ppm. At 1500 psi the excess hydrazine detected in the boiler water was less than 0.1 ppm, even though the amount in the feedwater was as high as 2 ppm. The amount of residual hydrazine which can be maintained in the boiler water appears to decrease as the pressure increases.

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The author's hypothesis of iron oxide acting as a catalyst for
the reaction is quite interesting. His observation on the color change of the iron oxide, suspended in the boiler water after start of hydrazine treatment, could indicate that suspended materials in the water play a part in the reaction. However, we would suspect that ferric oxide would be reduced to magnetite or hydrated magnetite, not to ferrous iron oxide. If oxides are good catalysts, reaction in the boiler would be accelerated due to the large surface of oxide film coating the boiler drum and tubes.

The possible catalyzing effects of other materials should not be overlooked. For example, copper salts, even in minute concentrations, are good catalysts for the room-temperature reaction between oxygen and hydrazine. It would be interesting to know if oxygen removal in Trial 5 of the author's Table 1 would be greater if a small amount of copper sulphate were added to the feedwater along with the hydrazine.

Decomposition of hydrazine to form ammonia can occur even when the boiler water contains much less than the 0.2 ppm N₂H₄ specified in the paper. The extent of decomposition does not depend alone on concentration. As shown in the paper by Baker and Marcy, temperature of the boiler water or steam is also quite important.

We have not found it necessary to destroy hydrazine in water samples prior to analyzing for dissolved oxygen. Our tests indicate that hydrazine does not interfere in the Modified Schwartz-Gurney or ASTM Referee Methods.

PIERO STURLA. The purpose of this discussion is to make further additions to this already complete and very interesting paper, by outlining the results obtained in the Emilia Power Plant of the Edison Company, Milano, Italy, after substituting the treatment by sodium sulphite with the treatment by hydrazine hydrate.

Concerning the possibility of the use of hydrazine as a reducing agent, Societa Edison received the first information regarding its practical use during the conference which was held in March, 1953, at Brussels, Belgium, by the Water Commission of Unipede (Union Internationale des Producteurs et Distributeurs d'Energie Electrique). It was on this occasion that Mr. Werner of Vereinigung Industrielle Kraftswirtschaft and Mr. H. Kohle of Grosskraftwerk Mannheim, confirmed the use of hydrazine by introduction into the feedwater system in a solution ranging from 2 per cent to 5 per cent. The ratio between oxygen and hydrazine being maintained at 1 to 1.5.

Hydrazine hydrate was used in place of sulphite because of the corrosion by SO₃.

During another conversation with Mr. Werner in Leverkusen, more detailed information was obtained.

The use of hydrazine hydrate in the Leverkusen Power Station of the Bayer Company was decided on for the following reasons:

1 By using hydrazine, the total amount of solids in the boiler does not increase. Nitrogen produced by the reaction of oxygen and hydrazine is simply removed by the condenser ejector or by the deaerator and, at any rate, it has no dangerous effect upon the system.

In the specific case, these considerations were most important because the temperature of the superheated steam reached 1070 °F, the pressure 2200 psig, and the make-up approximately 100 per cent.

2 Hydrazine produces ammonia when the temperature exceeds 212 °F, which is not dangerous to the system inasmuch as the increased pH, if controlled, may produce favorable results in the reduction of iron and copper pickup.

Of significance is the fact that it was possible to improve the speed of reaction between oxygen and hydrazine at ambient temperate by adding an activated carbon filter as a catalyst. Thus it was possible to control the reaction so that proportionally hydrazine and oxygen combined in the ratio of 1 to 1. The volume of the activated carbon filter used was 28 cu ft which was sufficient for a flow of 440 gpm. The filter, therefore, absorbed excess oxygen which could later react with the hydrazine residual in the boiler.

Another advantage of the filter was the removal of any traces of iron and copper in suspension.

Only four months ago it was possible to obtain in Italy the necessary amount of hydrazine to start conversion to the hydrazine treatment. This was effected as follows:

1 No filter was installed in order to simplify the system and also because the hydrazine would be fed after the boiler feed pump at which location the temperature is adequate to guarantee the rapid elimination of the residual oxygen.

2 For control, the hydrazine solution was added continuously in a ratio of 1:1.5 to the quantity of oxygen present.

3 The residual of hydrazine was controlled in the following three ways:

   (a) Direct titration by picryl chloride (colorimetric analysis by Mr. Zimmerman).

   (b) Control the reducing condition of the system by "dead-stop end point."

   (c) Control the feeding of hydrazine by analyzing very accurately the ammonia content. Since there is no natural ammonia present in the water at the Emilia Plant, the ammonia found is produced only by the decomposition of hydrazine.

The results of the treatment were very satisfactory. Starting from a ratio of oxygen-hydrazine 1:1.5 (the theoretical one being 1:1), it was later reduced to 1:1.2 and even under these conditions the reducing action in the cycle was maintained while the pH increased to 8.8 to 9.1 in the condensate due to the presence of 0.1 ppm of ammonia in the absence of CO₂.

Incidentally, it was found that the best method to control the hydrazine feed was to analyze very carefully the residual ammonia in the condensate and either increase or reduce the quantity of hydrazine fed accordingly.

In addition to the favorable results mentioned, we also noted the following possible disadvantages to this method of oxygen scavenging, which are being studied at our plant:

1 The effect of hydrazine on the protective iron-oxide film.

2 The possibility of too rapid dissociation of a substantial amount of the hydrazine with subsequent lack of protection to the system.

3 The possibility that dissociation may result not only in ammonia, which can be controlled, but also in other objectionable volatile substances such as NO, NO₂, and NO₃.

Items 1 and 2 were illustrated by the author. As for the third item, the Societa Edison still believes that the production of nitrous oxide is possible, especially at high pressure and temperature in the presence of metallic particles which act as catalysts. It is for this reason that it was decided, as soon as possible, to make a very thorough study of the gas emanating from the condenser ejector. This study will be made with the improved instruments such as the infrared spectrophotometer because of the presence of heavy molecules.

AUTHOR'S CLOSURE

In the intervening period between the submission of the paper in August, 1954, and the presentation at the Annual Meeting in New York, December, 1954, considerable advance was made in the work using the pilot-plant high-pressure boiler. For
LEICESTER—CHEMICAL DEAERATION OF BOILER WATER—USE OF HYDRAZINE COMPOUNDS

There have been five main developments in connection with this work:

1. To examine in more detail the relationship between hydrazine concentration in the feedwater, residual hydrazine in the boiler water, and ammonia content in the steam condensate.
2. A more detailed study of the amount of oxygen removed for a given excess of hydrazine added to the feed. This has been made with high and low initial oxygen values in the feedwater.
3. A study of the effect of feedwater temperature on the rate and amount of oxygen removal.
4. The effect of a catalyst, such as activated charcoal, on the rate and amount of oxygen removal.
5. The development of solid compounds offering increased reaction rate and more favorable handling and storage properties.

Work carried out under item 1 is summarized in Figs. 9 and 10, herewith. These graphs show the results of some 40 boiler trials and illustrate clearly the fixed relationship between the three variables.

The second phase of the work studied in more detail the amount of oxygen removed for a given excess of hydrazine and the results obtained are summarized in Figs. 11 and 12. The increase in percentage removal with increasing oxygen content is as would be expected from the law of mass action. The reaction temperature in the feedwater was approximately 150°F and in no case was the reaction complete. Finally, Fig. 13 summarizes the percentage of the original oxygen removed throughout these two series of trials.

In the third series of experiments, an attempt was made to determine the effect of feedwater temperature on the rate and degree of reaction. Quoting one typical experiment using hydrazine hydrate and a feed temperature of 203°F (an increase of 86 deg F), the amount of oxygen removed by the time the water reached the feed-pump sampling point had risen from about 60 to 81 per cent and in the boiler water from 85 to 94 per cent.

The fourth series of experiments was carried out to investigate the effect of a catalyst on the reaction rate. In these trials, hydrazine hydrate was again used with an activated charcoal catalyst. Considering the use of low-temperature feedwater at 150°F, the amount of oxygen removed is increased from 60 to 72 per cent at the feed-pump sampling point, and from 85 to 89 per cent.
per cent in the boiler water. Experiments are continuing to evaluate the dual effect of catalyst plus temperature increase.

The final work concerns the development of an alternative solid compound of hydrazine. It has been shown that in so far as oxygen scavenging is concerned, the use of dihydrazine phosphate is as efficient as hydrazine hydrate. However, one serious disadvantage with the use of this material is that it adversely affects the pH of the boiler water. Being a more acid compound than the trisodium phosphate added to the boiler for normal alkalinity control, the over-all pH is reduced, resulting in a demand for the addition of more trisodium phosphate and an increase in the total solids in the boiler water. This nullifies the effect sought by the use of hydrazine. It is not intended to carry out any further experiments with the dihydrazine-phosphate compound for use in steaming boilers.

The Geigy Company Ltd. of Manchester, England, recently has succeeded in developing for the Admiralty a hydrazine salt of dinaphthyl methane, disulphonic acid. The compound was required for several reasons:

(a) The material is a very active dispersing agent and thus assists in fluidizing solids in the boiler water.

(b) The material is alkaline in water solution and does not affect the pH control of the boiler water.

(c) In view of the known catalytic effect of ion-exchange resins on the hydrazine-oxygen reaction, it was thought that the sulphonated naphthaline radical of this compound might assist the reaction.

(d) The material contained approximately 11 to 15 per cent available hydrazine and was in the form of a dry, free-flowing, inert powder, very suitable for handling and storage under shipboard conditions. The powder also was immediately soluble in cold water and hence presented no difficulty when preparing a diluted solution.

Initial tests with this compound showed excellent promise and a series of trials have been carried out with feedwater temperatures of 150 and 203 F. At the lower temperature and adding sufficient compound to give an excess hydrazine concentration of 200 to 300 per cent over theoretical, the amount of oxygen removed at the feed pump (compared with straight hydrazine hydrate and no catalyst) is increased from 102 to 105 per cent, and in the boiler water from 86 to 91 per cent. At the higher feed temperature of 203 F, the oxygen removed at the feed-pump discharge showed an increase from 81 to 86 per cent and in the boiler water from 94 to 96 per cent. Table 2 of this closure summarizes the results of these later trials and shows how the percentage removal of oxygen has steadily increased.

It is along this very promising line that our work proceeds and it may well be that as our knowledge of the kinetics of the hydrazine-oxygen reaction increases, so we shall find even more efficient means of promoting this desirable reaction. It is obvious from the encouraging practical results obtained in the United States and so ably reported in this symposium, that studies of this nature are well worth while. I hope that the brief comments on the work taking place in Great Britain and in particular of the Admiralty team will have been of interest and value, and that they will stimulate discussion on what is undoubtedly a vital, complex, and fascinating subject for research.

Turning now to the points raised during the frank and valuable discussion:

Mr. Adams mentions the use of hydrazine for protection in idle boilers and throughout the superheaters, a very valuable suggestion and one which we have already investigated with success. In our particular application we found it of benefit to use the dihydrazine phosphate for the idle conditions. His further note on the presentation of data by smooth graphs and the omission of data points is quite valid. It must be pointed out, however, that in the ASME publication on "Hints to Authors," with which Mr. Adams is obviously au fait, one is encouraged to make the illustrations simple and free from extraneous markings. This fact was to the fore in the author's thoughts when preparing the present diagrams. Readers may be assured that these graphs represent the average of some 40 boiler trials.

The points raised by Mr. Adkins have been answered in the author's summary of the more recent work. His reference to the earlier ASME paper is of interest in view of the major effects that have been attributed to ferrous and ferric oxide. On the question of analytical control there is little to add although the author fully realizes its importance. It is not the function of his Division to investigate such techniques.

Mr. Finnigan stresses that our conclusions on the mechanism of the hydrazine-oxygen reaction may eventually have to be modified. We are the first to agree with him but, at least, in

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TABLE 2 SUMMARIZED RESULTS OF PILOT-PLANT BOILER EXPERIMENTS

<table>
<thead>
<tr>
<th>Trial series no.</th>
<th>Oxygen scavenger used</th>
<th>Oxygen in feedwater, ppm</th>
<th>Temp of original oxygen removed, deg F</th>
<th>Percentage of original oxygen removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Hydrazine hydrate</td>
<td>0.22</td>
<td>150</td>
<td>31</td>
</tr>
<tr>
<td>II</td>
<td>Dihydrazine phosphate</td>
<td>0.02</td>
<td>150</td>
<td>32</td>
</tr>
<tr>
<td>III</td>
<td>Hydrazine hydrate</td>
<td>0.20</td>
<td>150</td>
<td>60</td>
</tr>
<tr>
<td>IV</td>
<td>Dihydrazine phosphate</td>
<td>0.50</td>
<td>150</td>
<td>84</td>
</tr>
<tr>
<td>V</td>
<td>Hydrazine hydrate</td>
<td>0.20</td>
<td>203</td>
<td>81</td>
</tr>
<tr>
<td>VI</td>
<td>Hydrazine hydrate plus</td>
<td>an activated charcoal</td>
<td>150</td>
<td>72</td>
</tr>
<tr>
<td>VII</td>
<td>Hydrazine salt of dinaphthyl methane, disulphonic acid</td>
<td>0.20</td>
<td>150</td>
<td>78</td>
</tr>
<tr>
<td>VIII</td>
<td>Hydrazine salt of dinaphthyl methane, disulphonic acid</td>
<td>0.20</td>
<td>203</td>
<td>86</td>
</tr>
</tbody>
</table>
the course of modification we shall have learned a lot more about the reaction. In a like manner, we feel no remorse at having introduced the so-called "sour note" into the halcyon picture of the use of hydrazine. It would seem from the results of our own British survey and also from the many similar statements of American experience, that this fact should have been recognized much earlier.

Mr. Jacklin's experience with hydrazine treatments in his experimental boiler unit is very interesting. This work parallels closely our own pilot-plant experiments and it will be interesting to note whether or not our later experiments at 1500 psi confirm the difficulties of maintaining the residual hydrazine content in the boiler water. The present trend of our experiments up to 1000 psi agree with this statement. With regard to the observation about the breakdown of hydrazine at 1500 psi, giving rise to hydrogen, this is very interesting and it is a point that we must follow up during our experiments.

Mr. Marcy indicates that, in his opinion, the mechanism of reduction of ferric oxide is more likely to produce magnetite or hydrated magnetite in preference to ferrous oxide. The author is inclined to agree with him on this point and our later program is scheduled to investigate in more detail this reduction mechanism. With regard to his comments on the catalyzing effect of copper sulphate, undoubtedly the speed of this reaction would have been increased if the latter material had been present. However, from our experiments with various catalysts, activated charcoal has been found to be far superior for this purpose.

Mr. Sturla's final comments on the results obtained in the Imilia Power Plant at Milano, Italy, are very stimulating and, in general, agree well with our findings.

It is interesting to note that again attention is directed toward the dissociation products of hydrazine at high pressure and temperature. The results from this proposed comprehensive examination of gases, emanating from the condenser ejector, should be worth careful study.