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by

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INTRODUCTION

The formation of water-side deposits in drum-type utility boilers is a major concern to the heat transfer efficiency and availability of the unit. In recent years there have been major attempts made to correct the formation of deposits through the use of chemical cleaning and the development of improved feedwater chemical treatment. In simple terms the boiler water chemistry must be maintained in order to achieve a thin protective magnetic iron oxide scale at the I.D. surface of the tube. The scale should be sufficiently thin to allow adequate heat transfer to the water in the tube. Furthermore, the water should be sufficiently pure that there should be a minimum of deposition on the internal surface. Thick scale and deposits can cause the heat transfer to be decreased to such an extent that overheating of the tube occurs leading to blistering and eventual failure. Water chemistry is also maintained in order to minimize carryover from the drum into the steam circuit. Solids carryover into the steam decreases purity and can cause problems not only in tubes but at the turbine.

Another problem associated with water chemistry and water-side deposits is the corrosion of the tube. A common corrosion problem is the pitting of tubes due to the ingress of oxygen into the boiler water. The oxygen tends to attack welds and backing rings preferentially and can lead to eventual failure. In addition there are two major types of water-side attack of furnace tubes which can result in catastrophic failure of tubes and cause forced outages. These two types of corrosion mechanisms are caustic gouging and hydrogen damage. As the corrosion is derived predominantly from the water chemistry both types of corrosion can be widespread throughout the furnace tubes.

Caustic gouging is caused by relative enrichment of alkali in the water. This occurs in an area where there is a slight departure from nucleate boiling. This departure from nucleate boiling (DNB) is not sufficient to overheat the tube. However, due to the steaming in the tube (albeit transient) the water at the steam/water interface becomes enriched in alkali. This alkali can be very aggressive and strip off the protective scale and dissolve the underlying carbon steel. A characteristic of caustic gouging is the absence of scale in the region due to the aggressive nature of the alkali-rich water. Furthermore, the wastage of the tube usually occurs at the interface between the water and the steam forming long gouges at these locations while the other areas of the tube show no wastage.

Hydrogen damage occurs in the furnace walls of drum boilers operating at pressures over 1000 psig. The damage is caused by the accumulation of hydrogen under water-side deposits. The hydrogen originates from the reaction of water with iron:

$$H_2O + Fe = Fe_3O_4 + 4H$$

The hydrogen migrates toward the O.D. of the tube (fireside). However, under the conditions of hydrogen damage the concentrations of hydrogen are sufficient that some of the hydrogen reacts with the carbide phase (pearlite, Fe_3C) in the steel to form gaseous methane and ferrite:

$$4H + Fe_3C = CH_4 + Fe$$

It is the formation of methane which leads to the formation of short, discontinuous intergranular cracks at the I.D. of the tube. In some cases decarburization can be observed. The cracking progresses from the I.D. to the O.D. The Reference 1 paper advances the subject of hydrogen damage in utility boilers in greater detail.

ANALYTICAL TECHNIQUES FOR WATER-SIDE DEPOSITS

The material scientist charged with finding the cause of the failures and the corrective or control measures that can be recommended to the utility has a number of problems when faced with water-side chemistry. The first is the absence of some key evidence due to the failure itself. The catastrophic nature of a ruptured tube boiler tends to blow I.D. deposits from the surface of interest. The second problem is the lack of available tools for the analysis of the deposits. A third problem is the lack of knowledge of the history of the tube and feedwater-chemistry treatments including chemical cleaning. In the first case while, it is always important to analyze the failed tube sample as part of the failure analysts forensic report, additional value can be obtained by studying an intact water-wall tube from an adjacent area for evaluation. The second problem is the major focus of this paper and deals with a technique developed by DB Riley for the evaluation and characterization of water-side deposits.

Routine analysis of furnace tubes involves the determination of water-side deposit loading (Atwood-Hale Analysis) as a measure of deposit weight per unit area and the chemical composition of the deposit. Further analysis will include the determination of the microstructure of the steel including the scale at the O.D. and I.D. as well as the integrity and nature of the scale. Pitting and other forms of corrosion are also investigated. In some cases x-ray diffraction analysis is performed on the I.D. scale. While this technique gives valuable information on the crystalline phases present in the sample it has some major limitations. The first limitation is that the technique can only detect crystalline phases. The second limitation is that the sample is removed from the I.D. of the tube, mixed, ground, and then analyzed. This results in loss of spatial relationships between the deposit, scale, and base metal. In these circumstances the results may indicate the presence of iron oxide with some sodium salts. However, it is not possible to determine if the sodium salts were in contact with the iron oxide during service.

In many instances the deposit/scale is evaluated using scanning electron microscopy (SEM) with electron microprobe analysis. This analysis provides excellent high resolution observations of features of interest in the sample. The microprobe analysis (usually using an energy dispersive x-ray detector system) is used to determine the chemical characteristics of the features. The methods may include the elemental mapping of an area, the analysis of a point (limited to a minimum 1-3 microns in diameter), or the analysis of an area. The mapping is used to determine the general association of different elements. For example, it can show the differences in chemistry between the scale (predominantly iron oxide) and the deposit. However, the resolution of the mapping is insufficient to allow quantifiable assessment of chemical relationships with the region of interest. The analysis of a point is useful when there are specific, identifiable features to focus on. The data provided can be a full chemical composition of that point (using ZAF correction protocols). The disadvantage of analyzing points is that it is very subjective and time consuming. It is difficult to relate the compositions of a few points to the bulk processes involved in deposition and corrosion. The third type of analysis is the area analysis; the operator can select a region of interest and determine the average chemical composition of the region in a similar manner to the point analysis discussed above. The disadvantages of this method are that it is somewhat subjective and conclusions based on the analysis are limited.

As part of an on-going commitment to determine the integrity and reliability of pressure-part components it was evident that the present characterization techniques described above were not sufficient. A technique was adopted from extensive recent advances in the characterization of fireside deposition and corrosion to investigate water-side deposits. This technique was that of scanning electron microscopy point count (SEMPC) which is used primarily to establish the phase assemblage of complex inorganic systems. The analysis is quite simple but provides excellent data and information. The technique involves the use of a scanning electron microscope with electron microprobe facilities. A region is selected by the operator and then the instrument rasters over the region and analyzes approximately 250 points. The actual points are selected at random. The signals are collected and then converted to a chemical composition (fully quantitative). The data is then stored on file for subsequent evaluation. This evaluation is the key to the whole analysis and involves the processing of the data through various tailored specialized computer programs. The first program is used to determine the phase assemblage of the region. This involves the classification of each point into one of over 40 different phases common to deposition and corrosion processes in utility boilers. Due to the complexities of such systems, however, it is not possible to adequately classify all the points and some of these points will then be assigned to the "unclassified" group. As part of this program the average chemical composition is reported as well as the average chemical composition of the unclassified phases. A second program is used to establish the relationship between the various components for all points or for a selection of different phases such as the unclassifieds. This data is very useful to show the interaction and association of iron, for example, with components within the deposit. The advantages of the SEMPC technique are that it provides objective, statistically relevant chemical information from a region and that the data can be used to show relationships between selected components. The data from the SEMPC can be used to establish deposition and corrosion processes as well as for the determination of benchmark conditions. The ability to benchmark the condition of the boiler is useful when assessing the impact of chemical cleaning or change of water-treatment procedures. The following case studies illustrate the some of the uses for the SEMPC technique.

CASE STUDIES

The following two case studies illustrate the application of the SEMPC technique to the characterization of water-side deposits. As an original equipment manufacturer, DB Riley does not control feedwater treatment at utility sites. Recommendations for feedwater treatments are made in the service guidelines. However, through DB Riley's commitment to increasing reliability and availability the company maintains concern over how the water-side treatment can affect component integrity. By careful, and systematic evaluation of boiler tubes condition assessments can be made and reported to the utility. Part of this detailed evaluation is to determine the characteristics of the I.D. deposits and relate these results to corrosion or wastage mechanisms which can lead to forced unscheduled outages during service. Furthermore, by careful analysis guidelines for chemical treatment can be made including the need and specific requirements for chemical cleaning.

In recent years, there has been a major increase in hydrogen damage. This has prompted the need to study and investigate the root cause of the hydrogen damage in utility boilers. At this stage there is no consistent relationship between chemical treatment, deposits, location of damage, etc. However, while there is no consistent relationship available to date does not mean that such relationships should not be actively sought. The approach taken by DB Riley is to acquire data which can be used to establish relationships between the I.D. deposits, water chemical treatment, boiler operation and corrosion processes.

CASE STUDY #1

Hydrogen Damage Failure from Utility Boiler 1500 psig

Microstructural analysis of the tube in the laboratory confirmed that the mechanism of failure was hydrogen damage. The unit had recently changed water-treatment process from a coordinated phosphate to chelant treatment. Prior to this particular failure the unit had been in service for 15 years without a single water-wall tube failure. The utility was concerned with what effect the change in water chemical treatment may have had on the hydrogen damage. The study confirmed that the failure mechanism was indeed hydrogen damage. Of interest was the heavy I.D. deposits at the location of a flash tube weld. At this location significant gouging was observed. The deposit at the I.D. of the tube in the region of the hydrogen damage was analyzed using SEMPC. The deposit was analyzed in-situ in order to maintain relationships between the deposit and the steel.

Table 1 lists the phases observed in the deposit as determined by SEMPC. The major phase identified, as expected, was iron-based. The chemical composition of the deposit is listed in Table 2 and is derived from the averaging of all points analyzed. Also listed in Table 2 is the average composition of selected groups of phases including the unclassifieds. Examination of the data shows that the unclassified points were rich in sodium and phosphorus. Indeed, further evaluation revealed that a significant proportion of the points analyzed were predominantly iron, manganese, phosphorus, and sodium. Figure 1 shows a ternary graph of these three components of the points where $Na+P+Fe+Mn > 85$wt.% (on oxide free basis). These points were then examined to determine if there was a relationship between these components. This was achieved by converting the weight percent values as obtained from the SEMPC data to normalized three components on a molar basis. The use of mole concentrations is necessary in order to establish if there is any type of stoichiometry in the system. Representation of the data can be done in many ways, other graphs could be used to represent the relationship between the $Mn+Fe$ versus Na and P. The results show

Table 1 Phase Assemblage of Water-Side Deposit

Phase	Volume, %
Iron Oxide	23.4
Unclassified	76.6

Table 2 Chemical Composition of Bulk Deposit and Unclassified Phases, Wt%

	Si	Al	Fe	Ti	P	Na	K	Mn
Bulk	0.2	0.8	59.0	0.0	13.9	10.9	0.1	14.4
Unclassified	4.2	0.7	23.4	0.5	17.8	14.1	0.3	39.1

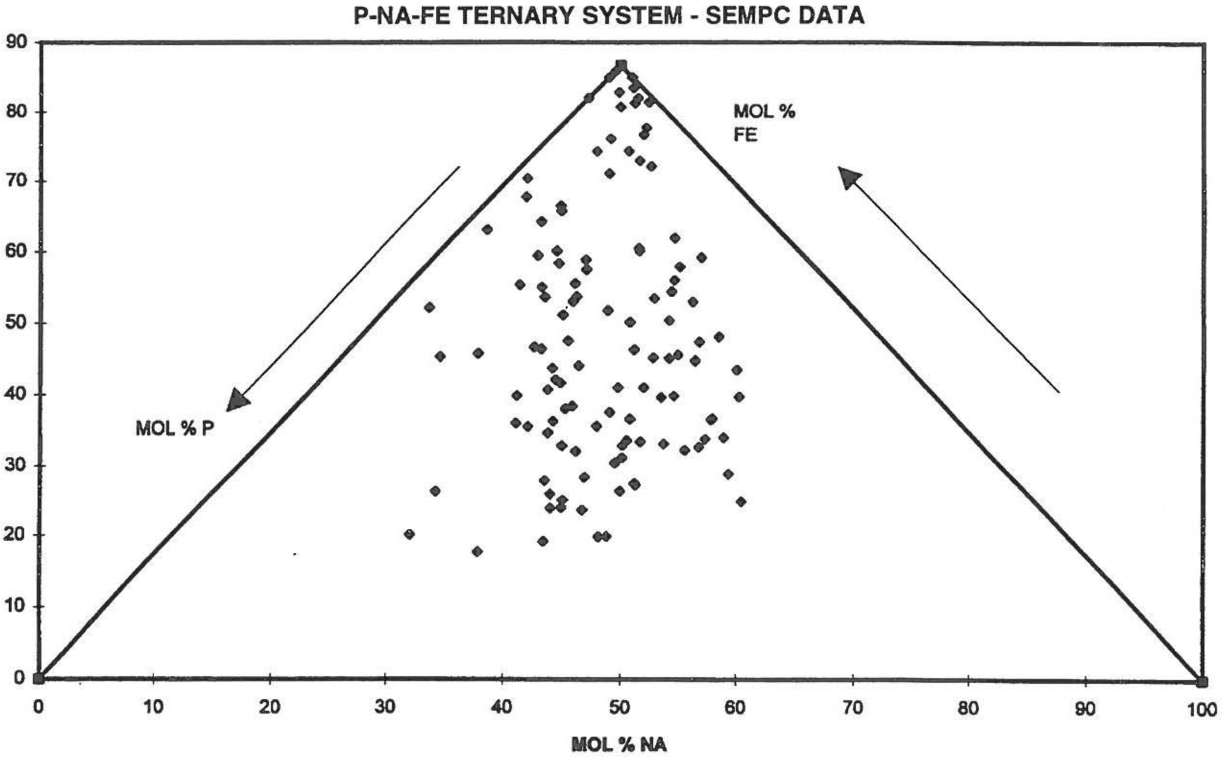

Figure 1 Ternary diagram representing the molar relationship between Iron - Phosphorous - Sodium in a deposit based on SEMPC data

that there was extensive interaction between the iron, phosphorus and sulfur. Indeed, all the points were rich in iron with on pure sodium phosphate phases observed (these phases would be represented by points along the x axis). The data also shows that the deposits were rich in sodium and may have had the potential to cause caustic attack.

The results of the analysis indicated to the utility the need to assess current water chemical treatment processes and the need to detect and remove areas affected by hydrogen damage. The data showed that while they changed from a phosphate-based treatment process, the deposits were phosphate rich. In many cases where there has been a switch to a different treatment the location, extent, and chemistry of the deposits are changed. Similar analysis of intact tube samples were recommended to determine if the modifications in the treatment program had resulted in improved deposit characteristics.

CASE STUDY #2

Hydrogen Damage of Tube - Utility Boiler 2500 psig

This sample was from a unit which has had a history of hydrogen damage failures in the water-walls over the last five years. The hydrogen damage was widespread in the regions of high heat flux and at tube bends. However, surveying of wall tubes showed that while there were heavy deposits at the I.D. crown, the presence of these deposits did not necessarily relate to hydrogen damage. The primary corrosion mechanism associated with the tubes was oxygen pitting with heavy, copper-rich deposits. The utility had a concern not only with the cause of the deposition but how they could remove the deposits to prevent further corrosion by oxygen pitting or hydrogen damage. It was known from discussions with the boiler operators that there was some corrosion of the feedwater heaters which allowed ingress of copper into the boiler circuits. While copper in water-side deposits is not unusual in utility boilers the role of the copper in corrosion processes, if any, has not been well defined.

Table 3 lists the results of the phase assemblage from SEMPC analysis of the I.D. deposit in the region of hydrogen damage. Table 4 presents the chemical composition of the bulk deposit. The deposit was analyzed in situ in order to maintain relationships between the deposit and the metal interface. The phase assemblage shows that the major phase was iron oxide. However, there were some zinc-rich and copper-rich phases. These phases are derived from corrosion of pre-boiler components such as the feedwater heaters. Of significance is the presence of calcium rich phases such as montmorillonite, calcium silicate, and

Table 3 Phase Assemblage of Water-Side Deposit

Phase	Volume, %
Calcium Silicate	1.2
Montmorillonite (Calcium-rich clay)	2.8
Pyrrhotite (FeS)	0.4
Anorthite ($CaO, Al_2O_3, 2SiO_2$)	0.4
Zinc-rich	3.4
Copper-rich	4.0
Iron oxide	23.4
Unclassified	69.2

Table 4 Chemical Composition of Bulk Deposit and Unclassified Phases, Wt%

	Si	Al	Fe	Ti	P	Na	Zn	Cu	Mn	O
Bulk	1.7	0.5	76.6	0.1	0.3	0.2	0.3	1.5	0.6	16.7
Unclassified	2.3	0.6	36.9	0.9	0.7	0.6	5.9	7.6	2.2	37.9

anorthite. These phases are presumed to be from the zeolite water-softener and indicates a major problem with the water-treatment equipment. It should be noted that these phases tend to be less sensitive to acid cleaning chemicals than the calcium-rich salts usually observed in boiler tubes.

Of interest was the potential effect of the copper and zinc in the deposit on the hydrogen damage. Figure 2 shows the relationship between copper, zinc, and iron for the points containing these components. It can be seen from the ternary diagram that there was extensive interaction between the copper and iron but limited interaction between iron or copper with zinc.

The results of the analysis showed that the deposit present in the region with hydrogen damage was a complex mixture of iron oxide, calcium rich-phases, and iron/copper rich points. Based on the information obtained it was recommended to the utility to chemically clean the boiler, review water chemistry, and continue monitoring tube deposit characteristics.

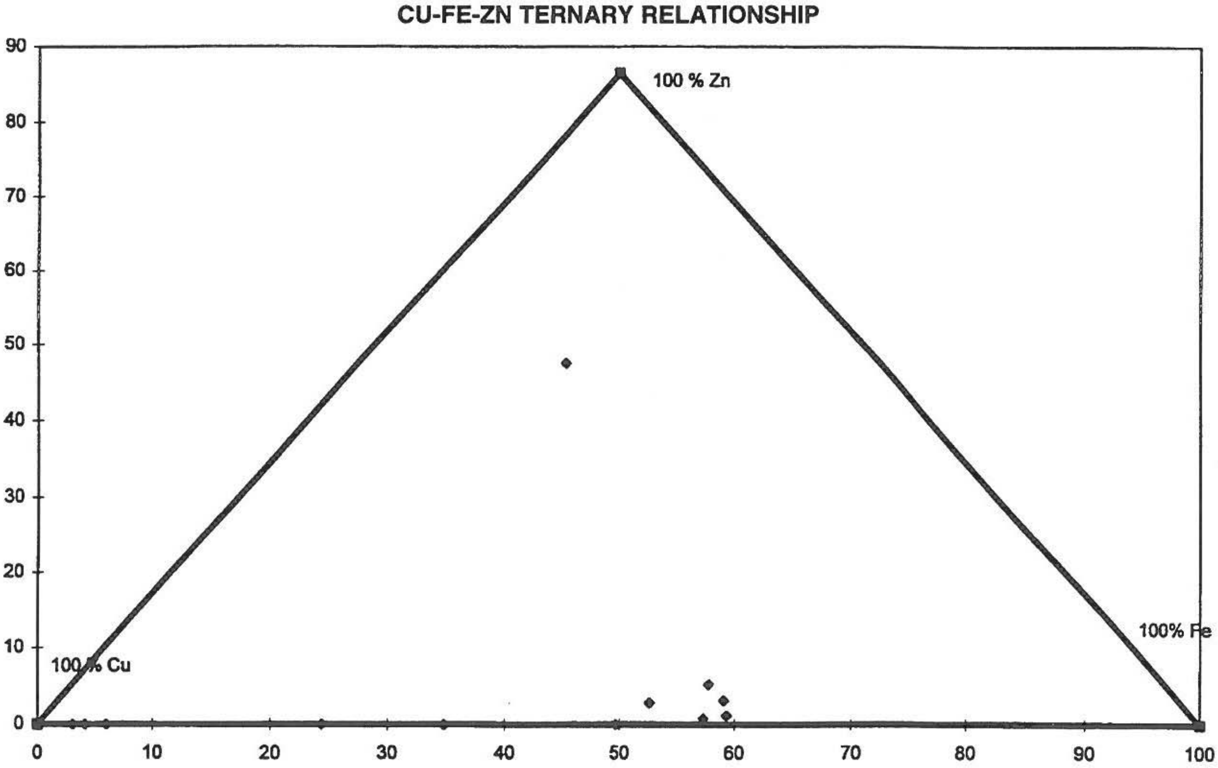

Figure 2 Ternary diagram representing the molar relationship between Iron - Copper - Zinc in a deposit based on SEMPC data

CONCLUSIONS

A technique has been developed which can be used to further characterize water-side deposits. The technique is based on microprobe analysis techniques and involves the analysis of approximately 250 random points within the scale and the corrosion interface. The data from the analysis is then used to determine the association and relationship between the various elements and components. Two case studies were presented which shows the application of the SEMPC technique to I.D. corrosion processes. It was shown that the SEMPC data gave valuable data on both the phase assemblage of the I.D. deposits and the interaction of the various components within the deposit with the base metal which may have contributed to the corrosion process.

The complexity and variability of water-side deposits in water-wall tubes precludes the simple correlation of deposit characteristics with corrosion processes such as caustic gouging and hydrogen damage. However, through systematic analysis and characterization of deposits and corrosion interfaces, mechanisms of deposition and corrosion can be developed. These mechanisms can then be used to improve operation of the unit by reducing maintenance costs and reducing forced outages due to water-wall failures. In order to achieve this outcome, however, it is necessary to establish a boiler tube evaluation program including both failed and intact tubes.

REFERENCES

1. Kalmanovitch, D. P., "Hydrogen Damage in Utility Boilers," presented at the International Conference on Boiler Tube Failures in Fossil Plants, San Diego, California, 1991. DB Riley Technical Paper RST-108.