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Hydrogen Damage in Utility Boilers

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INTRODUCTION

This paper deals with recent experience with hydrogen damage in utility boiler furnace wall tubing. The phenomena of hydrogen damage is discussed including the mechanism of formation and the techniques used to determine the extent of damage. Furthermore, three case studies of hydrogen damage in utility boilers are presented. These test cases will show how a detailed inspection of waterwalls where hydrogen damage has been observed has to include both extensive surveying and detailed metallographic analysis. A good balance between destructive and non-destructive testing can be very effective in determining cost effective and efficient assessment. These case studies are of relevance as they show some interesting manifestations of hydrogen damage. The results will show that while non-destructive testing (NDT) analysis such as ultrasound analysis is very useful in surveying a boiler, a rigorous tube sampling and evaluation program must be undertaken to confirm the results. A framework with which the NDT survey is combined with metallurgical analysis and interpretation is given in this paper. The interpretation of the hydrogen damage is crucial to the proper assessment of the extent of corrosion and the remedial or mitigating efforts that can be adopted.

Hydrogen damage is a major concern for the utility industry. While there have been extensive reports of the causes of hydrogen damage there is still significant confusion in the utility industry. This confusion is mainly derived from the inappropriate label of hydrogen embrittlement applied to the phenomena. It is hoped that this paper will help in the clarification of the problem. The occurrence of the thick-edge failures in the water-cooled surfaces should be regarded with alarm as it may be a small manifestation of serious internal (I.D.) corrosion of the water wall and potential for further failures and unscheduled outages. Hydrogen damage reflects a serious problem with the condition of the water wall tubing. Indeed, the phenomena is related to poor control of water chemistry, lay-up procedures, and high heat flux on the furnace walls. In simple terms it can be considered a cancer which has to be properly identified, located, and removed. Indeed, following the medical analogy further, subsequent to selective removal of the damaged material, regular monitoring of the condition of the I.D., including water chemistry, is crucial to maintaining unit availability and efficiency. This monitoring can detect any further occurrence or keep in check a minor condition.

HYDROGEN DAMAGE VERSUS HYDROGEN EMBRITTLEMENT

The phenomena of hydrogen damage, that of thick walled failures caused by I.D. corrosion of water walls in boilers has continued to be incorrectly labelled by some as hydrogen embrittlement. This is despite numerous publications on the subject[1,2,3]. The two phenomena are quite different and the labels convey different processes. The term embrittlement can best be described as the potential for failure. An embrittled steel does not necessarily imply damaged, it implies less elastic or ductile nature of the material. This condition is reversible as it is caused by the diffusion of hydrogen atoms into the molecular structure of the steel. Suitable heating or renormalizing of the steel will result in the exsolution of the hydrogen and subsequent transformation to the normal structure. Embrittlement occurs in hydrogen rich atmospheres such as found in ammonia synthesis plants, see references 4, 5, and 6. The embrittlement process can be detected by the determination of physical properties (destructive tests) or x-ray diffraction and not by non destructive means such as ultrasound. The change in the atomic structure of the steel caused by the embrittlement process results in a change in the lattice spacing of the crystals. This can be detected by x-ray diffraction methods. All steels are sensitive to hydrogen embrittlement given the right conditions of temperature and pressure as well as the partial pressure of hydrogen. Hydrogen embrittlement is not normally observed in utility boilers, and there have been no reported evidence of failures attributed to embrittlement.

Hydrogen damage is permanent damage caused by the reaction of hydrogen with the carbide phases present in carbon and low alloy carbon steels (pearlite colonies). Hydrogen damage does not occur in austenitic or martensitic steels. The hydrogen is formed under internal deposits on the fireside crown of the boiler tubes. The deposit encapsulates a "corrosion cell". In this cell the concentration of corrosive material, derived from the feedwater chemicals, can be significantly higher than the bulk water chemistry. The chemical reactions under the deposit includes the formation of molecular hydrogen and nascent hydrogen. Hydrogen is the smallest atom in nature and can permeate through all membranes including steels. Molecular hydrogen, while larger than the atom can also permeate through steels, albeit at relatively slower rates. Therefore, a fraction of the hydrogen formed will be forced into the steel. A portion of the hydrogen will diffuse along the grain boundaries to the pearlite colonies. The hydrogen can react with the carbide phase according to the reactions to produce methane (CH_4) via the reaction:

$$Fe_3C + 4H = 3Fe + CH_4$$

The molecular volume of CH_4 is significantly larger than the hydrogen atom. This results in the development of increased pressure along the grain boundaries. The pressure builds up and increases intergranular strain. This stress is relieved by increasing the volume of the grain boundary, causing crack formation or propagation. This has three effects: the decarburization of the carbide at the I.D., the formation of intergranular cracks, and the opening of channels for further diffusion of the hydrogen into the tube wall. Examination of the microstructure reveals short discontinuous cracks associated with decarburized pearlite colonies. The short cracks are due to the limited amount of methane that can form from a single pearlite colony. Once the pearlite has been exhausted no further methane will form at the grain boundary. Accumulation of these cracks or fissures results in the weakening of the structure of the tube and the reduction of the capacity of the tube to withstand the operating or local stresses. This ultimately leads to failure.

There have been many publications on the conditions required for hydrogen damage, see references 7, 8, 9, and 10. In general hydrogen damage occurs in high pressure units at metal temperatures above 900°F[1]. Carbon or low alloy steel is a requirement. A common observation, however, is the presence of heavy I.D. deposits, usually rich in copper. It is reasonable to assume that without these deposits hydrogen damage will not occur. Indeed, one can consider that the formation of the deposit is the rate-limiting step. One can only speculate on the characteristics of the deposit which can cause hydrogen damage. The common analysis performed on these deposits is chemical analysis or in some cases rudimentary scanning electron microscopy with energy dispersive spectrometry semi-quantitative analysis. There has been very little analysis of the various phases present in the deposits either by x-ray diffraction or advanced analytical techniques such as surface science (ESCA, Auger or SIMS). This detailed, fundamental work is required in order to accurately determine the role of the deposits on I.D. corrosion mechanisms including hydrogen damage and caustic gouging.

Some questions have been raised with respect to the rate of hydrogen damage formation. The rate of damage will be dependent on the nature of the corrosion cell, the pressure, the temperature, and wall thickness as well as the amount of carbon in the steel. As the rate of damage is dependent on the rate of formation and diffusion of hydrogen then these factors have to be considered. The conditions for the formation of hydrogen are sensitive to the nature of the deposit. Not all the water/steam in the "cell" will form nascent hydrogen. Furthermore, some hydrogen will pass through the steel without reacting with the carbide phase. Also the hydrogen can diffuse through the I.D. scale/deposit.

In terms of real experience, there appears to be some confusion about the rate of damage in utility boilers. It is of course very difficult to decouple the various effects and historical data associated with boiler I.D. conditions. The key aspect is that the manifestation of hydrogen damage indicates significant I.D. corrosion of the water-walls.

Testing for hydrogen damage includes ultrasound techniques and metallography. In recent years there has been extensive development of ultrasonic technology for NDT of boilers including I.D. analysis. The use of simple crushing tests do not in themselves verify the presence of hydrogen damage. The physical tests such as crushing of a ring section in a vise should be discouraged. Metallographic examination is relatively rapid and conclusive and should be used to confirm hydrogen damage. Developments in ultrasound technology have been used to obtain methods to determine the damaged microstructure at the I.D. These techniques include attenuation (shear-wave) and velocity reduction (longitudinal-wave) methods. Details of these techniques can be found elsewhere[11,12,13]. It should be mentioned that these techniques are incapable of detecting hydrogen embrittlement. The ultrasound methods detect a difference in the propagation of the sound wave. This different sound propagation is due to the altered microstructure in the metal or at the scale/metal interface.

The techniques can not distinguish between gouging, caustic gouging, pitting, or hydrogen damage by themselves. However, the UT methods are very useful in surveying a boiler for I.D. damage. The actual mechanism of damage can only be confirmed by the use of metallographic samples.

CASE STUDIES

The following are the results of three recent case studies at the DB Riley Metallurgical Laboratory involving hydrogen damage.

Case Study No. 1

This unit is a gas-fired boiler, about 25 years old, operating intermittently and with a maximum operating pressure of 1550 psig. Over the past ten years the boiler was only fired during peak system loads. During a recent outage, a detailed evaluation of the condition of the boiler was undertaken. Part of the evaluation involved an extensive ultrasound survey of the furnace floor, roof, and wall tubes. The unit had experienced many boiler tube failures over recent years. The bulk of the water-wall failures was attributed to hydrogen damage. The technique used to detect hydrogen damage was shear-wave, pitch-catch (sound attenuation). This technique is routinely used to determine the presence of I.D. damage such as pitting and hydrogen damage. In general, the results are reported as attenuation or dB drop. A drop of <5 dB is normal and indicates little or no I.D. damage. Drops in dB of between 6 and 12 are taken to indicate moderate damage and values above 12 indicate severe damage. Table 1 lists the results of the survey of 6 of the 11 tubes removed from the boiler. The selection of the tubes was based on location and measured dB drop. As can be seen in Table 1, the water-walls showed moderate damage based on attenuation values. High attenuation values were observed in the roof and floor tubes indicating severe damage. This result was quite surprising given the low heat flux in these regions and the relatively low dB drop values in the water walls. The tube samples were subjected to a detailed metallographic examination to confirm the results of the ultrasound survey. Hydrogen damage was observed in only one water-wall tube and a roof tube sample (see Figure 1). In the tubes where no hydrogen damage was observed there was also no pitting or other noticeable damage/corrosion to the I.D. This was despite the high dB drop observed in some samples. Review of the data showed that there was little correlation of hydrogen damage or pitting with dB drop. Further studies were undertaken. The analysis of the I.D. deposit showed that the deposit contained mainly iron and copper with a minor amount of nickel. Other components comprised only 1 wt% of the deposit. Furthermore, the I.D. loading analysis of the deposit revealed a very high value of 40 g/square foot. Subsequent lab-scale tests, performed by the ultrasound technicians, showed that heavy I.D. tenacious deposits can increase the dB drop or attenuate the signal.

Sample	Location	dB Drop	Damage
1	Roof	24	Severe
2	Front wall*	8	Moderate
3	Rear wall*	6	Moderate
4	Right wall*	8	Moderate
5	Left wall*	6	Moderate
6	Floor	24	Severe

* at or near a burner elevation

Table 1 Measured dB Drop for Selected Tubes

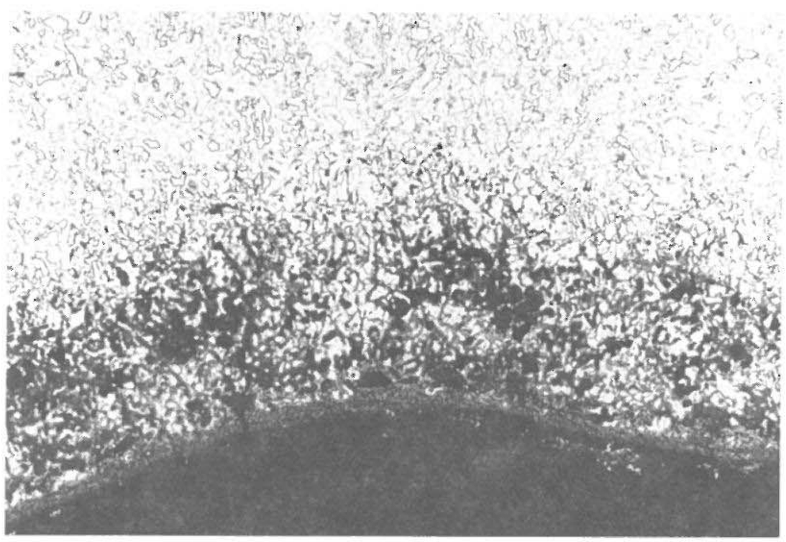

Figure 1 Waterwall Sample — Case Study No. 1
Note the I.D. voids, microcracks, and copper deposits typical of hydrogen damage (50X)

The results of this case study show that the ultrasound techniques are effective only when used in conjunction with systematic metallurgical analysis. Post-mortem analysis of the boiler survey showed that the hydrogen damage was not as extensive as indicated by the UT survey. The hydrogen damage in the roof tube was quite surprising and indicated a problem with boiler lay-up procedures. Certainly, the heavy I.D. deposits suggested a high propensity for I.D. corrosion and localized overheating of the tube. The lessons learned from this study have been used to develop a more systematic method of evaluating hydrogen damage in boilers.

Case Study No. 2

This boiler is a pulverized coal-fired unit operated at a pressure of 1575 psig. The unit was commissioned in 1967. Extensive water-wall failures were observed in the rear wall of the furnace at the burner elevations. Furthermore in all cases the hydrogen damage was present at flash weld locations. Metallographic examination of failures showed that there was slight misalignment of the tube ends at the flash welds. The misalignment combined with excess weld splatter at the I.D. formed a flow disrupter. This lead to heavy localized I.D. deposits and subsequent hydrogen damage, see Figures 2 and 3. The samples showed severe gouging and hydrogen damage in the weld metal. A survey of the condition of the water walls was undertaken using the longitudinal wave velocity reduction technique. The UT survey indicated possible hydrogen damage in the rear and side walls at the burner elevations. This corresponded very well with the failure history of the unit. Based on the survey the locations which showed positive or possible damage were replaced. The unit has not reported any water wall failures since repairs were made.

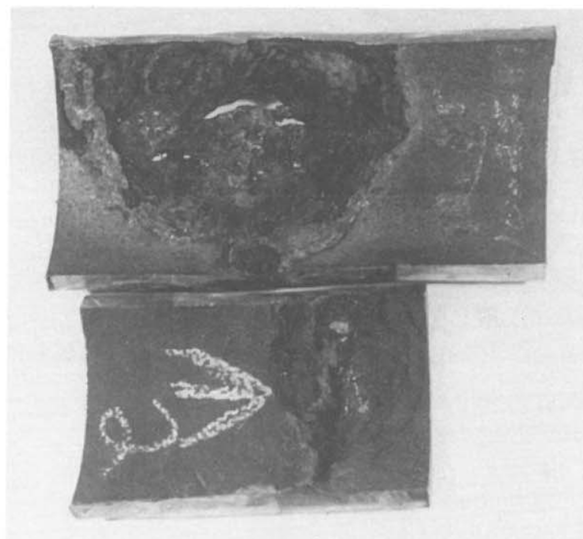

Figure 2 I.D. of As-Received Failed Tubes — Case Study No. 2
Note the Localized Deposits and Gouging at Welds

Figure 3 Hydrogen Damage Manifested as Cracks in Weld — Case Study No. 2 (500X)

Case Study No. 3

This unit was commissioned in 1965 and is rated to operate at 1260 psig. The boiler is designed for gas and oil. Multiple outages due to water-wall tube failures had been noted over recent years. A detailed inspection of the furnace was performed by DB Riley. The hydrogen damage was associated with welds and severe I.D. gouging (presumably by caustic attack). The location of the failures was at the west side wall and the roof. Significant thinning of the tubes had occurred. Field repairs had been made to the tubes and the ruptures had occurred at these repairs. The repairs were pad welds. Detailed analysis showed that the pad welds were made over damaged base material. The high localized heat input during welding may have increased the damage to the original tube. The result is interesting as it shows the effect of welding repairs of damaged base metal and the importance of determining the failure mechanism prior to adopting a repair procedure (see Figures 4 and 5).

Based on the failure mechanism the examination involved a UT survey for wall thinning only. This survey confirmed the presence of thinned tubes in the areas where failures due to hydrogen damage had occurred. The results lead to extensive replacement of affected areas. There have been no reports of failure from the unit since it re-entered service.

In all cases the solution to hydrogen damage is control of the water chemistry, maintenance of a clean I.D. and awareness of high heat flux zones. In boilers with hydrogen damage the affected material must be located, identified and removed. Chemical cleaning of the water-walls is a viable method of control only if the hydrogen damaged portions are removed and the cleaning is performed routinely.

RECOMMENDATIONS

The major recommendation based on these case studies is that boiler tube failures caused by hydrogen damage should be treated with alarm. A rigorous, extensive survey of affected areas should be scheduled at the earliest convenience. The failures are due to internal corrosion/damage process and must be addressed. The procedure for inspection should include the following.

- U.T. Survey of suspected areas (velocity reduction method).
- U.T. Survey of sensitive areas - furnace walls etc.
- Analysis of U.T. Survey.
- Determination of 'damaged' areas.
- Determination of 'possible' areas.
- Sampling of 'possible' tubes.
- Metallurgical analysis of samples including deposit loading and I.D. deposit analysis.
- Review of operating data and the location and historical data on tube failures.

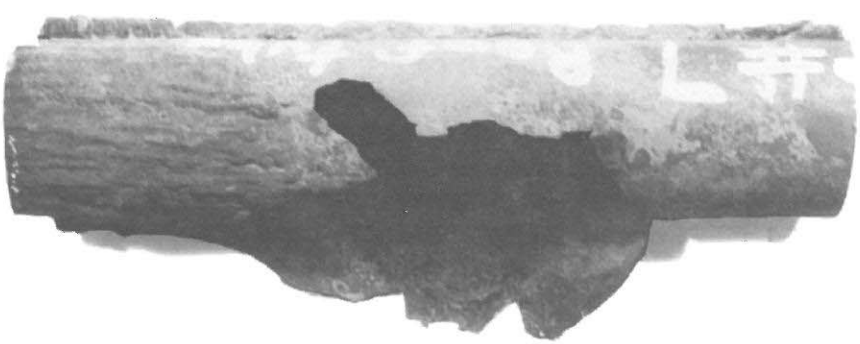

Figure 4 As Received, Failed Roof Tube Sample — Case Study No. 3

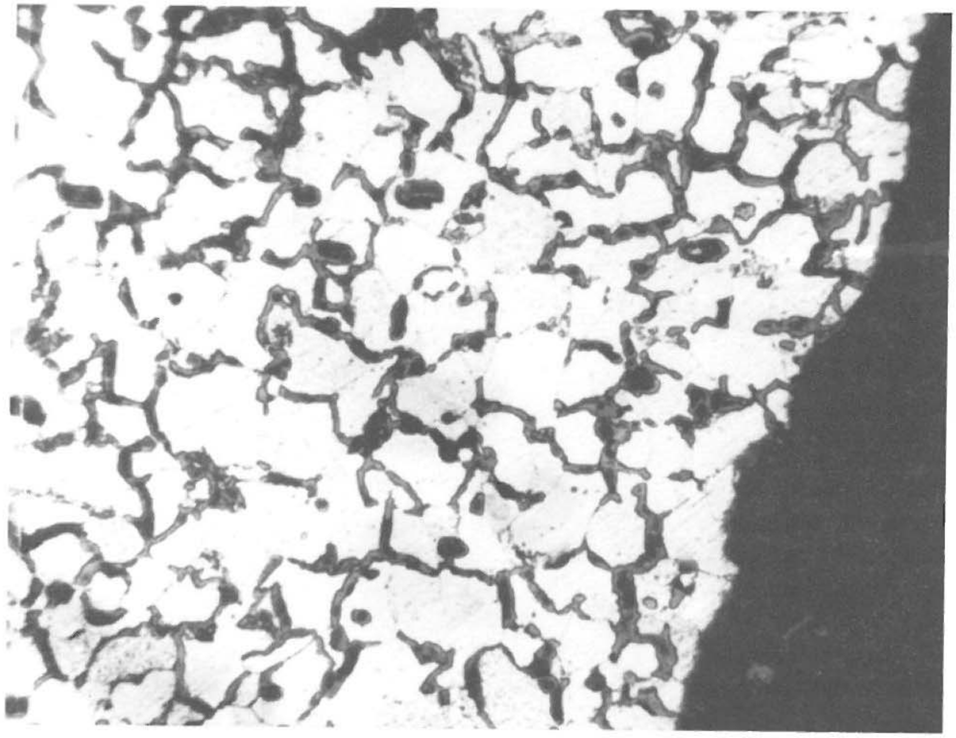

Figure 5 I.D. of Roof Tube Failure Edge — Case Study No. 3 (500X)
Note the Oxide-Filled Hydrogen Damage Cracks

In addition, fibrescopic video investigation of the failed or suspect areas can be very useful in determining the extent of I.D. deposit and gouging. This can give rapid insight into the condition of the I.D. and the optimum repair procedure.

The results of the inspection can be used to establish effective courses of action. These can include the chemical cleaning of the boiler, improvement of water chemistry treatment, selective replacement of water-wall tubes. The careful survey of the extent of hydrogen damage ensures that only the minimum amount of water-wall is replaced, if necessary. The advantages of such a detailed study gives confidence to continued operation.

The other conclusion of the study is that weld repairs at or adjacent to hydrogen damage regions are not effective in the long term. In reality, the weld repair procedure tends to exacerbate the problem. This was seen in two of the three case studies reported here. This indicates that surveying of damage should include welds and weld repairs in sensitive areas. Another observation is that ultrasound survey of the water-walls for hydrogen damage while useful have to be performed under supervised conditions with some effective calibration and qualification. The experience to date suggests that the longitudinal wave velocity reduction technique is superior to the attenuation method for determining I.D. damage, particularly hydrogen damage. It is strongly encouraged that the inspection team comprise experienced boiler inspection personnel as well as qualified ultrasound technicians. Acknowledgment has to be made to the limits of the ultrasound techniques and how other inspection techniques can be used to give a full definition of the condition of the water-wall tubes. There is no shortcut with hydrogen damage.

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