

# MODEL OF INFLUENCING FACTORS FOR HYDROGEN DAMAGES OF BOILER EVAPORATOR TUBES

M. DJUKIC<sup>1</sup>, V. SIJACKI ZERAVCIC<sup>1</sup>, G. BAKIC<sup>1</sup>, D. MILANOVIC<sup>2</sup>, B. ANDJELIC<sup>3</sup>

<sup>1</sup>Faculty of Mechanical Engineering, Department of Material Science, University of Belgrade, Serbia

<sup>2</sup>Vectram, Belgrade, Serbia

<sup>3</sup>Technical Faculty, Department of Physics & Materials, Cacak, University of Kragujevac, Serbia

## ABSTRACT

Hydrogen-induced fractures of metallic components of thermal fossil fuel power plants (TPP) presents very serious exploitation problem and often exert considerable influence on the loss of power plant availability. Hydrogen damage is one of the most disturbing of boiler tube failure mechanism, and from the international experience, remains as one of the leading causes of frequent outages of boiler tubing system. To clarify root causes and complexity of problems associated with hydrogen damages, it is necessary to apply a multidisciplinary approach which comprises research in the field of material quality, boiler design, operation and maintenance. The work reported here is based on the theory and, particularly, on the experimental tests performed on boiler evaporator tube samples, taken from a domestic 210 MW power plant, that had experienced hydrogen damages during service. Possible mechanisms for metal – hydrogen interaction are considered from materials point of view, fluid hydrodynamics in evaporator tubes and the complexity of structural – exploitation plant characteristics. The aim of this paper is to contribute to the analysis of hydrogen damaging in boiler evaporator tubes and to propose failure mechanism model based on "micro-departure from nucleate boiling" (micro-DNB) of working fluid. In addition, this paper elucidates some definitions of major root cause influences by proposing model for systematization of influencing and corresponding operating factors responsible for hydrogen damages of boiler evaporator tubes.

## 1 INTRODUCTION

Hydrogen damage of boiler evaporator tube, also called hydrogen attack, results in serious and irreparable damage to the tube steel and should not be confused with "hydrogen embrittlement" which is sometimes reversible adsorption of hydrogen into steel. It is generally accepted that term hydrogen damage describes the interaction process between atomic hydrogen with carbon in steel at elevated temperatures and high pressures resulting in the formation of methane gas along the ferrite grain boundaries. However, the hydrogen damage in boiler evaporator tubes of thermal power plants has a much wider meaning and includes hydrogen-induced corrosion damage (rupture) of metal. Ruptures of a large number of evaporator tubes over a short time interval is often a result of individual or combined effects of different damaging mechanisms whose initiation and evolution are closely related to the specific exploitation conditions of a particular boiler equipment [1]. The damage mechanisms responsible can be decarburizing, embrittlement and formation of molecular hydrogen and methane in the metal. Although each of these mechanisms is relatively well understood in the case of hydrogen corrosion-induced damage in boiler tube systems and evaporator tubes, these mechanisms are still not sufficiently investigated phenomena. This is due to very specific and complex interconnection of material quality, hydrodynamic of evaporating systems, mechanisms and consequences of hydrogen diffusion in metals, water-chemical treatment regime as well as design and operating characteristics of the boiler unit (Djukic et al. [2]). Based on the analysis of the hydrogen damaged carried out on domestic boilers, results of the studies conducted on samples removed from the damaged tubes and the results cited in the world literature, a model for initiation of hydrogen damage of boiler evaporator tube is proposed.

The model is based on the effects of local destabilization of nucleate boiling of working fluid (in accordance with the hypothesis of existence of "micro-departure from nucleate boiling") which, in turn, elucidates the phenomenon of hydrogen damage of boiler evaporator tubes. In addition, the tests results and proposed model form a basis for classification of the influencing and corresponding operating factors responsible for development of hydrogen damage.

## 2 BACKGROUND

During exploitation of one 210 MW fossil fuel power plant boiler, significant failures of evaporator (water wall) tubes occurred after 73000 hours and were found in the furnace zones with maximum heat fluxes. Water wall tubes ( $\varnothing 60 \times 6$ ), made of St 20 (GOST), were exposed to working conditions of  $P=15,5\text{MPa}$ ,  $t=350^\circ\text{C}$ . Failure analysis was carried out on a specimen, removed from the failed tube (Sijacki Zeravcic et al. [3]).

## 3 EXPERIMENTAL PROCEDURES

Several techniques were used to determine damage mechanism, main cause of damage, the microstructural state and mechanical characteristics of material. The wall thicknesses were measured at several locations along the length of the tube and in the fracture area. Chemical analysis of tube material was made by flame spectroscopy. The Vickers hardness measurements were made at 30 daN load. Tensile test was carried out at room temperature on the samples prepared from the tube fireside in the vicinity of fracture. Metallographic investigations of the damaged zones were carried out on numerous specimens using light microscopy.

## 4 RESULTS

Analysis of the samples cut from the damaged evaporator tubes revealed three types of damages on the fire side of tubes: 1) "window" type thick-edge fracture with characteristic partial crack opening and thinning of the tube walls at the edge of the fracture, 2) uneven local wall thinning on the inner side in the form of relative shallow gouging of irregular shape in the vicinity of the fracture, 3) many small micro-crack on the tube inner side. The damage propagates along the welded joint from one welded joint to the other with the origin at one of them. On the inner side of a tube, there were no deposits but only defective magnetite layers of variable thickness.

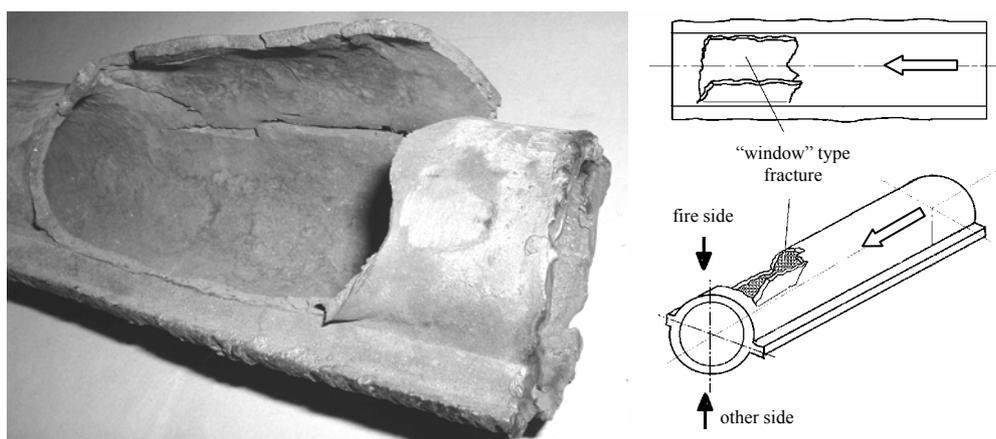


Figure 1: "Window" type fracture with schematic view of the damage.

Measured wall thicknesses along the edge of the fracture were in the range of 2.9-5.75mm, less than nominal value of 6.0mm. The zones outside the damaged one were intact with nominal thickness.

Chemical composition of investigated material is shown in Table 1. The results obtained for evaporator tubes are satisfactory and in accordance with standard data for St.20 (GOST – 1050 – 74) steel.

Table 1: Results of chemical analyses

Chemical composition, wt %	C	Si	Mn	S	P
Sample	0.171	0.267	0.678	0.021	0.020

Mechanical characteristics indicated a noticeable embrittlement of material. Yield strength of  $R_{0.2}=398$  MPa was significantly higher than minimal designed value,  $R_{0.2min}=216$  MPa, and it is close to the minimum value of standard tensile strength of  $R_m=420$  MPa. Tensile strength was  $R_m=481$  MPa while deformation characteristic, expressed by elongation,  $A_5=13.8\%$ , was much lower than recommended ( $A_{min}=24\%$ ) which is an indication of a significant increase of the material embrittlement.

The hardness values were in the range (147-174HV) and are higher than 145HV generally considered as the upper limit for steel St.20 in normalized state. This is in agreement with the tensile test results.

Microstructure of the central area of sample cross sections was as expected ferrite-pearlite with the presence of completely deteriorated pearlite. In these zones the presence of micro-fissures along the ferrite boundaries were observed as seen in Figure 2. Due to a complete decarburization, the microstructure was pure ferrite showing fractures along the boundaries as observed in the zones closer to the inner side, Figure 3. On the inner side shallow corrosion pits - gouges without any scalling were observed, Figure 4. Observed decarburization as well as the deterioration of pearlite microconstituent indicates that the hydrogen penetration occurred through the tube wall. Many discontinuous, intergranular cracks and fissures are the result of great pressure exerted by methane molecules or molecular hydrogen precipitated along the ferrite grain boundaries.

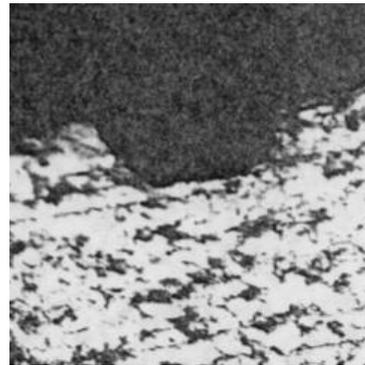
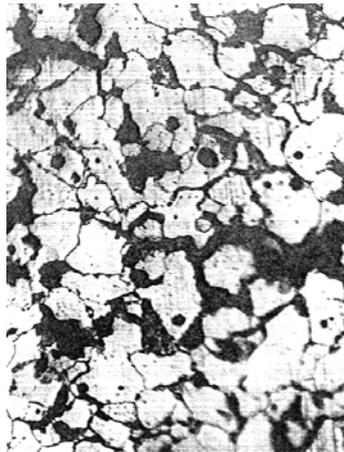


Figure 2: Ferrite – pearlite. Figures. 500x  
Figure 3: Ferrite. Decarburization. Intergranular cracks. 500x

Figure 4: Ferrite – pearlite. Cavities. 200x

## 5 FAILURE MECHANISM MODEL BASED ON

### "MICRO-DEPARTURE FROM NUCLEATE BOILING" OF WORKING FLUID

The observed corrosion gouging at the inner side of evaporator tube can be associated with an increased local concentration of basic or acid content at the boundary surface metal-water.

The porous deposit, essential for achieving a very high local concentration of basic compounds at the boundary surface (Port et al. [4]), are not present at all and also different ferrous oxides and multi-layered deposits in the pits are not present. Hence, it can be assumed that the observed gouging is a result of local reduction in pH value of working fluid in boundary layer and development of hydrogen corrosion. The results of microstructural analyses and mechanical testing confirmed this assumption. Analysis of boiler operation showed that there was no significant deviations from the nominal working parameters, water pH value and the amount of dissolved impurity content during the exploitation prior to damage occurrence. Disturbance in the flame spreading in the furnace were not observed (microstructure analyses confirmed the absence of overheating). The same applies to the hydrodynamic disturbance and thermal-hydrodynamic instabilities. In this case, the real cause of increase in the local concentration of acid ions at the boundary layer is unknown as well as the destruction of the magnetite layer.

The operating heat fluxes in the furnaces of coal-fired, drum type, natural circulation boilers up to 300 MW are substantially lower of the critical heat flux values (CHF). Therefore there is a very small probability that departure from nucleate boiling (DNB) of working fluid, under nominal operating conditions, would appear as a macro phenomenon over a wide area of the evaporator.

Contemporary studies of nucleate boiling destabilization are mainly devoted to the local and micro-hydrodynamic approach. Using "hydrodynamic instability model" Zuber [5] proposed that the regime of nucleate boiling regime can be divided into two subregimes: isolated bubble regime and bubble interaction regime (formation of dry-out patches). Similarly Kang and Bartsch [6] proposed a division of the nucleate boiling regime into stable and unstable regimes, which is in agreement with the Zuber model.

Recently, Nagai and Nishio [7] reported that contrary to conventional expectation on appearance of dry areas at DNB point, based on global macro hydrodynamic approach, "primary dry area" formed under bubbles, have appeared scattered even at low heat flux ( $q \sim 0,3 \text{CHF}$ ) nucleate boiling region. Despite the majority of the experimental studies conducted under the conditions of pool boiling and not for forced convective boiling of fluid, newer studies (Ha et al. [8]) demonstrated that the contemporary micro hydrodynamic models defining trigger mechanism for CHF can be successfully applied for both types of boiling.

Also, it was shown that modeling based on the global macro hydrodynamic approach is limited and confirmed that the local and micro hydrodynamics, in agreement with local phase change "drive", are ultimately responsible for the onset of DNB and thus even further removed from experimental observation. It can be concluded that DNB (subcooled and saturated) as a macro phenomena occurred due to accumulation and coalescences of dry spots formed as a result of bubble crowding and dryout of the micro layer under the bubbles (Ha et al. [8]).

However, neither of these models can explain clearly the observed damage mechanisms. In view of the limitations of the existing models and their limited application in this specific case, we propose a model to account for the reduced integrity of magnetite layer. It was assumed that the damage mechanism of the tube investigated requires formation of the micro dry spots and patches on the magnetite surface under stable saturated nucleate boiling of working fluid at heat fluxes much below CHF. A question arises as to whether this assumption has its merit? In our opinion, the confirmation of our assumption is justified by the contemporary approaches of both DNB (subcooled and saturated) despite the lack experimental data specifically for the boiler evaporator tubes. Based on this hypothesis, data from the plant exploitation history and the results of our

studies, we are of the opinion that during exploitation "micro-departure from nucleate boiling" (micro-DNB) of working fluid appears at heat fluxes considerably lower than the CHF (Djukic et al. [2,9]). Here, under the term "micro-departure from nucleate boiling" (micro-DNB) it is understood a local formation and disappearance of dry patches at the inner surface of the fire side due to micro-hydrodynamic perturbation in the vicinity of tube surface.

Intermittent formation of the dry patches at the tube inner surface during the micro-DNB provoke the wall temperature oscillations as well as the increase in the concentration of acid/base content within the boundary layer magnetite-fluid even in the absence of the porous deposit. At the sites where local damage of magnetite was formed as a result of the thermal cycling and its chemical decomposition, hydrogen is formed during steam-water corrosion of metal. The so-formed hydrogen diffused into the tube surface layer causing the hydrogen attack.

### 6 MODEL OF INFLUENCING FACTORS

Hydrogen damage is a specific damage mechanism due to numerous major root cause influences. The most common contributing features of the root cause are: dirty boiler, leading to extensive deposits, followed by a low pH excursion (Dooley et al. [10]). However, hydrogen damage of evaporator tubes can occur as a result of the number of influencing factors. As a result of experimental investigations and analysis of reliability of evaporators on domestic TPP conducted over many years, we propose classification of influencing and corresponding operating factors factors presented in Figure 5 (Djukic [11]). Four major operating parameters have direct impact on one or more influencing factors. Their relationships are presented in the left part of Figure 5 by arrow with inscribed numbers corresponding to influencing factors. Furthermore, numerous influencing factors are grouped by their effects on state of: A) corrosive potential of fluid, B) furnace heat absorption, C) deposit, D) oxide layers and E) unfavorable design/operating factors.

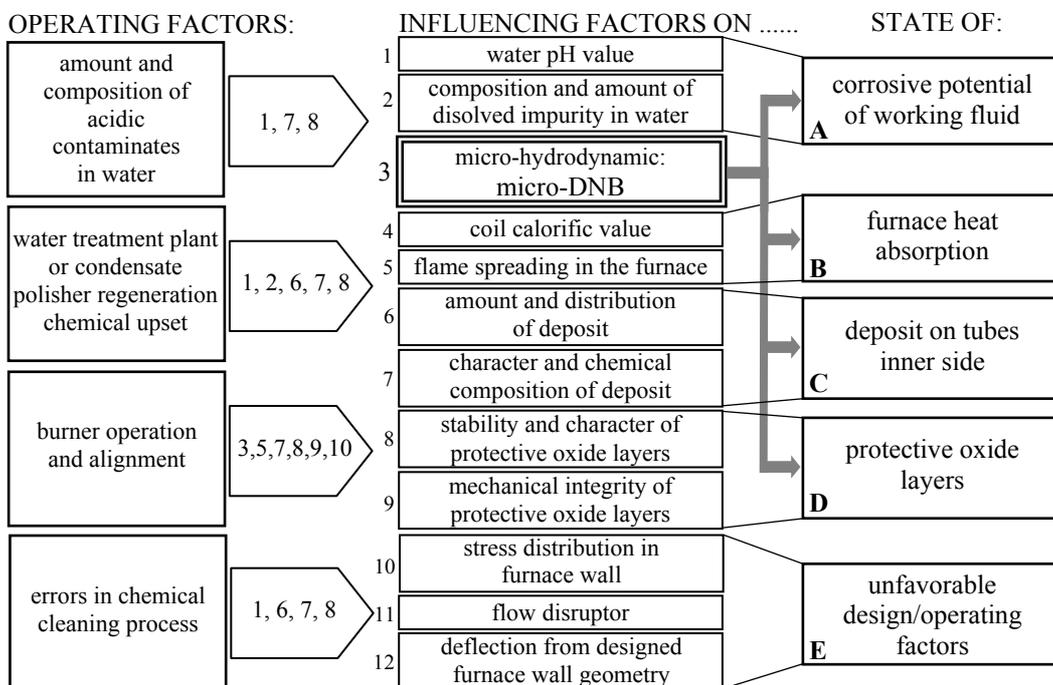


Figure 5: Summary of influencing factors for hydrogen damages of boiler evaporator tubes

The appearance of micro-DNB of working fluid, on tube inner surface, has very unbeneficial effect on integrity of protective oxide layers and also provoked the rise of corrosive potential of working fluid, increased rate of impurities deposition and oscillation of tube metal temperature. Hence, micro-DNB present very prominent influencing factor. The presented model of influencing factors is always applicable to root cause analysis of boiler evaporator hydrogen damage and could also be beneficial to define short and long – term preventive actions.

## 7 CONCLUSIONS

Due to the complexity of the processes involved and difficulties to simulated experimentally the operating conditions of evaporator tubes of steam drum boiler, there is a very limited information available in the world literature about micro-hydrodynamic phenomenon of low quality water nucleate boiling stability in evaporator tubes with natural and forced circulation. On the other hand, our experience indicate that all damage mechanisms of evaporator tubes are linked to the phenomena at the micro and sub-micro levels, whose accumulation exceeds the macro threshold level that causes the final rupture (Djukic et al. [2]). The proposed micro-DNB hypothesis defines the local destabilization of nucleate boiling and periodic appearance of dry patches irrespective of the absence of the conditions for the appearance of 1st order of boiling crisis (DNB) at the macro level ( $q < CHF$ ). The required conditions for the initiation and persistence of micro-DNB are not well understood despite the fact that the macro phenomena of DNB ( $q \sim CHF$ ) are relatively well known.

Based on the results of the present studies it is concluded that the integrity of the steam drum boiler evaporator tubes is greatly affected by numerous influencing factors where the local and micro hydrodynamics phenomena of two phase mixture boiling is of the significant importance (Djukic et al. [2], Djukic [11]). Hence, further experimental studies are required in order to elucidate the damage mechanism of boiler evaporator tubes including the hydrogen damages.

## REFERENCES

- [1] Corrosion of Thermal Power Plant, Fac. of Technology, Fac. of Mechanical Engineering, Nuclear Institute Vinca, Belgrade, 2002
- [2] Djukic M., Sijacki Zeravcic V., Contribution to the Methodology of Hydrogen Damages Analysis of Boiler Water Wall Tube and Condition of their Appearance, accepted for presentation at Conf. Corrosion 2004, Lviv, Ukraine
- [3] Sijacki Zeravcic V., Stamenic Z. et al., Hydrogen Embrittlement of the Furnace Walls Tubing, Proc. of 2<sup>nd</sup> Int. Colloq. Mat. Struc. and Micromec. of Frac., Brno, Czech Republic, pp.18-21,1998
- [4] Port R.D., Harvey M.H., The Nalco Guide to Boiler Failure Analysis, McGraw-Hill, 1991
- [5] Zuber N., Int. J. Heat Mass Transfer, Vol.6, pp. 53-58, 1963
- [6] Kang S. et al. Transition Between Stable and Unstable Nucleate Boiling Regions, Proc. of 2<sup>th</sup> European Thermal-Science Conf., Vol 1, Rome, Italy, p. 451, 1996
- [7] Nagai N., Nishio S., Study of Liquid-Solid Contact Phenomena, Proc. of ASME/JSME Thermal Eng. Book No. H0933b, pp. 239-246, 1995
- [8] Ha S.J., No H.C., Int. J. Heat Mass Transfer, Vol.41, No.2, pp. 303-311, 1998
- [9] Djukic M., Sijacki Zeravcic, Bakic G. et al., The Influence of Exploitation Conditions on Integrity of boiler evaporator tubes, Proc. of Dom. Thermal-Sc. Conf., pp. 303-311, 2003
- [10] Dooley R.B., McNaughton W.P., Boiler Tube Failures: Theory and Practice, Vol. 2, Water-Touched Tubes, EPRI, Paolo Alto, pp.15-2, 1988
- [11] Djukic M., Hydrogen damages of boiler furnace wall tube metal, MSc theses, Faculty of Mechanical Engineering of Belgrade University, Belgrade, p.124, 2002