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### LAB-SCALE STUDY ON FIRESIDE SUPERHEATERS CORROSION IN MSWI PLANTS

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#### ABSTRACT

Combustion of the municipal waste generates highly corrosive gases (HCl, SO<sub>2</sub>, NaCl, KCl and heavy metals chlorides) and ashes containing alkaline chlorides and sulphates. Currently, corrosion phenomena are particularly observed on superheater's tubes. Corrosion rates depend mainly on installation design, operating conditions i.e. gas and steam temperature and velocity of the flue gas containing ashes. This paper presents the results obtained using an innovative laboratory-scale corrosion pilot, which simulates MSWI boilers conditions characterized by a temperature gradient at metal tube on the presence of corrosive gases and ashes. The presented corrosion tests were realized on carbon steel at fixed metal temperature (400°C). The influence of the flue gas temperature, synthetic ashes composition and flue gas flow pattern were investigated. After corrosion test, cross section of tube samples were characterised to evaluate thickness loss and estimate corrosion rate while the elements present in corrosion layers were analysed.

Corrosion tests were carried out twice in order to validate the accuracy and reproducibility of results. First results highlight the key role of molten phase related to the ash composition and flue gas temperature as well as the deposit morphology, related to the flue gas flow pattern, on the mechanisms and corrosion rates.

**Keywords : Waste-to-Energy boiler, fireside corrosion, temperature gradient, velocity of flue gas**

#### INTRODUCTION

The recent revision of the European Waste Framework Directive paved the way by setting ambitious policy targets of 60% recycling and 40% energy recovery by 2020. More precisely, high energy efficiency thresholds have been fixed to classify MSWI plants as energy recovery facilities (Directive 2008/98/EC). Consequently, the EU encourages the Waste-to-Energy industry to play an essential role in both sustainable energy supply and environmentally sound waste management. In municipal solid waste incineration (MSWI) facilities, options for increasing the energy recovery efficiency consist to:

- i) promote, when it is possible, combined heat and power (CHP) generation instead of condensing power generation,
- ii) reduce boiler loss,
- iii) optimise the water/steam process.

This last case implies higher steam pressure and temperature to increase electrical efficiency. An increase of steam temperature, entering into a condensing turbine, from 400°C to 500°C lead to an increase of 20% of power generated. Nevertheless, combustion of waste with high chlorine and alkali content generate highly corrosive gases and ashes [1, 2, 3]. Fireside corrosion mechanisms of heat exchanger tubes includes simultaneously :

- corrosion by gaseous phase including "active oxidation" by chlorine (HCl, Cl<sub>2</sub>) [4,5],
- condensation of alkali and heavy metals chloride and/or sulfates [6],

- deposit induced corrosion and sulfidation of condensed chlorides [7],
- molten salts eutectics induce rapid dissolution of protective oxide scales and metallic tubes (“fluxage”) [8-10].

Higher steam temperature into heat exchanger tube is expected to increase the risks of corrosion, particularly on superheater tubes, along with important loss of materials, frequent shutdowns for repairs and high operational costs. Reported corrosion rates depend mainly on installation design and operating conditions, i.e. flue gas temperature and steam conditions (temperature gradient from flue gas to metal interface) [1, 11]. Moreover, velocity of the flue gas, containing abrasive ashes composed of silicate and aluminosilicate, can influence the tube degradation due to erosion-corrosion mechanisms [12]. Numerous materials for boiler tubes had been tested [13-15] in laboratory conditions simulating MSWI environment using various deposits composition in the presence or not of HCl and SO<sub>2</sub>. Nevertheless, the tested conditions rarely take into account simultaneously gas phase and ash phase corrosion, flue gas / metal temperature gradient and flue gas velocity. Consequently, the relative contribution of the different mechanisms (active oxidation, fluxing and erosion) on fireside corrosion is still unclear and open to discussion.

Thus, an innovative laboratory-scale corrosion pilot, which simulates MSWI boiler conditions, characterized by the presence of corrosive gases and ashes had been developed and used in this study. The specificity of our approach includes the simultaneous simulation of the temperature gradient at flue gas/tube interface and the velocity of flue gas containing synthetic ashes, while most studies already done in this field were restricted to isotherm and/or static conditions. The corrosion pilot had been validated by performing a set of experiments whose results had been compared with data coming from experience of MSWI plant boilers [16].

In this study, corrosion test are performed on carbon steel tube at 400°C. The effect of the following parameters are examined :

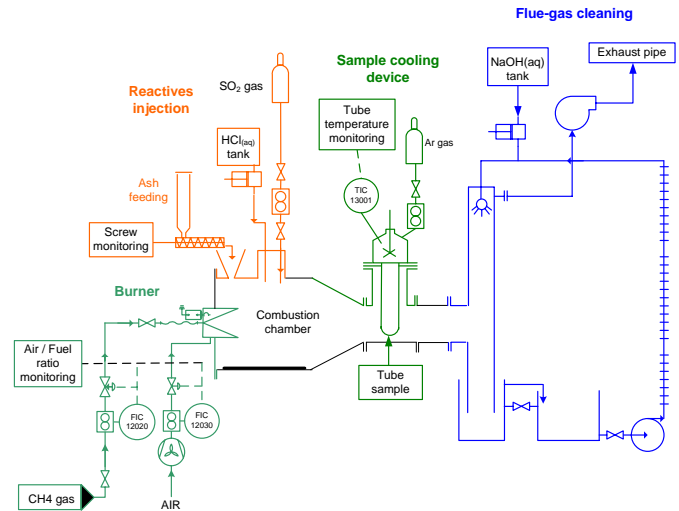
- flue gas temperature,
- flue gas flow direction,
- composition of synthetic ashes.

Our attention will be particularly focussed on the evaluation of corrosion rate and the analysis of the corrosion scales in order to discuss corrosion mechanism involved.

## EXPERIMENTAL PROCEDURE

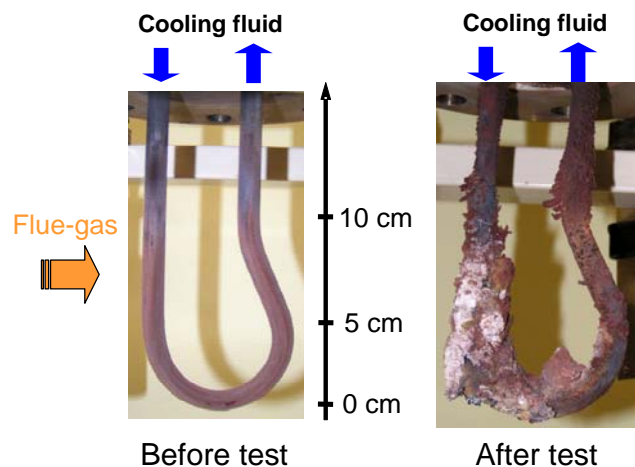
The laboratory scale pilot, describe elsewhere [16], is composed of a gas burner, a combustion chamber, a corrosive species injection device, a cooled metallic tube sample and a wet gas cleaning-up device (Fig. 1). The material to be tested is

a cylindrical pin shaped tube (Fig. 2). A thermal fluid circulates inside this tube to cool the tube and the monitoring system reproduces accurately the gradient temperature at flue gas / tube interface. The velocity of flue gas (gas and ashes) is ensured by the gas burner. Thus, corrosion tests with T<sub>gas</sub> ≠ T<sub>tube</sub> conditions are possible.



**Fig. 1 Drawing of the corrosion lab scale pilot**

In the present study, test duration is fixed at 48 hours and the SA192 carbon steel tested is commonly used as superheater tube. Flue gas temperatures investigated range from 450 to 850°C while the metal temperature is fixed at 400°C. After each corrosion test, deposited sample are embedded in a cold resin. Sections localised at 5, 6 and 7 centimetre from the bottom of the pin shaped sample (Fig. 2) are prepared for metallographic analysis [16]. Flue gas temperature recorded close to each section are reported in the table 1.



**Fig. 2 Sample and cross section preparation**

During all corrosion tests, the concentration of aqueous HCl solution introduced in the flame is calculated to maintain a  $O_2$  and  $H_2O_{(g)}$  content in combustion gases respectively around  $11 \pm 2\%$  and  $19 \pm 2\%$  (vol.%). Partial pressures of HCl and  $SO_2$  are fixed to maintain a HCl/ $SO_2$  ratio equal to 10. Partial pressures of gases ( $O_2$ , HCl,  $SO_2$ ,  $H_2O$  and  $CO_2$ ), gas velocity are quantified for each test.

**Table 1 : Flue gas temperature close to tube section analyzed.**

Test temperature (°C)	450	650	850
$T_{flue\ gas}$ at level 5 (5cm)	457	654	851
$T_{flue\ gas}$ at level 6 (6cm)	441	638	835
$T_{flue\ gas}$ at level 7 (7cm)	386	616	795

Three types of synthetic ashes are considered (Table 2). All of them are free of heavy metal. Ash 1 is free of chlorine and contain only sulphate salts while the Ash 2 and 3 contain different mixture of alkali sulphate and alkali chlorine.

**Table 2 Chemical composition of synthetic ashes used**

Constituents (wt.%)	Ash 1	Ash 2	Ash 3
$K_2SO_4$	7	5	5
$Na_2SO_4$	7	5	5
KCl	0	5	20
NaCl	0	5	20
$2SiO_2-Al_2O_3$	27	25	25
$Fe_2O_3$	7	5	5
$CaSO_4, 2H_2O$	52	50	20

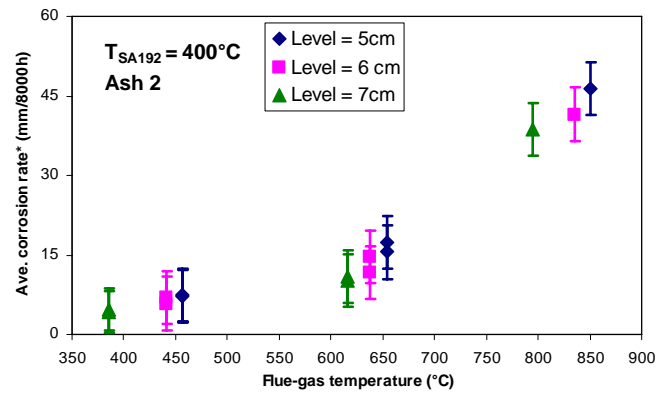
After corrosion test, tube thickness loss is measured to estimate corrosion rates, following the procedure described elsewhere [16] using a microprobe SX50. SEM observations and EDS analysis are performed to identify and localise the element in the corrosion layers.

## RESULTS

### Effect of flue gas temperature

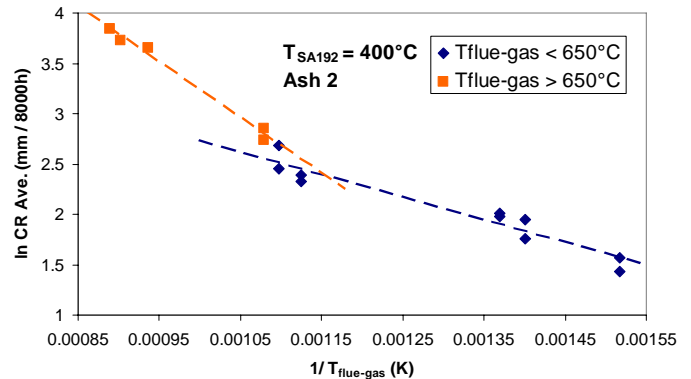
Average corrosion rate ( $CR_{Ave.}$ ) is estimated, for 8000 hours of operation per year, on the basis of a linear extrapolation of the average metal loss measured on the whole circumference of the tube after 48 hours. The  $CR_{Ave.}$  estimated for each section of each test performed with Ash 2 is presented on Fig. 3. Corrosion test performed twice at  $650^\circ C$  confirm the accuracy and reproducibility of the results. For metal temperature fixed at  $400^\circ C$  the  $CR_{Ave.}$  increased with flue gas temperature.  $CR_{Ave.}$  seems to follow an exponential acceleration with flue gas temperature. Nonetheless, Arrhenius plots of results (Fig. 4) indicate that 2 different kinetic stages are involved respectively

at flue gas temperature below  $650^\circ C$  and above  $650^\circ C$ . Mechanisms involved above  $650^\circ C$  present a higher activation energy demonstrating the acceleration of corrosion observed on Fig. 3.



\* calculated from metal loss after 48h

**Fig. 3 Average corrosion rate versus  $T_{flue\ gas}$  with Ash 2**

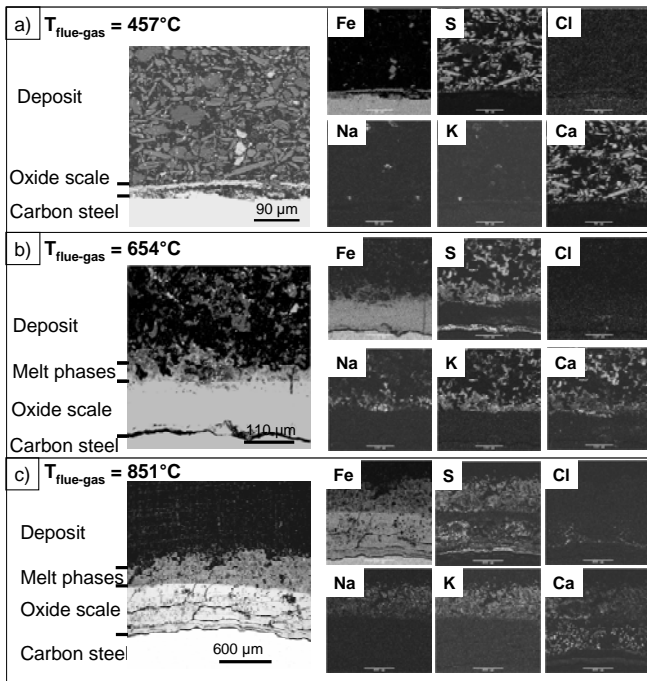


**Fig. 4 Arrhenius plots of  $CR_{Ave.}$  obtain with Ash 2**

Fig. 5 illustrates the morphology of the corrosion scales observed by SEM after 48 hours of corrosion test performed with ash 2. At low temperature ( $T_{flue\ gas} < 650^\circ C$ ), corrosion scale is constituted of mixed iron oxide scale ( $Fe_2O_3 + Fe_3O_4$ ) coated by ash particles deposit. Presence of iron sulphur mixed with iron oxide is also detected at the interface between metal and oxide scale. No trace of chlorine is detected within the oxide scale or the ash deposit. Alkali chlorides initially present in ashes are probably sulphated by  $SO_2(g)$  present in flue gas. At high temperature ( $T_{flue\ gas} > 650^\circ C$ ), iron sulphur is also identified and the oxide scale is mainly formed by hematite ( $Fe_2O_3$ ). With Ash 2, all test performed at  $850^\circ C$  revealed the presence of fused phase scale (Na, K, S) between the deposit and the protective oxide scale. This points out that melting point of ash had been reached and consequently that protective oxide scale should be dissolved by fluxing mechanism. On sample tested at  $650^\circ C$ , fused phase scales were occasionally observed. Melting point of ashes should be around this

temperature and local conditions probably promote or not the fusion.

Traces of chlorine were detected at the metal / oxide interface and within the oxide scale but no pitting was observed at metal oxide interface with ash 2 and HCl/SO<sub>2</sub> ratio = 10.



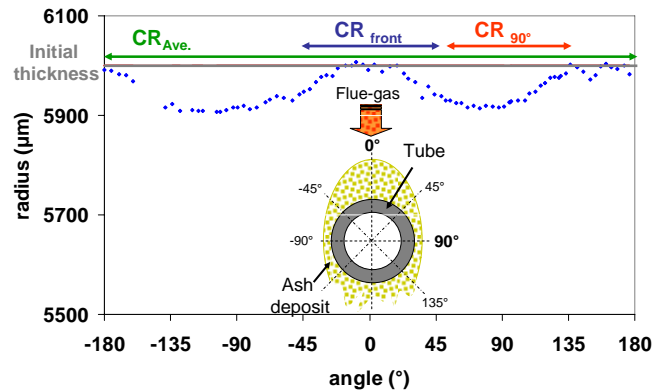
**Fig. 5 Morphology of corrosion scale formed at 457°C (a) 654°C (b) and 851°C (c).**

Commonly, the corrosion scales are poorly adhesives and incidence of cracks of the protective oxide scale increase with flue gas temperature and oxide scale thickness (Fig. 5b and Fig.5c). At 850°C the oxide scale is layered with corrosive species (Cl, S, Ca) intercalated.

### Flue gas flow and local corrosion relationship

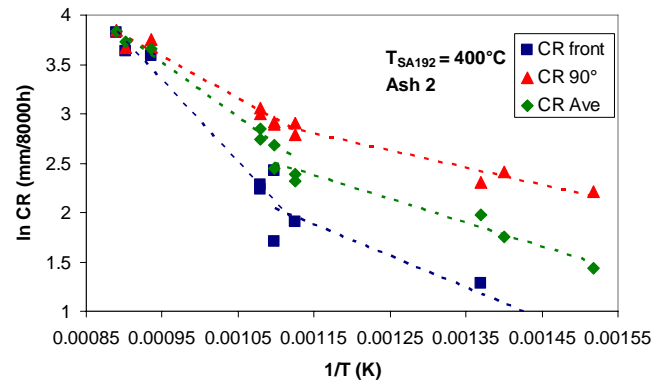
Previous results show that  $CR_{Ave}$  depends mainly on flue gas temperature nevertheless SEM observations point out, particularly at 650°C, that corrosion scale sequence could differ from one position on the tube to another. Hence, metal loss measurements had been examined in regards with the highest deposit crest located at 0° versus flue gas flow direction. This demonstrates that corrosion is not uniform and new local corrosion rates are determined.  $CR_{front}$  and  $CR_{90^\circ}$  are associated respectively to the average value measured from -45° to +45° and from +45° to 135° (Fig. 6) while  $CR_{Ave}$  is the average of all the thickness measurement. For all the test temperature, the tube is attacked all around the tube but  $CR_{front}$  is lower than  $CR_{90^\circ}$ . The most corroded area is located at ± 90° from the crest of the deposit (Fig.7). Nevertheless, this distinction between

local corrosion rate and average corrosion rate is less apparent at temperature above 650°C.



**Fig. 6 Distribution of metal loss around tube**

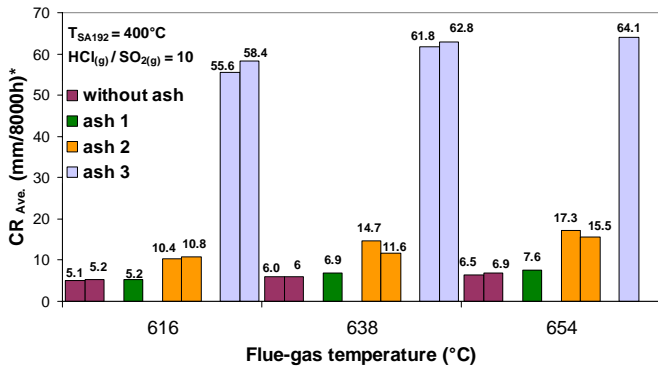
Accordingly, flue gas flow direction influence ash deposit morphology and the corrosion rate. Corrosion mechanisms involved at high temperature seems to be less sensitive to deposit morphology and more homogeneous.



**Fig. 7 Arrhenius plots of local corrosion rate**

### Effect of ash phase composition

The following experiments are conducted to investigate the effect of presence of ashes on corrosion rate as well as the effect of their composition, particularly the amount of chloride (Fig.8). As previously, results are quite reproducible and  $CR_{Ave}$  increase with flue gas temperature in presence or not of ash 1, 2 or 3. Average corrosion rates reported for test without ash or with ash free of chlorine (Ash 1) are similar and quite low compare to  $CR_{Ave}$  obtained with ash 2 and 3 (Fig.8). With ash 2 containing 10% of alkali chloride (wt.%),  $CR_{Ave}$  are twice the one obtained with free chlorine ash (Ash 1) and more than 4 time lower than the one measured with ash 3 containing 40% of alkali chloride.



**Fig. 8 Effect of ash composition on corrosion rate**

Fig. 9 illustrates the morphology of the corrosion scales formed after 48 hours of corrosion test performed at 650°C. In presence of ash 1, the ash deposit formed on the top of the protective oxide scale ( $\text{Fe}_2\text{O}_3$ ) is not fused. A layer of iron sulphate  $\text{Fe}_2(\text{SO}_4)_3$  is detected at this interface. As with ash 2, iron sulphur is detected at the metal/oxide interface. With ash 3, a large scale of fused phase containing chlorine is systematically observed while sporadic and partially melted phase is observed with ash 2. In addition, presence of  $\text{FeCl}_2$  and pitting are observed at the metal oxide interface with ash 3. This confirms that active oxidation is promoted with deposit containing high alkali chloride content. Chlorine still analysed in the unfused deposit indicating that  $\text{SO}_2$  contained in the flue gas cannot react with all the alkali chloride. The remaining chlorine contained in the deposit should act as reservoir of corrosive species in case of further sulphatation reactions.

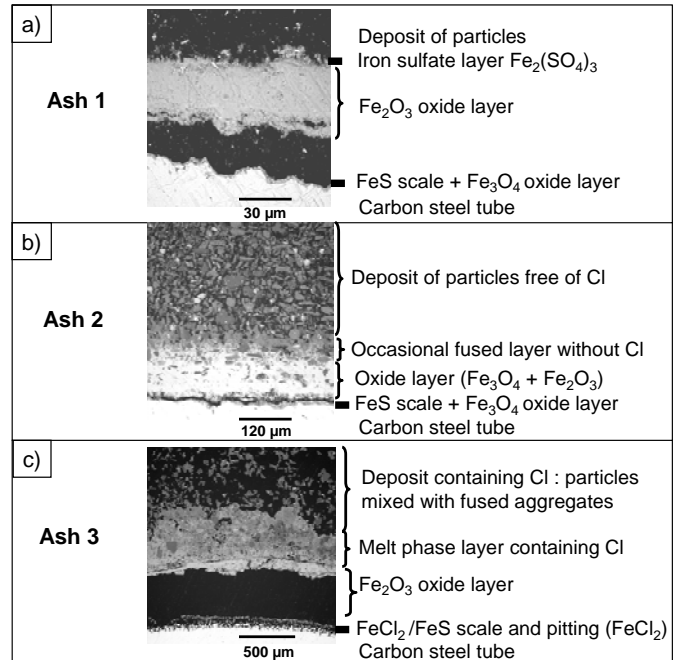
## DISCUSSION

Phenomenons currently observed on boiler tube, such as built up of deposit, cracks formation and penetration of corrosive species into a corrosion interface, are closely reproduced simulating the flue gas velocity and flue gas / tube temperature gradient.

Corrosion rate values extrapolated for 8000 hours and obtained from short duration test should be considered carefully, i. e. as relative value, because the linear hypothesis used for extrapolation is probably erroneous. Nonetheless, Krause [17] reported similar corrosion rates using a cooled corrosion probe in comparable conditions in a MSWI facility.

As expected at fixed metal temperature ( $T_{\text{metal}} = 400^\circ\text{C}$ ), the corrosion rate increases with flue gas temperature. Simultaneous corrosion mechanisms are implicated and corrosion acceleration observed at high temperature suggest that two different kinetic stages can be differentiated below and above  $T_{\text{flue gas}} = 650^\circ\text{C}$ . At  $T_{\text{flue gas}}$  above  $650^\circ\text{C}$ , higher corrosion rates measured are probably associated simultaneously to :

- the formation of molten phase above the protective oxide scale supporting iron oxide protective scale dissolution by “fluxing” [8, 9],
- the acceleration of the kinetic of sulfatation of alkali chloride above  $650^\circ\text{C}$  [18] that promotes induced deposit corrosion and “active oxidation” [4, 7].

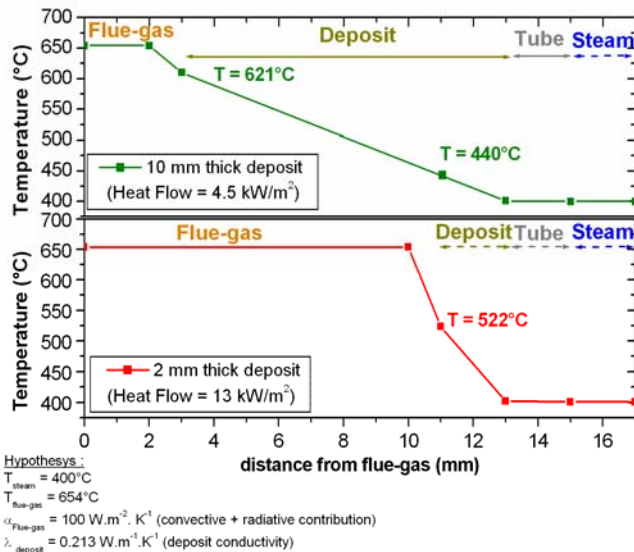


**Fig. 9 Effect of ash composition on corrosion rate at 654°C**

It is clearly demonstrated that alkali chloride amount in ash is a key factor on corrosion rates. Formation of eutectic compounds with lower melting temperature will enhanced fluxing mechanism at lower flue gas temperature. On the other hand, Pykkonen et al. [7] demonstrate that sulphatation of alkali chloride will be limited by  $\text{SO}_2$  transport and concentration close to the deposit. This can explain the remaining chlorine detected in deposit and oxide scale with chlorine rich ash (ash 3).

Finally, the present experiments point out that position of tube in regard with flue gas flow direction and the resulting deposit morphology also affect corrosion rates. Anderson et al. [19] demonstrate that deposit morphology, and particularly deposit thickness does affect strongly the formation of the protective scale. Corrosion rate increases up to about 1 mm of deposit and decrease for thicker deposit. Noguchi et al. also report that the corrosion rate increases with flue gas flow [20]. Thus, the flue gas flow pattern can explain that the preferential attacks were mainly observed at  $\pm 90^\circ$  from the crest deposit (Fig. 10). Similar behaviour had been observed in MSWI boiler on parallel flue gas flow superheater bundle tubes [11].

Furthermore, the lower thickness observed at 90° from flue gas flow related to erosion of deposit will affect heat transfer and increase temperature locally close to the metal / oxide interface. Fig. 10 show an example of the effect of thickness deposit on heat flow transfer estimated, as first approximation, using empirical conductive law. This example illustrates how the thickness of deposit affects the temperature within the deposit close to the metal / oxide interface. Higher temperature reached near to the interface when deposit is thinner will promote thermally activated corrosion mechanism.



**Fig. 10 : Example of temperature profile form flue gas side to steam side**

Nevertheless, results indicate that dependence of corrosion rate with flue gas flow pattern is less significant when temperature increase above 650°C while molten phase amount was higher. In this case, according to Anderson et al. study [19] the melt phases are supposed to fill the pores of the deposit, and thus hinder transport of gaseous corrosive species. Consequently, the effect of thickness deposit observed at lower temperature is counterbalanced at high temperature by the presence of molten phase that reduce permeability of deposit to corrosives gases. On the other hand, transport of corrosive gases and molten phase will be promoted by oxide scale cracks propagation observed above  $T_{\text{flue gas}} = 650^{\circ}\text{C}$ .

## CONCLUSION

The present results demonstrated that the corrosion lab-scale pilot is an effective test method to reproduce fireside corrosion phenomenon of heat exchanger tube materials in presence of thermal gradient and simulated MSWI flue gas (gas and ash).

The following results are established, for carbon steel tube at tube temperature fixed at 400°C and HCl(g)/SO<sub>2(g)</sub> ratio fixed to 10.

- i) The corrosion rate of carbon steel is governed by flue gas temperature. Kinetics of corrosion is accelerated above  $T_{\text{flue gas}} = 650^{\circ}\text{C}$ . It is partially explained by formation of molten phase and sulfatation of alkali chloride promoted at high temperature.
- ii) Deposit containing alkali chloride accelerates significantly the corrosion. Composition of ash will modify deposit composition and melting point. Low eutectic compound formation is promoted and favored accelerated corrosion rate at lower temperature.
- iii) The flue gas flow pattern modifies locally the deposit morphology and the local corrosion rate. Corrosion is promoted at  $\pm 90^{\circ}$  from the crest deposit, in the lower thickness deposit zone. Higher flue gas velocity and temperature close to the metal/oxide interface support this observation.
- iv) At high temperature ( $T > 650^{\circ}\text{C}$ ), relation between local corrosion rates and flue gas flow pattern is less important. Modification of the deposit permeability by molten phase is expected to modify transport of corrosive species.

Further investigations, will consist to apply this short duration test procedure on different materials to compare their corrosion rates. Higher metal temperature will also be investigated to identify resistant and cost effective tube materials able to be used to increase WtE condensing turbine efficiency.

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