

Fireside Corrosion of Superheater Materials in Chlorine Containing Flue Gas

T. Valente

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Corrosion resistance of three types of candidate materials for superheater sections under simulated waste incineration conditions was evaluated. A 9Cr1Mo steel, an AISI 310SS, and the Ni-based alloy Sanicro 28 were tested on a laboratory and on a pilot scale with different flue gas compositions (up to 2500 mg/Nm³ of HCl and 1500 mg/Nm³ of fly ash). Laboratory tests were carried out in a furnace up to 200 h. Metal and gas temperature were kept constant at 500 °C. Pilot scale tests were carried out by using a 0.3 × 0.3 m cross-sectional combustor, with flue gas velocity of 5 m/s. Air-cooled probes, designed to operate at a metal temperature of 500 °C and facing gas temperatures as high as 600 °C, were used for 200 h as maximum test time. Qualitative correspondence was found between results obtained by the two sets of experimental tests, but quantitative values were not comparable. Metallographic evaluations, metal loss measurements, and weight loss analysis evidenced as the most suitable alloy Sanicro28. Maximum metal loss observed was 240, 182, and 107 μm, respectively, for 9Cr1Mo, AISI310SS, and Sanicro 28 under the most aggressive conditions. Intergranular corrosion attack was evidenced for AISI310SS, limiting the choice of materials to 9Cr1Mo and Sanicro 28, depending upon the lifetime expected at the design stage.

Keywords 9 Cr1 Mo Steel, fireside corrosion, Sanicro 28 steel, type 310 stainless steel

1. Introduction

Nowadays, environmentally friendly managing systems for waste incineration plants are one of the major topics of concern. Modern flue gas cleaning equipment can meet very strict emission requirements, and, if heat or power is generated from incineration, alternative fuels are saved and waste incineration becomes a more attractive economical possibility. Household waste contains a number of different compounds that are very corrosive to the boiler tubes (evaporators and superheaters). Since material performance is strictly related to steam and flue gas temperatures, additional information on corrosion behavior of candidate metal alloys is needed for selecting materials to design new plants with higher operating temperatures. The type and extent of corrosion depends markedly on metal temperature and on the waste being burnt. When a high amount of plastics are burnt (*i.e.*, refuses containing PVC), chlorination seems to cause a major corrosion problem.^[1–6] Metal chlorides and oxychlorides are formed, which are generally nonprotective and tend to evaporate because of their high vapor pressure.^[7–10] In addition, attack by ashes, metal compounds, and alkali salts, which condense on the boiler tubes, can play an important role in corrosion attack.^[11–14] With these operating conditions, a proper selection of materials to be used in the high-temperature sections represent a very important item to reduce the risk of corrosion failures, taking into account also that material costs represent only a fraction of the entire component design and fabrication costs. This paper focuses on the evaluation of the

reliability of results obtained by means of simplified laboratory testing with respect to more realistic pilot scale testing,^[15] carried out to obtain experimental data for materials selection based on corrosion behavior in chlorine containing flue gas.

2. Materials and Testing Methods

Materials selected for the experimental program were a ferritic steel 9Cr1Mo (9Cr), an austenitic low carbon stainless steel AISI 310SS (310), and the Ni-Cr alloy Sanicro 28 (S28). Two test methodologies were adopted: (a) isothermal tests in a laboratory furnace with planned flue gas composition and low gas velocity (cm/s); and (b) tests on a fluidized bed combustor with selected gas composition and velocity of 5 m/s.

In both cases, solid sodium chloride particles and fly ashes were added to the aggressive gas environment. For case (a), they were placed in direct contact with all the specimens; and, for case (b), they were injected in the flue gas. Fly ashes were previously collected by an incineration plant working with municipal solid wastes; sodium chloride was used since the flue gas cleaning system to be realized on the real plant had to be based on a sodium compound as the absorbent medium. The solution was studied in order to minimize the release of airborne gaseous chemicals such as hydrogen chloride to the environment, which is one of the many components of the so called “acid rain.”^[16] All the controllable testing parameters were selected to be as close as possible to real operating conditions.

In case (a), samples were cylindrical specimens (8 mm diameter, 10 mm height). Before testing, they were measured with a digital micrometer, weighted, cleaned with acetone, and then placed in a ceramic crucible together with fly ashes and sodium chloride. After testing, all samples were weighted again and two for each type of tested materials were resin embedded and polished for metal loss measurements by scanning electron microscopy. Two test times were selected: 100 and 200 h.

T. Valente, Department of Chemical and Materials Engineering, Rome University “La Sapienza,” Via Eudossiana, 18-00184 Rome, Italy. Contact e-mail: teodoro.valente@ingchim.ing.uniroma1.it.

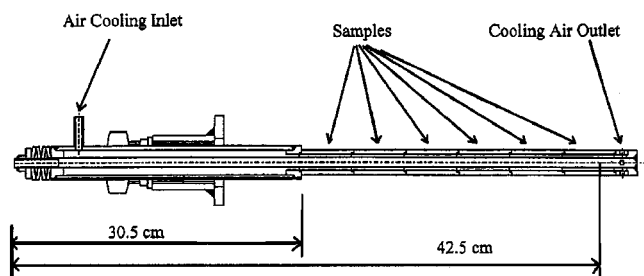


Fig. 1 Details of probe design

In case (b), a suitable probe design was adopted (Fig. 1) in order to operate at a constant metal temperature of about 500 °C. Each probe was independently supplied with cooling air; the air flow rate was measured on a rotameter and thermocouples were located at the interface between the probe body and first test specimen, to ensure the specified temperature was maintained during the test period. The selected flue gas temperature was 600 °C. Each probe was designed to carry on six specimens, and three probes were inserted into the combustor in well-defined locations, where test conditions were met. Each specimen was weighted before testing and measured at six different radial positions before being assembled on the probe carrier. Prior to assembly and measurements, samples were also cleaned with acetone to ensure that surfaces were free from dirt and grease. Four testing times were selected (20, 70, 130, 180, and 200 h). After each test, specimens were removed by the probe, weighted, and characterized by optical and scanning electron microscopy (energy dispersive spectroscopy included, SEM-EDS) and x-ray diffraction. A process and instrumentation diagram of the fluidized bed combustor is reported in Fig. 2. Main testing parameters for cases (a) and (b) are summarized in Tables 1 and 2.

3. Results and Discussion

Laboratory Tests

Corrosion behavior was studied in terms of metal loss measurements, weight changes, and microstructural investigations. The SEM metal loss measurements were affected by wide scattering, so that they were considered not really significant. Weight loss data (Fig. 3) allowed more consistent considerations: a significant difference between values measured after test 1 and after tests 2 and 3 was observed. Scattering for results of test 1 was the highest. The best behavior was obtained with S28, followed by 310 and 9Cr.

Test 1, with 2500 mg/Nm³ of HCl, represented the most aggressive environment. For 310 and S28 (materials with higher content of Cr and Ni), the difference among test 1 and tests 2 and 3 was very relevant after 200 h of exposure time: weight loss values reduced to about 40 and 20% of those measured after test 1. These results were consistent with the existence of a threshold value for HCl concentration of about 200 mg/Nm³ to rapidly accelerate the corrosion attack^[4] and also indicated that corrosion, for low HCl values, was essentially controlled by underdeposit attack due to the presence of solid fly ash and

NaCl. Only for 9Cr, less resistant to corrosion attack, is the difference among various tests always significant; less damage was still obtained with lower HCl concentration in the flue gas. The previous analysis has to be integrated with the results of microstructural characterization. Particular weight loss data obtained for 310 must be considered with great attention, because intergranular corrosion was revealed as evidenced in the metallographic section shown in Fig. 4.

Pilot Scale Tests

For each run and exposure time, average values of weight loss are reported in Fig. 5 to 7. As a general consideration, again test 1, with the highest concentration of HCl in flue gases, represented the most aggressive environmental condition. Starting from 70 h exposure time, a significant difference in weight loss was evidenced between test 1 and tests 2 and 3. Taking into account the calculated standard deviations, the possible threshold value of about 200 mg/Nm³ for HCl concentration was confirmed. Metal loss results after 200 h showed as maximum corrosion attack 240, 182, and 107 μm, respectively, for 9Cr, 310, and S28 under the most aggressive conditions. For 310, evident signs of intergranular corrosion attack were revealed. A comparison between results obtained in laboratory tests and those related to pilot scale experiments evidenced that laboratory tests gave an underestimation of corrosion attack, in particular, for test 1, when corrosion mechanisms were essentially dominated by the gas phase. Lower values were also obtained when spalling of corrosion products was observed on the pilot test as for 9Cr in tests 2 and 3. Metallographic analyses and SEM-EDS evaluations of the corrosion scale (morphology and composition) were consistent with a main damaging mechanism due to the formation of metal chlorides (mainly iron chlorides) for test 1 and oxychlorides and underdeposit attack for tests 2 and 3, as also confirmed by x-ray diffraction patterns on corrosion scales. Figures 8 and 9 show a cross section of sample 9Cr (test 2 for 200 h) and the elemental maps for Cl and Fe taken of the same area. Because the corrosion scale was composed of an outer layer (very rich in Cl due to solid deposits), an intermediate layer, and an inner layer (respectively rich in Fe and Cl), in agreement with the formation of metal chlorides, iron oxide and oxychlorides were also observed. Similar consideration can be made for 310 and S28, but a retained quantity of Cl in the scale decreased as Cr and Ni content of the material increased. In addition, for test 1, a porous and nonprotective scale was formed for all the three types of materials tested.

The results can be explained according to the cyclic oxidation model^[11,17-19] without excluding the eventual formation of the FeCl₃ compound not detected due to its higher vapor pressure with respect to FeCl₂.

No pitting corrosion was observed, but a combination of uniform wastage and erosion corrosion was revealed. The predominant attack was uniform wastage, particularly on the side facing the flue gas direction, suffering of direct impingement.^[10] In order to have a possible estimation of corrosion attack for exposure times higher than 200 h, experimental data were used for a regression analysis, in the cases of a supposed linear-parabolic kinetics (attack due to oxidation and metal chloride

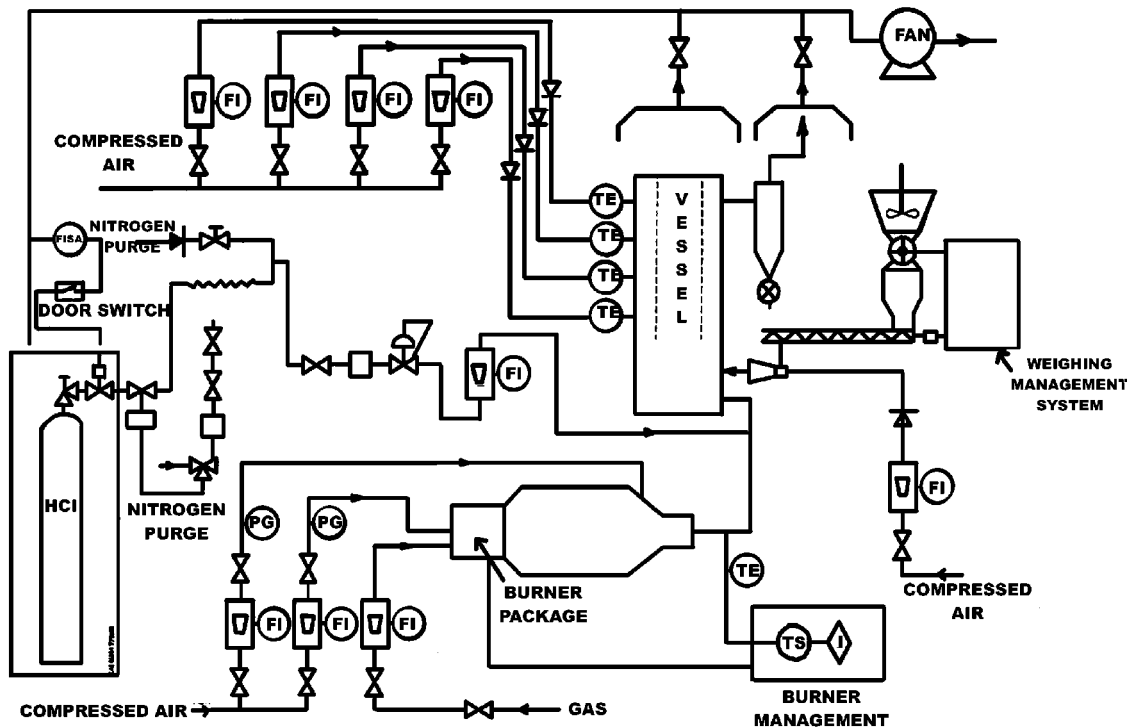


Fig. 2 Process and instrumentation diagram of the combustor, solids feeder, and HCl injection

Table 1 Testing conditions for laboratory investigations

Test run	Flue gas composition in addition to 9% O ₂ , 11% CO ₂ , 9% H ₂ O, N ₂ rem	Testing time (h)	Materials and number of specimens tested	
1	HCl 2500 mg/Nm ³	100	9Cr	6
			310	6
			S28	6
		200	9Cr	6
			310	6
			S28	6
2	HCl 200 mg/Nm ³	See test 1	See test 1	See test 1
3	HCl 20 mg/Nm ³	See test 1	See test 1	See test 1
Other conditions		Flue gas temperature 500 °C Materials (specimens) temperature 500 °C Fly ash, NaCl in contact with all tested specimens		

formation with evaporation, Eq I) and parabolic kinetics (oxidation attack, Eq II). The basic models are as follows:

$$d(WL)/dt = Kp/WL + K_v \quad (\text{Eq 1})$$

$$d(WL)/dt = Kp^*/WL \quad (\text{Eq 2})$$

with WL = weight loss and Kp and K_v = constant for parabolic and linear kinetic. Results should be used with care since some hypotheses are needed for the extrapolation procedure,^[20] such as uniform wastage, constant operating conditions, no acceleration of corrosion attack due to spalling phenomena or molten compounds,^[12,13] and no reduction of corrosion attack due to formation of a protective scale. With these assumptions, linear and parabolic extrapolated curves

are reported in Fig. 11 to 13. Adjusted R^2 values for the regression curves ranged from a minimum of 0.81 to a maximum of 0.99. A linear-parabolic kinetic represented the best fitting condition for all materials in test 1 and for 9Cr and 310 for test 2; in all other cases, a parabolic kinetic gave the best fitting results. With the estimated models, predicted corrosion attacks for 1 year of operation were prohibitive for all materials tested with 2500 mg/Nm³ HCl in flue gas (>5 mm/y for linear-parabolic and 1.0 to 1.5 mm/y for parabolic) and they reduced to 0.2 to 0.5 mm/y for 250 mg/Nm³ HCl in flue gas. The best behavior was obtained with S28 (about 0.20 mm/y for tests 2 and 3). A comparison among values obtained with the model and data related to exposure in real waste incineration plants (Högdalen incinerator^[14]) and other literature data^[4,9,11,21-23] gave good results up to 1000 h.

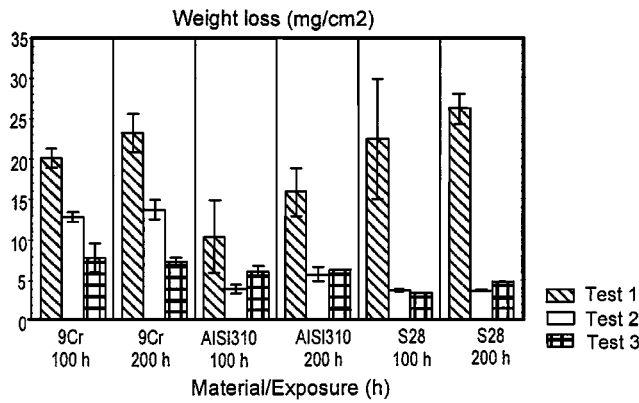


Fig. 3 Weight loss results after laboratory tests

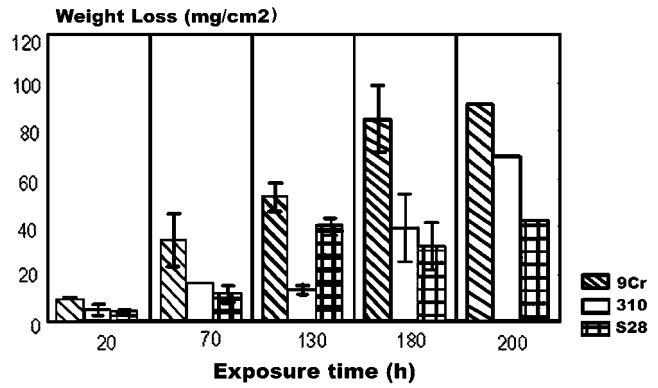


Fig. 5 Test 1—weight loss vs exposure time

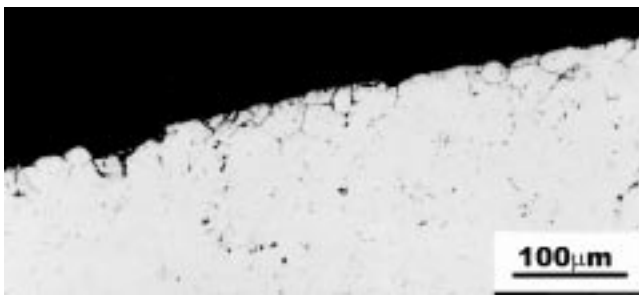


Fig. 4 AISI 310—test 2 after 200 h (chemical etching HNO₃-acetic acid HCl-glycerol, 30 s)

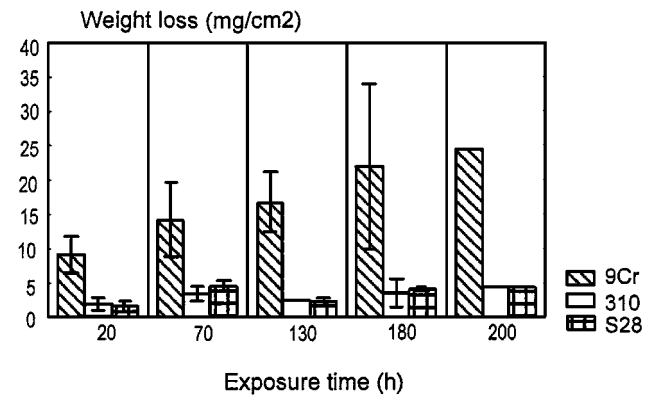


Fig. 6 Test 2—weight loss vs exposure time

Table 2 Testing conditions on the 0.3 × 0.3 combustor

Test run	Flue gas composition in addition to 9% O ₂ , 11% CO ₂ , 9% H ₂ O, N ₂ rem	Testing time (h)	Order of specimens in the probes						
1	Fly ash 1500 mg/Nm ³ HCl 2500 mg/Nm ³	20	9Cr	310	S28	9Cr	310	S28	
		70	310	S28	9Cr	310	S28	9Cr	
		130	310	S28	9Cr	310	S28	9Cr	
		180	9Cr	310	S28	9Cr	310	S28	
		200	S28	9Cr	310	S28	9Cr	310	
2	Fly ash 250 mg/Nm ³ HCl 200 mg/Nm ³ NaCl 250 mg/Nm ³	See test 1	See test 1						
		See test 1	See test 1						
3	Fly ash 250 mg/Nm ³ HCl 20 mg/Nm ³ NaCl 250 mg/Nm ³	See test 1	See test 1						
		See test 1	See test 1						
Other conditions		Flue gas temperature 600 °C Materials (specimens) temperature 500 °C Flue gas velocity 5 m/s							

4. Conclusions

Laboratory tests and pilot scale tests were carried out on three candidate materials for waste incinerator superheaters, 9Cr1Mo, AISI310SS, and Sanicro 28, for a total testing time

of 200 h and with particular concerns about chlorination. Qualitative correspondence was found between the two sets of experimental tests. Quantitative results were not comparable and pilot scale tests were more indicative of real material behavior. In the adopted testing condition, for high HCl content in flue gas,

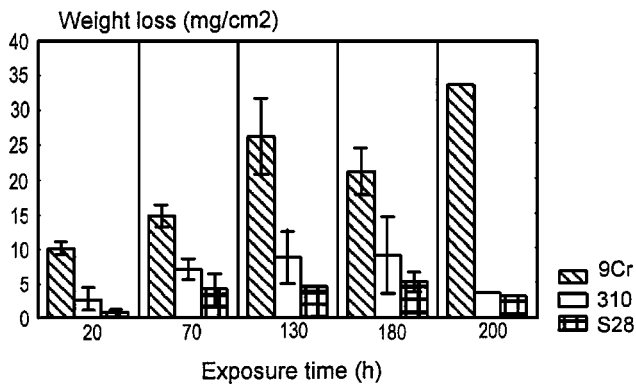


Fig. 7 Test 3—weight loss vs exposure time

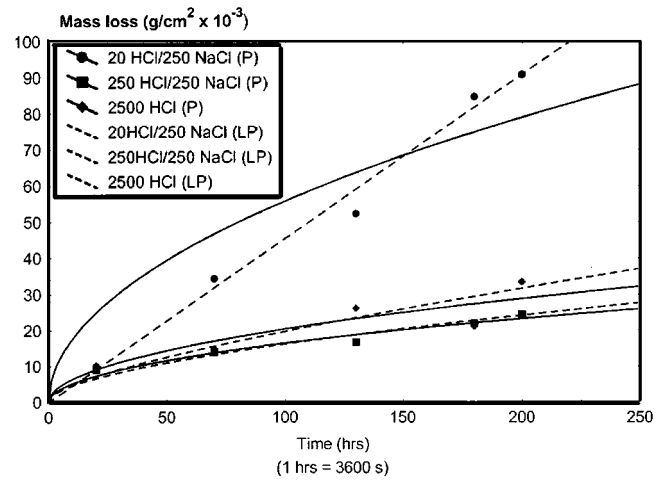


Fig. 11 Linear-parabolic (LP) and parabolic (P) kinetic regression curves for 9Cr (all testing conditions)

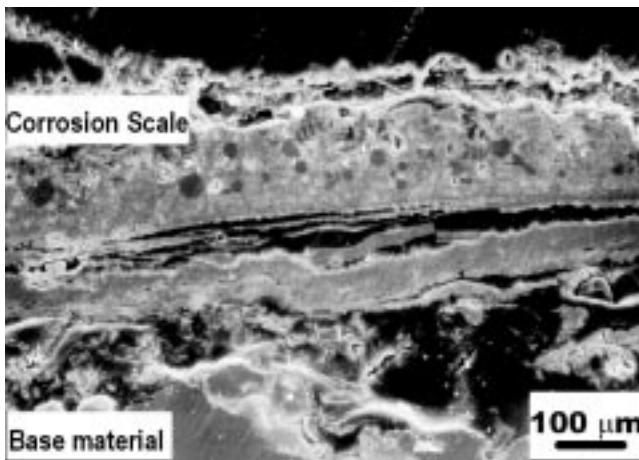


Fig. 8 Cross section of sample 9Cr after 200 h testing (test 2, SEM image)

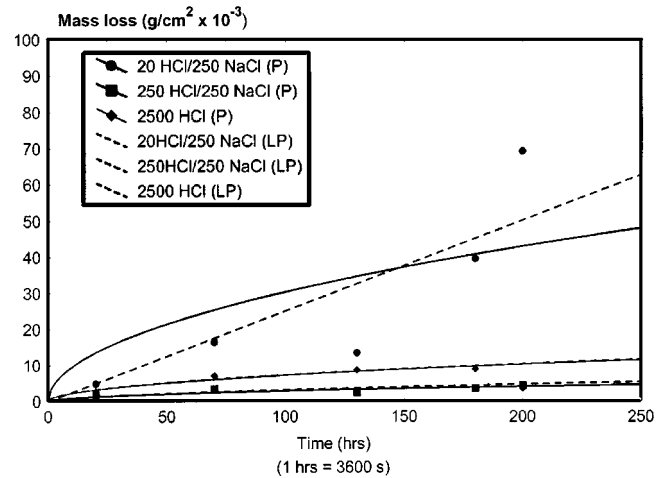


Fig. 12 Linear-parabolic (LP) and parabolic (P) kinetic regression curves for 310 (all testing conditions)

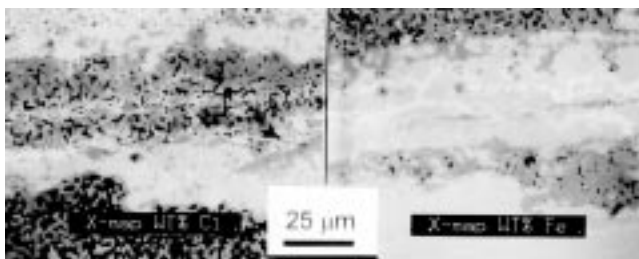


Fig. 9 Elemental mapping of Cl and Fe (wt.%) on a cross section of sample 9Cr after 200 h testing (test 2)

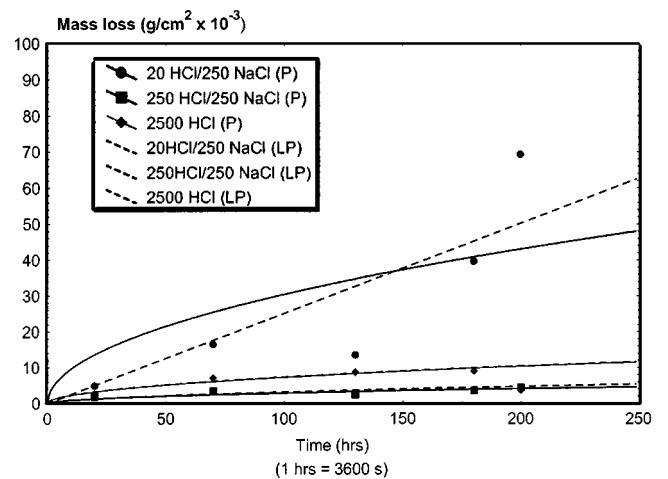


Fig. 13 Linear-parabolic (LP) and parabolic (P) kinetic regression curves for S28 (all testing conditions)

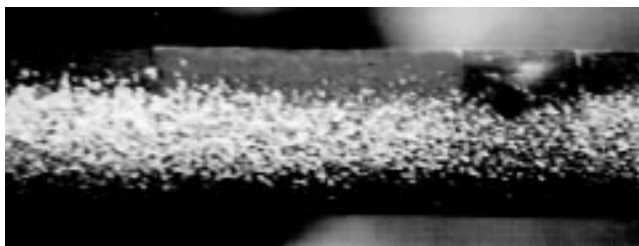


Fig. 10 Deposit built up on probe side directly exposed to flue gas after 70 h

iron chloride formation and evaporation are the main damaging mechanisms. With HCl concentration values higher than about 200 mg/Nm³ and a material temperature of 500 °C, the kinetics of the corrosion attack was linear rather than parabolic. In this case, in addition to metal chloride evaporation, the formed surface scale resulted which was also porous and nonprotective. The high chromium content (without σ phase formation) and the high nickel content in materials selected significantly reduced the corrosion attack, due to the higher vapor pressure of iron chlorides and to the tendency of chromium to form protective oxides up to 500 °C. This aspect explains the good results obtained with the alloy Sanicro 28, which showed a reduction of about 100% in metal loss with respect to the ferritic steel 9Cr1Mo. AISI310SS had an intermediate behavior, but the evidence of intergranular corrosion should induce care for selection of this material in terms of component structural integrity.

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