

HIGH TEMPERATURE CORROSION RESISTANCE OF METALLIC MATERIALS IN HARSH CONDITIONS

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Abstract

Highly efficient energy recovery from renewable sources and from waste incineration causes new problems of corrosion at high temperature. A similar situation exists for new recycling processes and new energy storage units. These corrosions are generally considered to be caused by ashes or molten salts, the composition of which differs considerably from one plant to another. Therefore, for the assessment of corrosion-resistance of advanced materials, it is essential to precisely evaluate the corrosion rate under conditions close to industrial conditions. To be able to advise their customers in selecting the right material or the right protective coating, the present authors are developing testing equipment and related procedures to assess the high temperature corrosion rate of metallic materials. This paper describes the testing equipment developed so far and presents the first results obtained in two corrosive environments: the aggressive condensates that affect waste incinerators (mixture of liquid/solid salts in oxidising conditions) and heat transfer fluids of electric power generating plants based on solar towers (mixture of liquid salts). Temperatures range from 400 to 650°C. Tested materials include 16Mo3 (0.3% molybdenum steel alloy), Inconel 625 (austenitic nickel-chromium-based superalloys), Nickel 200, Ni-57CrMoSiB (nickel-base coating with high chromium content and boron as additional element) and Grade 91 (9% chrome- 1% molybdenum steel alloy).

Keywords: High temperature corrosion testing, Waste incinerator, Solar salt, 16Mo3, Inconel 625, Nickel 200, Ni-57CrMoSiB, Grade 91

1. Introduction

Highly efficient energy recovery from renewable sources and from waste incineration causes new problems of corrosion at high temperature. A similar situation exists for new recycling processes and new energy storage units. These corrosions are generally considered to be caused by ashes or molten salts, the composition of which differs considerably from one plant to another.

High-temperature corrosion in waste incinerators has been widely studied [1-4] as a lot of plants suffered from wall thinning due to corrosion. In these waste to energy plants, the temperature is generally kept low (around 450°C) to avoid corrosion problems [2, 3]. Persson et al. studied high temperature corrosion in a 65 MW waste to energy plant [2]. They observed that the corrosion rate increased when extra chlorine was added to the fuel mix and extensive corrosion losses were found, even at low temperature materials (320 to 460°C). Phongphiphat et al. studied the high-temperature corrosion in a large scale municipal waste-to-energy plant [3]. They found that both temperature and deposits greatly influenced

corrosion rates. Ni-based alloy had lower corrosion rates than Fe-based alloy but they were more prone to localised corrosion.

Molten salts are already used in concentrated solar power (CSP) plants and studies have been conducted on the corrosion of metals in these salts [5-9]. For example, Fernandez et al. studied the corrosion of stainless steels and low-Cr steel at 390 and 550°C in solar salt [5]. They discuss the changes that occur in steels and solar salt after test. McConohy et al. evaluated thermophysical property changes and corrosion of nickel alloys at 600 and 680°C [6]. The authors conducted experiments on the metals and salt mixtures and found that the high operating temperatures of CSP plants result in physical and chemical changes. Gill et al presented the design of their molten salt corrosion test vessel [8]. Their vessel can work at temperatures up to 700°C.

Corrosion and the accompanying diffusion of impurities induce measurable changes in the properties of the material and the deterioration of the function of the technical systems [10-11]. Therefore, for the assessment of corrosion-resistance of advanced materials, it is essential to evaluate precisely the corrosion rate under conditions close to industrial conditions. To be able to advise their customers in selecting the right material or the right protective coating, the present authors are developing testing equipment and related procedures to assess the high temperature corrosion rate of metallic materials.

Two versatile equipment were designed to simulate environments mainly encountered in practice at high temperature.

The first one makes it possible to test samples in specific gaseous atmosphere or to combine the action of molten salt with the interaction of gaseous chemical elements.

The second type consist in a set of small reactors that enable to carry out a great number of tests under a large variety of testing conditions simultaneously, provided temperature is the same.

This paper describes the testing equipment developed so far and presents the first results obtained in two corrosive environments: the aggressive condensates that affect waste incinerators (mixture of liquid/solid salts in oxidising conditions) and heat transfer fluids of electric power generating plants based on solar towers (mixture of liquid salts).

2. Horizontal tubular furnace with controlled atmosphere

2.1 High temperature testing equipment

The testing equipment makes it possible to test samples in specific gaseous atmosphere or to combine the action of molten salt with the interaction of gaseous chemical elements. It

consists in a commercial tubular furnace through which a gas mixture with a controlled chemical composition flows (Figure 1). The design and the construction of the gas blending installation were achieved by the Industrial Solutions Unit of CRM.

The furnace can operate up to 1500°C. It has a heated length of 300 mm divided into three zones each with its own temperature controller to improve uniformity. The worktube has an inner diameter of 50 mm and a length of 1500 mm, which reduces the temperature of both ends of the tube and makes it possible to attach gas tight end seals. The temperature of the tube is monitored throughout its length by 10 thermocouples protected by an Inconel liner. In this way, the temperature of the samples can be determined accurately.



Figure 1: Tubular furnace and instrumentation

The gas blending installation is made of 4 mass flow controllers that enable to fine tune the composition and the flow rate of the mixtures to be injected into the furnace (Figure 2). If necessary, atmosphere can be humidified by a direct injection of water into the hot area of the furnace. Corrosion of the gas supply line is thus prevented by this separate injection.

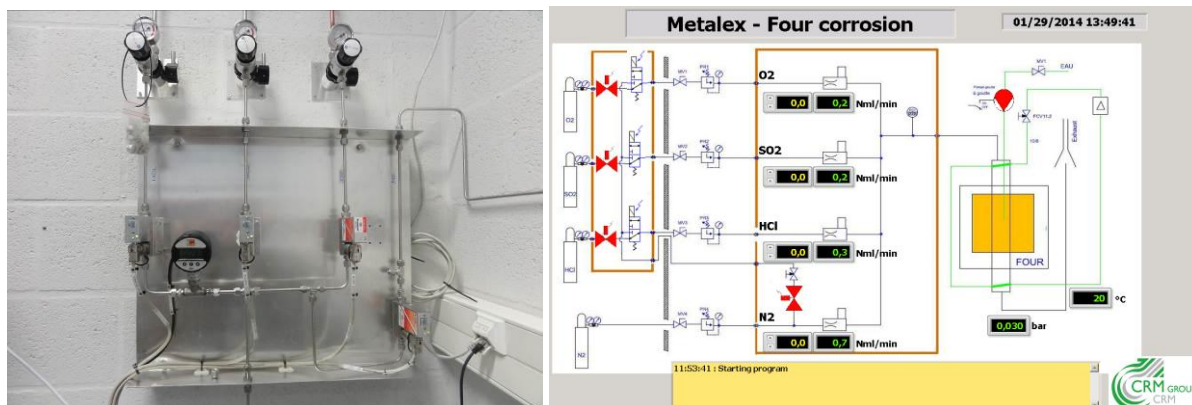


Figure 2: Gas blending installation

The complete installation is computer controlled through a graphic interface. It provides an automatic management of the temperature profile inside the furnace, the blending of gas and of security systems.

2.2 Trials in waste incinerator conditions

The tubular furnace was used to simulate the environment of the second path of the system that recovers the heat contained in the flue gases of a waste incinerator.

Table 1 summarizes the flue gas composition which is mainly made of nitrogen, water, carbon dioxide, oxygen and non-negligible amounts of hydrochloric acid and sulphur dioxide. The flow rate was adjusted so that the gas speed in the hottest area of the furnace was of 0.5 cm/s.

H ₂ O	18 % vol
O ₂	8 % vol
HCl	1000 or 1500 mg/Nm ³
SO ₂	150 or 300 mg/Nm ³
N ₂	Balance

Table 1: Gas composition

To test the samples under conditions that are most similar to real operating conditions, some of them were covered with ashes (Figure 3) taken from a municipal waste incinerator. A simplified chemical composition of ashes is given in Table 2.

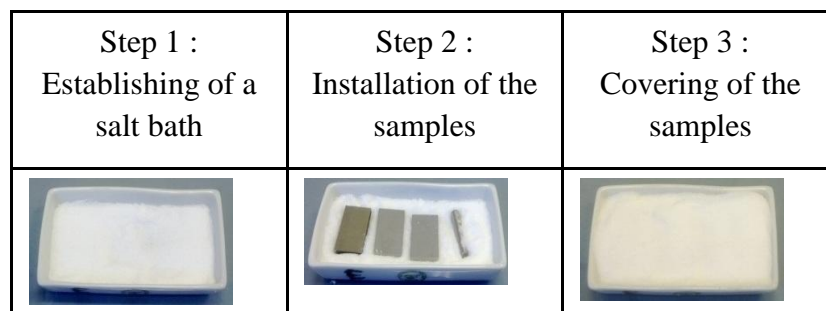


Figure 3: Establishment of the corrosion environment

	Al	Si	S	Cl	K	Ca	Zn	Pb
% wt.	1.1	2.9	8.2	3.6	4.1	27.9	2.6	0.5

Table 2: Ash composition

Three metallic alloys (Table 3) were subjected to the tests: 16Mo3, which is a carbon steel with improved creep resistance, Inconel 625, which is a nickel-based alloy increasingly used in waste incinerators and Nickel 200, which is an almost pure nickel grade.

	Fe	Ni	Cr	Mo	Autres
16Mo3	>98%	/	<0.3	0.25-0.35	Si, Mn, Cu, C
Inconel 625	<5	>58	20-23	8-10	Nb+Ta : 3.8-4.15
Nickel		≈99%			

Table 3: Metallic grade composition

The test plan described in Table 4 was undertaken to determine the influence of the amount of hydrochloric acid, of the amount of sulphur dioxide and of the presence of ashes on metallic wall corrosion.

	Trial nr. 1	Trial nr. 2	Trial nr. 3
[HCl] (mg/Nm ³)	1000	1500	1500
[SO ₂] (mg/Nm ³)	150	300	300
Ashes	No	No	Yes
Temperature	450°C	450°C	450°C
Duration	200h	200h	200h

Table 4: Experimental plan

The results (Figure 4 and Table 5) indicate that Inconel 625 is not corroded whatever testing conditions.

Nickel 200 is slightly corroded (< 6µm/y).

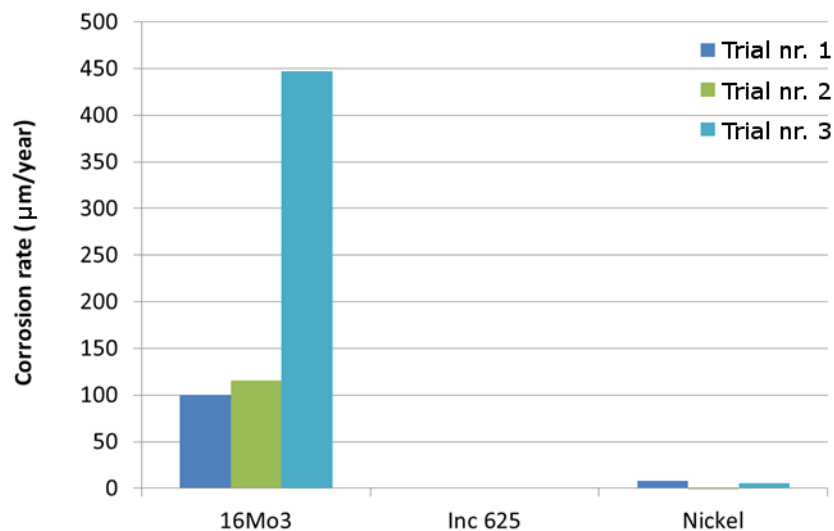


Figure 4: Corrosion rate (µm/y) based on the average mass loss of 3 samples

However, 16Mo3 is more corroded. For low levels of hydrochloric acid and sulphur dioxide, the corrosion rate is about 100 µm/y. For higher levels, a corrosion rate increase of 10% is

recorded. The presence of ashes considerably increases the corrosion rate to a value of 450 $\mu\text{m}/\text{y}$. This is confirmed by photographs of the sample after testing (Figure 5).

	Trial nr. 1	Trial nr. 2	Trial nr. 3
16Mo3	100 ± 14	115 ± 6	447 ± 195
Inc 625	0.3 ± 0.1	1 ± 1	1 ± 1
Nickel	8 ± 1	3 ± 1	5 ± 1

Table 5: Corrosion rate ($\mu\text{m}/\text{y}$) based on the average mass loss of 3 samples

Metallographic examinations of cross sections through 16Mo3 samples (Figure 6) reveal that the thicknesses of oxidation products are in a good accordance with the corrosion rate determined from mass loss measurements: Trial nr. 1 ($\sim 4 \mu\text{m}$) < Trial nr. 2 ($\sim 7 \mu\text{m}$) < Trial nr. 3 ($\sim 20 \mu\text{m}$). Evidences of chloridation are clearly visible in the oxide layer of the sample covered with ashes (Trial nr.3). Indeed, it is made of several layers that have teeth oriented towards the metallic interface.

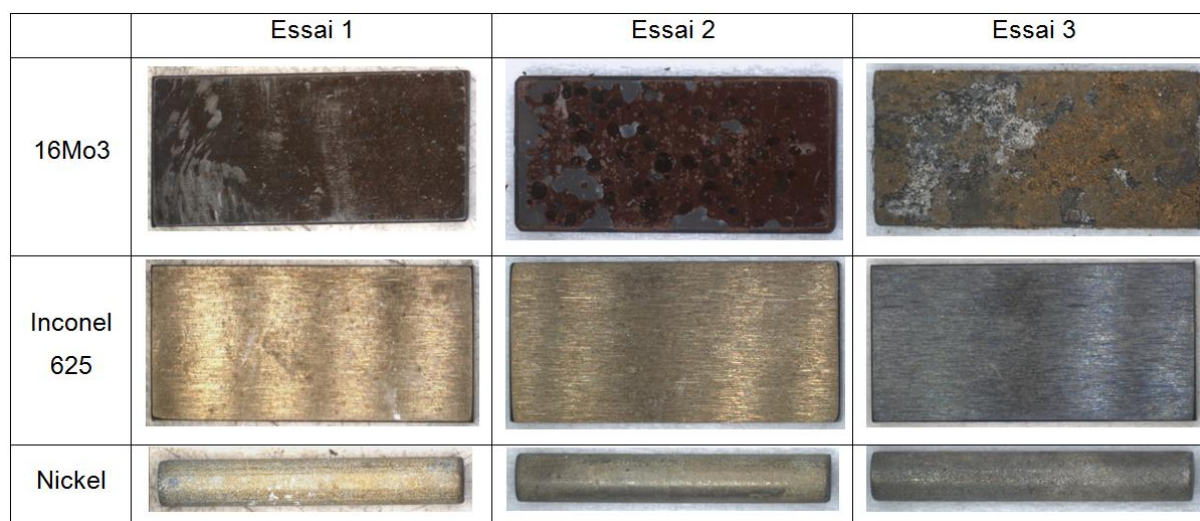


Figure 5 : Samples after trials

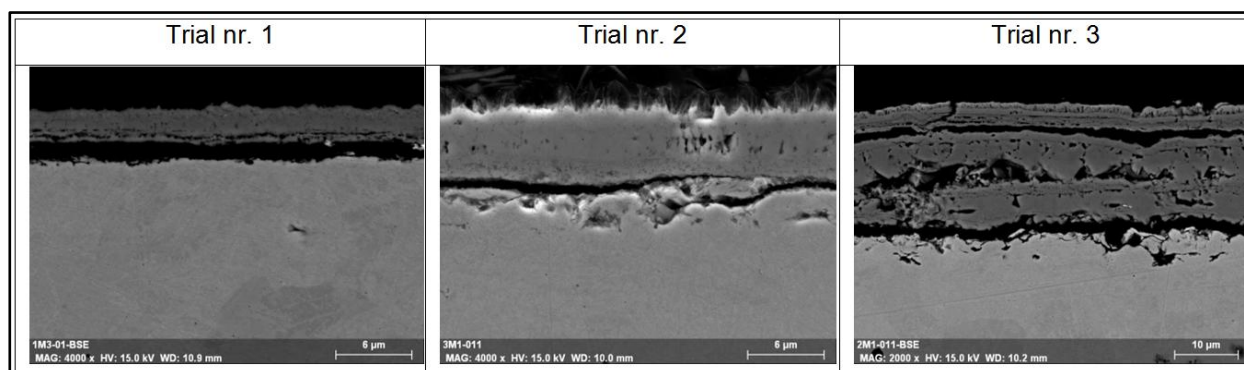


Figure 6: Metallographic cross sections of 16Mo3 samples

3. Tight reactors

2.1 High temperature testing equipment

Equipment described hereunder is devoted to corrosion tests in molten salt when gaseous chemical elements in the atmosphere do not interfere with the corrosion of immersed samples. It can also be used to test samples in the vapour phase due to salt volatilization. Two types of tight reactors are being developed in CRM. The first ones, which allow testing a large number of samples at the same time in a reduced volume of space, are made of quartz ampoules (Figure 7). They can withstand high temperatures (up to 1000°C) and a pressure of 5 bar.

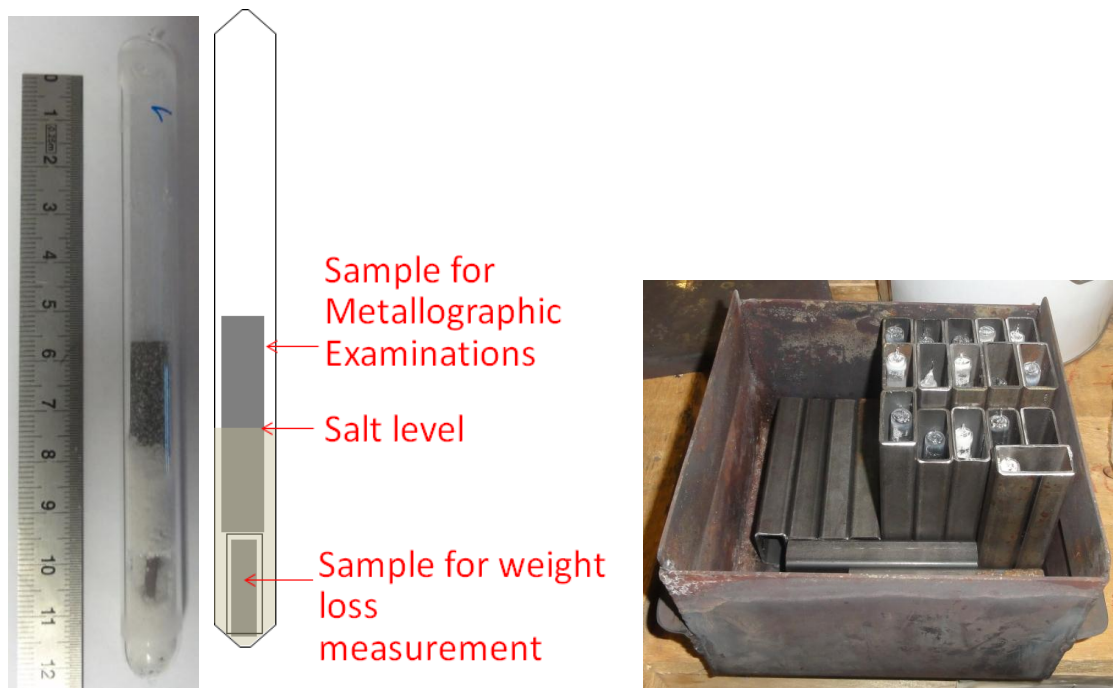


Figure 7: Quartz ampoules

For higher pressures or when quartz is not corrosion resistant, a tight metallic reactor, inside which a ceramic crucible is inserted to hold samples to test and salts (Figure 8), was designed. The pressure can rise up to 40 bar at 700°C.

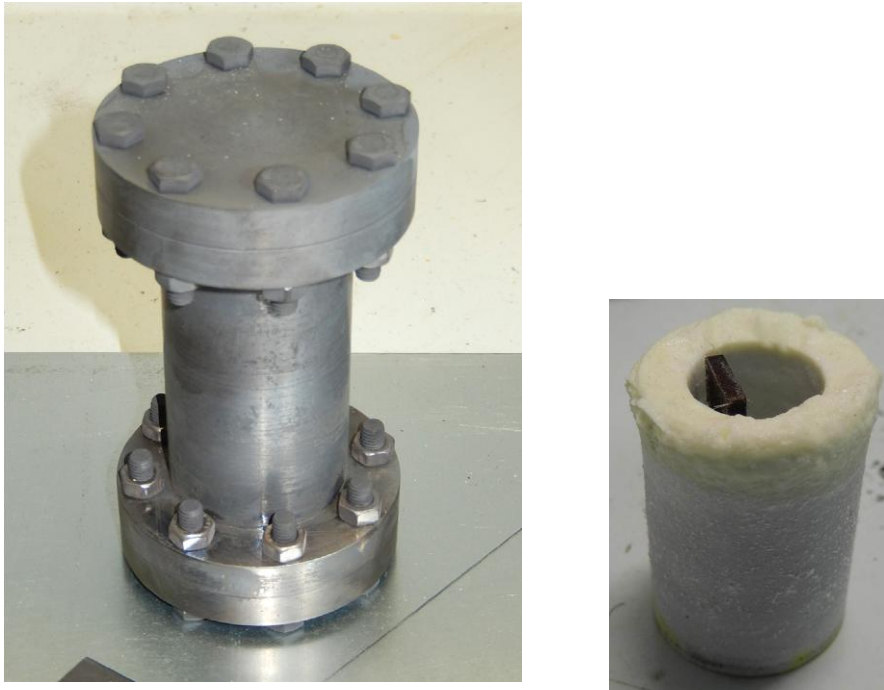


Figure 8: Tight metallic reactor and ceramic crucible

3.2 Trials in molten salt heat storage conditions

Tight reactors were used to determine the corrosion of ASTM P91 grade (Table 6) when subjected to nitrate and nitrite molten salts at 400°C. Molten salts are used as heat transfer fluids and for thermal energy storage in solar power plants.

	C	Cr	Mo	V	Nb
ASTM A335 Grade P91	0.1%	9%	1%	0.2	0.08

Table 6: Chemical composition of grade P91

Tests concern two commercially available salts. Binary mixture of sodium and potassium nitrate (Solar salt) and ternary mixture of potassium nitrate, sodium nitrate and sodium nitrite (Hitec). The influence of humidity and chlorides, which are unavoidable in industrial salt grades, was also observed. Testing conditions are summarised in Table 7.

Steel	Grade 91	
Temperature	400°C	
Salts	Salt 1 – Solar salt	NaNO ₃ 60% wt., KNO ₃ 40%
	Salt 2 – Hitec	NaNO ₃ 7% wt., KNO ₃ 53%, NaNO ₂ 40%
Impurities	Water	0% wt., 0.5% and 1.5 %
	Chlorides	0% wt., 1.65 %
Durations	100, 500 and 1000 h	

Tableau 7: Testing conditions

At 400°C, results show that uniform corrosion rates, obtained by mass loss measurements, are less than 25 µm/y. Moreover, corrosion rates decrease during the first thousand hours to

stabilise at a low value of about 15 $\mu\text{m}/\text{y}$. Chlorides content and water do not seem to have an influence on uniform corrosion. However, some pits have been detected on samples exposed to 1.65% wt. of chlorides. Further tests should be made to confirm that pitting really occurs.

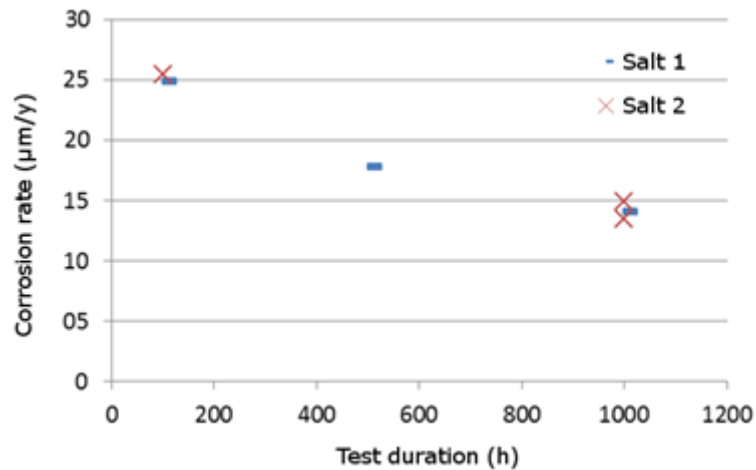


Figure 9: Corrosion rate versus test duration at 400°C

Furthermore, it seems that corrosion is more active in the vapour phase than in the liquid phase. Even if this needs to be confirmed, it would mean that special care should be given to the upper part of the storage tank which is in contact with the salt vapours.



Figure 10: Sample partially immersed in the salt

4. Synthesis

Two versatile equipment were designed to simulate environments mainly encountered in practice at high temperature:

- A tubular furnace through which a gas with a controlled chemical composition flows. It makes it possible to test samples in specific gaseous atmosphere or to combine the action of molten salt with the interaction of gaseous chemical elements.

- A set of tight reactors able to work at high temperature and pressure. They enable to carry out a great number of tests under a large variety of testing conditions simultaneously provided temperature is the same.

They were used to simulate two corrosive environments: aggressive condensates which affect waste incinerators (mixture of liquid/solid salts in oxidising conditions) and heat transfer fluids of electric power generating plants based on solar towers (mixture of liquid salts).

5. Acknowledgment

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