

# Cyclic High Temperature Corrosion in Coal Gasification Plant and DownTime Corrosion: A Procedure for Laboratory Tests to Simulate Industrial Experience

## Summary

A laboratory testing procedure that simulates downtime corrosion in coal gasification plant has been developed. The test comprises alternate exposures of specimens that had previously been coated in char, to simulated coal gasification atmospheres (CGA) at high temperature and at ambient temperature. Results from the test have been compared to those obtained from a test developed by EPRI and industrial experience for two alloys, Incoloy 800H and AISI 310 stainless steel. The new test is less aggressive than the EPRI test and produces microstructures and kinetics similar to those observed in industrial coal-fired plant. The specific procedure for coal gasification plant should be capable of modification to suit other plant operating with deposit formation in a cyclic mode where condensate formation occurs.

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## Background

All industrial plant operated at high temperatures will also be exposed to ambient conditions, and if the high temperature gases contain high moisture contents as, for example, in combustion or gasification of fossil fuels, condensates will form. These condensates are normally very corrosive comprising of acidic solutions so that severe attack of metallic components can occur, which is often called dewpoint or downtime corrosion (DTC). Flushing the plant with dry nitrogen during a shutdown period would largely avoid this form of attack, but this is not always practicable. Thus test methods are required to determine resistance to this form of attack.

## Introduction

Despite the current trend toward use of natural gas for the generation of electricity in combined cycle power plants, there remains strong interest in the development of clean, high efficiency coal-based systems for power generation [1]. Various designs of plants of this general specification exist, but one which has received widespread support is based on gasification of coal as part of a combined cycle unit [2]. In this system, designs frequently require an intermediate heat exchanger to allow clean-up of the so-called syngas before combustion in the gas turbine. The gas produced in the gasification unit is sulphidising both iron- and nickel-base materials which would be severely attacked if not alloyed with aluminium and chromium to allow formation of either alumina or chromia scales. In addition, the environment in the heat exchanger is such that during operation deposits form on the boiler tubes. These deposits are a mixture of coal ash and/or char and are found to contain relatively large amounts of condensed iron and alkali metal chlorides [3]. Downtime corrosion (DTC) as discussed above is also a major problem in this type of plant [3,4,5].

Although a large amount of information exists about materials behaviour in laboratory simulated coal gasification atmospheres (CGAs) free of HCl, the effects of chlorides in these conditions are less well characterised and conflicting results have been published in which the presence of HCl has been shown to both increase and decrease rates of attack for candidate alloys [4-10]. Experience in operating coal gasification pilot plants generally supports the view that HCl is deleterious [3] and in cases of severe attack a chloride-containing layer has often been found at the scale/alloy interface [3,4].

A particular problem is to design a laboratory test that accurately simulates the service conditions and forms a corrosion product representative of that found in an operating plant. The environment is very complex as discussed above so that in addition to the aggressive gas mixture, deposits should be incorporated in the test, and here it is clearly important to achieve the correct chemistry. The objective of the current research, therefore, is to develop a laboratory test method which can simulate the corrosion product morphology and the rates of attack found in operating plant. The test method is validated by a systematic study of all the various elements present in the syngas cooler to determine the effects of HCl additions to the gas, the presence of deposits with and without chloride-containing salt additions and intermittent exposure to downtime corrosion.

## Test Philosophy and Scope of Test

The test is based upon the simulation of high temperature plant returning to room temperature after a period of operation. In practice this may be carried out under an inert atmosphere if the shutdown is scheduled or under the process atmosphere in an emergency or failure situation. The shutdown is simulated by removing the test specimen from the hot zone to the cooler part of the test apparatus whilst either maintaining the flow of simulated plant gas or changing to nitrogen containing HCl/H<sub>2</sub>O or air.

This procedure has been developed and validated for the specific case of coal gasification plant. However, the procedure, with suitable modifications, can be applied to other high temperature plant operating under cyclic conditions where deposits are formed during high temperature operation and condensates form upon cooling.

## Equipment

The test procedure requires a furnace which is sealed with a gas-tight valve and airlock assembly that allow the specimens to be either entered into or withdrawn from the work tube under an argon atmosphere. A schematic representation of the furnace assembly is shown in [Figure 1](#).

Post test evaluation requires a scanning electron microscope (SEM) fitted with energy dispersive X-ray analysis facility (EDX) for visual and chemical investigation of the corrosion products. An automated measuring rig consisting of a PC-driven motorised XY-stage and an optical microscope with an interactive video imaging system is required for quantitative measurement of the metal loss.

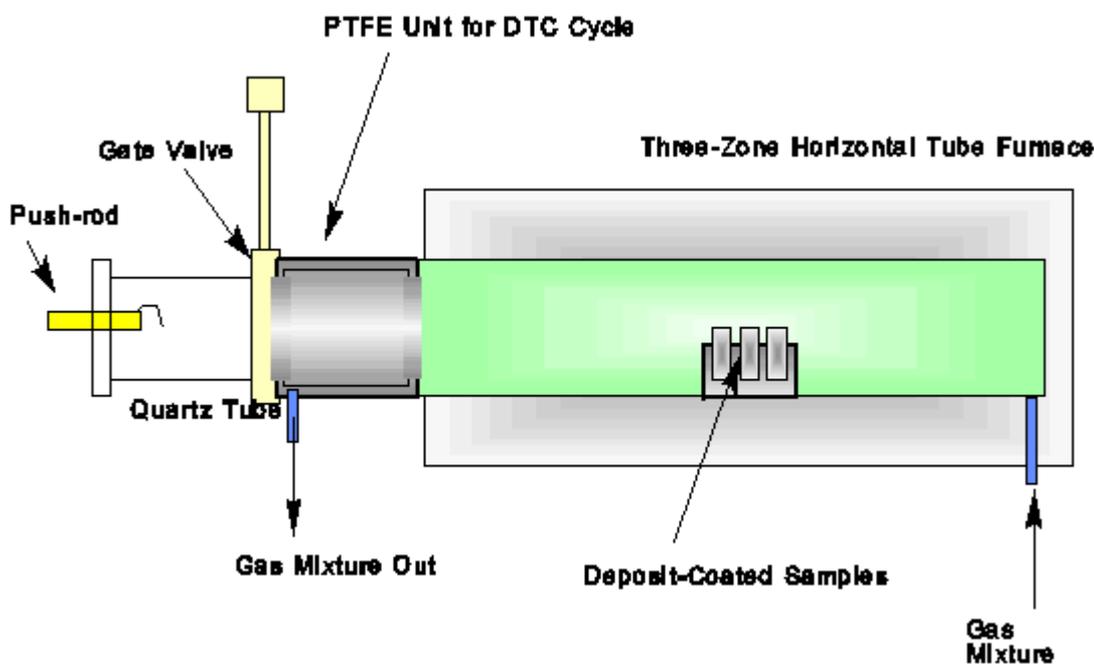


Figure 1 Diagram of the NPL CGA + DTC Testing System

## Specimen Preparation

Samples (suggested six approximately 10 x 10 x 2 mm) are prepared with a 600 grit SiC finish such that the major

surfaces are plane parallel to within 3  $\mu\text{m}$ . The thickness is determined by replicate measurements with a micrometer to an uncertainty of  $\pm 1 \mu\text{m}$ ; this measurement forms the basis of metal loss assessments and thus is of fundamental importance to the outcome of the test. The specimens are then cleaned in ethanol and air-dried before recording their initial mass.

Deposits taken from operating plants should be used as the basis for coatings on the specimens. A slurry of deposit is made by addition of ethanol. Alloy samples are then dipped in the slurry and placed in an alumina crucible and air dried at 125°C; typically the mass of deposit per unit area should be chosen such that the active species are not exhausted during the lifetime of the test. In some cases it may be necessary to replace the deposit, but if this is done some information would be lost on the development of the scale. **Care must be taken to ensure that the deposit is consistent between samples. Experience has shown that char composition can vary significantly within a nominally equivalent sample.**

## Specimen Exposure

Initial exposures to the process gas are carried out in a 3-zone furnace system at the chosen test temperature. Each test cycle is commenced by first purging the furnace tubes with commercial purity dry argon for 20-30 minutes, then changing to the selected gas mixture. Additions of HCl and H<sub>2</sub>O may be required to simulate the process gas correctly and are achieved by passing the dry gas mixture over a solution of HCl heated to an appropriate temperature. The proportions of HCl/H<sub>2</sub>O vapour can be varied by control of acid strength and temperature [11]. The flowrate of the gas must be sufficient to prevent depletion of the active elements but must also be slow enough to allow preheating of the gas stream. In practice a linear flow rate between 0.1 and 10 mm s<sup>-1</sup> satisfies these conditions in most cases. The composition of the gas leaving the furnace can be measured if required with a quadruple mass spectrometer to establish whether the gas reaches equilibrium. At temperatures below ~700°C non-equilibrium will be progressively the norm. However this situation is probably a better simulation of plant behaviour thus no attempt should be made to encourage equilibrium by the use of catalysts etc.

Temperature control during this high temperature exposure should be consistent with that proposed by Nicholls [12] for discontinuous corrosion testing viz:

- ± 3°C for temperatures, T, up to 600°C
- ± 4°C for T between 600°C and 800°C
- ± 5°C for T between 800°C and 1000°C
- ± 8°C for T between 1000°C and 1500°C
- ± 10°C for T greater than 1500°C

In order to introduce the downtime corrosion element of the test under continued exposure to CGA gas, specimens are simply withdrawn from the furnace to a cooler region such that condensate forms on the sample; the temperature of this zone is typically 28-30°C and the pH of the condensate is typically between 1 and 3. Alternatively the gas may be changed to a suitable nitrogen-based gas mixture containing the same acidic gases and moisture content as the process gas, simultaneously with withdrawal of the sample into the cool region.

The duration of each stage of the test can be tailored to suit the application required and to establish the process kinetics. An approximately geometrically increasing sequence of exposure times to CGA interspersed with fixed periods of DTC is recommended, eg a sequence of 4 h CGA + 24 h DTC + 16 h CGA + 24 h DTC + 50 h CGA + 24 h DTC + 100 h CGA + 24 h DTC + 240 h CGA + 24 h DTC + 480 h CGA + 24 h DTC has been used in the current validation exercise.

## Post-exposure Examination

Specimens should be slit and mounted; the cross-sections are then polished to a final finish of 1  $\mu\text{m}$  diamond. All preparation should be carried out without lubrication, otherwise soluble corrosion products may be lost.

Determination of the extent of corrosion is carried out by measurement of initial and residual thickness of alloy to assess the metal loss. The recommended method to measure metal loss is to use an automated measuring rig consisting of a PC-driven motorised XY-stage and an optical microscope with an interactive video imaging system. The maximum metal loss is determined from up to 20 random measurements of the maximum attack found in the field of view on each of the major planes on the sample. Metal loss values quoted are those that relate to one

surface and are the mean of the two planes. If pitting is observed then measurements should be made at the base of each pit. Accuracy of measurement better than 3  $\mu\text{m}$  can be achieved using this method. **This method will underestimate the maximum metal loss but it is considered that kinetic information will be valid. Alternative analyses using extreme value statistics approaches may be used to overcome any concerns.** Alternatively the operator may use the procedures specified in standards for measuring the thickness of metallic and oxide coatings [13,14].

Micrographs of the corrosion product are taken using backscattered imaging to give elemental contrast. Digimaps and/or semi-quantitative spot analysis is recommended.

## Presentation of Results

It is recommended that results presented from the test should include, as a minimum, the following information:

- objective of the test
- test materials
- initial dimensions of specimens
- composition of test atmosphere
- chemical composition of deposit and condensate
- exposure sequence (times and temperatures of each cycle)
- micrographs of representative areas
- semi quantitative analysis of corrosion product
- measurement of metal loss

\*uncertainties of measurement should be included for each measurement

## Statement of Uncertainty

In a measurement procedure of this nature it is not possible to quantify the total uncertainty of the test. Variations in test atmosphere, exposure temperature and deposit composition will affect the kinetics of corrosive attack in a complex (and interdependent) manner.

It is possible to quantify the uncertainties associated with individual aspects of the measurement procedure eg chemical analysis and metal loss measurements. The uncertainty in the measurement of metal loss is better than  $\pm 2 \mu\text{m}$  from the image analysis system in use at NPL - however the practical limit to the precision of this measurement is lack of knowledge of the position of the original surface.

Any measurements taken using semi-quantitative X-ray analysis should be treated with caution. The following statement (or one similar) should always be used to moderate the quoted results. "The results from the elemental analyses are processed using the net peak integrals. It should be noted that these values are approximate and represent the ratio of selected peak integrals. No corrections are made for zero or gain shift or unanalysed elements, nor have any ZAF calculations been made."

## Test Example

The test has been validated by comparison of results achieved using the new test procedure with those from an EPRI downtime corrosion test [3]. Two materials, Incoloy 800H and AISI 310 stainless steel were investigated under conditions relevant to coal gasification plant. The exposure conditions and sequences used are given in Table I.

**Table I Experimental conditions for validation of procedure**

Identifier	Description
1	CGA only, no coating
2	CGA only, char
3	CGA only, char + salt

4	CGA + NPL DTC, char
5	CGA + NPL DTC, char + salt
6	CGA + EPRI DTC, char
7	CGA + EPRI DTC, char + salt
Sequence: 4 h CGA + 24 h DTC + 16 h CGA + 24 h DTC + 50 h CGA + 24 h DTC + 100 h CGA + 24 h DTC + 240 h CGA + 24 h DTC	

Table II lists metal loss data for both alloys after exposure to all seven test conditions; for ease of comparison only the duration of the CGA cycles are used, but it should be remembered that for the tests with DTC the total times were 112 and 530 h, respectively, for the quoted 70 (4+16+50) and 410 (4+16+50+100+240) h exposures.

Figure 2 shows the maximum metal loss data for the tests 5 and 7 as a function of time (including the periods of DTC).

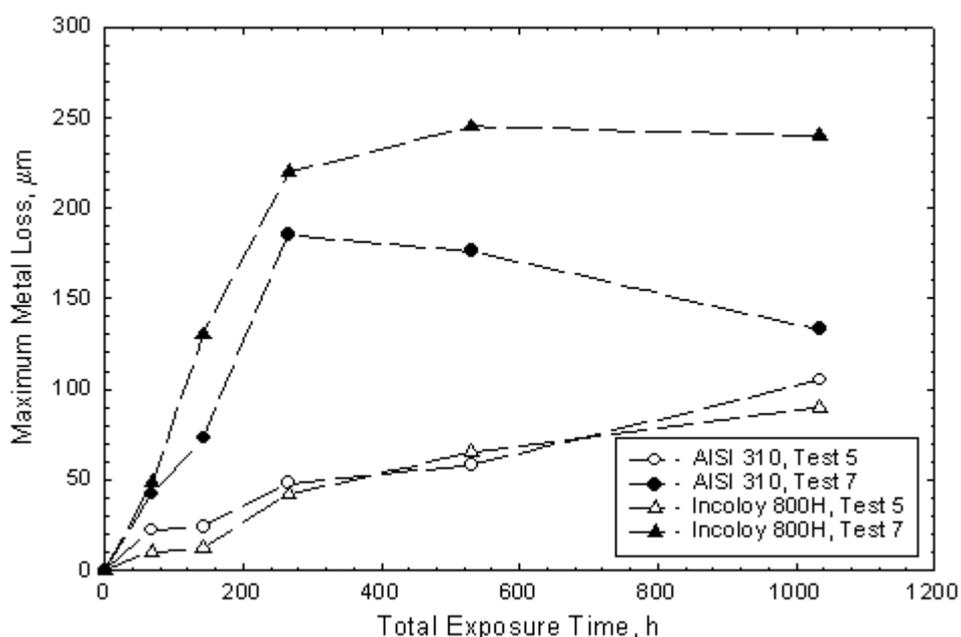


Figure 2 Metal loss as a function of time and test type

Using the data in Table 2 and Figure 2, the following general observations can be made:

- i. AISI 310 stainless steel is generally more resistant to attack than Incoloy 800H with the possible exception of tests when salt was added to the char.
- ii. The addition of salt to the char did not increase the maximum metal loss observed significantly, and in some test sequences actually decreased the corrosive attack.
- iii. Downtime corrosion cycles increased the severity of attack for both alloys, with the EPRI test producing the greatest attack.

Table II Metal loss data for test alloys for each test condition

Test Type	Maximum metal loss, µm			
	Incoloy 800 H		AISI 310 ss	
	70 h	410 h	70 h	410 h
1	1	5	< 1	
2	48.5		12.7	

3	6.8		22.8	
4	53.7		50.6	
5	13.7	66.0	24.6	62.9
6	125.6		61.2	
7	128.7	242.4	73.4	176.7

Detailed investigation of the corrosion product was carried out on the samples of both alloys and has been reported previously [17] for samples withdrawn from the tests after 70 h exposure for all seven exposure conditions, and at 410 h for tests 1, 5 and 7. The important features are illustrated in Figure 3 on an Incoloy 800H sample with char and salt deposit, exposed for a total of 70 h to CGA and incorporating the NPL DTC cycle. A sulphide scale is fully developed and a layer of chloride-containing materials was found at the scale alloy interface. Quantitative analyses of the thicker regions on the chlorine-containing layer indicated an average composition of 45.3 Cl, 17.7 Cr, 13.6 Fe, 10.6 Ni, 6.3 Si, 2.3 Al, 1.9 Ti (atom %). Similar chlorine-rich compounds were found in tests carried out in the authors' laboratory in CGA only but with the HCl level at 12000 ppm [8].

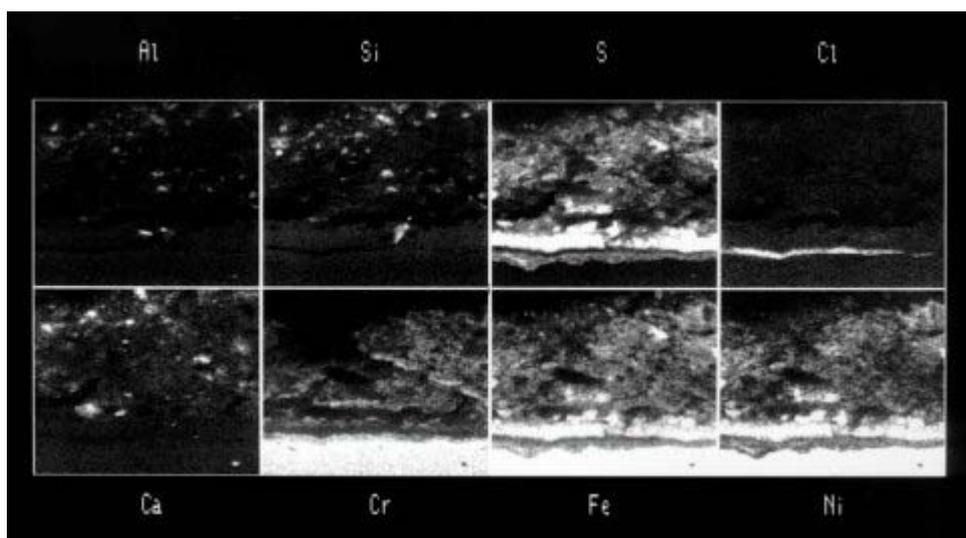
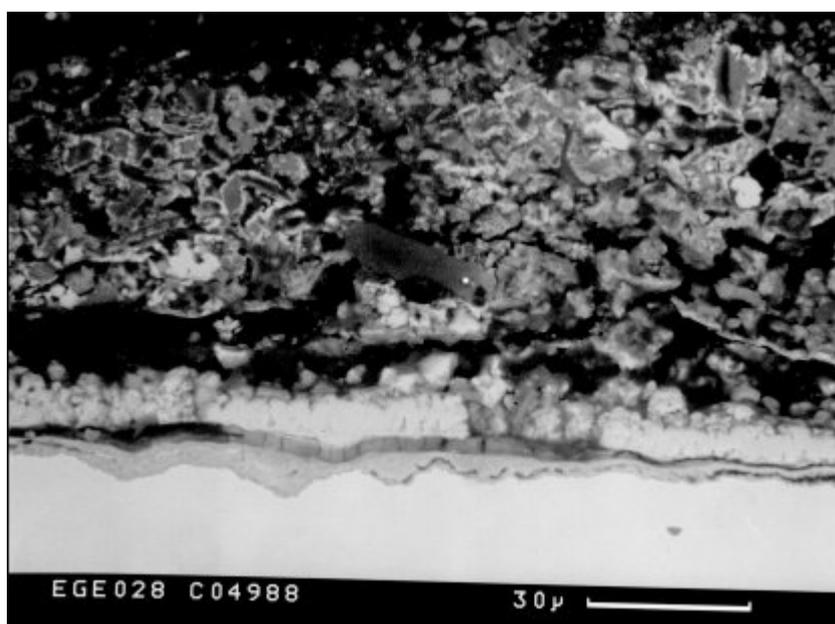


Figure 3 Backscattered electron micrographs and digimap of Incoloy 800H sample with char and salt coating, exposed to CGA+NPL DTC cycles for total exposure time of 70 h

## Comparison with Plant Experience

The metal loss rates observed for the laboratory tests incorporating deposits and DTC are in good agreement with some reports of metal loss from operating plant. For example, the pilot operated by CTDD resulted in an estimated metal loss 0.08 mm for Incoloy 800H at 550°C in 2000 h [4], and both Incoloy 800H and AISI 310 lost about 0.1 mm in 2100 h after exposure in the PRENFLO plant also at 550°C [16]. Using a linear extrapolation of the data obtained from the two longer-term tests in this work (Type 5 and 7) metal loss data at 2000 h for Incoloy 800H were 0.22 and 0.9 mm, respectively. The lower rate was from the test incorporating the NPL DTC cycle and the linear extrapolation is probably an overestimate so that it is believed that reasonably good agreement with observed metal loss from operating plant has been achieved in the test operating the more modest DTC cycle.

The corrosion product morphology is also similar to many reported examples in the literature, but of particular note is the ability to form a layer of metallic chlorides at the scale/alloy interface, which is also reported to be a characteristic of scales formed in operating plant [3]. The amount of chloride formed in this work is believed to be greater than that normally found on service exposed samples, and from the results presented here and in the literature it is evident that the development of the chloride layer is related to DTC. In order to develop a more realistic laboratory simulation of corrosion experience by syngas heat exchanger materials it seems clear, therefore, that the frequency of the DTC cycles in the laboratory tests should be reduced.

## Test Summary

- i. Addition of char deposits obtained from a coal gasification pilot plant containing condensed salts greatly increased rates of attack compared with test in simple CGA.
- ii. Attempts to increase the corrosiveness of the deposit by addition of iron and alkali metals chlorides proved to be ineffective.
- iii. Incorporation of DTC cycles in the tests with deposits resulted in a further increase in the aggressiveness of the test, and the EPRI DTC test was much more aggressive than one developed during the course of this work (NPL DTC).
- iv. Rates of attack in the test incorporating deposits and the NPL DTC cycles approximated to those found in operating plant.
- v. Corrosion product morphologies were also in good agreement with those found on alloys exposed to service conditions.

## Discussion

The advantages of the proposed new test procedure are flexibility, ease of experimentation and relevance to industrial situations. The flexibility of the new test procedure is self-evident: the times of exposure to simulated industrial atmospheres and simulated downtime are fully flexible and can be achieved without exposure of the specimens to laboratory air outside of the controlled furnace atmosphere, reducing the risk of contamination.

The apparatus is self-contained and more compact than the two chamber system required to reproduce the test conditions via the EPRI route.

The test reproduces the metallographic structure and kinetics of the industrial situation as shown by the validation exercise.

## Conclusions

A new testing procedure for downtime corrosion has been developed that provides a realistic simulation of material behaviour in industrial plant. The new procedure has been validated for Incoloy 800H and AISI 310 stainless steel under conditions simulating coal gasification plant.

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