EVALUATION OF MATERIALS' CORROSION AND CHEMISTRY ISSUES FOR ADVANCED GAS COOLED REACTOR STEAM GENERATORS USING FULL SCALE PLANT SIMULATIONS

By

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ABSTRACT

Advanced Gas Cooled Reactors (AGRs) employ once-through steam generators of unique design to provide steam at approximately 530° C and 155 bar to steam turbines of similar design to those of fossil plants. The steam generators are highly compact, and have either a serpentine or helical tube geometry. The tubes are heated on the outside by hot CO_2 gas, and steam is generated on the inside of the tubes. Each individual steam generator tube consists of a carbon steel feed and primary economiser section, a 9%Cr steel secondary economiser, evaporator and primary superheater, and a Type 316L austenitic stainless steel secondary superheater, all within a single tube pass.

The multi-material nature of the individual tube passes, the need to maintain specific thermohydraulic conditions within the different material sections, and the difficulties of steam generator inspection and repair, have required extensive corrosion-chemistry test programmes to ensure waterside corrosion does not present a challenge to their integrity. A major part of these programmes has been the use of a full scale steam generator test facility capable of simulating all aspects of the waterside conditions which exist in the plant. This facility has been used to address a wide variety of possible plant damage/degradation processes. These include; single- and two-phase flow accelerated corrosion of carbon steel, superheat margins requirements and the stress-corrosion behaviour of the austenitic superheaters, on-load corrosion of the evaporator materials, and iron transport and oxide deposition behaviour. The paper outlines a number of these, and indicates how they have been of value in helping to maintain reliable operation of the plant.

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1. INTRODUCTION

Advanced Gas Cooled Reactors (AGRs) employ once-through steam generators of unique design to provide steam at high temperature and pressure, approximately 530° C and 155 bar, to steam turbines similar to those of fossil plants. Steam is generated on the inside of the steam generator tubes, as a result of heat transfer from hot CO_2 gas on the outside. Each individual tube consists of a carbon steel feed and primary economiser section, a 9% chromium steel secondary economiser, evaporator and primary superheater, and a Type 316L stainless steel austenitic superheater. The three materials are joined by short tube transition pieces, within a single tube pass, inside the heat exchanger. Individual steam generator designs are highly compact, having either a serpentine or helical tube geometry. These design features make their inspection and repair extremely difficult.

The multi-material nature of the individual tube passes and thermohydraulic conditions within them present particular waterside corrosion concerns, and have required the development of specific feedwater chemistries to ensure waterside corrosion damage is minimised throughout the steam generators. To evaluate these, an extensive corrosion-chemistry research and development programme has been carried out, which has included extensive use of a steam generator test facility capable of full scale simulation of the waterside conditions within the plant. The test facility is also vital in demonstrating that the plant operating conditions are benign, due to the inability to fully inspect the plant.

The value of using such full scale plant simulations to resolve plant chemistry and corrosion issues is illustrated in the following sections. Before considering these, however, it is appropriate to give a brief description of the facility itself.

2. DESCRIPTION OF STEAM GENERATOR TEST FACILITY

Figure 1 shows a schematic diagram of the main parts of the test facility. The main test section illustrated in the figure has a serpentine configuration, which replicates a single tube of the Heysham 2 AGR steam generators.

Alternative test sections are available, and it is possible to switch between these quite simply, whilst still utilising the other main components of the rig's water circuits. The other main test sections available are: a helical tube test section, which simulates the Heysham 1 and Hartlepool AGR steam generators; a smaller serpentine test section fabricated entirely from 1%Cr steel, which simulates the decay heat boilers at Heysham 2, and a third serpentine test section fabricated from carbon steel tubing which simulates the once-through steam generators of the MAGNOX reactors at Wylfa. In each case the main test section is a single full size tube replicating that in the plant itself.

The tube materials and fabrication processes used to construct the main boiler test sections are also, as far as possible, those used in the plants themselves. It is possible, however, to introduce new sections of tubing or special test pieces as may be required by particular test programmes. The schematic diagram of Figure 1 illustrates this, showing an additional test assembly for flow accelerated corrosion (FAC) studies in the feed section of the rig. Such additional test assemblies are constructed in a manner to suit the individual requirements of the problem being addressed.

Feed heating is provided by a regenerative feed heater fed from the steam condensing part of the circuit (not shown), which heats the feed water to the main test section to a pre-determined temperature. For AGR steam generator studies this is typically around 150° C, but higher and lower temperatures are achievable.

The main boiler test section is heated by resistance heating of the tube itself using low voltage 50Hz current. The power input is in a three phase delta arrangement with one phase earthed and connected to the top and bottom of the heated section. This allows a stepwise replication of the boiler heat flux profile by using a number of heated sections without the need for insulating joints. The main test sections also have extensive temperature and pressure monitoring (including differential pressure measurements) to establish local thermohydraulic conditions throughout the rig.

The electrical heating can raise the fluid temperatures to those generated in the plant at full plant flow conditions, typically up to 530° C. For the helical boilers the full plant flow rates are around 0.21 kgs^{-1} per tube. Those for the serpentine boilers are higher, and the rig is capable of delivering flow rates of ~0.5 kgs^{-1} to the AGR serpentine boiler test section at full power conditions for all but one of the AGRs. These are equivalent to power inputs of ~500kW and over 1 MW respectively.

As indicated in Figure 1, the rig incorporates a wide variety of dosing and sampling points. These can be used to control and monitor the feedwater chemistry very precisely throughout the rig. Sampling from locations within the main boiler test section provides information which cannot be obtained in the plant itself. Accurate monitoring of all necessary chemical parameters on the rig is possible using a dedicated chemical analysis laboratory. All of the following chemical parameters can be routinely determined:

pH, ammonia, oxygen, hydrazine, direct conductivity, after cation conductivity, sodium, chloride, sulphate, iron, and silica.

Other species can be determined as necessary for specific tests, eg CO_2, H_2 etc. The accuracy of determination of ionic contaminants, such as sodium, chloride etc., is in most cases down to sub- μgkg^{-1} levels.

3. MATERIALS' CORROSION & CHEMISTRY TEST PROGRAMMES

The test facility has been used to address a variety of steam generator materials' corrosion and chemistry issues. These include:

Flow accelerated corrosion (FAC), of the carbon steel and 1%Cr feed and economiser tubing (later AGR designs adopted 1%Cr steel in place of carbon steel).

Two-phase FAC studies of carbon steel evaporator tubing, and the use of amine chemistry to control it, for MAGNOX once-through steam generators.

Stress-corrosion of the Type 316L SS superheater tubing when subject to wetting on-load, and the superheat margin at the transition to the austenitic section necessary to avoid this.

On-load corrosion behaviour of the 9%Cr and 1%Cr evaporator material when subject to chemistry fault conditions.

Iron transport and oxide deposition behaviour, and its influence on boiler pressure loss.

Various smaller programmes of work. For example, work related to issues such as alternative oxygen scavengers, and oxygen consumption by waterside oxides during fault conditions.

It is not possible to cover all of these here. Consequently aspects of specific examples, representative of issues which have arisen for each of the three main tube materials, will be described. In addition, oxide deposition studies will be discussed, since these involve all sections of the steam generator tube.

3.1 Flow Accelerated Corrosion Studies of Carbon Steel Feed & Economiser Tubing

Early studies of flow accelerated corrosion using the test facility were directed at establishing a feedwater chemistry which would avoid significant single phase corrosion damage of the carbon steel feed tubing in units having helical steam generators, while avoiding the possibility of introducing additional corrosion problems elsewhere in the generators and secondary circuits. These studies have been reported previously [1,2], and resulted in the adoption of a combined ammonia/oxygen/hydrazine feedwater chemistry for the boilers concerned. The feedwater chemistry initially adopted for these units, based on the test work, was:

pH_{25} 9.4 (NH_3)
O_2 15 μgkg^{-1}
N_2H_4 30 μgkg^{-1}

This feedwater chemistry was shown to prevent flow accelerated corrosion of the steam generator feed tubing (the most vulnerable section of carbon steel pipe work). This operates at 150° C, and protection is provided by the persistence of oxygen throughout this section of the generator. However, the hydrazine was shown to remove the oxygen in the higher temperature sections of the economiser, hence avoiding the possibility of enhanced corrosion and stress-corrosion in the evaporator and superheater sections due to the existence of oxidising conditions at those locations.

Operating experience with this chemistry regime has progressively led to reductions in the feedwater pH, and increases in the oxygen and hydrazine dose levels. This has been to accommodate operational factors related to the condensate polishing plants of the units concerned. At each stage the changes have been fully validated by additional full scale tests using the rig facility[3]. These have demonstrated that the pH can be reduced to at least as low as pH_{25} 8.5, without risking flow accelerated corrosion of 90° bends in the feed tubing, providing oxygen dose levels are sufficiently high (> 8 $\mu g kg^{-1}$). The current feedwater chemistry recommendations for AGR helical steam generators are therefore:

pH_{25}	>8.8 (NH_3)
O_2	25 $\mu g kg^{-1}$
N_2H_4	40 $\mu g kg^{-1}$

The plants have now operated with feedwater chemistry conditions within this range for over 60,000 hours without any failures due to flow accelerated corrosion. Plant inspections have also failed to detect any damage to date. This is consistent with the test work which indicates FAC rates at bends in the feed tubing should be < 0.03 mm/year, even at pHs down to 8.8, providing the elevated oxygen concentration is maintained.

Further single phase FAC studies have been conducted recently, which examined the influence of feedwater fault conditions on both FAC and iron transport behaviour. These were conducted primarily to support operation of units with serpentine steam generators, and examined behaviour which could result from ingress of CO_2 into the secondary water circuits, which can occur under certain fault conditions. This should lead to a reduction in the feedwater pH, and since the units normally operate with a fully deoxygenated feedwater chemistry (pH(NH_3) ~9.4), this could result in increased FAC damage of the carbon steel feed tubing.

For these tests the rig was operated in the manner set out in Figure 1, with an FAC test assembly installed in the main feed pipe work. The assembly comprised a series of four 90° bends fabricated in either carbon or 1%Cr steel, of which three were surface activated with ^{56}Co to monitor the FAC losses in-situ. These losses were monitored as a function of the feedwater chemistry, and in particular as a function of the level of CO_2 in the feedwater. Figure 2 shows a typical FAC response to variation in the level of CO_2 at 119° C, and constant ammonia concentration, in this case 1.1 $mg kg^{-1}$. It is evident from Figure 2 that increases in CO_2 initially have only a minor impact on the FAC rates for carbon steel at this ammonia concentration, but the rates increase substantially above a threshold value. This is as expected from considerations of the pH_T of the feedwater, and Figure 3 shows the correlation obtained between the FAC rate and pH obtained from a number of experiments. Below pH(119°C) 7.2, FAC rates rise rapidly, but above this value rates remain rather low.

Figure 2 also shows that FAC rates for the 1%Cr steel bends remain low regardless of the CO_2 level, within the range studied.

From studies of this type it has been possible to determine the correct operational response to fault conditions involving CO_2 ingress, and to define permitted operating times and concentrations for the plant under these conditions. The studies also confirmed the effectiveness of oxygen dosing for controlling FAC in the presence of CO_2 for units with helical steam generators.

3.2 On-Load Corrosion of 9%Cr Evaporator Tubing Under Feedwater Fault Chemistry Conditions

During normal operation, AGR feedwater impurity levels for ionic species such as Na^+, Cl^- and SO_4^{2-} are extremely low, typically well below 0.5µgkg^{-1}, with cation conductivities around 0.06 µScm^{-1}. Under these conditions on-load corrosion damage of the 9%Cr evaporator tubing is expected to be minimal.

The plants also have a feedwater trip protection system which protects the steam generators against major impurity ingress. eg from large condenser leaks which the condensate polishing plant (CPP) may not be capable of containing (also from possible ingress of CPP regenerant chemicals). These trip systems operate on feedwater conductivity, and are on the feedwater discharge from the CPP, upstream of any chemical dosing. The trip settings vary somewhat from plant to plant, and are typically around 1µScm^{-1}, with the highest set at 3µScm^{-1}. These settings correspond to impurity levels of 112 and 385 µgkg^{-1} SO_4^{2-} (as sulphuric acid) respectively. However, alarms also operate at conductivity values well below the trip settings.

Impurity ingress of this order has never occurred at any AGR to date. The highest impurity levels during normal operation have rarely exceeded a few µgkg^{-1} for short periods of time. The likely levels of corrosion damage which might result from impurity ingress at levels around the feedwater conductivity trip protection settings were established in order to permit proper evaluation of any significant chemistry faults which might occur in the future.

A number of tests have been carried out with both the serpentine and helical steam generator test sections to establish the likely level of corrosion damage. These involved dosing hydrochloric or sulphuric acid contaminants into the rig feedwater for a period of some 500 hours, and examining the extent of corrosion damage this produced in test pieces specifically introduced for this test programme. The test pieces were several metres in length, and the thermohydraulic conditions were maintained constant within them for the duration of each test, and from one test to the next. This ensured direct comparison between the corrosion resulting from different impurities and differing impurity concentrations used in separate tests.

The corrosion data from these tests are extensive, and will not be considered in detail. However, broadly speaking the levels of corrosion damage were lower with HCl contamination than H_2SO_4, due to the higher volatility of HCl. Damage was also lower in the helical tube geometry than the serpentine geometry. The latter can be related to the longer dryout boundary region which exists in the helical geometry. In the serpentine geometry the greatest damage tended to occur at the outlet of 180° bends operating at high steam quality, where the flow redistribution which takes place produces localised re-wetting and dryout.

The damage rates with acid sulphates were relatively high, of the order 1 mm/year, and the damage itself was similar in nature to that seen in autoclave experiments. However, the tests demonstrated that the steam generators should be tolerant of relatively large feedwater chemistry faults, providing they do not persist for long periods. Even after 500 hours, the tube wall penetration due to corrosion observed in the tests did not exceed 135 µm. This gives considerable reassurance that any significant feedwater faults which might occur on the plant would not significantly challenge its integrity. The plant is of course protected against large faults by the trip protection system.

3.3 Superheat Margins and Stress-corrosion Studies of Austentic Superheaters

All AGRs operate with a defined level of superheat at the transition between the 9%Cr superheater and the Type 316L SS austenitic superheater. This is to avoid the possibility of stress corrosion cracking of the austenitic material. The use of high purity feedwater also provides further protection for this region of the steam generator.

The required superheat to avoid wetting and stress-corrosion of the austenitic material can be estimated from thermohydraulic analysis of the likely penetration of droplets into the superheater region. Ultimately, though, unless the operational superheat margins are very large, the level of superheat needed to avoid damage requires experimental confirmation. This can only really be provided by corrosion test work. For this reason tests have been carried out to examine the corrosion damage produced in the transition joint to the austenitic superheater, and the Type 316L tubing itself, as a function of the degree of superheat at the transition joint.

The tests used the helical steam generator test section at full plant operating conditions, and employed a multiple transition joint test piece, with several transition joints and sections of Type 316L tubing in series. The test piece is illustrated schematically in Figure 4. These were operated at fixed thermohydraulic conditions, with the steam quality and superheat varying from one transition piece to the next, over the range ~ 80% steam quality to ~40° C superheat.

Initial tests were run with acid sulphate dosing of the feedwater, with levels of the order 10 $\mu g kg^{-1}$ sulphate. These levels of contamination are well above those expected on the plant, as indicated previously. The tests demonstrated that corrosion damage, in the form of intergranular attack and stress-corrosion cracking, was restricted to tubing operating with less than 10° C superheat. Maximum damage occurred close to 100% steam quality/1° C superheat. This is illustrated in Figure 5.

The tests therefore demonstrate that only a limited superheat margin is necessary to protect the austenitic superheater against the risk of stress-corrosion cracking for the helical tube geometry.

More recently, this test programme has been extended to quantify the stress-corrosion risks as a function of the feedwater chemistry, in the event that the austenitic sections are wetted.

It has been established from autoclave tests and modelling work that acidic sulphate environments were likely to represent the greatest risk of stress-corrosion within the boilers. The risks should, therefore, be significantly reduced by operating with a slightly alkaline ionic balance for the feedwater contaminants. Figure 6 shows the variation in damage rate as a function of the sodium to sulphate ratio in the feedwater from full scale steam generator rig tests of the type described previously. This clearly shows the benefit of operating with a slightly alkaline balance for the ionic contaminants present in the feedwater.

All AGRs seek to operate with the lowest level of feedwater contaminants practicable. However, based partly on the evidence provided by such full scale test work they also seek to maintain a slightly alkaline balance for ionic contaminants to further minimise corrosion risks.

3.4 Oxide Deposition and Boiler Pressure Loss Studies

While performing many of the stress-corrosion tests described in the previous section, the pressure loss changes in various parts of the steam generator tubing were monitored. These established that pressure loss in the evaporator section responded to changes in the feedwater chemistry. This is illustrated in Figure 7, for both an acid contaminant dose and an alkaline one. It is clear that the pressure loss rose for the acid case, but diminished slightly with alkaline dosing. This effect, while small over the timescale of the tests, was quite reproducible, and correlated with the pH at temperature in the two-phase region where the pressure loss measurements were made. This is shown in Figure 8.

The pressure loss in this region of the steam generator is associated with the presence of rippled magnetite. Examination of the rippled magnetite deposits present in the test section showed them to be highly crystalline, and therefore formed almost entirely by crystallisation from iron in solution. The influence of the chemistry in the evaporator region on rippled magnetite formation therefore arises from its influence on soluble iron within the test section, and offers a means of controlling the deposition behaviour. This is of limited value for once-through boilers if the pH changes are generated by ionic species, since they are likely to cause corrosion damage of the evaporator. However, amines such as dimethylamine, which are much stronger bases at high temperature than ammonia, should produce similar effects. These are currently under investigation as a means of controlling boiler pressure loss in once-through boilers. Initial test results have confirmed that dimethylamine does indeed help to limit the development of boiler pressure loss in this manner.

4. SUMMARY

The examples given in the previous section illustrate how the use of full scale plant testing facilities for AGR steam generators has been of great value in establishing satisfactory operating chemistry regimes and thermohydraulic conditions for the steam generators. These have helped avoid significant materials' corrosion problems and, to date, there have been very few tube leaks in the plants themselves. Of those which have occurred, the majority have not been the result of any on-load corrosion damage mechanism. The oldest plants have now accumulated over 120,000 hours operation.

The facility itself still continues to be of value, even after almost 20 years operation in support of AGRs, and is currently being used to evaluate issues related to steam generator pressure loss.

5. ACKNOWLEDGEMENTS

This paper is published with the permission of Nuclear Electric Ltd. The authors also wish to thank the numerous individuals who have contributed to the successful operation of the test facility over many years. In particular, we wish to thank J D Tyldesley and G G Lewis who managed the rig's operation until March 1997, and who also made considerable contributions to some of the work programmes described.

6. REFERENCES

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2. D Penfold, G M Gill, J C Greene, G S Harrison and M A Walker; 'Chemical and Hydrothermal Studies on Once Through Boilers using a Full Scale Replica', The Nuclear Engineer, Vol. 28, No. 2, 1987.

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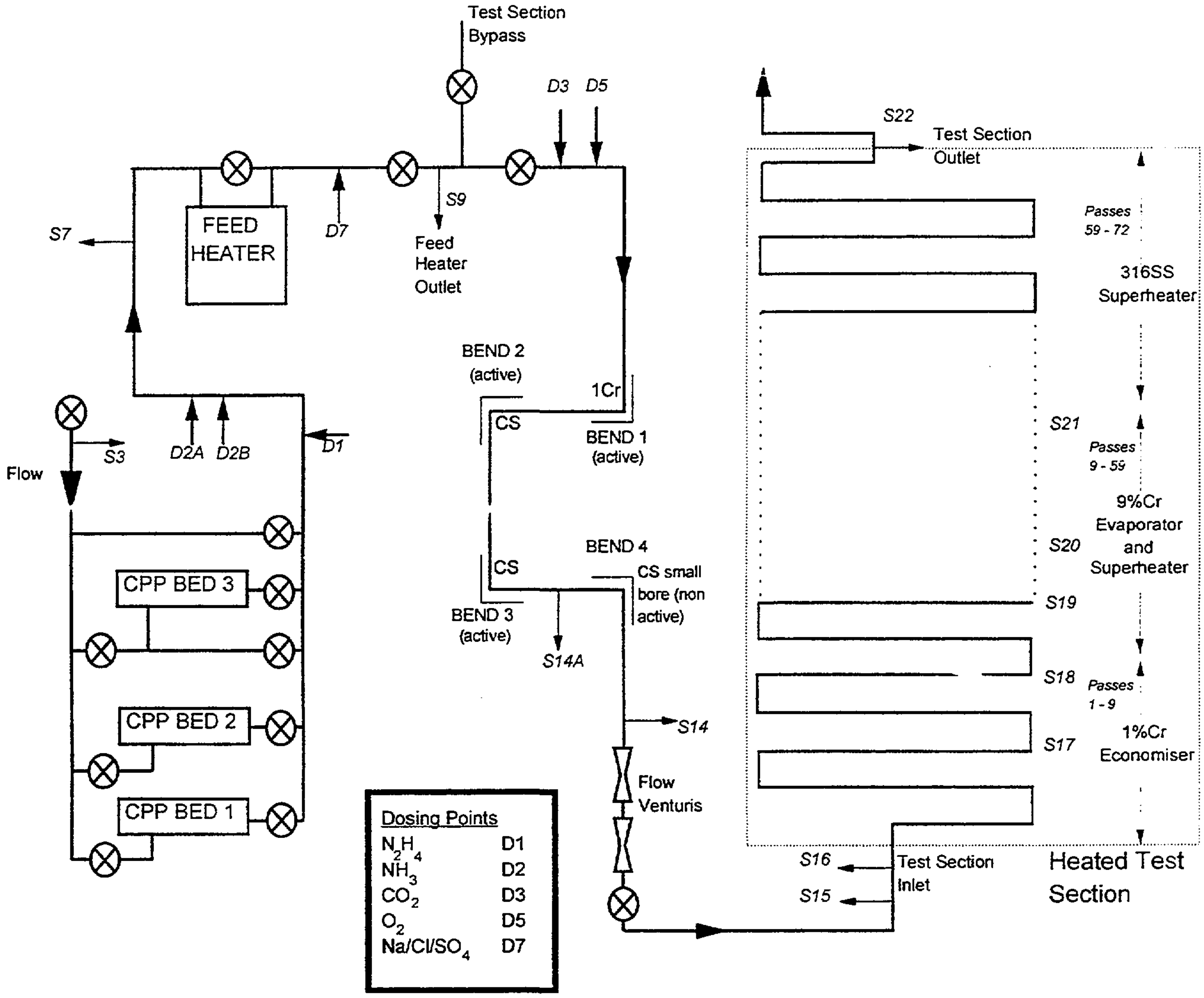


FIGURE 1: Schematic Diagram of the Serpentine Test Section Showing Dosing Points (D) and Sampling Points (S)

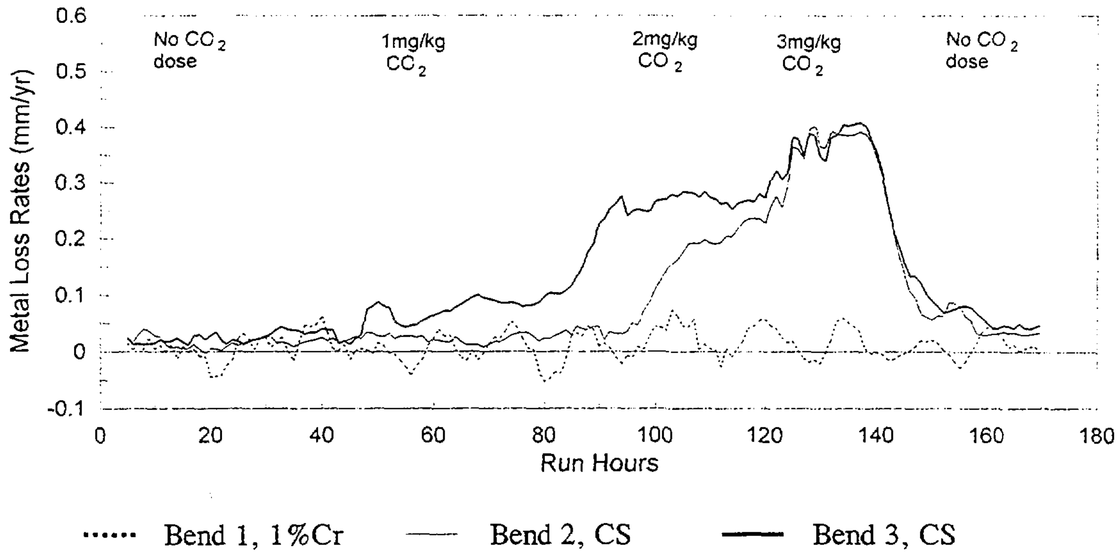


FIGURE 2: Effect of Feedwater Carbon Dioxide Levels on FAC rates at 1.1 mg/kg ammonia

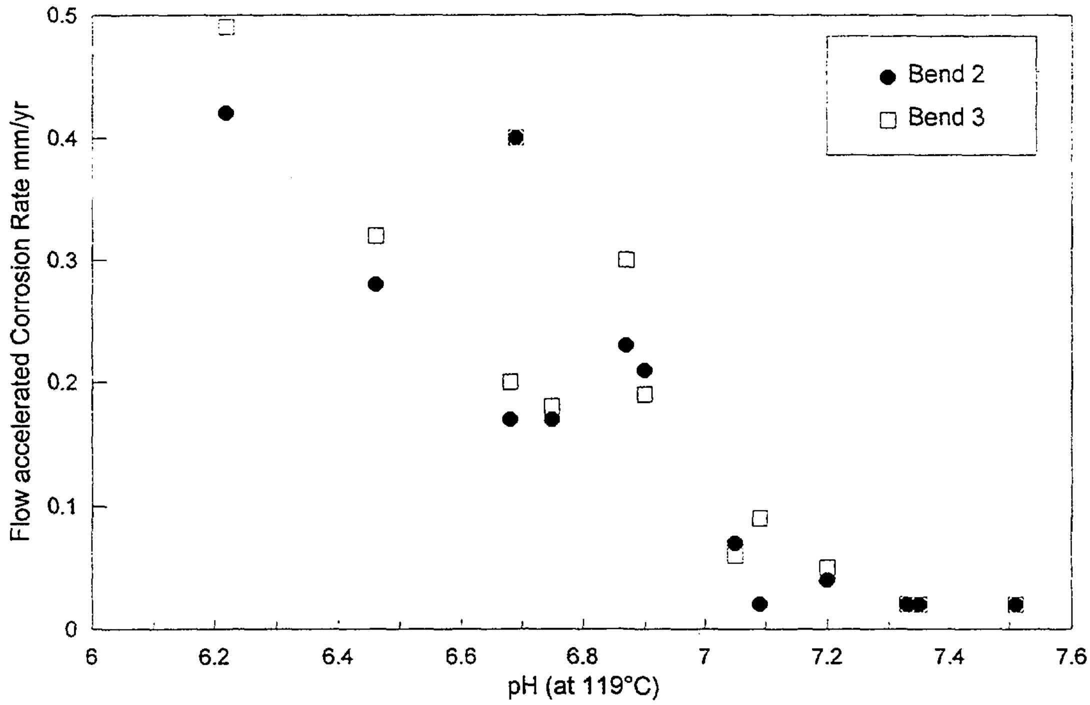
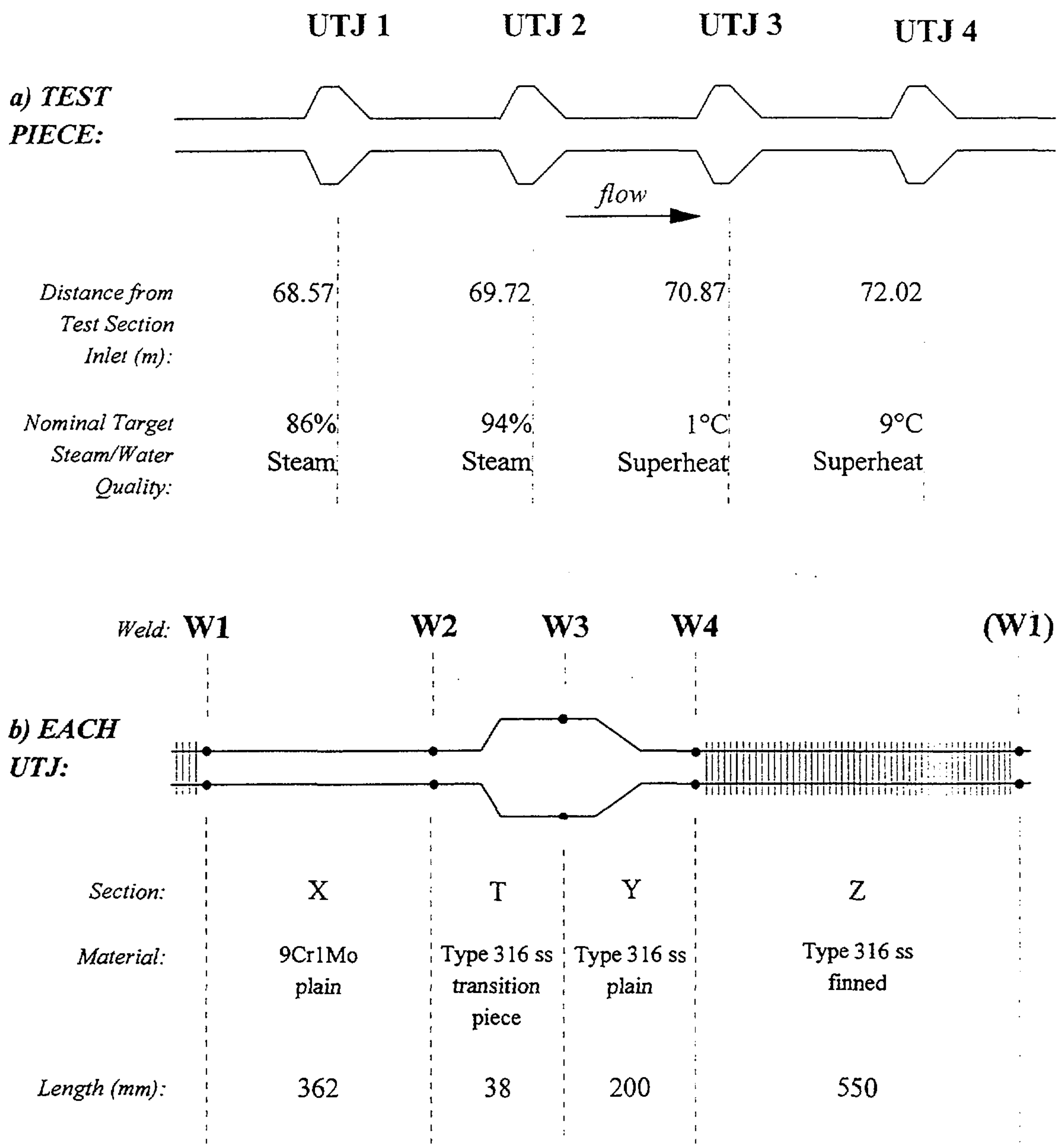


FIGURE 3: Relationship Between FAC and pH (119°C) for Carbon Steel Bends



Notes:

1. W1 of UTJ 1 connected the Test Piece to the end of the Rig 9Cr1Mo superheater section
2. There was one further weld at the end of UTJ 4 which connected the Test Piece to the start of the Rig Type 316 SS superheater section

FIGURE 4 : Schematic Diagram of the Test Piece

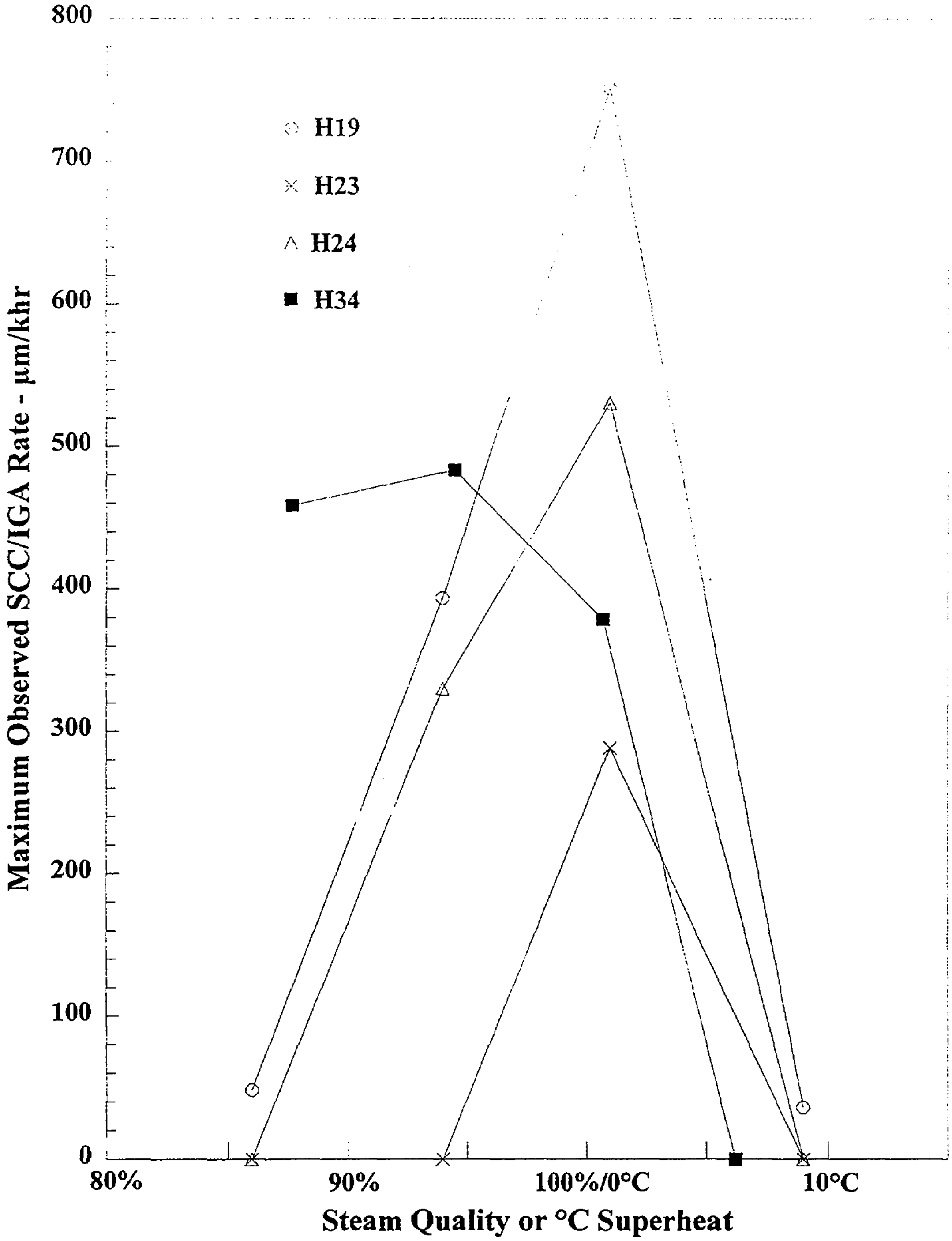


FIGURE 5: Maximum Observed SCC/IGA Penetration as a Function of Hydrothermal Conditions

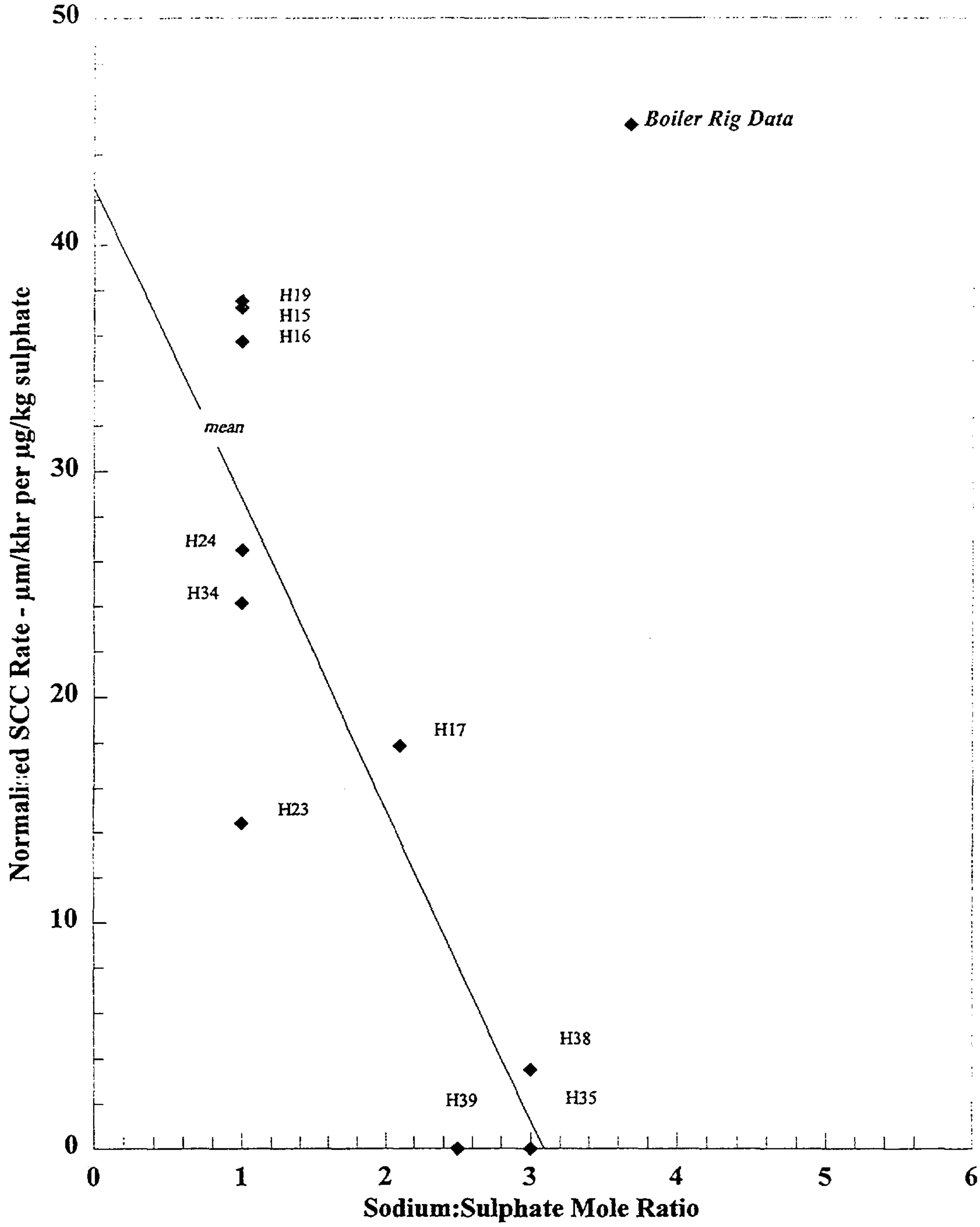


FIGURE 6: Effect of Feedwater Sodium:Sulphate ratio on SCC damage rate

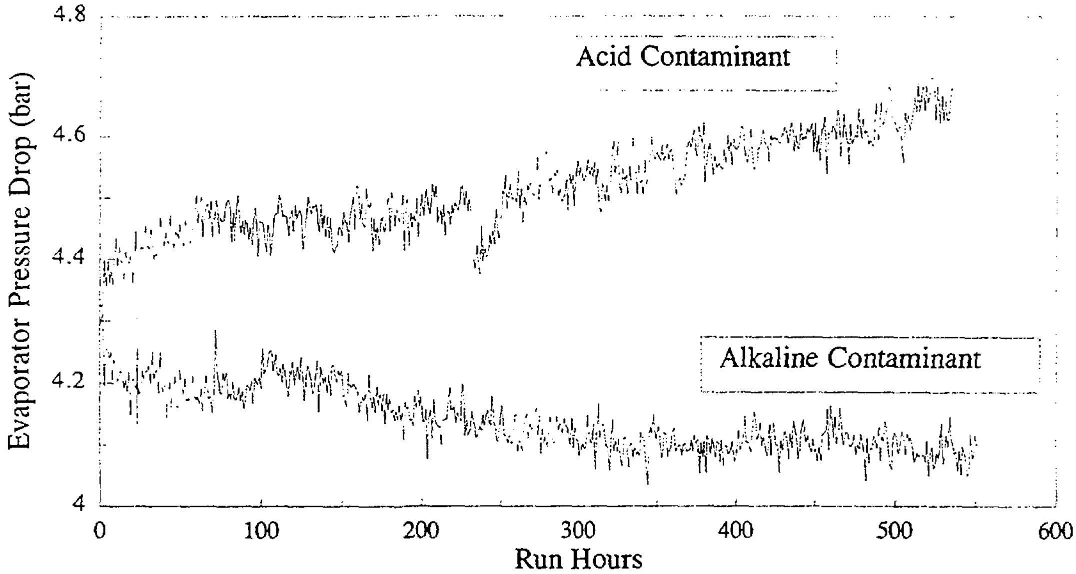


FIGURE 7: Effect of Feedwater Chemistry on Evaporator Pressure Drop

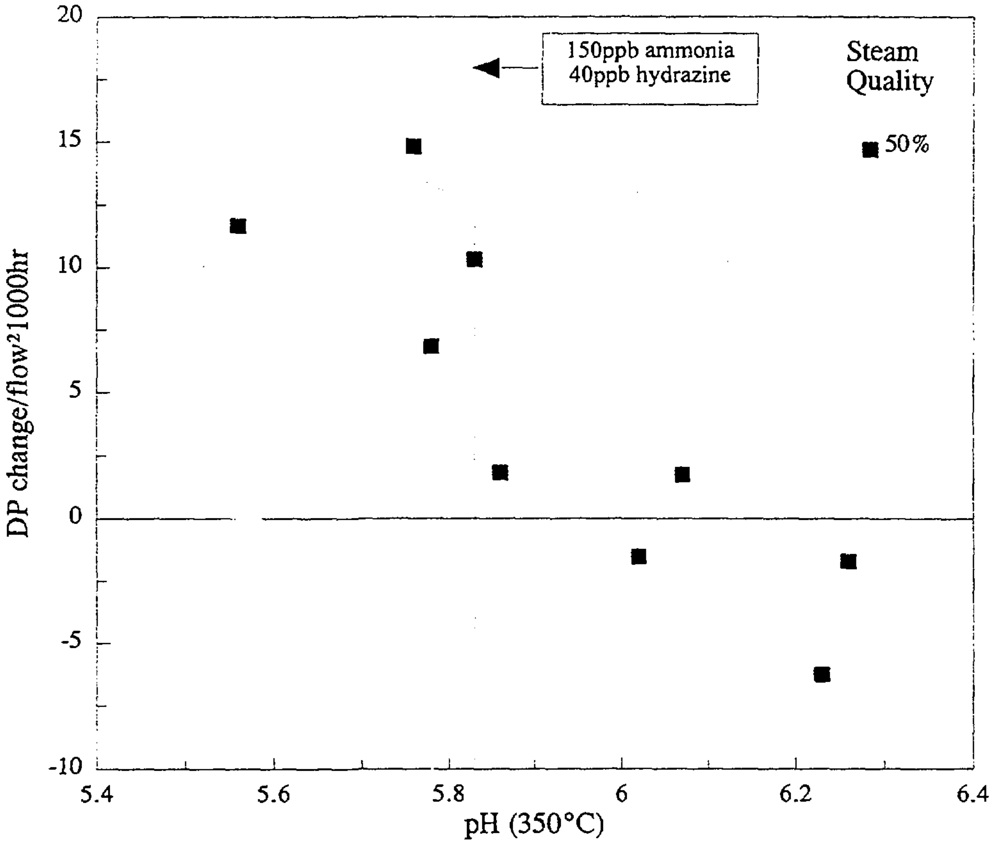


FIGURE 8: pH Dependence of Evaporator Pressure Drop

DISCUSSION

Authors: I.S. Woolsey, A.J. Rudge, D.J. Vincent, Nuclear Electric Ltd.

Paper: Evaluation of Materials' Corrosion and Chemistry Issues for Advanced Gas Cooled Reactor Steam Generators Using Full Scale Plant Simulations

Questioner: R. Crovetto

Question/Comment:

Could you elaborate more about the geometry of the 56 points where you find the ripple magnetite? And the possible mechanism of the formation of that ripple magnetite?

Response:

The rippled magnetite we observe is in the evaporator section of the steam generator, which is fabricated from the 9% Cr 1% Mo steel. The deposits, however, are derived at least partly from the upstream 9% Cr 1% Mo economizer by internal transport of iron in solution. The ripple structure of the deposits derives from the hydrodynamics of the deposition process, and naturally occurring ripple roughness is seen in a wide range of situations; e.g. silica deposition in pipeline flows. It can also occur as a result of the hydrodynamic influence on dissolution processes; e.g., FAC and ice dissolution in flowing water.

Questioner: J. Gorman

Question/Comment:

Have you identified the species involved in the SCC of Type 316? Are they reduced sulfur species? More broadly, have you defined the ECP, pH and species involved in the SCC?

Response:

The IGA/SCC of Type 316 in acidic sulphate environments occurs with the formation of sulphites from the sulphate, although both of these are carried over in the steam in the steam generator. The corrosion process also generates metallic sulphides, particularly NiS and these are found in both the general corrosion film and down stress-corrosion cracks. I would expect some H_2S may also be formed, but we have not detected this in our rig experiments. Extensive autoclave studies were carried out in acidic sulphate environments prior to the steam generator tests, and the corrosion behaviour was similar in both cases, but the rig work allows definition of the feedwater levels likely to produce damage.

Questioner: P.L. Frattini, EPRI

Question/Comment:

Concerning iron transport in model boiler tests using DMA: do you have an understanding of what fraction of the iron feed to the test section is in soluble form versus particulate oxide form?

Response:

The iron measured within the test section is derived mainly from intermediate temperature parts of the test section, which then redeposits in the evaporation region. The feedwater contains only sub-ppb levels of iron. Since the low temperature sections operate under oxidizing conditions, where iron (hematite) solubilities are very low, it is the intermediate temperature section (>250°C) which supplies most of the internal iron transport. This is because all the oxygen has been removed by ~250°C in the test section and reducing conditions are maintained by the residual hydrazine. We believe the iron is predominantly in the soluble form. The deposits formed are highly crystalline, and this is consistent with the expectation that the iron is mainly soluble, but we have not carried out a full speciation of the depositing iron.