

STEAM GENERATOR MATERIALS CONSTRAINTS IN UK DESIGN GAS-COOLED REACTORS

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Abstract

A widely reported problem with Magnox-type reactors was the oxidation of carbon steel components in gas circuits and steam generators. The effects of temperature, pressure, gas composition and steel composition on oxidation kinetics have been determined, thus allowing the probabilities of failure of critical components to be predicted for a given set of operating conditions. This risk analysis, coupled with regular inspection of reactor and boiler internals, has allowed continued operation of all U.K. Magnox plant.

The Advanced Gas Cooled Reactor (AGR) is a direct development of the Magnox design. The first four AGRs commenced operation in 1976, at Hinkley Point 'B' and at Hunterston 'B'. All known materials problems with the steam generators have been diagnosed and solved by the development of appropriate operational strategies, together with minor plant modifications. Materials constraints no longer impose any restrictions to full load performance from the steam generators throughout the predicted life of the plant.

Problems discussed in detail are:-

1. Oxidation of the 9 Cr - 1 Mo superheater.
2. Stress corrosion of the austenitic superheater.
3. Creep of the transition joints between the 9 Cr - 1 Mo and austenitic sections.

With the 9 Cr - 1 Mo oxidation maximum temperature restriction virtually removed and creep constraints properly quantified, boiler operation is now favourably placed. Stress corrosion research has allowed the risk of tube failure to be related to time, temperature, stress and chemistry. As a result, the rigorous "no wetting" policy has been relaxed for the normally high quality AGR feedwater, and the superheat margin has been reduced to 23°C. This has increased the size of the operating window and reduced the number of expensive, and potentially harmful, plant trips.

1. INTRODUCTION

The world's first commercial gas-cooled reactor commenced operation at the Berkeley (U.K.) Power Station in 1962. Since then, "Magnox"-type gas-cooled reactors have been built in the United Kingdom, France, Italy and Japan. Magnox reactors have performed well with high availabilities. Sizewell became the first nuclear power station to gross more than 50,000,000 MWh, marginally ahead of the Connecticut Yankee pressurized water reactor plant.

Most of the early difficulties associated with Magnox steam generators have been reported widely and are now history. The only difficulty that is discussed here is the oxidation of mild steel components in reactors and steam generators. This was undoubtedly the most severe problem encountered with the Magnox stations and is responsible for the continued derating of certain reactors.

Hunterston 'B' and Hinkley Point 'B' were the first advanced gas cooled reactor (AGR) stations to be commissioned. They both achieved power ratings in early 1976. The principal change from "Magnox" reactors is the use of oxide fuel in stainless steel cans. This allows higher reactor temperatures and steam conditions commensurate with modern fossil-fired plant (160 bar, 538°C main and 538°C reheat).

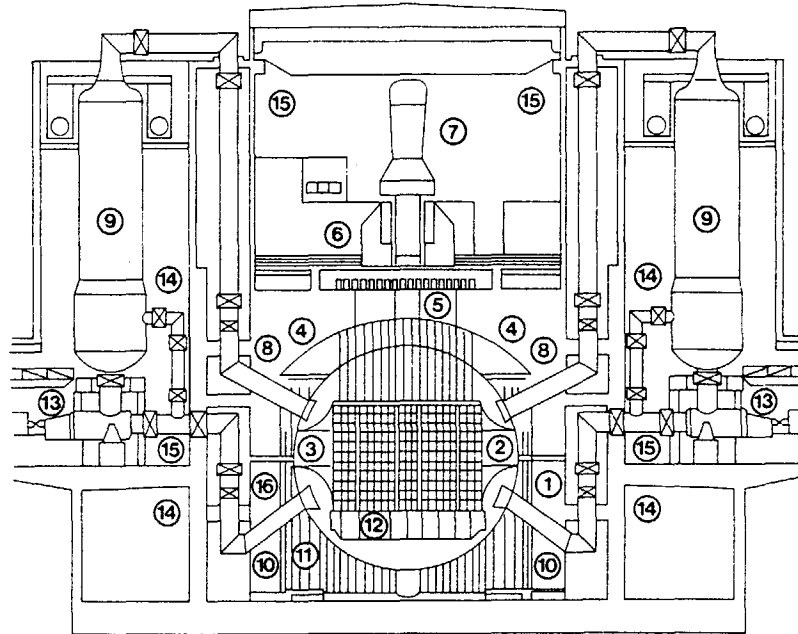
Ten AGRs are now operating, with a further four due to be commissioned in the near future. All are designed to generate 660MW(electric). Early operational experience has been good. Although steam generator problems have occurred they have been solved and now constitute no limit to full load performance. This paper deals with three such problems at Hinkley and Hunterston:-

1. gas-side oxidation of the 9Cr-1Mo superheater.
2. stress corrosion of the austenitic superheater.
3. creep of the transition joint between the 9Cr-1Mo and austenitic superheaters.

These problems imposed temperature constraints (high and low) that necessitated development of a special operational strategy.

2. OXIDATION OF MILD STEEL IN MAGNOX REACTOR STEAM GENERATORS

The principle of the Magnox reactor system is that nuclear fuel, encased in magnesium alloy (Magnox) cans in a graphite moderator core, generates heat that is transferred by carbon dioxide at high pressure to steam generators (see Fig. 1). Mild steel is used for virtually all the structural steel work in the boilers and reactors. Its chief advantages are that it is low cost, readily available, easy to fabricate, less active than stainless steel when exposed to a neutron flux, and has better heat transfer characteristics than higher alloy steels. It was recognized that oxidation would take



- | | |
|--------------------------------|------------------------------------|
| ① REACTOR PRESSURE VESSEL | ⑨ BOILERS (SIX PER REACTOR) |
| ② FUEL ELEMENTS | ⑩ COOL GAS INLETS TO REACTOR |
| ③ GRAPHITE MODERATOR | ⑪ THERMAL SHIELD |
| ④ CHARGE TUBES | ⑫ DIAGRID |
| ⑤ CONTROL ROD STANDPIPES | ⑬ MAIN CIRCULATORS |
| ⑥ CHARGE FLOOR | ⑭ GAS ISOLATING VALVES |
| ⑦ CHARGE/DISCHARGE MACHINE | ⑮ HINGED EXPANSION BELLOWS |
| ⑧ HOT GAS OUTLETS FROM REACTOR | ⑯ CAN-FAILURE DETECTION STANDPIPES |

Fig.1 Cross section through Magnox reactor.

place, but this too can be an advantage as oxide-free surfaces or sliding components can gall and seize.

The oxidation reaction is described by Eq.(1) as:



Extensive laboratory studies showed that the oxide should remain protective under normal operating conditions although higher temperatures and pressures would give rise to a different oxide morphology with much faster kinetics. After a few years of operation, it was discovered that the more aggressive oxidation mechanism could occur under service conditions. Maximum oxide thicknesses were still very small and unlikely to give rise to major difficulties during the design lifetime. In 1968, however, the bolts securing a specimen basket in a reactor at Bradwell were found to be broken. The cause was diagnosed to be oxide jacking at interfaces in the bolt/washer/component assembly.

A characteristic of the "breakaway" oxide is that it is porous and continues to form even after interfacial gaps have been filled. It was, therefore, expected that other, more critical, bolts would be affected. Certain weld geometries, too, would be at risk. The following actions were taken:-

1. Carefully inspect all accessible reactor/boiler internals.
2. Reduce maximum gas temperature to 360°C.
3. Reduce water levels in CO₂ coolant.
4. Review emergency shutdown capability.
5. Initiate major investigative programme.

Work on CO₂ oxidation in laboratory autoclaves had already shown that actions 2 and 3 would be beneficial. What was now needed was an understanding of the mechanism of oxidation and means whereby its effects on operation might be minimized.

It must be stated that this particular phenomenon of breakaway oxidation is peculiar to high-pressure CO₂. At lower pressures (unfortunately too low to be of commercial advantage), the effect disappears. Our current understanding of the mechanism is that metal ions diffuse through the protective oxide leaving vacancies behind, which coalesce to form pores. Carbon monoxide produced by the oxidation reaction (Eq. 1) fills these pores, thus promoting the Boudouard reaction:



The carbon thus formed diffuses into the steel and produces cementite, which acts as a catalyst for the above reaction. The CO₂ causes further oxidation at the base of the scale; thus, the reaction is self-sustaining.

Apart from quantifying the effects of temperature, pressure, gas composition, and steel composition on reaction kinetics, the research programme also investigated the application of gas phase inhibitors acting as catalytic poisons. Undoubtedly, however, the most important outcome of the work was that the probabilities of failure of critical components could be predicted for a given set of operating conditions. This risk analysis, coupled with regular inspection of reactor and boiler internals to provide confirmatory evidence, has been sufficient to satisfy the British Nuclear Installation Inspectorate as to the overall safety of the plant.

Accumulated experience, together with a more precise knowledge of oxidation kinetics has permitted the initial restricted maximum gas temperature (360°C) to be relaxed under carefully controlled circumstances, thereby allowing higher outputs to be achieved.

Commercial Magnox reactors have now operated for 25 years with projected lives well into the 1990s.

3. STEAM GENERATOR PROBLEMS IN ADVANCED GAS-COOLED REACTORS

3.1. Steam Generator Design Parameters.

The steam generators at Hinkley Point and Hunterston are located around the reactor within the pressure vessel. Gas circulators in the lower part of the pressure vessel walls drive carbon dioxide coolant around the circuit. Each of the four steam generators is divided into six independently fed "half units". A "once-through" design with serpentine tubes is utilized. Relevant design parameters are given in Table 1.

TABLE 1.

Hinkley Point 'B' Design Parameters.

| | |
|---|---------|
| Electrical output, gross (MW) | 2 x 660 |
| Overall thermal efficiency (%) | 41.6 |
| Reactor thermal power (MW) | 1493 |
| Mean channel gas temperature, inlet (°C) | 319 |
| Mean channel gas temperature, outlet (°C) | 645 |
| Core gas mass flow (kg/s) | 3667 |
| Coolant pressure (bottom slab) bar (abs) | 42.4 |
| Vessel internal diameter (m) | 18.9 |
| Vessel internal height (m) | 19.38 |

Coolant gas composition has varied since commissioning but is typically in accordance with the following upper limits:-



Water chemistry is controlled by zero solids (all volatile) treatment. Full flow condensate polishing is provided.

Mild steel is used for the economizer tubes and supports; 9Cr-1Mo for the evaporator and primary superheater, and austenitic stainless steel for the secondary superheater and re-heater as shown in Fig. 2.

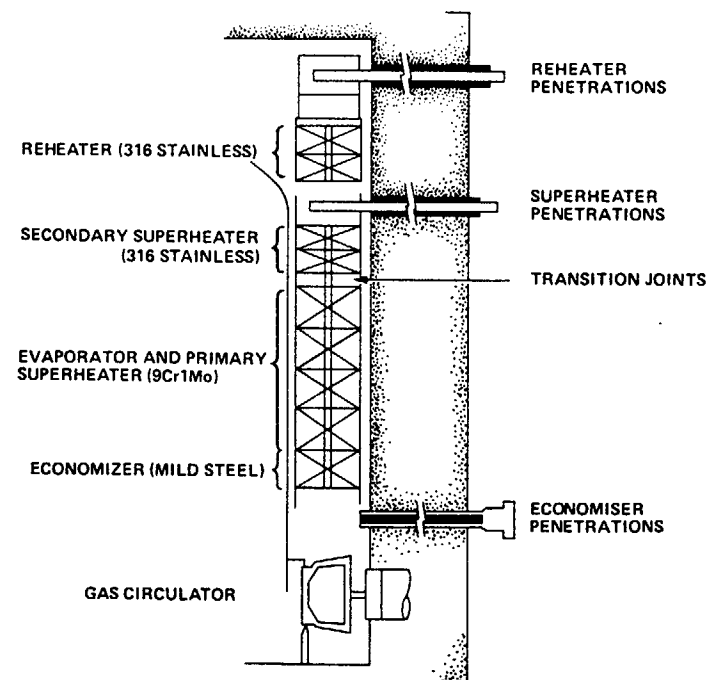


Fig.2 Schematic of Hinkley Point/Hunterston AGR steam generators.

4. HISTORICAL REVIEW OF PROBLEMS

This section introduces each problem as it occurred in chronological sequence. Each subject will then be discussed in greater detail in subsequent sections.

A minimum superheat margin of 106°C between the dryout point and the 9Cr-1Mo to Type 316 stainless steel transition joint was specified in the original design to eliminate the risk of wetting the stainless steel, which was known to be sensitive to stress corrosion. The discovery, before reactor commissioning, that 9Cr-1Mo steel could be prone to breakaway oxidation required that the temperature at the top

of the 9Cr-1Mo section (i.e. at the transition joint) should be temporarily reduced from the 485°C design value to 446°C pending further investigation of the oxidation process. The boiler operating conditions were re-optimized around this new limit and the superheat margin reduced to 90°C. Maximum load was thereby restricted to 82% (535 MW) of the design rating. A substantial research programme was launched to study the factors governing stress corrosion of Type 316 stainless steel since further relaxation of the superheat margin could allow some recovery of steam generator output.

The revised operating constraints led to frequent low steam temperature trips. By this stage, however, the conditions governing 9Cr-1Mo oxidation were becoming better understood, thus allowing sufficient relaxation of the upper temperature limit to reduce trip frequency.

As the 9Cr-1Mo restrictions were relaxed, concern was focused on the Sanicro 71 (72Ni-16Cr-10Fe) transition joints. Small defects had been discovered in these joints during Hunterston B construction, and it was necessary to assume their presence at both Hinkley and Hunterston. This led to the possibility of creep crack growth during service. The creep properties were investigated and these studies, together with transition joint temperature distribution determinations, enabled definition of tube failure probabilities at given temperatures. A statistical approach was then developed to allow operators to determine the probability of a given tube running outside the imposed constraints for any observed mean and standard deviation of transition joint thermocouple readings.

5. 9Cr-1Mo STEEL OXIDATION

When the evaporator and primary superheater sections were designed it was expected (from 20,000 hour laboratory data) that protective oxidation kinetics would apply at 520°C for 200,000 hours. Maximum metal temperatures were therefore set at 485°C for tubes, and 518°C for the support structure.

The laboratory data were extended to longer periods during construction and commissioning and, in the late 1960s, a non-protective oxide possessing rapid growth characteristics was discovered. Of prime importance was the time to breakaway when rapid loss of section occurred. Even if the risk of tube failure is low, accumulation of oxide debris within the gas circuit could significantly impair reactor operation and maintenance.

Maximum tube temperatures were, therefore, reduced from 485°C to 446°C and a large investigative programme was established.

The original laboratory tests were carried out on coupons having a large edge-to-surface ratio. Breakaway corrosion occurs in much shorter times and at lower temperatures at such locations than would be expected on a large, smooth, surface such as a tube or support strap. Coupon-to-tube correlations were therefore sought. When

these geometry effects were taken into account quantitatively and proper allowance made for gas and materials composition effects, it became clear that the upper temperature limits would be relieved to such an extent that full load operation could be restored.

6. STRESS CORROSION

Stress corrosion damage is difficult to predict in a quantitative manner as it arises from a complex interaction of stress, material, temperature, pressure and environment. The original design concept was to avoid wetting the austenitic superheater section. This was achieved by defining a minimum superheat margin of 106°C at the bottom of the austenitic section (9Cr-1Mo to austenitic transition joint). However, the upper temperature limit imposed by 9Cr-1Mo oxidation previously referred to, meant that reductions in superheat margin were necessary. A major research programme was therefore aimed at defining the conditions under which wetting of the austenitic superheater could be tolerated.

The first step was to recalculate the minimum superheat margin. The lifetime of water droplets can be calculated if their initial size and evaporation rate are known. Once the droplet size falls below a certain radius, it will stay entrained within the gas stream even on a 180-deg. bend. This defines the limit beyond which tube walls cannot be wetted. Evaporation rates depend on the impurities in the droplet. As evaporation proceeds, salts concentrate and raise the boiling point so that evaporation rates slow down. Hence, minimum superheat margins depend on water purity. Calculations, combined with confirmatory tests on tube rigs, indicated that a minimum margin of 23°C should be sufficient to keep the transition joints dry under steady-state conditions. Clearly, however, tube temperatures vary from one transition joint to another; thus, the operational margin must be increased to allow for this variation. Nevertheless, a considerable improvement on the original 106°C margin was possible. A detailed study of feedwater purity was undertaken covering all known operating conditions and faults. Stress corrosion tests were then carried out in an attempt to cover, in matrix fashion, the whole range of material and environmental variables. One such test utilized a simulated full-size boiler element in which once-through boiling conditions and feedwater chemistry were carefully controlled.

The research results showed that austenitic superheater tubes could be wetted for short periods (e.g. start-up and reactor trip conditions) provided that such periods did not coincide with an "out-of-specification" condition for feedwater chemistry such as might occur, for instance, during a particularly severe series of condenser leaks. Implementation of these recommendations led to a dramatic decrease of reactor trips and an eventual return to full-load capability for the steam generators.

7. CREEP OF TRANSITION JOINTS

When small defects were found in the root run of transition welds between the 9Cr-1Mo and Sanicro transition pieces at Hunterston, concern was expressed for the long-term integrity of such welds at Hinkley and Hunterston. If further reductions in maximum transition joint temperature were required this would mean that the existing superheat margin would have to be further reduced. Replacement of defective joints, however, would be an extremely difficult and costly exercise. Thus it was necessary to quantify the possibility of joint failure in service and to devise operational methods to reduce such a risk to an acceptable level.

The transition between the ferritic and austenitic parts of the boiler is made through a high nickel transition piece, Sanicro 71 (basically 72% Ni, 16% Cr, 10% Fe), with the Sanicro 71/9Cr-1Mo weld being made with 9Cr-1Mo filler wire and the Sanicro 71/316 weld with 316 filler wire, Fig. 3. The defects are caused by the transfer of nickel from the Sanicro 71 into the weld pool. In general, cracks do not extend beyond the limit of the root run (~ 1.5mm) and are both axial and circumferential in orientation.

Loadings likely to influence crack behaviour were identified as residual stress, pressure stress, thermal discontinuity stresses due to varying weld composition, and tube bank system stress arising from differential thermal movement between tubes and casing. Three modes of crack propagation were identified: creep, fatigue and waterside stress corrosion.

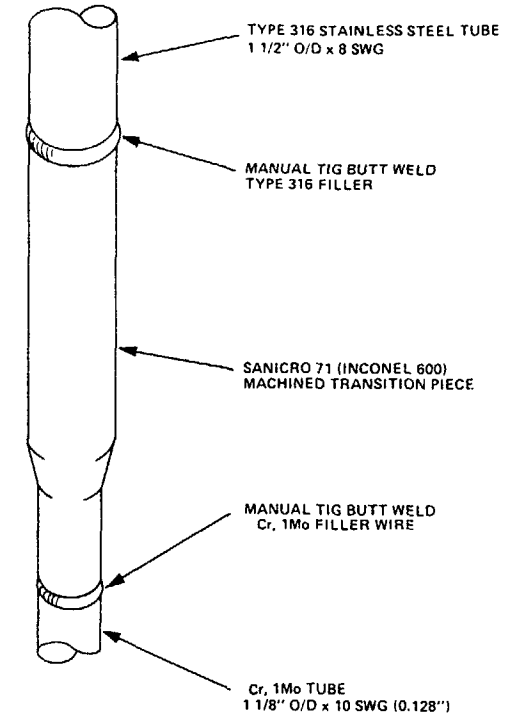
An extensive testing programme was mounted to determine materials composition and thermal expansion coefficients of the components forming the transition joint, together with tensile, creep, corrosion and fatigue properties of the weldments on both uniaxial and tubular specimens.

It was concluded that failure due to stress corrosion and fatigue (both high and low cycle) was unlikely provided the weld was operated in a dry environment, hence re-emphasising the need to maintain an adequate superheat margin.

Creep and creep crack growth, under the combined effects of axial pressure and system stresses (calculated to be 88 MNm²) could not be discounted, however, as possible failure mechanisms, and further longer term creep tests were commissioned. In the meantime, peak weld temperatures were restricted.

8. STATISTICAL MODEL

Having generated appropriate oxidation, stress corrosion and creep data, it is necessary to apply this information to the operation of the boilers. If an absolute limit is imposed beyond which the temperature of critical components never deviates, then plant inflexibility and commercial penalties result. From a practical point of view a comprehensive and continuous temperature monitoring



| CHEMICAL COMPOSITION OF PARENT METAL % | | | | | | | | |
|--|-----|------|------|-----|------|------|------|-------|
| ELEMENT MATERIAL | Mo | Ni | Cr | Fe | Si | Mn | Ti | c |
| 9% Cr | 1.0 | | 9.0 | | 0.65 | 0.45 | | 0.10 |
| SANICRO 71 | | 71.8 | 17.1 | 8.1 | 0.5 | 0.49 | 0.39 | 0.03 |
| TP 316H | 2.3 | 13.5 | 16.5 | | 0.6 | 1.7 | | 0.055 |

Fig.3 Transition joint between 9Cr 1Mo and austenitic superheaters.

system would be required. Access and instrumentation feed-through limitations render this impossible in the present situation at Hinkley and Hunterston.

A far better approach is to devise a risk criterion such that the probability of tube failure arising from a given mechanism can be predicted for any combination of time and temperature. Provided that we know how many tube failures can be tolerated within a given time, it should be a relatively simple matter to control the plant accordingly. For Hinkley Point 'B' it has been decided that not more

than 2% of all tubes may be allowed to fail within the plant lifetime (30 years). It must be emphasized that the term "risk" refers to commercial risk - none of the issues discussed in this report create any impediment to the overall safety of the plant.

8.1. Creep Failure Probability

The methods originally developed for predicting creep failure probabilities are discussed in detail in Ref. 1. They involved the extrapolation of stress rupture and creep strain data to the stresses and temperatures prevailing in the plant. Transition joint failure probabilities were then calculated as a function of temperature, assuming a plant lifetime of 30 full power years, Fig. 4.

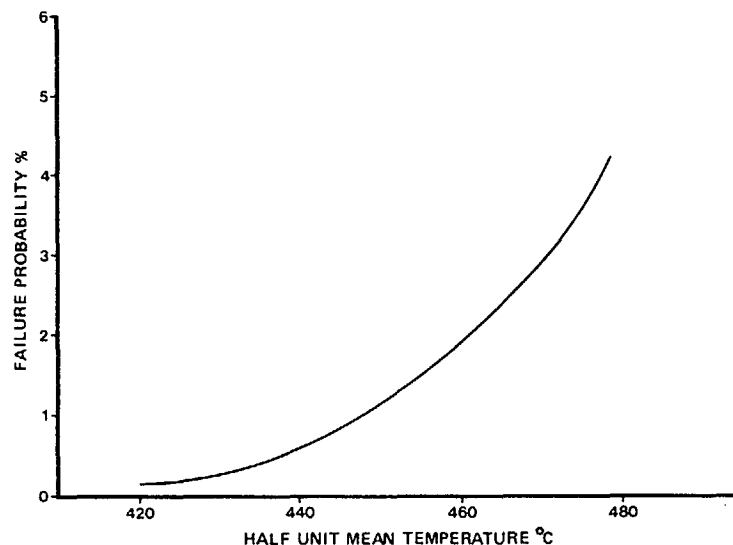


Fig. 4 Transition joint creep failure probabilities over 30 years as a function of half unit mean temperature.

The early methods have since been refined to allow for the different system stresses obtained in different tubes and to allow for the relaxation of these stresses during normal plant operation.

Steam generator control is based on the boiler "half-units" referred to in Section 3. Each half-unit contains 44 transition joints of which 3 have thermocouples attached, from which a half-unit "mean" temperature is derived. This temperature is controlled by adjustments

to the boiler water feed flow valve on each half-unit. A standard deviation of 18.5°C for all transition joint temperatures was used to derive the curve shown in Fig. 4.

8.2. Oxidation Failure Probability

Section 5 dealt with the problem of 9Cr-1Mo steel oxidation and the generation of laboratory data. The statistical treatment of these data is discussed elsewhere (Refs. 2 and 3). It is sufficient to say that we can now predict the number of tubes that will fail within a given time at a given temperature. It is assumed that failure occurs when the tube wall reduces to a cross section which is unable to support the imposed stresses.

8.3. Stress Corrosion Failure Probability

Calculation of failure probabilities is relatively straightforward for the cases of creep and oxidation failures since there exists a large amount of data (time to rupture, oxide growth rates, etc) on which to base statistical analysis of tube failure probabilities.

Definition of the lower (stress corrosion) limit, however, cannot be handled in quite the same way as insufficient stress corrosion data are available, for type 316 stainless steel in the appropriate environment, to allow meaningful statistical analysis of failure probability (Ref. 3). At present it is assumed that a tube will fail due to stress corrosion only if its minimum (transition joint) temperature is maintained continuously below 370°C at 80% of full load. (This is equivalent to a saturated steam temperature of 340°C, a superheat margin of 23°C and a steam-to-metal temperature difference of 7°C).

9. APPLICATION TO STEAM GENERATOR OPERATION

The plant control problem is simplified because the critical component is the same (upper transition joint) for all three tube failure mechanisms. Stress corrosion determines the lower temperature limit for the transition joint whereas the upper temperature will be fixed by the more restrictive of the creep and oxidation limits. For any mean half-unit temperature one can determine the probability that a given tube is above or below a given temperature. It then remains to combine this probability with the probability derived in the preceding section that a tube would fail in a given time if its temperature were maintained continuously above a given temperature (for creep and oxidation) or below the given temperature (for stress corrosion).

These three sets of probability data are combined in Fig. 5 using a distribution typical of measured transition joint temperatures with a standard deviation of 18 °C. Half unit temperatures are controlled so that no more than 2% of tubes should fail in 30 years. This corresponds to a temperature range, read from the total probability curve, of 409°C to 457°C. This is well within the capability of the

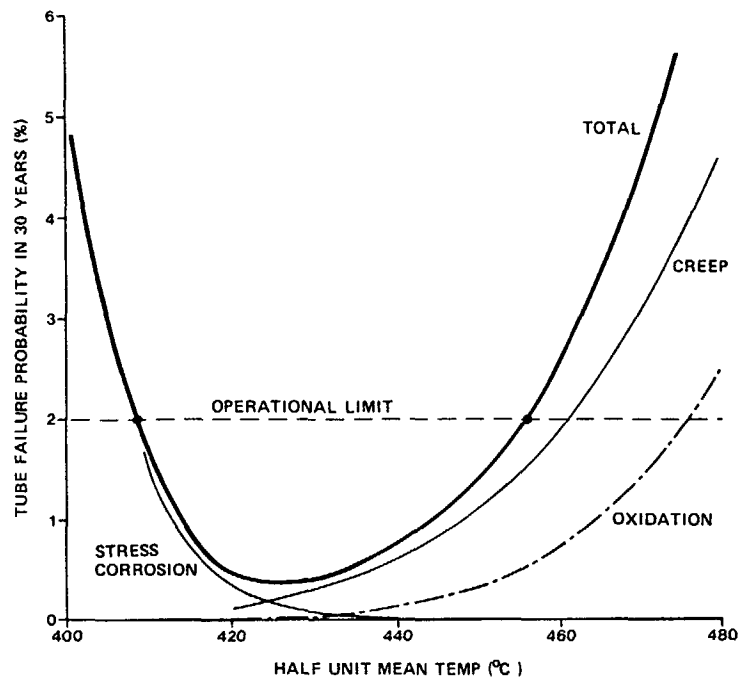


Fig. 5 Tube failure probabilities for stress corrosion of superheaters, creep of transition joints and oxidation of 9Cr 1Mo, expressed as a function of half unit mean temperatures.

plant and allows full load operation of the boilers without contravention of materials constraints. Fig. 5 also shows that transition joint creep effectively determines maximum operating temperatures rather than oxidation of 9Cr-1Mo.

The probabilistic approach to boiler operation also lends itself to improved control systems. It has been possible to arrange feedback of half-unit mean temperatures to adjust the position of the half-unit feed flow control valve, thereby allowing fully automated boiler control within the limits defined by materials constraints

Finally, Fig. 5 can be presented in a "life-fraction" format displayed in the Power Station control room. This permits increased flexibility of operation by allowing temperature constraints to be violated for limited periods (when increased output is required for example), provided that a subsequent period at reduced output allows the plant to be operated well within the normal constraints.

10. CONCLUSIONS

With the oxidation constraint virtually removed as a result of research effort, boiler operation is now in a favourable position. The stress corrosion programme has allowed the risk of failure to be assessed in terms of time, temperature stress, and chemistry. As a result, it has been possible to relax the rigorous "no-wetting" constraint for the normally high quality AGR feedwater and to reduce the normal minimum superheat margin to 23°C. In operational terms this allows a more controlled start-up procedure (since reactor temperature may be ramped at a slower rate), and has increased the size of the operational window within which it is required to maintain the boiler.

Now it is no longer considered necessary to trip the reactor every time the low temperature limit is transgressed for short periods. Transition joint creep limitations are well quantified.

The steam generators at Hinkley and Hunterston can be operated well within the temperature window, thereby allowing the plant to achieve the design output (of 660 MW) without impediment to plant life or safety. To date, after 11 years of continuous operation, and a total of more than 50 reactor-years for all AGR plant, there have been no transition joint failures.

11. ACKNOWLEDGEMENTS

The author wishes to thank all colleagues within the Central Electricity Generating Board and in companies involved in the design and construction of British gas-cooled reactors who contributed to the work described in this paper.

Permission to publish is granted by the Central Electricity Generating Board.

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