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An Overview of Materials Degradation by Stress Corrosion in PWRs

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Abstract

The aging of water cooled and moderated nuclear steam supply systems has given rise to many material corrosion problems of which stress corrosion cracking has proved to be one of the most serious. The aim of this paper is to review some examples of corrosion and particularly stress corrosion problems from the author's experience of interpreting and modelling these phenomena in PWR systems.

Examples of stress corrosion cracking in PWR systems described include the major issue of Alloy 600 intergranular cracking in primary PWR coolants, for which it is generally perceived that both adequate life prediction models and remedial measures now exist. Intergranular corrosion and stress corrosion cracking of Alloy 600 steam generator tubes that occur in occluded superheated crevices on the secondary side of steam generators due to hide-out and concentration of water borne impurities are also addressed.

Rather less extensive or well known examples are discussed such as the stress corrosion cracking of carbon and low alloy steels and of stainless steels in occluded dead-leg situations where it is sometimes difficult to guarantee adequate control of water chemistry, particularly at plant start-up. Reference is also be made to the use of high strength fastener materials in PWR systems as well as to the emerging issue of the effect of high neutron doses on the stress corrosion resistance of core structural components fabricated from austenitic stainless steels.

Keywords: Stress corrosion cracking, intergranular attack, hydrogen embrittlement, corrosion fatigue, PWR

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Introduction

Most of the world's nuclear steam supply systems for generating electricity are based on water cooled and moderated systems of which the most widespread designs are the Pressurized Water Reactor (PWR) and the Boiling Water Reactor (BWR). Such power production systems are initially designed to operate for up to 40 years and extension to 60 years is now being envisaged in many cases. It is perhaps often overlooked that the materials of construction that typically rely on their passivity in the aqueous environment for corrosion protection are being, or are intended to be used for significantly longer periods than in most other industries. Thus, long term operating experience is really only now being gained as many such nuclear power plants have reached 20 to 30 years old. It is not surprising, therefore, that as plants have aged, some serious corrosion problems have been encountered and remedied or repaired, of which one of the most serious is stress corrosion cracking.

The main difference between a PWR and a BWR is that in the former sub-cooled primary water cools the nuclear fuel and exchanges its heat via steam generators to create steam to drive a turbine and alternator in a secondary circuit. In the latter, water is boiled directly by the nuclear fuel and the steam is then separated and dried before passing directly to the turbine. Operating temperatures range between about 280 and 320°C except for the PWR primary circuit pressurizer which operates at 343°C. The fundamentals of water reactor chemistry treatment and control are described in reference [1] and a recent overview of PWR water chemistry operating experience in reference [2].

From a corrosion perspective, the operating environments in PWRs and BWRs are radically different as illustrated in Figure 1 on a Pourbaix diagram for nickel and iron at 300°C. (This figure also indicates the corrosion conditions for some common stress corrosion phenomena in both PWRs and BWRs that will be described later.) Thus, in PWRs, the water of the primary and secondary circuits are alkali treated and essentially oxygen-free to ensure minimum general corrosion and corrosion product release rates of the structural materials. PWR primary water also contains about 3 ppm of dissolved hydrogen to suppress water radiolysis and, as a consequence, primary circuit corrosion potentials are about 200 mV lower compared to the secondary side, in both cases being close to the H_2/H^+ redox potential for virtually all structural materials. In direct cycle BWRs by contrast, extremely pure water is used to ensure the lowest possible general corrosion rates. For those BWR plants on Normal Water Chemistry (NWC), radiolytic decomposition of water in combination with removal of non-condensable gases at the turbine condenser establishes electrochemically significant concentrations of dissolved oxygen and hydrogen peroxide in the recirculating water and consequently corrosion potentials are around 500 mV more positive than in PWR primary coolant circuits. In the case of the Hydrogen Water Chemistry (HWC) variant for BWRs, hydrogen at about 10% of the concentration typical of PWR primary circuits is used to depress corrosion potentials to values intermediate between those of BWR NWC and PWR primary circuits, specifically with the intention of protecting sensitized and cold worked stainless steels from Intergranular Stress Corrosion Cracking (IGSCC), as described briefly later.

The main emphasis of the examples of corrosion related material failures described hereafter come mainly from the author's experience of interpreting and modelling stress corrosion of structural materials in PWR systems. However, some examples of BWR experience are also provided for comparison as well as to illustrate the significantly different experience in many cases between the two water cooled nuclear reactor systems.

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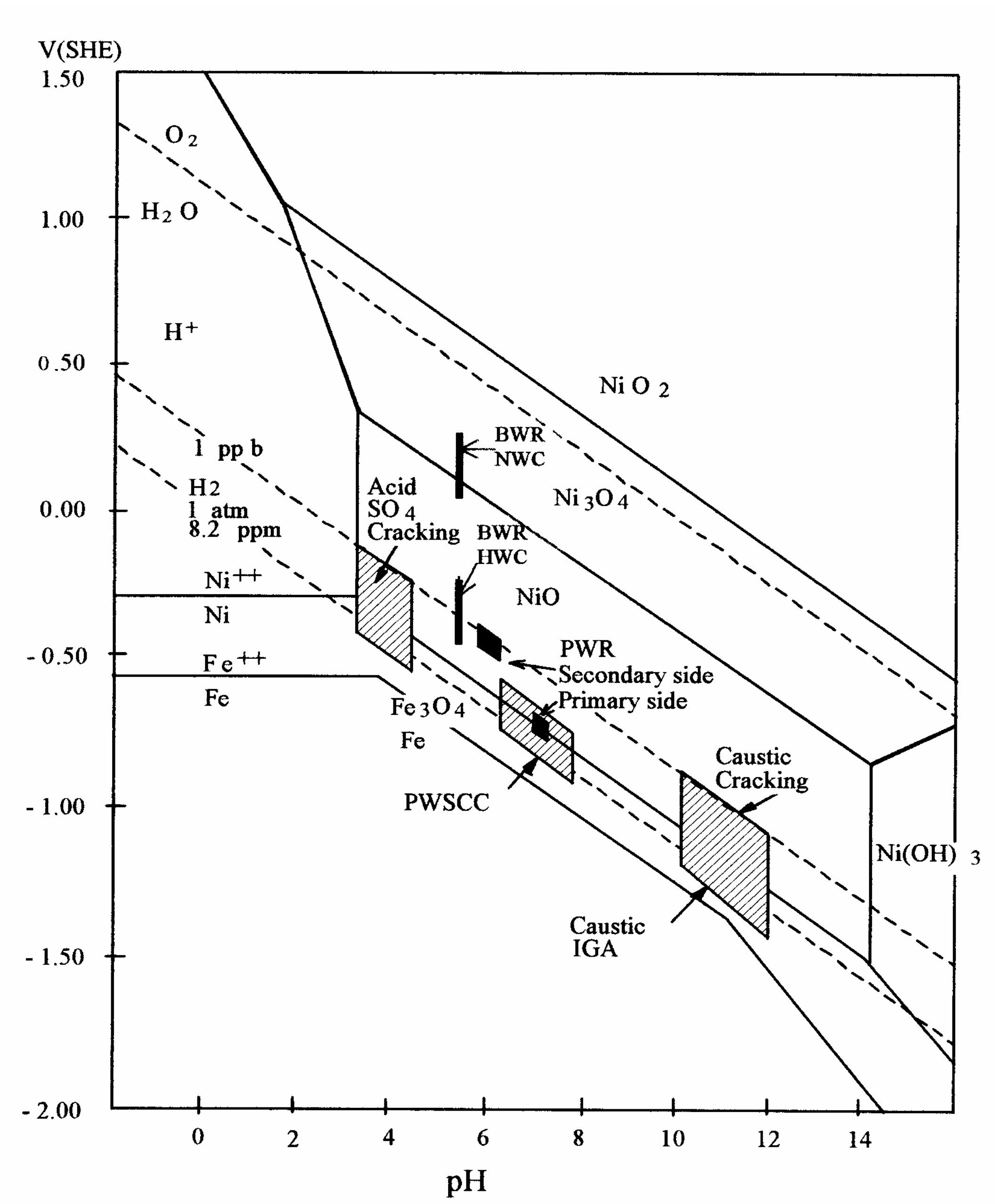

Figure 1: Simplified Pourbaix diagram for nickel and iron at 300°C showing the principal pH-potential combinations for PWR primary and secondary water, BWR Normal Water Chemistry (NWC) and BWR Hydrogen Water Chemistry (HWC) and the modes of stress corrosion cracking of Alloy 600.

Nickel base alloys in PWR primary water

The most severe stress corrosion problem to affect PWRs is IGSCC of Alloy 600 in PWR primary water (sometimes called PWSCC for Pressurized Water Stress Corrosion Cracking, as in Figure 1). It has become a generic issue rivalling that of IGSCC of sensitized and/or cold worked stainless steels in BWRs in terms of unanticipated outages and cost of repairs. In addition, high strength nickel base alloy fasteners and springs fabricated from precipitation hardened Alloys X750 or 718 are used extensively in PWR primary circuits and some service failures of these items have also occurred.

Alloy 600, a nickel base alloy containing 14-17% Cr and 6-10% Fe plus various minor elements was initially adopted for use in PWRs for steam generator tubes because of its excellent resistance to chloride cracking (from the secondary side) compared to stainless steel. It was also attractive for primary circuit components because of the close similarity of its coefficient of thermal expansion to that of the low alloy steel used to fabricate the reactor pressure vessel, pressurizer and steam generator shells.

The susceptibility of Alloy 600 to IGSCC in operational service in PWR primary water was first revealed in steam generator tubing in the early 1970s in tight U-bends and in rolled, cold-worked transitions in diameter within or just above the tube sheet [3]. This then became a major cause of steam generator tube cracking in the 1980s, and later, premature steam generator retirement and replacement. IGSCC of pressurizer nozzles and Control Rod Drive Mechanism (CRDM) penetrations in the upper heads of PWR reactor pressure vessels followed in the late 1980's and has continued for over a decade [4, 5]. Apparently interdendritic, but in fact intergranular, stress corrosion cracking of the compatible weld metals Alloys 182 and 82, the former having a composition similar to that of Alloy 600, has also been observed more recently in major primary circuit welds of several PWR plants, often after very long periods in service ranging between 17 and 27 years [5]. To these can be added the experience of extensive IGSCC in the γ' strengthened analogue of Alloy 600, Alloy X750, which is used for split pins attaching the CRDM guide tubes to the upper core plate. Even Alloy 718, a high strength nickel base alloy containing 17-21% Cr, which is normally considered a very reliable high strength material in PWR primary water use, has occasionally exhibited IGSCC [4].

A common feature of service failures of Alloy 600 and its compatible weld metals is the presence of very high residual stresses exceeding the nominal yield strength, usually coupled with a roughly machined or heavily ground surface finish. High residual stresses may be induced by rolling operations as with steam generator tube expansion into the steam generator tube sheet mentioned above or by nearby welding operations as in the case of CRDM nozzles. If thermal or mechanical plastic straining results in a plastic compression / tension hysteresis cycle, then very high tensile stresses easily up to 1000 MPa can be generated. By contrast, stress relief (in practice of attached low alloy steel components) has a very favourable effect on IGSCC resistance and no failures of Alloy 600 components so stress relieved have occurred in service. The other major factors influencing IGSCC susceptibility are the material microstructure and the temperature, an activation energy of 44 kcal/mole being generally admitted for crack initiation. Much research into the metallurgical parameters affecting IGSCC of Alloy 600 and similar materials in PWR primary water has shown that chromium carbides precipitated on the grain boundaries improve resistance while intragranular carbides have the opposite effect. Thus material procurement specifications were developed to ensure that products were delivered with the carbon precipitated as far as possible as carbides on grain boundaries. Even "sensitized" materials, that is those with grain boundary carbides but an adjacent narrow zone of chromium depletion have improved IGSCC resistance in PWR primary water, in sharp contrast to their very poor resistance in oxygenated BWR NWC.

The generic mechanism IGSCC of the nickel base Alloy 600 and its high strength analogue, Alloy X750, in PWR primary water has been extensively studied. Despite considerable experimental efforts, no consensus exists as to the nature of the cracking mechanism [1] and both life modelling and remedial measures have relied on empirical, phenomenological correlations. In addition to the major influencing parameters of stress, cold work, temperature and carbide morphology mentioned above, a profound influence of hydrogen partial pressure (or corrosion potential) has been identified with a worst case centred on corrosion potentials near the Ni/NiO equilibrium (Figure 1). The mechanism of cracking also does not apparently change between 300°C sub-cooled water and 400°C superheated steam.

It is interesting to note that despite the intense debate concerning the mechanism of IGSCC of Alloy 600 in PWR primary water, the most recent models incorporate the idea that solid state grain boundary diffusion is rate controlling [6]. This is independent of whether the mechanistic model considers that cracks advance by an oxidation process at the crack tip or due to embrittlement caused by hydrogen discharged by the matching cathodic reaction. Such models provide physically based support for the high value of the apparent activation energy, which is typical of solid state grain boundary diffusion in nickel. Physical support for a fourth power dependency of IGSCC on applied stress comes mainly from studies of grain boundary sliding (itself dependent on grain boundary diffusion) observed during primary creep in Alloy 600 at temperatures between 325 and 360°C. Grain boundary sliding rates are also observed to depend on grain boundary carbide coverage, greater coverage being associated with slower grain boundary sliding rates and higher resistance to IGSCC.

Various empirical models have been developed to predict IGSCC of Alloy 600 and similar materials in PWR primary circuits until, as sometimes is the case, replacement becomes unavoidable. The only presently perceived sure remedy for susceptible Alloy 600 components is replacement, usually by Alloy 690 (28-31% Cr and 7-11% Fe) and its compatible weld metals, Alloys 152 and 52, which have proved to be resistant to IGSCC in PWR primary water both in severe laboratory tests and, to date, after up to 15 years in service.

Predictive equations for IGSCC in Alloy 600 were first developed for steam generator tubes and later extended to pressurizer nozzles and upper head CRDM penetrations [7, 8]. Both deterministic and probabilistic methods have been developed. Modelling of Alloy 600 component life is often based on the following empirical equation:

$$t_f = C\,\frac{\sigma^{-4}}{I_m}\exp\left(\frac{E}{RT}\right) \tag{1}$$

where:

t_f is the failure time (hours),
C is a constant,
σ is the applied stress (MPa),
I_m is a material susceptibility index (e.g. Table 1),
E is the apparent activation energy (44 kcal/mole),
R is the universal gas constant (1.987 cal/mole/°K),
T is the absolute temperature (°K).

Establishing the stress including residual fabrication stress on a given component is not trivial but well tried and proven approaches based on finite element stress analysis or experimental techniques applied to mock-ups are available. Dealing with material variability in susceptibility to IGSCC is not so straightforward, however, and in the case of classification of the susceptibility of CRDM nozzle cracking in US PWRs, has been ignored.

One method to account for variability in material resistance to IGSCC has been based on a system of material indices, I_m, in equation (1) [9]. At its simplest, with no direct information about IGSCC susceptibility of individual heats, the guidelines given in Table 1 were adopted. They were based on observations of minimum times to failure of plant components or, in

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cases where no service failures have been observed, of laboratory specimens in accelerated tests of representative plant materials. The constant C in equation (1) was adjusted so that an index of unity corresponds to a minimum failure time of 10,000 hours at a temperature of 325°C and an applied stress of 450MPa, as observed in practice in plant and in laboratory tests. In addition, temperature and stress indices were defined relative to the reference conditions of 325°C and 450 MPa consistent with equation (1) as follows:

$$I_\theta = \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T} - \frac{1}{598}\right)\right] \qquad I_\sigma = \left(\frac{\sigma}{450}\right)^4 \qquad (2)$$

Thus:

$$t_f = \frac{10000}{I_m . I_\theta . I_\sigma} \qquad (3)$$

In this way, the minimum time to cracking of each generic Alloy 600 primary circuit component was assessed after determining its operating temperature and stress. The results for different generic components of PWR primary circuits are shown in Table 1. Appropriate surveillance strategies were then established.

Table 1: Minimum failure times for IGSCC of Alloy 600 components in PWR primary circuits (Ref 9).

Ref.	Alloy 600 parts	Material index	Stress index	Temperature index	Overall index	Time (hours)	Observation *
1	Hydraulic expansion	0.2	0.4	1	0.08	80000	NC
2	Divider plate	0.5	0.3	0.9	0.14	80000	NC
3	Hard rolling on cold leg (Ringhals 2)	2	2.2	0.1	0.44	48000	C
4	Pressurizer nozzle (San Onofre 3)	0.5	0.1	3.3	0.17	56000	C
5	Nozzle (San Onofre)	0.5	0.9	3.3	1.49	8000	C
6	Pressurizer nozzle (ANO1)	0.5	0.3	3.3	0.5	84336	C
7	Pressurizer nozzle (Palo Verde 1)	0.5	0.4	3.3	0.66	33320	C
8	Nozzle (Palo Verde 2)	0.5	1.5	1.1	0.83	25000	C
9	Explosive expansion Fessenheim 1	1	0.4	1	0.4	75000	C
10	Hard rolling on SG hot leg (Gravelines 6)	0.5	2.2	1	1.1	30000	C
11	Hydraulic expansion (Doel 2)	2	0.4	1	0.8	30000	C
12	Small U-bends Vallourec	2	2.2	0.3	1.32	30000	C
13	Small U-bends Westinghouse	2	10	0.3	6	6000	C
14	Sensitive hard rolling on SG hot leg	1	2.2	1	2.2	20000	C
15	Very sensitive hard rolling on SG hot leg	2	2.2	1	4.4	8000	C
16	1300 MW Pressurizer Nozzle	0.5	3.2	3.3	5.28	8000	C
17	Mechanical pluggs	0.5	1	1	0.5	40000	C
18	French CRDM Nozzles	0.5	1.5	0.5	0.4	80000	C
		0.5	1.5	0.5	0.4	26800	C
		1.1	2.8	0.08	0.24	72909	C
		1.1	2.5	0.08	0.22	48427	C
		1.1	2.5	0.08	0.22	58868	C
		1.1	2.5	0.08	0.2	90777	C

* : NC : non cracked; C : cracked

The quantification of variability of Alloy 600 heat susceptibility to IGSCC has been developed further to assess cracking encountered in the upper head CRDM nozzles of French PWRs and extended to other large Alloy 600 primary circuit components [8]. Three main types of microstructure were recognized and related to the carbon content, thermal treatment, especially the temperature at the end of forging or rolling operations, and yield strength after hot-working:

- class A with mainly intergranular carbide precipitates;
- class B re-crystallized with carbides mainly on a prior grain boundary network;
- class C re-crystallized with randomized intragranular carbides as well as carbides on prior grain boundaries.

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These classes were then linked to their IGSCC resistance (i.e. material susceptibility index) as determined from operating experience or in accelerated laboratory tests of archive materials mainly at 360°C.

Inevitably, such an approach to assessing IGSCC susceptibility reveals significant scatter in the susceptibility indices for different heats about the mean associated with each class. This dispersion in material properties combined with the dispersion of stress values for any particular component gives rise to a distribution of failures with time that can be fitted to an appropriate function such as the Weibull distribution. The main advantage of the Weibull distribution is that it has a linear transform that can be fitted to the early failures in order to give a reliable prediction of the increase in stress corrosion failures with time [7, 8].

Further improvements in estimating the progression of IGSCC failures in Alloy 600 with time as well as the uncertainty in those predictions have come about by applying the Monte Carlo simulation technique of randomly sampling distributions of the input parameters in equation (1) [8]. An example of the results using the Monte Carlo approach is shown in Figure 3 in the form of a Weibull distribution comparing the results of these simulations with the inspection results for upper head penetrations in each susceptibility class of Alloy 600. When the Monte Carlo simulations are repeated many times, the dispersion in the resulting Weibull distribution of failure times is relatively small because the number of penetrations considered for each PWR plant series is quite large (over 1000). It can be shown that the progression of the problem for each design series of PWRs has relatively little inherent uncertainty. On the other hand, if the problem is considered on a plant by plant basis, then the statistical uncertainty in predictions of the proportion that will crack in a given operating time is much greater because there are less than a hundred CRDM penetrations per upper head. For a given upper head, this statistical uncertainty can be of the order of ±1 to ±5 on the mean prediction, which is easily demonstrated and quantified in a probabilistic sense using the Monte Carlo simulation technique.

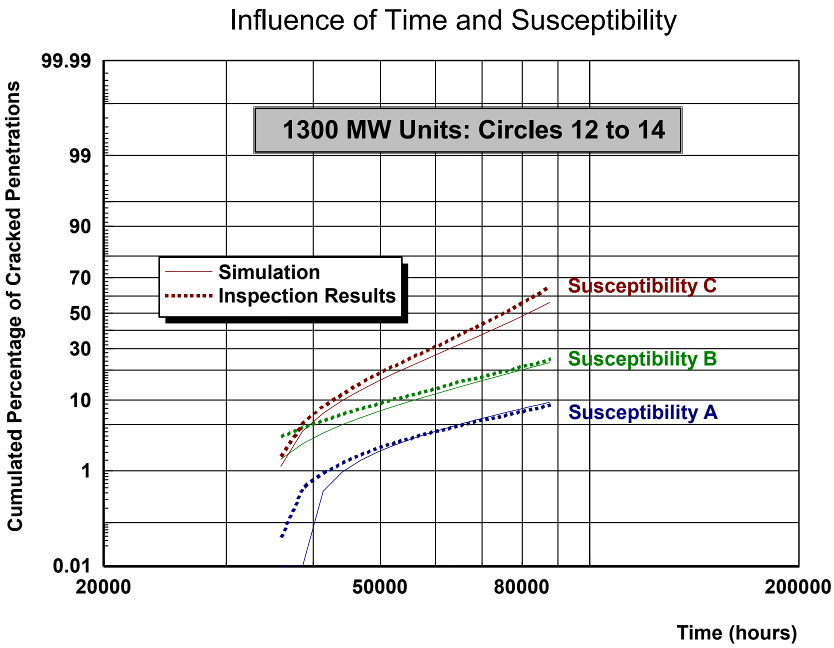

Figure 3: Results of Monte Carlo simulations of IGSCC in upper head CRDM penetrations of 1300 MWe French PWRs and comparison with inspection results for each class of alloy 600 [8].

Once a stress corrosion crack has been detected by non-destructive examination in a PWR primary circuit component, an essential step in the justification of structural integrity and further operation without repair or replacement of the affected component is an assessment of crack growth during the next few operating cycles. Practical approaches to assessing crack growth by IGSCC in Alloy 600 components have relied on empirical measurements of crack growth rates as a function of crack tip stress intensity, K_I, of the form [10, 11]:

$$\frac{da}{dt} = C.(K_I - 9)^n \qquad \left(K_I \ in \ MPa\sqrt{m}\right) \tag{4}$$

The values of the coefficients *C* and *n* for given practical circumstances vary between different publications but there is a reasonable consensus that the apparent or effective activation energy to be used for adjusting the coefficient *C* for temperature is ~31 kcal/mole.

<u>Nickel base alloys on the secondary side of PWR steam generators</u>

The main type of PWR steam generator in general use is the vertical Recirculating Steam Generator (RSG) with tube bundles, depending on age, made from either mill annealed or thermally treated Alloy 600, or thermally treated Alloy 690, or Alloy 800. Thermal treatment is carried out at ~700°C with the objective of precipitating dissolved carbon as chromium carbides on the grain boundaries. Sub-cooled primary water flows through inside of the tubes and boils secondary water on the shell side of the tubes. The steam quality of the water-steam mixture entering the steam driers of RSGs is typically 10% and the superheat across the tubes may vary from 10 to 40°C.

Vertical PWR steam generators have experienced a variety of corrosion-induced problems and many have been replaced, usually because of corrosion induced cracking of mill annealed Alloy 600 steam generator tubes. Only a very few thermally treated tubes have experienced such problems and they appear to be due to isolated failures of the thermal treatment to ensure an adequate grain boundary carbide microstructure. Some steam generators with mill annealed Alloy 600 tubes have been replaced after only 8 to 12 years of operation, which is well short of the usual initially licensed plant operating period of 40 years. New or replacement RSGs are supplied with thermally treated Alloy 690 or Alloy 800 tubing, which to date have resisted both primary and secondary corrosion problems.

Secondary side steam generator tube corrosion problems involving mill annealed Alloy 600 include denting, wastage, intergranular attack, IGSCC, and pitting on the outside surfaces of the steam generator tubes [3, 12]. The evolution of steam generator tube corrosion with time in terms of relative importance of each damage mechanism is shown in Figure 4.

Many secondary side corrosion problems with mill annealed Alloy 600 tubes have been associated with the interstices between the tubes and the tube supports. The tube support structures for most of the early units were made of carbon steel, while later units switched to Types 405, 409, and 410 ferritic stainless steels for greater corrosion resistance. Tube support structures of early units used plates with drilled holes, then plates with trefoil or quatrefoil broached holes, initially with concave lands and then flat lands, or lattice bars (egg crates).The objective of the more open tube support designs is to reduce the accumulation of impurities in the interstices by the phenomenon of hideout (see later).

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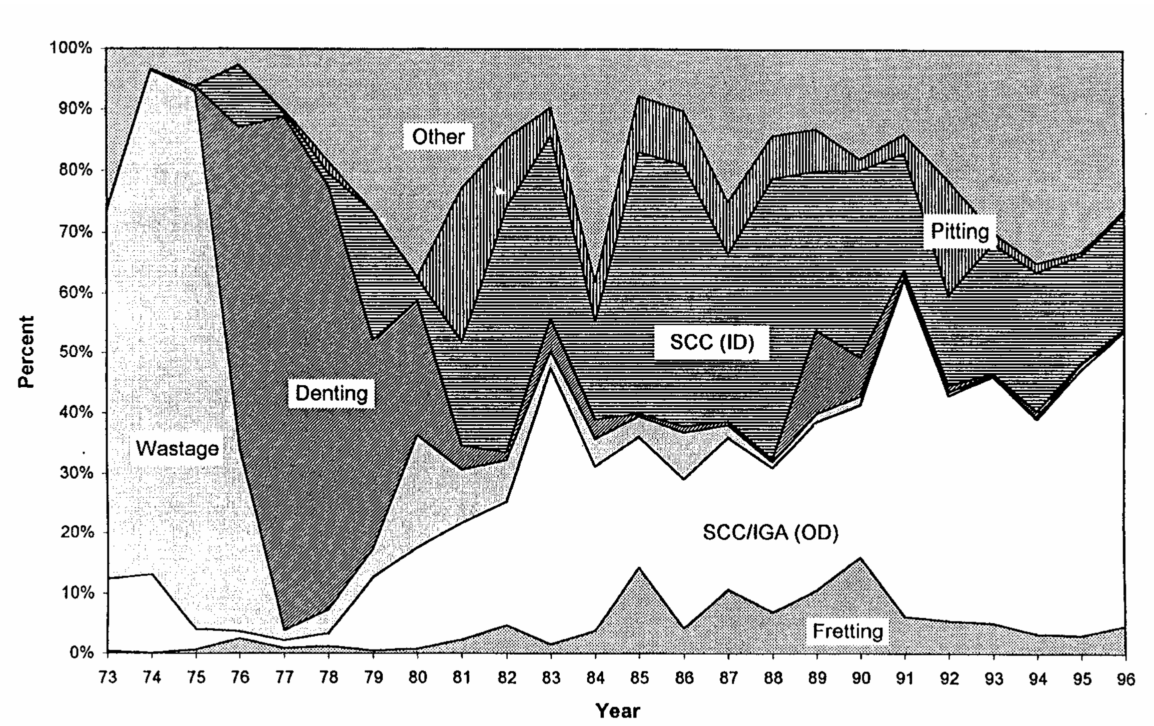

Figure 4: World wide causes of steam generator tube plugging [12].

Another corrosion sensitive zone for steam generator tubes has been in and just above the tubesheet. In some of the very early RSG designs, the tubes were only partly expanded just above the seal weld with the lower tubesheet face, thus leaving a crevice between the outside diameter of the tube and the inside diameter of the hole in the tubesheet. Later, the tubes were expanded into the tubesheet along nearly their full length in order to close all but the last ~4 mm of the tube to tubesheet crevice. Tube expansion has been achieved by various methods, mechanical rolling, hydraulic, and explosive. Each expansion method generated its own characteristic residual stress fields in the tubes that have influenced subsequent stress corrosion behaviour if, or when, impurities concentrate by hideout either in the tube sheet crevice or under sludge that accumulates on the upper face of the tubesheet.

The underlying cause of all forms of localized corrosion observed on the secondary side of steam generators is the phenomenon of hideout of low volatility solutes in superheated crevices with restricted water circulation. Most impurities entering recirculating steam generators in the feed water are relatively insoluble in the steam phase and can concentrate by potentially many orders of magnitude in occluded superheated crevices by a wick boiling mechanism. Due to the potential variety of impurities entering the steam generators, many complex mixtures of concentrated chemicals can be envisaged. This severely complicates the task of understanding the mechanisms of tube attack and defining adequate remedies. Tube damage such as wastage, pitting and denting has been attributed to the local formation of strong acids and, evidently, has been largely eliminated by appropriate management of secondary water chemistry (Figure 4). By contrast, the steadily rising trend in IGA/IGSCC (Figure 4) suggests that counter measures have not been completely effective, probably because the mechanism has not always been correctly identified.

The morphology of IGSCC in mill annealed Alloy 600 steam generator tubing consists of single or multiple major cracks with minor-to-moderate amounts of branching that are essentially 100% intergranular. Experience suggests that secondary side IGSCC requires stresses greater than 0.5 yield in order to propagate rapidly. At lower levels, propagation rates may approach zero, or the corrosion may take the form of intergranular attack (IGA). IGA is the second generally recognized form of secondary side corrosion attack of mill annealed Alloy 600 where there is substantial volumetric attack of every grain boundary. Stress is not strictly necessary for IGA to occur, which distinguishes it from IGSCC. Nevertheless, the two are clearly closely related.

IGA/IGSCC varies greatly with height of the tube support plate in recirculating steam generators, being much more prevalent at the lower levels where the temperature difference between the primary and secondary fluids is greatest. This is clearly strong evidence for the importance of impurity hideout, which increases as a function of the available superheat on the secondary side. Broached tube support plates minimize the extent of the narrow gap between the tube and its support plate and hence substantially reduce the tendency for impurity hideout in such locations.

When the fraction of tubes affected by IGA/IGSCC at tube support plate intersections is plotted as a function of time on Weibull distribution coordinates, it is observed that the slopes of the Weibull plots are rather high, typically between 4 and 9 [7, 13]. This indicates that once IGA/IGSCC starts, its progression to other tubes is rather rapid and relatively consistent between different plants. On the other hand, incubation periods before cracking starts vary considerably. In some cases, IGA/IGSCC has not been observed at all, even on mill annealed Alloy 600 tube bundles after very long periods of operation. There is a tendency to attribute this variability between plants mainly to differences in secondary water chemistry and impurities. However, heat to heat variability in sensitivity of mill annealed Alloy 600 to IGA/IGSCC is very important in this respect and the proportion of very sensitive heats varies markedly between different plants [4, 13].

Following the retirement of some steam generators with degraded tubing, it has been possible to extract and observe metallographically complete tube/tube support plate intersections [14]. These studies have revealed that the crevice between the tube and tube support plate is typically plugged at its entrance and exit with a very low porosity (<10%) solid mixture of magnetite and silica. In the centre of the crevice, the deposit is mainly magnetite and its porosity is much higher at around 50%. This fouling and plugging of the crevices between tubes and carbon steel tube support plates with cylindrical tube holes is generally acknowledged to be widespread. Very high forces have systematically become necessary to extract tubes for destructive examination, indicating that the tubes no longer slide easily in the tube support plates as intended by the design. Extensive detailed examinations have also been made of the deposits found on extracted steam generator tubes [15]. On the tube free spans, magnetite deposits are observed overlying a protective nickel/chromium spinel oxide. Within the tube support plate crevices, thin layers rich in alumino-silicates have been observed on the heat transfer surfaces associated with poorly protective oxide films and the presence of IGA/IGSCC.

At least seven classes of environmental contaminants have been postulated at various times to explain the occurrence of IGA/IGSCC of mill annealed Alloy 600 [16, 17]:

- high concentrations of sodium hydroxide (NaOH) and/or potassium hydroxide (KOH);
- the products from the reaction of sulphate ions with hydrazine or hydrogen (reactive sulphur-bearing species are postulated);

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- the products of thermal decomposition of ion exchange resins (sulphates and organic residuals);
- highly concentrated salt solutions at neutral or nearly neutral pH (these salt solutions are the natural consequences of condenser leakage concentrated to high levels by the boiling process in the steam generator);
- alkaline carbonates and/or their reaction or hydrolysis products and alumino-silicate deposits (believed to affect the nature of the passive film on the alloy surface);
- lead contamination;
- polluted steam.

All these different modes of secondary cracking of Alloy 600 have been recently extensively reviewed [18]. Evaluation and modelling of mill annealed Alloy 600 tube damage by IGA/IGSCC has, nevertheless, traditionally been based on the assumed formation of solutions in occluded superheated crevices with extreme values of pH less than 5 or greater than 10 at temperature. In practice, most cases have been attributed to caustic cracking and extreme care is now taken to restrict as much as possible sodium impurities entering steam generators. A few cases of stress corrosion cracking in operating steam generators have been clearly caused by lead, sometimes, but not necessarily, with a marked transgranular component to the cracking. Lead induced cracking occurs across the whole feasible range of pH; it is one of the few types of tube degradation for which there is unequivocal evidence that it occurs in the mid-range, moderately alkaline pH targeted by the secondary water chemistry treatment to minimize general corrosion. Whether the minor amounts of lead found in practically every steam generator have a critical influence on IGA/IGSCC behaviour of Alloy 600 as distinct from aggravating another underlying degradation mechanism remains unresolved [19]. The latter option seems likely in the view of the widely varying and erratic distributions of lead traces found on steam generator tubes.

Modification of the crevice environment appears at first sight to be the most straightforward method of preventing or arresting secondary side corrosion although implementation can be complicated due to existing deposits impeding access of secondary water to the occluded zone. Attempts to modify the crevice environment have included several factors, such as lowering the temperature, adding a pH neutralizer or buffering agent such as boric acid, removing the aggressive species by flushing or soaking, and changing the concentration and/or anion to cation ratio of bulk water contaminants [3]. Laboratory studies with model boilers have shown the benefit of several of these corrective measures and some have been applied to operating steam generators. Minimizing sludge entry and fouling of steam generators also contributes to reducing the hideout and concentration of impurities.

Stainless steels in PWR primary circuits

Primary pressure boundary

Type 304 and 316 austenitic stainless steels are the main materials used for the pressure boundary piping of PWR primary circuits. The internal surfaces of low alloy steel components are also clad with Type 308/309 stainless steel weld overlays. Operating experience with these stainless steels over many tens of years has generally been excellent. Those stress corrosion failures that have occurred have in most cases, if not all, been due to internal or external surface contamination by chlorides or to out-of-specification chemistry in dead-legs or other occluded volumes where primary water chemistry control can be difficult (such as the transient presence of oxygen for significant periods) [4]. Excessive cold work with the attendant risk of martensite formation in Type 304 stainless steel has also been a contributing factor in some cases.

CRDM housings above the main reactor vessel and associated canopy seals that ensure the leak tightness of threaded joints in the housings are an example of dead-leg locations that have experienced some stress corrosion, mainly Transgranular Stress Corrosion Cracking (TGSCC) attributed primarily to chloride contamination. However, sulphate either as a surface impurity on threaded surfaces or from thermal decomposition of any resin fines that find their way accidentally into the hot parts of the primary circuit may also contribute since sulphate in combination with oxygen is well known to cause stress corrosion in BWRs, albeit usually intergranular.

Although low carbon grades of Types 304 and 316 stainless steels have often been used to minimize the risk of sensitization (by grain boundary chromium depletion) of weld heat affected zones, there is little doubt that such sensitized materials exist in many older PWRs. Nevertheless, practical experience shows that de-oxygenated, hydrogenated PWR primary water does not cause IGSCC in such sensitized materials, in contrast to BWR experience with oxygenated NWC water.

Core internals
Another major use of Type 304 and 316 austenitic stainless steels is for the structures supporting the nuclear core in the reactor pressure vessel. This is generally a bolted structure of horizontal formers and vertical baffle plates that, because of its proximity to the nuclear fuel, is very heavily neutron irradiated. Unlike the stainless steel components of fuel elements that are discharged and replaced after a few reactor cycles, the core support structure is intended to remain for the whole reactor life.

Irradiation-Assisted Stress Corrosion Cracking (IASCC) is a term that defines cracking phenomena in core structural materials of water cooled and/or moderated nuclear power reactors in which neutron and/or γ irradiation contributes directly to the initiation and propagation of stress corrosion cracking. By implication, in the absence of material damage by fast neutrons and/or modification of the environmental chemistry by ionizing radiations, cracking either does not occur or is significantly less severe. Laboratory and field data show that intergranular stress corrosion cracking of austenitic steels can result from long-term exposure to high-energy neutron radiation in both PWR and BWR systems [20, 21].

Neutron irradiation causes atom displacements from their equilibrium crystallographic locations thereby creating point defects (vacancies and interstitials) that may either recombine or diffuse to traps such as grain boundaries, dislocations and second phase interfaces. The diffusion and agglomeration of point defects leads to significant changes in microstructure and mechanical properties that alter resistance to stress corrosion cracking. One consequence is a significant hardening of materials due to the formation of many interstitial (Frank) dislocation loops of nanometre dimensions. Hardening saturates after fast neutron doses of about 5×10^{21} n/cm^2 (E > 1MeV) with yield stresses typically in the range 800 to 1100 MPa. Point defect trapping at grain boundaries leads to changes of local elemental composition in a zone about ±5 nm wide due to atoms of different elements exchanging at different rates with the diffusing point defects. Typically chromium, iron and molybdenum depletion and nickel and silicon enrichment are observed. More generalized changes in elemental composition may also be caused by nuclear transmutation reactions

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In the case of the oxygenated coolants of BWRs, the modification of grain boundary composition due to neutron irradiation, particularly chromium depletion, has been shown to be an important precursor of IASCC. Neutron doses exceeding $5x10^{20}$ n/cm^2 (E > 1MeV) are associated with the occurrence of IASCC in BWRs, this being the dose required to develop sufficient irradiation-induced chromium depletion at grain boundaries. (Note that the maximum end-of-life dose to the core internals of BWRs is about $8x10^{21}$ n/cm^2 (E > 1MeV), which is about an order of magnitude less than that anticipated for PWRs due to the wider water gaps between the fuel and internals in the former case.) In addition, the formation of oxidizing species, oxygen and hydrogen peroxide, by radiolysis plays an important role in this manifestation of IASCC in BWRs, which is absent in PWRs due to the hydrogen added to PWR primary water.

Nevertheless, PWR field experience has also shown that intergranular cracking of highly irradiated core components can occur. Type 304 cladding of control rods and cold worked Type 316 core baffle-former bolts of some first generation (CP0 series) 900 MWe French PWRs have cracked intergranularly in service [21]. Fast neutron doses of $>2x10^{21}$ n/cm^2 (E > 1 MeV) and strains >0.1 % have been implicated in the cracking. Clearly, the absence of oxidizing species, oxygen and hydrogen peroxide, is an obvious environmental difference compared to BWRs that renders grain boundary chromium depletion of no particular consequence in PWR primary water. However, the considerable hardening that occurs very probably plays an important role (as indeed it also does in BWRs) [22].

In addition to the phenomena of radiation induced hardening and changes to grain boundary composition, other radiation damage processes could have an important influence on the development of IASCC. Helium bubble formation, particularly if it occurs on grain boundaries, may have an adverse effect on intergranular stress corrosion resistance. Irradiation creep can relax residual and applied stresses and is independent of temperature in the range of interest to light water reactors. Swelling, hitherto only considered of importance to fast reactors, could in principle also appear at the high neutron doses associated with the second half of life of PWRs and affect the loads applied to components such as baffle bolts due to differential swelling rates between Type 304 and 316 stainless steels. Thus, although significant advances have been made in the understanding of IASCC, much remains to be learned, and it is today a very active field of research in the context of both BWR and PWR plant aging.

High strength fasteners

Precipitation hardened high strength nickel base alloys have already been mentioned earlier but high strength stainless steels are also widely used in PWRs for components such as bolts, springs and valve stems. The main ones are A286 precipitation hardened austenitic stainless steel, A410 and similar martensitic stainless steels, and 17-4PH precipitation hardened martensitic stainless steel. Small numbers of such components have cracked over the years due to stress corrosion or hydrogen embrittlement and on occasions, loose parts have been generated in the primary circuit.

A286, an austenitic, precipitation hardened, stainless steel is strengthened by γ', $Ni_3(Ti,Al)$, formed during aging at 720°C. Its use is favoured where the expansion coefficient relative to other austenitic stainless steels is an important design factor. Unfortunately, it is susceptible to IGSCC in PWR primary water when loaded at or above the room temperature yield stress, typically 700 MPa. [23, 24]. Cold work prior to aging in combination with the lower of two commonly used solution annealing temperatures of 900 and 980°C has a particularly adverse effect on resistance to IGSCC. Hot heading of bolts, which can create a heat-affected zone between the head and shank, is another known adverse factor. Nevertheless, even if these metallurgical factors are optimized, immunity from cracking cannot be assured unless the stresses are maintained below the room temperature yield stress, which necessitates strictly controlled bolt loading procedures. There is also strong circumstantial evidence that superimposed fatigue stresses can lower the mean threshold stress for IGSCC even further. Finally, impurities, including oxygen introduced during plant shut down and possibly consumed only slowly in confined crevices, may help crack initiation. Once initiated, cracks grow relatively easily even in well-controlled PWR primary water.

Components such as valve stems, bolts and tie rods requiring rather high strength combined with good corrosion resistance in PWR primary circuit water have been typically fabricated from martensitic stainless steels such as Type 410 and 17-4 PH. Significant numbers of failures of Type 410 and similar martensitic stainless steels have occurred [25]. In most cases, the affected components have usually entered service too hard due to tempering at too low a temperature. No in-service aging seems to have been involved. An additional problem has been caused by galvanic corrosion with graphite containing materials in the packing glands of valves, sometimes leading to valve stem seizure. The preferred replacement material has often been 17-4 PH with its higher chromium and molybdenum content no doubt conferring better resistance to crevice corrosion.

Service failures of 17-4 PH precipitation hardening stainless steel have also occurred in PWR primary water [26, 27]. Initially, intergranular cracking by stress corrosion / hydrogen embrittlement was associated with the lowest temperature aging heat treatment at 480°C (900°F) designated H900. This gives a minimum Vickers hardness value of 435HV clearly in excess of the limit of 350HV commonly observed to limit the risk of hydrogen embrittlement. The 593°C (H1100) aging heat treatment was subsequently widely adopted and normally yields a hardness value below 350HV. Nevertheless, a small number of failures have continued to occur. The origin of these failures appears to be thermal aging in service rather than "reversible temper embrittlement" that is related to the diffusion of phosphorus to grain boundaries at aging temperatures generally above 400°C. Thermal aging of precipitation hardened stainless steels such as of 17-4 PH arises from an intra-granular decomposition of the martensitic matrix into two phases, α which is rich in iron, and α' which is chromium rich. A progressive generalized increase in hardness is observed with corresponding increases in strength and ductile / brittle transition temperature and loss of fracture toughness. The hardening cannot be reversed without re-solution annealing. French studies have shown that this aging mechanism can occur in 17-4 PH steels on time scales relevant to the design lives of PWRs at temperatures exceeding 250°C and quantitative models for component assessment have been developed [26]. Intergranular failures have been associated with hardness values following in-service aging that have significantly exceeded 350HV and have also been apparently aggravated by impurities coming from valve packing gland materials.

Low alloy steels

Secondary circuit components
A small number of potentially serious failures caused by transgranular stress corrosion/corrosion fatigue have occurred in low alloy steel steam generator shells and carbon steel feedwater piping that are directly exposed to secondary water. The combination of fabrication and operational factors necessary for such cracking to occur in carbon and low alloy steels in steam-raising plant has ensured that it has in reality been highly plant specific.

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Extensive circumferential cracking of the upper shell to cone girth welds of all the Indian Point 3 steam generators was found in 1982 following a steam leak through one of more than a hundred circumferential cracks [28]. Subsequently, the steam generator shells of six other plants located in the United States and Europe were also observed to be cracked in the same location. In some cases, cracking recurred after local repairs had been made by contour grinding. The steam generator shell cracking was caused by an environmentally assisted cracking mechanism and has been variously called "corrosion fatigue", "stress corrosion cracking", or "strain-induced corrosion cracking". In fact, the last term seems most appropriate since it recognizes that although the cracking is environmentally controlled, a dynamic strain is necessary to maintain crack propagation [29]. Consequently, crack extension tends to occur intermittently alternating with pitting at the crack tip during quiescent periods.

This environmentally assisted cracking (EAC) mechanism observed for steam generator shell materials is well known and characterized both for bainitic low alloy steels as well as for ferritic-pearlitic carbon manganese steels used extensively in both conventional and nuclear steam-raising plant [29, 30, 31]. In addition to the dynamic loading requirement usually caused by large thermal transients, cracking has been associated in practice with high residual welding stresses due to poor or non-existent stress relief. The worst affected plants had been weld repaired during fabrication of the final closure weld. In one case, the girth weld had to be completely remade and stress relieved at a higher temperature of 607°C compared to 538°C originally. Water chemistry transients, particularly oxygen ingress, occurring at the same time as dynamic loading have also been strongly linked to the observed cracking. The effect of oxygen was observed to be greatly exaggerated if copper corrosion products (e.g. from brass condenser tubes) were also present [28]. The only metallurgical factors that appeared to play a role were the sulphur impurity content of the steel in the form of manganese sulphide, where the risk of cracking was greater the higher the sulphur content, and possibly also the free nitrogen content via the phenomenon of strain aging [31]. Practical resolution of steam generator shell cracking has been mainly achieved by contour grinding of existing cracks and by ensuring that auxiliary feed water is properly de-oxygenated prior to use, particularly during plant start-up.

In addition to these reported incidents of steam generator shell cracking, a very large technical literature exists concerning EAC of carbon and low alloy steels in both nuclear and conventional steam-raising plant [29, 30, 31]. The observed cracking is usually transgranular cleavage-like in appearance although can occasionally be intergranular without any obvious involvement of other chemical pollutants.

High strength fasteners

High strength martensitic and maraging steels are used in many external fastener applications in nuclear power plants as well as for some internal fasteners in PWR secondary circuits. A significant number of corrosion related failures of external fasteners used for support bolting and pressure boundary flanges have occurred [32]. Failures of low alloy (AISI 4340 and 4140) and maraging steel support bolting have been attributed mainly to hydrogen embrittlement. Steels with ultra high yield strengths greater than 1000 MPa have failed due to a combination of too high applied stresses and humid or wet environments collecting around the bases of components. Pitting often precedes cracking in such cases. Steels with lower yield strengths have also failed due to poor heat treatment or material variability. Hydrogen cracking is usually avoided by specifying an upper bound strength limit (normally defined by a hardness level acceptance criterion of <350HV).

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A second category of bolt failures has concerned the integrity of the primary pressure boundary at locations such as flanges of manway covers and valves. Most of these incidents have been caused by erosion-corrosion in PWR primary water leaks. A small number of failures among this category of bolt have been associated, however, with environment assisted cracking rather than wastage [32]. The ferritic bolting steels involved were not out of specification but had been in contact with molybdenum disulfide lubricants. It has been postulated that the lubricant dissociated on contact with hot water to yield hydrogen sulphide, which is a severe hydrogen embrittling agent for ferritic steels. Prevention of this type of failure therefore includes avoiding leaks at flanges by improved gasket design and eliminating the use of sulphide containing lubricants.

Concluding remarks

The aging of light water cooled and moderated nuclear power plants such as BWRs and PWRs has been accompanied by many cases of corrosion related material failures, particularly stress corrosion cracking. A small proportion of these material failures have arisen from failures to apply existing knowledge and have then been remedied by tightening quality assurance procedures. Others were not predictable in advance because of the very long operating times involved and have sometimes proved to be widespread and generic. These have been carefully studied and effective predictive models have been developed in parallel with practical and economic repair strategies. This is an essential continuing process that will increase in importance as these power plants enter the second half of their original design lives. In many cases, plant life extension beyond the original design life is a practical and economic option but continued vigilance for unexpected long term aging and corrosion processes will be essential.

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