

# A Perspective on the Early Corrosion Problems of Magnox and AGR Commercial Nuclear Power Stations.

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## Abstract

A personal review of laboratory studies concerning possible and actual corrosion problems at Magnox and AGR nuclear power stations, up to 1972, is given. The main problem was the breakaway oxidation of mild steel interfaces, causing distortion of retaining structures and failure of bolts and welds. It was predicted in 1964. Action at the design stage of Wylfa NPS was taken, and at the design stage of AGRs, but action at operating Magnox stations was not taken until a reactor problem occurred in 1967. Relationships between researchers and operational and design engineers, and the change after 1964, are discussed. The difficulty of ensuring the relevance of laboratory data is considered with examples.

**Keywords:** corrosion, oxidation, nuclear power stations, early problems

## Introduction

During the period 1956 to 1972, when I was in charge of the corrosion section of the nuclear design company at Whetstone, Leicestershire, major problems of the commercial Magnox and AGR stations due to corrosion were encountered. Very little was published of these corrosion problems, or of their solutions, except for several media stories on the so-called Magnox corrosion problem, for commercial reasons. My intention is to give a brief historical account of the generic problems as a tribute to the staff, both scientific and engineering, who ensured that these problems were adequately addressed, and to

illustrate the relation at that time between scientists and engineers. The problems generally demonstrated the natural reluctance of designers and operators to act sufficiently quickly on new laboratory data, and for scientists to act too quickly. There were also specific corrosion problems at each nuclear power station (NPS), but I have only included one unique problem at Wylfa NPS as an example. Sufficient time has now passed for all of this information to have no commercial importance.

During this period, all the commercial Magnox NPSs were built, whilst the first AGR NPSs were designed and some construction started.

### Cooling Pond Water Treatment

The AEA decided in the early 1950s that discharged fuel from commercial Magnox NPSs would be temporarily stored in ponds for about 90 days before being sent to Windscale for processing. Chemists at their Culcheth laboratories had determined that deionised water at pH 10.5 should passivate the magnesium alloy canning of the fuel elements. However, they were uncertain of the permissible chloride level. We were doing oxidation tests of canning materials under fault conditions, and hence were able to provide specimens that had a representative oxide coating formed in high pressure CO<sub>2</sub> gas. Preliminary tests on these oxidised specimens showed passivity only when chloride levels were very low. A set of tests involving 5 laboratories was arranged, using oxidised specimens produced at Whetstone. These tests defined the pond water as deionised, at pH 10 to 11 by caustic soda dosing, and a chloride level as low as possible, and certainly below 2 ppm.

Unfortunately, when operation of ponds commenced, insufficient attention to pond conditions was made until serious corrosion had commenced. It was then impossible to stop this corrosion, and took much effort by operators to achieve good pond conditions. All ponds had initially no roof, allowing some sea spray to enter. However, one of the worst ponds was at Trawsfynydd station, which was inland. The cost of the building changes to provide a roof, and cleanup operations,

was considerable. It was a clear case of the operators ignoring laboratory data until there was a corrosion problem. Surprisingly, some station chemists were not aware of these laboratory data, and of the dangers of allowing corrosion to start, and then being unable to re-instate passivity due to the action of the corrosion products.

## **A Unique Problem at Wylfa Nuclear Power Station**

In the design of Wylfa station, discharged fuel elements were dry stored, eliminating the problems of cooling ponds. The discharged fuel elements were stored vertically in mild steel tubes. The tubes were about 25feet long, 1 foot diameter, welded into a steel charge face, and had an internal atmosphere of carbon dioxide. There were three such facilities, housed in a concrete structure, which allowed natural convective cooling of the outside of the tubes by the local sea air, which was not filtered. A corrosion protection system for the outside of the tubes was required. Salient factors were:

- The protection had to last at least 40 years
- Inspection, including visual, was not possible because of the high radiation dose
- The protection had to resist the calculated 40 year radiation dose
- The protection had to resist regular sharp increases in temperature to about 150°C followed by slow cooling over about 90 days, and the concomitant changes in diameter and length of the tubes
- The atmosphere was sea air at the coast of Anglesey, with ambient temperatures varying seasonally from freezing up to 35°C. There would be periods when particular tubes were not in use, and subject to wet salty conditions.
- Though there was no obvious crevice corrosion problem, there were supports, which the tubes might rub against.

I decided that organic coatings were highly likely to fail. Silicon based coatings, sprayed coatings, and metal dipped coatings were closely studied. Galvanising was favoured, but there were practical problems. Metal sprayed coatings seemed best from all aspects, though a life of 40 years was outside existing experience. The then chief chemist at metallisation was extremely helpful, and we jointly picked a particular sprayed aluminium coating. We did agonise on the advantages and disadvantages of sealing the coating with a conventional system, but decided that it could fail the coating under some conditions. For example, heating could cause boiling of water trapped in the coating under the sealant, and radiation might degrade the sealant. His help was invaluable, and went far beyond the commercial requirements. After the facility was built and sent to Wylfa site, he took a portable repair kit to site, and individually inspected every tube for any coating faults. He personally repaired any blemishes or scratches with his repair kit. There was no better quality system, and no paperwork. The protection system worked well, and I understand that it is still causing no problems after more than 30 years of service.

## Clean Conditions

The concept of Clean Conditions was a unique problem in the construction of the Magnox and AGR stations. The constructors had to ensure that no foreign materials should be in the reactors on completion of construction, which might affect the nucleonics, the fuel, or the graphite stack. Any metal that formed a eutectic with magnesium in the fuel cladding, such as zinc, was banned. Steel alloys were not banned, though some alloying elements were suspect. We undertook several tests of the compatibility of various steels with the fuel canning alloy, Magnox, at operating temperatures. We discovered that it was possible for a nickel/ aluminium intermetallic to form in the grain boundaries of the Magnox from contact with austenitic stainless steel. Such steel was used for various purposes, including the sheathing of thermocouples embedded in some Magnox fuel cans. We devised a solution of a ferritic steel cap on the thermocouple, but it was not used by the operators. Fortunately, this possible problem has

not occurred in practise, probably because of oxide films preventing good contact. It seemed to us an unnecessary risk. It was another example of laboratory results being ignored by operators in the absence of a site problem.

A quirk of clean conditions was that rust must not be present in the reactor. The reason was a very early AEA experiment which showed that the thermal oxidation rate in air of graphite was greatly increased if it had been soaked in ferrous sulphate solution. The test was not relevant, but nevertheless the operators banned rust. A few years later a relevant test showed no effect of rust on graphite properties.

In order to prevent rusting of mild steel surfaces in the reactor, they were generally shot-blasted then painted. Bradwell, the first commercial station to be commissioned, used a graphite based anti-friction coating, because it was used at Calder Hall. It had no protective ability, but rust was no longer visible. Unfortunately, it released a gas of phthalic anhydride during hot commissioning tests at Bradwell, which condensed in cooler regions of the gas circuit. This effect did not occur at Calder Hall due to a different commissioning procedure. For Hinckley Point station, Federated Paints proposed a modified etch primer, containing grade A graphite, called PA 21. Our tests showed it had excellent protective properties with only a single coat, and gave no problems in simulated hot commissioning tests. Unfortunately, the Bradwell experience caused phthalic esters to be banned. Though we were certain that the phthalic ester in PA 21 would not cause a commissioning problem, it had to be removed. Fortunately, our tests showed that this modified PA21 was still adequate. Provided that the coat was at least 0.5 thou. (0.0125 mm) thick, it gave at least 6 months protection to a coastal atmosphere. Modified PA 21 was extensively used for other Magnox reactors, and no Bradwell-type commissioning problems were experienced.

As with all paints, conventional problems did occur with PA21, but I was fortunate in having the support of an enthusiastic chief chemist at Federated Paints. For example, an unusual case of poor application, we

discovered after an urgent midnight trip to Wylfa site, was due to employing a one-eyed labourer with no training to spray a large structure, the Wylfa gas baffle, that night in poor lighting without supervision. We had it immediately painted again next morning by an expert. The paint film was now extremely thick, but it worked. The operators were not told of this problem!

## Oxidation of Grey Cast Iron

Grey cast iron should not have been used in the hot regions of reactors, but it was. Studies by GEC researchers in 1956 showed that grey cast iron suffered from internal oxidation in simulated reactor conditions. Within a year, oxidation caused gross swelling and some mechanical failure of specimens. Grey cast iron was immediately banned from internal reactor components. However, designers sometimes ignored this decision, probably because the decision was not properly disseminated.

The first case was in 1965. As described in a later section, we surveyed all reactor materials being used in Wylfa to select those for the oxidation monitoring scheme. We were amazed to find very large cast iron plates suspended above the reactor graphite pile. We immediately tested some samples in simulated reactor conditions, and were not surprised to find that they swelled alarmingly within a few weeks. Fortunately, commissioning had not started, and the blocks were immediately removed at considerable cost to the designers. Ironically, new studies showed that the blocks were not actually required. The reason for having cast iron was a late design change from mild steel to cast iron, which was not properly assessed. If Wylfa had started up with these blocks in place, the resultant swelling would have probably occurred too quickly for adequate countermeasures, and caused either a severe accident or sufficient difficulties for the station to be closed permanently.

A second case was in 1967. A standpipe mechanism at Dungeness A station malfunctioned and was removed. Examination showed that a



bearing had been made of grey cast iron, and had failed. I was surprised that it had not failed much earlier. There was also considerable oxidation of the mild steel interfaces, as discussed in a later section. There was a further example of this problem of grey cast iron some years later, but not of importance.

## Chromel – Almel Thermocouples

Magnesia insulated Chromel – Almel thermocouples sheathed in stainless steel were well known for their reliability and good thermal characteristics, and consequently were used in nuclear reactors, and laboratories. However, they occasionally failed in our laboratory. In 1957, out of curiosity, we unsheathed a failed couple. The Almel was brittle for about 1 inch from the hot junction, and broken into several pieces. Metallography revealed extensive intergranular oxidation, which surprised us.

The manufacturer, BICC, was initially dismissive of our findings. BICC had historical evidence that the Chromel always failed first, and only in sulphurous atmospheres. We eventually convinced them that the sulphur content of the magnesia was not the cause, and that it was the Almel which was failing. We examined several failed, and several operating, thermocouples, and the results confirmed our original findings. In addition, only the 1/16<sup>th</sup> inch (1.6 mm) diameter thermocouples failed. 1/8<sup>th</sup> inch (3.1 mm) diameter thermocouples did not fail though their Almel at the hot junction showed some intergranular oxidation, but never enough to cause failure. Surprisingly, thermocouples from other manufacturers were better, which threw suspicion on the type of Almel used. We discussed material sources and manufacturing methods with BICC, and learnt that the hot-junction seal was made by oxy-acetylene welding, though BICC were now developing an electron beam welding method. I then realised what was the cause of the embrittlement. The welding process produced steam, which was partly absorbed by the magnesia insulation at the hot junction. During usage at high temperatures, the absorbed water would become steam. Almel is nickel with some

aluminium. Nickel is not oxidised by steam. Thus only the aluminium is oxidised by steam, and being of low concentration, it caused a classical example of intergranular oxidation of the aluminium. The Alumel wire in 1/16<sup>th</sup> inch (1.6 mm) thermocouples was sufficiently thin for the extent of intergranular oxidation to be the full diameter, but this was not the case for 1/8<sup>th</sup> inch (3.1 mm) thermocouples where the limited quantity of absorbed steam was insufficient to affect the full diameter of the Alumel.

Fortunately, the change to electron beam welding solved the problem, and only these 1/16<sup>th</sup> inch (1.6 mm) thermocouples should have been used in the reactors. Some original 1/8<sup>th</sup> inch (3.1 mm) thermocouples were used, but they were acceptable. I am not aware of any loss of operational couples due to intergranular oxidation in the Alumel.

A related consequence of the intergranular oxidation was the possibility of the resultant heterogeneity along the Alumel conductor having an effect on the voltage/temperature characteristics of the couple, because it would be in a thermal gradient during reactor operation. Research on this general topic was already under way at UKAEA Risley using a thermal gradient rig. There was also very little information on the effect of in-pile radiation on Chromel–Alumel thermocouples, which was surprising in view of their extensive use in all nuclear reactors.

No conclusive answers were reached, nor on where exactly the voltage was produced, because of the variable extent of heterogeneity in a temperature gradient. It was assumed that the effects of heterogeneity and radiation were encompassed by the general assumption of an error in reading of + or – 3°C for all Chromel–Alumel couples.

An obvious way of eliminating the embrittlement problem was to use pure Nickel instead of Alumel. In spite of reports that pure metals gave unreliable thermocouples, BICC agreed to make several 1/16 inch (1.6 mm) thermocouples of Chromel/Nickel for me to test.



The thermocouples had a very good temperature/voltage relationship which was reliable and stable when tested for long times. Deliberate reduction in insulation resistance to very low values, and even deliberate failing of the sheath integrity, had no effect. However, Chromel/Alumel was too well established for a change to Chromel/Nickel.

## **Oxidation of Mild Steel**

The possible and actual safety and commercial problems caused by interface breakaway oxidation of mild steel components in Magnox reactors had several profound effects, particularly after the operators recognised fully the problems and took remedial actions. Outlet gas temperatures were reduced, causing significant loss of electrical outputs, boiler and reactor control systems had to be altered, and new fault studies were made. Reactor gas composition control was much improved. Biennial inspections of reactors were introduced. Novel in-core inspection tools were quickly developed. Detailed theoretical studies on possible in-core consequences were undertaken. Oxidation monitoring schemes were started. Scientists became as much involved in the operation of the reactors as the engineering staff. The media were very much involved, and it was called the 'Magnox corrosion' problem.

Historically, the problem evolved in three distinct phases:

- acceptance of breakaway oxidation at outlet gas temperatures
- acceptance of interface breakaway oxidation at outlet gas temperatures
- acceptance of interface breakaway oxidation as a reactor problem,

which are briefly reviewed.

## **Breakaway Oxidation**

The first oxidation tests on mild steels in simulated reactor conditions were conducted by AEI Manchester, and started in 1954. They found by 1955 that the normal protective oxidation process on mild steel could change to a high linear rate of oxidation, which was called 'breakaway oxidation'. The oxide film surface became rough and so-called 'excrecences' formed in a random fashion. Rimming steels were much worse than killed steels, and high phosphorus content caused higher oxidation rates. By 1956, five corrosion laboratories had formed in the nuclear consortia. We were able to discuss our work freely, and form collaborative programmes. An immediate unanimous decision was that the AEI tests were poorly done. The tests used coupons suspended in graphite holders within autoclaves pressurised with carbon dioxide gas, and then sealed. At the typical test temperature of 450°C, the gas quickly changed composition to have a high moisture content and up to about 18% carbon monoxide. Such gas compositions were not considered possible in reactors. The results were rejected, but new more relevant tests, typically at 200psig pressure in flowing dry gas with 2% carbon monoxide, were started in other laboratories. These tests almost always gave no cause for concern. At Whetstone, we did tests on pressure vessel steel coupons at 350°C, which ran for over 100,000 hours without any test problems except for a slight overheat one night on one of the four autoclaves. There was no obvious breakaway oxidation on any specimen. These and other oxidation tests at Whetstone must be the longest oxidation tests in history.

When it was clear that Wylfa station would operate at 400psig, we started in 1963 a series of mild steel oxidation tests at 400psig in a simulated CO<sub>2</sub> reactor gas. We were surprised at the extent that breakaway oxidation occurred, though it sometimes took several thousand hours to be clearly established. Combining these test results with others then available from other laboratories, I was able to establish some quantitative relationships between the silicon content of the steel, temperature and the linear breakaway rate. The relation of the water content of the gas, and gas pressure, with the breakaway rate was essentially qualitative, as was an apparent effect of the

phosphorus and manganese content of the steel. The pre-breakaway time was strongly dependent on the surface finish. A rough surface went immediately into breakaway, but a smooth surface could take of the order of 5000 hours. The linear breakaway rate was not affected by surface finish.

Breakaway oxidation of mild steels in reactor outlet gas conditions was accepted in 1964 as a real laboratory effect, but engineers needed much persuading that it was a real effect in nuclear reactors. In 1967 at Whetstone, we also started tests at 600 psig gas pressure, simulating AGR gas conditions, whose results helped to improve the accuracy of our relationships, and did not exhibit any new problems except that breakaway times were shorter, and the linear breakaway rates were higher.

The mechanism of breakaway was never fully established. The breakaway oxide was fully adherent except on very rare occasions, but spalling of oxide did not affect the breakaway rate. The breakaway rates, once established during test, never altered over at least 100,000 hours of test on several hundred specimens. The rate was always constant. Clearly, the rate controlling mechanism must be a solid state surface reaction, or a film of constant thickness, at the oxide/metal interface. CEGB studies showed some carburisation of the metal under breakaway oxide. The mechanism of how carbide formation gave rise to breakaway, and what was the rate controlling process, was never explained. We could also not explain why the breakaway oxide had such open porosity, and why carbon dioxide gas at pressure could diffuse through quite thick oxide layers and not limit the oxidation rate.

## Interface Oxidation

Also in 1964, in the midst of the discussions on breakaway oxidation, a design engineer asked my opinion on a theoretical fatigue problem at Wylfa. The gas baffle above the reactor core was a large bolted structure, and calculations and experiments predicted high frequency

fatigue failure of the bolts. However, he suspected that oxidation would essentially tighten the structure and prevent fatigue failure. I agreed, believing that all interfaces would fill with oxide, become sealed, and increase the fatigue resistance. A demonstration oxidation test of a bolted assembly was undertaken. An assembly of two ½ inch (12.5 mm) mild steel plates held by two ½ inch (12.5 mm) carbon steel bolts was used, and exposed to an accelerated test condition at 450°C. It was probably the first oxidation test in the world on a full scale engineered component. Examination after 1 week showed oxide filling the interfaces, and stiffening of the assembly, as we predicted. Examination after 6 weeks, equivalent to 30 years reactor operation, gave us all a great shock. One bolt was broken at the end of its screw thread, and the other was similarly cracked. Breakaway oxidation had generally formed on all interface surfaces to the same depth as on the open surfaces. The resultant strain on the bolts had caused their failure. We could not explain how oxidation could proceed at a sealed interface filled with oxide, nor did we or any other researchers ever explain it.

Not surprisingly, there was much discussion of this result, and a suspicion that we had somehow made a mistake. We urgently repeated the test, but subject to rigorous independent scrutiny at all times. The same terrible result was obtained, and a new operational problem was revealed having enormous potential for causing component failures. We started a major programme of oxidation tests on bolted and welded assemblies of various designs under several test conditions. Breakaway oxidation started at most interfaces quicker than at free surfaces. It continued at the same oxidation rate as that for free surfaces. The oxide always deformed the assembly to accommodate its growth without the oxide being apparently compressed in thickness. Bolts and welds were deformed or strained to failure, if necessary. Even using high tensile Nimonic 80A bolts had no restraining effect. Tests on 'pin in a tight fitting hole' assemblies gave useful data on the shear strength of oxide films filling the circular interface. The tensile strengths of bolt/nut screw threads after various

extents of oxidation, up to complete oxidation of the threads, were measured.

Unfortunately, CEGB, SSEB, AEA and HMNI took no immediate action at any operating NPS, presumably because there was suspicion of the relevance of our tests, and the absence of any related operating problem. CEGB did make one immediate decision. In the contract tender for Wylfa station, written about 1962, I had stated that we expected operation over the predicted life of 30 years to cause oxidation of mild steels in the outlet gas regions to a maximum metal depth of .009 inches (0.225 mm). I had naturally assumed only pre-breakaway oxidation. In 1964, I predicted .036 inches (0.9 mm) of metal loss due to breakaway. CEGB insisted that Wylfa was redesigned to accept .009 inches (0.225 mm) of metal loss at all interfaces with the commensurate breakaway oxide growth, at no expense to CEGB. English Electric bore the cost of about £5M, and I was not popular. An EE director had the Professor of Metallurgy at Imperial College review our work. It was a great relief when Professor Ball supported the actions we had taken.

#### Interface Oxidation at Operating Stations.

In 1967, a standpipe assembly stuck in a reactor, and was difficult to remove. Examination by CEGB staff revealed substantial interface oxidation, and a failed cast iron bearing, see earlier section on cast iron. The extent of oxidation was greater than predicted by my data according to these staff, who concluded that there was a radiation effect. Fortunately, I was able to examine some offcuts. The material was rimming steel, and not fully killed as assumed by CEGB staff, and the extent of oxidation agreed well with my predictions. We had discussed in 1956 the possibility of a radiation effect, but no tests were ever done. We totally relied on a simple calculation on the increased density of vacancies in the protective oxide, which implied no effect. We have been very lucky that no radiation effect on breakaway oxidation kinetics has been experienced, so far as I am aware.

In 1968, some bolts holding a specimen basket in a reactor at Bradwell station were found broken due to interface oxidation. This experience finally convinced the operators that interface oxidation was a reactor problem. The CEGB engineering manager, Bob Rutter, moved quickly to set up a working committee of CEGB design engineers, and myself. The design of each commercial Magnox reactor was systematically examined in detail to determine the possible operational consequences of the predicted oxide growth. Major co-operation from many organisations was required to obtain detailed designs and metal quality data. We agreed that a 'breathing space' of at least a year was urgently needed to assess the final results, by reducing outlet gas temperatures to 360°C, and gas moisture levels to less than 10 ppm, when breakaway rates would be very small. The committee finished its work in less than one year, and reported in 1968, a tremendous achievement, which was never given the accolade it deserved. Outlet gas temperatures were reduced to typically 360°C, though we did allow a short time each year at 380°C.

Perhaps the most worrying immediate finding was the possibility that the core restraint in some reactors had failed because it relied on a sliding movement, which should have become impossible due to oxide growth. Movement transducers were quickly designed and installed, and showed freedom of movement. The reason was not understood, but it was a great relief. Loss of movement would have caused immediate closure of these reactors. Unfortunately, the operators were not convinced for several years that some outlet temperatures could be safely increased above 360°C, and even then they had difficulty in convincing the regulator. The lowering in temperature caused several operational problems, and major loss in electrical output. Though Wylfa station was designed to accept some interface oxidation, it was also limited to 360°C, causing an electrical output reduction of about 400 Megawatts. Whether effective action in 1964 at all stations would have prevented the 'Magnox corrosion' problem is difficult to determine, though I believe it would. The position in 1968 of many components being close to failure, or even predicted to have failed, would have been avoided. Immediate control of the moisture content



of the reactor gas, and a small reduction in temperature at some reactors could have been sufficient. However, it could be argued that laboratory data were not a basis for assuming a major engineering problem, and the regulator, though fully informed, took no obvious action. There was also the fact of no apparent problem at the older Calder and Chapelcross reactors, though this was partly due to the lower outlet temperature and lower gas pressure. Nevertheless, when I was allowed to inspect one of the boilers at Calder Hall in about 1966, there were clear signs of breakaway oxidation on boiler tubing. The solving of the many engineering problems faced by the operators after 1968 is a fantastic story, which should be recorded, but it is outside my competence.

### **Wylfa Oxidation Monitoring Scheme**

In 1968, construction of Wylfa station had only recently started. In consequence, CEBG decided that it was possible to build an in-pile oxidation monitoring scheme using offcuts from components exposed to the outlet gas conditions. They also decided to have two similar out-of-pile facilities, one on site using reactor gas, and one in my laboratory at Whetstone. Several contractors were involved to get the offcuts, particularly the boiler manufacturer, Babcock and Wilcox. The latter did a marvellous job of getting the various types of boiler offcuts, and deciding what to test. I was involved in co-ordinating much of the work, particularly at site, which was a difficult challenge. Suitable offcuts were securely positioned in a cage near the top of one boiler, selected by B and W, though there were some reservations on its accessibility. At Whetstone, we were able to use some very large furnaces that had become available, fitted them with autoclaves big enough to take the offcuts, and built a large pressurised gas supply system. All of these facilities were commissioned successfully by about 1970, and were a unique undertaking for any nuclear reactor or laboratory. Unfortunately, the on-site facility was perhaps too ambitious, and did not operate too well. Building on this experience, in-pile oxidation monitoring schemes for AGR stations were started in

1970 as well as the compilation of oxidation schedules for every in-pile component.

## Inhibition of Breakaway Oxidation

Towards the end of 1966, the MD of the English Electric nuclear consortium told me to find an inhibitor of breakaway oxidation within 18 months, so it might be used at Wylfa station before start of operation. I was given free run of all facilities and full co-operation of all the engineers. There was no obvious precedent in any literature of anyone looking for an inhibitor of high temperature oxidation. However, the initial treatment might be applied before any oxidation had occurred, which appeared to be a help. If repeat treatment in service was required, it could only be when the reactor was shutdown. It was not conceivable under conditions of criticality. There was considerable discussion on the maximum temperature possible without nuclear heating, but 350°C was the probable limit. Initially, 380°C seemed possible, even without nuclear heating.

The presence of the graphite stack in particular precluded any liquid treatment, though some preliminary tests used silicon based liquids and gases. There were also several plastic seals in the reactor circuit, which had to be compatible with the treatment. I eventually decided that the only way was to initially provide the mild steel surfaces with a protective film, but not from a carbon containing gas, so that there was no underlying carburisation. Some coatings using liquids and gases were tried but were rejected for practical reasons. The second stage was to measure how long it took for this film to resist breakaway. If there was a clear benefit, we would then re-treat these specimens and see if the benefit was further maintained. I decided to try treatments in a limited range of possible gases, including steam and ammonia. The latter was included because a separate study we had made of bearing materials had shown nitrided steels to have excellent oxidation resistance and no breakaway.

One weekend, we prepared about 1000 specimens, which were coupons, bolted assemblies, and welded assemblies, and started the tests. Specimens were treated in the various test gases or coatings at 380°C for up to 1000 hours. They were subsequently oxidised either in a simulated reactor condition at 550°C for up to 2000 hours, or at 380°C for typically 10,000 hours. Some specimens were pre-oxidised to simulate some reactor period of operation, subject to the treatment, and then subject again to oxidation at the 550 or 380°C condition.

All treatments delayed the time to breakaway under accelerated test conditions. The delay was not too encouraging except for steam and ammonia treated specimens. We decided to concentrate on ammonia, because of the condensation problems with steam. We also discovered that ammonia worked by nitriding the surfaces. If the ammonia was diluted with nitrogen, any oxide was not affected, but the underlying metal was nitrided, causing a thin film of iron nitride and some underlying nitride needles in the steel. The treatment was clearly very effective in delaying or preventing breakaway oxidation on unoxidised specimens, and in halting breakaway oxidation on oxidised specimens for a time of the order of 2 years. We surveyed all the possible problems of filling Wylfa reactors with an ammonia/nitrogen 1:9 mix at 135psig (circulator requirement), and heating at 350°C for up to 1000 hours, before start of operation. Additional oxidation tests on graphite core materials, side shield graphite, and fuel cans showed no problems. We also surveyed the post treatment problems and their solutions. Surprisingly, the survey showed that it was practicable, and rough estimates of cost were made. By this time we had shown that the treatment would need to be repeated at about two yearly intervals.

Senior staff at Whetstone reviewed the proposal and gave it their support. We met the 18 months deadline. A meeting was arranged with CEGB to report our findings, and hopefully get their agreement. They had been aware of our investigation, and had given it some encouragement. However, at the end of the meeting, they stated that it would not be economical to have Wylfa shut down for 1000 hours every two years. They were also not prepared to consider it for

operating stations. Their decision was a severe disappointment. The treatment was clearly novel, and handling of a large quantity of ammonia could have caused difficult problems. But it could have allowed Wylfa to operate at full power, particularly as it had been redesigned to accept some interface oxidation, giving a higher output by 400 megawatts. An immediate consequence was the stopping of any further work, including writing a final report. Thus a large unique body of research was never properly recorded. CEGB researchers later repeated our work with ammonia, got the same results and published their findings without mentioning our earlier work, which was another disappointment to all of my staff who had worked intensively for two years.

### **AGR Boiler Tubing**

The mild steel oxidation limit of 350°C, and the need for the stainless steel superheat boiler tubing not to run the risk of stress corrosion on the steam side, caused the introduction of a third type of boiler tubing to cover the gas side temperature range of 350°C to about 550°C. 9% chrome ferritic steel was chosen because it was easier to weld than the more common 12% steel used in other industries.

About 1967, we started a range of oxidation tests on various types of chrome steels and 18/8 stainless steels under simulated AGR gas conditions at temperatures from 450 to 650°C. The expected protective oxide films and parabolic kinetics were found for fairly long periods of time. Then, after typical times of at least 5000 hours, some 9% steel specimens went into a form of breakaway oxidation with a constant linear rate of oxidation. Some of the later tests on 18/8 steels also showed an increase in oxidation rate, but it was not a strongly marked effect.

Examination of the 9% steel results concerning breakaway did not reveal a relationship with steel composition. However, I was able to show that breakaway oxidation of 9% steel did not start until a minimum extent of oxidation had occurred. It was often much greater,

or not at all, as shown by tests which extended eventually to 100,000 hours. The evidence was sufficient to show a risk of breakaway on 9% steel boiler tubing unless the gas side temperature was reduced to about 500°C. I was surprised at the sudden acceptance of my opinion in 1969, and the resultant immediate actions by the operators, largely because of their experience of the 'Magnox corrosion' problem. The latest, at that time, AGRs at Heysham and Hartlepool had a section of 9% steel plain tubing inserted to avoid the problem, as well as changes to the boiler control systems.

## Oxide Spalling

Spalling of oxide from structural steel specimens was a rare event. It was experienced to a very limited extent in the operation of the Magnox reactors, but caused no operational or safety problems. I was reasonably confident that spalling of oxide from structural steels in AGRs would also not be a significant problem. Thus the possible problems from significant oxide spalling from structural steels, such as enhanced radiation in boilers, filters, and BCD systems, were neither anticipated nor met in practice. Unfortunately, spalling from the stainless steel canning on AGR fuel elements could have been a problem. During a study at Whetstone of the oxidation of AGR fuel canning under simulated fault conditions, though the results gave no cause for concern on the integrity of fuel cans, we observed that some oxide spalled. Such oxide in a reactor would be extremely radioactive and would cause difficult maintenance problems.

Specific tests revealed that oxide spalled only when the specimens cooled sufficiently from the hot test conditions. About 40% of the oxide formed in a test period always spalled when cooled to room temperature at the end of that period. However, spalling had no effect on the oxidation rate, which was always adequately low. When these results were established by 1968, the operators took some immediate action, because of the 'Magnox corrosion' problem experience. Filters were designed and fitted into the top of fuel channels at the first AGR.

However, during operation of all AGRs, oxide spalling from the fuel cans was not experienced. We were wrong.

The reason for the absence of spalling is clear. Experiments on simple specimens are not representative of reactor conditions. The specimens were short tubular sections of fuel cans. They were not subject to any of the strains and stresses of a fuel can, and oxidised internally as well as externally. Henry Cowen at the AEA in 1968 told me privately of an experiment he had done in which a short length of a fuel can was oxidised as normal, but severely restrained from shrinking when cooled to room temperature. No oxide spalled. He concluded that the comparable restraint imposed on a fuel can during operation would probably prevent spalling of oxide. I believe he was correct. He did not publish this result, and did no other tests.

It was an embarrassing example of the need for great care in extrapolating laboratory data to engineering assemblies, particularly something as complex as a fuel pin unless properly designed tests are used. Clearly, oxidation tests on sections of fuel cans were too simplistic, but nobody in the nuclear industry including all the substantial research staffs ever publicly realised the error in our tests.

## **AGR Concrete Pressure Vessels**

The AGR concrete pressure vessels (CPVs) presented two unique corrosion problems.

The first concerned the vessel cooling system. The steel liner of the pressure vessel was externally clad in mild steel pipes carrying a flow of water to keep the temperature of the adjacent concrete below 80°C. The array of pipes was extremely complex, and its length could be calculated in miles. All CPVs had this design feature, but the details varied. Heysham and Hartlepool used 2inch (50 mm) square pipes joined by welded sleeves. Great care was taken to prevent internal corrosion during erection.



During operation, the flowing water was subject to radiation, which would release hydrogen, and some hydrogen peroxide. To passivate the surface and minimise the radiation effect, we decided to treat the water with lithium hydroxide to pH 10.5 and have an overpressure of hydrogen gas. We may have been overcautious as early operation showed no need of the overpressure. We were also worried at the possibility of crevice corrosion at the pipe sleeves, but eventually accepted that the risk should be minimal.

The second novel problem was corrosion protection of the pre-stressing cables. Each consortium used different cable systems. For Heysham and Hartlepool, each cable was formed on site from several strands. Each strand consisted of six wires wrapped closely around a king pin wire. The corrosion protection devised by Taylor Woodrow was impressive. The wires were deeply phosphated, each strand was completely coated in a special radiation resistant grease formulated by Shell, and the completed cables were additionally greased. The cables ran in steel lined ducts, sealed at each end. In practice, the cables could be re-tensioned during operation, and even replaced. My only reservation at the time was whether moisture could access the king pin and cause some accelerated (crevice) corrosion, but seeing the actual production dissuaded me. There was also a problem during erection of 'concrete juice' in some ducts, but it was dealt with. I was also concerned at the possibility of microbiological corrosion. The microbes in the grease could have become active during reactor operation when the temperature could rise to 40C. Fortunately, the problem was not found in practice.

A theoretical corrosion problem occurred to me when it was clear that AGR gas would have a significant moisture level. It raised the possibility of condensation of water saturated with carbon dioxide in the cold parts of the gas circuit, particularly when the reactor was shutdown, but not depressurised. The acidity of the water might cause accelerated corrosion of mild steel surfaces, even though oxygen levels were extremely low. I experimented with mild steel specimens partly immersed in water contained in glass autoclaves pressurised

with carbon dioxide at 600 psig. In tests up to 5000 hours, there was no visual sign of corrosion. However, when the autoclaves were opened, the water became cloudy and iron carbonates were precipitated. I concluded that corrosion occurred until the water was saturated with ferrous carbonate, and then essentially ceased. Subsequent exposure to air caused oxidation to ferric carbonate, which was much less soluble and came out of solution. My opinion that the extent of any such corrosion in an AGR was not likely to cause a reactor problem was accepted. I am not aware that this possible problem has ever occurred in practice.

## Review

During this period from 1956 to 1972, several unique corrosion problems were experienced in practice, some of which were predicted beforehand. Other possible corrosion problems were identified at the design stage and remedial measures were taken. The outstanding problem was interface oxidation of mild steels. It was partly predicted in 1956, not established in laboratory tests until 1964, not established in reactors until 1967, and remedial measures taken in 1968. In the laboratory we should have immediately looked further into the relevance of the 1956 data, realised the need to test engineering assemblies, and looked further into the conditions that could cause breakaway oxidation. If we had, the 'Magnox corrosion' problem should have been identified by about 1960, allowing effective remedial measures at the Magnox stations. We and other laboratories were too academic in our work, an attitude which persisted for many years, and gave the industry the 'Magnox corrosion' problem and later the pressure vessel problem. Similarly, engineers had little faith in laboratory advice, and great belief in their ability to fix any problem, causing the 'Magnox corrosion' problem to 'grow' for a further 4 years, after which they probably acted too quickly on new laboratory data. Though we had excellent relations with the engineering staff at whetstone, it was difficult at first to get action on the 1964 data. Unfortunately, the operators did not accept the data until 1968. Subsequently, it was gratifying and worrying to see how quickly

operators acted on new laboratory data. We were probably right concerning 9% boiler tubing, but clearly wrong on AGR fuel can spalling. However, for all the more conventional site problems, such as misuse of PA21, chlorine corrosion of header tanks from cathodic protection, pond water quality, paint failures, cleaning reactor internals after a fire, protection of fuel stores etc., there was good co-operation at whetstone between us and the relevant engineers, including staff of the operators.. In my opinion, by about 1968, the attitudes of scientists and engineers to each other, and their roles, throughout the commercial nuclear industry had become much healthier. As a scientist, by about 1970, I felt much humbler about the relevance of laboratory work, and the need to be very careful on its applicability to reactors. I also had a clearer understanding of the need for relevant tests to be on engineering components, and not to be obsessed with academic tests on simple material samples.

A considerable benefit was the open collaboration between the industrial Consortia laboratories, which was partly shared by AEA and CEGB laboratories. There was very close collaboration on all oxidation studies until about 1965, when the other oxidation laboratories had generally closed down.

This period from 1956 to 1972 in my laboratory was one of considerable activity, and occasional excitement such as the first test of a bolted assembly causing the bolts to fail. Testing engineering assemblies in large autoclaves was a major challenge. Having typically 1000 specimens on test in about 50 autoclaves, and other types of test, was another major challenge to ensure the high quality needed. Our work was mainly high temperature tests. Since reactors were designed to last at least 30 years, I decided in 1956 that conventional oxidation tests lasting up to 100 hours were not sufficient, and our tests should be for at least 10,000 hours. I later extended this timescale to 100,000 hours. Such long term tests run the risk of failure, but only two autoclaves ever overheated, and only for a short time, in this period. There was also the question of relevance, with specimens being examined typically every 1000 hours, but some

control tests with either very frequent or infrequent examinations showed no difference in results. We also did some early tests on the effects of fatigue, creep, strain, and thermal cycling on high temperature oxidation, and found no effect. It was not glamorous work, not academically attractive, and often boringly routine because of the long test periods. Nevertheless, I had a very loyal staff, 12 initially, and 23 by 1964. I made sure that we always had too much to do, if only to prevent any direct redundancy in the uncertain times after about 1966.

We were fortunate in working on the same site as design and project engineers, which allowed joint discussion of laboratory and engineering problems, usually informally. We often found ourselves involved with site corrosion problems, of which I only review 'PA 21' and pond corrosion. Though our laboratory data were treated with commendable suspicion until 1964, our advice on site corrosion problems was often sought and accepted.

Not surprisingly, corrosion problems have been experienced after 1972, when this review ended, and no doubt will continue to test both scientists and engineers until the last Magnox and AGR stations is shut down.

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END

