PROPERTIES OF MATERIALS
FOR WATER REACTOR FUEL ELEMENTS
AND METHODS OF MEASUREMENT

PROCEEDINGS OF A TECHNICAL COMMITTEE MEETING
ON PROPERTIES OF MATERIALS
FOR WATER REACTOR FUEL ELEMENTS
AND METHODS OF MEASUREMENT
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN VIENNA, 13-16 OCTOBER 1986

INTERNATIONAL ATOMIC ENERGY AGENCY. VIENNA, 1987
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FOREWORD

The present meeting was scheduled by the International Atomic Energy Agency upon the proposal of the Members of the International Working Group on Water Reactor Fuel Performance and Technology and held in the IAEA Headquarters in Vienna from 13 to 16 October 1986.

Nineteen participants from 11 countries attended the meeting. Fifteen papers were presented in three sessions covering the following subjects: cladding materials, fuel materials and influence of material properties on fuel rod behaviour. Three working group meetings covered the above-mentioned topics were held in order to discuss, in depth, the presentation of papers and to develop the recommendations for future activities aimed at improving properties of cladding and fuel materials for water cooled power reactors.

The Agency would like to express its thanks to the Session Chairmen, Messrs. O. Barta, P.K. De, G. Sukhanov and Messrs. F. Garzarolli, M. Lippens and C. Lemaignan, M.V. Speight, D.R. Tice and P.A. Jackson who, together with the above-mentioned persons, organized the working group meetings.

The IAEA Scientific Secretary of the Technical Committee meeting was Mr. V. Onufriev of the Division of Nuclear Fuel Cycle.
EDITORIAL NOTE

In preparing this material for the press, staff of the International Atomic Energy Agency have mounted and paginated the original manuscripts as submitted by the authors and given some attention to the presentation.

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SUMMARY REPORT

SESSION I  CLADDING MATERIALS
Chairman: O. Báta

1. Summaries of the presentations

There were six presentations in this session. Contributions from five different countries covered a wide range of activities investigating the properties of cladding materials.

1.1 The first French contribution presented the results of an investigation of stress corrosion and corrosion fatigue of Zircaloy-4 and pure zirconium in an iodine environment. The effect of in reactor irradiation was simulated using heavy ion irradiation which resulted in initiation of small cracks. This suggests that in-pile irradiation may result in the formation of defects which act as initiation sites for iodine stress corrosion. A smaller effect of irradiation on crack initiation was observed for pure zirconium. This could provide an explanation for the effectiveness of zirconium lined cladding for PCI resistance. The stress corrosion tests showed the importance of anisotropy in iodine stress corrosion of Zircaloy-4 and also the importance of the initiation step in SCC. The corrosion fatigue tests showed enhancement of crack growth by up to a factor of four. There was also a reduction of fatigue resistance in the medium stress range, but no effect on fatigue limit.

1.2 The Indian contribution studied the influence of iodine vapour and cadmium in PCI/SCC of Zircaloy-2, with various treatments (graphite coating, pre-oxidation and hydriding). Graphite coating was found to improve SCC resistance. Cadmium in intimate contact with the surface was found to produce embrittlement, but less in the presence of iodine.

1.3 A USSR paper compared advantages of Zr1Nb 0.130 and Zr1Nb 1 Sn 0.5 Fe with the standard Zr1Nb cladding. The modified alloys had better mechanical properties, and were both more resistant to iodine SCC than Zr1Nb. The Sn/Fe containing alloys also had improved
irradiation creep properties and improved resistance to waterside corrosion.

1.4 The PEG paper compared the behaviour of various Zircaloy-4 treatments with regard to mechanical properties and irradiation growth. A combination of β-quenching and subsequent cold work provided the best combination of mechanical properties and low irradiation growth. A Zr-2.5 Nb alloy had highest yield strength and low irradiation growth.

1.5 The British contribution described the initial results of an investigation into the possible effects of lithium and boron hideout on corrosion behaviour of Zircaloy-4. Corrosion rates in standard PWR coolant were similar to those in pure water. Only a small accelerating effect of a high Li/B environment was observed in contrast to reported observations on the effect of LiOH alone; but exposure times were relatively short.

1.6 The second French paper reported the results of in-pile measurement of external corrosion and cladding growth at burnups up to 56 GWD/tU at relatively low heat generation rates. The results showed very good cladding performance. A correlation was observed between initial elongation and irradiation growth. Maximum corrosion scale thickness was 65 μm, but there were large axial and azimuthal variations. The azimuthal variation could be explained by the influence of local thermohydraulic conditions. The axial variation correlated with local clad surface temperature.

2 Conclusions and Recommendations of the Working Group I
Chairmen: F. Garzarolli, P.A. Jackson

2.1 Pellet-clad interaction

Simple stress corrosion tests in simulated fission product environments such as iodine or cadmium can be used for preselection of different alloys, heat treatments, surface coatings etc. However, final confirmation of PCI resistance requires the use of more realistic testing, e.g. ramp tests.
Ion irradiation tests have indicated the possibility that the fission recoil zone at the innermost surface of the clad may play an important role in crack initiation. This possibility should be confirmed on actual cladding irradiated to various burnups.

Work carried out under cyclic load conditions in a stress corrosion initiating environment resulted in some increase in crack growth at medium stress levels, but negligible effect on fatigue limit. These beneficial results obtained at room temperature should be confirmed at realistic temperatures in iodine vapour or other fission product environments, as usually used for stress corrosion testing.

2.2 Irradiation growth

A significant lot to lot variation was noted for irradiation growth of standard Zircaloy cladding. Further analysis of the reasons for variability with regard to material composition and microstructure is required.

The effect of final heat treatment on irradiation growth is well understood. There is a close correlation of growth with texture and yield strength.

2.3 External corrosion

Increased corrosion rates at higher burnups in PWR were again confirmed by measurements on experimental fuel of up to 56 GWD/tU burnup. It should be borne in mind that linear heat generation rate also has a strong influence on cladding corrosion. Therefore, high burnup experiments with linear heat generation rates representative of the future applications should be performed. It has been speculated that this increase of corrosion rate is due to concentration of lithium within the oxide layer under heat flux conditions. Accelerated corrosion in lithia-containing water has been previously reported. It was shown that these data obtained in pure lithia solution may not be relevant to the PWR environment which also contains boric acid. The beneficial effect of boron revealed by the new observations provides some support for a proposed increase in lithia content for the purpose of man rem reduction. Therefore work to assess the significance of increasing
lithium concentration in the presence of boric acid should be intensified, and extended to more realistic test conditions, i.e. under heat flux.

Initial results of an interesting trial method of shortening the long term corrosion tests which are usually necessary by the use of preoxidation were reported. Further work is necessary to confirm the validity of such tests in predicting corrosion behaviour.

2.4 Alternative alloys

For prospective applications of higher burn-up or higher power density there is a possible advantage to be gained from the use of modified alloys compared to standard Zircaloy or Zr-1% Nb. In-pile tests of fuel rods are recommended to confirm the behaviour of these alloys, especially as regards PCI and external corrosion. In these tests both current alloys (Zircaloy and Zr-1% Nb) should be included as controls. An investigation of the effect of fabrication route, e.g. heat treatment and cold work, for the new alloys is also recommended.

SESSION II   FUEL MATERIALS
Chairman: G. Sukhanov

1. Summaries of the presentations

1.1 Post-irradiation examinations are part of an integrated quality assurance system at KWU and provide the basis for further development in fuel element design and technology.

The standard techniques used for the examination of appropriate fuel samples are briefly described. However, emphasis is put on more elaborate techniques for fuel characterization such as:

- micro-gamma scanning
- micro-coring
- measurement of density and open porosity
- optical and scanning electron microscopy.
Micro-gamma scanning and micro-coring are applied to determine the fission product and fission gas distribution across the fuel pellet. Open porosity measurements are of importance for the fission gas retention behaviour. Optical and scanning electron microscopy are used to characterize the fuel microstructure and the pore size distribution. The overall swelling behaviour of the fuel is determined by Hg-pycnometry.

1.2 The Belgian paper described typical characteristics of the microstructural evolution under irradiation of MOX fuel prepared by mechanical blending of UO₂ and PuO₂ powders. The first part of the paper described briefly the MOX microstructure before irradiation; the second part dealt with basic conclusions of the demonstration programme and illustrated the post-irradiation MOX microstructure revealed by ceramographic and electron microprobe techniques.

1.3 The French paper described the measurements that have been made on the thermal and physical properties of fuels doped with gadolinia to concentrations up to 12 wt %. The measurements covered a temperature range up to about 2000 K. The alloy was found single phased. Thermal expansion and melting point are similar in (U-Gd)O₂ and UO₂. Heat capacity and thermal conductivity of (U-Gd)O₂ are lower than those of UO₂ at low temperatures but at high temperatures (above 1100 K) are not significantly different from UO₂. In-pile measurements have confirmed out-of-pile results on thermal conductivity.

Fission gas release rates from Gd-doped fuel are the same as those from UO₂ operated at the same linear heat rating.

1.4 The Japanese paper described various techniques in post-irradiation examination of water reactor fuel that have been developed in Japan. Prominent among these is the use of shadows formed under light or X-ray illumination to monitor the ballooning to failure of unirradiated and irradiated zircaloy during tube burst testing.
2. Conclusions and Recommendations of the Working Group II
   Chairman: M. Lippens, D.R. Tice

2.1.1 With good control of temperature mercury pycnometry can provide density determinations of irradiated fuel samples to an accuracy of 0.01 g cm$^{-3}$. At normal atmospheric pressure the mercury fails to penetrate open porosity and so a geometrical density of the fuel is provided. With increasing pressure mercury can penetrate open pores with smaller and small radii such that at 1865 bars pores of radii greater than 40 A are filled with mercury. Using a range of mercury pressures a distribution of open pores among the various size ranges can be determined.

2.1.2 Micro-gammascanning is used to assess the radial and circumferential distribution of fission products, mainly $^{137}$Cs and $^{134}$Cs, that remain in the fuel at the end of life. At low irradiation temperatures, where fission product migration does not occur, the results of gammascanning provide a measure of the local burn-up variations and hence rating differences across the pellet. At higher irradiation temperatures indications of the release and redistribution of fission products are obtained. Microcoring of the fuel and subsequent dissolution of the samples in nitric acid provides additional information on the local concentrations of fission products; fission gases, caesium, and isotopes of uranium and plutonium. This is a powerful technique but its application is limited by the experimental difficulties of obtaining many samples.

2.1.3 To obtain detailed information on fuel microstructural changes at the sub-micron level electron-optical techniques for the examination of irradiated fuel are required. The scanning electron microscope with use of replicas can provide information on pores and fission gas bubbles at sizes down to 100 A. With the use of replicas there is no need to shield the microscope. Direct examination of small fuel samples can also be carried out in the unshielded microscope.
2.2 Main results: Ceramographic techniques and Electron probe micro-analysis applied to irradiated Uranium-Plutonium oxides.

2.2.1 Demonstration programme

- Integrity of MOX fuel has always been found to be as good as that of UO₂ fuel under similar irradiation conditions.
- Power/burn-up targets have been achieved with thermal-mechanical behaviour similar to UO₂.
- Fission gas release is increased and pellet-clad mechanical interaction is decreased compared to UO₂.
- Technical feasibility of MOX recycling in LWRs has been demonstrated.

2.2.2 MOX microstructure after irradiation

Low temperature behaviour

- no significant change in the as-fabricated fuel microstructure;
- heterogeneous distribution of fission products;
- high concentration of pores in plutonium rich particles;
- UO₂ matrix remains free of fission products;
- Pu homogenization starts at low temperature with disappearance of Pu particles < 10 μm

High temperature behaviour

- massive Pu homogenization starts with grain growth;
- complete homogenization accompanies grain growth from 5 μm - 15 μm.

2.2.3 FGR increase

Pu particles create preferential paths for gas release:

- open porosity is increased due to interlinkage of pores in and between particles;
- diffusion assisted by the fission process is strongly enhanced in Pu particles.
2.2.4 **PCMI decrease**

- no definitive explanation of the exact mechanism of swelling reduction compared to $\text{UO}_2$ when Pu is heterogeneously distributed;
- questionable validity of existing swelling laws when local burnup exceeds 300,000 MWD/tU

2.3 It was concluded that no particular problems should arise from the use of Gd as a burnable poison in solid solution within $\text{UO}_2$.

2.4 As a result of the Japanese programme a recommendation was proposed and accepted by ASTM to modify the testing procedure for zircaloy tubing to reduce the influence of the presence of the mandrel on the overall diametral strain to failure during burst testing and on the total axial strain during tensile testing. Additionally it was shown that relaxation of spring forces in the spacer grids would lead to no enhanced fretting at the end of life in elements subjected to "re-sizing". Due to lower grid forces these elements subject to "re-sizing" have developed negligible bow during life.

2.5 It was concluded that no particular problems arise from the use of Gd as a burnable absorber in solid solution within $\text{UO}_2$.

3. **Recommendations**

3.1 Many advantages would accrue from the installation in hot cells of equipment capable of providing detailed information on fission product chemistry effects and on $\text{O}/\text{U}$ stoichiometry changes in irradiated fuel.

3.2 MOX fuel behaviour under transient conditions is known to a limited extent. On the basis of the results obtained in steady state conditions less PCMI is expected for MOX fuel during ramp tests. This must be confirmed by experiment.

On the other hand, microstructural investigations made up to now have provided numerous results on the MOX fuel behaviour under irradiation, but they are not sufficient to establish definitely the
mechanisms of gas release increase, and fuel swelling reduction compared to $\text{UO}_2$. For this, more detailed investigations are necessary; future experiments will focus on local chemical analysis and quantitative microstructural determinations.

3.3. During the course of the work presented here and previous work on high burn up fuels, it has been shown that accurate knowledge of the radial power distribution is necessary for a good modelling of the fuel behaviour. We therefore strongly recommend further work (computation or experiments) that could lead to an improved description of radial power history ($\text{Pu}$ formation, Gd consumption etc.) Measurements of the melting points of irradiated fuels, including gadolinia bearing fuels, are required.

**General recommendations**

- Little is known on the properties on irradiated fuel in accidental conditions, e.g. after melting. Effort in this field is necessary.

**SESSION III INFLUENCE OF MATERIAL PROPERTIES ON FUEL ROD BEHAVIOUR**

Chairman: P.K. De

Session III was devoted to the influence of material properties on fuel rod behaviour.

1. **Summaries of the presentation**

1.1 The first USSR paper presented the current approach to requirements for reference parameters and properties of materials for WWER-1000 fuel elements, and to the evaluation of their effects on fuel reliability. It included some results of investigations into the interconnection between the reference parameters and fuel material properties, as well as the criteria of operational reliability.

1.2 In the Argentinian paper, the behaviour of two different types of fuels were analysed: the Embalse fuel (CANDU type) and the Atucha
fuel (similar to PWR rods). In both cases, power ramping due to on-power fuel re-shuffling was studied.

1.3 In the GDR paper, the results of model calculations on the operating performance of a VVER-440 type fuel element with a mean burnup of about 60 GWD/tU were presented and discussed. The STOFFEL-1 code used for the model calculations makes possible the simultaneous estimation of several important fuel element parameters.

1.4 The second paper from the USSR presented a report on the results of the irradiation for ten years of experimental fuel rods using uranium dioxide as fuel and zirconium – 1% niobium alloy as the cladding in an experimental loop within the MR research reactor.

1.5 The Czechoslovakian paper presented the evaluation of fuel element cladding state by the analysis of fission product behaviour in PWR primary coolant. The results of the DFE code were checked against two different sipping tests.

2. Conclusions and Recommendations of the Working Group III
Chairmen: C. Lemaignan, M.V. Speight

From these presentations the following statements were concluded:

2.1.1 Experience has shown that the potential abilities of zirconium/Nb alloy clad oxide fuels are far from being exhausted and the main trend is to improve the existing fuel assembly and rod design and the fuel quality during manufacture as well as to optimize operating conditions with the aim of increasing reliability and practicability.

2.1.2 Process chips (fraction of UO₂ pellet broken during manufacturing process) can move in the gap or between pellets inducing pellet to pellet gap or pellet eccentricity. 10 to 15 mm pellet-pellet gaps have been shown to be thermally acceptable.

2.1.3 Under Accident Conditions of different inner pressure at a similar rate of heating the modes of clad straining differ
significantly: at low heating rates and at temperatures of 850-950°C clads can show an extended creep strain. This mode of loading is characteristic of "low leaks", and the peculiar features of straining are accounted for by phase transitions of the alloy, inducing a "superplasticity effect". Relatively low ballooning and ruptures of clads are observed at high rates of heating, where corrosion processes will occur.

However, circumferential variations of temperature may be induced by pellet eccentricity. In this case differences in strain behaviour have to be accounted for.

2.1.4 The danger of a fuel failure under transient conditions depends upon its state prior to a power ramp. The most dangerous is a situation when there is no fuel-clad gap and fuel thermal expansion is transmitted to a clad giving rise to high tensile stresses.

The level of tensile stresses in a clad can be reduced through some technological and design solutions:
- filling of a fuel rod with helium at increased pressure;
- use of pellets having a central hole.

2.1.5 The commercial technology of tubes and methods of their control ensure defects in as manufactured fuel clads - ≤ 50 microns deep. The occurrence of load follow induces cyclic stresses in the cladding and under those circumstances, the defect permissible sizes in fuel clads have to be reduced.

2.2 Using the Baco code

A porosity distribution having a high volume fraction of fine pores was compared to a coarser porosity was analysed. Fine pores led to high in-pile densification, improving the power ramping performance due to a delay in hard pellet-clad mechanical interaction. In the short CANDU fuel benefit can be taken from this effect, while in the long Atucha rod it was established that proper care must be taken of eventual pellet stack interruption in the case of high densification.
Differences in Zry mechanical anisotropy due to changes in fabrication route were also analyzed. Their influence on the power ramping performance of the Atucha fuel was determined. It is concluded that acceptance tests should be improved in order to avoid high diametral creep.

2.3 The results of the model calculations show that none of the fuel element parameters investigated reaches critical values. These are e.g.: internal pressure much lower than coolant pressure and cladding stress much less than rupture strength. However, it has to be considered that a long operation takes place with closed gap. This fact may increase the probability of cladding failure by PCI, especially on changing loads. Additionally, it has to be noted that the programme used does not give any conclusions about structural components of fuel assemblies and about interactions between fuel elements and structural components.

2.4 Nodular corrosion was observed with a maximum nodule diameter of 1 mm and a depth of 110 micron. The maximum amount of hydride inclusion was only 0.0069 Wt%. In the central regions of the fuel rods, the cladding diameter increased by a maximum of 0.47 mm (3.5%). The cladding still remained ductile after irradiation: The deformation to rupture was measured to be 6–9% at 20°C and 10–12% at 350°C. Some diffusional fuel cladding interaction was evident at some points around the pellet periphery. For the maximum fuel rod BU achieved (91.4 GWD/tU) the fission gas release was 27% (maximum power at BOL near 600 W/cm). Thus the Zr 1% Nb may be used as cladding in the fuel element design for extended burnup operation.

2.5 Using a simplified method to assess the fuel integrity, as part of a software package for automatic gamma spectroscopy, the number of failed rods may be forecast by monitoring the coolant activity. The comparison of the result of sipping tests during an outage showed good agreement between code predictions and measurements.
3. **Recommendations**

3.1 If NPPs operate under load-follow conditions the capacity factor is reduced to 0.5 - 0.6, and therefore at the same burnup, the time during which fuels remain in the core is increased approximately by a factor of 2, to 6-7 years. This circumstance requires additional investigation of fuel performance under operational conditions of this type.

3.2 To promote exchange of information on material properties influencing fuel integrity, such as:

- SCC of irradiated Zr alloys (both Zry and Zr-Nb).
- Burnable-poisons effect on UO₂ properties (creep and fracture strength).
- Fission gas release and swelling under extended burn-up and under load-following operation.

3.3 To promote a modelling effort being able to incorporate all this experience into the assessment of fuel integrity under different operating conditions (burn-up extension and load following).

3.4 This should lead the IAEA to increase the number of delegates at these meetings in order to have people of different fields working together (material, irradiation behaviour, code, etc.).

Emphasis should be made on comparison with data rather than on the results of code predictions.
STRESS CORROSION AND FATIGUE CORROSION OF ZIRCALOY IN IODINE ENVIRONMENT

C. LEMAIGNAN
CEA, Institut de recherche technologique et de développement industriel

I. SCHUSTER
CEA, Département de métallurgie de Grenoble
Grenoble, France

Abstract

As pellet cladding interaction (PCI) limits the performance of PWR fuel rods, the mechanisms of cladding failure by PCI must be intensively studied. It is commonly accepted that it involves a stress corrosion cracking (SCC) phenomenon induced by iodine created during fission.

To complement standard SCC tests performed on different cladding tubes in order to observe crack growth rate, the crack initiation step was analysed by simulation using irradiation by heavy ions: after irradiation with $^{84}$Kr at 97.5 MeV to a dose of $8 \times 10^{14}$ ions cm$^{-2}$, severe surface embrittlement was observed on stress relieved Zry4 cladding tubes; on the other hand, this effect was less significant on pure recrystallised Zr plate. This observation is discussed with respect to the use of Zr liner as a PCI remedy.

Due to the increasing tendency towards load-following operation, fatigue behaviour must be analysed. As the existence of I-SCC induces the possible occurrence of a Zry fatigue corrosion phenomenon under the same environment conditions, fatigue crack growth rate and fatigue life measurements were carried out on RX Zry4 plates. They show a drastic reduction in fatigue resistance when iodine is present. The results of fatigue corrosion tests and fractography can be analysed as a grain-to-grain association of I-SCC and standard crack growth, depending on grain orientation.
1. INTRODUCTION

Owing to its impact on PWR performance, cladding failure induced by pellet-cladding interaction (PCI) is a problem of major concern. Studies on this phenomenon have led to common agreement as to the origin of this failure: stress-corrosion cracking (SCC) due to released fission products (the most suspicious being iodine), acting on the cladding when stressed by oxide expansion during power ramps. These findings are supported by a great deal of experimental work on Zry iodine SCC [1-4]. The aim of this paper is to describe recent investigations in this field, including:

- analysis of 1-SCC crack growth rate in cladding tubes,
- simulation of fission recoil induced damage in the inner wall of the cladding,
- and fatigue corrosion life and crack growth rate.

2. IODINE INDUCED STRESS CORROSION CRACK GROWTH RATE

Stress corrosion behaviour was analysed using a standard pressurisation test in an iodine environment (≈1.5 mg cm⁻² Zry) at 350°C. For the measurement of crack growth rate through the cladding wall, a special procedure was developed to induce a small fatigue crack at a given point in the inner wall of the cladding tube. The procedure used, described in detail elsewhere [5], is based on compression of the tube using a loading device which enables the fatigue crack to be positioned at the required point. Figure 1 shows a sketch of this loading scheme used on a fatigue machine.

Figure 2 is a photomicrograph of a cladding tube in which three different fatigue cracks acted as crack starters for subsequent 1-SCC. As can be seen, the difference in aspect is clearly visible and the crack growth rate can be analysed.

For a given test, the mean crack growth rate is computed from the initial fatigue crack to the final unstable ligament. The initial value of the stress intensity factor $K_I$ at the crack tip was obtained using the results of Kabayashi [6], for the stress intensity factor of a small elliptical crack in the inner wall of a pressurised tube.

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Figure 1: Loading device used to induce a small fatigue crack in the inner wall of a cladding tube.

Figure 2: Internal fatigue crack acting as starter for 1-SCC in order to measure crack growth rate.
Figure 3: Crack growth rate data obtained from fatigue precracked specimens.

Figure 3 gives the results for a particular stress-relieved cladding tube. The value of $K_{1,SCC}$ was measured with great accuracy:

$$K_{1,SCC} = 3.4 \pm 0.2 \text{ MPa}\sqrt{\text{m}}$$

This value can be used to analyse fuel behaviour with respect to PCI once an initial crack length has been defined. The usual procedure is to take the minimum surface flow not detected by NDE at the fabrication plant, or the grain size, as $I$-SCC starts with intergranular cracks [7]. Other mechanisms may be proposed for the initiation step. Strain incompatibilities between grains or local corrosion points around Fe-bearing precipitates have been demonstrated in recrystallised materials [8, 9]. However, other mechanisms may be involved such as surface embrittlement induced by ions implanted as recoil fragments.

3. INNER WALL DAMAGE INDUCED BY FISSION RECOIL

3.1 Introduction

For typical PWR conditions, the fission rate is approximately $1.3 \times 10^{13}$ fissions cm$^{-2}$ sec$^{-1}$. Each fission gives rise to the creation of two fission products of mass and energy values in the range 140 - 95 AMU and 70 - 98 MeV. Given their high energy, they have stopping ranges of the order of 0.7 - 0.8 $\mu$m in UO$_2$ [10] and 8.2 - 10.4 $\mu$m in Zr [11, 12]. These fission rate and recoil range values give a flux of high-energy fission products incident to the inner surface of the cladding, equivalent to $5 \times 10^{19}$ ions cm$^{-2}$ sec$^{-1}$. They lead to a layer of about 10 $\mu$m depth bearing more than 2% of foreign atoms at standard burn-up. Of the various fission products, some will induce only collision damage, e.g. Zr, while others will add a chemical effect (gases, halogens, etc.). In order to find any possible damage of this irradiation on the cladding surface, specific experiments are mandatory.

3.2 Experimental procedure

Tensile specimens were machined out of standard stress-relieved Zry 4 cladding tubes and out of pure Zr cold-worked recrystallised plates. The samples were oriented in order to have the tensile direction in the longitudinal axis of the product. The cladding samples were irradiated on the inner surface in the as-received condition (sand blasted), while the Zr samples were electropolished before the experiment.

The samples were irradiated using the heavy ion linear accelerator ALICE (Institut de Physique Nucléaire, Orsay, France) which can generate a beam of $^{84}$Kr$^{8+}$ ions with an energy of 97.5 MeV. Typical irradiation times were two hours, giving a dose of $8 \times 10^{14}$ ions cm$^{-2}$. After irradiation, slow tensile tests were performed on the various samples. They were performed in an argon atmosphere at $350^\circ$C at a tensile rate of 5 $\mu$m min$^{-1}$. This type of test was developed to analyse $I$-SCC of Zr alloys [4]. It has been shown that, for the orientation of the samples chosen in this study, due to texture effects, there is no loss of ductility nor embrittlement even under iodine. The tensile tests were interrupted after 3% plastic deformation, i.e. near neck formation. After tensile tests, the samples were examined using standard metallography procedures for optical or SEM observations.
3.3 Results

The surface aspect of the unirradiated reference cladding specimen (Fig. 4-a) and the sample that received a Kr dose of \(8 \times 10^{14}\) ions cm\(^{-2}\) (Fig. 4-b) can be compared. It appears clearly that, after irradiation by heavy ions, a small amount of plastic deformation induces an array of short cracks perpendicular to the tensile direction. The crack length varied between 5 to 25 \(\mu\)m for a crack depth of 5 to 15 \(\mu\)m as measured by transverse metallography. The average crack density was \(3 \times 10^4\) cracks mm\(^{-2}\). In comparison, the reference sample is free from any defects for the same deformation or even at higher strain.

For the recrystallised plate of pure Zr, Fig. 5-a and 5-b show both sides of the sample at the same location. Deformation bands are clearly visible due to large grains and to the soft fresh surface obtained after electropolishing. In addition, many small cracks are observed on the side irradiated with an \(8 \times 10^{14}\) ions cm\(^{-2}\) dose. The length of these cracks is limited by the distance between slip bands and rarely exceeds 5 \(\mu\)m. Crack depth is small (about 1 to 2 \(\mu\)m) and their density is higher than for Zry samples (about \(1.5 \times 10^5\) mm\(^{-2}\)).

From the observations made, it appears that the irradiation of cladding material by heavy ions induces surface embrittlement which leads to a lattice of surface cracks after a small amount of plastic deformation. Several mechanisms may be involved in the embrittlement process, including chemical effects due to doping by implantation and ion-induced atomic displacement damage.

In any case, if the surface cracks observed in the brittle layer can be considered as the initiation step for PCI cladding cracks, the difference between Zry 4 and pure Zr may be the origin of the improvements of the Zr liner cladding tubes with respect to PCI [13].

4. Fatigue Corrosion

As a result of the development of load-following operation of power plants and subsequent cyclic loading of fuel cladding, fatigue behaviour of Zry is of great concern for fuel design. As Zry is very sensitive to stress corrosion cracking in iodine, the possibility of some degree of corrosion fatigue in the same environment must be considered. This is the reason why fatigue corrosion was studied on Zry. Lifetime (number of cycles to failure) and crack growth rates...
Figure 5-a Slip bands on a pure Zr plate, 3% plastic strained after electropolishing.

Figure 5-b Fine cracks on the irradiated face (dose = $8 \times 10^{14}$ Kr ions cm$^{-2}$) before 3% plastic strain.

Figure 6 Fatigue crack growth rate for RX Zry4, measured in RX Zircaloy 4 plates [14]. Using a standard procedure for this type of measurement, the behavior of Zry4 plate under corrosion-fatigue conditions in methyl alcohol with 1% {iodine} was studied for different crack orientations.

The crack growth rate measured using DCB compact specimens is plotted on Figure 6, with a comparison being made between ambient air, taken as reference environment, and the mildly aggressive solution of iodine in methyl alcohol. An increase in crack growth rate in the iodine environment is clearly apparent, equivalent to a fourfold increase at about 10 MPa√m and 0.1 Hz. The effect of test frequency is of secondary importance, but an increase in crack growth rate can be obtained by reducing the frequency.
The corrosion fatigue life was measured on standard tensile specimens machined out of a thin RX plate (1 mm). The results are presented in Figure 7 and confirm the important effect of fatigue corrosion. However, a very uncommon type of behaviour is observed: in the general case of corrosion fatigue, both time to failure and fatigue limit are reduced. However, in the case of Zry4 plate, the time to failure was found to be eight times shorter only in the intermediate stress range, with no reduction in the fatigue limit stress level. This surprising behaviour can be explained by the fatigue surface analysis.

Figure 8 gives a typical SEM view of a corrosion fatigue fracture of Zry. The fracture surface is a mixture of crack growth by stress corrosion, as observed with quasi-cleavage in certain grains, while other grains have been subject to plastic fatigue crack growth. The manner in which the crack grows, according to one or other of these two mechanisms, depends on the grain orientation with respect to the loading direction. Consequently, corrosion fatigue cracks can only initiate if the stress level is sufficiently high to induce corrosion cracking and inert fatigue leading to a corrosion fatigue stress threshold similar to the fatigue threshold.

5. CONCLUSIONS

The work undertaken on the subject of fission product induced stress corrosion and other FCI-related phenomena has provided a means of:

- determining the stress corrosion threshold for crack growth with a high degree of accuracy: \( K_{S C C} = 3.4 \pm 0.2 \) MPa \( \sqrt{m} \)
- showing that the irradiation of the inner surface of the cladding by fission recoil can induce a brittle surface layer which can act as an I-SCC initiation site.
giving the intensity of the corrosion fatigue for the crack growth rate and failure life, and explaining the corrosion fatigue in Zry as a combination of stress corrosion and plastic fatigue grain fracture.

All this information is used as input data for fuel behaviour modelling during transients and cyclic behaviour.

References

ENVIRONMENT INDUCED CRACKING OF ZIRCALOY-2 FUEL CLADDING TUBE

S.K. GHOSAL, P.K. DE
Metallurgy Division,
Bhabha Atomic Research Centre,
Bombay, India

Abstract
This paper is based on some studies on the influence of iodine, vapour and cadmium on pellet clad interaction (PCI) stress corrosion cracking (SCC) of different types of zircaloy 2 fuel cladding tubes bare, graphite coated, pre-oxidized and prehydrided meant for use in pressurized heavy water reactors (PHWR).

Experiments were conducted using the internal pressurisation technique and the hoop stress applied on the tube was varied from 16 kg/mm² to 37 kg/mm² at temperatures 573 K to 773 K. Iodine concentration inside the tube was maintained at 1 to 10 mg/cm². The susceptibility to SCC of the bare tubes increased with increasing iodine concentration, stress level and temperature. The applied stress at which SCC occurred was close to the yield stress of the material and was virtually independent of the iodine content. Depending on the applied stress, the tubes fractured either by pin-hole damage or by complete bursting with only 3-10% circumferential strain.

The graphite coated and the pre-oxidized tubes demonstrated enhanced resistance to SCC failure. The life of graphite coated tubes was more than 10 times longer as compared with that of uncoated tubes at 673 K in the presence of 1 mg/cm² of iodine. The life time of graphite coated tubes under simulated power ramp conditions, in which the temperature was raised suddenly from 573 K to 773 K, was seen to be about 1.5 times longer than that of bare tubes.

Cadmium, when in direct contact with zircaloy surface (as in the case of acid cleaned tubes), promoted embrittlement. In the presence of both cadmium and iodine, a strong influence of the applied stress was noticed. At low applied stresses, no failure could be detected in the presence of both the species. Prehydrided zircaloy tubes showed enhanced stress corrosion susceptibility.

Localised attack, such as pitting, was detected on the inside surface of those tubes which failed by iodine-SCC. The presence of corrosion products on or near the
fracture surface suggested a chemical interaction of iodine with the cladding surface. Fracture surfaces were found to have a flute type morphology, typical of PCI-SCC failure in iodine environment. The mechanism of PCI-SCC failure appeared to be one of stress-assisted chemical attack by iodine or cadmium.

1. INTRODUCTION

Zircaloy-2 tubing is widely used for fuel cladding in water cooled nuclear power reactors because of the good resistance of this alloy to corrosion by high temperature water and its low neutron absorption cross-section. During operation, the zircaloy clad has to withstand multiaxial stresses caused by pellet-clad mechanical interaction. In addition, the inside surfaces of the cladding tubes are exposed to a variety of fission products, such as, iodine, cesium, cadmium etc. Of all the causes of fuel element failure in water cooled reactors, stress corrosion cracking (SCC) of zircaloy cladding due to mechanical and fission product induced chemical pellet-clad interaction (PCI) is considered to be most important. In-reactor experience suggests that these failures are predominantly due to fission product iodine stress corrosion cracking. Out-of-pile investigations in several laboratories have also established that zircaloy is susceptible to SCC in the presence of iodine [1-10]. However, the reported results are not all consistent in respect of the required iodine concentration, critical stress and strain and of various metallurgical factors, such as, second phase distribution, cold work, crystallographic texture and residual stress for SCC to occur. This divergence in results can be attributed to the differences in the manufacturing processes of zircaloy tubes and in the methods of carrying out laboratory SCC experiments.

In the present study, the SCC behaviour of typical bare PHWR zircaloy-2 cladding tubes in iodine vapour was evaluated by the internal pressurisation technique. Iodine concentration, stress and temperature were varied to obtain their respective influences on the SCC behaviour. In addition, the SCC behaviour of zircaloy tubes was determined under thermal cycling conditions.

In order to evaluate the effect of graphite and oxide coating, some graphite coated and pre-oxidised tubes were exposed to iodine environment at different temperatures and applied stress levels. The SCC behaviour of the graphite coated/oxidised tubes was compared with that of bare tubes.

The influence of hydrogen uptake in zircaloy tubes on the iodine-SCC behaviour was also studied. Stressed zircaloy tubes with cadmium coating were tested at 573 - 673 K to find the effect of cadmium on SCC susceptibility.

2. EXPERIMENTAL

Stress-relieved reactor grade zircaloy-2 tubes, 150 mm long, with 15.275 mm OD and 0.427 mm wall thickness, were used for the SCC tests. One end of the tube was closed by the help of a mechanical seal, while the other end was connected to the pressurising system through stainless steel pressure fittings. A schematic diagram of the experimental set up is shown in Fig. 1. A calculated amount of solid iodine was kept inside the tube which was internally pressurised with high purity argon. The temperature of the assembly was brought to the desired value by heating the autoclave externally. High purity argon was circulated inside the autoclave to prevent excessive oxidation of the outside surface of the tube. The internal pressurisation led to a biaxial state of stress with a stress ratio between 0.5 to 1. Under in-reactor operating conditions a similar state of stress is generally achieved at the tube at the pellet-clad interfaces. Thus, this type of test could simulate the actual in-reactor condition quite well.
time-to-failure was noted by recording the drop in the internal pressure in the tube.

Iodine concentration was varied from 1 to 10 mg/cm$^2$ of the exposed tube surface while the applied hoop stress was varied from 16 to 37 kg/mm$^2$. SCC tests were carried out at temperatures in the range 573-773 K. In addition, some experiments were carried out in which the temperature was changed rapidly from 573 K to 773 K. This type of experiments were expected to simulate the power ramp condition in a broad sense.

For the tests with the graphite coated tubes, only the inside surfaces of the tubes were coated with graphite. The coating thickness was maintained within 6-10 $\mu$m. To find the effect of oxide layer, tubes were preoxidised in steam at 673 K and 104 kg/cm$^2$ for 7 days. Experiments were also carried out with hydrided tubes containing 44 to 84 ppm of hydrogen. These tubes were prehydrided in gaseous $H_2$ at 627 K for 10-30 minutes.

To find the effect of cadmium, the inside surfaces of the tubes were coated with cadmium by electroless plating, using a cadmium oxide-sodium fluoride bath. Before coating, the tubes were pretreated either in warm sodium hydrogen phosphate solution (a sil pretreatment) or in a mixture of hydrofluoric acid and nitric acid solution (acid pretreatment) for 5 seconds. In some cases, cadmium oxide powder along with zirconium hydride powder was spread on the inside surfaces of the tubes so that at higher temperatures zirconium hydride could dissociate and liberate hydrogen which in turn could react with cadmium oxide, giving free cadmium.

Circumferential strains at failure were measured for all the failed tubes and the fracture surfaces were examined under optical and scanning electron microscopes.

3. RESULTS AND DISCUSSIONS
3.1 Effects of Iodine, Stress and Temperature

The effects of iodine concentration, applied hoop stress and temperature on the SCC behaviour of zircaloy-2 tubes, as observed in the laboratory tests, are shown in Table 1. It was observed that an increase in iodine concentration reduced the time-to-failure drastically.
Table 1

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Iodine concentration (mg/cm²)</th>
<th>Temperature (°C)</th>
<th>Applied hoop stress (kg/mm²)</th>
<th>Circumferential strain at failure (%)</th>
<th>Time to failure (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>400</td>
<td>32.29</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>400</td>
<td>19.87</td>
<td>44</td>
<td>50-70</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>400</td>
<td>32.29</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>350</td>
<td>36.8</td>
<td>8.5</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>300</td>
<td>30.93</td>
<td>10</td>
<td>190</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>300</td>
<td>16.0</td>
<td>-</td>
<td>NF</td>
</tr>
<tr>
<td>7</td>
<td>nil</td>
<td>400</td>
<td>32.29</td>
<td>-</td>
<td>NF</td>
</tr>
<tr>
<td>8</td>
<td>nil</td>
<td>300</td>
<td>19.87</td>
<td>-</td>
<td>NF</td>
</tr>
</tbody>
</table>

NF - Not failed

At 673 K, with 1 mg/cm² iodine the time-to-failure was 10 hrs. but with 10 mg/cm² iodine, it was reduced to 0.1 hrs. Wood (4) has observed similar changes in time-to-failure due to variations in iodine concentration. He has also reported that below a certain concentration, i.e., 10⁻² mg/cm² iodine, there was no failure within the period of test.

In general, stress corrosion cracking is strongly dependent on the applied stress. Sometimes a threshold stress exists below which no SCC occurs. A similar stress level seemed to exist in the present case. Table 1 shows that failure of tubes was much influenced by the applied hoop stress. Most of the failures occurred at stresses which were around the yield stress of the material; below a particular stress level, no failure was observed. Similar observations have been made by Videm and Lunde (7) in their tube pressurisation tests. They have noticed that SCC threshold stress could be correlated more closely with the burst strength of zircaloy tubes than with any other mechanical property. However, Garlick (11) has observed that the SCC threshold stress is closer to the yield strength determined by the burst test. Wood (4) has reported a value of 21 kg/mm² as the threshold stress for iodine-SCC of zircaloy-2 at 573 K. These differences in the results could arise from differences in the manufacturing process of the tubes, the heat treatment schedule and also the crystallographic texture (12-15).

Iodine-SCC failure of zircaloy-2 is also strongly influenced by temperature. Table 1 shows that with 1 mg/cm² iodine, the time-to-failure was 10 hrs. at 673 K whereas at 623 and 573 K, it was 80 and 190 hrs. respectively. This variation in failure time might be due to the variation in the ratio of the applied stress to the yield stress at different test temperatures. Wood (4) has observed a similar behaviour in split ring tests in the temperature range 493-573 K in the presence of 3 x 10⁻³ gm/cm² iodine. He has also noted that iodine-SCC occurs even below 503 K.

3.2 Mode of Failure and Fracture Surface Characteristics

The failure of the tubes was either of the pinhole type or showed complete bursting, depending on the applied stress. At lower stresses, pinhole failure was predominant whereas at higher stresses complete bursting was observed. However, in all the cases the circumferential elongation was within 10%. Fig.2(a) shows a typical pinhole at the place marked 'X', detected on tubes after SCC test at stress levels lower than or around the yield strength of the material. The strain-to-failure at such places was seen to be minimum.
Figs. 2(a), 2(b), and 2(c) show, respectively, a Zircaloy-2 tube exposed in iodine vapour at 300°C, bursting of a Zircaloy-2 tube exposed in iodine vapour at 650-800°C, and bursting of a graphite-coated Zircaloy-2 tube exposed in iodine vapour at 300°C.

Enlarged views of this pinhole are shown in Figs. 3 and 4. Several micro-cracks formed around this pinhole as can be seen in Fig. 3. This type of failure, with very small circumferential strain, is considered to be a typical mode of failure by iodine SCC and has been observed by many investigators. Busby et al. (6) have reported that pinhole failures occur in Zircaloy-4 at lower stress levels while at higher stresses, the mode of failure is transgranular (bursting). Fig. 2(b) shows a burst type failure observed in this study due to the application of a high stress (above yield strength) at a high temperature (> 673 K). Under such circumstances stress rupture type failure was noticed. The tubes deformed uniformly up to the point of instability but ultimately ruptured after some localised bulging.
Garlick\textsuperscript{(11)} has reported pinhole failure at a stress level slightly higher than 0.2\% yield stress. Yaggee and Cho-Yu-Li\textsuperscript{(15)} have noticed pinhole failure in stainless steel tubing and have suggested that this type of failure is controlled by grain boundary sliding (intergranular). A cross-sectional view of a tube which failed by pinhole formation is shown in Fig.5. The initiation of the fracture was not clear but the final fracture appeared to be due to mechanical overloading. Recently Haddad and Cox\textsuperscript{(8)} have shown that transgranular cracks in zircaloy-2 tubes exposed to iodine vapour, initiated from slightly pitted areas.

Shimada and Nagai\textsuperscript{(17)} have produced pinholes as well as axial cracks in laboratory tests of \textsuperscript{6}C-radiated zircaloy-2 tubes, failed at 673 K at 1000 stress values corresponding to 56-70\% of the 0.2\% yield strength of the tubes. They have observed both intergranular and transgranular fracture to be always associated with the cracking mode.

SEM examinations revealed that iodine chemically attacked the zircaloy tube. Fig.6 shows the nature of attack on the inside surface of a tube which may be characterised as pitting. Pits were clearly visible on the inside surface of the tube, as illustrated in Fig.7(a). A few of these pits were seen to be associated with cracks [Fig.7(b)]. It appeared that chemical attack by iodine, leading to the localised formation of pits, was the first step of the cracking process. These pits acted as the potential sites for crack initiation. Gangloff\textsuperscript{(18)} et al have reported the initiation of cracks at the bases of pits formed by corrosion. They have presumed that pits form prior to cracking. However, this assumption has not been verified experimentally. Initiation of incipient stress corrosion cracks at the bases of the pits has also been noticed by Cox and Wood\textsuperscript{(5)}. Propagation of such cracks appeared to occur in the later stages through the corroded zircaloy surface as depicted in Fig.8.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig3.png}
\caption{Cross-sectional view of a zircaloy tube failed by pinhole mode in iodine vapour. X 200.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig6.png}
\caption{Inside surface appearance of a zircaloy tube on exposure to iodine vapour, showing chemical attack. X 600.}
\end{figure}
Initiation of cracks at the roots of pits formed on the inside surface of a zircaloy tube exposed in iodine vapour. X 2000.

A number of small pits have also been observed by Shimada and Nagai\(^8, 17\) on transgranular fracture surfaces and cleavage facets adjacent to the inner surface of a tube specimen. Such pits have not been observed on cleavage facets far from the inner surface. They have suggested that the cleavage facet was attacked by iodine after the cracking took place.

In the present investigation, electron probe microanalysis (EPMA) and Auger electron spectroscopy (AES) were carried out and it was seen that iodine did not penetrate the tubing material. This suggested that iodine-SCC is a surface phenomenon where chemical interaction takes place between iodine and zircaloy at the tube surface.

Fig. 8 indicates the flute like morphology, which is a typical fracture surface crack morphology found in iodine-SCC. Similar features have also been reported by other authors\(^5, 17, 19\). Aitchinson and Cox\(^19\) have attributed...
these fluted regions to internal necking by slip. With the idea of observing the appearance of the fracture surface in the absence of iodine, a few tests were carried out at room temperature in which the tubes were pressurised to failure by argon gas pressure. These tests produced dimpled fracture, as shown in Fig.10. This mode of fracture involves microvoid nucleation, growth and coalescence.

3.3 Effect of Graphite Coating and Preoxidation

In order to mitigate iodine-SCC in zircaloy cladding, graphite is usually applied as a thin layer on the cladding inside surface (CANLUB). The graphite interlayers between UO₂-fuel pellets and cladding surfaces are meant to provide lubrication. In addition, they may affect the chemical reaction between iodine and zircaloy. In the context of pellet clad interaction, Wood et al. have found that graphite coating provided effective lubrication even in dry low oxygen potential environments such as those existing at UO₂-zircaloy interfaces. Graphite coated tubes have also been reported to have higher resistance to defects caused by power ramping.

In the present study, an attempt was made to evaluate the SCC behaviour of graphite coated zircaloy-2 tubes by the internal pressurisation technique. It was felt that in these tests one would perhaps be able to find out whether graphite interlayers could act as barriers to the chemical reaction between iodine and zircaloy. Table 2 gives the

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Iodine concentration (mg/cm²)</th>
<th>Temperature (°C)</th>
<th>Applied hoop stress (kg/mm²)</th>
<th>Time to failure (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Graphite coated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) nil</td>
<td>300</td>
<td>33.09</td>
<td>NF (384)</td>
<td></td>
</tr>
<tr>
<td>(ii) 1</td>
<td>300</td>
<td>30.93</td>
<td>NF (260)</td>
<td></td>
</tr>
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<td>(iii) 1</td>
<td>400</td>
<td>30.93</td>
<td>NF (144)</td>
<td></td>
</tr>
<tr>
<td>(iv) Un-coated</td>
<td>1</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. Oxidised</td>
<td>1</td>
<td>300</td>
<td>30.93</td>
<td>NF (72)</td>
</tr>
<tr>
<td>C. Hydrided</td>
<td>(i) 44 ppm nil</td>
<td>300</td>
<td>26.08</td>
<td>NF (120)</td>
</tr>
<tr>
<td>(ii) 44 ppm 1</td>
<td>300</td>
<td>26.11</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(iii) 80 ppm nil</td>
<td>300</td>
<td>26.11</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(iv) 84 ppm 1</td>
<td>300</td>
<td>26.11</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

NF - Not failed.
The number in bracket indicates duration of test in hours.
results obtained with the graphite coated tubes. It could be seen that a considerable improvement towards resistance to SCC could be achieved with this coating. At high stress levels at 673 K, with 1 mg/cm² of iodine, the graphite coated tube did not fail in 144 hrs. whereas the uncoated tube failed within 10 hrs., under similar conditions of testing. This clearly indicated that the chemical reaction between the zircaloy surface and the iodine vapour is significantly affected in the presence of graphite interlayers. In order to confirm this cross-sections of uncoated and graphite coated tubes, exposed to iodine vapour, were examined microscopically. The uncoated tubes showed localised reduction in wall thickness while graphite coated tubes showed no such feature. It appeared, therefore, that graphite coating acted as an effective barrier to the chemical reaction. Cubicciotti et al (22) have found that the crack initiation sites in zircaloy tubing are associated with local inhomogeneities in the material. Graphite coating, though porous, can certainly cover some such potent crack initiation sites and thereby can increase resistance to SCC. EPMA studies revealed that iodine did not penetrate the matrix of the graphite coated tubes. Fig.2(c) shows a photograph of a failed graphite coated tube.

The results obtained with the preoxidised tubes are also given in Table 2. The oxide layer on the tube surface acted as a barrier to chemical reaction and improved SCC resistance. UNE (23) has reported complete absence of SCC in iodine atmosphere containing oxygen partial pressure above 28 torr at 573 K and 9 torr at 623 K. Mattas et al (24) have shown that the presence of a thick unbreached oxide layer on the inside surface reduced the susceptibility of irradiated zircaloy cladding to iodine-SCC.

Results obtained under thermal cycling conditions are given in Table 3. In this situation the graphite coated tubes also became susceptible to failure in iodine environment. However, the strain to failure was much higher than those obtained in tests at any fixed temperature and without graphite coating. Under thermal cycling, the failure could be termed ductile stress rupture which was different from the typical iodine-SCC failure. Similar observations have been made by Garlick (11) in experiments where the internal pressure has been changed rapidly in iodine-argon environment at high temperatures.

Table 3

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Iodine concentration (mg/cm²)</th>
<th>Temperature cycling range (°C)</th>
<th>Maximum applied hoop stress (kg/mm²)</th>
<th>Circumferential strain at failure (%)</th>
<th>Time to failure (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncrusted</td>
<td>1</td>
<td>300-450</td>
<td>30.93</td>
<td>29.8</td>
<td>25.7</td>
</tr>
<tr>
<td>Uncrusted</td>
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<td>300-500</td>
<td>30.93</td>
<td>29.8</td>
<td>25.7</td>
</tr>
<tr>
<td>Uncrusted</td>
<td>nil</td>
<td>300-450</td>
<td>30.93</td>
<td>29.8</td>
<td>25.7</td>
</tr>
<tr>
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<td>26.0</td>
<td>74.64</td>
</tr>
<tr>
<td>Crusted</td>
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<td>300-450</td>
<td>27.16</td>
<td>27.16</td>
<td>NF (528)</td>
</tr>
</tbody>
</table>

NF - Not failed.
The number in bracket indicates duration of test in hours.
3.4 Effect of Hydriding

The influence of hydrogen pick up on the iodine-SCC behaviour of zircaloy tubing was studied and the results are presented in Table 2. These indicated that as low as 34 ppm of Hydrogen could seriously affect the SCC resistance of zircaloy-2. Tubes containing about 80 ppm of hydrogen were found to have a very short time-to-failure even in the absence of iodine. However, this burst test was conducted at a stress above the yield stress - a situation not likely to be attained under normal operating conditions. Nevertheless it could be concluded that PCI type failures of zircaloy cladding may be accelerated due to hydrogen up-take.

3.5 Effect of Cadmium

SCC behaviour of zircaloy-2 in the presence of cadmium has not been studied as extensively as in the presence of iodine. Cadmium is one of the fission products released during the fission reactions in the reactor and its yield is about twenty times smaller than that of iodine. Grubb and co-workers were the first to discover the ability of cadmium to promote SCC of zircaloy.

In the present study, cadmium coating was seen to be harmful in terms of its embrittling capacity. Table 4 gives the time-to-failure as well as the circumferential elongation at failure of the tubes pretreated either in acids or in alkali. Tubes pretreated in acids failed within a very short time. Alkali-treated tubes did not fail within the test duration. It seemed that a proper contact between cadmium and zircaloy tube surface is needed for cracking to occur. Possibly the oxide film on zircaloy surface could not be removed by only alkali cleaning and remained effective in preventing a direct contact between zircaloy and cadmium. A similar situation might have been obtained when a mixture of cadmium oxide and zirconium hydride powders were spread on the tube surface and the embrittling effect was absent. Acid cleaning makes the surface free of oxides and thus, cadmium comes in direct contact with the tube's metallic surface, leading to brittle failure. Coffin and Gangloff clamped a thin foil of cadmium to the grooved gauge section of a zircaloy tensile specimen which was pulled at a slow strain rate at 573 K. They observed brittle transgranular failure accompanied by a flute-like morphology. Cubicciotti could not produce cracks when they placed pieces of Cd on the surfaces of zircaloy samples, but numerous cracks were developed when Cd was rubbed against the surfaces. They suspected that the small amounts of oxygen present during

<table>
<thead>
<tr>
<th>Test Condition &amp; pretreatment</th>
<th>Temperature (°C)</th>
<th>Applied Hoop stress (kg/mm²)</th>
<th>Time-to-failure (hrs)</th>
<th>Circumferential strain at failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali pretreatment + Cd coating</td>
<td>350</td>
<td>24.5</td>
<td>NF (150)</td>
<td>-</td>
</tr>
<tr>
<td>Acid pretreatment + Cd coating</td>
<td>350</td>
<td>24.5</td>
<td>2.5</td>
<td>30</td>
</tr>
<tr>
<td>Acid pretreatment + Cd coating</td>
<td>350</td>
<td>27.0</td>
<td>0.5</td>
<td>35</td>
</tr>
<tr>
<td>Acid pretreatment + Cd coating + I₂</td>
<td>350-400</td>
<td>21.0</td>
<td>NF (200)</td>
<td>-</td>
</tr>
<tr>
<td>CdO + ZrH₂</td>
<td>350</td>
<td>25.5</td>
<td>NF (164)</td>
<td>-</td>
</tr>
<tr>
<td>I₂ (1mg/cm²)</td>
<td>350</td>
<td>33.0</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

NF - Not failed.
The number in bracket indicates duration of test in hours.
the tests were sufficient to form films that prevented reaction of cadmium and zirconium except when the cadmium was forced into intimate contact with the zirconium metal by abrasion.

Shann and Olander(29) also have produced cleavage failures in zircaloy-4 in the presence of cadmium. In their experiments a molecular beam of cadmium with a well defined vapour pressure was directed onto the surface because cadmium in the vapour phase was expected to have a better contact with the zircaloy metallic surface. They have also shown that for Cd-SCC, there is a greater sensitivity to surface chemical or physical inhomogeneities than for fracture caused by iodine or metal iodides.

Shimada et al have reported similar observations in their experiments with cadmium iodide powder where they produced low-ductility failures in iodide-contacting specimens in which cadmium iodide powder was spread on the inner surface of the specimen which was heated to 673 K. At this temperature cadmium iodide is expected to be in the liquid condition, the melting point of CdI being 663K. But in the iodide non-contacting method, the powder was kept on a mandrel inside the tube and the tube failed in a ductile manner.

Time-to-failure was seen to be dependent on the applied stress. Acid cleaned tubes stressed at 24.5 kg/mm² failed within 2.5 hrs. whereas similar tubes stressed at 27 kg/mm² failed within half an hour. Moreover, tubes stressed at 21 kg/mm², but containing both cadmium and iodine did not fail within the period of the test. The fracture strain was much higher with cadmium than with iodine. It appears, therefore, that the degree of embrittlement due to Cd is less than that due to iodine.

4. CONCLUSION

In the present investigation it has been observed that zircaloy-2 cladding tubes are susceptible to iodine-SCC at a stress level close to the yield stress of the material. The time-to-failure is dependent on the iodine concentration, temperature and hydrogen pick up. Graphite coated and preoxidised tubings have been found to resist iodine-SCC. Thermal cycling shortens the life of tubes both in the presence and absence of iodine. However, graphite coating improves the rupture behaviour even under thermal cycling conditions. Cadmium, when in intimate contact with zircaloy surface, causes embrittlement.

5. ACKNOWLEDGEMENTS

The authors express their gratitude to Dr. C.K. Gupta Head, Metallurgy Division and to Dr. H.S. Gadiyar, Head, Corrosion and Electrometallurgy Section, Metallurgy Division, Bhabha Atomic Research Centre for their encouragement during the course of this investigation. The authors also gratefully acknowledge the assistance of Dr. G. Eswara Prasad and Mr. M. Sundararaman for SEM and AES analysis respectively.

REFERENCES

FRAGEMA ZIRCALOY CLADDING BEHAVIOUR IN FRENCH PWR

O. LAVOINE, A. RAYBAUD
Electricité de France,
Villeurbanne

B. HOUDAILE
CEA, Département de technologie,
Saclay

G. RAVIER
Division Combustible,
Framatome,
Lyon

France

Abstract

For several years, EDF, FRAGEMA and CEA, with the cooperation of Westinghouse in some cases, have developed R and D programs to study the FRAGEMA fuel behaviour under reactor operating conditions. These programs include dimensional on-site examinations and physical hot cell examinations of fuel rods.

An important objective of these programs is a better understanding of the zircaloy cladding behaviour under irradiation. In this paper, the cladding growth and corrosion are presented.

Cladding growth

Measurements have been carried out on fuel rods irradiated up to 56 GWd/tU. The measurements show a large scatter in the values. The impact on rod growth of cladding physical characteristics has been analyzed.

Cladding external corrosion

Cladding external corrosion has been measured on fuel rods in hot cells. The discharge burnup ranged from 10 to 56 GWd/tU. The results show a scatter in the values. An important azimuthal variations were observed on several fuel rods; this phenomenon is perhaps due to the local thermohydraulic conditions.

INTRODUCTION

For several years, EDF, FRAGEMA and CEA, with the cooperation of Westinghouse in some cases, have developed R and D programs to study the FRAGEMA fuel behaviour under reactor operating conditions. These programs include on-site examinations of characterised assemblies and fuel rods PIE in hot cells.

The results include among other data the zircaloy cladding behaviour under irradiation in power reactors.

In this paper, the main results that will be presented concern the cladding dimensional variations (growth and diametral variations) and the cladding external corrosion.

CLADDING GROWTH

The fuel rod cladding is made of stress-relieved zircaloy 4. To prevent interference between the rods and the assembly tips, rod-to-nozzle gaps are provided at the top and the bottom of assemblies.

The peripheral rods of around 60 FRAGEMA assemblies were examined on site to determine their growth. The assemblies were examined over a wide range of burnups, up to 56 GWd/tU. The results are presented on Figure 1. They show a steady dependency of growth on burnup. The rod-to-nozzle gaps are sufficient to accommodate the fuel rod growth. It was noted that the rod-to-nozzle bottom gap is generally filled after three cycles.

The analysis of the results relative to early fabrications shows a scatter in the measurements for a similar burnup, even in the same assembly. This scatter cannot be explained by irradiation-induced conditions only. The various growth behaviours are closely related to the manufacturing batches; an example is given for one fuel assembly on Figure 2. The origin of this scatter has been investigated in the manufacturing conditions, keeping in mind that each fabrication step contributes towards final cladding properties: ingot chemical composition, trex manufacturing (see Figure 3), heat treatments.
In a first step, a statistical analysis was developed to correlate the cladding growth and the as-fabricated cladding batch properties. The cladding mechanical properties are representative of material metallurgical structure; because the cladding growth can be interpreted in terms of modifications of the metallurgical structure under fast neutron flux, one of our analyses was focused on the tube mechanical properties, as characterized during the fabrication process.

This analysis was applied to an interesting case in which a large scatter of cladding growth was observed on 5 assemblies and is given as an example.

Three characteristics are currently measured in fabrication:

- Ultimate strength
- Yield strength (0.2% offset)
- Elongation.

For these three parameters, a statistical analysis of the variance was developed to compare the respective correlation of each parameter with the growth.
In the fuel rod population we distinguish three classes according to their growth value:

- growth below 0.7 Z
- growth between 0.7 Z and 1.0 Z
- growth above 1.0 Z.

For each parameter calculation is made of a variance ratio defined by $F = \frac{V_A}{V_P}$, where $V_A$ is the intra-class variance and $V_P$ the inter-class variance. This factor is then compared with the Fisher-Snedecor law to assess the irradiation behaviour homogeneity for each mechanical characteristic.

The results show in this particular case that the best indication of the irradiation behaviour is the elongation: for a large elongation, the cladding growth should be low (see Figure 4).

This first statistical approach of the phenomenon is limited and not exhaustive. It has appeared necessary to extend it to other growth results and to search for the fabrication parameters (chemical composition, heat treatments) which can explain this growth behaviour scatter. This analysis has already given results which confirm that the present FRAGEMA cladding product does not exhibit such growth scatter.

CLADDING DIAMETER CHANGE

Profilometry measurements in hot cells were carried out on many fuel rods. Figure 5 shows the results obtained. We can observe a scatter of the data, but the general tendency seems clear: the cladding reduction is due to the creepdown until a burnup of around 25 GWD/tU. This creepdown is stopped at this burnup value. This trend suggests that cladding diameter decreases until pellet-cladding contact occurs.

Up to higher burnup (50 GWD/tU) there is no change in the cladding diameter behaviour, which shows that pellet swelling is low or non-existent.
Fuel cycle cost optimization and grid requirements have led EDF to increase the fuel discharge burnup and to operate the reactors under load follow and frequency control.

Longer irradiation times, higher cladding temperature and more aggressive thermal hydraulic environments can be considered as potential problems for zircaloy cladding corrosion.

To improve our knowledge of cladding external corrosion, extensive programs including theoretical studies, experimental tests and fuel rod examinations in hot cells have been carried out. The on-site measurements are in progress. The results of fuel rod examinations in hot cells are presented below.

These fuel rods were characterized by discharge burnups between 12 and 56 GWd/tU. For each rod four axial evolution measurements along the cladding have been carried out with an eddy current probe. Metallographic measurements were made to confirm the eddy current measurements and to observe the oxide layer thickness distribution. (Figure 6 shows the peak oxide thickness measured versus burnup). Typical examples of axial zirconium oxide thickness evolution along the fuel rod length are shown on Figure 7. The maximum value corresponds to 65 μm for a burnup of 56 GWd/tU.

Fuel rod cladding corrosion appears to be a scattered phenomenon; corrosion values can vary by a factor 2 or 3 under identical irradiation conditions. In particular, azimuthal variations in zirconium oxide layer thickness were observed on some fuel rods; examples of zirconium oxide layer thickness distributions measured by metallography are shown on Figure 8. The search of the origin in the scatter of oxide thickness shows the potential influence of thermal/hydraulic conditions due to rod flow for example. These analyses are in progress.

Hydrogen measurements were taken from fuel rod claddings. The measurements show that around 20% of the hydrogen produced by the oxidation reaction is absorbed by the cladding.
CONCLUSION

The measurements on EDF sites and in the CEA hot cells proved the good behaviour of the FRAGEMA fuel rod cladding under irradiation.

Further analysis is in progress to determine the influence of fabrication parameters on cladding growth and external corrosion.

REFERENCES


IRRADIATION GROWTH AND STRENGTH OF ZIRCONIUM ALLOYS

F. GARZAROLI, P. DEWES, R. MANZEL, A. JÜTTNER
Kraftwerk Union AG.
Erlangen, Federal Republic of Germany

Abstract

Irradiation growth of Zircaloy and zirconium base alloys was studied in PWRs for up to four operational cycles, corresponding to fast neutron fluences of about $9 \times 10^{21} \text{ cm}^{-2} (E > 0.82 \text{ MeV})$. For standard Zircaloy tubing there exists a strong interrelation between irradiation growth and as-fabricated yield strength. Higher yield strength usually results in higher growth. An effective means of reducing irradiation growth is final $\beta$-quenching of the tubing. A combination of high yield strength and low irradiation growth can be achieved by $\beta$-quenching and subsequent cold working. Zr 2.5 Nb shows a significantly smaller growth rate even at high yield strength compared to Zircaloy.

1. Introduction

The standard fabrication routine for Zircaloy tubing leads to a pronounced crystallographic texture. As a consequence, irradiation results in growth in the axial direction. This irradiation growth is an important issue that has to be considered in the design of fuel assemblies and fuel rods. However, for the selection of the appropriate material condition the strength requirements have to be considered too.

It has been shown in the past \cite{1,2,7} that material with high strength, such as cold worked Zircaloy, exhibits significantly higher irradiation growth than lower strength, fully recrystallized Zircaloy. Experiments have been conducted to study the irradiation growth behaviour of various material conditions and to look for materials that combine both low growth and higher strength.

2. Materials and Irradiation Conditions

The materials studied are listed in Tab. 1. The materials comprise standard Zircaloy with various final heat treatments, e.g. stress relieved, partially recrystallized, and fully recrystallized. The yield strength at 340 °C ranges from 300 to 120 N/mm². The effective volume fraction of material with {0002} crystallographic pole orientation in axial direction (the so-called $f$-parameter) is generally 0.05.

$\beta$-quenching was considered to be an effective means of reducing irradiation growth due to the nearly isotropic crystal orientation. The Zircaloy studied had an $f$-parameter of 0.23 in axial direction, much larger than the standard Zircaloy with $f = 0.05$, but nevertheless not totally isotropic ($f = 0.33$). The yield strength of the $\beta$-quenched Zircaloy was, at 150 N/mm², only slightly higher than that of fully recrystallized Zircaloy at 120 N/mm². 5% cold working of $\beta$-quenched Zircaloy resulted in an increase in yield strength to 240 N/mm² and a slight decrease in the $f$-parameter.

The material with the highest yield strength within this study was Zr 2.5 Nb in the stress relieved condition fabricated according to conventional techniques with $f = 0.05$. The material Zr 3 Nb 1 Sn also had a high yield strength even in the fully recrystallized condition, due to the high alloying content. The $f$-parameter for this alloy was likewise 0.05.

All samples studied were from tubing with an outer diameter of 10.75 mm and a wall thickness of 0.72 mm. The growth behaviour of these samples has been compared to the behaviour of Zircaloy control rod guide tubes of standard PWR fuel assemblies.

<table>
<thead>
<tr>
<th>Material/Condition</th>
<th>$R_{0.2}$ (N/mm²)</th>
<th>Degree of Recryst. (%)</th>
<th>Texture $f$-parameter*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zry, Fully Recryst.</td>
<td>120</td>
<td>&gt; 95</td>
<td>0.05</td>
</tr>
<tr>
<td>Zry, Partially Recryst.</td>
<td>230/270</td>
<td>~ 30</td>
<td>0.05</td>
</tr>
<tr>
<td>Zry, Stress Relieved</td>
<td>300</td>
<td>&lt; 5</td>
<td>0.05</td>
</tr>
<tr>
<td>Zry, $\beta$-quenched</td>
<td>150</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>Zry, $\beta$-quenched + 5% CW</td>
<td>210</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>Zr 2.5 Nb, Stress Relieved</td>
<td>330</td>
<td>&lt; 5</td>
<td>0.05</td>
</tr>
<tr>
<td>Zr 3 Nb 1 Sn, CW + 540 °C/16 h</td>
<td>260</td>
<td>&gt; 95</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* Effective volume fraction of material with {0002}-crystallographic pole orientation in axial direction
**Tab. 2 Irradiation Conditions**

<table>
<thead>
<tr>
<th>Material/Condition</th>
<th>Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zry, Fully Recrystallized</td>
<td>a) Guide Tubes of PWR Fuel Assemblies in PWR A, B and C</td>
</tr>
<tr>
<td>Zry, Partially Recrystallized</td>
<td>b) Water Tubes at Fuel Rod Positions in PWR-A and</td>
</tr>
<tr>
<td>Zry, Stress Relieved</td>
<td>c) Special Growth Samples (1)</td>
</tr>
<tr>
<td>Zry, B-quenched</td>
<td>Special Growth Samples (1)</td>
</tr>
<tr>
<td>Zry, B-quenched</td>
<td></td>
</tr>
<tr>
<td>Zr 2.5 Nb - Stress Relieved</td>
<td>Water Tubes at Fuel Rod Positions in PWR-A</td>
</tr>
<tr>
<td>Zr 3 Nb 1 Sn, CW 54°C/16 h</td>
<td></td>
</tr>
</tbody>
</table>

(1) Tubular sample with a length of 2260 mm positioned inside of the guide tube of a PWR assembly and held down by a special flow restrictor in PWR-A

---

**Fig. 1 Schematic Diagram of Growth Samples in a PWR Fuel Assembly**

**Fig. 2 Length Changes of PWR-Fuel Assemblies with Different Zircaloy Control Rod Guide Tubes as a Function of Fast Neutron Fluence**

Irradiation took place in three German PWR's designated as PWR A, B, and C. The different irradiation conditions are summarized in Tab. 2. Two types of material samples were used. One type were cladding tubes with a length of 2915 mm replacing fuel rods within PWR fuel assemblies. The other type were special growth samples (Fig. 1) with a length of 2260 mm, inserted in control rod guide tubes of a PWR fuel assembly and held in position by a modified flow restrictor. The B-quenched Zircaloy, Zr 2.5 Nb, and Zr 3 Nb 1 Sn were studied only in samples, whilst growth of the various commercial conditions of Zircaloy was evaluated from samples and guide tubes.

Irradiation lasted up to 4 reactor cycles, corresponding to about 1200 EFPD and a fast neutron fluence of 9 x 10^21 cm^-2 (E > 0.82 MeV). In general, length measurements were performed after each cycle.
3. Results and Discussion

The results of the length measurements on control rod guide tubes are shown in Fig. 2 as a function of fast fluence. Growth of guide tubes of stress-relieved Zircaloy reveals an almost linear fast fluence dependence and by far the highest growth rate. Fully recrystallized Zircaloy guide tubes show the least growth and a tendency to saturation in the fluence range studied. Partially recrystallized Zircaloy is between these two materials.

Fig. 3 summarizes the results of the growth samples. Again, for a given fluence, stress relieved Zircaloy shows the highest growth, fully recrystallized Zircaloy significantly less growth, and partially recrystallized Zircaloy falls in between. From a comparison of Figs. 2 and 3 it is evident that growth of Zircaloy guide tubes is somewhat less than that of stress free empty tubes. This is due to the axial forces imposed by the assembly hold-down springs, although the stresses are rather low. Whilst the growth samples of partially recrystalized Zircaloy exhibit a growth behaviour closer to stress relieved material, the partially recrystalized guide tubes behave more like fully recrystallized ones.

These differences are due to differences in the yield strength which was 230 N/mm² in the case of the guide tubes compared to 270 N/mm² in the case of the growth samples. The differences in yield strength reflect the differences in dislocation densities. It is believed that the increasing growth with increasing dislocation density is due to a contribution from irradiation-induced dislocation climbing.

The lowest growth rate was found, as expected, for β-quenched Zircaloy. At fast fluences between $2 \times 10^{21}$ cm⁻² and $10 \times 10^{21}$ cm⁻², the growth rate of β-quenched Zircaloy is only about 35 % of that of fully recrystallized Zircaloy. This corresponds to the differences in the f-parameter which influences growth according to the following general correlation:

$$L_0 = \text{const.} \cdot (t)^n \cdot (1 - 3f)^{-3.7}$$

$\Delta L = \text{fast fluence}$

$n = \text{growth exponent}$

$f = \text{texture parameter}$

Using the f-parameter given in Tab. 1, the correlation predicts for β-quenched Zircaloy 35 % of the growth rate of fully recrystallized material, in good agreement with the above stated observation.

β-quenched and 5 % cold worked Zircaloy shows an initial contraction followed by later growth. It is suggested that the initial contraction is due to a release of the internal stresses generated by the final cold deformation step (drawing). Although the f-parameter of this material is relatively high, the later growth rate is about equal to that of fully recrystallized material with small f-parameter. This can be explained by the increased dislocation density due to the final cold deformation.

In Fig. 4, the irradiation growth of Zr 2.5 Nb and Zr 3 Nb 1 Sn is compared to stress relieved and fully recrystallized Zircaloy. Included are literature data from on annealed Zr 2.5 Nb. In general, Zr 2.5 Nb exhibits a growth behaviour similar to that of Zircaloy. Stress relieved Zr 2.5 Nb shows a linear dependence on fast fluence, and annealed Zr 2.5 Nb shows a tendency to saturation. However, the absolute growth of both material con-
For design application it should be mentioned that all materials experience significant irradiation hardening after short exposure times. In commercial Zircaloy tubing, irradiation growth is almost directly correlated to as-fabricated yield strength. Effective means of reducing irradiation growth is a final β-quenching treatment. A combination of high yield strength and low irradiation growth can be achieved by β-quenching and subsequent cold working.

The highest yield strength and low irradiation growth is found in stress relieved Zr 2.5 Nb.
CORROSION OF ZIRCALOY-4 FUEL CLADDING IN CONDITIONS SIMULATING EXTENDED BURN-UP IN PWR

D.R. TICE, G. HUDDART
Springfields Nuclear Power Development Laboratories, United Kingdom Atomic Energy Authority, Sallows, Preston, Lancashire, United Kingdom

Abstract

The possibility of increased corrosion of Zircaloy-4 fuel cladding due to hideout of lithium at the extended fuel burn-ups now being proposed for pressurised water reactors is being investigated. The test programme includes isothermal testing in simulated start-of-cycle coolant chemistry, and in a high lithium/boron environment simulating that which might be produced under heat flux conditions due to 'hideout' of lithium and boron compounds in porous oxide or crud. Tests under heat flux conditions with local boiling are planned, to investigate the conditions which might result in hideout in practice.

The present paper presents results of the isothermal test after one year's specimen exposure. These results show no significant difference between corrosion rates in PWR coolant and in the simulated hideout environment prior to the transition from cubic to approximately linear kinetics, but a small degree of acceleration of corrosion in simulated hideout conditions is observed subsequently. There are also differences between the various environments in the extent of lithium incorporation in the oxide film. Specimen exposures have not yet reached the time at which the greatest effect of the environment would be expected.

1. INTRODUCTION

Waterside corrosion of the Zircaloy-4 fuel cladding in pressurised water reactors (PWRs) is not generally considered to be limiting under normal operating conditions. However, as part of the continuing development of commercial reactors there is a move towards increased fuel burn-up and higher fuel temperatures to improve the economics of operation. Both factors will result in increased clad corrosion, but as this is of no concern. However the increased oxide thickness produced will result in an increase in the temperature of the metal-oxide interface which will further accelerate corrosion. Increased temperatures will also result in some local boiling which may produce a concentration of lithium within either porous oxide or a crud layer which may be present on the fuel. This hideout of lithium may result in enhancement of corrosion rates above those which might be expected due to increased temperature.

Available data (1) on the influence of lithium on Zircaloy corrosion have been obtained in solutions with only lithium present, which results in a higher pH than would occur in a lithiated, borated environment relevant to commercial PWRs. The current programme aims to investigate the effects on the corrosion of Zircaloy-4 of a lithiated and borated environment which would be expected to be produced by concentration due to hideout under conditions relevant to operation of a modern PWR.

The experimental programme includes isothermal testing in autoclaves in both standard start of cycle coolant chemistry (2.2 ppm Li as LiOH • 1000 ppm B as boric acid) to compare corrosion behaviour with that previously generated in pure water, and similar tests in an environment simulating that which may be generated by hideout. These latter tests are being conducted in an environment with a hundred-fold increase in the concentration of lithium which is believed to be possible due to hideout under local boiling conditions. To calculate the likely concentration of boron under these conditions requires knowledge of the dissociation constants for several borate anion-boric acid equilibria:

\[
\begin{align*}
\begin{array}{l}
B(OH)_4^- & \rightleftharpoons H_2BO_3^- + OH^- \\
B_2(OH)_7^- & \rightleftharpoons 2H_2BO_3^- + OH^- \\
B_3(OH)_{10}^+ & \rightleftharpoons 3H_2BO_3^- + OH^- \\
B_4(OH)_{14}^+ & \rightleftharpoons 4H_2BO_3^- + 2OH^- 
\end{array}
\end{align*}
\]

Account must also be taken of volatilisation of boric acid. Trowell (2) has calculated that under conditions leading to a 100-fold concentration of lithium (i.e. 220 ppm Li) the relevant boron concentration is between 6000 and 8000 ppm. A solution of 220 ppm Li • 8000 ppm B was thus used for the simulated hideout tests. This is estimated to have a pH at 350°C of 8.4 compared to 7.3 for start of cycle coolant and 13.1 for 220 ppm Li as LiOH in the absence of boric acid. The observed effects of LiOH on corrosion are believed to be a synergistic effect of Li and pH. Thus a considerably lower enhancement of corrosion is expected for the environment used for these tests than for the same lithium concentration in the absence of boric acid, (1)

Additional tests are planned to assess whether concentration processes leading to lithium hideout can in fact occur under relevant heat flux conditions. These tests will use an electrically heated simulated fuel rod exposed to a lithiated, borated environment. Local boiling conditions will be attainable.

The present paper describes the results of the first year's autoclave testing in both standard and simulated hideout environments, and compares the data with that previously generated in pure water or in steam.

2. EXPERIMENTAL PROCEDURE

The isothermal tests were performed in two static autoclaves, of internal dimensions 950 mm x 100 mm diameter, one of which was used for each test environment. The specimens were cut from standard PWR cladding tubing, and were 50 mm long and 9.5 mm diameter; the ends of the tube were
Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.5%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1%</td>
</tr>
<tr>
<td>Fe + Cr</td>
<td>0.3%</td>
</tr>
<tr>
<td>Al</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>W</td>
<td>&lt; 30 ppm</td>
</tr>
<tr>
<td>B</td>
<td>&lt; 0.3 ppm</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.3 ppm</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Co</td>
<td>35 ppm</td>
</tr>
<tr>
<td>Hf</td>
<td>40 ppm</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 20 ppm</td>
</tr>
</tbody>
</table>

Mechanical Properties

Yield Strength (0.2%) 516 MPa
Tensile Strength 685 MPa
Elongation 22%

Chemical composition and mechanical properties of the material tested are given in Table 1. The weighed specimens were mounted in purpose-built jigs, to minimise contact between the jig and the specimen, and inserted in the autoclaves. The autoclaves were filled with a volume of liquid calculated to be sufficient to cover all specimens at temperature. After closure of the vessels they were purged with argon prior to heating to 350°C, monitored via thermocouples in the water. Throughout exposure the pressure was maintained at the saturation vapour pressure at 350°C. Twelve specimens were initially put on test in the standard coolant environment, and 24 specimens under simulated hideout conditions. In addition, eighteen specimens were pre-oxidised in steam at 550°C to produce an oxide film intended to simulate a period of prior exposure to PWR coolant. These specimens were then exposed to the standard coolant environment. Specimens were removed for weighing every 28 days. At the start of each successive exposure period two additional virgin specimens were inserted, to provide a comparison of oxidation behaviour during each corrosion run.

After approximately 300 days, four specimens previously exposed to standard coolant were transferred to the high lithium environment, to simulate the effect of hideout after a period of standard operation. At the same time four specimens were transferred from the high to the low lithium environment.

3. RESULTS

3.1 CORROSION DATA

Figure 1 illustrates the average weight gains for the three initial batches of specimens which have all reached exposures approaching 350 days. For the virgin specimens in standard PWR coolant, the general corrosion behaviour is similar to that previously reported for Zircaloy exposed to pure water in the temperature range 300 to 360°C. Thus the corrosion kinetics initially followed an approximately cubic rate law until transition to a somewhat more linear region was reached, after ~ 140 days. Until relatively recently the approximately linear behaviour following transition was believed to be representative of steady state corrosion behaviour, but it is now known(3) that this assumption may underestimate final corrosion rates by as much as a factor of two. In fact an intermediate "transitory" region exists comprising repeated cycles with cubic kinetics. It has been suggested that this behaviour is due to the formation of a new protective oxide layer at the metal-oxide interface on each cycle. The data on virgin samples in PWR coolant are consistent with this behaviour, with the time to second transition being ~ 250 days.

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In the high Li/B environment simulating hideout, the initial corrosion rate was very similar to that in standard coolant, but some acceleration in corrosion rate was observed after about 100 days exposure, i.e. just before the first transition. The total weight gain after 300 days was about 15% greater than in standard coolant.

The preoxidised specimens showed a more linear rate of corrosion with time, although even in this case some cyclic behaviour can be detected. The weight gain due to steam oxidation for these specimens averaged 180 mg/dm² which is about three times that which occurred in 300 days at 350°C. There is an indication of a slight acceleration in corrosion rate towards the end of the exposure period for these specimens.

Figure 2 compares the corrosion behaviour of the initial charges of virgin specimens with that of specimens introduced later for control purposes. Whilst there are minor differences in behaviour it is clear that the overall behaviour is very similar to the original specimens. The interspecimen variability is considerably greater for the high lithium/boron environment.

Figure 1 also shows the effect of transferring four specimens from standard to high Li/B conditions, and vice versa. There is a considerable acceleration in corrosion rate when specimens were transferred to the high Li/B environment, and a deceleration when the reverse transfer was made.

3.2 CHARACTERISATION OF THE CORROSION LAYER

During the autoclave tests, two samples were removed for destructive characterisation of the oxide scale. These had been subjected to standard coolant for 168 days, and to the high lithium environments for 56 days, respectively. Further characterisation is planned for samples which have been exposed for longer periods. The main technique used was x-ray diffraction (XRD), but some Auger Spectroscopy was also carried out.

X-ray diffraction patterns were measured for both specimens. The major phase present was monoclinic ZrO₂, with around 2% cubic ZrO₂. Three lithium zirconate phases were present. These, with their mole per cent concentrations for the low and high lithium environments, respectively were:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Low Li/B</th>
<th>High Li/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₆Zr₂O₇</td>
<td>0.4%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Li₄ZrO₅</td>
<td>0.4%</td>
<td>1.2%</td>
</tr>
<tr>
<td>Li₂ZrO₃</td>
<td>0.45%</td>
<td>0.45%</td>
</tr>
</tbody>
</table>

This is equivalent to a lithium concentration in the high lithium environment about twice that in the low lithium environment.

Auger spectroscopic examination of the scale revealed no boron was present either on the surface, or through the depth of the scale, as exposed by ion etching. Although a peak indicative of lithium was detected on both samples, which was larger on the high Li/B sample, there is some uncertainty concerning the identification of this peak.

4. DISCUSSION

The short term corrosion data in standard and high lithium PWR coolant shown in Fig. 1 are consistent with other data obtained in this laboratory(5) in pure water at 316 and 360°C and 1 atm at 360 and 400°C and with data obtained by Garzaroli(6) in pure water at 350°C, as shown by the Arrhenius plot in Fig. 3. For this plot, pretransition corrosion rates were averaged between the beginning and end of the cubic cycle up to either the first or second transition. Despite the relatively short exposure times reached to date, the activation energy for these data is similar to that generally accepted for post-transition corrosion between 300 and 400°C. Using this activation energy of 28.2 kJ/mol, the data obtained previously(5) in water and steam at 360°C can be compared with the current data, Fig. 4. After allowing for the effect of test temperature, corrosion rates are quite similar for all the data.

Prior to exposure to PWR coolant the pre-oxidised specimens had a total weight gain equivalent to four times that produced in 300 hours at 350°C. Overall corrosion rates in standard coolant were quite similar to those of virgin specimens, although the kinetics approximated more closely to linear, and there was some acceleration towards the end of the exposure period. It is planned to transfer some of the specimens to the simulated hideout environment.
McDonald et al.(1) and Hiller et al.(7) have studied the effects of lithium hydroxide (without boric acid) on corrosion of Zircaloy-4 and Zircaloy-2 respectively. Their data at 360°C, Fig. 5, indicate that whereas at high lithium concentrations (≥ 0.1 molal) there is no obvious pretransition region, at lower concentrations (0.01-0.06 molal) there is a definite pretransition region, where the presence of LiOH has little effect, an intermediate region where there is a small accelerating effect of LiOH, and finally a post transition region where the corrosion kinetics are linear but sharply accelerated.

For comparison, the lithium hydroxide concentration in the simulated hideout environment used in the current tests was 0.03 molal, but the pH was much lower due to the presence of boric acid. Even in the absence of boric acid, only a fairly small effect of LiOH would be expected in the intermediate region at this concentration, but a much larger effect might be anticipated once the post transition region is reached. In practice the effect of LiOH is likely to be a synergistic effect of Li⁺ concentration and pH. The observed effect of LiOH alone on the post transition corrosion rate was described by McDonald et al using a modified Arrhenius equation:

\[ \ln \frac{dw}{dt} = \frac{25.39 + 185.6 [\text{LiOH}] - 407.4 [\text{LiOH}]^2 - 32660 + 110540 [\text{LiOH}]}{RT} \]

which predicts an enhancement by more than an order of magnitude for 0.03 molal LiOH. However, if it is postulated that the effect of pH can be allowed for by replacing [LiOH] in this equation by [Li⁺][OH⁻]², then with the simultaneous presence of 8000 ppm boron as boric acid an enhancement of 50% is calculated. This is more than the degree of enhancement currently being observed (Fig. 5), but exposure has not yet
been long enough to reach the true post-transition region. It should be
emphasised that this form of dependence on [Li+] and [OH–] is specula
tive only, although probably closer to the truth than assuming dependence just
on [Li+]. A number of assumptions concerning the equilibrium constants of
the various boric acid-borate reactions (Section 1) and the extent of
volatilisation of boric acid were necessary to select a representative
hideout environment and to calculate the resultant pH.

Although only a small effect of the simulated hideout environment has
so far been detected for specimens exposed to this environment through-
out, a significant increase in corrosion rate was observed for samples
transferred from a standard coolant environment. Further work is required
to determine the reasons for this behaviour and the long term corrosion
rate of these specimens. Nevertheless this may have some relevance to the
effect of a hideout environment developing on cladding which has become
oxidised during exposure to standard coolant.

The measurements of lithium uptake in the oxide film reported here
are preliminary, since they refer only to specimens which have seen short
periods of exposure: in the case of the simulated hideout environment only
56 days. This latter specimen had a lithium uptake over twice that of the
specimen exposed to standard coolant for 168 days. McDonald et
al.1 report a correlation between corrosion rate and lithium uptake, so
further work is planned to assess the significance of lithium
incorporation in the oxide scale in the present system.

5. CONCLUSIONS

1. Corrosion tests on Zircaloy-4 fuel cladding in standard PWR coolant
indicate no enhancement over tests in pure water for exposures up to
350 days at 350°C.

2. Pretransition corrosion rates in a high lithium/boron environment
simulating hideout are similar to those in standard coolant, but there is
a small amount of subsequent acceleration of corrosion compared to
standard coolant.

3. Accelerated corrosion is observed when specimens are transferred from
standard coolant to simulated hideout conditions.

4. The observed acceleration of corrosion rates in lithiumated/borated
conditions is much lower than that reported in the same lithium
concentration in the absence of boron.

5. There is some lithium but no boron incorporation in the scale in both
environments, the concentration being over twice as great in the high
lithia environment.

6. Specimens preoxidised in steam to three times the 300 day weight gain
in 350°C water show slightly higher corrosion rates than virgin specimens
in standard PWR coolant.

7. While there is evidence for only slightly enhanced corrosion in
conditions simulating lithium hideout, this is not unexpected since
corrosion is still in a 'transitory' region and has not reached steady
state.

6. ACKNOWLEDGEMENTS

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data reduction, Dr B Riley for performing Auger Spectroscopy and
Mr A Bell for X-ray diffraction analysis.

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EVOLUTION OF Zr-Nb BASE ALLOYS FOR LWR FUEL CLADS

V.M. GRIGORIEV, A.V. NIKULINA, M.M. PEREGUD
All-Union Scientific Research Institute for Inorganic Materials,
Moscow, Union of Soviet Socialist Republics

Abstract
The properties of Zr-1% Nb-0.13% O and Zr-1% Nb-1% Sn-0.5% Fe alloys as fuel clads have been investigated in comparison with the properties of Zr-1% Nb. The investigation included short-term mechanical and creep tests, definition of tendency to uniform corrosion, hydrogen pick-up and iodine corrosion cracking. Tests were carried out under out- and in-pile conditions.

Apart from the optimization of the structure, evolution of alloys based on Zr-Nb composition proceeds on two lines: increase of oxygen content to 0.13-0.16% mass., or additional alloying with tin (0.8-1.3% mass.) and iron (0.3-0.6% mass.).

The role of each element in the alloying of zirconium is rather well known [1,2]. The properties of Zr-1% Nb-0.13% O and Zr-1% Nb-1% Sn-0.5% Fe alloys as fuel clads have been investigated for some years in comparison with the properties of Zr-1% Nb. The analysis of the main results of these studies forms the basis of this paper.

For the sake of brevity the paper uses the following designations:

- A alloy - Zr-1% Nb;
- B alloy - Zr-1% Nb-0.13% O;
- C alloy - Zr-1% Nb-1% Sn-0.5% Fe.

Short-Term Mechanical Properties

Typical mechanical properties of fuel clads 9.15 dia. manufactured from A, B and C alloys are tabulated in Table 1 [1]. If at 20°C the strength of B and C alloys practically coincides, at 350-380°C the strengthening effect of oxygen on B alloy becomes weaker as compared to the effect of alloying on C alloy. In spite of the fact that at 350-380°C the yield strength of C alloy is by a factor of 1.5-2 higher than that of A and B alloys, the total percent elongation of C alloy remains at the level of 40-45%.

All the alloys in the form of annular specimens as irradiated by neutron fluxes of the density up to 9x10^{14} n/cm^2 s (E>0.1 MeV) to the fluence ~5x10^{21} n/cm^2 at 350-380°C showed a factor of 1.8-2.0 increase of the yield strength and a similar decrease of the total percent elongation. In spite of the fact that C alloy specimens have a factor of 2 higher yield strength as compared to that of A alloy, the uniform elongation is similar for both the alloys.

Creep

The results of out-of-pile tests of internally pressurized tubes show, that alloys with higher short-term mechanical properties have an improved creep resistance. After 1000 h test at a temperature of 400°C and stress of 100 MPa the following creep rates were derived as calculated from the rate of a change of a tubular specimen diameter:

- A alloy - 2.5x10^{-3}/h;
- B alloy - 5x10^{-4}/h;
- C alloy - 5x10^{-5}/h.
The creep resistance of all the alloys at 400°C increases through a rise of the temperature of anneal of the finished tubes up to 650°C.

In-pile tests for a long-term stability under external pressure at 400 and 420-450°C confirmed the higher creep resistance of B and C alloys [3].

The data on the creep of externally pressurized tubes indicate that the specimens as irradiated to a fluence of $10^{20}-10^{22}$ n/cm² ($E > 0.1$ Mev) at 350-400°C show the same averaged creep rate as in out-of-pile tests. In this case as a first approximation the following relation is noted for the creep rates of A, B and C alloys:

$$\dot{\varepsilon}_A : \dot{\varepsilon}_B : \dot{\varepsilon}_C \sim 10:3:1.$$ 

Uniform Corrosion

In the first stage of studying zirconium alloy corrosion a characteristic feature of A alloy was noted, viz, its susceptibility to oxygen [4,5]. Air present in a steam-water mixture at 350°C resulted in a factor of 3-4 acceleration of corrosion as compared to the corrosion rate in the same atmosphere without air (fig.1). The corrosion rate of A alloy accelerated not only with an increase of the oxygen content of the environment but also under neutron irradiation. Reactor core loop irradiation for 4000 h in a water flow at the rate 4-5 m/s at 290°C and pressure of 10 MPa increased the oxidation intensity by a factor of 5-6 as compared to the oxidation in the same loop without irradiation.
Since the corrosion behaviour of A and B alloys is practically the same, it is interesting to compare A and C alloys.

The simultaneous investigation of A and C alloys in different corrosive environments showed [5] that in out-of-pile tests at ~300°C in a steam-water mixture containing 10-36 mg/kg oxygen the A alloy gained in weight approximately by a factor of 2 more than in autoclave tests in water containing 0.3-0.6 mg/kg oxygen (fig.2). Under the same conditions C alloy proved to be unsusceptible to oxygen content and had similar weight gains in the both environments.

Under reactor conditions the influence of oxygen is much stronger. The weight gained by A alloy during tests in a loop outside the core was approximately by a factor of 3 more than in laboratory tests in the atmosphere containing the same amount of oxygen and reached 150 mg/dm² (fig.2). Under the above conditions C alloy was less susceptible to oxygen: its weight gains arose less than by a factor of 2 and did not exceed 50 mg/dm².
Under the conditions discussed (the coolant temperature of 280-300°C, pressure of 8 MPa, steam content up to 22%) the neutron irradiation at the flux density of $3 \times 10^{13}$ n/cm$^2$s insignificantly increased the weight gains of both the alloys.

In the other series of in-pile experiments the irradiation was carried out at 300°C in pressurized water of low oxygen content. The neutron irradiation did not practically influence the weight gains of A alloy (as compared to the experimental site of this reactor) and increased the weight gain of C alloy by a factor of 3.5 (fig. 3). Under the both conditions the weight gains of C alloy tested for 6230 hours were lower than those of A alloy.

The in-pile tests of A and C alloys under boiling conditions at 300°C showed that the weight gains of C alloy were a factor of 2-3 more than those of A alloy after both 17460 and 30000 hour tests; no indications of breakdown in the oxidation kinetics being observed for either alloy.

It was shown [6, 7] that niobium containing zirconium alloys have a higher resistance to nodular corrosion as compared to zircalloys. It is also reported [8] that the resistance of zircalloys grows significantly with the saturation of the matrix with elements such as ferrum and niobium. It is C alloy has this combination of alloying elements which must impart a higher nodular corrosion resistance to it. This conclusion is confirmed by the results of in-pile tests.

**Hydrogen Pickup**

The hydrogen pickups of niobium containing zirconium alloys during the process of corrosion are lower than for zircalloys [7-8, 9]. Comparison between niobium containing alloys shows that C alloy has a higher pickups compared with A alloy [9].

The influence of tensile stresses on hydrogen pickup and hydride orientation is similar for both the alloys. It is noted that at the stress level of up to 1.2 of the yield strength an increase of hydrogen pickup in corrosion tests does not exceed a factor of 1.5-2.5 as compared to unstressed specimens. The influence of tensile stresses grows with the temperature of testing. Mainly tangential orientation of hydrides was observed in the specimens of both the alloys at stresses about 0.2 of the yield strength.
The investigation of specimens in-pile tested for more than 30,000 h at 300°C did not show any difference in the extent of A and C alloy hydriding; the hydrogen content of all the specimens did not exceed 0.0156 mas.

**Iodine Corrosion Cracking**

The investigation of A, B and C alloy resistance to ISCC was carried out at 400°C in the neutron irradiation field of the density $4 \times 10^{13}$ and $3 \times 10^{12}$ n/cm$^2$.s ($E > 0.1$ MeV) [10], using internally pressurised tubular specimens.

The data on A alloy are given in fig.4. Iodine vapours present at the concentration of 13 mg/cm$^2$ in the irradiation test of the alloy reduce its time to failure approximately by an order of magnitude at the stress of 130 MPa (curves 1 and 3 in fig.4). With the iodine concentration decreased by a factor of 10 the time to failure significantly increases (curves 1 and 2).

A, B and C alloy specimens tested at 400°C in the atmosphere containing iodine at the concentration of 13 mg/cm$^2$ showed under irradiation essentially different time to failure under the same conditions of loading (fig.5). At the stresses of 155-160 MPa A, B and C alloys withstood without failure during 470 and 800 h, respectively.

Fig.6 illustrates the results of processing the data of work [10]. It can be seen that at similar relative stresses the time to failure for all the three alloys lies in the same region. This evidences to the fact that for the alloys discussed the differences in the time-to-failure are chiefly related to different yield
strengths, but not to a difference in the character of the inci­
pience and growth of corrosion cracks. The stresses at which the
alloys did not rupture in the presence of iodine for 1000 h and
more are equal for each alloy to a value close to 0.75 of the yield
strength (fig.6).

The character of the dependence in fig.6 is quite similar to
the regularity noted in [11] for A alloy under out-of-pile condi­
tions at slightly higher stresses but at a lower concentration of
iodine vapours (fig.7).

Along with Zr-1\% Nb (A alloy) that proved to be beneficial,
Zr-1\% Nb-0.13\% O₂ (B alloy) and Zr-1\% Nb-1\% Sn-0.5\% Fe (C alloy)
are under study.

Additional alloying of A alloy leads to an improvement of
short-term strength properties of B and C alloys and insignificant
decrease of their ductility. Compared to A alloy, specimens
of C alloy as irradiated to a fluence of 5x10²¹ n/cm² (E > 0.1 MeV)
at 350-380°C have a factor of 2 higher yield strength and the same
uniform elongation.

Additional alloying had a larger effect on the creep resistance
of B and C alloys. At temperatures of 350-400°C the rates of out-of
and in-pile creep of each alloy practically coincide. In this case

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**Fig. 6.** Dependence of time to failure on the amount of relative
stresses (σ/σ₀₂₀) in A (○), B (•) and C (×) al­loy specimens in a neutron flux at 400°C and iodine
vapour concentration of 13 mg/cm² (data of [10]).

**Fig. 7.** Interrelation between time to failure under out-of-pile
conditions and hoop stresses in A alloy specimens
internally pressurised at 380°C and iodine vapour con­
centration of 0.2 mg/cm² (data of [11]).

**Conclusion**

Along with Zr-1\% Nb (A alloy) that proved to be beneficial,
Zr-1\% Nb-0.13\% O₂ (B alloy) and Zr-1\% Nb-1\% Sn-0.5\% Fe (C alloy)
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Additional alloying had a larger effect on the creep resistance
of B and C alloys. At temperatures of 350-400°C the rates of out-of
and in-pile creep of each alloy practically coincide. In this case
the following relationship is observed for the creep rates of A, B and C alloys as a first approximation:

\[ \dot{\varepsilon}_A : \dot{\varepsilon}_B : \dot{\varepsilon}_C \approx 10 : 3 : 1. \]

Compared to A alloy, the rate of uniform corrosion of C alloy is less dependent on the oxygen content of the environment both under in- and out-of-pile conditions. The results show that A and C alloys will insignificantly differ by their corrosion rates and absolute values of weight gains both in pressurized and boiling water at temperatures \( \leq 350^\circ C \).

Based on the lower susceptibility of C alloy to oxygen dissolved in a coolant and the favourable combination of alloying elements one can expect C alloy to have the improved resistance to nodular corrosion among other niobium containing alloys.

A correlation is noted between the resistance to hydrogen stress corrosion cracking and the yield strength of the alloys.

References

ADVANCED EXPERIMENTAL TECHNIQUES FOR POST-IRRADIATION EXAMINATION OF LWR FUEL RODS

H. SCHÖNFELD, R. MANZEL, R. WÜRTZ
Kraftwerk Union AG,
Erlangen, Federal Republic of Germany

Abstract

Today post-irradiation examinations are performed to extend the data base to higher target burnups, to determine performance limitations and to characterize new fuel types (e.g. U/Pu-oxide, U/Gd-fuel).

After a survey of the post-irradiation examination techniques applied by KWU in the spent fuel pool and the Hot Cells a description will be given of some new Hot Cell techniques for a more in depth characterization of the fuel: fuel density measurement, micro-coring, micro-gammascanning, open porosity determination, SEM-examination.

1. INTRODUCTION

Post-irradiation examinations of PWR- and BWR-fuel rods are part of an integrated quality assurance system at KWU. In the early days of Light Water Power Reactors, post-irradiation examinations were concentrated on defective fuel rods in order to find the cause of defects. Meanwhile, a high degree of reliability has been achieved in the performance of LWR-fuel rods with extremely low defect rates. Therefore, today post-irradiation examinations are geared to extend the data base to higher target burnups, to determine performance limitations and to characterize new fuel types such as U/Pu-mixed oxide and U/Gd-fuel. The results provide the basis for further developments in fuel element design and technology.
At present, economic considerations as well as the task of improved uranium utilization provide strong incentives for an increase in discharge burnup of LWR-fuel assemblies. Efforts have therefore been concentrated on extending the average discharge burn-up from presently 33 GWd/tU to 50 GWd/tU for PWR- and from 28 GWd/tU to 40 GWd/tU for BWR-fuel assemblies and to further reduce parasitic neutron absorption.

This has led to the development of high burnup fuel with a pore structure specially tailored to reduce densification early in life but provide sufficient porosity late in life to compensate fuel swelling. The fuel structure is also optimized with regard to low fission gas release and good PCI-behaviour.

Post-irradiation examination techniques have been developed to allow the in depth characterization of the fuel.

2. POST-IRRADIATION EXAMINATION TECHNIQUES

Table I gives a survey of post-irradiation techniques applied by KWU in the spent fuel pool. Pool examinations provide the basis for selection of fuel rods for more detailed post-irradiation examinations in the Hot Cells. The post-irradiation examination techniques available in the Hot Cells are summarized in Table II.

The following description concentrates on new techniques that are being applied for a detailed characterization of the fuel.

| TABLE I: Pool Post-irradiation Examination Techniques in Use at KWU |
| VISUAL INSPECTION with TV-unit, video recorder and polaroid camera |
| LVDT (LINEAR VARIABLE DISPLACEMENT TRANSDUCER) MEASUREMENT for dimension control, e.g. rod diameter |
| EDDY CURRENT TESTING for detection of cladding defects and determination of the oxid layer thickness on cladding surface |
| GAMMASCANNING for determination of the burnup distribution in fuel element |
| MECHANICAL MEASUREMENT of rod length |
| CRUD COLLECTION for crud analyses |
| FORCE MEASUREMENT at the withdrawal of fuel rods for determination the relaxation of spacer springs |
| DISTANCE MEASUREMENT for determination of rod-rod spacing |
TABLE II: Hot Cell Post-irradiation Examination Techniques in Use at KWU

VISUAL INSPECTION
with stereo periscope and standard scale for visual examination and length measurement

EDDY CURRENT TEST
for detection of inside and outside defects at the cladding and determination of the oxid layer thickness

AXIAL GAMMASCANNING
for determination of the burnup distribution, the fuel stack length and fuel relocation

LVDT MEASUREMENT
for rod diameter determination

CLADDING OVALISATION
for determination of the pellet/cladding gap

METALLO-/CERAMOGRAPHY
with optical and scanning electron microscope for structure and surface examinations

X-RAY-SPECTROMETRIC ANALYSIS
on SEM for analyses of chemical elements

AUTORADIOGRAPHY (ALPHA AND BETA/GAMMA)
for determination of the distribution of radioactive material on sections

MICRO-GAMMASCANNING
for determination of fission product distribution in fuel rod cross sections

MICRO-CORING
for examination of axial and radial distribution of fission products especially the fission gas and the U/Pu-isotopes

DENSITY MEASUREMENT
for examination of density changes

POROSITY MEASUREMENT
for determination of the open porosity

3. HOT CELL EXAMINATION TECHNIQUES FOR FUEL CHARACTERISATION

Apart from standard ceramographic examinations, the following techniques are applied for a more in depth fuel characterization:

- fuel density measurement
- measurement of open porosity
- micro-gammascanning
- micro-coring
- SEM-examination.

It should be mentioned that on-line computers are increasingly used in the field of post-irradiation examinations for the operation of the equipment and data acquisition and evaluation.
3.1 Density Measurements

Density measurements on irradiated fuel pellets provide the basis for an evaluation of the densification characteristics and the matrix swelling rate. During the first period of irradiation densification is the dominant process, resulting in an increase in fuel density. Then the continuous generation of fission products leads to a decrease in density. This decrease in density is attributed to fuel swelling.

The bulk-density of the fuel is determined on individual pellets using a mercury pycnometer. Fuel pellets are usually cracked because of thermal gradients during irradiation. For density measurements all larger fragments (8 - 16) of one pellet representing about 75% of the total pellet volume are used. The fragments are weighted with an accuracy of 1 mg. The weight of the pycnometer is determined, first completely filled with mercury and second filled with mercury and the pellet fragments. Because of its high surface tension, the mercury does not penetrate into the open pores of the fuel fragments at standard pressure. Hence, the mercury displaced by the pellet fragments is a direct measure of the fragment volume. From the weight of the fragments and the volume, the density can be calculated. Determining the working temperature to an accuracy of 0.1 °C and the mercury density to 0.0001 g/cm³ results in an accuracy of the fuel density value of ± 0.01 g/cm³.

Density values determined by this technique are plotted as a function of burnup in fig. 1. As can be seen from this figure, there is a clear difference between the swelling characteristic of standard fuel operated below centre temperatures of 1300 °C without gaseous swelling and experimental high power fuel.

FIG. 1: Density of Irradiated Pellets as Function of Burnup /3/
operated at about 1650 °C with a significant amount of gaseous swelling.

3.2 Micro-Coring

In order to quantitatively determine the radial distribution of fission products, e.g. Cs-137, the radial distribution of U- and Pu-isotopes as well as retained fission gases within a pellet microsamples are analysed.

Microsamples are preferably taken from ceramographic cross sections at various radial positions. Sampling is performed using a hollow drill ultrasonically excited in longitudinal direction. The cross section is precisely positioned using a x-y-table and then electrodynamically pressed against the drill. Drilling operation is performed in a diamond/methanol suspension continuously circulating through the hollow drill and the bore hole. The diameter of the cores resulting from the drilling operation can vary between 0.8 to 1.3 mm depending on the size of the hollow drill. The cores have a length of about 10 mm and their weight does usually range from 10 to 50 mg.

Fig. 2 shows a ceramographic cross section of a fuel rod with three bore holes resulting from micro-coring.

The micro-cores are weighted, dissolved under vacuum in airless nitric acid and the gas phase analysed using a mass spectrometer. Other fission products such as Cs-134, Cs-137, Ru-106 and Ce-144 are determined by gamma-spectrometry. The uranium content of each micro-core is either determined by spectral photometry or using a mass spectrometer.

The radial distribution of Xenon and Cs-137 as determined from an analyses of micro-cores is shown in fig. 3.

FIG. 2: Fuel Pellet Micro Section after Drilling Micro Samples

FIG. 3: Radial Distribution of Xe and Cs-137 in a Ramped Fuel Pellet /4/
3.3 Micro-Gammascanning

In addition to the quantitative data on fission gas and solid fission product concentrations received from micro-sample analyses, the radial distribution of radioactive isotopes is determined by micro-gamma-scanning of fuel pellet cross sections. The high local resolution of this method gives valuable information on migration and release of volatile fission products.

Normally ceramographic samples are used for these measurements allowing a comparison with the structural data received from the ceramography.

The experimental equipment for micro-gammascanning primarily consists of a collimator with a square aperture of 0.5 x 0.5 mm and of a stepping motor driven cross slide to allow two dimensional motions by 0.5 mm steps. Radiation is recorded by an intrinsic germanium solid state detector in order to cover the gamma- and x-ray-radiation region. Stepping motors, multichannel analyzer systems and data handling are computer controlled so that automatic longterm measurements can be performed. Measuring times of several hours or days are used depending on the irradiation conditions of the samples and the isotopes to be investigated.

Examples of Cs-137 and Cs-134 micro-gammascans of fuel samples with different burnup and linear heat rating are given in fig. 4.

3.4 Determination of Open Porosity

An important property with respect to fission gas release and swelling of the irradiated fuel is the porosity and especially the portion of open porosity within the fuel matrix.
While information of total porosity obtained from mercury immersion density measurements had been available since a long time for the determination of the open porosity and the pore size distribution a new device has been installed in the Hot Cells.

The principle of measurement is based on high pressure mercury penetrating into the fuel and thereby recording of the pressure and volume of the mercury entering the pores.

Pore size \((r)\) and pressure \((p)\) are related according to the expression

\[ r = \frac{2 \sigma \cos \theta}{p} \]

where \(\sigma\) is the surface tension of the mercury and \(\theta\) is the wetting angle of mercury and \(UO_2\). With \(\sigma = 480 \times 10^{-5} \text{ N/cm}^2\) and \(\theta = 141.3^\circ\) the expression given above results in

\[ r (\AA) = \frac{76,200}{p(\text{bar})} \]

The maximum pressure achievable with the porosimeter used (porosimeter 2000, Carlo Erba) limits the minimum pore size to be determined to 38 \(\AA\). A further limitation of the method consists in the assumption of cylindrical pores rather than the irregular shape of real pores.

The measurements are carried out in an autoclave equipped with a capillary tube and an inductive measuring system for detecting the amount of mercury intruding into the fuel sample. Fuel samples of 0.5 to 20 g are used.

The accuracy of the method is mainly influenced by volume and density changes of the mercury due to gas residues trapped. High accuracy is achieved at sample sizes above 10 g. The detection limit is about 0.2 \(\text{mm}^3/\text{g}\).

Irradiated fuel of LWR's examined by this method exhibited open porosities between 0.2 and 1.5 \(\text{mm}^3/\text{g}\) corresponding to 2 to 15 % of the total porosity.

Fig. 5 shows a computer record of an open porosity measurement.

A histogramme of the pore size distribution of a fuel sample is given in fig. 6.

### 3.5 SEM Examinations

Light microscopical examination of irradiated fuel in Hot Cells is limited to magnifications of about 500 : 1 and therefore the resolution is restricted to objects larger than 1 \(\mu\text{m}\).

Smaller objects within the fuel e. g. small pores, segregations of fission products only become visible at larger magnifications which can be achieved by SEM.

Even irradiated fuel can be examined at magnifications between 2,000 : 1 and 10,000 : 1.

Since it did not seem practical to completely install a SEM in a Hot Cell, the sample sizes of the highly radioactive material have to be reduced to a few milligrams or replicas of the sample surfaces have to be prepared.

Sample size reduction normally is carried out by cutting and grinding down ceramographic samples to 0.2 to 0.5 mm and taking fractions of this material.
The negative replicas of sample surfaces can easily be transformed to positive replicas without losing information.

In fig. 7 replica pictures of a fuel sample at magnifications of 2,000 : 1; 5,000 : 1 and 10,000 : 1 are shown, where small pores down to a size of 0.01 µm can be detected.

An intercrystalline fracture surface of a small fuel sample is shown in fig. 8, exhibiting few large open pores within the general fine porosity of the irradiated fuel.
FIG. 7: Replica Pictures of a Fuel Pellet Cross Section

FIG. 8: Intercrystalline Fracture surface from a Micro Sample of a Fuel Pellet
CERAMOGRAPHIC TECHNIQUES AND ELECTRON PROBE MICRO-ANALYSIS APPLIED TO URANIUM-PLUTONIUM OXIDES

M. LIPPENS
Belgonucléaire SA,
Brussels

C. VAN LOON, J. KETELS
Centre d'étude de l'énergie nucléaire (CEN/SCK),
Mol
Belgium

Abstract

Feasibility of plutonium recycling in LWR's is a reality in Europe. This result has been obtained by BELGONUCLEAIRE through constant progresses made in the field of uranium-plutonium mixed oxide (MOX) fuel fabrication, of neutronic calculations, and of fuel rod design. These efforts were supported by an extensive programme of demonstration in PWR's and BWR's, associated to post-irradiation examinations focused on neutronic, thermomechanical and microstructural behaviour of MOX fuels.

The present paper aims to described typical characteristics of the microstructural evolution under irradiation of the MOX fuel prepared by mechanical blending of the UO₂ and PuO₂ powders. The first part of the paper describes briefly the MOX microstructure before irradiation; the second part deals with basic conclusions of the demonstration programme and illustrates the post-irradiation MOX microstructure revealed by the ceramographic and microprobe techniques. Finally, further developments on the MOX fuel are summarized.

1. AS-FABRICATED MOX MICROSTRUCTURE

1.1. Fabrication route

One of the essential problems in the MOX fuel fabrication is to obtain a uranium-plutonium blend which is homogeneous in the plutonium repartition at the pellet scale. This goal is achieved today by various fabrication processes, going from a fine mechanical blending up to the co-precipitation of uranium and plutonium containing ingredients; the mixture has a plutonium content equal to the one imposed for the final pellet,
or forms a master-blend with about 30% plutonium, which is diluted in UO₂ in order to reach the final plutonium content. A micronization step of the uranium-plutonium blend prepared mechanically is introduced to meet the high plutonium solubility imposed by the fuel reprocessing.

BELGONUCLEAIRE MOX fuels in the years 1967-1984 were prepared by a fine mechanical blending of UO₂ and PuO₂ powders without micronization step; the early fabrications used a non free-flowing (ex-ADU) UO₂ powder imposing its granulation before blending. This fabrication step has been eliminated from 1974 by using free-flowing (ex-AUC) UO₂ powder (Fig. 1).

This fabrication method (named “reference” hereafter) was stopped in 1984 and replaced by the MIMAS process, introducing a micronization step of a master-blend; neither compaction, nor granulation was necessary due to the utilization of ex-AUC free-flowing powder (Fig. 1).

Plutonium is spatially distributed homogeneously at the pellet scale (Fig. 2), but is heterogeneous when looked at the micron scale; the alpha-autoradiography shows black spots corresponding to plutonium rich particles inserted in a UO₂ matrix of low plutonium content. Typical plutonium particle size, determined by alpha-autoradiography, ranges between 0 and 100 microns; the frequency distribution which is centred on the 15 micron class size, has a very reduced population above 50 microns and an average size around 30 microns.

These characteristics are representative of reference and MIMAS fuels. The plutonium content in the plutonium rich particles, determined by electronprobe micro-analysis (EPMA), varies on a wide scale, reaching locally 100% in the reference MOX fuel and limited to the master-blend plutonium content in the MIMAS process.

Plutonium diffusion in the UO₂ matrix, emphasised by etching, occurs without creation of macropores in the plutonium rich particles. The uranium-plutonium interdiffusion is more pronounced in the MIMAS fuel; one observes also for this fuel, UO₂ grain boundaries rich in plutonium, indicating an important plutonium diffusion by intergranular process.

Pore and grain characteristics of reference and MIMAS fuels are identical to those found for ex-AUC UO₂ fuel prepared in the same conditions. Pore number density increases with decreasing size, leading to a pore population mainly in the submicron range; pores above 50 microns are scarce. The volume distribution is monomodal, centred on the 5 micron class size, with a median pore diameter of 5 microns. The grain size, measured in the UO₂ matrix, is small with an average value of 5 microns.

2. MAIN POSTIRRADIATION EXAMINATION RESULTS

2.1. Conclusions of the MOX demonstration programme

The in-reactor behaviour of MOX fuel prepared following the three main fabrication routes (ex-ADU, reference and MIMAS) has been or is still being evaluated by performing irradiations with a broad range of operating conditions (linear power up to 600 W/cm, burnup above 90,000 MWd/tU and rod design (235 enrichment and plutonium content, pellet density and geometry, fuel clad-gap, initial pressurization, relative plenum volume, clad diameter and material).

Single MOX fuel rods were tested in the BR2 reactor at 1 W/cm in irradiation devices having different pressures (13 to 150 bars) and coolant temperatures (40 to 350°C), whereas
The demonstration programmes on the feasibility of plutonium recycling in LWRs and in the DDEHAARD, GARRIGLIO and OSHABMAH BNBr's. A total of more than 6,000 MOX fuel rods have been irradiated in the frame of the demonstration programmes as part of a normal reload, such as presently in BR3 with 48% of MOX rods and a maximum fissile plutonium content reaching 10%.

The first and essential conclusion of this demonstration programme is the integrity of MOX fuel rods, which have always been found as good as that of UO2 fuel rods; the second conclusion is the achievement of the power and burnup targets with a thermal-mechanical behaviour similar to the UO2 rods. This favourable situation for the MOX fuel demonstrates the technical feasibility of plutonium recycling in LWRs. As third conclusion of the programme, one has observed a higher fission gas release (FGR) and a lower pellet-clad mechanical interaction (PCMI) in MOX than in UO2 fuel. Consolidation of these experimental observations is given by fuel design code calculations, which evidence a too low FGR and excessive fuel swelling when MOX fuel is simulated by UO2 or by a MOX fuel with homogeneous plutonium distribution. The particular microstructure of the heterogeneous MOX fuel seems thus to play a significant role in the in-reactor evolution of some macroscopic properties.

2.2. MOX microstructure after irradiation.

2.2.1. Low temperature behaviour

(a) Stability

The as-fabricated microstructure remains extremely stable for irradiation temperatures corresponding to negligible FGR and unobservable grain growth in UO2 fuel. The heterogeneous plutonium distribution is maintained during irradiation (Fig. 3) and the majority of the beta/gamma emitting fission products remains in the plutonium rich particles. This heterogeneity has no observable effect at the macroscopic scale.

(b) Fission products

In the MOX fuel combining high plutonium content and natural uranium, most of the fissions occur in the plutonium rich particles; this heterogeneity in the fission rate decreases with pellet average burnup due to the progressive lowering of the initial local plutonium content and the build-up of fresh plutonium in the UO2 matrix.
The high burnup in the plutonium rich particles leads to high concentrations of fission products. Plutonium presence (white zones) revealed by stain-etched ceramicographic samples (Fig. 4.a) indicates that the gaseous fission products precipitate in bubbles, creating a new pore population concentrated in the plutonium rich particles. EPMA in the line-scan mode of uranium and plutonium elements confirms the low uranium-plutonium interdiffusion and the pore concentration in the plutonium rich particles. Scanning electron microscopy of irradiated heterogeneous MOX fuel indicates a spongy morphology of the plutonium rich particles.
Solid fission products appear to remain in the plutonium-rich particles, where they have been created; metallic fission products like Pd, Ru, ... precipitate in the plutonium-rich zones (Fig. 5a), whereas caesium remains in or close to the place where it has been generated. Presence of Cs-137 emphasized by beta counting and radiography (Fig. 1) demonstrates that caesium remains in majority in the plutonium-rich particles; another sign of the relative stability of solid fission products is the massive decohesion of the grains in the plutonium rich particles (Fig. 6a). However, a preferential attack of grain boundaries of the UO₂ matrix occurs in regions close to the plutonium rich particles, indicating a local transport of caesium.

**Fig. 5a - METALLIC PRECIPITATES IN Pu RICH PARTICLES AT LOW TEMPERATURE**

**Fig. 5b - METALLIC PRECIPITATES IN Pu RICH PARTICLES OPERATING AT MODERATE TEMPERATURE**
The microstructure of the fuel is not strongly modified during irradiation, except for an accumulation of bubbles in the plutonium rich particles; no new pore population has been created in the UO$_2$ matrix. The grain size in the plutonium rich particles is not easily determined owing to the abundance of bubbles and resistance to etching of plutonium rich material; however, grain structure can be determined when fission products accumulate at grain boundaries and moderate grain decohesion occurs; the grain size observed in these conditions is not higher than in the surrounding UO$_2$ matrix.

The grain size in the UO$_2$ matrix generally remains unchanged. However, some observations showed local UO$_2$ grain growth in the close vicinity of high plutonium content particles.

2.2.2. Influence of operating conditions

(a) Moderate temperature

For moderate temperature but not sufficient for grain growth, an evolution of the plutonium rich particles is already observed; plutonium rich particles at pellet centre show the disappearance of the small pore population, in favour of one macropore around 20 micron size centred on the plutonium rich zone (Fig. 4.b). An identical behaviour is sometimes noted for the metallic fission products, which, instead of being finely dispersed in the plutonium rich particles, form one large precipitate occupying part of the macropore (Fig. 5.b).

The average plutonium particle size is not modified at the pellet outer rim, but one observes by EPMA the disappearance of most of the particles of less than 10 micron size, indicating uranium-plutonium interdiffusion due to the fission process.

(b) High temperature

When grain growth starts, important modifications occur in the plutonium rich particles. One notes simultaneously a decrease of the pore number density and pore size, as well as a spreading of the zones of high pore concentration (Fig. 7). The metallic fission products follow the same route; they are of small size and found in larger areas. The observations correspond to a decrease of the plutonium content in the plutonium rich particles, associated to an increase in size of the plutonium rich area. EPMA (Fig. 8) and alpha-autograph show this plutonium homogenization, which is already achieved when the grain size still reaches 15 microns.

(c) Burnup effects in MOX fuel

Burnup effects result from the buildup of fission products and fresh plutonium, involving changes in the MOX fuel chemical state. The first and macroscopically observable effect related to the burnup is the appearance in MOX fuel enriched in U235 of a transition zone of high concentration of intragranular porosity starting around pellet mid-radius and extending up to pellet centre in low rated fuel; in moderately rated fuel, this intragranular porosity disappears progressively with grain growth, starting by denuded zones (no pores) near grain boundaries.

A second effect related to the burnup is the presence, in MOX fuel utilizing natural uranium, of acicular phases in the UO$_2$ matrix outer edge, close to the plutonium rich particles; they look like UO$_2$ phase precipitating along preferential crystalline planes of the UO$_2$ grains.
Fig. 7 - DECREASE OF PORE CONCENTRATION IN Pu RICH PARTICLES WITH TEMPERATURE INCREASE

Fig. 8 - U AND Pu LINE SCAN AT MODERATE RATING
Fresh plutonium buildup occurs preferentially at pellet rim. The alpha-autoradiography does not show this buildup due to the presence of the heterogeneously distributed plutonium, but it is clearly seen by EPMA and stain-etching.

3. CONCLUSIONS AND FURTHER DEVELOPMENTS

The microstructural analysis of MOX fuel concludes on deep and spectacular local modifications due to the irradiation: high concentrations of gas bubbles are found in the plutonium rich particles, whereas negligible transport of solid fission products occurs towards UO₂ matrix. This last one does not seem to be strongly affected by the irradiation, in particular, no local overheating has been noted.

These microstructural events do not produce significant macroscopic effect, the MOX behaving like a UO₂ fuel excepted for a higher FGR and a lower PCH. The FGR increase in heterogeneous MOX fuel results of the concentration of gaseous fission products following preferential paths imposed by the plutonium distribution, negligible transport occurring through the UO₂ matrix; open porosity is increased by the pore interlinkage in and between the plutonium rich particles, as well as by microcracks propagating between the plutonium particles. Moreover, a significant diffusion by irradiation exists in the plutonium rich particles, leading to a faster propagation of the gaseous fission products.

It must be pointed out that the small penalty on FGR paid by the heterogeneously MOX fuel has no practical consequence on the general performance of pressurized fuel rods introduced in modern PWR's, but can lead to thermal instability in absence of initial rod pressurization. An alternative to the problem cannot easily been found; it requires the complete micronization of the MOX fuel batch before pelletizing and, in case of non free flowing powder, imposes a granulation step. The flat pores between the granules strongly reduce the fuel thermal conductivity which, in turn, increases the fission gas release.

The smaller fuel swelling in the heterogeneous MOX fuel has not been completely clarified. The high concentration of gaseous and solid fission products are due to the local burnup which must be counted in terms of X FIMA, rendering hazardous the extrapolation of swelling laws based on low burnup data; on the other hand, the local swelling of a plutonium rich particle is probably less than expected due to the compressive forces acting on it. Finally, the mechanical behaviour of a fuel is different when the porosity is distributed uniformly or in scattered zones with a strong concentration of pores.

The data accumulated so far on irradiated MOX fuel give an advantage to this fuel in case of power ramp, less PCI and a higher power failure threshold being expected. On the other hand, an enhancement of FGR is probable in transient power conditions. These power change effects are the object of the future PRIMO programme managed by BELGONUCLEAIRE, consisting in transient and ramp tests on MOX fuels of different design, fabrication route and base irradiation conditions. These tests are followed by detailed postirradiation examinations.

The microstructural investigations made up to now provide indications of the MOX fuel behaviour under irradiation, but are not sufficient to establish definitively the mechanisms of gas release and fuel swelling. More detailed and numerous investigations will be performed in the future, in order to characterize the microstructure, the fission product distribution and the chemical state of the fuel, as well as to quantify on a large scale the characteristics resulting from the plutonium heterogeneous distribution such as pore, grain and plutonium rich particle size. Part of these objectives is fulfilled by two experimental devices newly installed in the CEN/SCK hot cells, the LEITZ texture analysis system for the quantification of the ceramographic samples, and the CAMEBAX-MICRO for detailed chemical inventory and its automatic data processing.
OUT OF PILE PHYSICAL PROPERTIES AND IN PILE THERMAL CONDUCTIVITY OF (U, Gd)O₂

A. CHOTARD, P. MELIN
Division Combustible,
Framatome,
Lyon

M. BRUET, B. FRANÇOIS
CEA, Institut de recherche technologique et de développement industriel,
Grenoble
France

Abstract

The following physical properties of (U, Gd)O₂:

- Lattice parameter
- Thermal expansion (from 300 K to 2000 K)
- Melting point
- Specific heat (from 300 K to 1000 K)
- Thermal conductivity (from 400 K to 1300 K)
- Thermal diffusivity (from 300 K to 2100 K)

have been studied out of pile for Gd₂O₃ contents up to 12 weight per cent. The study of the thermal conductivity has been completed with in pile measurements for Gd₂O₃ contents of 5 and 8 weight per cent.

Except for thermal conductivity and lattice parameter which depend on gadolinia content, the results obtained are close to UO₂ values. In particular, out of pile values for thermal expansion are equivalent to those obtained for pure UO₂ whatever the Gd₂O₃ content may be, in the studied range. Also in this range, the solidus and liquidus are very close and no significant difference has been found between UO₂ and (U, Gd)O₂ melting point. The specific heat has been found nearly identical to pure UO₂ values.

Measurements of thermal conductivity by radial heat flow and thermal diffusivity by the 'Flash Laser' method have allowed to confirm the decrease of these properties with gadolinia content, which has been further confirmed by in pile measurements. These results are discussed and compared to the published data.

INTRODUCTION

A significant improvement in PWR fuel utilisation (extended cycles, cycle flexibility ...) can be obtained by using Gd₂O₃-poisoned UO₂ fuel, with the gadolinium acting as a burnable poison. The need to qualify this fuel and evaluate the margins it provides from operating limits led to the implementation of a joint CEA-FRAGENA program centering on the following: fabrication processes, out of pile physical properties, thermomechanical behavior and fission product releases, gadolinium worth and optimization of gadolinium incore distribution.

This paper sets forth the results yielded by determination of non-irradiated fuel physical properties and thermal conductivity under irradiation conditions.
1 - FABRICATION AND CHARACTERIZATION OF ANALYZED PRODUCTS

The conditions of fabrication of gadolinium-bearing \( \text{UO}_2 \) pellets containing 0 (reference), 4-8 and 12 weight per cent of \( \text{Gd}_2\text{O}_3 \) are such as to meet the following requirements:

- density close to 95% TD
- good homogeneity of gadolinium distribution
- near-stoichiometric O/M ratio
- correct, homogeneous microstructure

1.1 FABRICATION CONDITIONS

The \( \text{UO}_2 \) powder is produced by the "Dry Route" conversion process.

Powder blending: the two processes used, i.e. wet co-ball milling and dry co-blending yielded products of comparable quality. The pore former for obtaining the required density is added at this stage.

Granulation: granulation is by isostatic compression followed by crushing and sieving, producing a granulate of size 6-1 mm. The granulate is lubricated with zinc stearate.

Pellet pressing: by uniaxial compression of the granulate.

Sintering: 4 hours at 1973 K in a humidified H\(_2\) atmosphere.

1.2 CHARACTERIZATION OF SAMPLES

The results of the chemical analyses (Gd concentration, impurity content, O/M ratio) are given in Table 1.

The final density is 94.5 ± 0.2% TD.

The resintering test (1993 K during 24 h in a controlled atmosphere) led to a densification of 0.6%.

Pellet ceramographic examination revealed a grain size distribution around 12 \( \mu \)m and a pore size distribution containing two peaks: one at 13 \( \mu \)m (pore former pores) and a smaller one around 1 \( \mu \)m (residual sintering pores).

Table 1

| Sample type: \( \text{UO}_2 \) + \( \text{UO}_2 \) + \( \text{Gd}_2\text{O}_3 \) | ANALYSIS RESULTS (ppm/U) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( \text{U}^\circ \) | Al | Si | Cr | Cu | Na | Mg | Ca | Fe | Ni | Si | SiO\(_2\) | \( \text{Gd}_2\text{O}_3 \) |
| 1 | 27 | < 0.3 | 3 | < 3 | 25 | < 3 | < 10 | < 10 | 30 | 2,0015 | 2,094 | 4,14 ± 0,06 |
| 2 | 15 | < 0.3 | 3 | < 3 | 25 | < 3 | < 10 | < 10 | 15 | 2,0313 | 84,39 | 0,04 ± 0,06 |
| 3 | 15 | < 0.3 | 3 | < 3 | 25 | < 3 | < 10 | < 10 | 15 | 2,0656 | 0,06 | 1,4 ± 1 |
| 4 | 15 | < 0.3 | 3 | < 3 | 25 | < 3 | < 10 | < 10 | 15 | 3,0000 | 77,06 | 12,03 ± 0,06 |
2 - PHYSICAL PROPERTIES OF NON-IRRADIATED (U,Gd)O_2

2.1 LATTICE PARAMETER AND THEORETICAL DENSITY

For all the analyzed Gd_2O_3 concentrations, the fluorite-type center-face cubic structure is observed. The variation in the lattice parameter with Gd_2O_3 content X is given by the formula:

\[ a = 0.5470 - 0.0251 X \]

Equally, density is given by:

\[ \rho = 0.1096 \times 10^5 - 0.20413 \times 10^4 X^1 + 0.15355 \times 10^6 X^2 \]

The results are in perfect agreement with the literature.

2.2 THERMAL EXPANSION COEFFICIENT

Over the temperature range (300 - 2000 K) and concentration range (0 - 12% Gd_2O_3) analyzed, the thermal expansion coefficient is the same as for pure UO_2.

2.3 SPECIFIC HEAT

The specific heat of pure UO_2 samples and samples containing 8 weight per cent by weight of Gd_2O_3 was measured between 300 K and 1000 K by differential microcalorimetry.

To take the measurements, the samples are sealed within stainless steel crucibles. A measurement of enthalpy variation during thermal cycles provides the specific heat value.

The test results are expressed for the temperature range considered, as follows:

\[ C_p (J/Kg^{-1} . K^{-1}) = 337.7 - 1.823 \times 10^2 T - 0.997 \times 10^7 T^{-2} \]

The scatter of data points about this equation does not exceed 2.5%.

Over the 500 - 1000 K range there is no significant difference between UO_2 and 8 weight per cent of Gd_2O_3 and no deviation from the results published in the literature (1), (2).

2.4 SOLIDIFICATION TEMPERATURE

The solidification temperature was measured for pure UO_2 samples and samples of 4-8 and 12 weight per cent of Gd_2O_3 by weight per cent Gd_2O_3.

The cylindrical samples (\( \Theta = 8 \, mm \); \( L = 5 \, mm \)) placed inside a quartz vessel containing a mixture of argon combined with 5% by volume of hydrogen at 0.3 MPa (for maintaining stoichiometry) are arranged at the center of focus of an arc image furnace.

A twin modulator conceals the heating beam during pyrometer scanning at a frequency of 10 Hz; observation is provided of the solidification plateau during sample loss of energy by radiation.
The pyrometer is calibrated by observing $\text{Al}_2\text{O}_3$, $\text{Er}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$ and $\text{Gd}_2\text{O}_3$ under the same solidification conditions. Finally, the solidification temperatures yielded at ± 30 K are as follows:

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>T SOLIDIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}_2\text{O}_3$</td>
<td>3125 K</td>
</tr>
<tr>
<td>$\text{U}_2\text{O}_3/4%\text{Gd}_2\text{O}_3$</td>
<td>3137 K</td>
</tr>
<tr>
<td>$\text{U}_2\text{O}_3/6%\text{Gd}_2\text{O}_3$</td>
<td>3131 K</td>
</tr>
<tr>
<td>$\text{U}_2\text{O}_3/12%\text{Gd}_2\text{O}_3$</td>
<td>3127 K</td>
</tr>
</tbody>
</table>

During these measurements, the phase diagram is entered by the liquidus. However, the cooling experimental curves exhibit no perceptible dip indicating crossing of the solidus. It can therefore be assumed that the solidification temperature and melting point are very close over the analyzed concentration range, which is in agreement with the observations of GROSSMAN (3) and that combining up to 12 weight per cent of Gd$_2$O$_3$ has no detectable impact on UO$_2$ solidification/melting temperature.

2.5 THERMAL CONDUCTIVITY

Two methods were used:

- another method involving direct measurement of thermal conductivity by steady-state radial heat flow between 400 and 1300 K at 0 and 8 weight per cent of Gd$_2$O$_3$.

2.5.1. Thermal diffusivity measurements

The measurements were taken by the "Flash Laser" pulse method. The response of the samples to heat pulses was detected by thermocouple up to 970 K and by infrared photodetector at higher temperatures. The signals were processed by the DEGIOVANNI method (4).

Thermal conductivity $\lambda$ was then deduced from diffusivity $a$ by the equation:

$$\lambda = a \rho C_p$$

where:

$\rho =$ density and $C_p =$ specific heat of the solid.

The experimental results are used to express the thermal diffusion values in polynomial form for $300 K < T < 2200 K$. The corresponding calculated thermal conductivity values are shown graphically in Figure 1.

2.5.2. Measurements by steady-state radial heat flow for 8 weight per cent of Gd$_2$O$_3$

The test device is shown in Figure 2. The temperatures detected on radii $R_{11}$, $R_{12}$, $R_{21}$ and $R_{22}$ by four Cr-Al thermocouples as a function of the power generated by the central tungsten rod
**Table 2**

<table>
<thead>
<tr>
<th>TEMP. (°C)</th>
<th>Gd₂O₃ Wt%</th>
<th>TEMP. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>.88</td>
<td>473</td>
</tr>
<tr>
<td>400</td>
<td>.91</td>
<td>673</td>
</tr>
<tr>
<td>600</td>
<td>.93</td>
<td>873</td>
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<tr>
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<tr>
<td>1000</td>
<td>.96</td>
<td>1273</td>
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<tr>
<td>1200</td>
<td>.98</td>
<td>1473</td>
</tr>
<tr>
<td>1400</td>
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<tr>
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</tr>
<tr>
<td>1800</td>
<td>.99</td>
<td>2073</td>
</tr>
<tr>
<td>0/M</td>
<td>2.001</td>
<td>1.991</td>
</tr>
</tbody>
</table>

(UGd)₀₂/U₀₂ thermal conductivity ratio, as a function of temperature.

**Fig. 1.**

Thermal conductivity of U₀₂ and (UGd)₀₂ versus temperature.

**Fig. 2.**

Radial conduction measurement.
and of the temperature at the cell boundary allow
determination of the oxide thermal conductivity
integral over a given temperature range.

$U\text{O}_2$ thermal conductivity can be broadly
represented by:

$K(T) = (A + BT)^{-1} + CT^2$

Over the analyzed temperature range, gadolinium
oxide conductivity is well represented by the
formula:

$K(T) = (0.220 + 1.49 \times 10^{-4}T)^{-1}$

This result is in quite good agreement with the
diffusivity measurements, as Figure 1 shows.

Table II shows the variation in gadolinium oxide
thermal conductivity in relation to $U\text{O}_2$ versus
$Gd_2O_3$ content and versus temperature.

As Figure 3 demonstrates, the observed decrease in
$K$ is smaller than that given by FUKUSHIMA (5).

3 - THERMAL CONDUCTIVITY UNDER IRRADIATION CONDITIONS

The GdGRIF I and II experiments run at Grenoble in
the SILOE reactor and detailed in (6), (7)
determined gadolinium oxide thermal conductivity
under irradiation conditions at 5 and 8 weight per
cent of $Gd_2O_3$.

3.1. BRIEF DESCRIPTION OF THE EXPERIMENTS (Fig. 4)

Each experiment involves two superimposed rods:
the top rod contains the $(U,Gd)O_2$ pellet stack;

![FIG. 3. Thermal conductivity of $U\text{O}_2$ and $(U,Gd)O_2$ versus temperature](image)

![FIG. 4. GdGRIF experiments](image)
It is instrumented by a 5/26 % W/Re central thermocouple and a helium purging line for collecting and measuring stable and radioactive fission gas releases as well as variations in pressure drop across the fuel stack.

The bottom rod consists of a UO₂ reference stack and is only instrumented by a W/Re central thermocouple. The rod fill gas is 1 MWh helium. The two instrumented rods are placed inside the "GRIFFON" pressurized water loop operating in coaxial thermosiphon at 13 MWh.

3.2 CHARACTERISTICS OF ANALYZED (U, Gd)O₂ OXIDES AND OF REFERENCE UO₂

The 5 weight per cent of Gd₂O₃ (U, Gd) O₂ pellets used in the GDGRIF I experiment and the 8 weight per cent of Gd₂O₃ pellets used in the GDGRIF II experiment had a density of 95 % TD and a respective enrichment of 1.5 and 1.8 % U 235; they were fabricated by the same process as the pellets used in the out of pile physical measurements and therefore have the same grain size, pore size distribution, thermal stability characteristics.

The same applies to the UO₂ pellets constituting the reference stacks which were also enriched at 1.5 and 1.8 % respectively.

3.3. RUNNING OF EXPERIMENT AND PROCESSING OF RESULTS

Irradiation of the GDGRIF I device at a nominal incident neutron flux of 1 \(10^{14}\) n cm \(^{-2}\) s \(^{-1}\) lasted 3.3. SILOE cycles, the (U, Gd)O₂ reaching 1750 MWdU\(^{-1}\). The total fuel linear power increased from 9.5 to 24 kW m\(^{-1}\) during irradiation.

Irradiation of GDGRIF II at the same nominal flux lasted 7.5 SILOE cycles up to a burnup of 7400 MWdU\(^{-1}\). Gadolinium-bearing rod power increased from 9.1 to 33.5 kW m\(^{-1}\).

The thermal results were processed as follows:

- The temperature rise inside the gadolinium-poisoned fuel was determined at a given power level,
- The thermal conductivity integral in the fuel was calculated,
- Based on this integral and on the fuel surface temperature, the temperature rise that would exist in UO₂ fuel of equal porosity was calculated. The ratio \(\Delta T_{UO₂}/\Delta T_{(U,Gd)O₂}\) was used to compare the average thermal conductivities of the two fuels over the considered temperature range.

3.3.1 POWER DETERMINATION

The incident neutron flux is continuously monitored by 4 electron probes (collectrons) placed inside the loop cooling sleeve.

Based on the current they supply and the integrated flux since the beginning of irradiation, the fission power and its radial
distribution are continuously calculated inside the \((U,\text{Gd})_2\) and \(\text{U}_2\) rods by means of the 99 energy group code "APOLLO". Some code input parameters (energy spectrum calibration etc) were previously determined by irradiation of a neutron mock-up.

This fission power must be combined with the power generated by \(\text{Gd}_{155}\) and \(\text{Gd}_{157}\) captures whose radial distribution and variation are also determined by the "APOLLO" code and with the power introduced into the fuel by \(\gamma\) radiation from the reactor core. This \(\gamma\) power was determined in the chosen irradiation location by \(\gamma\) calorimetry. In addition, fission power and its radial distribution are subsequently checked by axial and transverse \(\gamma\) scanning (radial distribution) performed between cycles on the bench set up in the reactor cavity.

The consistency of these results leads us to conclude that rod generated power accuracy is about 5%.

### 3.3.2 Determination of Cladding External Temperature \((T_e)\)

The reduced-thickness flow path loop configuration chosen to harden the neutron spectrum for similarity with PWR conditions implies thermal/hydraulic conditions leading to rod subcooling over the entire attained power range. Hence the rod cladding external temperature was continuously determined as a function of:

- power generated,
- water temperatures at the entry and exit of the loop hot flow path,
- the hot flow path water velocity measured by correlation of the thermal noise from three thermocouples placed just above the rods.

The temperature values obtained were checked at the end of irradiation by slow loop depressurisation during operation: the cladding temperature varied with pressure at constant power as soon as the pressure dropped below water saturated steam pressure at the relevant cladding temperature.

### 3.3.3 Determination of Fuel Surface Temperature \((T_f)\)

Knowing zircaloy cladding thermal conductivity and power, heatup inside the cladding is easily calculated.

Heatup in the fuel/cladding gap is then calculated by means of the heat transfer coefficient model published in (8).

This gives

\[ T_s = T_{ec} + \Delta T_{cl} + \Delta T_{gap} \]

and finally

\[ \Delta T_{fuel} = T_c - T_s \]
3.3.4 CALCULATION OF OXIDE THERMAL CONDUCTIVITY INTEGRAL

We have seen that the "APOLLO" code computes for a given incident flux and fluence the neutron power radial distribution: \( q_n(r) \) and the capture radial distribution for isotopes \( \text{Gd}_{155} \) and \( \text{Gd}_{157} \): \( q_{\text{cap}}(r) \).

Also taking into account the power introduced into the fuel by the \( \gamma \) radiation from the reactor core (its distribution in the fuel is assumed to be practically homogeneous): \( q_{\gamma} \), the fuel thermal conductivity integral is calculated as follows:

\[
I = \int_{r_{\text{int}}}^{r_{\text{ext}}} \frac{q(r) dr}{r} = \int_{T_s}^{T_c} K(T) dT
\]

\[
q(r) = \gamma \int_{r_{\text{int}}}^{r} r[q_n(r) + q_{\text{cap}}(r) + q_{\gamma}(r)] dr
\]

with \( q(r) \) = heat flux through the \( r \) radius cylinder.

Knowing the thermal conductivity integral law for \( \text{UO}_2 \) of under irradiation (9), the temperature increase that would be exhibited in a \( \text{UO}_2 \) pellet under the same surface temperature and power distribution conditions as the \( (\text{U}, \text{Gd})_2 \) pellet is easily obtained by:

\[
I = \int_{T_s}^{T_c} K(T) dT
\]

The \( \Delta T \) \( \text{UO}_2/\Delta T (\text{U}, \text{Gd})_2 \) ratio is used to estimate the ratio of average thermal conductivities between \( T_s \) and \( T_c \) at average fuel temperature (\( \bar{\Delta T} \) \( (\text{U}, \text{Gd})_2/\Delta \text{UO}_2 \)) fuel.

The best fit curve for all the results is shown in Figure 5 where they are compared with the values recommended by FUKUSHINA (5). As regards 5 weight per cent of \( \text{Gd}_2\text{O}_3 \) oxide, the thermal conductivity measured under irradiation is (at low temperature 700 K) better than the FUKUSHINA prediction (ratio with \( \text{UO}_2 \): 0.74 for 0.66) but still slightly less than the out of reactor values (Figure 3). At high temperatures, the deviation from the FUKUSHINA values is greater (0.90 for 0.75 at 1100 K) and the values under irradiation are the same as those measured ex-reactor. As far as 8 weight per cent of \( \text{Gd}_2\text{O}_3 \) oxide is concerned, the measurements under irradiation conditions are in agreement with the FUKUSHINA predictions at low temperature but low in relation to the out of reactor values.

![Figure 5: In pile thermal conductivity versus temperature](image-url)
However, they are the same as the latter at high temperature \((\bar{\lambda} (U, Gd)O_2 / \bar{\lambda} UO_2}\) approaches 0.95 whereas the FUKUSHIMA values remain about 0.70.

These results lead to the conclusion that for gadolinium concentrations up to 8 weight per cent of Gd_2O_3, even if thermal conductivity is significantly less at low temperature while the oxide at BOL operates at very low power (which is not therefore a problem), it improves sharply when the fuel operates at normal power or at overpower. For example, at BOL of the GDPII II experiment the centerline temperature reached 1720 K for a power of 33.5 kW m\(^{-1}\) which is scarcely at variance with the centerline temperatures recorded under the same conditions for UO_2 in PWR reactors.

**CONCLUSIONS**

Over the entire concentration range under analysis, the physical properties of gadolinium-bearing fuel (specific heat, melting point) are not significantly different from those of pure UO_2.

After the disappearance of the gadolinium neutron absorption effect and for Gd_2O_3 content less or equal to 8 weight per cent, the thermal conductivity values measured in pile and out of pile are only slightly degraded in relation to those for pure UO_2.

**ACKNOWLEDGEMENTS**

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- Messieurs J.M. BONNEROT, M. GUERY, J. MICHEL and E. PORROT of CEA/IRDI/DMECN for their contribution to the measurement of out of pile and in pile specific heat and thermal conductivity and diffusivity.

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JAPANESE STUDY ON WATER REACTOR FUEL ELEMENT MATERIALS AND METHOD OF MEASUREMENT

Y. MISHIMA
Faculty of Engineering,
University of Tokyo,
Tokyo, Japan

Abstract

So many studies have been carried out in Japan on water reactor fuel element materials and the method of measuring their properties. Some topics will be highlighted in this report to give an idea of what they have been doing in Japan.

Studies on the properties of zircaloy, including the development work for modified alloy have been performed since later 1950s, both in fundamental work at universities and research organizations and development work for zircaloy tube commercial production in metal industry. Among them, the latest work on the creep characteristics of zircaloy tube is presented.

For other material used in fuel element than cladding tube, spacer-spring will be discussed as the second topic. Reduction of spring force was carried out in Japan PWR fuel spacer to reduce rod bow in early 1970s which could successfully eliminate the problem since 1977. Relaxation of spring force against burn-up has been discussed in the so-called reliability test program of both BWR and PWR on then standard fuel since 1975 which was reported at Stockholm symposium in September 1986. The data obtained will be presented.
As the study for the method of measurement, the author proposed a modified testing procedure for tensile and burst test for zircaloy tubing, at ASTM-B10 Committee in 1976, to emphasize the shape of mandrel in the tensile test which has a significant effect on elongation values.

Various measurement techniques in post irradiation examination of water reactor fuel have been developed in Japan, among which the shadow measurement of tube during ballooning to burst will be described.

Well before the first LWR was put into commercial operation in 1970, development work for domestic introduction of zirconium alloy cladding tube had been carried out by metal industry people. This can be traced back to 1957. Fundamental study of zirconium alloys in my university laboratory started at least 5 years before 1957.

To accept zircaloy tubing for the re-load fuel of JPDR—small BWR which began to operate in JAERI to demonstrate electricity generation by LWR in 1963, various methods for testing cladding tube; metallography to measure grain size, hydride distribution, tensile and burst test, as well as corrosion test were specified by JAERI and the co-operative work including round robin was carried out among tube venders and JAERI plus research organization people, conducted by the author. Examination and testing methods Specialist Committee in Atomic Fuel Corporation (which later re-organized into PNC.) co-operated.

MITI standard from the point of view of regulatory work was also established this time for power reactor fuel element parts. The draft was prepared by a committee in Japan Electric Association (JEA), also chaired by the author.

As the information have been accumulated and newer knowledges on zircaloy behavior were introduced, NEN-AN-SEN—Fuel Safety Specialist Committee of Nuclear Safety Research Association (established in 1960 under chairmanship of the author)—carried out the necessary work in co-operation among the member organizations: JAERI, PNC, other government research organizations, universities, tube venders, reactor constructors and electric utilities.

After the LWR was put into commercial operation, various monitoring and verification test programs started to demonstrate LWR reliability by Nuclear Power Engineering Test Center (NUPEC) and later Japan Atomic Power Engineering & Inspection Corporation (JAPECIC). They are so-called Reliability tests.

Here in this report, the author would like to describe some items, in order to give an idea, what has been done in Japan in the field of material properties and methods of measurements for LWR fuel elements.

As there are so many works to be pointed out, only several among them will be highlighted here.

1. Properties of zircaloy tubing.

Our work on the testing procedure on zircaloy tubing was reported by the author in 1976 at ASTM-B10 Committee as a
special lecture,\(^1\) when the special emphasis was placed on
the shape of the mandrel in tube tensile test and the correct
location of O-ring at the tube burst test. If the dimensional
shrinkage is interfered by the mandrel inside in tensile test,
the lower elongation value will be obtained. In case of burst
test, longitudinal change of the tube should not be assisted
or interfered by the end fitting device, to observe correct
ballooning characteristics. Recommendations for the modifi-
cation of ASTM standard was made at that time.

NEN-AN-SEN carried out the work in 1975-82, on the creep
down behavior of non-irradiated and irradiated zircaloy tubing.
They are reported in detail in a NEN-AN-SEN Report\(^2\) and so,
only the outline will be described here.

Based on the various data obtained, the following experimental
formulas have been drawn for internal pressure creep
characteristics in Zircaloy-2 tubing for BWR and Zircaloy-4
tubing for PWR, respectively:

For BWR: 
\[
\varepsilon = 0.96 t \exp (0.29 \sigma) \exp \left(-\left(38 \sigma + 4760\right)/T\right)
\]
\[
\sigma = 0.0047 T + 0.01 e^{-2.79}
\]

\(\varepsilon\): creep strain (%)
\(t\): time (hr) \(t \leq 3000\)
\(\sigma\): stress (kg/mm\(^2\)) \(11 \leq \sigma \leq 20\)
\(T\): temperature (K) \(623 \leq T \leq 763\)

For PWR: 
\[
\varepsilon = K t^n
\]
\[
K = \exp \left(-11.5 + \left(-0.191 + 0.003822 T\right) \sigma + 0.00659 T\right)
\]
\[
\sigma = -0.539 + \left(-0.0144 + 0.0000727 T\right) \sigma + 0.00195 T
\]
\(\varepsilon\): creep strain (%)
\(t\): time (hr) \(t \leq 3000\)
\(\sigma\): stress (kg/mm\(^2\)) \(\sigma \leq 20\)
\(T\): temperature (K) \(603 \leq T \leq 693\)

And also, internal pressure creep test of Zircaloy-4 tubing for
PWR under neutron irradiation was carried out by NUPEC.

Besides this, Mitsubishi Atomic Power Industry (MAPI) carried
out an experimental work on creep in Zircaloy-4 PWR cladding tube.
This was reported already in the IAEA WG-FPT Specialists Meeting
in Tokyo in 1984.\(^3\) Fig. 1 shows the satisfactory consistency
between the experimental data and calculated value.

2. Relaxation of spring force in LWR fuel assembly spacer grids.

During the so-called Reliability Test Program, carried out
by NUPEC for both BWR and PWR fuel of 8X8\(^4\) and 15X15,\(^5\)
respectively, spring properties of Inconel springs for their
spacer grid were measured at the end of each reactor cycle.

Spring force was evaluated through withdrawal force of a rod
from the assembly. The results are shown in Fig. 2-4. Although
the Inconel itself is irradiation-hardened, spring constant was
almost kept constant as shown is Fig. 2 for BWR. The shape of
the respective spacer spring, however, was changed in the
**Fig. 1** Prediction by the Derived Equation

**Fig. 2** Burnup Dependence of Fuel Rod Expansion Spring (BWR)

**Fig. 3** Burnup Dependence of Fuel Rod Withdrawal Force (BWR)

**Fig. 4** Burnup Dependence of Fuel Rod Drag Force (PWR)
direction of reducing spring force, which would occur due to creep deformation accelerated by irradiation. The stress to cause creep came from the rejective force from the fuel rod against spring.

When the rod bow in PWR fuel was discussed in Japan in early 1970s, the author recommended to reduce the spring force of the PWR grid (so-called re-sizing) by inserting a rod with a little bit larger diameter than the fuel rod.

A criticism came out, where they insist that if the initial spring force is thus reduced, the force at the later life of the fuel becomes too low and so fretting should be worried about. The author did not think so. The reduction in the spring force will reduce the creep deformation of the spring due to the reduced rejective force from the fuel rod, which will retard creep rate. Therefore, at the end of life of the fuel, not so much difference is expected in the spring force of the spacer spring and so, there is no need to worry about fretting.

The relaxation of spring force actually measured on the spacer grid spring against burn up is plotted by the data obtained at the end of the respective reactor cycles as shown in Fig.3 for BWR and Fig.4 for PWR.

From these data, we are convinced now that the fretting is no more to be worried about even at the end of life of the fuel. No problem was found in the "re-sized" PWR grid spring in Japan. Moreover, after 1977, significant rod bow has been completely eliminated in Japan, as a result of the re-sizing.

3. Ballooning and Burst characteristics of Zircaloy tubing.

The first burst test of cladding tube of both zircaloy and austenitic stainless steel was carried out in Japan around 1960 by NEN-AN-SEN. The results were reported in 1964 in the 3rd International Conference for the Peaceful Uses of Atomic Energy in Geneva by the author. Since then, various experimental data on the ballooning and burst characteristics of zircaloy tubing have been obtained in Japan as a part of the experimental work on the tube behavior at LOCA.

Here, the author would like to mention only one of the results. Although the details of this study was already reported in 1981 at IWG-FPT Tokyo meeting, the newly developed test method to observe profile change of the tube by the shadow made by illumination device is mentioned here. This is developed by NFD people as a part of the PIE test for so-called Reliability Test of BWR 8X8 type, which the author reported in IWG-FPT Stockholm meeting in Sep. 1986.

Rough drawing of the test apparatus is shown in Fig.5 and the picture is shown in Fig.6. The pictures of the shadow during ballooning are shown in Fig.7 and 8 on both unirradiated and irradiated tubing, respectively. Although additional effort is needed to get more satisfactory results for irradiated tubing, that is after used in the reactor as the power reactor fuel rod, because it is more difficult to get good adjustment in the hot laboratory work. Illumination by Xray other than light may be useful in some cases, where so-called "Vinicon"
Fig. 5 Gas pressure burst test apparatus.

Fig. 6 High resolution ITV camera and optical system for burst test apparatus.

Fig. 7 Tube profile of unirradiated test specimen.

Fig. 8 Tube profile of irradiated test specimen.
TV camera developed in Japan, which can accept X-ray directly into TV system through beryllium window can be applicable.

4. Conclusion

Among so many research works, several are highlighted here to give an idea of what they have been doing in Japan.

References
INFLUENCE OF MATERIAL PROPERTIES ON FUEL ROD BEHAVIOUR
(Session III)
Chairman
P.K. De
India

THE EFFECT OF REFERENCE PARAMETERS AND PROPERTIES OF MATERIALS FOR WWER-TYPE FUEL ELEMENTS ON THEIR RELIABILITY

All-Union Scientific Research Institute for Inorganic Materials, Moscow, Union of Soviet Socialist Republics

Abstract

Present approach to requirements for reference parameters and properties of materials for WWER-1000 fuel elements is presented as well as evaluation of their effects on fuel reliability. Some results of investigations with the aim of improving fuel element reliability in operational NPP conditions are discussed.

1. Introduction

WWER-type reactors receive greatest attention in the programme of development of nuclear power in the USSR. WWER-440 reactors have been successfully operated for many years. Experience is being accumulated on the operational reliability of WWER-1000. At present time 7 units of 4 NPP are operated. In the nearest future a series of WWER-1000 units are planned to be brought into commission.

WWER-1000 is a Soviet version of a typical modern most common PWR. The first loads in WWER-1000 reactors were designed for a two year cycle at the maximum burnup up to 40 GWD/t. The accumu-
iated positive experience made it possible to start transition to a three cycle operation of fuels at a burnup of up to 60 GwD/t(max) and in future all the reactors of the WWER-1000 type will operate in a three year cycle. The technical characteristics of WWER cores of different generations are listed in table 1. It can be seen that an increase of a unit power is achieved through an increase of a linear heat generation rate (LHGR), a coolant rate and pressure and a fuel clad temperature.

One of the main directions of improvement of a PWR fuel cycle is a significant extension of burnup. The burnup of 60 GwD/t(max) will reduce the consumption of uranium, the load exerted on fuel production and reprocessing plants. The task is to produce fuels designed not only for an extended fuel cycle and high burnup but also for the obligatory retention of reliability at the modern level attained (the rate of failure ≤ 0.01%).

Therefore, the interrelation between the reference parameters of fuels and the fuel performance is one of the key problems of PWR fuel technology. For the current mass production and operation of fuels their reliability is a major criterion that reflects the level of technology and quality of fuel.

Experience shows that the potential abilities of zirconium alloy clad oxide fuels are far from being exhausted and the main trend is to improve the existent fuel assembly and element design and the fuel quality during manufacture as well as to optimize operation conditions with the aim of increasing reliability and practicability. The economic factor becomes the principal one in the selection of optimum solutions in the system: fuel design - manufacture - operation; the retention of the attained level of reliability being obligatory. Losses at one stage can be counterbalanced by a significant effect at others.

Of principal importance is the approach to the guarantee of a variable schedule of network loads on account of an increased fraction of NPP in the energy balance of the European part of the USSR. Here, two alternatives are possible: to operate a larger portion of NPP under follow-up conditions within the limited range of a power change or to assign with this purpose in view special NPP that permit load following with a high amplitude. When NPP operate under load follow the capacity factor is reduced to 0.5-0.6. Therefore, at the same burnup the time during which fuels remain in the core is increased approximately by a factor of 2, to 6-7 years. This circumstance requires additional invest-

<table>
<thead>
<tr>
<th>TABLE 1 DESIGN PARAMETERS FOR WWER REACTORS</th>
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<tbody>
<tr>
<td>PARAMETER</td>
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<tr>
<td>REACTOR HEAT RATING, MW</td>
</tr>
<tr>
<td>AVERAGE LINEAR HEATING OF FUELS, W/cm</td>
</tr>
<tr>
<td>MAXIMUM LINEAR HEATING OF FUELS, W/cm</td>
</tr>
<tr>
<td>COOLANT PRESSURE, kgf/cm²</td>
</tr>
<tr>
<td>COOLANT TEMPERATURE</td>
</tr>
<tr>
<td>INLET, °C</td>
</tr>
<tr>
<td>OUTLET, °C</td>
</tr>
<tr>
<td>COOLANT VELOCITY, m/sec</td>
</tr>
<tr>
<td>MAXIMUM TEMPERATURE OF CLAD SURFACE, °C</td>
</tr>
<tr>
<td>BURNUP OF DISCHARGED FUEL, GW.day/t</td>
</tr>
</tbody>
</table>
tigation of fuel performance under operational conditions of this type.

All the indicated modern trends in the usage of PWR fuel are closely related to the technical problems of optimisation of reference parameters and improvement of fuel rod material properties. It is in the interconnection between the reference parameters and fuel material properties, on the one hand, and the criteria of operational reliability, on the other, that the paper discusses some aspects of PWR fuel technology.

2. Requirements for Reference Parameters and Properties of Materials WWER-1000 fuel elements

Requirements for fuel design and performance are specified on the basis of a detail analysis of operation and processes defining fuel serviceability. Determination of nominal values of reference parameters takes into account ultimate operation conditions. The major physico-mechanical and chemical properties determine the most critical parameters of fuels that basically determine their performance. The most important reference characteristics of WWER-1000 fuel are tabulated in table 2. According to the operation conditions the reference parameters can be divided into three groups.

The 1st group comprises the most important parameters. Failure to fulfil the requirements for those parameters may be the cause of a premature failure of fuels. The 1st group includes:

- hydrogen, moisture, fluorine, carbon, nitrogen content of fuel pellets
- fuel stoichiometry
- fuel density
- pellet diameter and clad geometry
- finished fuel defects
- fuel element leak-tightness
- quality of weldments
- process gases in fuel
- hydride insertion in clads
- fuel microstructure
- helium pressure
- fluorine contamination of clad inner surface
- continuity of a fuel column.

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>WWER-440</th>
<th>WWER-1000 2 YEARS</th>
<th>WWER-1000 3 YEARS</th>
</tr>
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<tbody>
<tr>
<td>CLAD OUTER DIAMETER, mm</td>
<td>9.1</td>
<td>9.1</td>
<td>8.1</td>
</tr>
<tr>
<td>MINIMUM CLAD THICKNESS, mm</td>
<td>0.60</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>FUEL ROD LENGTH, mm</td>
<td>2570</td>
<td>3840</td>
<td>3840</td>
</tr>
<tr>
<td>FUEL COLUMN LENGTH, mm</td>
<td>2420</td>
<td>3530</td>
<td>3530</td>
</tr>
<tr>
<td>MINIMUM FUEL DENSITY, g/cm³</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>MOISTURE CONTENT, % mass</td>
<td>0.0007</td>
<td>0.0007</td>
<td></td>
</tr>
<tr>
<td>CENTRAL HOLE DIAMETER, mm</td>
<td>1.2</td>
<td>1.4</td>
<td>2.2</td>
</tr>
<tr>
<td>HELIUM PRESSURE UNDERNEATH  CLAD, kgf/cm²</td>
<td>1</td>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>GAS PLENUM VOLUME, cm³</td>
<td>4</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>FUEL-CLAD DIAMETRAL GAP, mm</td>
<td>0.12-0.27</td>
<td>0.19-0.32</td>
<td>0.15-0.27</td>
</tr>
<tr>
<td>HEIGHT/DIAMETER RATIO OF PELLET</td>
<td>1.2-1.5</td>
<td></td>
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</table>
Practically all the main physical and chemical properties of fuel and clad are reflected in those parameters, viz., thermodynamic properties, heat conductivity, thermal expansion, density, structure, chemical reactivity.

The II\textsuperscript{nd} group covers the parameters the deviation from which can result in the deterioration of technico-economic parameters of NPP. The deviations of the parameters can be as a rule estimated with design studies.

The II\textsuperscript{nd} group includes
- properties and structure of a clad material, including the anisotropy of properties and corrosion resistance
- reworking of fuel
- clad ovality
- fuel enrichment
- total boron equivalent
- pellet height
- external view of pellet
- fuel mass per a rod
- fluorine contamination of the outer surface of fuels.

The III\textsuperscript{rd} group includes mainly the rest of the parameters that are either ensured by the technology or the statistical methods of control.

The interrelation between certain parameters and properties on the one hand and fuel performance on the other is described below.

2.1. Fuel Column Characteristics

Depending on the fuel design the following requirements are placed upon a fuel column:
- length within specified limits
- weigh with a specified allowance
- amount of chips in a free volume not higher than specified
- continuity of a fuel column with a permissible unit gap.

The allowance for a fuel column length is substantiated based on the core physics and technological abilities of fuel loading. The accepted allowances are a trade-off between process abilities and physical design of a core.

For the design of a fuel rod the initial fuel-clad gap is taken sufficient to compensate for thermal expansions. At a certain moment the fuel can start to fill the gap and exert a perimeter uniform pressure on a clad. However, if U\textsubscript{2}O\textsubscript{3} particles as process or pellet chips escape to a gap, the fuel exerts a local load on a clad when going to a nominal power, even at low specific heat loads. By process chips are meant uranium dioxide particles of fine fractions brought to or resulting in a fuel rod during assemblage that are capable of escaping to initial gaps sticking in them at different heights of a fuel column. The linear dimensions of those particles do not exceed the maximum value of the diametral fuel-clad initial gap.

During power changes characteristic of power reactors the thermal expansion of fuel pellets is capable of inducing very high local loads on a clad, which in practice are, however, limited by the strength of fuel particles.

Design-experimental studies to predict the behaviour of a chip-containing fuel have been performed. An analytical model and a computer programme have been developed to calculate the stress-strained condition of fuel clads that simulate the conditions of U\textsubscript{2}O\textsubscript{3}-particle-clad interaction. The amount of a permissible unit gap and the sum of gaps were specified based
on the thermotechnical reliability of a core under normal and accident operation conditions. An increase of a fuel core temperature at discontinuity sites is permissible for fuel performance even at 10-15 mm discontinuities (fig. 1,2).

**2.2. Influence of Fuel Parameters on its Behaviour under Accident Conditions**

From the standpoint of estimation of fuel behaviour under accident conditions it is important to point out the following design and technological parameters:

- initial pressure under a clad
- radial fuel-clad gap
- filler gas composition (dilution of helium with gas fragments with an increase of fuel burnup and the presence of fission products chemically aggressive to a clad)
- axial gap between pellets (up to 15 mm)
- fuel pellet density
- heat loads.
Thus, under the conditions of different inner excessive pressures at a similar rate of heating up the modes of clad straining differ significantly. At low rates of heating up and at temperatures of 850-950°C clads can show an extended portion of high accumulated creep strain. This mode of loading is characteristic of "low leaks", and the peculiar features of straining are accounted for by phase transitions of the alloy used for cladding with straining rate and clad temperature combined in a specific manner the "superplasticity effect" shows up. Relatively low ballooning and ruptures of clads are observed at high rates of heating. Here corrosion processes have an effect (fig. 3, 4).

<table>
<thead>
<tr>
<th>PARAMETERS OF FAILURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRESSURE, MPa</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>8-10</td>
</tr>
<tr>
<td>2-2.5</td>
</tr>
<tr>
<td>5-6</td>
</tr>
</tbody>
</table>

FIG. 4 FAILURE OF CLADS UNDER INTERNAL PRESSURE IN STEAM ATMOSPHERE

FIG. 5 CHANGE OF MAXIMUM TEMPERATURE VARIATION IN WER FUEL CLAD WITH INITIAL ECCENTRICITY OF PELLET RELATIVELY CLAD
Another example deals with a variation of a radial fuel-clad gap. With the evolution of eccentricity there appear high azimuthal temperature non-uniformities which substantially affect the extent of hoop breaking strain (fig.5).

2.3. Requirements on Fuels for Reactors of Load Follow NPP

Experience gained in operation of water reactor cores shows that important factor limiting the fuel performance under transient conditions is a thermomechanical pellet-clad interaction (PCI). The physical base that characterizes the behaviour of fuels under transient conditions is a relatively fast variation of their temperature fields.

With an increase of specific power rating a thermomechanical PCI is realized in a fuel rod. The PCI results from the fact that the levels of temperature variations are different in fuel and clad, and the linear expansion coefficient of zirconium clad is lower than that of oxide fuel.

The most dangerous transient is a power ramp, i.e., a relatively fast (going ahead of stress relaxation in a clad and fuel at the expense of creep) increase of specific power rating above the preceding rather long steady-state level. The danger of a fuel failure under transient conditions depends upon its state prior to a power ramp: concentration of aggressive fission products on a clad and a fuel-clad contact. The most dangerous is a situation when there is no fuel-clad gap and the full thermal expansion is transmitted to a clad giving rise to high tensile stresses. In the presence of aggressive fission fragments the clad will fail by corrosion cracking. If the rate of loading is decreased to a level comparable to the rate of relaxation processes conditioned by the creep of fuel and clad, the clad stresses are reduced, which favourably affects the fuel performance.

However, this solution of the problem is acceptable only for base NPP.

The developed and presently recommended parameters of transients for base NPP operation contemplate to raise the power in such a way, that during a transient clad stresses might relax at the expense of UO₂ creep. If the time of a transient (power rise, is comparable to the time of the relaxation of fuel stresses, the stresses developing in clads will be low. The time of stress relaxation to 40-50% (at the expense of creep) in UO₂ is 12-15 hours, i.e., the permissible rates of fuel loading must not exceed 3.0-4.0% per hour.

The level of tensile stresses in a clad can be reduced through some technological and design solutions:
- filling of a fuel rod with helium at increased pressure (fig.6),
- use of pellets having a central hole.

In this case the insignificant reduction of a fuel weight per a fuel unit length lowers the fuel temperature and it becomes possible to lower the level of clad tensile stresses at the expense of the plastic deformation of fuel. The largest effectiveness of this design solution manifests at relatively high specific loads above 300-330 W/cm when the temperature level of fuel is sufficient for the mechanisms of plastic straining and creep during the time interval which characterizes a transient process.
- use of higher plasticity pellets (lower temperature of the brittle-plastic transition and higher creep rate)
- use of chamfered pellets with a reduced I/d.

Among the design solutions the most promising is considered to be the use of a barrier layer on the inner surface of a clad. In all the cases the fundamental circumstance is defects available in a clad. The commercial technology of tubes and methods of their control ensure defects in as manufactured fuel clads ≤50 mm deep. For WWER-1000 base NPP such defects are already at the level of maximum permissible. In a defect the concentration of aggressive fission products is sharply increased which lowers the threshold of corrosion cracking. Besides, even at the low level of tensile stresses (significantly less than the threshold of corrosion cracking) there occurs a cyclic plastic strain at the tip of a defect which sharply reduces the maximum amplitude of loading with a day control. Special comparative investigations were performed to study corrosion cracking using clads both without defects and with deliberately made ones. This made it possible to estimate the time before the incipience of a crack and the rate of its propagation until a through rupture of a clad takes place. This circumstance demands that the amount of a defect permissible in fuel clads for load-follow NPP be reduced (fig. 7) /4/.

**FIG. 6** HOOP STRESSES IN WWER-1000 FUEL CLAD AS A FUNCTION OF BURNUP AT DIFFERENT INITIAL HELIUM PRESSURE UNDERWRATH CLAD (Increase power 70% → 100% at rate 25 in min)

**FIG. 7** RELATIONSHIP BETWEEN TIME-TO-FAILUR AND HOOP STRESSES OF ZR-1Nb ALLOY SPECIMENS BY INTERNAL PRESSURE OF IODINE CONTAINING ATMOSPHERE
TABLE 3  POSSIBLE EFFECTS PRODUCED BY INCREASED BURNUP OF WWER FUELS

<table>
<thead>
<tr>
<th>CHANGE OF PARAMETERS</th>
<th>POSSIBLE PROCESSES AND THEIR EFFECTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>INCREASE OF BURNUP</td>
<td>- INCREASED ACCUMULATION OF FISSION PRODUCTS IN FUEL</td>
</tr>
<tr>
<td></td>
<td>- INCREASED SWELLING (GAS AND SOLID)</td>
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<td></td>
<td>- INCREASED GAS RELEASE</td>
</tr>
<tr>
<td></td>
<td>- INCREASED AMOUNT OF AGGRESSIVE FISSION PRODUCTS</td>
</tr>
<tr>
<td></td>
<td>- MORE INTIMATE FUEL-CLAD CONTACT</td>
</tr>
<tr>
<td>INCREASE OF DURATION</td>
<td>- HIGHER CORROSION EFFECT OF COOLANT OR CLAD</td>
</tr>
<tr>
<td></td>
<td>- INCREASED LAMINATION OF CLAD MATERIAL</td>
</tr>
<tr>
<td></td>
<td>- INCREASED NUMBER OF CYCLES UNDER TRANSIENT CONDITIONS</td>
</tr>
<tr>
<td></td>
<td>- INCREASED ACCUMULATED RESIDUAL COMPRESSION STRAIN OR CREEP</td>
</tr>
<tr>
<td></td>
<td>- HIGH IRRADIATION INDUCED GROWTH</td>
</tr>
<tr>
<td>INCREASED SHUFFLING (REARRANGEMENT) OF SUBASSEMBLIES FUEL</td>
<td>- INCREASED HANDLING OF FUEL</td>
</tr>
<tr>
<td></td>
<td>- INCREASED DISPLACEMENT OF FUEL PELLETS AND THEIR FRAGMENTS</td>
</tr>
</tbody>
</table>

2.4. Change of Fuel Performance Criteria at Extended Burnup.

To solve the problem of reliable operation of fuels at extended burnup investigations, new technical solutions and optimization of existing parameters are required on such lines as:

- increased fuel enrichment
- decreased non-uniformities of power rating
- optimization of fuel reloads
- re-use of assemblies that were not burnt at the initial stage of operation.

Fuels as most responsible components of a core are the main object of studies to reach high burnup.

During the last period of operation, the so-called period of wear, the main reasons for fuel failures at high burnup can be:

- swelling of $\text{UO}_2$, release of gas fragments as well as corrosion and embrittlement of clad due to high neutron fluence.

Extended burnup operation of fuels can significantly influence their performance. Processes possible due to a change of operation conditions and its consequences are tabulated in table 3.

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PREDICTION OF THE INFLUENCE OF MATERIAL PROPERTIES ON FUEL ROD BEHAVIOUR

S. HARRAGUE, D. AGUERO, J. LÓPEZ PUMAREGA, A. MARINO
Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

Abstract

There is an increasing interest on the influence of material properties on fuel rod behaviour under constant power, power ramping and load-following operation of a nuclear power plant. Analytical tools are required in order to determine the effect of the modification of given material properties, as well as to analyze actual irradiation behaviour and PIE results.

CNEA has developed the BACO Code for the analysis of fuel rod behaviour under irradiation. Its modular structure and detailed coupling of thermo-mechanical and irradiation-induced phenomena makes it an interesting tool for the prediction of the influence of material properties on the fuel rod performance and integrity.

In this paper, we present a study of the effect of some material properties -i.e. fuel porosity, densification, Zircaloy mechanical properties and anisotropy, among others- on fuel rod behaviour. The study covers constant power, and power ramping. Power ramping due to fuel reshuffling in HWRs is specially analysed, as well as the influence of ramp velocity and pre-conditioning on the fuel rod integrity.

A brief discussion is included regarding the interrelation between basic fuel design, material properties, operating conditions and fuel integrity.

1. INTRODUCTION

There is a generalized interest in improving fuel performance in water reactors under more demanding operating conditions, such as burn-up extension, load following operation and/or faster power ramps. This situation, in turn, requires a better understanding of the properties of fuel rod materials.

The strong coupling between thermal, mechanical and irradiation-induced processes in a fuel rod under reactor conditions, makes the effect of a given material property difficult to understand. For this reason, fuel modelling is necessary in the analysis of experimental results, planning experiments, in understanding the influence of each material property on the overall behaviour of the fuel and in the extrapolation of some experiments to actual reactor conditions.

CNEA has developed the BACO Code [1] for the simulation of a fuel rod behaviour under irradiation. The Code has a modular structure, and consequently it can easily incorporate different material properties. This flexibility allows the Code to analyze different fuel rod designs and operating conditions; it has been used for simulating PWR, PHWR, CANDU, PFR and experimental fuel rods [2], [3], [4]. The Code is based on a physically sound description of the phenomena taking place in a fuel rod, and therefore, it describes the coupling between stress-strain evolution, thermal field and irradiation induced effects.

In this work some applications of the Code, showing the influence of material properties on fuel rod behaviour, are shown. Most of them are related to the fast power ramps resulting from on-power fuel reshuffling in Heavy Water Reactors and on the effect of burn-up on the integrity of the cladding.

Conclusions are presented showing that the effect of some material properties depends strongly on the basic fuel rod design.

2. ANALYSIS OF FUEL ROD BEHAVIOUR UNDER POWER RAMPS - BACO CODE CAPABILITY

Argentina has two nuclear power stations in operation: Atucha-I (a pressurized heavy water reactor), and Embalse (CANDU 600 type). In both cases, on-power fuel reshuffling causes fast power ramps on the fuel. Basic fuel design is different in each of the two cases. The Atucha fuel assembly consists of 36 pre-pressurized, self-standing 600 cm long fuel rods, similar to the PWR rod except on its unusual length. The CANDU fuel bundle has 37 non-pressurized, collapsable, 50 cm long fuel rods. In both cases, stress-relieved Zry-4 cladding and non-enriched UO2 pellets are used.

In natural uranium fuel, final burn-up is low (around 7000 MWd/tU). Nevertheless, burn-up extension by U-235 enrichment, Thorium cycle, etc., is foreseen in these reactors. Load-following operation has also been tested in both power stations.

The fuel for the two power stations is currently produced in the country.

The situation just described has led to a study of the influence of material properties on the fuel behaviour under power ramps and cyclic operation at different burn-ups. Here, some power ramp predictions of the BACO Code are presented.

Fuel integrity under power ramping depends on many factors: burn-up, ramp height, initial LHGR ('pre-conditioning') and previous time at that power level, ramp velocity, etc.
Despite the low burn-ups at which HWR fuel operates, stress corrosion cracking has been identified as a failure mechanism [5].

It is necessary to have a given concentration of corrosive fission products, a given strain rate and a minimum tensile stress applied during certain time in order to produce SCC failure in Zry claddings. Threshold values for all these variables are inter-dependent.

Previous experience [6] has shown that, for a fixed ramp velocity, the hoop stress predicted by BACO at the inner surface of the cladding correlates with the fuel failure probability over a wide range of pre-conditioned powers and power increments during the ramp. In Fig. 1, the hoop stress at the cladding inner surface is plotted as a function of time for five Atucha fuel rods ramped from the same initial power $q_0$ to the same final power $q_0 + \Delta q$ at five different ramp rates. Ramp rates shown here cover the range between on-power fuel re-shuffling, to reactor start-up. BACO predicts the maximum tensile stress at the end of the ramp, afterwards cladding stress relaxes while power is kept at its peak value $q_0 + \Delta q$. This stress relaxation is mainly due to $\text{UO}_2$ creep into pellet dishing and cracks; BACO predicts a stress relaxation depending on the initial power $q_0$, the ramped power $q_0 + \Delta q$, and the ramp rate $\dot{q}$.

The predictions agree qualitatively with the experimental knowledge on fuel rod behaviour: low ramp rates are safe, because the thermal strain rate imposed by the power ramp on the cladding is comparable to the creep rate of $\text{UO}_2$, and therefore stress relaxation via creeping into dishing and fuel cracks can occur; consequently, no high stresses are imposed on the cladding. On the other extreme, very high ramp rates (as case 1 in Fig. 1) lead to high peak stresses in the cladding but also to a very fast stress relaxation; as the time the cladding stays under high tensile stresses is low, the probability of SCC failure falls.

In other words, at high ramp rates and high stress relaxation, the cladding can stand higher stresses without perforating.

It can also be seen in Fig. 1 that ramp rates regarded usually as safe, i.e., $\dot{q} \leq 5 \text{ W/cm}^2$ [7], are the ones leading to a very low tensile hoop stresses at the cladding inner surface.

A more quantitative image of the BACO Code capability to describe fuel behaviour under power ramping is given by the analysis of CANDU fuel. Based on actual experience of power ramping due to fuel re-shuffling in nuclear power stations, AECL has published bounds for safe operation. Usually [5], the maximum power increase and maximum power such that fuel operation below these values present (statistically) no failures, are given as a function of burn-up.

In Fig. 2a) and 2b) show the experimental bounds for power increase and maximum power corresponding to the Pickering Stations [5]. Power histories simulating re-shuffling were simulated with the BACO Code. In the Code, the criterion for safe operation was based on the maximum hoop stress at the cladding inner surface; this is related to susceptibility to stress corrosion cracking. A threshold hoop stress of 280 MPa tensile was adopted. It can be seen in Figs. 2a) and 2b) that BACO results are in good agreement with AECL data; even the mispredictions can be explained on a physical basis. At low burn-ups, BACO overpredicts SCC susceptibility, and at high burn-ups, it is lightly underpredicting it; that is consistent with an SCC criterion in which threshold stress is burn-up independent or, in other words, where the role of dwell time and corrosive products concentration is not included.

3. THE INFLUENCE OF PELLET DENSIFICATION

3.1 CANDU fuel

The CANDU fuel has some design characteristics which make the influence of material properties on its behaviour different in some cases from a PWR fuel. Two of these design characteristics
FIG. 2a: Variation of threshold power increase (for no fuel failure) with reshuffling burn-up.

AECL: values for Pickering NGS (Ref. 5)
BACO: BACO predictions

FIG. 2b: Variation of threshold ramped power (for no fuel failure) with reshuffling burn-up.

AECL: values for Pickering NGS (Ref. 5)
BACO: BACO predictions

FIG. 3: Standard CANDU fuel power cycle.

\( b_0 \) is the reshuffling burn-up; \( q \) and \( B \) in arbitrary units.

must be remarked: a thin, collapsable cladding, and no pre-pressurization. As a consequence, once in the reactor, the cladding early collapses on the fuel stack. Nevertheless, complete gap closure and, consequently, PCM I, may take a longer time depending on the actual irradiation conditions.

BACO, despite its axisymmetric analysis of a fuel rod, distinguishes between cladding collapse— influencing the heat transfer through the gap but leading to no important mechanical interactions—and complete gap closure leading to PCM I. This is achieved by a gap conductance model that takes into account a partial gap closure, in a way similar to the one proposed by Broughton and MacDonald \( 8 \).

In CANDU reactors, fuel reshuffling is done under reactor operation. During the reshuffling operation the fuel undergoes a power ramp due to the power distribution along the fuel channel.

For this reason, it is interesting to study the behaviour of a CANDU fuel under fast (10-20 min long) power ramps. The HGR before the ramp, the burn-up at which the ramp occurs, and the ramp height, cover a wide range. FIG. 3 schematizes the kind of power histories to be analyzed: at power \( q_0 \) and burn-up \( b_0 \) the fuel is ramped to power \( q_0 + \Delta q \); time for power increment \( \Delta q \) is in the range 10-20 minutes; at the end of reshuffling the fuel stays at a constant power \( q_f \).
With the purpose of studying susceptibility to SCC, the RMC Code is used to determine, for given initial power \( q_0 \) and reshuffling burn-up \( B_0 \), the power increment at which the hoop stress at the cladding inner surface reaches a fixed value \( \sigma_{SCC} \). Due to the fact that the fuel stays at the peak power \( q_0 + \Delta q \) only for a few minutes, \( \sigma_{SCC} \) is taken as higher than the usually accepted threshold stress for SCC (170-190 MPa). In this case, \( \sigma_{SCC} = 280 \) MPa.

In order to determine the effect of pellet densification on fuel behaviour, two different densification values were considered: 1.7% in volume, and 2.7% in volume. In-pile densification is assumed to end at 1000 MWd/tU burn-up.

FIG. 4 shows the power increment \( \Delta q \) needed to reach a 280 MPa hoop stress as a function of initial power \( q_0 \). At burn-up, \( B_0 = 3000 \) MWd/tU and \( B_0 = 5000 \) MWd/tU. The highly densifying fuel can stand much higher power ramps at the lower burn-up because a higher initial power is necessary for complete gap closure. As a matter of fact, gap closure (and PCMI) is reached in that case at 3000 MWd/tU burn-up for initial powers over 250 W/cm. For the 1.7% densifying fuel, gap closure at \( B_0 \) burn-up is reached at any initial power \( q_0 > 150 \) W/cm.

FIG. 5 shows the peak power \( q_0 + \Delta q \) necessary to reach a hoop stress \( \sigma_{SCC} \) at the cladding, as a function of \( q_0 \). Curves corresponding to 1.7 and 2.7% volume densification show a different behaviour at 3000 MWd/tU burn-up. At 1.7% densification, the pellet-clad gap has closed before the beginning of the power ramp for all values of \( q_0 \). FIG. 5 shows a typical evolution of the hoop stress at the cladding inner surface as a function of burn-up for a case where pellet-clad contact is reached at constant power \( q_0 \); \( \sigma_h \) is compressive when the gap is opened; once contact is reached, \( \sigma_h \) increases gradually due to pellet swelling until it reaches a constant, and low, saturation value where an equilibrium is established between pellet swelling and creep, cladding strain rate and coolant conditions. This implies that, if the fuel is ramped after pellet-clad closure, the power increment \( \Delta q \) necessary for reaching a given stress \( \sigma_{SCC} \) at the cladding will tend to become independent of initial power \( q_0 \) as \( q_0 \) (or \( B_0 \)) become higher.
In other words, going back to FIG.6, when \( q_0 \) (or \( B_0 \)) increases, the cladding stress reaches the saturation value before the ramp starts. This effect can be seen in FIG.4, where the curve corresponding to 1.7% tends to level as \( q_0 \) increases. If \( q_0 + \Delta q \) is plotted, as in FIG.5, as \( \Delta q \) tends to become independent of \( q_0 \), \( q_0 + \Delta q \) increases with \( q_0 \).

If the gap is opened at the beginning of the power ramp, as in the case with the higher densification, part of the ramp is required to close the gap. The higher the initial power \( q_0 \) is, the smaller will be the gap at the same burn-up \( B_0 \), and the smaller the power increment needed to close the gap. This is clearly seen in FIG.4, where \( q \) decrease with \( q_0 \) in the 2.7% case and 3000 MWd/tU burn-up, until the gap is closed before the ramp starts. On the other side, FIG.5 shows that the total power \( q_0 + \Delta q \) needed to reach the stress level \( \sigma_{cc} \) decreases with \( q_0 \) when the gap is initially open; this is due to non-linear effects such as temperature dependence of Zry creep, pellet creep, decrease of \( \Delta q \), thermal conductivity with temperature, temperature dependence of fission gas release. All of this non-linear effects, considered by the BACO Code, tend to diminish the gap at the beginning of the ramp.

As a conclusion, a higher densification delays hard pellet-clad contact, and makes the CANDU fuel more resistant to power ramping. Being the CANDU fuel only 50 cm long, the possibility of fuel stack interruption due to high densification is very low. The effect of densification gets smaller as the burn-up at which the fuel is ramped grows.

3.2 Atucha Fuel

As already said, the Atucha fuel rod is 600 cm long, with Zry-4 cladding and natural uranium UO2 pellets. Dimensional stability of the pellet is important due to the unusual length of the pellet stack. For this reason, the effect of 1% volume densification will be studied, and compared to non-densifying pellets. On-power re-shuffling is analyzed, corresponding to a power history shown in FIG.7, where now, \( \Delta q \) refers to the permanent power increase between two reactor channels, and not -as in FIG.3 for CANDU fuel- to the instantaneous, short-lived ramp during the re-shuffling.

As in the case of the CANDU fuel, safe operation limits for the fuel are studied. Now, \( q_0 \), \( B_0 \), \( \Delta q \) will refer to local power and burn-up at the axial position of the fuel rod undergoing the maximum power after the ramp. Another difference with the CANDU
situation is that a lower threshold hoop stress at the cladding inner surface is adopted for safe operation; the reason for it is that the fuel is now kept at the higher power position.

Results shown here correspond to $\sigma_{SC} = 170$ MPa.

FIG. 8 shows the power increase $q$ for reaching 170 MPa hoop stress in the cladding as a function of power $q_0$ before the ramp. Results for a non-densifying fuel (A), and a 1X densifying fuel (F), are given at three re-shuffling local burn-ups: 3000, 6000, and 9000 Mwd/1U. FIG. 9 shows the maximum power $q_0 + \Delta q$ for the same cases.

The benefits for a rather small densification are remarkable at low initial powers and/or low re-shuffling burn-ups. As burn-up, or initial power increases, the effect of densification tends to vanish.

As in the CANDU case, fuel behaviour changes according to whether the pellet-cladding gap was opened or already closed at the beginning of the ramp. Initial powers for which the gap closes before burn-up $q_0$ are marked in FIGS. 8 and 9; as expected, a densifying fuel requires a higher power to close the gap.

As already explained for the CANDU fuel, if the ramp starts with an open gap, part of the ramped power closes the gap, and the total power $q_0 + \Delta q$ required to reach a given stress at the cladding falls slightly with initial power $q_0$, due to non-linear effects such as $UO_2$ creep, gap thermal conductance, fission gas release, temperature and fast flux dependence of Zry creep. This behaviour is seen here at low powers and burn-up.

If the gap has been closed for some time before the power ramp, tensile stresses in the cladding due to PCMI become gradually relaxed, mainly by $UO_2$ creep into dishing and pellet cracks, as was shown in FIG. 6. As the initial power $q_0$ and/or burn-up $u_0$ increase, the cladding stress at the beginning of the ramp tends to the saturation stress shown in FIG. 6. This is seen in FIG. 8.
FIG. 10a): Pore size distribution for pellet "A". 
$\rho_p$ is pore radius (\(\mu\text{m}\)) and $f$ is volume fraction of porosity having radius $\rho_p$. (Volume fractions have been normalized to 1).

FIG. 10b): Pore size distribution for pellet B. Same notation as in FIG. 10a).

FIG. 11a): Radial distribution of porosity in pellet "A", at different burn-ups (CANDU cycle). 
$B_1 = 0$ corresponds to the beginning of the cycle, $B_1 = 3000$ MWd/tU to refueling, and $B_2 = 7000$ MWd/tU to end of cycle. 
$p$ in volume fraction; $R$: outer pellet radius.

FIG. 11b): Radial distribution of porosity in pellet "B" at different burn-ups, (CANDU cycle). Same notation as FIG. 11a).
where in those cases the power increase $q$ tends to become independent of initial power $q_0$. Finally, for very high initial power $q_0$ (500 W/cm), all curves tend to the same point. BACO predicts in that case the same, small initial cladding hoop stress independently of burn-up.

4. INFLUENCE OF PELLET POROSITY DISTRIBUTION

Even if the main effect of the pore size distribution is on fuel densification, a separate analysis of its influence on rod behaviour will be made here.

It is well known that small pores easily disappear by irradiation effects, while larger pores are more stable. Here, the influence of pellet pore size distribution on the behaviour of CANDU and Atucha fuel is analyzed. BACO modelling of pore size effects is based on the model proposed by Stehle et al. 9.

FIG. 10 shows the two pore size distributions considered: A with many fine pores and B with a coarser porosity. Distribution A is based on some CANDU pellets [18], while B is similar to the one presented in [9].

4.1 CANDU fuel

The power cycle shown in FIG. 3 is studied with:

$q_0 = 200$ W/cm; $q_1 = 350$ W/cm; $q_2 = 450$ W/cm; $B_0 = 3000$ MWd/tU, and a final burn-up of 7000 MWd/tU.

FIG.11a) gives the porosity distribution as a function of pellet radius, at different burn-ups, for case A. The as-fabricated porosity is assumed to be homogeneous ($B = 0$). After 3000 MWd/tU at low power, the fine pores have disappeared from the pellet, and thermal densification has removed some pore volume from the central, higher temperature region.

At 7000 MWd/tU, and due to the higher power, more densification has taken place. In FIG. 11b) the radial distribution of porosity is shown for case B; as expected, densification is much smaller.

FIG.12 shows the burn-up evolution of the pellet surface and centerline temperatures for both pore distributions: no major differences exist in surface temperature, a result to be expected for in a collapsable cladding fuel. However, an increasing difference in centerline temperature (100 degC at EOL) exists, with the more stable fuel having higher temperature. This is due to the porosity dependence of UO$_2$ thermal conductivity: as porosity disappears in the highly densifying pellet, thermal conductivity increases and temperature drops.

FIG.13 shows the volume of fission gas released, larger for the higher temperature pellet.
FIG. 14a) Radial gap as a function of burn-up for pellets "A" and "B" under a CANDU cycle. (In both cases, gap is closed before reshuffling).

FIG. 14b) Hoop stress at the cladding inner surface vs. burn-up for pellets "A" and "B" under a CANDU cycle. Compressive stresses before reshuffling are not shown.

FIGS. 14a) and 14b) show the burn-up evolution of pellet-cladding gap and, after the power-up ramp, the hoop stress at the cladding inner surface. Due to the fast densification of fine porosity, in case A the gap first reopens, and as densification slows down and cladding creep down keeps on going, it starts to close. In case B, cladding creep down is dominant since the beginning of irradiation.

Peak hoop stress at the end of the power ramp is slightly higher in case B, where earlier contact has occurred. Consequently, cladding stress relaxation is slower in that case. For both pore distributions, cladding stresses at 6000 MWd/ton are similar and low.

4.2 ATUCHA fuel

The power history for the higher power axial zone of an Atucha fuel rod is the one shown in FIG. 7, with: $q_c = 350$ W/cm; $q_f = 300$ W/cm; $B_0 = 3500$ Mwd/tU and $B_f = 6400$ Mwd/tU.

FIGS. 15a) and 15b) show the radial distribution of porosity for the two types of pellets; as compared to the CANDU case, higher power has produced a higher densification in this fuel.

FIG. 16 shows the burn-up evolution of pellet surface and centerline temperatures. The higher densification in case A leads to a larger gap, and consequently to a higher pellet surface temperature. Nevertheless, higher $UO_2$ thermal conductivity in the densified fuel A leads to a lower pellet centerline temperature. This, in turn, leads to less fission gas release, as shown in FIG. 17.

FIGS. 18a) and 18b) give the burn-up evolution of pellet-cladding gap, and after the power ramp, hoop stress at the cladding inner surface. High densification of fine porosity makes the gap to initially increase in case A; in case B, cladding creep down is always dominant and the gap steadily closes. For case B, the gap closes during the power-up ramp; the cladding hoop stress has a peak, then it relaxes and, afterwards, slowly grows due to pellet swelling. In case A, a larger densification leads to a much later gap closure, at almost 5000 Mwd/tU burn-up. Cladding stress starts to become less compressive as pellet-cladding contact pressure starts to grow.

It must be kept in mind that, even if the power ramping behavior of unstable pellets in the Atucha fuel is good, the unusual length of the fuel rod makes it dangerous to operate with a highly densifying fuel.
FIG. 15a): Radial distribution of porosity in pellet "A", at different burn-ups (ATUCHA cycle).

\( B_0 = 0 \) corresponds to BOL, \( B_1 = 3500 \text{ Mwd/} \text{t} \text{U} \) is local burn-up at reshuffling, and \( B_2 = 6400 \text{ Mwd/} \text{t} \text{U} \) corresponds to EOL.

\( p \) in volume fraction; \( R \): outer pellet radius.

FIG. 15b): Radial distribution of porosity in pellet "B" at different burn-ups (ATUCHA cycle). Same notation as FIG. 15a).

FIG. 16: Burn-up evolution of fuel centerline temperature \( T_c \) and surface temperature \( T_s \) for pellets "A" and "B" under an ATUCHA cycle.

FIG. 17: Volume of fission gas released (arbitrary units) vs. Burn-up for pellets "A" and "B" under an ATUCHA cycle.
FIG. 18a): Radial gap as a function of burn-up for pellets "A" and "B" under an ATUCHA cycle. In case "B" gap closes during reshuffling, while in case "A" it keeps open until a higher burn-up.

FIG. 18b): Hoop stress at the cladding inner surface vs. burn-up for pellets "A" and "B" under an ATUCHA cycle. Stresses before reshuffling are not shown.

5. INFLUENCE OF ZIRCALOY MECHANICAL ANISOTROPY

Hill's description [11] of mechanical anisotropy is adopted in the BACO Code for cladding plasticity and creep; more sophisticated models have also been included [2].

Here, four different cladding anisotropies are considered; Table I gives Hill's anisotropy coefficients as taken from Tenckhoff [12]. The four Zry claddings correspond to different suppliers.

FIG. 19 shows the time evolution of the cladding radius for a power cycle where fuel reshuffling is done at \( t = 0.2 \text{d} \). Different mechanical anisotropy leads to marked differences in cladding creep down; consequently, the pellet-cladding gap at the beginning of the ramp is quite different in the four cases. This causes a much higher hoop stress with the cladding that starts the ramp with the lower gap, as shown in FIG. 20.

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hill's Coefficients</td>
</tr>
<tr>
<td>CASE</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

Notation: \( c_{eq}^2 = F(\sigma_0 - c_r^2) + G(\sigma_0 - c_r^2) + H(\sigma_0 - c_r^2) \)
6. CONCLUSIONS

The advantages of carefully describing the coupling between different phenomena in a fuel rod—as done by the BACO Code—have been pointed out.

Power ramps due to on-power reshuffling in Heavy Water Reactors have been studied. Bounds on power increase and total power have been established on the basis of the hoop stress at the cladding inner surface. The relation between safe operation and hoop stress at the inner surface of the cladding has been proved valid in the case of the CANDU fuel; a good correlation between BACO predictions based on that criterion, and AECL experimentally determined bounds for the Pickering reactors, is shown in this work. Nevertheless, for burn-ups higher than those associated to power ramping in HWR's, a more elaborated SCC model should be introduced.

The effect of pellet in-pile densification in raising the limit for safe operation has been marked; this effect looses importance as fuel burn-up increases. A general prediction of BACO is that the capacity of the fuel to undergo power ramping decreases markedly with burn-up.

The analysis of pore-size distribution shows its influence on pellet densification. The increase in UO2 thermal conductivity due to pore shrinkage has, in the cases shown here, an important effect both on fuel temperatures and fission gas release.

The basic design differences between the CANDU and Atucha fuel lead to different behaviour under changes in a given material property. This is specially remarked in the role of densification: in the short CANDU rod, use can be made of the advantages of a rather large densification on improving fuel performance under power ramping. That is not the case with the long Atucha rod, where the danger of pellet stack interruption due to high densification must be taken into account.

ACKNOWLEDGEMENT

The authors wish to thank Dr. C.A. BAIGORRIA for elucidating discussions during the final part of this work.

REFERENCES

PERFORMANCE ANALYSIS OF VVER-440 TYPE FUEL ELEMENTS WITH HIGH BURNUPS

H. KARL, D. REINFRIED, H. STEINKOPFF
Zentralinstitut für Kernforschung Rossendorf,
Akademie der Wissenschaften der DDR,
Dresden, German Democratic Republic

Abstract

According to present knowledge optimum utilization of fuel in the VVER-440 type reactor is reached at a mean discharge burnup of 45 up to 50 GWd/tU using an annual refuelling cycle. This optimum can only be achieved with a refuelling fraction of about 1/5 and an enrichment of the new fuel of about 4.4%. By means of burnup calculations carried out for this mode of operation peak values for the mean and local burnup of a fuel element have been found to be about 60 GWd/tU and 67.5 GWd/tU, respectively.

In this paper the results of model calculations on the operating performance of this fuel element are presented and discussed.

1. Introduction

Out of different possibilities to improve the fuel utilization in PWR increasing burnup by means of extension of exposition time of fuel elements has been used in many countries for some years. Because of the favourable economy predicted corresponding investigations are carried out also in the GDR with the operating performance as central point of interest.

According to present knowledge optimum utilization of fuel in the VVER-440 reactor is reached at a mean discharge burnup of 45 up to 50 GWd/tU using an annual refuelling cycle. This optimum can only be achieved with a refuelling fraction of about 1/5 and an enrichment of the new fuel of about 4.4%.
By means of burnup calculations carried out for this mode of operation peak values for the mean and local burnup of a fuel element have been found to be about 60 GWD/tU and 67.5 GWD/tU, respectively.

In this paper the results of model calculations on the operating performance of this fuel element are presented and discussed. The code STOFFEL-1 /2/ was used for the model calculations. This code makes possible the simultaneous estimation of several important fuel element parameters.

2. Results and discussion

Fig. 1 shows the fuel central temperature versus exposition time. High linear heat ratings and an open gap between fuel and cladding cause maximum temperatures at the beginning of the first and second fuel cycles. Power and gap reduction lead to a rapid lowering of temperature during the first two cycles. The temperature drop slows down after closing the gap. The power reduction is greater than the deterioration of fuel thermal conductivity by burnup. Consequently, there is no fuel central temperature increase in the following cycles. Fig. 2 gives some information about size changes of fuel and cladding and about the development of contact pressure and cladding stress. Thermal fuel strain and fuel cracking cause an increase of the fuel radius connected with a decrease of the gap when the reactor is put into operation. Further size changes of fuel until gap closure depend mainly on the linear heat ratings and the inverse time-dependent processes of swelling and densification. The radial thermal strain of cladding is almost compensated by the elastic deformation of cladding caused by the coolant pressure at the beginning of operation. Consequently, the increase of the cladding radius amounts only to 5 μm. Time-dependent primary creep of cladding leads to a quick decrease of the cladding radius during the initial phase of exposition time.

Fig. 1 fuel central temperature versus exposition time
(axial area 4)

Fig. 2 Important parameters of the fuel element with the maximum burnup versus exposition time
(axial area 4)
The following slower decrease is initiated by secondary creep. The inverse size changes of fuel and cladding lead to gap closure, i.e., in the axial area of the fuel element after an exposition time of about 520 eff. days. The development of contact pressure between fuel and cladding diminishes the tangential cladding stress. This diminution relieves the cladding on stationary operation. The fuel size follows the size change of cladding during further exposition time. Thus, the fuel swelling does not produce an inverse strain of cladding at the mode of operation under discussion. It is characteristic of the internal pressure that it increases when the reactor is put into operation by a factor of about 2.5 (Tab. 1). The small fission gas release leads only to a small pressure during further exposition time.

Tab. 1: Important parameters of the fuel element with the maximum burnup at the end of exposition time.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean burnup (GWd/1U)</td>
<td>58.86</td>
</tr>
<tr>
<td>Amount of U-235 (lg)</td>
<td>3.10</td>
</tr>
<tr>
<td>Amount of Pu (lg)</td>
<td>8.76</td>
</tr>
<tr>
<td>Fuel column length change (%)</td>
<td>1.55</td>
</tr>
<tr>
<td>Fission gas release (%)</td>
<td>8.37 x 10^-7</td>
</tr>
<tr>
<td>Fission gas volume (1 cm^3)</td>
<td>1.48</td>
</tr>
<tr>
<td>Total gas volume (1 cm^3)</td>
<td>14.86</td>
</tr>
<tr>
<td>Gas pressure (MPa)</td>
<td>0.40</td>
</tr>
<tr>
<td>Cladding length change (%)</td>
<td>0.49</td>
</tr>
</tbody>
</table>

3. Conclusions

The results of the model calculations show that all the fuel element parameters investigated do not reach critical values. These are e.g.:

- Internal pressure < coolant pressure
- Fission stress < rupture stress.

Consequently, such effects as:

- Fission gas release and internal pressure
- Size changes of fuel and cladding

do not limit the exposition time of VVER-440 type fuel elements at the mode of operation under discussion. However, it has to be considered that a longer operation takes place with closed gap. This fact may increase the probability of cladding failure by PCI especially on changing load.

Our model calculations are assumed to contain uncertainties up to 10%. Additionally, it has to be noted that our programs do not give any conclusions about construction materials of fuel assemblies and about interactions between fuel elements and construction materials. Therefore, a final solution of the problem discussed requires corresponding postirradiation examinations.

Additional information about the operating performance of VVER-type fuel elements with high burnups are given in ref. /3-5/.

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/2/ D. Reinfried, H. Steinkopff, ZfK-522, 1984


/5/ H. Carl, et. al., Kernenergie 29 (1986), S. 193
RESULTS OF MR EXPERIMENTS ON TEN YEARS IRRADIATION OF EXPERIMENTAL URANIUM DIOXIDE ZIRCONIUM CLADDING FUEL ELEMENTS

V.V. GONCHAROV, K.P. DUBROVIN, E.G. IVANOV, A.B. KRUGLOV, V.A. SHESTERNIN
I.V. Kurchatov Institute of Atomic Energy, Moscow, Union of Soviet Socialist Republics

Abstract

The report presents the results on investigation of the experimental fuel elements with uranium dioxide and claddings made of 1% Nb-Zr alloy. Investigations were carried out in the I.V. Kurchatov Institute of Atomic Energy in Moscow. The experimental fuel elements have been irradiated in the MR reactor for about 10 years in boiling, neutral, uncorrected water-chemical regime with the steam quality up to 8.6 wt. %, at linear ratings up to 600 W/cm, at numerous changes of power and temperature (about 600 cycles), up to a maximum fuel burn-up of 91.4 MW.d/kgU.

The design of experimental fuel elements and assembly and in-pile test conditions are described in the report; the results of investigation are given, including neutron radiography of fuel elements, gamma-scanning, measurement of geometrical dimensions and volume of gas fission products released inside the cladding, the metallography and ceramography, determination of the mechanical properties of claddings.

It is shown that:
- the average fuel burn-up in the fuel elements ranged from 53.7 to 71.4 MW.d/kgU, maximum burn-up was from 68.7 to 91.4 MW.d/kgU;
- the corrosion damage of the cladding material is of nodular nature i.e. the corrosion centres with a maximum extension of 1 mm and a maximum depth of 110μm form, the number of the centres and their total extension are larger in the parts with higher linear rating;
- in the central parts the diameter of fuel elements was increased and the end dishes of fuel pellets disappeared, the maximum increase of the diameter made up 0.47 mm (3.5%);
- the maximum quantity of gas fission products released from fuel made up 584 cm³, the caesium migration to the ends of the fuel pellets in the central sections of the fuel elements is observed;
- there are fine hydride inclusions in the irradiated claddings with favourable tangential orientation, maximum amount of hydrogen was 0.0069 wt.%;
- in the central parts of the fuel elements the recrystallization of uranium dioxide took place without the formation of column zone;
- in certain parts of the pellet perimeters there was the diffusion fuel-cladding interaction with forming a layer having a maximum width of 45μm and total extension of 3.5 mm;
- the irradiated cladding conserved the sufficient plasticity (6-9% at 20°C and 10-12% at 350°C) which supposes possibility of their more extended in-pile operation;
- the untightness of one fuel element resulted from the deformation of the cladding under the effect of the internal pressure of gas fission products with the possible localization of deformation in the thinned parts of the cladding.
It was concluded that:
- the 1% Nb - Zr alloy cladding material is capable of work under condition of the reactor irradiation in water-steam mixture conditions for a long time at the large ratings and numerous changes of power and temperature;
- in the fuel element design intended for the extended operation and large burn-ups, it is necessary to foresee the sufficient plenum and measures to prevent the diffusion fuel-cladding interaction.

I. INTRODUCTION

The extended tests of the experimental fuel elements of power reactors are fulfilled in the MR reactor of the I.V. Kurchatov Institute of Atomic Energy. The results of such tests and post-irradiation examination may be used for designing of the good performance fuel elements of power reactors (for example, in connection with the transition to the four years fuel cycle in the NPP with the VVER reactors or with the development of heat supply nuclear plants in which the working period of the fuel elements will be 6-8 years). Besides, these results may be used to predict the performance of some reactor construction elements made of the zirconium alloys (for example, the RBMK reactor channels which are to be in the reactor during all its life).

The report presents the results of the post irradiation examination of the experimental fuel elements which have been tested in the MR reactor for about 10 years in the boiling regime to the maximum fuel burn-up of more than 90 MWd/kgU.

2. Construction of the experimental fuel assembly and fuel elements.

The experimental fuel assembly (FA) consisted of the 11 fuel elements and one rod with the specimens, arranged in a row around the central tube. The fastening and the spacing of the fuel elements in the FA was realized by the two rigid zirconium alloy grids and the two elastic spacers made of the stainless steel.

The standard RBMK fuel element cladding tubes made of 1% Nb-Zr alloy (H-I) were used for the claddings of experimental fuel elements. As a fuel were used the dished pellets from uranium dioxide with the density of 10.34-10.45 g/cm³, enriched by uranium -235 up to 6.5%. The fuel element was pressurized to about 0.1 MPa with helium gas. The leak tightness of the fuel elements was accomplished by standard technology with electron-beam and argon-arc weldings.

The main nominal geometric dimensions of the fuel elements were the following:
- the overall length was 1230 mm;
- the length of the fuel column was 1000 mm;
- the external diameter was 13.5 mm;
- the diameter of the fuel pellet was 11.52 mm;
- the diametral fuel-to-cladding gap was 0.18...0.38 mm;
- the volume of the free space inside the fuel element in the initial state was about 11 cm³.

3. Test conditions of the FA

The FA was placed into the loop channel having the construction of the tube in tube. The coolant flowed down in the central tube and flowed up in the external tube cooling the fuel elements.
The tests began on the 22nd of November 1974 and continued up to the 10th of April 1984. The location of the loop channel in the core of the MR reactor is given in Fig. 1. The main parameters of the PA test are given in Table I.

**TABLE I. Parameters of the PA test**

<table>
<thead>
<tr>
<th>MN</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power, kW</td>
<td>400...200</td>
</tr>
<tr>
<td>2</td>
<td>Test time on power, h</td>
<td>609.71</td>
</tr>
<tr>
<td>3</td>
<td>Test time in water-steam mixture, h</td>
<td>449.39</td>
</tr>
<tr>
<td>4</td>
<td>Heat production, MW.d</td>
<td>604.6</td>
</tr>
<tr>
<td>5</td>
<td>Fuel burn-up, MW.d/kgU:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- average</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>- maximum</td>
<td>91.4</td>
</tr>
<tr>
<td>6</td>
<td>Maximum linear rating, W/cm</td>
<td>600...300</td>
</tr>
<tr>
<td>7</td>
<td>Pressure of the coolant at the loop collector, MPa</td>
<td>9.8</td>
</tr>
<tr>
<td>8</td>
<td>Coolant velocity at the PA inlet, m/s</td>
<td>1.3</td>
</tr>
<tr>
<td>9</td>
<td>Coolant temperature, inlet °C</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>outlet °C</td>
<td>300...294</td>
</tr>
<tr>
<td>10</td>
<td>Maximum outlet steam quality, wt.%</td>
<td>8.6</td>
</tr>
<tr>
<td>11</td>
<td>Initial coefficients of power distribution:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- along the height</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>- over the cross-section</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>The number of shutdowns by signal of safety system</td>
<td>505</td>
</tr>
<tr>
<td>13</td>
<td>The number of planned shutdowns</td>
<td>153</td>
</tr>
</tbody>
</table>

The fuel assembly test was performed in the boiling, neutral, uncorrected water-chemical regime, corresponding to that of the RBMK reactor coolant.

Fig. 1. Dislocation of the loop channel relative to the centre of the MR reactor core and the arrangement of the fuel element in the PA.
For a long time the fuel assembly (over 4 years) was tested at the power level of 400...300 kW, the maximum linear rating of the fuel elements was 600...450 W/cm. Subsequently due to the fuel burn-up the fuel assembly power was gradually decreased and in the middle of 1979 it was nearly 200 kW (the maximum linear rating of the fuel elements was 300 W/cm).

The fuel assembly underwent the numerous changes of power during the test. It is enough to say that the number of planned shutdowns and shutdowns by the signals of the safety system was 658. Three times the FA was unloaded into the reactor pool for the spent fuel during the change of the loop channels. The FA test was stopped due to untightness of one fuel element. The untight FA operated nearly 1700 hours with the maximum linear rating of 240 W/cm.

4. Post-irradiation examination.

4.1. Visual inspection of FA and fuel rods and FA demounting.

The fuel element surface was covered by a relatively thin layer of the corrosion products of the loop. In the central, the most heat rating part the surface of the fuel elements underwent the nodular corrosion with the formation of the scaling oxide films of white colour. The diameter of the irradiated fuel elements increased, thus it was difficult to remove them from the FA. In demounting, untight fuel element N 042 was destroyed. The condition of the fuel element surface and the location of the destruction on the fuel element N042 is shown in Fig. 2.

4.2. The neutron radiography of fuel rods.

The analysis of neutron radiographs for the 10 leak tight fuel elements made it possible to determine that:

- the fuel pellets were stacked tightly with no gaps between the fuel pellets (except for fuel element N 46);
- pellets in the top and bottom parts of the fuel column had the dished ends and in the central parts the dishes between the pellets were not observed;
- in the central part of the fuel column in fuel element N 46 there was a 20 mm gap, filled with fuel fragments.

The internal conic holes appeared in pellets being close to the gap (Fig. 3), it was connected with the increased power in the given parts of pellets (see Fig. 4).

Fig. 2. The condition of the surface of the fuel elements and the location of the destroyed fuel element N042.
4.3. Gamma scanning of fuel elements

More than a year passed from the moment when the FA was removed from the reactor core up to the moment of the gamma scanning. Therefore the fuel element activity was mainly caused by the activity of Co isotopes. The gamma-scanning curves of the central fuel element parts have the saw-teeth shape (Fig. 4). The peaks on the curves correspond to the pellet ends. This evidences a redistribution of Cs isotopes within the fuel element pellets. The fuel element ends are characterized by a comparatively smooth gamma-scanning curves. On the basis of the gamma-scanning curves, ma-

Fig. 3. Neutronradiographs of fuel element N46 in the part with the gap between fuel pellets.

Fig. 4. The curve of gamma-scanning of fuel element N46 having the gap between fuel pellets.
de for the 10 leak tight fuel elements it was defined that the fuel burn-up in untight fuel element N 042 was close to the maximum one. The average fuel burn-up in the fuel elements was ranged from 53.7 to 71.4 MW.d/kgU and the maximum one from 68.7 to 91.4 MW.d/kgU.

The final coefficients of the burn-up distribution was along the height - 1.28, over the cross-section - 1.14. Such difference between the final coefficients and the initial ones (1.37, 1.2) may be explained by the deep fuel burn-up in the fuel elements of the given PA.


The results of measurement of the geometric dimensions showed the negligible change in the length of the fuel elements (less than 1 mm) mainly in the direction to decreasing. In the central parts of the fuel elements increased the diameter more than on the ends and the fuel elements became barrel-shaped. A relative increment in diameter made up from 1.2 to 3.5%. The fuel element with a greater amount of gas released were swelled to greater extent. This evidences that the cladding underwent creep strain under internal gas pressure in course of irradiation. The quantity of the gas fission products released from fuel was determined by the puncture of the cladding under the water layer and by gathering gas into the volumetric flask. It ranged from 300 cm³ to 580 cm³, i.e. from 20% to 36% in reference to the total amount of the generated gas fission products.

The results of measurement of the fuel element diameter, the volume of the released gas fission products and the fuel burn-up in the fuel elements are presented in Table 2.

<table>
<thead>
<tr>
<th>Number</th>
<th>Diameter increase in center of fuel element (mm)</th>
<th>Gas volume inside cladding under normal conditions (cm³)</th>
<th>Fuel burn-up in fuel element, MW.d/kgU</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21</td>
<td>300</td>
<td>53.7</td>
</tr>
<tr>
<td>2</td>
<td>0.47</td>
<td>480</td>
<td>54.1</td>
</tr>
<tr>
<td>3</td>
<td>0.24</td>
<td>367</td>
<td>56.2</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>370</td>
<td>59.2</td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>300</td>
<td>62.5</td>
</tr>
<tr>
<td>6</td>
<td>0.44</td>
<td>584</td>
<td>63.5</td>
</tr>
<tr>
<td>7</td>
<td>0.39</td>
<td>514</td>
<td>63.9</td>
</tr>
<tr>
<td>8</td>
<td>0.44</td>
<td>300</td>
<td>65.6</td>
</tr>
<tr>
<td>9</td>
<td>0.15</td>
<td>300</td>
<td>68.7</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>~70.3</td>
<td>~90.0</td>
</tr>
<tr>
<td>11</td>
<td>0.39</td>
<td>500</td>
<td>71.4</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>~91.4</td>
<td>~1.14</td>
</tr>
</tbody>
</table>

4.5. Metallographic examinations.

The specimens for the metallographic examination of fuel and claddings were cut from the bottom, central and top parts of three fuel elements NW 040, 40, 47. As mentioned above during irradiation the external surface of the fuel element cladding was subjected to the nodular corrosion. The nodular corrosion was characterized by the centres of the relative deep corrosion damage with
Fig. 5. The corrosion damage on the external surface and the view of hydride inclusions.

The dimension of corrosion centres ranged from 0.1 to 1 mm. Data on the number of centres over the cross-section, their extension, corrosion penetration etc. for various parts of the three examined fuel elements are given in Table 3.

<table>
<thead>
<tr>
<th>NH of fuel element</th>
<th>Fuel element section</th>
<th>Number of corrosion centres</th>
<th>Total extent of corrosion centres % from perimeter</th>
<th>Average corrosion penetration in centres</th>
<th>Average corrosion penetration over the perimeter</th>
<th>Maximum corrosion penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>bottom</td>
<td>59</td>
<td>3</td>
<td>54</td>
<td>21</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>centre</td>
<td>60</td>
<td>49</td>
<td>45</td>
<td>22</td>
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<tr>
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</tr>
<tr>
<td>0.40</td>
<td>bottom</td>
<td>26</td>
<td>28</td>
<td>51</td>
<td>14</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>centre</td>
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<td>58</td>
<td>48</td>
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<td></td>
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<td>23</td>
<td>53</td>
<td>12</td>
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<td>0.47</td>
<td>bottom</td>
<td>23</td>
<td>18</td>
<td>42</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>centre</td>
<td>31</td>
<td>49</td>
<td>47</td>
<td>23</td>
<td>110</td>
</tr>
<tr>
<td></td>
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<td>45</td>
<td>22</td>
<td>42</td>
<td>9</td>
<td>110</td>
</tr>
</tbody>
</table>

According to the results, the corrosion damage (column 6) grows with the increase of linear rating i.e. it increases from the fuel element ends to its centre. It should be noted that the corrosion penetration in the centres (column 5) is practically the same for all parts (of all rating levels) and the oxidation degree increased according to the increase of the numbers of the corrosion centres and their total extension (columns 3 and 4). The maximum depth of corrosion damage was 110 µm. The fuel element
Claddings were not practically subjected to the nodular corrosion in the zone of the plenum.

The hydride inclusions in the irradiated claddings have a small extension and favorable tangential orientation. The hydrogen content in the claddings was determined by analysing the specimens, cut from the bottom, central and top parts of the fuel elements with the automatic analyser of hydrogen RH-2 LECO (USA). The hydrogen content was for the bottom part - 0.0050 wt.%, for the central one - 0.0063 wt.%, for the top one - 0.0069 wt.%.

The microstructural investigations of the uranium dioxide showed that the dioxide recrystallization took place in the central sections of the fuel elements but the column zone was not formed. There was the diffusion uranium dioxide - cladding interaction in the separate zones along the perimeter of the pellets. The maximum width of the diffusion interaction layer made up 45 μm, the total extension of interaction in the cross-section did not exceed 3.5 mm (the internal perimeter of the cladding is 37 mm). Fig. 6 and 7 present the microphotos of the recrystallized uranium dioxide and the layer of the diffusion fuel-cladding interaction.

4.6. The mechanical properties of claddings.

The mechanical properties of the claddings were determined by the transversal tension of the ring 3 mm height specimens at 20 and 350°C. The specimens were cut from the bottom, central and top parts of fuel elements N 046, N 40, N 041, N 47. The results of the mechanical tests of the ring specimens are presented in Table 4.

Fig. 6. The microstructure of the recrystallized uranium dioxide.

Fig. 7. The layer of the diffusion fuel-cladding interaction.
TABLE 4. Results of the mechanical tests

<table>
<thead>
<tr>
<th>The place of cutting the specimens</th>
<th>Neutron fluence $10^{21}$ neut./cm$^2$ (E&gt;0.5 MeV)</th>
<th>Mechanical properties averaged by the fuel elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$</td>
<td>$\delta$</td>
</tr>
<tr>
<td></td>
<td>$G_\beta$</td>
<td>$\sigma$</td>
</tr>
<tr>
<td></td>
<td>$G_\alpha$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>$G_\sigma$</td>
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<tr>
<td>bottom</td>
<td>3.6</td>
<td>57.8</td>
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<td>53.3</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>31.2</td>
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<tr>
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<td></td>
<td>29.0</td>
</tr>
<tr>
<td></td>
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<td>10.7</td>
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<td>46.5</td>
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<td></td>
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<td></td>
<td>11.5</td>
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<tr>
<td>initial material</td>
<td>34.7</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.9</td>
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<td>10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.6</td>
</tr>
</tbody>
</table>

The mechanical properties of the claddings in the given parts of all the investigated fuel elements slightly differed from one another. Therefore Table 4 presents the mean values, obtained for all fuel elements. The irradiated claddings were sufficiently plastic, that supposes the possibility of their more extended operation. The strength of the claddings cut from the central parts of the fuel elements was less than ones cut from the ends. This difference may be explained in this way: the cross-section area of specimens cut from the central parts decreased in comparison with the nominal one (according to which the mechanical strength characteristics were calculated) as a result of the diametral deformation, corrosion damage and interaction with fuel.

CONCLUSION

The performed test and investigations showed that the 1% Nb-Zr alloy cladding material is capable to work for a long time under condition of the reactor irradiation in water-steam mixture, at the large ratings and numerous changes of power and temperature. The untightness of the fuel element (N 042) probably resulted from the deformation of the cladding under the internal pressure of gas fission products. The untightness was helped by the deformation localization in the thinned parts of the cladding, which were formed from the external corrosion and fuel interaction.

The performed experiment showed that in the fuel elements design intended for the extended operation and large burn-up, it is necessary to foresee the sufficient plenum and measures to prevent the diffusion fuel-cladding interaction.

Our thanks are extended to V.I. Vihrov, L.A. Goncharov, V.T. Kornev and L.M. Lebedev, working in the I.V. Kurchatov Institute of Atomic Energy for their efforts during investigations.
EVALUATION OF THE CLADDING INTEGRITY ON THE BASIS OF THE RADIATION SET-UP IN PRIMARY CIRCUIT OF PWRs

O. Bárta,
Nuclear Research Institute,
Reš

J. Běňa, V. Kapisovský
Research Institute of Nuclear Power Stations,
Jaslovské Bohunice

J. Smíško
Nuclear Power Station,
Jaslovské Bohunice

Czechoslovakia

Abstract

A part of the software package of an autonomous gamma spectrometry monitor of primary coolant is described. Computer code enables, on the basis of the analysis of the radiation set-up at the primary coolant at the steady-state conditions, which has been measured by "in-line" gamma spectrometry monitor, to estimate the total number of defective fuel rods and their deterioration.

The comparison of the DFE-code results to sipping test results after a fuel cycle of the 1st unit of the VI power station is presented.

1. Introduction

The primary coolant of the pressurized water reactors in operation is continually under surveillance. Periodic measurements of activity levels of main nuclides allow, among others, to detect the presence of defective fuel rods.

All checked methods of the fuel rods integrity during the power-reactor-operation are based on the analysis of the fission products activity in the primary coolant. Usual measuring methods of fission products activity levels suppose sampling of the coolant and following radiochemical analysis. Small number of measured nuclides and difficulties with quantitative description of their chemical behaviour at the balanced fuel-gap-coolant system do not permit to develop a reliable checking method which could give us both the information about the total number of failed fuel elements and about their damage range.

Therefore, in the same time, when the development of the continuous gamma-spectrometry monitor of primary coolant as a part of the radiation safety systems improvement was started, the software package was prepared, particularly for:

- fuel rods integrity-checking during the power-reactor-operation,
- prediction of the main fission products activity levels during transients.

Namely the "in-line" gamma spectrometry measurement of primary coolant of the PWR removes a great part of sampling methods imperfections. It enables to obtain nearly immediately information about the activity levels of a great number of various nuclides, not only radioiodine but rare gases too. Continuous watching of fission products behaviour facilitates to pick out the optimal time period for fuel rods checking, i.e. actually the steady-state conditions.

The application of the "in-line" gamma-spectrometry in the 1st unit of the VI power station /1/ together with the development of more sophistical model of the fission gas release /2,3/ and actual information about the application of similar methods /4/ allow to develop fast, simple, checking method of the fuel rods cladding integrity /5/.

2. Fuel rods checking method - DFE-code

The DFE-code supposes following basic simplifications:

- fission products redistribution in the balanced fuel-gap-coolant system is made up of i) the fission products release out of fuel, which can be described by the (R/B) ratio,
  ii) the mass transfer between the plenum of the failed fuel rod and primary coolant, which can be characterised by the rate constant Ygi,
  iii) the escape of fission products out of the primary coolant, that is given by the rate constant qf,
- all defective fuel elements at the core have the same linear power;
- each of the two groups of measured nuclides, i.e., volatile chemical reactive fission products and rare gases, has different rate constants Ygi and qf, but there is no difference among rate constants of nuclides from the same group;
- recoil is a predominant mechanism of the fission on products release from uranium-contaminated primary circuits surfaces.
Then the total activity of \( i \)-th nuclide in the primary coolant can be expressed by the equation

\[
\alpha_i^c = \frac{B_R y_i}{(\lambda_i + q_i)} \cdot \sum_{j=1}^{m} \frac{v_j^f}{v_j^c} \cdot \frac{y_j^f y_j^i}{(\lambda_j + q_j)(\lambda_i + y_j^f)} \cdot (R/B) \cdot \beta_j
\]

where

- \( \lambda_i^c \) = activity level of \( i \)-th fission product,
- \( y_i B_R \) = background release rate,
- \( V_j^f, V_j^c \) = volume of fuel in failed fuel rod, and coolant,
- \( y_j \) = cumulative fission yield,
- \( \lambda_j \) = decay constant,
- \( \beta_j \) = fission rate of defective fuel rod,
- \( m \) = number of failed rods.

The direct solution of balanced equations is not possible to obtain due to the unknowledge of some rate constants and different sensitivity of various nuclides to their change.

2.1 The estimate of the \((R/B)\) ratio

The \((R/B)\) ratios of volatile and gaseous fission products, that have been used in the DFE-code, were calculated by the microstructure-dependent model for stable and radioactive fission products release and swelling in uranium dioxide fuel - RELA /2,3/. In accordance with the experimental results /6/, the RELA-code considers, in the range of conditions of PWR's fuel elements, the diffusion the dominant mechanism of fission gas release.

Then during the steady-state conditions the \((R/B)\) ratio of short lived nuclides may be written as

\[
(R/B)_i = \frac{S}{V} \cdot \sqrt{\frac{D}{\lambda_i}}
\]

where \( D \) is diffusion coefficient, and \( S/V \) = surface to volume ratio.

The effective diffusion coefficient value has been calculated with using the three-components-single-gas-atom diffusion coefficient model, that has been developed from experiments on single crystal and small sinters of uranium dioxide by Turnbull et al. /8/. Without a great loss of accuracy this may be written as /6/

\[
D = 7.6 \cdot 10^{-10} \exp(-75000/T) + 1.41 \cdot 10^{21} \beta^{1/2} \exp(-13800/T) \cdot 2.0 \cdot 10^{-24} \beta^{1/2} \quad \text{(m}^2\text{s})
\]

where \( \beta \) is a fission rate and \( T \) = temperature.

The oxygen balance in the failed fuel is calculated too, and the increase of the O/M ratio is taken into account. The first component of the Turnbull's expression is correlated in accordance with Mathews and Woods approximation /9/.

The actual \( S/V \) ratio value depends both on the burnup and on the previous power history. The \( S/V \) ratio value has been calculated from empirical correlation between density and free surface of sintered uranium dioxide. The calculation of the fuel density actual value takes into account all important processes, as densification, grain boundary bubbles and open porosity, equiaxed and columnar grain growth etc.

The comparison of model prediction to experimental data is illustrated in fig. 1.

2.2 Mass transfer between gap and coolant

The emission of fission products by a pressurized-water-fuel-rod containing a defect was experimentally studied, using the pressurized water loops /10,11/. The results show that the release rate of fission products out of fuel is higher for failed pins than for the intact ones, but the transfer into the coolant is a function of thermal regimes in the gap, and the size and the location of the failure.

Practically in each the fuel rods there are unsteady thermohydraulic zones in which water is in a vapour state on the uranium dioxides surface and in the liquid state on the cold surface. If the equivalent diameter of the defect is relatively large (0.1 mm), the sustained coming and going of the coolant sweeps away the fission products. If the defect is "fine cracks" (\( < 1 \) \( \mu \)m) the unsteady regime occurs after any drop of pressure. Then the rod is filled with water, but after several hours or days this effect dies away.

At these conditions the quantitative description of the fission products transfer through the failure of cladding has not been possible. Taking into consider the measurable range of the rate constant \( y_{gi} \) the following simplification can be made:

- let only three types of defects be presented at the core; each type can be characterised by the fixed rate constant: the small one \( y_{g1} = 10^{-6} \text{s}^{-1} \), the middle one \( y_{g2} = 10^{-4.5} \text{s}^{-1} \) and the large one \( y_{g3} = 10^{3.3} \text{s}^{-1} \).
Fig. 1 Comparison of the MELA codes production of fission gas release to experimental data [11].

Fig. 2 The purification rate constant measurement - rare gases.

Fig. 3 The purification rate constant measurement - radionuclides.
This simplification allows to find out the damage distribution of failed rods, but only from the point of view of fission products emission rate.

2.3 The purification rate constant measurement

The last rate constant of the balanced equation for both groups of fission products can be obtained by "in-line" measurement of activity levels after the transients (see fig. 2 and 3). While the purification rate of volatile chemical reactive fission products at normal conditions can be calculated from the efficiency of the purification system, for the rare gases only the "in-line" measurement is possible.

The rate-constant $q$ value at the 1st unit of the VI power station was $2.73 \cdot 10^{-5}$ s$^{-1}$ for chemical reactive fission products, and $4.9 \cdot 10^{-6}$ s$^{-1}$ for rare gases.

2.4 The choice of suitable fission products

The group of volatile and gaseous fission products, which can be measured by continuous gamma-spectrometry is summarised in Tab. 1.

Table 1. Measurable fission products

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>Kr$^{85m}$, Kr$^{87}$, Kr$^{88}$, Kr$^{89}$</td>
</tr>
<tr>
<td>Rb</td>
<td>Rb$^{88}$, Rb$^{89}$</td>
</tr>
<tr>
<td>Te</td>
<td>Te$^{132}$</td>
</tr>
<tr>
<td>I</td>
<td>I$^{113}$, I$^{113m}$, I$^{113S}$, I$^{113T}$</td>
</tr>
<tr>
<td>Xe</td>
<td>Xe$^{133}$, Xe$^{133m}$, Xe$^{135}$, Xe$^{135m}$, Xe$^{137}$, Xe$^{138}$</td>
</tr>
<tr>
<td>Cs</td>
<td>Cs$^{134}$, Cs$^{137}$, Cs$^{138}$, Cs$^{139}$</td>
</tr>
</tbody>
</table>

Theoretically all isotopes mentioned above can be used for the fuel rod checking. However, the accuracy of the activity level measurements is necessary to take into account. This accuracy depends on the regime of power reactor (transient or steady-state) and on the complexity of the gamma spectrum. For example during the steady-state conditions the presence of a considerable amount of some corrosion products in the primary coolant (particularly Ag$^{110m}$) does not permit the measurement neither Cs$^{137}$ nor long-lived iodine (I$^{113}$ and I$^{113m}$), with reasonable accuracy.

Besides, only a part of the measured fission products has been sensitive to the change of $q$ rate constant. If their decay constant is greater than $10^{-3}$ s$^{-1}$ or less than $10^{-6}$ s$^{-1}$, they cannot be used for the fuel rods deterioration analysis, and are suitable for estimating either the level of contamination or the total number of failed fuel rods. Suitable fission products, which has been used for the fuel rods integrity checking are summarised in Table II.

Table II. Fission products suitable for continuous fuel rods checking (fission products, which are sensitive to the change of $q$ rate constant are underscored)

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>Kr$^{85m}$, Kr$^{87}$, Kr$^{88}$</td>
</tr>
<tr>
<td>Rb</td>
<td>Rb$^{88}$, Rb$^{89}$</td>
</tr>
<tr>
<td>I</td>
<td>I$^{113}$, I$^{113m}$, I$^{113S}$, I$^{113T}$</td>
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<td>Xe</td>
<td>Xe$^{133}$, Xe$^{133m}$, Xe$^{135}$, Xe$^{135m}$, Xe$^{137}$, Xe$^{138}$</td>
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<tr>
<td>Cs</td>
<td>Cs$^{134}$, Cs$^{137}$, Cs$^{138}$, Cs$^{139}$</td>
</tr>
</tbody>
</table>

2.5 Solution of balanced equations at the steady-state conditions

With regard to the previous simplifications and after introducing new formal unknown quantities

$$Y_i = A_i \frac{\lambda_i}{\lambda_1} + \frac{\gamma_i}{\gamma_1} \frac{X}{X} \quad \text{and} \quad X_i = \frac{\gamma_i}{\gamma_1} \frac{Y}{Y} + \frac{\gamma_1}{\gamma_1} \frac{X}{X}$$

the balanced equations can be transformed into the form

$$Y_i = n_0 + \sum_{j=1}^{3} n_j X_j$$

and can be solved by the multiple linear regression method for the unknown number of defective fuel rods with the defined type of the defect ($Y_i$).

3. Comparison of the model prediction to results of fuel rod checking during refuelling

The reliability of the developed method (DFE-code) has been tested in the 1st unit of the VI power station. On the basis of the fission products activity levels, which were measured by the "in-line" gamma-spectrometry
before and during the shut-down period, the estimate of the fuel rods cladding state was obtained. After calculation during the refuelling period all fuel assemblies were checked with using two independent methods, "in-core sipping" and standard "wet sipping".

3.1 Results of the DFE-code

Activity levels of volatile and gaseous fission products in the coolant during the time period immediately before the shut-down period, which were used for the checking by the DFE-code are given in the Table III.

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Activity (kBq/l) - 10.03.86</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>02.29</td>
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<tr>
<td>Xe 133</td>
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<td>Kr 85m</td>
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<tr>
<td>Kr 87</td>
<td>381</td>
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<tr>
<td>Kr 88</td>
<td>874</td>
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<tr>
<td>I 132</td>
<td>987</td>
</tr>
<tr>
<td>I 134</td>
<td>1725</td>
</tr>
<tr>
<td>I 135</td>
<td>894</td>
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</tbody>
</table>

The character of the radiation set-up in the coolant during this time period is shown in fig. 4. The slope of the curve of the dependence log (R/B)eff ~ log λ, including all mass-transfer processes taking part at the final fission products redistribution indicates the presence of the failed fuel rods in the core of the power reactor. The DFE-code predicts two failed fuel rods with the middle and small range of the damage. The estimate of the defective fuel rods burnup, which was obtained from the activity levels of Cs 134 and Cs 137 immediately after the transient condition (see fig. 5), indicates the presence of defective fuel elements in the fuel assemblies after the 3rd fuel cycle.

3.2 Results of sipping tests

The fuel assemblies checking during refuelling has been performed by two independent methods:
- "in-core sipping" with using KWU device, and
- standard "wet sipping" test.

The "in-core sipping" is based on the temporary increasing of fuel elements temperature (owing to worse heat transfer for a short time period) and following increasing of mass transfer between defective fuel element and coolant. The sample of coolant has been taken away and activity levels of various nuclides (I 131, Cs 134, Cs 137, etc.) have been measured.

By the standard "wet sipping" test, the fuel assemblies are removed from the core to the reactor's pool and located to the hermetic loop. The sample of the coolant, in which the activity levels of I 131, Cs 134 and Cs 137 are measured, is taken away after the drop of pressure.
Fig. 5 Development of the $A(\text{Cs}^{134})/A(\text{Cs}^{137})$ ratio after transient

Fig. 6 Results of the "in-core sipping" test - $^{131}I$

Fig. 7 Results of the "in-core sipping" test - $\text{Cs}^{134}$
All fuel assemblies were firstly checked by "in-core sipping". Results of the test are shown in fig. 6-8 /12/. After then suspicious fuel assemblies activity levels of which were outside the normal distribution (100–300 times higher than average values) together with a check set of fuel assemblies one by one were removed to the reactor's pool and tested by the standard "wet sipping" method. Results of measurements are summarised in Tab. IV.

<table>
<thead>
<tr>
<th>Table IV. Results of &quot;wet sipping&quot; test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assembly No.</td>
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<tr>
<td>1</td>
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<td>13</td>
</tr>
</tbody>
</table>

Both methods indicated the presence of failed fuel rod in two fuel assemblies. The burnup of these assemblies was 30981 MWD/tU and 28809 MWD/tU.

4. Conclusion

All used methods indicate, that only two of total number of fuel assemblies contain a defective fuel elements. The burnup of these assemblies was 30981 (MWD/tU) and 28809 (MWD/tU), respectively.

The DFE-code prediction, which was obtained on the basis of the analysis of radiation set-up immediately before shut-down period at the steady-state operation conditions, predicted the presence of two defective fuel elements at the fuel assemblies with a burnup about 29 000 - 31 000 (MWD/tU).

The comparison of results has shown the reasonable agreement between model prediction and real state of rods cladding. The available experimental techniques at the power station do not permit the visual check of failed fuel assemblies and failed fuel rods. Hence the entire verification of model prediction, taking into account not only the total number of failed fuel rods, but also the range of their damage, is not possible.
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/9/ Matthews J. R., Wood M. H., Stoner H. C.: AERE-M.3152
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LIST OF PARTICIPANTS

ARGENTINA
Mr. S. Harriagu*  
Comisión Nacional de Energía Atómica  
Av. Libertador 8250  
1429 Buenos Aires

BELGIUM
Mr. M. Lipptns  
Belgonucléaire  
rue du Champ de Mars, 25  
B-1050 Brussels

CZECHOSLOVAKIA
Mr. O. Bart*  
Nuclear Research Institute  
25068 Res near Prague  
c/o Czechoslovak Atomic Energy Commission  
Slezaska 9  
Prague 2

FRANCE
Mr. C. Lemaignan  
DNG/CEN Grenoble  
B.P. No 85  
Centre de Tri  
F-38041 Grenoble Cedex

Mr. O. Lavoine  
EDF  
12 Avenue Dutrievot  
F-69628 Villeurbanne Cedex

Mr. A. Chotard  
FRAGEMA  
B P. No 83  
119 Cour. Lafayette  
F-69398 Lyon Cedex 3

FEDERAL REPUBLIC OF GERMANY
Mr. H. Schönfeld  
Kraftwerk Union AG  
Selingenstädtstrasse 8  
D-8157 Karlsruhe

Mr. F. Garzarolli  
Kraftwerk Union AG  
Hammerbacherstrasse 12 + 14  
D-8120 Erlangen

GERMAN DEMOCRATIC REPUBLIC
Mr. H. Karl  
Zentralinstitut für Kernforschung  
Rossendorf  
PSF 19  
Dresden 8051

INDIA
Mr. P.K. De  
Metallurgy Division  
Bhabha Atomic Research Centre  
Modular Laboratories  
Trombay, Bombay - 400 085

JAPAN
Mr. Y. Mishima  
3-30-11 Matsunoki  
Suginami-ku  
Tokyo 166

POLAND
Mr. E. Szpunar  
Institute of Atomic Energy  
05-400 Swierk-Otwock

UNITED KINGDOM
Mr. M.V. Speight  
Central Electricity Generating Board  
Berkeley Nuclear Laboratories  
Berkeley, Gloucestershire

Mr. D.R. Tice  
UKAEA  
Springfields Nuclear Labs.  
Selwick  
Preston PR4 OXJ

Mr. P.A. Jackson  
British Nuclear Fuels plc.  
Springfields Works, Selwick  
Preston, Lancashire PR4 OXJ

USSR
Mr. G. Sukhanov  
Mr. V. Grigorev  
Mr. V. Shesternin  
State Committee on the Utilization of Atomic Energy  
Staromoskovsky perulok 26  
Moscow 109180

YUGOSLAVIA
Mr. R. Ilic  
"Joze Stefan" Institute Ljubljana  
Jamova 39  
P08 100  
61111 Ljubljana