IMPACT OF REACTOR WATER CHEMISTRY ON CLADDING PERFORMANCE

B. COX

Centre for Nuclear Engineering
University of Toronto
184 College St.,
Toronto, ON. M5S 3E4

ABSTRACT:

Water chemistry may have a major impact on fuel cladding performance in PWRs. If the saturation temperature on the surface of fuel cladding is exceeded, either because of the thermal hydraulics of the system, or because of crud deposition, then LiOH concentration can occur within thick porous oxide films on the cladding. This can degrade the protective film and accelerate the corrosion rate of the cladding. If sufficient boric acid is also present in the coolant then these effects may be mitigated. This is normally the case through most of any reactor fuel cycle. Extensive surface boiling may disrupt this equilibrium because of the volatility of boric acid in steam. Under such conditions severe cladding corrosion can ensue. The potential for such effects on high burnup cladding in CANDU reactors, where boric acid is not present in the primary coolant, is discussed.

INTRODUCTION

CANDU reactors use a standard (i.e. 1.5%Sn) Zircaloy - 4 cladding, without any specific adjustments to other alloying additions to improve its corrosion resistance and hydrogen uptake. This cladding had proved eminently satisfactory for the typical lifetime of about one year, and the relatively low outlet temperature (~ 310°C) compared with PWRs. Hydrogen uptakes have been sufficiently low that the thin wall (0.4mm) of CANDU cladding compared with PWR cladding (≥0.6mm) has not resulted in hydrogen embrittlement problems. This has been true despite observations of locally high hydrogen concentrations in braze and weld heat affected zones. Proposals to burn plutonium or slightly enriched uranium in CANDU reactors could raise the burnup at end of life to 20,000 MWd/te or higher. Under these conditions, would we expect any phenomena that might limit the fuel lifetime to appear?.

The water chemistry in CANDU reactors is ~pH 10.5 LiOD in D_2O. If boric acid is needed to control the overall core reactivity it is added to the moderator and not to the primary coolant. In this respect, therefore the CANDU fuel cladding sees a very different water chemistry from that of typical PWR fuel cladding. During a typical fuel cycle in a PWR, depending on the expected cycle length, the initial boric acid concentration in the primary water can range from 1000-2000 ppm B. To minimise the initial boric acid concentration for long cycles (and thereby minimise the LiOH concentration that must be added to maintain an alkaline pH) some utilities are now using enriched ^{10}B [1]. It has been known for a long time that concentrated LiOH solutions severely degrade the corrosion resistance of Zircaloy cladding [2-6] and the protective effects of boric acid. against this attack, were demonstrated ten years ago [7,8.].

Typical reactor water chemistries operate at LiOH concentrations several orders of magnitude below those where effects of degradation by LiOH begin to appear, so that a major concentrating mechanism would be necessary before any adverse effect of LiOH might be expected. This concentration can be most readily achieved by boiling heat-transfer in the presence of thick porous oxide films on the Zircaloy cladding. The elevation of the boiling point by LiOH is sufficient that a 5°C temperature rise above the saturation temperature across a porous oxide film would be sufficient to produce a 1.0 molar LiOH solution at the bottom of the pores [9]. Depending upon the heat flux, and the morphology of the pores in the oxide, this might be achieved once the oxide film was thicker than about $10\mu m$. However, if the boric acid were equally concentrated by the same process then it might still protect the oxide on the cladding from degradation. Boric acid is volatile in steam, unfortunately, so that extensive surface boiling, particularly in the second half of a fuel cycle when bulk boric acid levels have been reduced to low values, might deplete the boric acid at the oxide surface to the point where no protection was provided. Low concentrations of boric acid in concentrated LiOH give worse corrosion than no boric acid [8].

One situation where serious corrosion may have resulted from concentration of LiOH and depletion of boric acid may be the high outlet temperature Siemens KONVOI plants, where extensive subchannel boiling is present [10]. Enhanced corrosion begins at the onset of boiling at an oxide thickness of $\sim 10\mu m$ and a burnup <20,000MWd/te (figure 1). Siemens, however, have an explanation based on the formation of solid hydride layers at the cladding surface on the oxidation rate [11]. However, there is no good evidence for a large enough effect of hydride to explain this or for the presence of solid hydride layers before the acceleration of corrosion. Could such effects appear in high burnup CANDU fuel?.

MECHANISM OF LiOH AND H_3BO_3 EFFECTS

We have concentrated our efforts on understanding the mechanisms by which LiOH degrades ZrO_2 films (figure 2), and H_3BO_3 (figure 3) protects them [12-15]. These mechanisms seem to be very simple, and the basis of them can be readily understood.

- Zirconium oxide films on the Zircaloys consist of a mixture of nanocrystallites of monoclinic -ZrO_2 and tetragonal -ZrO_2. The monoclinic-ZrO_2 is the stable form at reactor temperatures; the tetragonal form must be stabilised by compressive stresses, impurities (eg. Fe) or a combination of the two. Because of the compressive stresses that develop in zirconia films the oxide crystallites develop a columnar texture with the long axis normal to the specimen surface. The column diameters remain in the range 20-50nm at reactor temperature, while the length may 0.5-1.0μm.

- Above a critical LiOH concentration (~ 0.1 Molar) the t-ZrO_2 crystallites are almost completely dissolved at 300-350°C to give pores that penetrate essentially right through the oxide (figure 4). Below this critical concentration dissolution occurs at the surface to form an array of superficial pores (figure 5).

- At high concentrations boric acid precipitates a bulky lithium zirconate/borate that plugs the holes when its solubility product is exceeded (figure 6). Incomplete plugging (at low boric acid concentrations) can restrict interdiffusion of the solution in the pores with the bulk solution to give higher LiOH concentrations in the pores, and higher corrosion rates (figure 7) than when there is no boric acid present.

- Other minor phases that may be present in the oxide films (iron and chromium oxides or silica) are not known at present to play a significant part in the oxide degradation process in LiOH solutions, but may be more significant in pure water because of their higher solubility than ZrO_2. Niobium oxide crystallites may perform a similar role in oxides on pressure tubes [16].

IMPORTANCE OF VARIOUS OTHER FACTORS

A number of other factors have been argued to be important in Zircaloy corrosion. Not all of them now seem to be so important.

Fast Neutron Irradiation. Direct effects of fast neutron irradiation on the corrosion process have never been found to be large, compared with the effects of concentrated LiOH [17]. They may become more important in pure water environments (eg. BWR conditions), and local dissolution of disordered primary knock-on spikes has been suggested as a mechanism for such a direct effect, but at present it appears to be possibly only a small contributor [18].

Indirect effects of irradiation, for instance by redistributing alloying elements like iron, have small effects on the post-irradiation corrosion rate [19]. Since Fe appears able to migrate fairly readily in the oxide anyway, the irradiation induced migration of Fe may not result in a large factorial increase in oxidation rate in-reactor.

Dissolved Oxygen or Hydrogen in the Water. The big difference in Zircaloy corrosion behaviour between oxygenated (BWR) and hydrogenated (PWR) water chemistries have often been blamed on direct effects of radiolytic oxygen species. There is still no well established explanation for these differences [20], and oxygen or hydrogen overpressures have only minor effects on corrosion rates in concentrated LiOH solutions [21]. Synergistic effects of LiOH and F^- on corrosion are present only in hydrogenated solutions and are absent in oxygenated solutions [22]. Specimens exposed in the laboratory to LiOH + F^- solutions show "blister" type oxide failures very similar to those reported for PWR cladding [23, 24]. F^- is produced in reactors in small quantities.

Crud Deposition. Fuel failures as a result of crud deposition do not necessarily require a very large temperature rise through the crud. Raising the cladding surface temperature above saturation could concentrate LiOH enough to lead to failures [25, 26].

SOLUTIONS

Because excessive corrosion of fuel cladding depends on several factors there are several possible approaches to ameliorating the situation:-

Improved Zircaloy - 4. Most fuel vendors have adopted an "improved" or "adjusted" version of Zircaloy-4 to deal with moderately severe operating conditions. This remains within the Zircaloy-4 specification, thus simplifying regulatory approval. For an "improved" Zircaloy-4 the tin content is usually held at the low end of the specification (1.3% Sn), Fe and Cr are held at the upper end of the specification and impurities such as Si and C are controlled in a narrow band. Cladding of this type does not perform well under severe conditions (figure 1) [11].

New Zirconium Alloys. For severe conditions most vendors have now developed new alloys. Most experience has been obtained with ZIRLO (1% Sn, 1% Nb, 0.1% Fe) a variant of the Russian alloy 635 developed by Westinghouse (figure 8) [27]. Siemens have developed an extra low tin (ELS) alloy with 0.8% Sn and 0.4% Fe, used as a duplex cladding because of its low mechanical strength [11]. A number of other new alloys are at earlier stages of development [29].

Change to KOH/NH_4OH Water Chemistry. The Russians obtain very low oxide thicknesses and hydrogen contents in VVER 1000 plants with Zr-1% Nb alloy cladding (figure 8) and a KOH/ammonia water chemistry [30]. Zr-1% Nb often behaves poorly in LiOH chemistry; it is not known whether low tin Zircaloy-4 will behave better in KOH/ammonia than in LiOH. This will be tested in the first core of Temelin-1 (Czech Rep.).

Add Boric Acid to CANDU Coolant. If protection by boric acid is a key part of the satisfactory behaviour in PWRs then separated ^{11}B could be used in CANDU.

Don't Boil. This might involve too high an economic penalty, but should be considered an option.

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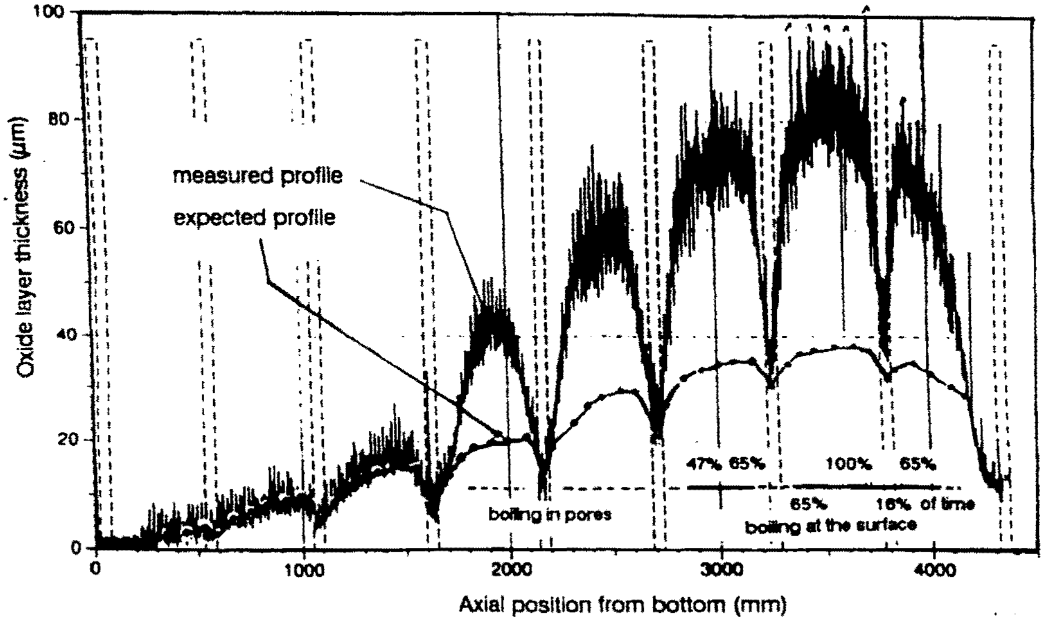

FIGURE 1. ACCELERATED CORROSION OF A FUEL ROD EXPOSED FOR TWO CYCLES IN A PWR [10]

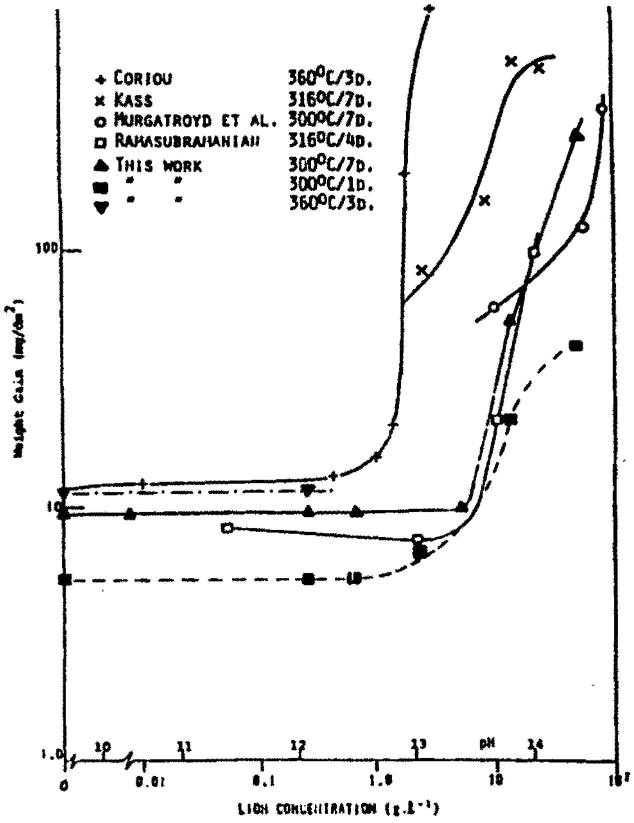

FIGURE 2. ACCELERATION OF CORROSION BY LiOH [12]

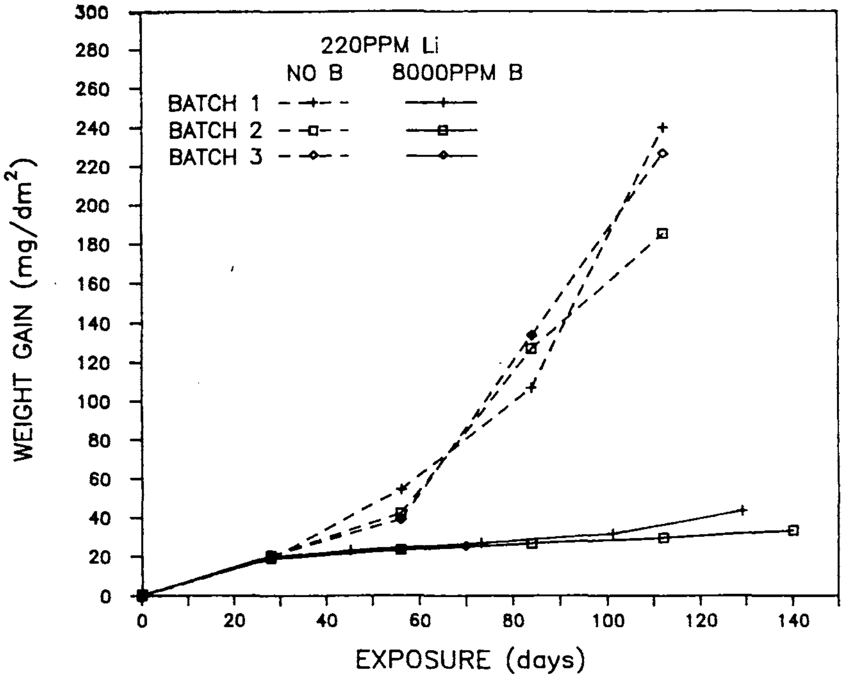

FIGURE 3. INHIBITION OF LiOH EFFECT BY H_3BO_3 AT 360°C [8]

FIGURE 4. HOLES PENETRATING THROUGH OXIDE AFTER 1 DAY IN lM.LiOH [15]

(SUPERFICIAL PORES SHOW ONLY SLIGHT CONTRAST IN THE BACKGROUND)

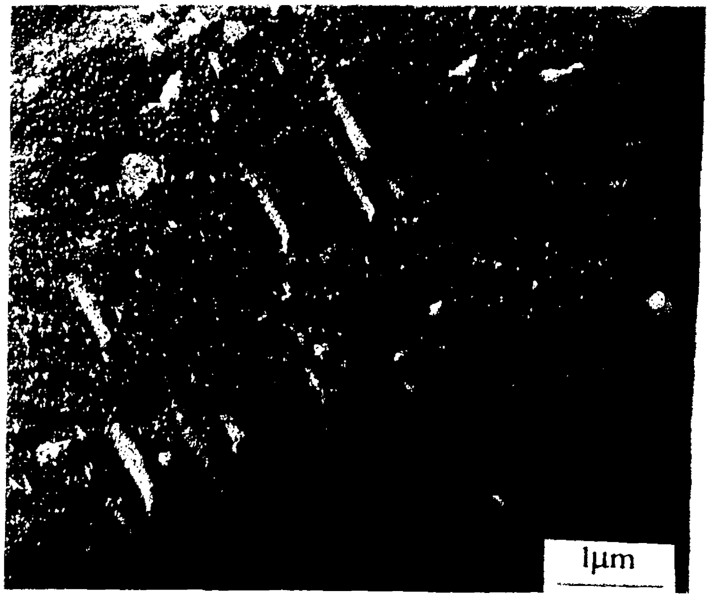

FIGURE 5. SUPERFICIAL PORES FORMED IN OXIDE IN pH13 LiOH, 360°C [13]
(TEM REPLICA OF SURFACE)

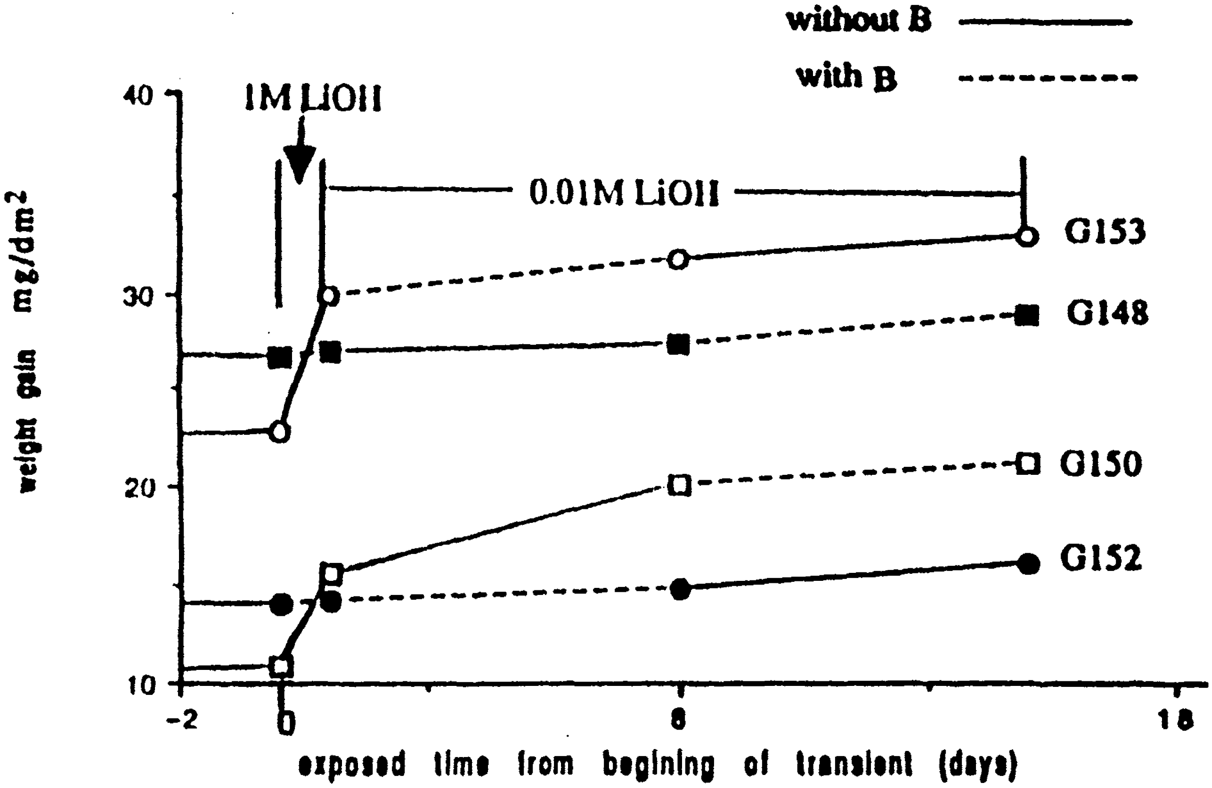

FIGURE 6. ELIMINATION OF TRANSIENT CAUSED BY t-ZrO_2 DISSOLUTION WITH H_3BO_3 ADDITION [14]

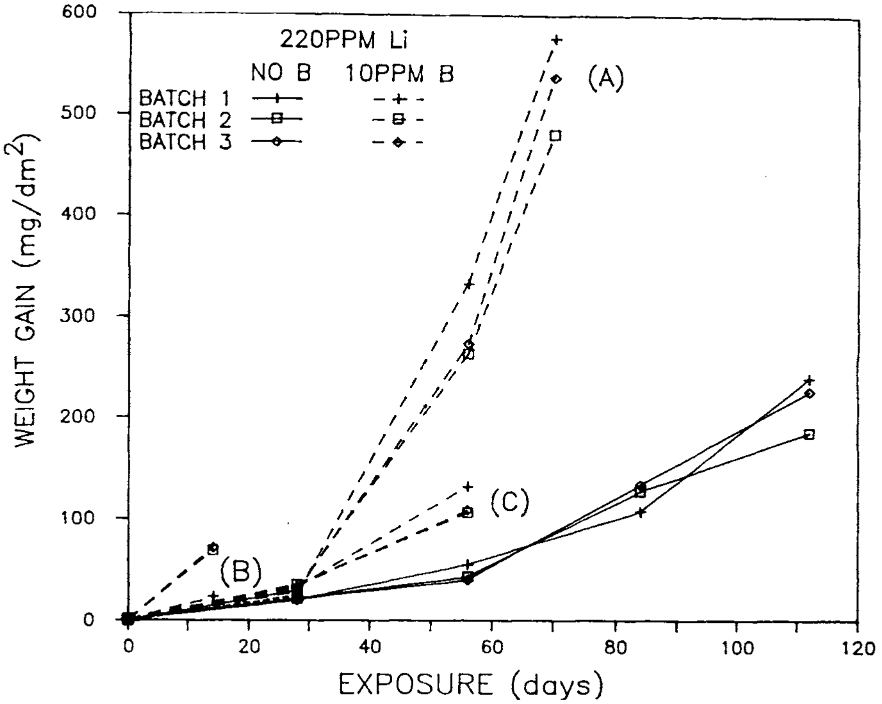

FIGURE 7. HIGHER CORROSION RATE WITH INSUFFICIENT H_3BO_3 THAN WITH NONE [8]

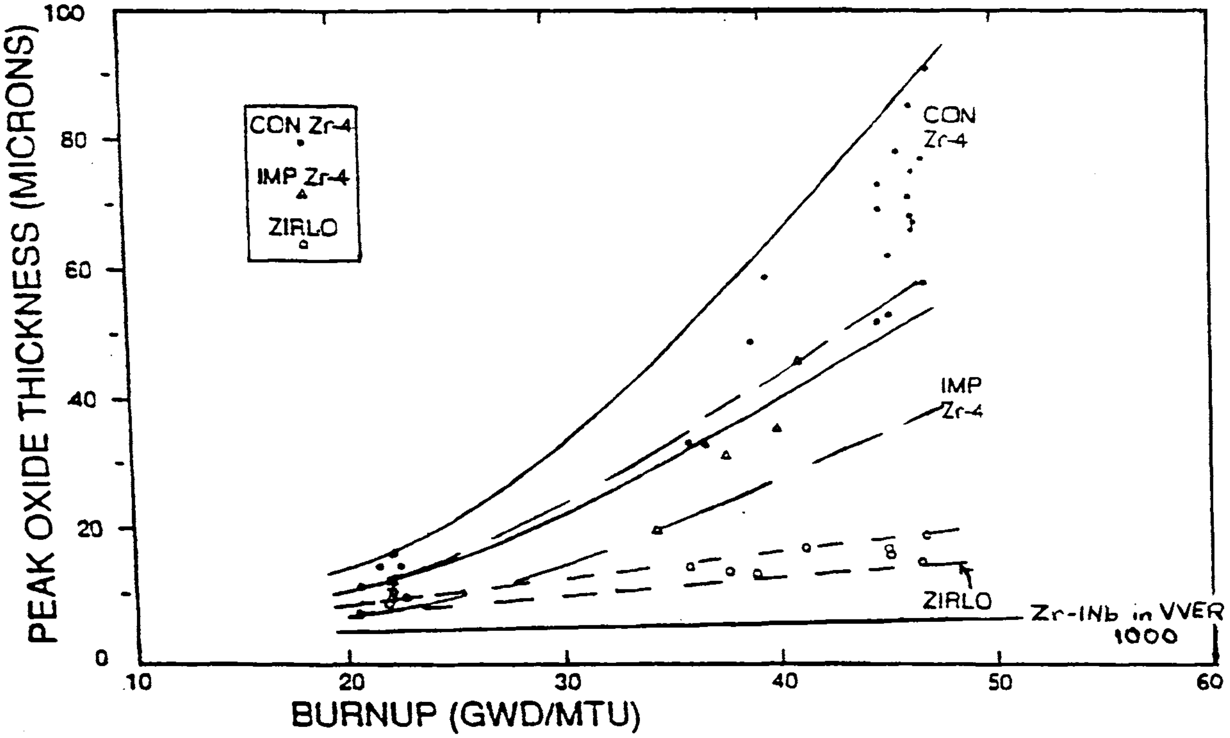

FIGURE 8. IMPROVED BEHAVIOUR OF ZIRLO COMPARED WITH ZIRCALOY-4 IN MILLSTONE-1, AND Zr-INb DATA FROM A VVER-1000