SPANISH INVESTIGATION OF AXIAL OFFSET ANOMALIES AOA

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Axial Offset Anomalies (AOA), observed in some PWR Nuclear Power Plants due to boron compound precipitation on the fuel rod surface, have very important economic (cycle length reduction, power limitations, ...) and safety implications (shutdown margin reduction, operational problems, ...).

An experimental project has been jointly initiated by ENUSA Industrias Avanzadas, S.A. and three Spanish Utilities (IBERDROLA GENERACION S.A., ASOCIACION NUCLEAR ASCO-VANDELLÓS II A.I.E. and A.I.E. CC.NN. ALMARAZ-TRILLO). The objective of the activities that are being performed in Studsvik Nuclear AB Laboratories in Sweden is to check out experimentally the basic mechanisms that take place, which will help to understand the AOA phenomenon as well as to define ways to minimize it. This article summarizes the most important results and future research plans.

INTRODUCTION

The small radial and axial power anomalies that occur in some Spanish PWR reactors, as well as much more important axial anomalies (Axial Offset Anomalies, AOA) that we know of in some American PWR reactors, led us in 1993 to study this problem.

To do so, various operating data from six cycles of five different Spanish PWR plants were correlated: boron concentration, Axial Offset (AO) measured ex-core and in-core, measured pH, pH calculated as a function of boron, lithium and coolant temperature.

Considering that a three-dimensional distribution of the local temperature produces a three-dimensional local distribution of the pH, a detailed analysis of all these data led us to formulate a new assumption to explain the anomalous behavior of the AO and boron concentration:

"When there is boron in the coolant, and the pH (function of the boron, lithium, temperature, ...) exceeds a threshold value (between 7.2 and 7.4), some mechanism causes precipitation of the coolant boron in the deposits on the fuel rod surface (crud). When this coolant pH falls below this threshold, the boron redissolves in the coolant."

It is also known that operation below a pH (Taverage) of 6.9 is not recommended because it decreases the solubility of the in-core corrosion products (ferrites and nickel-ferrites), which can result in a greater buildup of crud.

Therefore, we should seek a new mechanism responsible for the formation of crud when plant operation causes the coolant pH value to go above a certain threshold by considering another class of corrosion products. These deposits include boron compounds.

SUMMARY OF THE PROPOSED THEORY

According to the two current official theories, the root cause of AOA is boron deposition in the crud that has previously formed on the fuel rod surfaces. Three conditions are necessary for this to happen:

- Subcooled boiling conditions around the rod.
- Presence of corrosion products in the coolant.
- Presence of boron in the coolant.

Subcooled boiling accelerates corrosion products deposition in the fuel rods. When the crud is sufficiently thick and porous, evaporation occurs at the steam-liquid interface within pores in these deposits. Surface tension forces reduce pressure on the liquid side, drawing liquid into the deposit. Evaporation concentrates chemical species within the crud deposit.

The two theories differ only in the boron deposition mechanism. The first is precipitation of lithium metaborate ($LiBO_2$), which has retrograde solubility with temperature. But a very high concentration factor is needed for precipitation to occur. The second boron deposition theory is boric acid physisorption, in which non-ionic H_3BO_3 (or perhaps the borated anion) is physically adsorbed onto porous crud. This mechanism also requires a local (near-clad) boric acid concentration.

The most important experiments on the root cause of AOA based on these theories, carried out in the last 4 years as part of the EPRI RFP (Robust Fuel Program), have failed in two fundamental ways:

- They have not been capable of laboratory precipitation of the "typical" deposits observed in plants with AOA (achieving neither the quantity nor similar characteristics).
- And in experiments with previously deposited crud (thick and porous), they have not been capable of precipitating the boron compounds.

The new theory proposed by ENUSA to explain Axial Offset Anomalies (AOA), the boron hideout that has been observed in some PWR reactors and some localized corrosion process in these reactors, has already been presented in Spain and in some

international meetings (Refs. 1, 2, 3 and 4) and is briefly described below:

Precipitation of metallic cations in a PWR (especially nickel cations) in the form of hydroxides, when the local pH exceeds the threshold precipitation pH, can cause two significant effects:

- Co-precipitation of some boron ions. This would lead to formation of lithium metaborate in the fuel crud and could be the cause of the Axial Offset Anomalies (AOA) observed.
- Precipitation of the hydroxide occurs locally if the pH is higher than this threshold and if the hydraulic conditions are favorable for production of this deposit (subcooled boiling, laminar flow, zones with stagnant or little forced flow, ...). In these zones, the local pH would drop abruptly (on forming an occluded cell between the precipitates and the fuel cladding, Ref. 5) and could cause localized acid corrosion with dissolution of metal and production of hydrogen (H_2).

Based on this theory, the most advisable short-term primary chemistry strategy to prevent AOA from occurring would be to keep pH below the threshold pH of precipitation but always higher than the lower limit of 6.9. It is also preferable to keep a constant pH so that the metallic cations that form in the first part of the cycle remain in the coolant, thus preventing their precipitation on the fuel and other metal surfaces.

AOA SPANISH EXPERIMENT

These Axial Offset Anomalies (AOA) also have major safety implications (Ref. 6), such as a reduced shutdown margin and other operational and also economic problems, e.g. shortened cycle length or power reductions required to recover the safety margins.

For this reason, ENUSA Industrias Avanzadas, S.A., in collaboration with the Spanish utilities IBERDROLA GENERACION S.A., ASOCIACIÓN NUCLEAR ASCÓ-VANDELLÓS II A.I.E. and A.I.E. CC.NN. ALMARAZ-TRILLO, has been developing a testing program since 2001 in Studsvik Nuclear AB Laboratories in Sweden in order to discover the causes of these anomalies and the ways to prevent them.

This project's primary purpose is to experimentally check out the basic mechanisms that control the occurrence of the AOA phenomenon according to the theory proposed by ENUSA. Therefore, the project would fit in with the objectives of the Robust Fuel Program (Working Group 1, WG1) in its search for the root cause of AOA, and with those of WG4 to determine the failures caused by localized corrosion in TMI, Seabrook and Palo Verde.

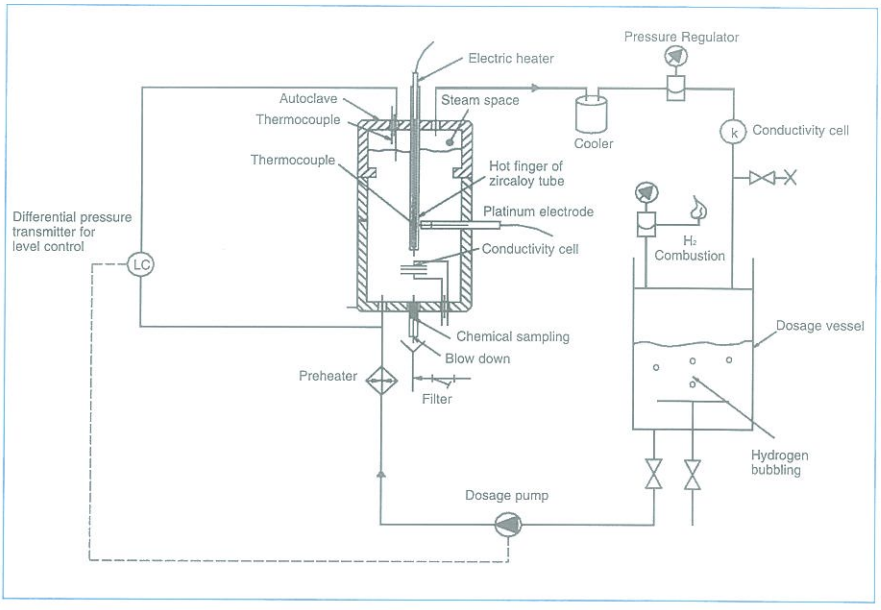

Figure 1. Phase 1 Autoclave System Illustration

RESULTS OF THE FIRST PHASE

The experimental tests are performed by simulating the operating conditions of a PWR reactor in an autoclave. Heated fuel claddings are used. The formation of precipitates related to the AOA phenomenon is tracked online. When this formation is detected, the precipitates are separated under operating conditions (hot blow-down) and subsequently analyzed by SEM/EDS (Scanning Electron Microscopy/Energy Dispersive Spectroscopy), XRD (X-Ray Powder Diffraction) and LSR (Laser Raman Spectroscopy).

Figure 1 shows a diagram of the autoclave system used for this first phase. This phase of the experiment was concluded in late 2001 with very promising results (Ref. 7). In this phase, tests were performed with and without the presence of boiling, and the online conductivity measurements confirm phenomena of formation and redissolution of precipitates containing lithium and boron.

Without boiling, only the formation of a deposit containing a small quantity of boric acid has been observed. Extensive precipitation of lithium borates ($LiBO_2$ and $Li_2B_4O_7$) is observed under conditions of boiling, high pH and low potential, and to a lesser degree under conditions of subcooled boiling, high pH and high potential (Figure 2).

Under conditions of subcooled boiling and high potential and pH, nickel oxide (NiO) is precipitated in significant quantities in the presence of oxidant concentrations.

These results indicate that the formation of lithium borates depends on the boiling conditions and pH value, and that it is less sensitive to the electrochemical potential of water. $LiBO_2$ precipitation seems to be very dependent on the boiling and subcooled boiling conditions if the pH is high enough because, if it is not, lithium and boron compound precipitation phenomena are not observed even if there is boiling.

SECOND PHASE

On the basis of these results, the decision was made to carry on with a second phase of the experiment, the purpose of which would be to test, also on a surface previously covered with a layer of crud, the precipitation mechanisms of boron and nickel compounds and their influence on the AOA phenomenon.

The aim was also to obtain the threshold pH at which these boron compounds are precipitated and to study the influence of Ni^{2+} concentrations in this process. Some windows were provided in the autoclave in this second phase for purposes of the online Laser Raman Spectroscopy (LRS) measurements and display.

Figure 2. Photograph of Lithium Borate Deposits

much higher than in the previous deposit.

There are now plans to carry out parametric studies to assess the influence of pH and Ni^{2+} on the formation of these precipitates, both on clean rods and on previously crudded claddings. These experiments are due to be concluded around February 2004.

POSSIBLE AOA SOLUTIONS (THIRD PHASE)

In view of the results obtained to date and the capacities of the experimental device used, a preliminary programming of experiments for a third phase (2004-2005) has been drawn up in collaboration with EPRI experts (Ref. 10).

In addition to the current Spanish partners, this phase will be co-funded by the EPRI Robust Fuel Program (RFP).

This third phase has been divided into 3 parts:

1) AOA mitigation experiments with the use of enriched boric acid (EBA):

These experiments are intended to verify whether or not the use of enriched boron in isotope B-10 helps to mitigate or prevent AOA. The experiments will be performed with previously crudded rods.

2) AOA mitigation experiments based on the use of potassium hydroxide:

Since potassium borates are much more soluble than lithium borates, it may be possible that the use of potassium hydroxide instead of lithium hydroxide to control the pH in PWR reactors can help to mitigate or prevent AOA problems. Experiments with clean rods and with previously crudded rods are planned.

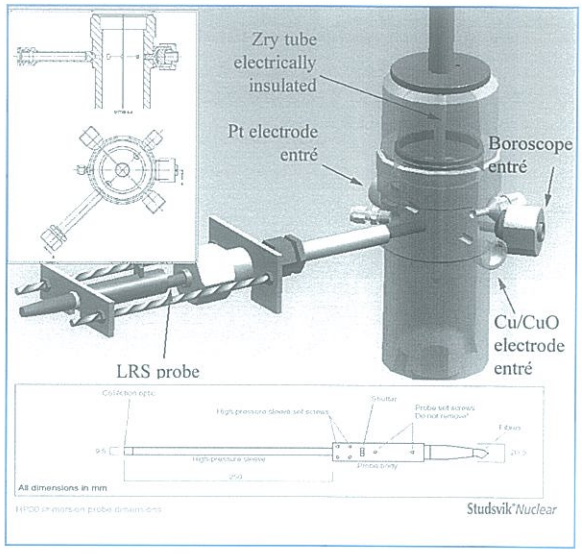

Figure 3. Illustration of the Second Phase Autoclave Window System.

The phase 1 devices have continued to be used in this second phase, together with specific devices for visual observation and LRS measurements. In addition, an electrochemical potential control loop has been added to keep the potential during the experiments around values similar to those produced inside PWR reactor cores (Ref. 8).

Figures 3, 4 and 5 give an idea of the complex experimental device that is used in this second experimental phase.

Several rods were previously prepared with a crud-covered surface. This crud has been characterized to confirm that it meets a series of minimum thickness and porosity requirements.

First of all, the experiment performed under conditions of subcooled boiling and high pH has been repeated in a way similar to the first phase but on a cladding that has a specific crud thickness.

The results of this first experiment are as follows (Ref. 9):

- The precipitates that occur are not easily detected either visually or using the online LRS system. Certain changes must be made to improve the sensitivity of the Raman system.
- Examination of the precipitates on the cladding surface, after the hot autoclave blow-down, shows clear evidence of the presence of lithium, boron and oxygen compounds, although to a lesser extent that on a clean rod.
- It has also been verified that the resulting nickel content of the crud is

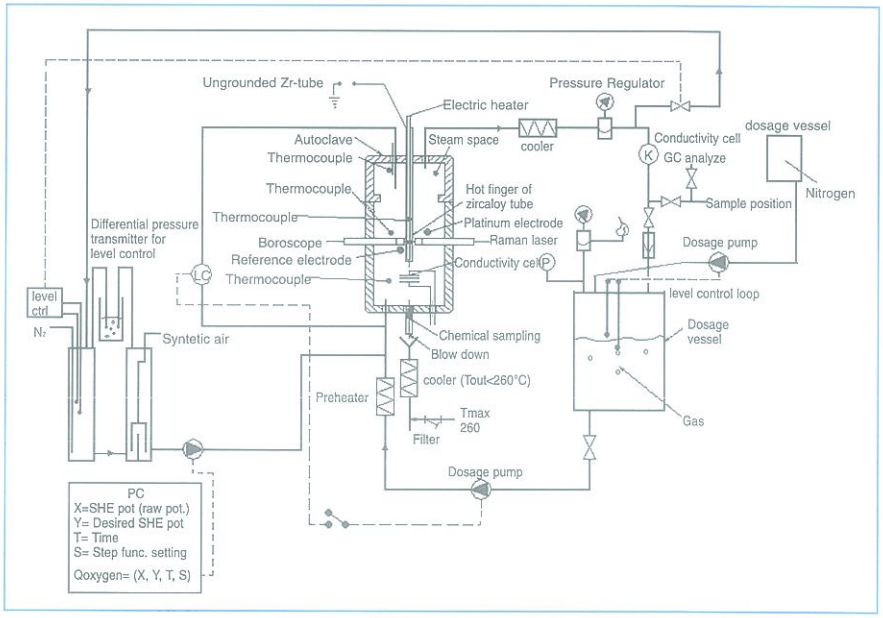

Figure 4. Illustration of the Second Phase Experimental Device.

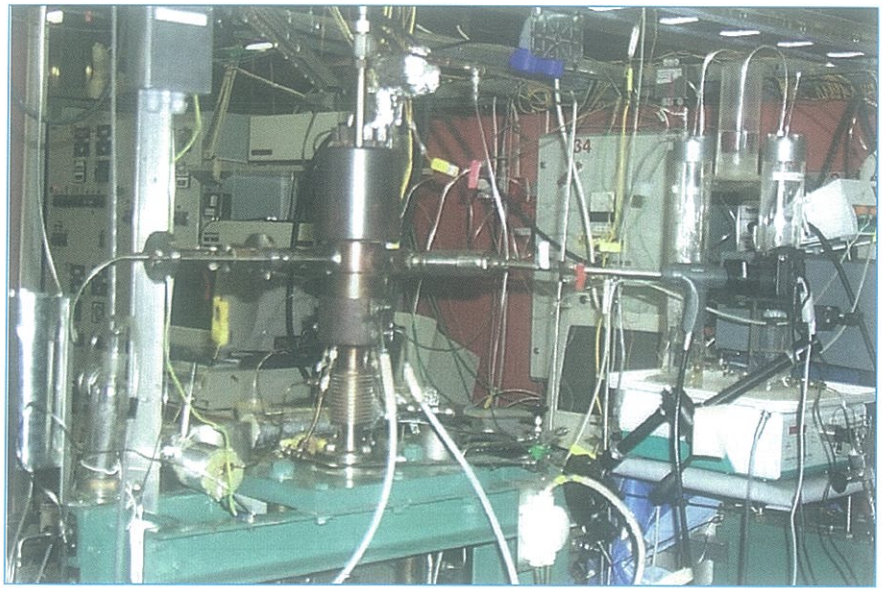

Figure 5. Photograph of a Part of the Second Phase Experimental Device.

Since the use of KOH under reactor irradiation conditions results in small amounts of LiOH, experiments with a mixture of both compounds are also planned.

3) Experiments with zinc injection:

Zinc injection is used in both BWR and PWR reactors to reduce dose rates. However, we want to confirm with these experiments if zinc could play a role in the reactor core similar to the role we believe that nickel plays, which would mean it could increase the risk of axial anomalies.

CONCLUSIONS

This experimental program has demonstrated how to precipitate certain boron compounds under some typical PWR reactor conditions and what some of the most important factors are that contribute to these precipitations (pH and boiling).

Therefore, we are in the process of discovering the mechanism that causes the occurrence of Axial Offset Anomalies (AOA).

In addition, once the mechanism whereby boron is precipitated is known, we have the most suitable experimental tool for testing mitigation strategies for this problem.

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