



**WARNING:**  
Please read the License Agreement  
on the back cover before removing  
the Wrapping Material



# Potassium Hydroxide

*A Potential Mitigation for AOA*

**TE-114158**

Effective December 6, 2006, this report has been made publicly available in accordance with Section 734.3(b)(3) and published in accordance with Section 734.7 of the U.S. Export Administration Regulations. As a result of this publication, this report is subject to only copyright protection and does not require any license agreement from EPRI. This notice supersedes the export control restrictions and any proprietary licensed material notices embedded in the document prior to publication.



# **Potassium Hydroxide**

*A Potential Mitigation for AOA*

TE-114158

Technical Review, December 1999

EPRI Project Manager

P. Frattini

## **DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES**

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

**George P. Sabol, Consultant**

## **ORDERING INFORMATION**

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (800) 313-3774.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 1999 Electric Power Research Institute, Inc. All rights reserved.

## CITATIONS

This document was prepared by

George P. Sabol, Consultant.  
37 Morris Street  
Export, PA 15632

Principal Authors

G.P. Sabol.

J. Philippe Berge, Consultant

M. Kenneth Johnson, Duke Power Corp.

This document describes research sponsored by EPRI.

The publication is a corporate document that should be cited in the literature in the following manner:

*Potassium Hydroxide, A Potential Mitigation for AOA*, EPRI, Palo Alto, CA: 1999. TE-114158.



## EPRI PERSPECTIVE

The original EPRI axial offset anomaly (AOA) root cause analysis (TR-108320, 6/97) suggested that AOA in pressurized water reactors (PWRs) occurs when the accumulation of slightly soluble boron salts on fuel surfaces acts to depress the local neutron flux. The less-soluble borates can precipitate under sub-cooled boiling heat transfer conditions, due in principle to boiling concentration within porous corrosion deposits on the fuel. The most probable species is lithium metaborate ( $\text{LiBO}_2$ ) since this compound is least soluble of the common lithium/boron salts. Besides its low solubility, the solubility is also inversely related to temperature, thus the likelihood of precipitation increases at higher temperatures. Lithium is always present at some concentration in the PWR primary coolant as a result of the  $(n,\alpha)$  reaction on  $^{10}\text{B}$ . But when  $\text{LiOH}$  is used for pH buffering, its concentration may be high enough locally near the cladding to precipitate the metaborate salt.

Some reactor types, notably the Russian-designed VVER reactors, use potassium hydroxide,  $\text{KOH}$ , instead of  $\text{LiOH}$  to adjust the primary coolant pH. These plants have not experienced AOA. Several reasons have been postulated for this observation, including the decreased likelihood of precipitating  $\text{KBO}_2$ . The potassium salts of boron are much more soluble than the lithium salts, and also exhibit a “normal” solubility curve, i.e., increasing solubility with increasing temperature. It is therefore of interest to investigate the consequences of a switch to potassium chemistry for control of AOA in US-designed PWRs.

This report examines issues that would arise in converting from lithium to potassium chemistry, including effects on fuel cladding, steam generator and reactor vessel internal materials, CVCS operation, and impact on fuel deposits. The report concludes that Western PWRs could adopt  $\text{KOH}$  chemistry pending further investigation of unknown effects, viz.:

- a) Effect of  $\text{KOH}$  on steam generator tube PWSCC,
- b) Effect of  $\text{KOH}$  on SCC of baffle/ and barrel/former bolts,
- c) Solubility characteristics of mixed cation ( $\text{Li}^+/\text{K}^+$ ) borate solubility characteristics, and
- d) CVCS operability under  $\text{KOH}$  chemistry in candidate test plants, particularly with respect to maintaining Li control.

Since  $\text{KOH}$  currently offers the only potential chemistry-based solution to AOA caused by  $\text{LiBO}_2$  hideout, efforts should be stepped up to answer the above questions. Some of these issues may well be addressed inexpensively through loop studies, while others may require more elaborate test programs at candidate demonstration plants.





# **CONTENTS**

<b>ACKNOWLEDGEMENTS.....</b>	<b>ix</b>
<b>ABSTRACT.....</b>	<b>1</b>
<b>1. INTRODUCTION.....</b>	<b>1</b>
<b>2. SOLUBILITY COMPARISONS OF LI AND K-BORATES .....</b>	<b>2</b>
2.1 LITHIUM BORATE .....	2
2.2 POTASSIUM BORATES .....	2
<b>3. CONSIDERATION FOR KOH USAGE FOR PH CONTROL .....</b>	<b>4</b>
3.1 COMPATIBILITY OF KOH WITH FUEL.....	6
3.2 K/B <sub>3</sub> (OH) <sub>3</sub> STRATEGY AND PH REGIMES FOR NORMAL OPERATION.....	6
3.3 EFFECT OF KOH ON SYSTEM MATERIALS .....	7
3.3.1 <i>Comparisons of Corrosion Product Concentrations in PRWs and VVERs</i> .....	8
3.3.2 <i>PWR Experience with Potassium Hydroxide Chemistry</i> .....	9
3.4 IMPACT OF CVCS OPERATION.....	12
3.5 IMPACT ON KOH WASTES.....	13
<b>4. DISCUSSION AND RECOMMENDATIONS.....</b>	<b>14</b>
<b>5. REFERENCES .....</b>	<b>17</b>



**TABLES**

TABLE 1 VISUAL OBSERVATIONS AND SOLUBILITY DATA FOR THE VARIOUS K-BORATES IN  
WATER. .... 20

TABLE 2 COMPARISON OF THE PRIMARY COOLANT CHEMISTRIES IN VVERS AND DOMESTIC  
PWRS..... 21



## **FIGURES**

FIGURE 1 SOLUBILITY OF $\text{LiBO}_2$ AS PRESENTED BY COHEN.....	23
FIGURE 2 SOLUBILITY OF SOLID PHASES IN THE $\text{KBO}_2\text{-H}_2\text{O}$ AND $\text{K}_2\text{B}_4\text{O}_7\text{-H}_2\text{O}$ SYSTEMS IN THE PRESENCE OF VAPOR. ....	24
FIGURE 3 SOLUBILITY OF SOLID PHASES IN THE $\text{NaB}_5\text{O}_8\text{-H}_2\text{O}$ AND $\text{KB}_5\text{O}_8\text{-H}_2\text{O}$ SYSTEMS IN THE PRESENCE OF VAPOR. ....	25
FIGURE 4 EFFECT OF $\text{LiOH}$ ON THE CORROSION BEHAVIOR OF ZIRCALOY.....	26
FIGURE 5 COMPARISON OF THE EFFECTS OF $\text{LiOH}$ AND $\text{KOH}$ ON THE CORROSION KINETICS OF ZIRCALOY-2 AND -4. ....	27
FIGURE 6 EFFECTS OF $\text{LiOH}$ , $\text{KOH}$ , AND $\text{NH}_4\text{OH}$ ON THE CORROSION WEIGHT GAIN OF ZIRCALOY-2 AND -4 AFTER THREE DAY TESTS AT 360 C. ....	28
FIGURE 7 WEIGHT GAIN AND HYDROGEN PICKUP FRACTION OF ZIRCALOY-4 AT 350 C VERSUS IONIC RADIUS OF THE ALKALI HYDROXIDE CATION. ....	29
FIGURE 8 COMPARISON OF THE $\text{Li/H}_3\text{BO}_3$ AND $\text{K/H}_3\text{BO}_3$ STRATEGIES USED IN PWRs AND VVERs, RESPECTIVELY. ....	30
FIGURE 9 OPERATIONAL DATA OF THE $\text{Li}$ AND $\text{K}$ CONCENTRATIONS IN A VVER CYCLE .....	31
FIGURE 10 COMPARISON OF THE SOLUBLE CORROSION PRODUCTS, $\text{Fe}$ , $\text{Ni}$ , $\text{Co}$ , $\text{Mn}$ , AND $\text{Zn}$ FOR DIFFERENT REACTOR TYPES. ....	32
FIGURE 11 COMPARISON OF THE INSOLUBLE CORROSION PRODUCTS, $\text{Fe}$ , $\text{Ni}$ , $\text{Co}$ , $\text{Mn}$ , AND $\text{Zn}$ FOR DIFFERENT REACTOR TYPES. ....	33
FIGURE 12 TREND OF COOLANT ACTIVITY AT LOVIISA 1 AND CONTRIBUTION OF $^{42}\text{K}$ . ....	34



## Acknowledgments

The author wishes to acknowledge the contributions of the following individuals for providing information and for stimulating discussions throughout the course of this effort: Mr. Jeff Deshon, of North Atlantic Energy, for communication with the chemists at the Loviisa plants, for providing information on coolant activity, and for review of the report. Ms. Gail Gary, of Ameren-UE, provided critical review of the report. Dr. Milan Zmitko and Dr. Jan Kysela, of the Czech Research Institute, NRI/Rez, provided valuable information and references on the coolant chemistry in VVERs. Dr. W. Art Byers, of Westinghouse, for discussions on the solubility of the lithium and potassium borates. Mr. M. Kenneth Johnson, of Duke Power, provided the section on the effect of KOH on CVCS performance and operation. Dr. J. Philippe Berge provided the section on the effect on KOH on system internals, and through his efforts direct contacts with ENEL have been established with Chemists at Trino and ENEL. More precise information on Trino can be obtained through this cooperation, which has been excellent. These contacts are the following:

In Rome Dr. L. Noviello - Director of Engineering & Technology Enel Nuclear Plant Management . Via Torino No6 00184 Roma  
Fax (+39 6) 85095961

In Trino Mr. Ghioni - Trino Superintendant  
Mr. Pisani - Main chemist fax No (+ 39 1) 61805275

Finally, the guidance and encouragement of the EPRI Program Manger, Dr. Paul Frattini, is sincerely appreciated.





## KOH – A Potential Mitigation for the Axial Offset Anomaly

### **ABSTRACT**

Axial Offset Anomaly (AOA) is believed caused by the precipitation of solid lithium borate,  $\text{LiBO}_2$ , within porous crud deposits due to concentration of Li and B under sub-cooled boiling heat transfer. Of the common alkali borates,  $\text{LiBO}_2$  has the lowest solubility, and the solubility decreases with increasing temperature. Potassium borates, on the other hand, have solubilities more than two orders of magnitude greater than that of  $\text{LiBO}_2$ , and their solubilities continue to increase with increasing temperature. These favorable solubility characteristics have made the use of KOH a potential mitigation for AOA. An evaluation of the use of KOH as a replacement for LiOH as the pH control agent in PWRs has been performed based on information in the literature and from VVER experience. Sufficient data exists to indicate good compatibility between the Zr-based alloy fuel cladding and components and the KOH/ $\text{H}_3\text{BO}_3$  coolant chemistry. VVER experience also indicates good compatibility with the KOH coolant and stainless steel components. However, the Ni-based alloys used in steam generators have not been extensively tested in KOH solutions, and evaluation of SCC concerns with these materials may be necessary prior to full plant implementation. This evaluation should include the assessment of crevice areas to assure avoidance of conditions where KOH may concentrate to levels deleterious to SCC performance. Also, because some lithium will always be present due to neutron capture by boron, the solubility characteristics of mixed potassium plus lithium borates should be evaluated.

### **1. INTRODUCTION**

The mechanisms of the Axial Offset Anomaly as currently understood is the concentration of Li and B in porous crud deposits under the action of sub-cooled boiling to the extent that boron precipitates within the deposits as lithium borate,  $\text{LiBO}_2$ <sup>1,2</sup>. Although  $\text{LiBO}_2$  has not been conclusively identified, boron in some solid form is required to produce the flux depressions observed<sup>1</sup>, and lithium return data coupled with AOA changes during downpower support dissolution of a compound of Li and B having a 1:1 molar ratio. This evidence, albeit circumstantial, strongly implies the solid boron compound is  $\text{LiBO}_2$ , probably in some hydrated form. The retrograde solubility of  $\text{LiBO}_2$

is consistent with the hideout return behavior of boron during power maneuvers. Precipitation at the hot surface of the fuel cladding could be avoided if the boron compound had a normal, or positive, temperature coefficient of solubility. Furthermore, the margin to the solubility limit on the boiling surface increases in direct proportion to the absolute solubility. These two attributes, positive temperature coefficient of solubility and higher absolute solubility are possessed by the potassium borates. It is for these reasons, and the knowledge that KOH is a strong base with similar dissociation behavior to LiOH, that interest in KOH as a substitute for LiOH was stimulated.

## **2. SOLUBILITY COMPARISONS OF Li AND K-BORATES**

### **2.1 Lithium Borate**

The solubility of  $\text{LiBO}_2$  is both retrograde and low. Figure 1, reproduced from Cohen<sup>3</sup>, gives the solubility of  $\text{LiBO}_2$  as a function of temperature. At a boiling surface the saturation temperature is about 345° C (653° F), and the solubility is about 0.12 moles/liter, and it decreases with increasing temperature. These solubility data were essentially confirmed by Byers, et. al., as presented in Appendix F of Reference 1. The solubility of  $\text{LiBO}_2$  over the temperature range of 300-360° C was determined<sup>1</sup> to be the following:

$$S = (5 \times 10^{-6})T^2 - (6 \times 10^{-3})T + 1.5889$$

where  $S$  = solubility in moles/kg

$T$  = temperature in °C.

These new data give a solubility of 0.114 moles/kg at 345° C and the temperature coefficient of solubility is  $-2.55 \times 10^{-3}$  moles/kg C°.

### **2.2 Potassium Borates**

The solubilities of the borates of potassium have been reported by Urusova and Valyashko.<sup>4</sup> Measurements were performed on three borates; the mono or metaborate,

$\text{KBO}_2$ , the tetraborate,  $\text{K}_2\text{B}_4\text{O}_7$ , and the pentaborate,  $\text{KB}_5\text{O}_8$ . Solubilities of high temperatures were determined by use of two methods; visual observation of the water-salt system in the presence of the vapor phase in sealed quartz ampoules at temperatures up to about  $400^\circ\text{C}$ , and by heating in steel autoclaves and sampling the liquid phases at elevated temperatures. Figures 2 and 3 show the solubility curves for the K-borates, and that of  $\text{NaB}_5\text{O}_8$  is included in Figure 3. These curves show previously published data (source not given) as the solid lines, with the new data represented by the dashed lines. Whereas, retrograde solubility was believed to exist starting at about  $250^\circ\text{C}$ , the new data show that the solubilities of these borates continue to increase with increasing temperature. Tabular data of the solubilities as given by Urusova and Valyashko<sup>4</sup> are listed in Table 1. From these data, the solubilities of the K-borates at  $350^\circ\text{C}$  are the following:

	Wt %	Moles/kgH <sub>2</sub> O
$\text{KBO}_2$	~75	36.6
$\text{K}_2\text{B}_4\text{O}_7$	~80	17.1
$\text{KB}_5\text{O}_8$	~80	~18.1

As is noted in Table 1, the data for the  $\text{KB}_5\text{O}_8$  was from sampling the autoclave at  $360^\circ\text{C}$ . These solubility data may be compared with the solubility of  $\text{LiBO}_2$  of 0.101 moles/kgH<sub>2</sub>O at  $350^\circ\text{C}$  as calculated by the solubility equation described in Section 2.1. Thus, the K-borates have solubilities at least two orders of magnitude greater than that of  $\text{LiBO}_2$  at the local surface temperatures of high duty fuel rods. Additionally, the most recent solubility data indicate that the temperature coefficient of solubility of the K-borates is positive at high temperatures, in contrast to the retrograde solubility displayed by  $\text{LiBO}_2$ . These favorable solubility characteristics provided the impetus for a more thorough evaluation of KOH as a substitute for LiOH for pH control in PWRs.

### **3. CONSIDERATION FOR KOH USAGE FOR pH CONTROL**

Use of KOH for pH control in PWR reactor systems is not unique. Although all domestic and western PWRs use LiOH for pH control, the Russian designed VVER plants exclusively use KOH to buffer the acidity of boric acid. Thus, there is operating experience in over 40 plants with KOH, but the accessibility of information from VVER plants is difficult at times, and there are material and operational differences between eastern and western PWRs that require consideration of the impact of KOH usage. A complete discussion of all items requiring evaluation prior to implementation of KOH is beyond the scope of this report. However, several key-items are compatibility with the fuel and system internal materials, pH regimes in plant operation, impact on CVCS operation and performance, and the effect on the dose related activity of liquid wastes. Although all of the above are important for ultimate implementation, the compatibility with fuel and plant materials is of prime importance for assurance of fuel and system integrity.

#### **3.1 Compatibility of KOH with Fuel**

At the concentrations of Li typically used in PWRs, less than 3.5 ppm, there is only a minimal enhancement of zirconium alloy corrosion caused by Li<sup>5</sup>. The greater threat to fuel rod integrity is the possibility of Li concentration to much higher values, as may occur at boiling surfaces within crud deposits or within the pores of post-transition oxide films. It is well known that concentrated LiOH is detrimental to the corrosion behavior of Zr-based alloys such as Zircaloy-2 and -4. Li-acceleration of the corrosion rate in the presence of elevated levels of LiOH was clearly demonstrated in 1962 by Hillner and Chirigos,<sup>6</sup> as shown in Figure 4. The effect of LiOH is insignificant until the pH<sub>(RT)</sub> increases to about 11.5 (22 ppm Li), and then the deleterious effect of Li becomes very pronounced with increasing LiOH concentration. In Reference 6, the effect of KOH was also evaluated, and a comparison of the effects of LiOH with KOH on an equimolar basis is shown in Figure 5. Concentrated KOH is much less aggressive than LiOH by at least an order of magnitude in concentration. That is, 1.0M KOH is less aggressive than 0.1M LiOH as noted from the longer time to transition and lower post-transition corrosion rate in the 1.0M KOH solution.

The less aggressive nature of KOH vs LiOH was reported independently by Coriou, et. al,<sup>7</sup> Figure 6. For a more valid comparison, to eliminate the effect of pH the data can be put on an equimolar basis by dividing the KOH concentration by the ratio of the molecular weight of KOH and LiOH,  $56.1/24 = 2.34$ . But even with the correction, the less aggressive behavior of KOH relative to that of LiOH is obvious.

Substitution of KOH for LiOH in PWRs found renewed interest in the 1990's. Henzel<sup>8</sup> reported that after screening a number of potential pH control agents, only KOH and RbOH were feasible replacements for LiOH. Of these two, KOH is most favored because of cost and availability. Jeong, Ruhmann and Garzarolli<sup>9</sup> reported on the influence of the hydroxides of Li, Na, K, Rb, and Cs on the corrosion resistance of several Zr-based alloys based upon the Zr-Sn, Zr-Nb, and Zr-Sn-Nb systems with transition metal additions. Testing was performed for up to 150 days in autoclaves at 350° C in solutions containing 0.32, 4.3, and 31.5 mmole of the hydroxides. For LiOH, these concentrations correspond to 2.2, 30, and 220 ppm Li. In these tests the most aggressive environment was the LiOH, particularly in the more concentrated solutions. The least aggressive was CsOH, and in general the rate of corrosion was inversely proportional to the ionic size of the cation of the hydroxide. Thus KOH was superior to both NaOH and LiOH. RbOH was an exception in that in some of the cases it resulted in higher corrosion than expected. These data confirmed the earlier data of Coriou, et. al.<sup>7</sup> on the relative effects of Li, Na, and K, and expanded the data base on relative effects of LiOH and KOH on the corrosion resistance of Zr-based alloys. CsOH would not be considered as a pH control agent because of the generation of dose-rate relevant radionuclides.

In additional work on the effect of the alkali hydroxides, Jeong, Kim, Jung, and Ruhmann<sup>10</sup> reported on Zircaloy-4 tested to 500 days in the various alkali hydroxides. These data were combined with the results of microstructural characterization of the ZrO<sub>2</sub> corrosion films formed in the various solutions and reported by Jeong, Baek, Kim, Kim, and Ruhmann<sup>11</sup>. The beneficial effect of KOH versus LiOH on both corrosion and hydrogen pickup in autoclave tests at 350° C is clearly shown in Figure 7, in which weight gain and hydrogen pickup are shown as functions of the cation radius of the hydroxides.

In summary, all of the autoclave testing of Zircaloy and other Zr-based alloys in KOH solutions has been positive. Concentrated KOH is much less aggressive than equimolar concentrations of LiOH. Thus, use of KOH to replace LiOH poses no threat to fuel corrosion. All of the data, in fact, suggests that such substitution may be beneficial for fuel because of the lower corrosion observed in concentrated KOH vs LiOH solutions.

### 3.2 K/B<sub>3</sub>(OH)<sub>3</sub> Strategy and pH Regimes for Normal Operation

KOH is used as the alkalizing agent in VVERs, and the primary coolant chemistry of these units have been described in detail elsewhere<sup>12-14</sup>. What follows is a very brief description of the K/H<sub>3</sub>BO<sub>3</sub> control strategies used and a comparison to the Li/H<sub>3</sub>BO<sub>3</sub> strategies used in western PWRs.

KOH is a strong base with a temperature dependence of dissociation very similar to that of LiOH. Thus, on a molar basis the pH values with KOH and LiOH are identical, and the mass relations between Li and K is simply the ratio of their molecular weights, i.e., 39.6 g K/7 g Li = 5.59 g K/1 g Li.

The pH regimes used in VVERs are shown in Figure 8. A nominal pH of 7.2<sub>(300)</sub> is used in most VVER-440 plants, and a nominal pH of 7.1<sub>(300)</sub> is followed in VVER-1000 plants. The core average temperatures are 284° and 306° C for the -440 and -1000 units, respectively. This so-called “Modified” chemistry, which allows the pH to be essentially constant during the cycle, evolved from a pH regime that was intended to be constant at about 6.9, but, due to erroneous dissociation constants, varied continuously from a nominal pH slightly less than 6.9 at BOC to about 7.3 at EOC. This older pH control is termed “Standard” control. Most VVERs have transitioned to the Modified pH control, but some (Loviisa, Paks, Kozloduy) still use the Standard chemistry.

Figure 8 also shows a comparison between the VVER pH Guidelines with KOH and the EPRI guidelines with LiOH. The VVER guidelines are essentially the equivalent of 3.5 ppm Li max, with a constant pH of 7.1-7.2 for the two types of units. As most VVERs are on annual cycles, the pH is essentially constant throughout the cycle. Note also that this pH strategy is currently being implemented in a number of domestic PWRs as means of mitigating BOC crud deposition on the fuel.

Typical guidelines for the primary coolant in VVERs during power operation are given in Table 2, and these are compared to values in the EPRI Guidelines. Except for the use of KOH and the presence of some ammonia, the primary coolant chemistry of VVERs is very similar to that of western PWRs. Ammonia is added to VVERs to supply hydrogen via radiolytic decomposition. The hydrogen levels, however, are very similar. Chloride and fluoride are low in VVERs, as is the silica. The suspended solids of <0.2 ppm is consistent with U. S. Utility practice.

One of the great advantages of using LiOH for pH control is that there is no chemical distinction between the  $^7\text{Li}$  added as the hydroxide and that formed from the  $^{10}\text{B}(n, \alpha)$  reaction. Thus, only a singular cation is added to the coolant, and the Li level is controlled by the CVCS. With KOH, both K and Li cations will be present. Initially, only K is added to the coolant for pH control, but as  $^{10}\text{B}$  burns out, the Li concentration builds and typically peaks at about 0.5 ppm Li in a VVER cycle with a beginning of life B of 1000 ppm. The Li generation rate is proportional to the boron concentration, so as the boron concentration decreases during the cycle, so does the Li generation rate. The resultant relationship between Li, K, and B for an operational cycle in a VVER-440 is shown in Figure 9. The Li builds to ~0.5 ppm near mid-cycle, and then decreases due to removal along with K by CVCS ion-exchange and a diminishing generation rate. Consideration of the effects of KOH on CVCS operation is discussed in Section 3.4.

The presence of both K and Li on the potential for precipitation of a mixed (Li + K)-borate within crud deposits with sub-cooled boiling is an uncertainty at this time. It is recommended, therefore, that the solubility characteristics of such mixed borates be established prior to conversion to KOH for mitigation of AOA.

### 3.3 Effect of KOH on System Materials

There is no direct comparison of KOH and LiOH on system materials for the same reactor system. However, because the corrosion of stainless steel and Ni-based alloy are more strongly influenced by pH than the specific cations of the alkalizing agent, and the pH regimes are essentially the same with LiOH and KOH, the shift to use of KOH should not have a significant effect on general system corrosion. This principle has

been reinforced by the absence of significant corrosion concerns in the VVER plants, which utilize stainless steel steam generator materials.

### 3.3.1 Comparison of Corrosion Product Concentrations in PWRs and VVERs.

Consistent with the corrosion similarity between KOH and LiOH, the corrosion product concentrations in the coolants of PWRs and VVERs are similar. Coolant samples from a number of European PWRs and VVERs have been collected and analyzed by AEA technology and the results summarized by Zmitko and Kysela<sup>13</sup>. The concentrations of Fe, Ni, Co, Mn, and Zn were determined for samples taken downstream of the heat exchangers in the letdown loops. Samples were filtered through 0.45  $\mu\text{m}$  micron filters and analyses were performed on both the soluble and insoluble portions. Typical data are shown in Figures 10 and 11. The Loviisa, Dukovany and Paks plants are VVER-440s with stainless steel S/G tubing. Ringhals 2 and Sizewell B have Alloy 690 S/G tubing, and Gronde, Phillipsburg, Neckar 2 and Brockdorf are large PWRs in Germany and have Incoloy 800 S/G tubing. Trillo, in Spain, also has Alloy 800 S/G tubing. The corrosion products in the plants show large variability, but the absolute values of even the highest concentration are low; total insolubles mostly being less than 1 ppb, and total solubles being less than 4 ppb, except for Sizewell B, for which solubles were up to about 6 ppb. For all units, the Fe is usually higher than the Ni concentration, both for solubles and insolubles, and this is especially true of the VVER units, as may be expected because of the stainless steel S/G tubing. Most importantly, the levels of corrosion products, both soluble and insoluble, in the coolants of VVERs and are similar to those of PWRs, supporting the belief that use of KOH in place of LiOH has no significant effect on corrosion of plant system materials. The only caveat in this comparison is that there are no data for plants using KOH and having the Ni-based alloys, 600 or 690, for steam generator tubing. It is generally believed, however, that the corrosion and release rates of these two Ni-based alloys are similar to those of stainless steel<sup>15,16</sup>, albeit the corrosion rate of Alloy 690 may be somewhat lower<sup>16</sup> because of the high level of chromium in the alloy.



### 3.3.2 PWR Experience with Potassium Hydroxide Chemistry – by Dr. J. Philippe Berge

In the early 1980's EdF began an evaluation of KOH in an effort to reduce dose rates in their plants. An evaluation of the dose rates at Loviisa was made by the French CEA. It was found that the very low doses can be related to causes such as use of electropolished tubes and low cobalt materials, but the favorable role of KOH chemistry is not impossible. The only experience with KOH in a western PWR is the Italian plant, Trino Vercellese. The Trino plant had lower doses than the similar SENA Chooz plant, which operated with LiOH control. As was the case with Loviisa, the data indicated that use of KOH may have been at least partially responsible for the lower doses at Trino. This EdF evaluation of KOH was recently reviewed and a summary of the Trino experience and other comments on use of KOH on PWR internal components follows. Much of this information was obtained at a meeting held in Trino on February 2, 1999, with the management and the chemists of the plant, and Dr. Philippe Berge, consultant to EPRI.

#### 3.3.2.1 Experience at Trino ENEL, Italy

The only experience of a western type PWR, operating with potassium hydroxide as the neutralizing agent in the primary coolant is the Italian plant, Trino Vercellese. The Trino plant is a 270 MWe PWR, manufactured by Westinghouse, and operated by SELNI-ENEL, in the north of Italy, from October 1964 to August 1988. It was shut down after the Italian referendum, which led to the shut down of all the nuclear reactors in Italy. The reactor operated with Westinghouse fuel, clad with stainless steel. The four steam generators had stainless steel tubing.

#### Operation

Two major shut down periods were caused by reactor internals repair ( 1968-1969) and ECCS modification (1979-1984). These shut downs had nothing to do with the chemistry. Apart these two periods, the load factor was high and the total production of Trino was 24,905 GWh.

### Chemical Specifications

The primary coolant specifications were the usual specs for PWR, at a date where no special requirement was given for a constant pH. The usual lithium concentration of 0.7 to 2.2ppm was replaced by the potassium hydroxide equivalent of 4 to 13 ppm

### Lithium formation

As for VVERs, the main problem was related to the formation of lithium with the boron neutron reaction. The production of  $^7\text{Li}$  is given as  $0.036\text{E-}3$  ppb/MW(t)/ppmB-day, with a fuel burnup rate of 2ppm of B a day and a main coolant leakage rate of 200 liters/day.

Maintaining the alkalinity within the specifications, and, nowadays, within the requirement of the EPRI primary guidelines, would require a plant specific study. The Trino chemists have resolved the problem with conditions of dilution and purification which are specific to Trino, but can give indications on how to manage the situation with a modern PWR. This information can be obtained with direct contacts with the Trino plant chemist (see acknowledgements).

### Health Physics

The integrated doses and the dose rates outside the circuits were extremely low compared to a sister plant in France (Chooz of the SENA). There are factors of four for the integrated doses and two to three for the dose rates between Chooz and Trino. The only significant and known difference between the two plants was the use of potassium hydroxide in Trino and the usual lithium chemistry in Chooz.

At the request of EDF, a complete and detailed evaluation of the activities of the corrosion products between the two plants was performed by the CEA with the use of the Pactole code ( see reference). As for the evaluation of the low dose of Loviisa, the conclusion was that the differences could be explained with other factors than the chemistry, but that the use of potassium hydroxide was either better or equivalent to lithium.

The possibility of getting an improvement in health physics with the potassium hydroxide chemistry, and the absence of clear drawback, led EdF, in 1983, to evaluate the

possibility of applying the KOH chemistry in the 900 MW plant of Blayais 3. Additional tests were performed at EdF to confirm the absence of risk to the components. They confirmed the lower oxidation rate of the zirconium alloys for the fuel cladding. However, they also confirmed previous CEA results on stress corrosion cracking of cold worked stainless steels that showed an increased susceptibility in concentrated potassium hydroxide compared to lithium hydroxide. The concern about the local dry out in the baffle/former bolts (which had not cracked at that time) due to gamma heating led Edf to give up this modification of the primary chemistry. As second generation baffle bolts have circulation to prevent the risk of dry out, the risk of SCC should now be eliminated. In the absence of concentration of the coolant, for steam generators tubing or vessel head penetrations, for instance, the application of potassium hydroxide chemistry should not lead to an increased risk of SCC.

### Conclusions

The Trino plant operated successfully with KOH/H<sub>3</sub>BO<sub>3</sub> chemistry. The unique experience of Trino can be useful for possible application of potassium hydroxide chemistry in a modern PWR, despite the differences in size and materials.

### References

- SELNI Valutazione della produzione giornaliera media di litio-7 ( evaluation of the average daily production of Lithium-7) October 1965 Internal Trino report.
- P. BESLU Comparaison des activites deposees des reacteurs CNA-Enrico Fermi(Trino), Rapport SEN 81/110 CEA France.
- Several internal reports of SELNI on lithium production and chemistry , with unknown references are available.

### 3.4 Impact on CVCS Operation – by M. Kenneth Johnson

While using LiOH for pH control, the normal practice for operating CVCS demineralizers is to use a mixed bed demineralizer in the lithium - borate form for continuous purification and a second demineralizer for intermittent removal of lithium produced via the  $^{10}\text{B}(n,\alpha)$  reaction. The delithiation bed may be either a hydrogen form cation bed or a hydrogen – borate form mixed bed. Under KOH chemistry, the purification bed will start out in the potassium – borate form. During operation, Li-7 will be produced and the purification bed will remove a portion of the Li-7, exchanging it for potassium. The amount of lithium that will be exchanged for potassium is determined by the relative ionic concentrations and the resin selectivity:

$$K_{Li/K} = \frac{(RLi) [K^+]}{(RK) [Li^+]}$$

$K_{Li/K}$  = Resin Selectivity for Li over Potassium,  
~0.34 for a typical cation resin

$(RLi), (RK)$  = Concentrations of Li and K on the resin

$[K^+], [Li^+]$  = Concentrations in the Liquid

The exchange of Li for potassium will occur on an equimolar basis. Thus, the net increase in excess of base due to Li production will be the same as under lithium chemistry. The same cation capacity in the delithiation bed will be able to remove this excess base. Since this cation capacity is in the hydrogen form, both potassium and lithium will be removed. As a result, the ratio of lithium to potassium in the coolant will increase throughout the cycle. The rate of increase in Li/K will be dependent on the plant specific Li-7 production rate, purification bed cation capacity, and cation resin selectivity.

One approach to lowering the Li/K ratio would be to make small potassium additions to RCS. The increase in potassium will release lithium from the purification bed, which can then be taken out with additional usage of the “delithiation” bed since the hydrogen form resin in the delithiation bed will remove both potassium and lithium at their ratio in

coolant rather than based on the relative selectivities. This approach would likely require usage and disposal of additional cation resin. This cost may be somewhat offset by the lower costs for potassium compared to Li-7.

The other potential problem with the CVCS purification demineralizer operation is that, since the resins have a higher selectivity for potassium than for lithium, the relative equilibrium concentration of other cations, such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{Cs}^+$ , in the RCS will be higher. However, cationic impurities, in the absence of significant failed fuel, are not generally a problem. As with lithium, other cations could be shifted to the de-lithiating demineralizer by making repeated small additions of potassium.

### 3.5 Impact KOH on Wastes

Natural K is made up of 93.26%  $^{39}\text{K}$ , 6.73%  $^{41}\text{K}$ , and 0.01%  $^{40}\text{K}$ . Additional  $^{40}\text{K}$  is formed from  $^{39}\text{K}$  from  $^1_0\text{n}$ ,  $\gamma$  reaction. The half-life of  $^{40}\text{K}$  is  $1.26 \times 10^9$  y, so it is a relatively stable isotope. It decays by  $\beta^-$  and  $\beta^+$  decay, with the emissions of 1.31 and 1.51 MeV gamma. However, the low cross-section of  $^{39}\text{K}$ , 2.1 b, and low concentrations of K in the coolant indicate that the activity of  $^{40}\text{K}$  should be minimal. The effect of  $^{40}\text{K}$  on waste activity was discussed with both NRI/Rez, and Imatran Voima Oy, the operators of the Loviisa plants. Both organizations say there is absolutely no problem, nor concern, with  $^{40}\text{K}$  causing high activities. In response to direct questions on the effect of  $^{40}\text{K}$ , the following responses were obtained from the personnel at the Loviisa plant.

Q1. What are the typical effluent release values to the environment for  $^{40}\text{K}$ ?  
What are the effluent limits for  $^{40}\text{K}$  proposed by the regulators?

A1. Potassium-40 is not detected. K-42 is the predominant activation product. During the 1<sup>st</sup> quarter, 1998, 4.1EO1 Bq were released from Loviisa. Because of the short half-life, do not normally detect K-42 in effluents. No K-42 was detected in releases during 1997.

Q2. Please provide trend curves of reactor coolant K-40 and H-3?

- A2. Potassium-40 is not detected in the RCS. The predominant activation product is K-42. K-42 ranges from  $4\text{E}06 \text{ kBq/m}^3$  (BOC) to  $1.5\text{E}06 \text{ kBq/m}^3$  (EOC). Half-life of K-42 is 12.4 hours. This trend curve is faxed.

The trend curve for the K-42 is shown in Figure 12. As a comparison,  $4\text{E}06 \text{ kBq/m}^3$  is equivalent to  $0.11 \text{ } \mu\text{Ci/cc}$ , which is comparable to the total activity of the coolant in a western PWR operating with LiOH control.

#### **4. DISCUSSION AND RECOMMENDATIONS**

Recent solubility studies of potassium borates have shown that these borates are much more soluble than lithium borate at the temperatures characteristic of the surface of high duty fuel rods, and the temperature coefficient of solubility is positive, in contrast to the retrograde solubility of  $\text{LiBO}_2$ . These data suggest that use of KOH in place of LiOH as the alkalizing agent for PWR coolant would greatly curtail the precipitation of normally soluble borates at the surface of fuel rods with crud deposits operating with sub-cooled boiling. Thus, the risk of precipitation of borates within the crud would decrease, and the occurrence of AOA would be greatly mitigated.

The solubility characteristics of the potassium borates are indeed favorable for KOH utilization. A concern, however, is that lithium will also be present in the coolant due to the  $^{10}\text{B}(n, \alpha)$  reaction, and the possibility of precipitation of mixed (K + Li) borates cannot be ruled out. As there are no known data on the solubility of these mixed borates, it seems prudent that their solubility behavior be established to the extent sufficient to ensure high solubility with a positive temperature coefficient, i.e., behavior more typical of the potassium borates than of lithium borate. Included in this investigation should be confirmation of the recent solubility data<sup>4</sup> on the potassium borates.

Potassium hydroxide possesses many of the attributes of lithium hydroxide and can be used as a pH control agent in western PWRs. The use of KOH in over 40 VVER reactors operating with boric acid and with pH control strategies similar to those currently used in PWRs attests to its applicability in high temperature water reactor systems. VVER operational experience establishes compatibility of Zr-Nb binary alloys and stainless steel with reactor coolant containing KOH and  $\text{H}_3\text{BO}_3$ . Furthermore, numerous laboratory studies support the VVER experience with Zr-Nb alloys and extend this compatibility to Zircaloy-4 and other Zr-based alloys. At the usual concentrations of Li and K present in the bulk coolants, less than about 3.5 ppm Li and 20 ppm K, neither Li nor K has a marked effect on the corrosion of Zr-based alloys. However, at elevated concentrations, such as may exist within crevices or in the pores of the zirconium oxide corrosion film, KOH is much less aggressive than LiOH toward Zircaloy and other Zr-based alloys. Thus, transition from LiOH to KOH for pH control of the primary coolant poses no concerns with the performance of Zr-alloy fuel cladding and structural components.

General corrosion of stainless steel and Ni-based alloys, such as Alloy 600, is affected more by pH than the alkalizing cation. Thus, there should be no significant effect of transitioning to KOH from LiOH on system corrosion. The favorable comparison of the soluble and insoluble corrosion products in the reactor coolant of VVERs and PWRs supports this position. Stress corrosion cracking, however, remains an open issue. It is generally believed that concentrated KOH is more aggressive to the SCC performance of stainless steel and other austenitic alloys than is similarly concentrated LiOH. In general, such concentration is not likely at the system internal surfaces, other than fuel, due to lack of a significant heat flux to support the mechanism for concentration. However, baffle/former bolts may be an exception due to gamma heating of the crevices in the bolted cavity. This concern has been alleviated in second-generation baffle assemblies that allow a circulation of the coolant in the bolt cavity to prevent the potential for dryout. A similar argument applies to barrel/former bolts, although the heat generation rates are usually lower in these than in the baffle bolts. This issue with baffle and barrel bolts would likely have to be addressed on a plant specific basis for evaluation of the susceptibility of these bolts to SCC.

Although enhanced susceptibility to PWSCC is not expected with KOH, extensive laboratory SCC testing has been performed with Li/H<sub>3</sub>BO<sub>3</sub> solutions, and a small negative effect of Li at levels below 3.5 ppm on PWSCC susceptibility was noted. These data have been summarized in the EPRI PWR Primary Water Chemistry Guidelines, Revision 4. Because of this deleterious effect of Li, it may be necessary to evaluate the effect of KOH on PWSCC of S/G tubing prior to plant implementation. Such an evaluation may consist of reviewing the existing database, performing some type of screening tests, or performing a technical assessment of the comparative effects of potassium and lithium based on the mechanism of SCC.

In summary, use of KOH for pH control in PWRs appears very promising, and its use offers the potential for mitigation of AOA in high boiling duty plants by affecting the solubility of the borate phase that precipitates readily within crud deposits in lithiated coolants. However, there are uncertainties with use of KOH that should be addressed prior to plant conversion from LiOH to KOH. The most significant of these concerns include the following:

- Determine the solubility characteristics of mixed borates of potassium plus lithium.
- Verify acceptable SCC performance of steam generator materials in KOH/H<sub>3</sub>BO<sub>3</sub> solutions.
- Perform plant specific evaluations of geometries in critical components that may be susceptible to KOH concentration and subsequent SCC and justify acceptability.
- Operability issues in the CVCS should be identified at a candidate demonstration plant.



## 5. REFERENCES

1. G. P. Sabol, J. R. Secker, J. Kormuth, H. Kunishi, and D. L. Nuhfer, "Rootcause Investigation of Axial Power Offset Anomaly", EPRI TR-108320, Final Report (June, 1997).
2. G. P. Sabol, J. R. Secker, H. Kunishi, and B. Cheng, "Characteristics of Corrosion Product Deposits on Fuel in High Temperature Plants", Proceedings SFEN/ENS International Symposium, Fontevraud IV – Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors, Vol. 2, 1159 (September, 1998).
3. P. Cohen, Water Coolant Technology of Power Reactors, Gordon and Breach Science Publishers, New York (1969).
4. M. A. Urusova and V. M. Valyashko, "Phase Equilibria in Hydrothermal Systems Containing Sodium and Potassium Borates", Russian Journal of Inorganic Chemistry, 38, 662 (1993).
5. IAEA, "Waterside Corrosion of Zirconium Alloys in Nuclear Power Plants", IAEA-TECDOC-996, IAEA, Vienna (January, 1998).
6. E. Hillner and J. N. Chirigos, "The Effect of Lithium Hydroxide and Related Solutions on the Corrosion Rate of Zircaloy in 680° F Water", WAPD-TM-307, Westinghouse Electric Corp., Bettis Atomic Power Laboratory, Pittsburgh, PA (August, 1962).
7. H. Coriou, L. Grall, J. Neunier, M. Pelras, and H. Willermoz, "The Corrosion of Zircaloy in Various Alkaline Media at High Temperature", Corrosion of Reactor Materials, Vol. II, 193, IAEA, Vienna (1962).
8. N. Henzel, "Alternative Water Chemistry for the Primary Loop of PWR Plants", Paper Presented at the IAEA Technical Committee Meeting on the Influence of Water Chemistry on Fuel Cladding Behavior, REZ, Czech Republic, (October, 1993).
9. Y. H. Jeong, H. Ruhmann, and F. Garzarolli, "Influence of Alkali Metal Hydroxides on Corrosion of Zr-Based Alloys", Paper Presented at the IAEA Technical Committee Meeting on the Influence of Water Chemistry on Fuel Cladding Behavior, REZ, Czech Republic, (October, 1993).
10. Y. H. Jeong, H. G. Kim, Y. H. Jung, and H. Ruhmann, "Effect of LiOH, NaOH, and KOH on Corrosion and Oxide Microstructure of Zr-Based Alloys", Paper Presented at the IAEA Technical Committee Meeting on Water Chemistry and Corrosion Control of Cladding and Primary Circuit Components, Hluboka nad Vltavou, Czech Republic, (September 28-October 2, 1998).

## EPRI Licensed Material

11. Y. H. Jeong, J. H. Baek, S. J. Kim, H. G. Kim, and H. Ruhmann, "Corrosion Characteristics and Oxide Microstructures of Zircaloy-4 in Aqueous Alkali Hydroxide Solutions", J. Nuclear Mater., 270, 322 (1999).
12. J. Kysela, M. Zmitko, V. A. Yurmanov, and V. K. Tiapkov, "Primary Coolant Chemistry in VVER Units", Proceeding, SFEN/ENS Conference on Chemistry in Water Reactors: Operating Experience and New Developments, Nice, France, Vol. 1, 17 (April, 1994).
13. Characteristics of Corrosion Products in the Loop and VVER Plant Primary Systems: Support of Axial Offset Anomaly Studies, EPRI, Palo Alto, CA: 1999. TP114132
14. M. Zmitko and J. Kysela, "The Water Regime of the VVER-440 and VVER-1000 Primary Circuits", the Rez Institute of Nuclear Research, plc, NRI Rez Report No. 10105 (December, 1993) (Translated from Czech).
15. D. H. Lister and R. D. Davidson, "Corrosion-Product Release in Light Water Reactors", EPRI-NP12, Final Report (September, 1989).
16. J. Robertson, "The Mechanism of High Temperature Aqueous Corrosion of Stainless Steel", Corrosion Science, 32, 443 (1991).

## TABLES

Table 1.

**Visual Observations and Solubility Data for the Various K-Borates in Water.**  
 (From Urusova and Valyashko<sup>4</sup>)

Borate	Salt Content wt %	Parameters of Phase Disappearance		Max Heating Temp, °C
		T, °C	Solution Conc. <sup>(1)</sup> Wt %	
KBO <sub>2</sub>	30.3			382
	36.9			365
	62.4	<200		360
	65.0	<200		411
	71.6	~250	~73	413
	75.1	350 <sup>(2)</sup>	~75	406
K <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	31.0			400
	31.9			393
	38.9			355
	76.0	~350	~80	370
KB <sub>5</sub> O <sub>8</sub>	30.3			403
	32.4	140	32.5	403
	54.1	200	54.5	410
	54.7	180	55.0	404
KB <sub>5</sub> O <sub>8</sub> <sup>(3)</sup>	80	360	80	-----

<sup>(1)</sup> Corrected for water in vapor phase

<sup>(2)</sup> Very small number of crystals

<sup>(3)</sup> Data from autoclave samples. Observation of phase disappearance not possible.

Table 2.  
**Comparison of the Primary Coolant Chemistries  
 In VVERs and Domestic PWRs**

Parameter	VVER	EPRI Guidelines
pH	440 – 7.1 to 7.3 @ 300° C 1000 – 7.0 to 7.2	6.9 to 7.4 at Temp
Li (ppm)		<3.5
K (equivalent) (ppm)	0.8-20	(<19.55 as 3.5 ppm Li)
NH <sub>3</sub> (ppm)	>5 (normally 10)	-----
H <sub>2</sub> (cc/kg)	30-60	25-50
Cl <sup>-</sup> , F <sup>-</sup> (ppm)	<0.05	<0.15
SiO <sub>2</sub> (ppm)	<0.2	<~3
H <sub>3</sub> BO <sub>3</sub> (g/l)	0-8	~0-10
Suspended solids (ppm)	<0.2	-----

## FIGURES

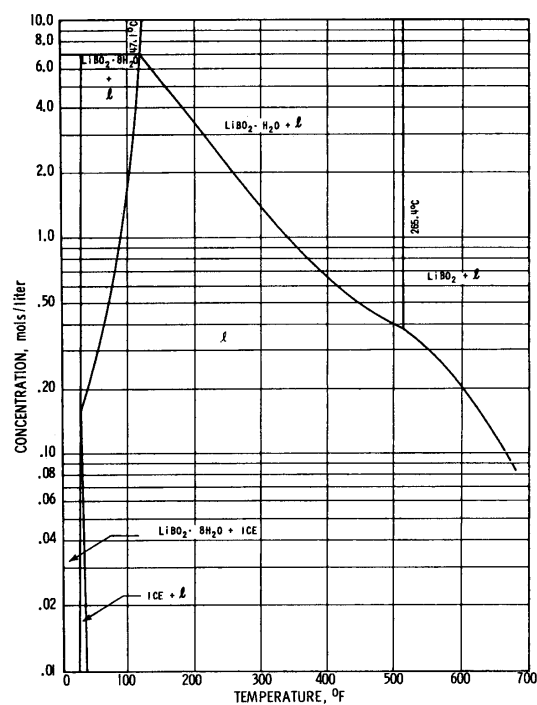


Figure 1 Solubility of  $\text{LiBO}_2$  as presented by Cohen.<sup>3</sup>

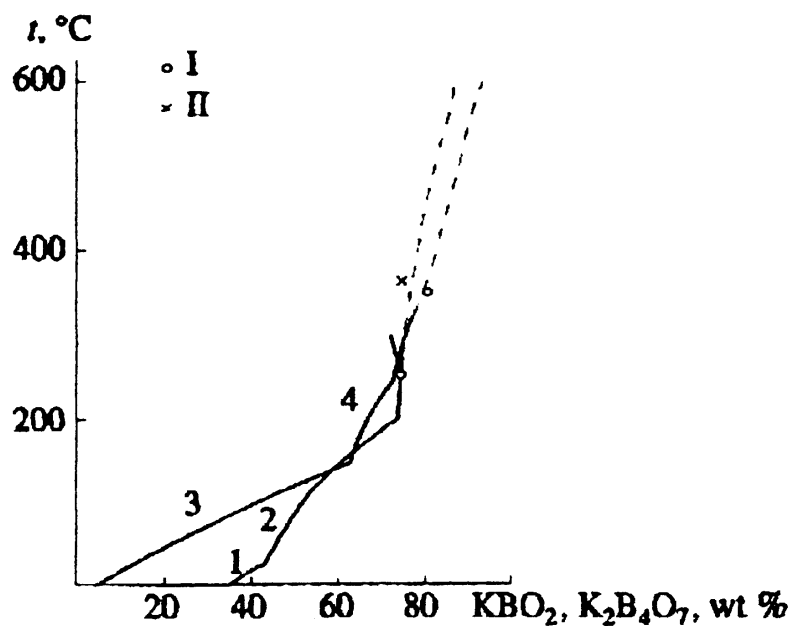


Figure 2 Solubility of solid phases in the  $\text{KBO}_2\text{-H}_2\text{O}$  and  $\text{K}_2\text{B}_4\text{O}_7\text{-H}_2\text{O}$  systems in the presence of vapor. (I) the solubility was determined in ampoules; (ii) the solution is unsaturated. Compositions of the solid phases: (1)  $\text{KBO}_2 \cdot 4\text{H}_2\text{O}$ , (2)  $\text{KBO}_2 \cdot 1.25\text{H}_2\text{O}$ , (3)  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , and (4)  $\text{K}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$ . From Urusova and Valyashko.<sup>4</sup>



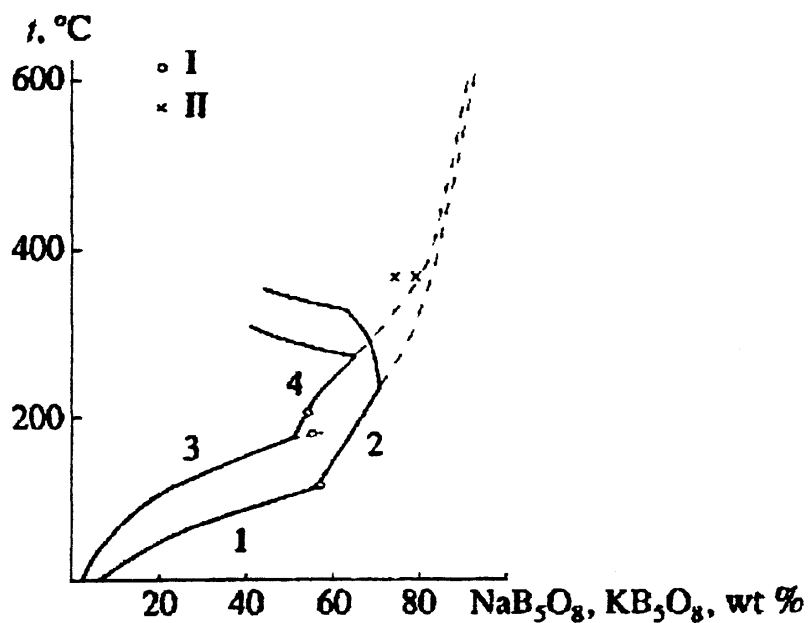


Figure 3 Solubility of solid phases in the  $\text{NaB}_5\text{O}_8\text{-H}_2\text{O}$  and  $\text{KB}_5\text{O}_8\text{-H}_2\text{O}$  systems in the presence of vapor. (I) the solubility was determined in ampoules; (II) the solution is unsaturated. Compositions of the solid phases: (1)  $\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ , (2)  $\text{NaB}_5\text{O}_8 \cdot \text{H}_2\text{O}$ , (3)  $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ , and (4)  $\text{KB}_5\text{O}_8 \cdot \text{H}_2\text{O}$ . Solid lines published data, dashed lines this study. From Urusova and Valyashko.<sup>4</sup>

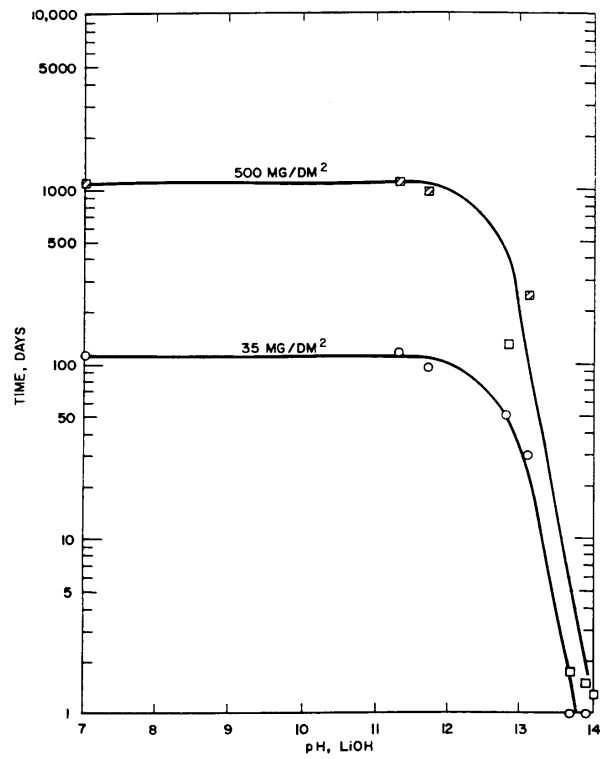


Figure 4 Effect of LiOH on the corrosion behavior of Zircaloy. Time required to reach a particular weight gain in autoclave tests at 360°C. The pH values are those at room temperature. From Hillner and Chirigos.<sup>6</sup>

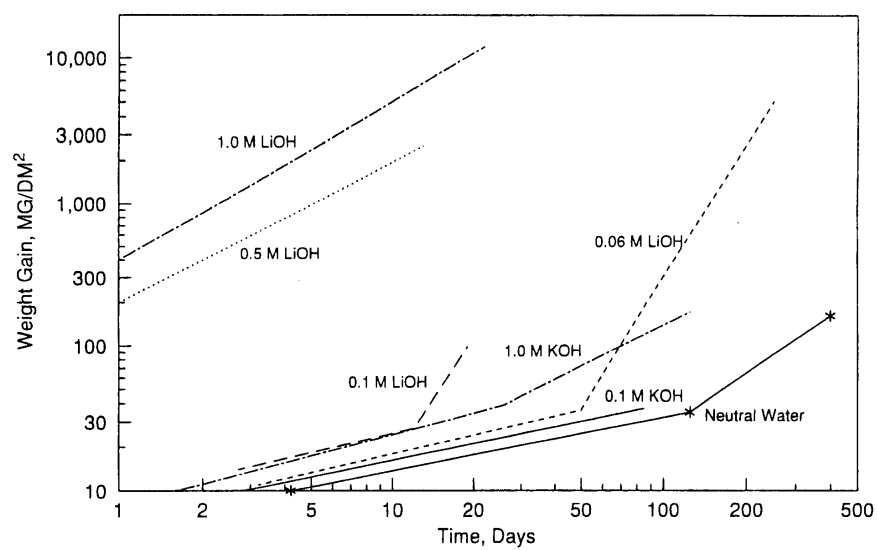


Figure 5 Comparison of the effects of LiOH and KOH on the corrosion kinetics of Zircaloy-2 and -4. KOH is much less aggressive to Zircaloy than LiOH. From Hillner and Chirigos.<sup>6</sup>

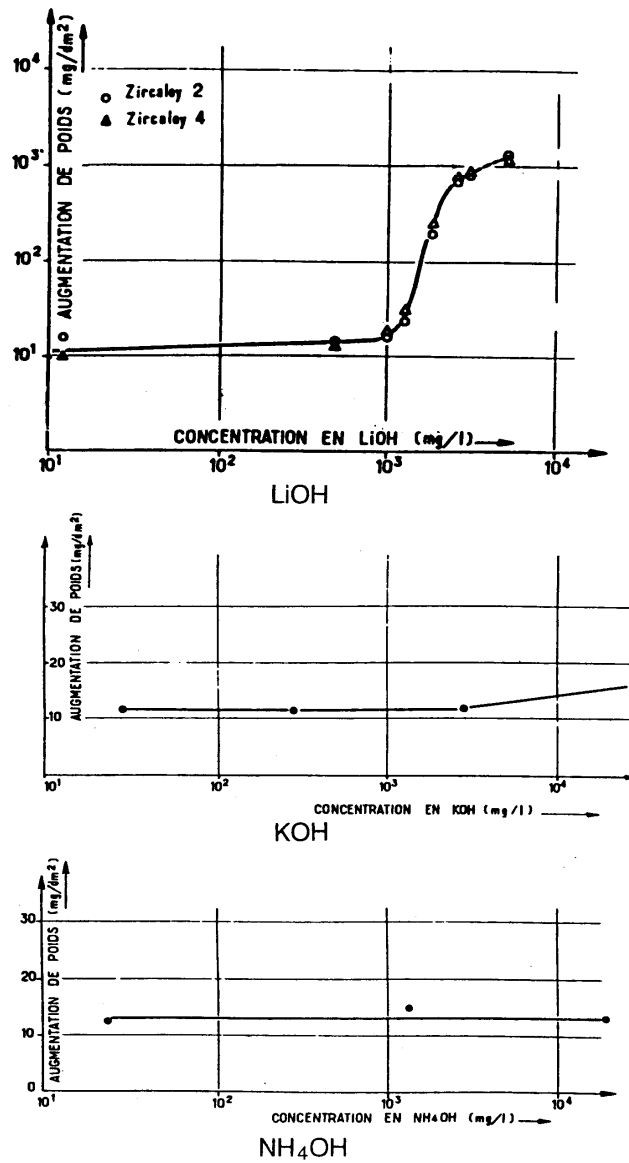


Figure 6 Effects of LiOH, KOH, and NH<sub>4</sub>OH on the corrosion weight gain of Zircaloy-2 and -4 after three day tests at 360°C. From Coriou, et. al.<sup>7</sup>

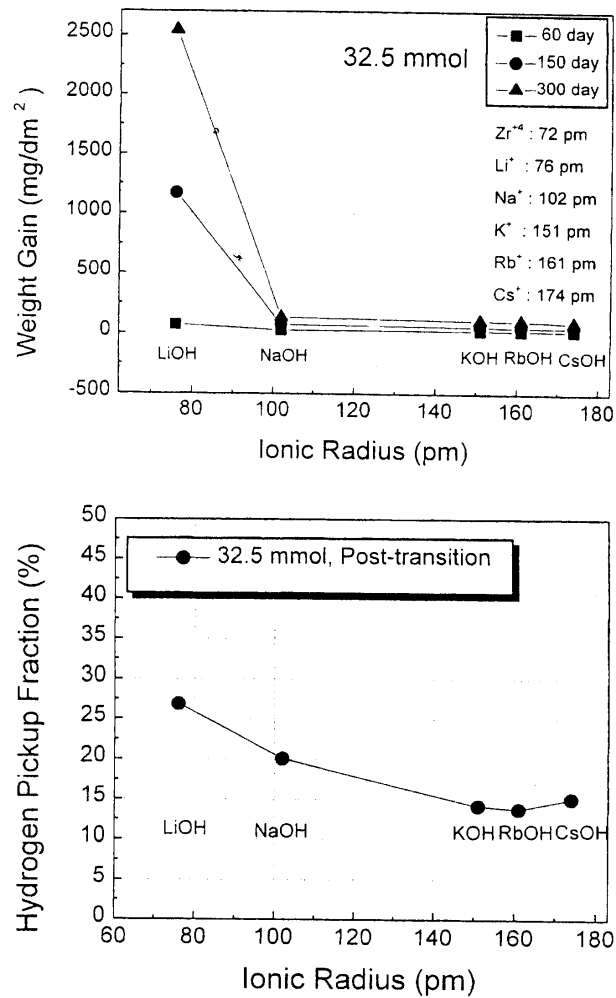


Figure 7 Weight gain and hydrogen pickup fraction of Zircaloy-4 tested at 350°C versus ionic radius of the alkali hydroxide cation (32.5 mmol is equivalent to 226 ppm Li). From Jeong, et. al.<sup>11</sup>

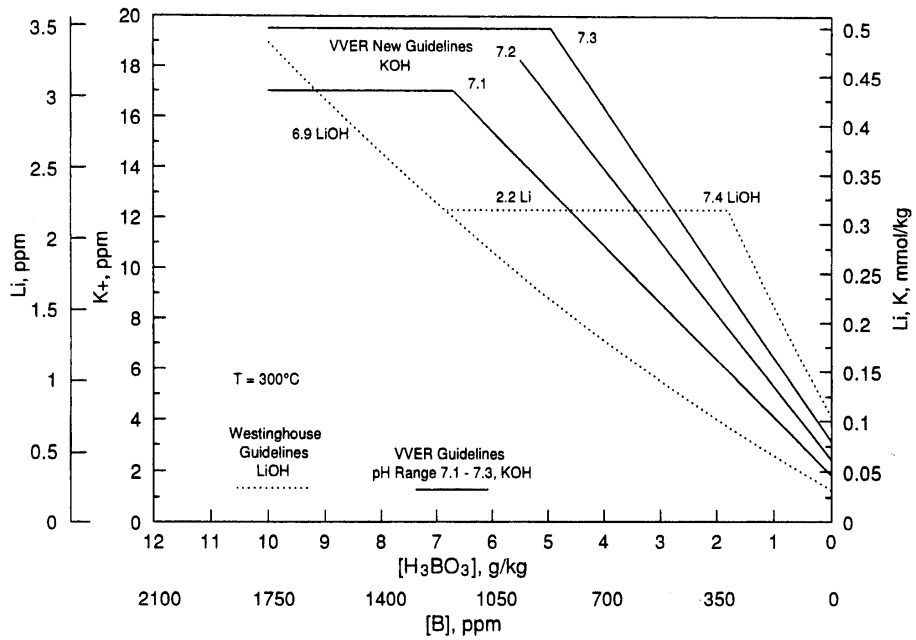


Figure 8 Comparison of the  $Li/H_3BO_3$  and  $K/H_3BO_3$  strategies used in PWRs and VVERs, respectively.

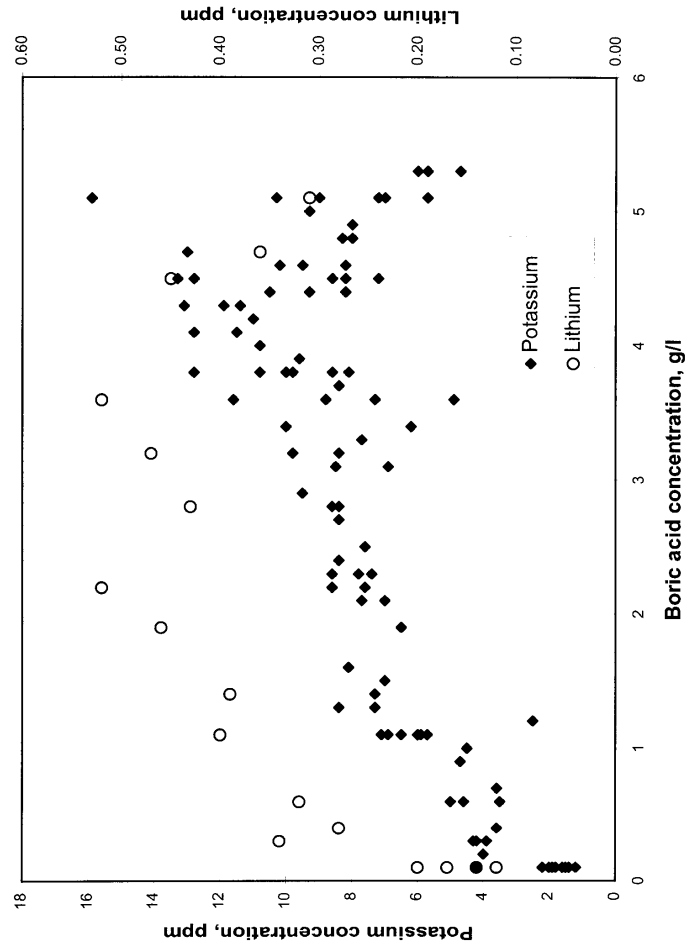


Figure 9 Operational data of the Li and K concentrations in a VVER cycle starting at about 927 ppm B (5.3 g/l  $H_3BO_3$ ) at 100% power. (From NRI/Rez)

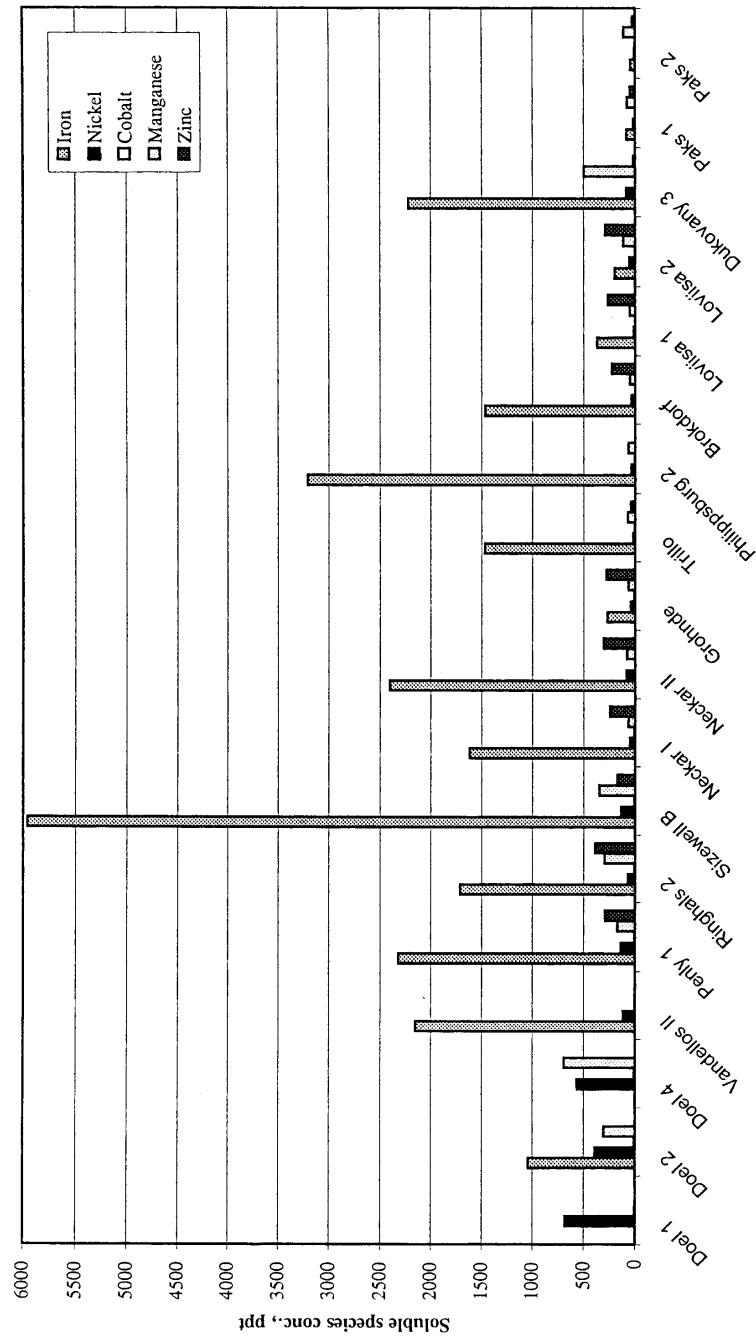


Figure 10 Comparison of the soluble corrosion products, Fe, Ni, Co, Mn, and Zn, for different reactor types. From reference 13.



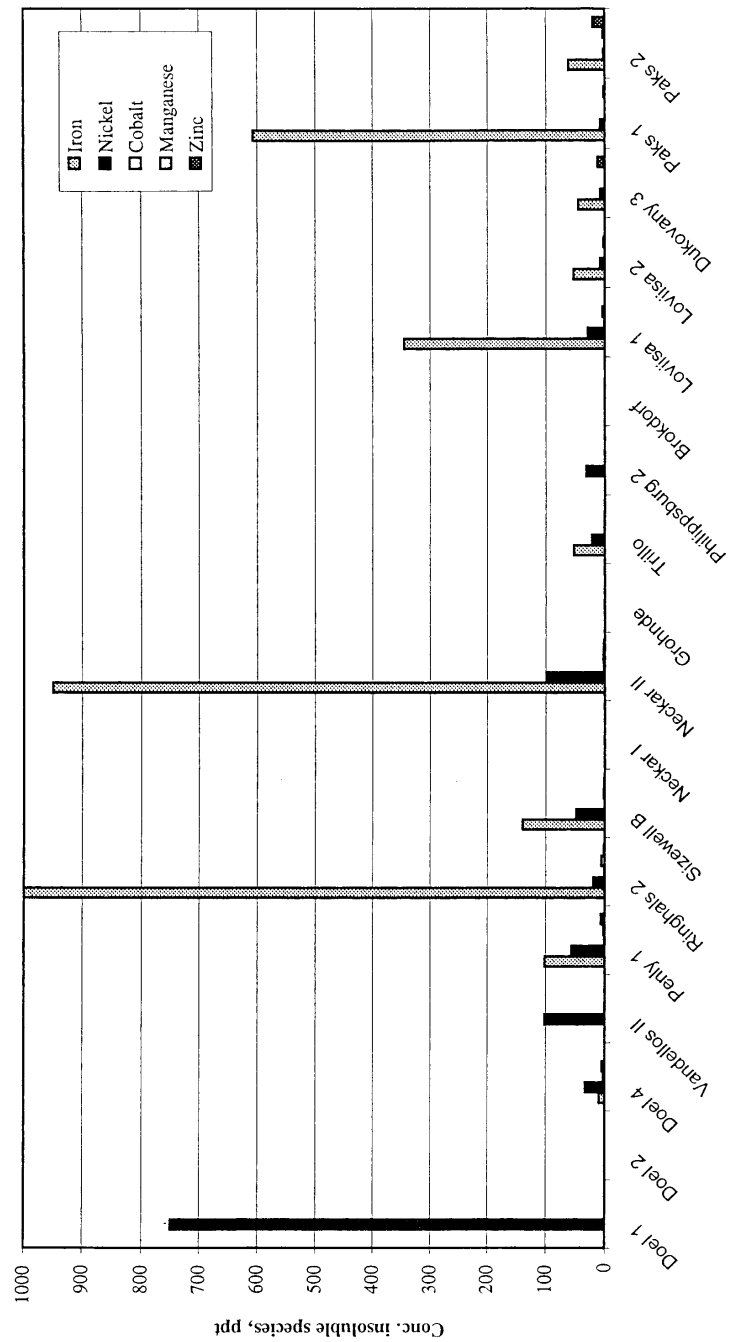


Figure 11 Comparison of the insoluble corrosion products, Fe, Ni, Co, Mn, and Zn for different reactor types. From reference 13.

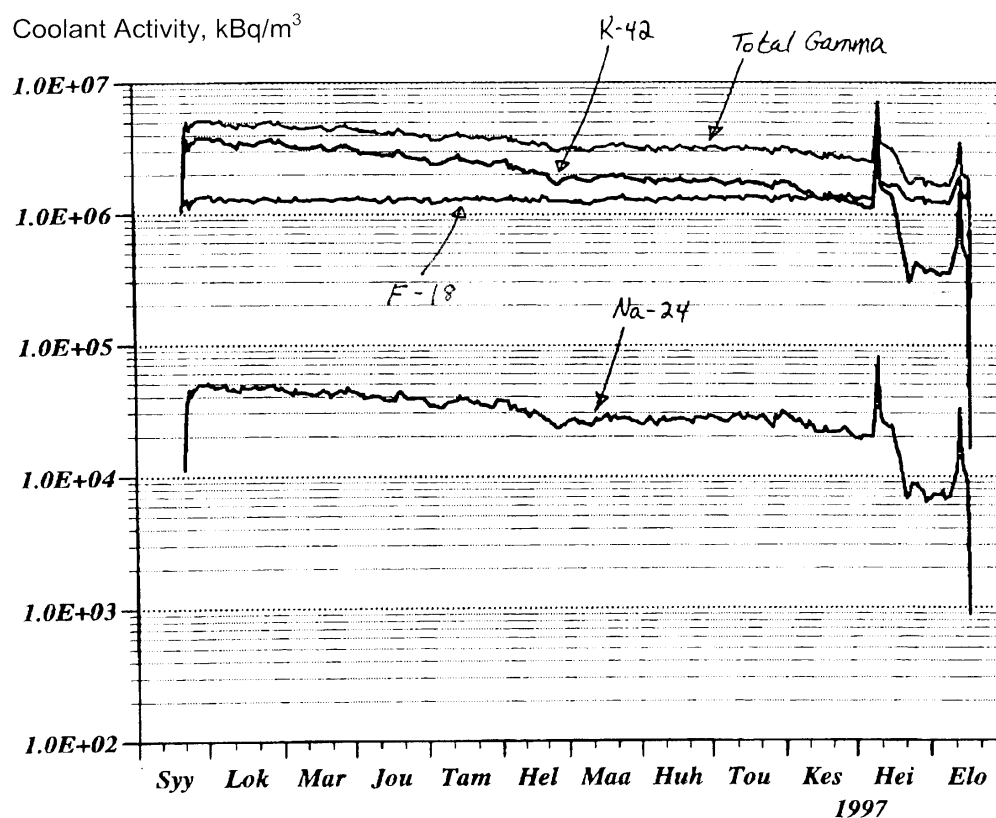


Figure 12 Trend of coolant activity at Loviisa 1 and contribution of <sup>42</sup>K. Data from September, 1996 to August, 1997 (Data provided by Loviisa plant personnel).




## About EPRI

EPRI creates science and technology solutions for the global energy and energy services industry. U.S. electric utilities established the Electric Power Research Institute in 1973 as a nonprofit research consortium for the benefit of utility members, their customers, and society. Now known simply as EPRI, the company provides a wide range of innovative products and services to more than 1000 energy-related organizations in 40 countries. EPRI's multidisciplinary team of scientists and engineers draws on a worldwide network of technical and business expertise to help solve today's toughest energy and environmental problems.

EPRI. Powering Progress

© 1999 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

TE-114158

 Printed on recycled paper in the United States of America

## SINGLE USER LICENSE AGREEMENT

**THIS IS A LEGALLY BINDING AGREEMENT BETWEEN YOU AND THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). PLEASE READ IT CAREFULLY REMOVING THE WRAPPING MATERIAL.**

BY OPENING THIS SEALED PACKAGE YOU ARE AGREEING TO THE TERMS OF THIS AGREEMENT. IF YOU DO NOT AGREE TO THE TERMS OF THIS AGREEMENT, PROMPTLY RETURN THE UNOPENED PACKAGE TO EPRI AND THE PURCHASE PRICE WILL BE REFUNDED.

### 1. GRANT OF LICENSE

EPRI grants you the nonexclusive and nontransferable right during the term of this agreement to use this package only for your own benefit and the benefit of your organization. This means that the following may use this package: (I) your company (at any site owned or operated by your company); (II) its subsidiaries or other related entities; and (III) a consultant to your company or related entities, if the consultant has entered into a contract agreeing not to disclose the package outside of its organization or to use the package for its own benefit or the benefit of any party other than your company.

This shrink-wrap license agreement is subordinate to the terms of the Master Utility License Agreement between most U.S. EPRI member utilities and EPRI. Any EPRI member utility that does not have a Master Utility License Agreement may get one on request.

### 2. COPYRIGHT

This package, including the information contained in it, is either licensed to EPRI or owned by EPRI and is protected by United States and international copyright laws. You may not, without the prior written permission of EPRI, reproduce, translate or modify this package, in any form, in whole or in part, or prepare any derivative work based on this package.

### 3. RESTRICTIONS

You may not rent, lease, license, disclose or give this package to any person or organization, or use the information contained in this package, for the benefit of any third party or for any purpose other than as specified above unless such use is with the prior written permission of EPRI. You agree to take all reasonable steps to prevent unauthorized disclosure or use of this package. Except as specified above, this agreement does not grant you any right to patents, copyrights, trade secrets, trade names, trademarks or any other intellectual property, rights or licenses in respect of this package.

### 4. TERM AND TERMINATION

This license and this agreement are effective until terminated. You may terminate them at any time by destroying this package. EPRI has the right to terminate the license and this agreement immediately if you fail to comply with any term or condition of this agreement. Upon any termination you may destroy this package, but all obligations of nondisclosure will remain in effect.

### 5. DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, NOR ANY PERSON OR ORGANIZATION ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS PACKAGE IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS PACKAGE OR ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE.

### 6. EXPORT

The laws and regulations of the United States restrict the export and re-export of any portion of this package, and you agree not to export or re-export this package or any related technical data in any form without the appropriate United States and foreign government approvals.

### 7. CHOICE OF LAW

This agreement will be governed by the laws of the State of California as applied to transactions taking place entirely in California between California residents.

### 8. INTEGRATION

You have read and understand this agreement, and acknowledge that it is the final, complete and exclusive agreement between you and EPRI concerning its subject matter, superseding any prior related understanding or agreement. No waiver, variation or different terms of this agreement will be enforceable against EPRI unless EPRI gives its prior written consent, signed by an officer of EPRI.