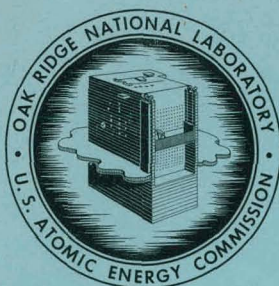


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WATER CHEMISTRY IN THE N.S. SAVANNAH REACTOR - - EFFECT OF A CORE  
COMPONENT CHANGE FROM 304 STAINLESS STEEL TO ZIRCALOY-4

C.L. Whitmarsh

ABSTRACT

Effect of changing the material of construction of the fuel element container, a structural component in the core of the N.S. SAVANNAH reactor, from 304 stainless steel to Zircaloy-4 was considered with respect to the water chemistry of the primary coolant system. No detrimental effects could be foreseen from the standpoints of crud characteristics and chemical effects on material properties. Consequently, no changes would be necessary to the primary loop purification system.

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WATER CHEMISTRY IN THE N. S. SAVANNAH REACTOR  
EFFECT OF A CORE COMPONENT CHANGE FROM 304 STAINLESS STEEL TO ZIRCALOY-4

Introduction

A change in the material of construction of the NMSR fuel element container from 304 stainless steel to Zircaloy-4 is being investigated as part of a study of means for reducing fuel-cycle costs of future SAVANNAH cores. This will increase the amount of Zircaloy surface area exposed to the primary coolant to ~ 17% in the reactor core and ~ 5% in the total primary system. Of principal interest in this report is the effect on crud behavior as related to the primary purification system in the N. S. SAVANNAH reactor and any effect on the Zircaloy-4 component due to the water chemistry.

Radioactivity associated with the crud in pressurized-water-type reactors results from corrosion of activated core components, activation of corrosion products from out-of-flux regions, fissioning of heavy elements contained as impurities in metal components of the core, and activation of impurities in the water. This crud tends to deposit at various points in the primary system, thereby fouling heat-transfer surfaces and/or creating high-activity levels in maintenance regions. Consequently, removal of crud from the primary coolant with a purification system is desirable.

Experience to date with pressurized-water reactors<sup>1</sup> has shown that the principal contributors to long-lived activity in crud are  $\text{Co}^{58}$  and  $\text{Co}^{60}$ , which result from the reactions  $\text{Ni}^{58} (n,p) \text{Co}^{58}$  and  $\text{Co}^{59} (n,\gamma) \text{Co}^{60}$ ,

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<sup>1</sup>C. R. Breden, AEC-Euratom Conference on Aqueous Corrosion of Reactor Materials, TID-7587 (July 1960), pp. 48-70.

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respectively. These materials are present in reactor cores as alloying agents and/or impurities.

### N. S. SAVANNAH Purification System<sup>2</sup>

The primary function of the purification system is to remove impurities, both dissolved and particulate, from the primary cooling water. The equipment consists of two letdown coolers, three demineralizers, and two filters. During reactor operation a side stream is continuously withdrawn from the primary system, cooled, depressurized, and then routed through the demineralizers and filters.

The resin bed<sup>3</sup> in the demineralizers is a mixture of a hydrogen-form, strong acid, cation exchange resin (Rohm & Haas XE-77) and a hydroxyl-form, strong base, anion exchange resin (Rohm & Haas XE-78). This resin adjusts the pH of the water to within the range 6.5 to 8.5. Each demineralizer is designed to give a minimum of 50 days' service in removing corrosion products formed at a maximum rate of 10 mg/dm<sup>2</sup>/month. Soluble impurities are removed by ion exchange and particulate matter by filtration. The following design specifications<sup>4</sup> for primary-system water are based on a 20-gpm (cold) blow-down rate.

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<sup>2</sup>B&W Specification No. AEC-421-4/482100, "NMSR Final System Design Specification for Primary Loop Purification System," April 29, 1959.

<sup>3</sup>B&W Specification No. AEC-205-2/482134, Change No. 5, October 7, 1959, "NMSR Final Equipment Specification for Demineralizer" (May 12, 1959).

<sup>4</sup>N. S. Savannah Plant Operating Manual, Volume II, Chapter I, Article 1.8.1.

## Corrosion Product Activity

<u>Radioisotope</u>	<u>Activity (<math>\mu\text{c/ml}</math>)</u>
Mn <sup>56</sup>	$5.42 \times 10^{-2}$
Fe <sup>59</sup>	$5.49 \times 10^{-4}$
Cr <sup>51</sup>	$4.00 \times 10^{-2}$
Co <sup>58</sup>	$2.16 \times 10^{-3}$
Co <sup>60</sup>	$1.19 \times 10^{-2}$

## Impurities in the Water

<u>Radioisotope</u>	<u>Activity (<math>\mu\text{c/ml}</math>)</u>
Ar <sup>41</sup>	$7.8 \times 10^{-2}$
Na <sup>24</sup>	$8.9 \times 10^{-3}$

Fission Products from Maximum Failure  
of Fuel Elements

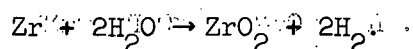
<u>Radioisotope</u>	<u>Activity (<math>\mu\text{c/ml}</math>)</u>
Cs <sup>136</sup>	$0.16 \times 10^{-1}$
Cs <sup>137</sup>	$0.33 \times 10^{-1}$
Cs <sup>138</sup>	$0.19 \times 10^0$
I <sup>131</sup>	$0.83 \times 10^0$
I <sup>132</sup>	$0.12 \times 10^1$
I <sup>133</sup>	$0.13 \times 10^1$
Br <sup>83</sup>	$0.33 \times 10^{-1}$
Sr <sup>89</sup>	$0.13 \times 10^{-2}$
Sr <sup>90</sup>	$0.33 \times 10^{-4}$
Ba <sup>139</sup>	$0.36 \times 10^{-1}$
Ba <sup>140</sup>	$0.14 \times 10^{-1}$
Cs <sup>140</sup>	$0.56 \times 10^{-2}$
Br <sup>84</sup>	$2.3 \times 10^{-2}$
Kr <sup>88</sup>	$3.3 \times 10^{-1}$



Additional equipment is necessary for hydrogen addition to the primary loop during normal operation to eliminate any dissolved oxygen and for hydrazine addition to remove oxygen at startup. Dissolved hydrogen in the coolant water is maintained at 1.8 to 3.6 ppm at all times; hydrazine concentration is 20 to 25 ppm at startup and nil during operation. Total solids are limited to 1.0 ppm and chloride content to < 0.1 ppm (maximum of 1.0 ppm allowed for periods of < 1 day).

#### Corrosion Products

Corrosion of Zircaloy in water may be represented by the reaction



At the proposed reactor conditions, the resulting  $\text{ZrO}_2$  film will be of the protective, adherent type. Corrosion rate may be represented by a weight gain of 0.6 to 0.9  $\text{mg}/\text{dm}^2/\text{month}$  exclusive of any mechanical wear.<sup>5</sup> (By using the stoichiometry of the corrosion reaction, this represents 1.5 to 2.6  $\text{mg}/\text{dm}^2/\text{month}$  of Zircaloy metal.) However, for conservative design, a value of 5  $\text{mg}/\text{dm}^2/\text{month}$  is used; 5 to 10  $\text{mg}/\text{dm}^2/\text{month}$  is generally used for 304 stainless steel design calculations. With respect to the crud problem, an additional conservative feature is the fact that these corrosion products not only must be formed but they must also be removed from that surface and transported through the system.

From an activation standpoint the principal Zircaloy-4 corrosion product is  $\text{Zr}^{95}$ , which has a 65-day half-life and  $\gamma$  radiation of  $\sim 0.8$  Mev. Other, quantitatively less important, activated isotopes result from various alloying metals and impurities in Zircaloy-4.

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<sup>5</sup>E. C. W. Perryman, A Review of Zircaloy-2 and Zircaloy-4 Properties Relating to the Design Stress of CANDU Pressure Tubes, CRMet-937 (June 1960).

Zircaloy-4 Composition<sup>6</sup>

<u>Component</u>	<u>Weight %</u>
Sn	1.2 to 1.7
Cr	0.05 to 0.15
Fe	0.12 to 0.18

<u>Impurity</u>	<u>Maximum ppm</u>
Al	75
B	0.5
Cd	0.5
C	500
Co	20
Cu	50
Hf	200
Mg	20
Mn	59
Mo	50
Ni	70
N	70
Pb	130
Si	100
Ti	50
W	100
V	50
U	3.5

Of these, the more important resulting activities are Co<sup>60</sup>, Co<sup>58</sup>, Hf<sup>181</sup>, Hf<sup>175</sup>, Mn<sup>54</sup>, Fe<sup>59</sup>, and Cr<sup>51</sup>.

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<sup>6</sup>Zirconium Data File, The Carborundum Metal Company, Akron, New York.

In stainless steel systems long-lived crud activity is primarily due to  $\text{Co}^{58}$  and  $\text{Co}^{60}$ . Type 304 stainless steel contains 8 to 12% Ni (parent of  $\text{Co}^{58}$ ) as an alloying component and up to 0.1% Co as an impurity ( $\sim 0.05$  wt % in the SM-1). For in-core reactor applications, cobalt specifications in 304 stainless steel have sometimes been set at  $< 0.010\%$  with an aim of  $< 0.005\%$ .

Relative amounts of nuclides observed in coolant systems of the S-1-W, SM-1, and PWR reactors have been measured.<sup>7,8</sup> The S-1-W core contained Zircaloy fuel cladding, hafnium control rods, and a small amount of stainless steel; the SM-1 core was essentially all stainless steel plus a significant amount of Haynes-25 alloy in a high-flux region; and the PWR core contained Zircaloy clad fuel elements, hafnium control rods, and significant amounts of 304 stainless steel and stellite. Although the tabulated values below represent widely scattered data, the following observations were noted: (1) very little activity was contributed by the Zircaloy cladding; (2) the principal source of activity was  $\text{Co}^{60}$  and  $\text{Co}^{58}$  from the 304 stainless steel, Haynes-25, and stellite core components; and (3) hafnium activity in the S-1-W probably resulted from wear on the control rod rubbing shoes. No direct comparison of the data appears valid because of different reactor conditions, sampling, and operating procedures.

Chemical analysis of crud in the PWR<sup>9</sup> showed 90% to 95% iron as  $\text{Fe}_3\text{O}_4$ . Concentration of particulate matter in the circulating coolant was only 3 to 5 ppb, with a specific activity of  $\sim 2 \times 10^7$  cpm/mg.

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<sup>7</sup>Breden, op. cit.

<sup>8</sup>C. A. Bergman, SM-1 Research and Development Program, Long-Lived Induced Activity Buildup during SM-1 Core I Lifetime, Task XVII, Phase I, APAE No. 77 (November 30, 1960), p. 77.

<sup>9</sup>Shippingport Operations from Start-Up to First Refueling - December 1957 to October 1959, pp. IV-40 to IV-60.

<u>Nuclide</u>	<u>S-1-W*</u> <u>(% of total)</u>	<u>SM-1</u> <u>(% of total</u> <u>after 1440 EFPH)</u>	<u>PWR</u> <u>(% of total</u> <u>after 1440 EFPH)</u>
Co <sup>60</sup>	19.5	10.8	39.2
Co <sup>58</sup>	5.5	58.0	16.9
Cr <sup>51</sup>	1.1	13.5	14.8
Zr <sup>95</sup>	0.7		6.5
Fe <sup>59</sup>	0.7	13.8	12.1
Hf <sup>181(175)</sup>	53.3		5.1
Mn <sup>54</sup>	—	<u>3.9</u>	<u>5.4</u>
TOTAL	80.8	100.0	100.0

Principal difference in water chemistry between the SAVANNAH and the PWR is the water alkalinity--6.5 to 8.5 in SAVANNAH and 9.5 to 10.5 in PWR. High pH has been demonstrated to decrease corrosion rate of stainless steel, decrease transport of crud, and increase filterability of crud.<sup>10</sup> Although Zircaloy represents 5 to 10% of the surface area in both primary coolant systems, its function is as fuel element cladding in PWR and as a structural component in SAVANNAH.

Preliminary tests indicate that the corrosion rate of Zircaloy in 680°F lithiated water (pH = 9.5 to 10.5) is ~ 1.2 times that for neutral water. More extensive tests are in progress at Bettis Atomic Power Laboratory.

#### Fission Products

The N. S. SAVANNAH primary coolant is routinely monitored for fission products in order to detect possible fuel-element failure and to determine when and if the radioactivity level is acceptable for discharge.

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\*Insoluble crud (average 9 values). Time of sampling unknown.

<sup>10</sup>Brcdcn, op. cit.

Fissionable material is present as an impurity (3.5 ppm maximum natural U) in Zircaloy. Thus, small amounts of fission products can enter the coolant during reactor operation by the process of fission fragment recoil, thereby creating an activity background which could interfere with the monitoring system for defected fuel elements. In general, only strontium and iodine activities are monitored since these nuclides are indicative of the fission product spectrum.

Analytical measurements of Zircaloy from the PWR showed uranium concentrations of  $1.35 \pm 0.2$  ppm as a bulk contaminant.<sup>11</sup> Measured fission product activity in the primary system was greater, however, than could be accounted for by this method and was, therefore, attributed to defected fuel elements. Measured fission product activity backgrounds in other reactors indicate uranium contaminations of 1 to 2 ppm in the Zircaloy. Because of the fuel-element fabrication procedures in which zirconium and uranium must necessarily be processed together, a large part of this uranium probably was the result of surface contamination on the Zircaloy-clad fuel elements. However, the use of Zircaloy as a structural component in the SAVANNAH should minimize surface contamination with uranium during fabrication and thereby decrease fission product activity from that source.

#### Effect on Zircaloy-4 Properties

Of the water chemistry specifications for the N. S. SAVANNAH,<sup>12</sup> only excess hydrogen need be considered with respect to the physical properties of Zircaloy-4. The effect of pH on corrosion was considered previously under Corrosion Products.

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<sup>11</sup>P. W. Frank, "Evaluation of the Fission Product Activities in the Primary Coolant of Shippingport," Bettis Technical Review, WAPD-BT-12 (April 1959), pp. 118-128.

<sup>12</sup>Plant Operating Manual, N. S. SAVANNAH Nuclear Power Plant, Operating Procedures, Volume II, The Babcock & Wilcox Company, Section 1.8.

Absorption of hydrogen with its resulting embrittlement tends to be a limiting condition for Zircaloy in reactor service of the type being considered here.<sup>13</sup> Although experimenters agree that hydrogen concentrations of 1.8 to 3.6 ppm increase absorption in Zircaloy, the magnitude of this effect is in considerable doubt.<sup>14,15</sup> The continued use of Zircalloys in existing and future reactors of the pressurized-water and the pressure-tube types, however, indicates that this situation is probably not serious.

Even though the above results were reported for Zircaloy-2, they are probably applicable to Zircaloy-4 and can be considered conservative since the only major difference between the two materials is a lower tendency to absorb hydrogen by Zircaloy-4.<sup>16</sup>

#### Conclusions

The information reviewed in this report is summarized below:

1. Experience with pressurized-water reactors containing a substantial amount of stainless steel has indicated that Zircaloy contributes very little to crud activity. Long-lived crud activity resulting from corrosion products (excepting abnormal wear) is due primarily to Co<sup>58</sup> and Co<sup>60</sup>. The target nucleus in each case, Ni<sup>58</sup> and Co<sup>59</sup>, respectively, is present to a lesser degree in Zircaloy than in 304 stainless steel.
2. No prohibitive effects on Zircaloy resulting from the primary system water chemistry conditions in the N. S. SAVANNAH are indicated.

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<sup>13</sup>Shippingport Operations from Start-Up to First Refueling - December 1957 to October 1959.

<sup>14</sup>J. D. Eichenberg, et al., Irradiation of UO<sub>2</sub> Fuel Rods--The X-1-L Experiment, WAPD-208 (April 1960), p. 16.

<sup>15</sup>G. J. Biefer, et al., Hydrogen Pick-Up in Zirconium Alloys, A Review of Data up to June 1, 1959, CRMet-849, pp. 23-25.

<sup>16</sup>E. C. W. Perryman, op. cit.



3. Fission-product activity in the crud resulting from fissioning of uranium contained in Zircaloy as a contaminant, while measurable, is sufficiently low so as not to represent a problem.

Therefore, it may be concluded that changing the material of construction of the fuel element container in the N. S. SAVANNAH from 304 stainless steel to Zircaloy-4 will necessitate no changes in the design of the primary coolant system for Core I and will, in fact, reduce somewhat the principal source of long-lived crud activity.

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