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EFFECT OF FLUORIDE IONS ON THE AQUEOUS CORROSION OF ZIRCONIUM ALLOYS

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ABSTRACT

A review has been made of the effects of fluoride ions on the corrosion behavior of zirconium alloys in high-temperature water. Corrosion was found to occur as the result of contamination of the water or the zirconium surface. A major source of fluorides is undue delay in rinsing the HF-HNO₃ pickling solution during surface preparation. The oxide on corrosion-resistant material has been found to contain up to 7600 ppm fluoride from this source. The threshold concentration of fluoride in the oxide film which produces poor corrosion resistance ranges from 8500 to 17,000 ppm. Accelerated corrosion from fluorides in water at 300 to 360 C occurs at about 100 ppm, although increased corrosion has been reported at 10 ppm fluoride in water at 300 C. Fluorocarbon plastics degrade and contribute fluorides to the high-temperature water or to the alloy surface when in direct contact with zirconium. Chlorides (1 to 10,000 ppm) and iodides (1270 ppm) do not adversely affect the corrosion behavior of zirconium alloys in water at 360 C. The mechanism of corrosion is not well understood but apparently is related to the formation of insoluble zirconium oxyfluorides during pickling and during exposure to fluoride-contaminated water.

INTRODUCTION

Although zirconium is one of the more corrosion resistant metals, it is rapidly attacked by hydrofluoric acid and acid fluoride solutions at room temperature. This fact is taken advantage of in preparing zirconium alloy surfaces for use in the high-temperature water environments of pressurized-water and boiling-water reactors. A solution containing approximately 40 per cent (by volume) of 70 per cent HNO_3 and 3.5 per cent by volume of 50 per cent HF is used to remove 1.5 to 2 mils of metal. This ensures the removal of a worked surface layer which if left in place would result in lowered corrosion resistance. Thus, it is not surprising that accelerated corrosion occurs in high-temperature water with fluoride ions in solution or in contact with zirconium alloys. This is one of the possible causes of premature failure of zirconium alloys in reactor environments. The source of the fluoride may be (1) residual etchant left on the surface after pickling or (2) materials or actions which contribute fluoride to the water. The latter might include (1) breakdown of fluorocarbon plastics in gasketing materials, (2) residual etchants leached from other components in the reactor, (3) accidental introduction of contaminated water into the primary coolant circuits, or (4) as in at least one case, fluoride contamination from the fissionable nuclear fuel.

The effect of the fluoride is to hasten the formation of white stoichiometric ZrO_2 on the zirconium alloy surface. Under severe contamination this could result in excessive pitting or general metal wastage with accompanying loss of structural strength. With only mild

contamination a superficial white oxide film may form which poses no threat to structural properties but is very undesirable in fuel element cladding. The white ZrO_2 is more of an insulator than the substoichiometric black ZrO_2 which normally forms on good quality zirconium alloys in high-temperature water. The black oxide eventually transforms to the white oxide with an accompanying transition in corrosion kinetics.⁽¹⁾ This transformation is strongly temperature dependent. Thus, a superficial film on a nuclear fuel element will tend to slow down the heat transfer rate. This will increase the surface temperature and hasten the time to conversion to the white oxide. This reduction in heat transfer results in (1) the nuclear fuel being operated at higher temperatures, or (2) an increase in coolant flow rate to keep the fuel temperature within design specifications.

THE ETCHANT PROBLEM

Early in the nuclear reactors program it was recognized that Grade 1 crystal bar zirconium would corrode in high-temperature water if the HF-HNO_3 etching solution was not immediately and thoroughly rinsed.⁽²⁾ Subsequent work was directed toward defining the conditions which cause this phenomenon and means of avoiding it.^(3,4,5,6,7,8,9)

Kass⁽³⁾ has shown that variations in delay time between pickling and rinsing markedly affect the corrosion behavior of Zircaloy-2 (sponge zirconium plus 1.5 Sn, 0.12 Fe, 0.10 Cr, 0.03 Ni). No delay

produced excellent corrosion resistance. One to 5 minutes delay resulted in cloudy surfaces and initially high weight gains during corrosion. However, upon continued exposure, the corrosion rate paralleled that of uncontaminated Zircaloy-2. Twenty-four to 72-hour delays produced severely contaminated surfaces and spalling oxide films in 360 C water and 400 C-1500 psi steam (the corrosion test conditions for qualifying zirconium alloys). After an initial period of spalling in 400 C steam, the severely contaminated Zircaloy-2 gained weight at a slightly higher rate than that for uncontaminated surfaces. However, in high-temperature water, the severely contaminated specimens continued to exhibit spalling oxide.

Kass, et al.,⁽⁴⁾ investigated the effect of various rinses and of additives to the pickling solution on the contamination problem. Dilute HNO_3 or NaOH rinses were found to be helpful. The addition of wetting agents to the HF-HNO_3 pickle bath did not improve the rinsing characteristics. It was found H_2SO_4 could be substituted wholly or in part for HNO_3 in the pickling bath without adverse effects on corrosion. On the other hand, an HCl-HF solution was not satisfactory. A fluoride-free etchant consisting of 96 per cent H_2SO_4 and 120 grams per liter NaNO_2 was as effective as HF-HNO_3 .

Shannon and Griggs⁽⁶⁾ also investigated rinsing techniques and found that the addition of 10 per cent $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ to the rinse water was effective in preventing acid staining. Any fluoride ion from dragover apparently is tied up as an aluminum fluoride complex.

Shannon and Griggs⁽⁶⁾ have speculated on the mechanism of acid staining by HF-HNO_3 etchants and its adverse effect on the corrosion

of zirconium. They believe the compound which precipitates on the surface has the general formula $H_2ZrO_xF_y(H_2O)_z$. Included in the possibilities are H_2ZrF_6 , H_2ZrOF_4 , or $H_2ZrO_2F_2$. ($H_2ZrOF_4 \cdot 2 H_2O$ was found in the white precipitate which forms in the $HF-HNO_3$ bath with excess pickling of zirconium). These compounds, once precipitated, are only slowly dissolved. Upon heating in high-temperature water, they are believed to be converted to the oxyfluoride $ZrOF_2$. Fluorides deposited from other sources are also believed to form $ZrOF_2$ on the surface.

Analytical studies have been made of the surface fluoride after pickling and after exposure to high-temperature water or steam. Beg and Brown,⁽⁷⁾ using radioactive tracer techniques, have shown that pickling of Zircaloy in $HF-HNO_3$ solutions resulted in attachment of about $50 \mu g/dm^2$ (about 10 atom layers) of fluorine. Their results are shown in Table 1. This was firmly bound and could not be removed by water or NH_4F solutions at 100 C as shown in Table 2. Mechanical abrasion or oxidation in 500 C steam reduced the fluorine level apparently by removing a surface layer of metal. This analytical technique indicated no difference in fluoride content between "good" pickled surfaces and "poor" pickled surfaces. The latter are attributed to inadequate stirring during pickling which produces stains. Increased corrosion rates are frequently observed at these stains during corrosion in high-temperature water.

Beg and Brown⁽⁷⁾ also found that Zircaloy-2 picked up 10 to $20 \mu g/dm^2$ fluorine from a solution containing 5 ppm F^- (as NH_4F) at room temperature. Fluoride was lost from these specimens immediately

TABLE 1. FLUORINE PICKUP ON ZIRCALOY-2 FROM
PICKLING IN HF-HNO₃ SOLUTIONS
(Ref. 7)

Specimen No.	Surface Preparation Prior to Pickling	Pickling Time, Min.	Fluoride Pickup, μg (b)
1	Polished	2	7.2
		4	6.2
		16	6.9
2	Abraded	4	6.0
3	Abraded	4	6.1
4	Abraded	4	6.8
5	Pickled (c)	4	6.1
6	Pickled (c)	4	6.0
7	Pickled (c)	4	6.2

(a) Pickling solution = 39 vol. % HNO₃ (70%)-3.5 vol. % HF (50%)-
balance water.

(b) Surface area = 13.5 cm².

(c) 7.1 μg F⁻ initially present from prior pickling.

TABLE 2. RESULTS OF ATTEMPTS TO REMOVE FLUORIDE
PICKED UP FROM PICKLING OF ZIRCALLOY-2
(Ref. 7)

F Uptake, $\mu\text{g(a)}$	Treatment	Duration, Min.	F Retained, %
6.9	Boiling water	208	100
7.1	Boiling NH_4F solution 5 ppm F	214	100
6.0	NH_4F solution 5 ppm F at room temperature	110	95
6.1	Anodic oxidation ^(b)	30	93
7.0	Cathodization ^(b)	30	100
6.1	Steam oxidation ^(c)	15	Not Detectable

- (a) Specimen area = 13.5 cm^2
 (b) 42 milliamps to 165 V
 (c) 500 C at atmospheric pressure

upon immersion in distilled water suggesting that the uptake of fluoride under these conditions was related to the ion-exchange properties of the zirconium oxide film.

Rynasiewicz⁽⁸⁾ has found evidence for at least $27 \mu\text{g F/dm}^2$ on as-pickled Zircaloy-2 surfaces. His results were based on the amount of fluoride which hydrolyzed from the surface of corrosion tested specimens and entered the autoclave water. Other experiments by Rynasiewicz⁽⁸⁾ on Zircaloy-2 intentionally doped with $1050 \mu\text{g}$ fluoride indicated two-thirds of the fluoride was lost to the autoclave water at 360°C supposedly by hydrolysis as indicated in the following equations:

The surfaces of stainless steel autoclaves have been found to contain approximately $20 \mu\text{g F/dm}^2$. Carefully controlled experiments have shown (1) that this fluoride can be released to the high-temperature water, and (2) the source of this fluoride is that released from HF-pickled Zircaloy specimens.⁽⁸⁾

Using pyrohydrolysis-distillation followed by colorimetric analysis of fluoride in the condensate, Rynasiewicz⁽⁸⁾ has also found that the oxide films on corrosion-resistant Zircaloy-2 specimens contain up to $760 \mu\text{g F/dm}^2$ (7600 ppm) while the threshold concentration for white oxide formation lies between 850 and $1700 \mu\text{g F/dm}^2$ (8500 to 17,000 ppm). However, he was able to produce a ring of white oxide by evaporating as little as $88 \mu\text{g F/dm}^2$ on a pickled Zircaloy

coupon and then exposing the specimen to water at 360 C for 14 days. (Shannon and Griggs⁽⁶⁾ obtained similar results upon drying one drop of 6 ppm HF solution, about 1 μ g HF, on Zircaloy and then autoclaving.) Ryansciewicz found that the extent of white oxide formation was proportional to the amount of HF evaporated in the range of 88 to 52,500 μ g F/dm². This effect is shown in Figure 1, and suggests that the rings of white oxide formed at low HF levels are due to localized concentration of the HF during evaporation of the water.

CONTAMINATION FROM FLUOROCARBONS

The corrosion of zirconium alloys in direct contact with, or in the vicinity of, fluorocarbon plastics in high-temperature water has been attributed to leached fluorides by at least two investigators.^(10,11)

Krenz⁽¹⁰⁾ leached Viton "A" at 200 C and passed this water over Zircaloy-2 at 300 C in a recirculating system. The initial pH dropped from 10 (LiOH) to 3.8 while the fluoride content of the water ranged from 3 to 10 ppm with one analysis running 73 ppm just before completion of a 190-hour test. The Zircaloy-2 exhibited small blisters and patches of white oxide. Its weight gain was 54 mg/dm² and hydrogen pickup was 235 ppm, compared with weight gains of 10 mg/dm² and hydrogen pickup of 16 ppm for Zircaloy in pure water at this temperature. The hydride was uniformly distributed in these specimens.

Moore and Rau⁽¹²⁾ have also studied fluoride leaching from fluorocarbons in 205 to 230 C water. Their results are summarized in Table 3. They found Viton A or B contributed up to 30 ppm fluoride

14 days exposure

0 0.88 2.63 4.37 6.13 8.80

3 days exposure

0 8.5 17.0 25.5

3 days exposure

175

350

525

WHITE-PRODUCT FORMATION PRODUCED BY EVAPORATING FLUORIDE
ON ZIRCOLOY AND THEN EXPOSING TO WATER AT 360C.
(Indicated quantities are μ g of fluoride)

TABLE 3. FLUORIDE LEACHED FROM FLUOROCARBON
PLASTICS IN HIGH-TEMPERATURE WATER
(Ref. 12)

Plastic	Temperature, C	Exposure Time, hr	pH		Fluoride Pickup, ppm
			Initial	Final	
Viton A	205	28.5	8.2(NH ₃)	3.3	33
	205	10	10.4(LiOH)	3.6	29
Teflon	205	48	6.9	5.5	0.05
	230	48	6.9	5.9	0.35

after one day's exposure to water at 205 C. Teflon, on the other hand, contributed 0.05 ppm fluoride to water at 205 C and 0.35 ppm fluoride at 230 C. Tolstaya, et al.,⁽¹¹⁾ also report negligible fluoride contamination by Teflon in water at 263 to 310 C, although accelerated corrosion was observed when the Teflon and zirconium alloys were in direct contact.

FLUORIDE IN SOLUTION

The effect of fluorides in solution on the corrosion behavior of zirconium alloys in high-temperature water has been reported by several investigators.^(4,5,13,14,15)

Kass, et. al.,^(4,5) reported severe attack of mating faces at crevices between unalloyed zirconium exposed to 343 C water containing 90 ppm fluoride as NaF. Little or no attack was observed on individually mounted specimens or on electrically coupled specimens (no crevice).

Only slight attack was observed on mating faces in the steam above this solution with little or no attack on uncoupled pieces. Photographs of these specimens are shown in Figure 2.

Krenz⁽¹³⁾ observed accelerated corrosion of Zircaloy-2 in water at 300 C containing 10 ppm fluoride at pH 10 (LiOH). After 7 to 8 days' exposure, specimens exhibited pitting, a gray product on their surface, and increased hydrogen pickup. Intergranular attack to a depth of 4 mils was detected on the tension side of U-bend specimens, but no such attack was observed on the compression side.

On the other hand, Berry, et. al.,⁽¹⁴⁾ have found that Zircaloy-4 (sponge zirconium plus 1.5 Sn, 0.20 Fe, 0.10 Cr, <0.007 Ni) did not corrode excessively in 360 C pH 10.5 water containing 19 ppm fluoride (as LiF or NH_4F), but did exhibit accelerated corrosion with 190 ppm fluoride. Freshly pickled specimens corroded uniformly but precoated specimens (autoclaved in high-temperature high-purity water) pitted severely in the water containing 190 ppm fluoride at 360 C. This is shown in the photographs in Figure 3. Severe hydriding accompanied this attack being more concentrated in the metal beneath the areas of heaviest corrosion. This is illustrated in Figure 4.

Large quantities of crud (Fe_3O_4 corrosion product) appeared to adsorb the fluoride ion reducing its concentration from 190 to 19 ppm where no accelerated corrosion occurred. Up to 1.8 mg F/g crud was detected by chemical analysis.

In these same tests,⁽¹⁴⁾ the white oxide which formed on specimens exposed to 190 ppm fluoride (as NH_4F), was found to contain

Physical Contact-Water

Electrical Contact-Water

Individually Mounted-Water

Physical Contact-Steam

Individually Mounted-Steam

FIGURE 2. CORROSION OF ZIRCONIUM IN 343 C WATER AND STEAM CONTAINING 200 PPM SODIUM FLUORIDE - FOUR DAYS EXPOSURE

a. Exposed to LiF

b. Exposed to NH_4F

FIGURE 3. APPEARANCE OF ZIRCALOY-4 SPECIMENS AFTER 3 DAYS' EXPOSURE TO 360 C pH 10.5 WATER CONTAINING 190 PPM FLUORIDES ⁽¹⁴⁾

Precoated specimens at left, as-pickled specimen at right.

a. Beneath White Oxide (1300 PPM of Hydrogen)

b. Beneath Black Oxide (567 PPM of Hydrogen)

FIGURE 4. CROSS SECTIONS OF A ZIRCALOY-4 SPECIMEN EXPOSED TO 360C WATER CONTAINING 190 PPM FLUORIDES AS NH_4F AT pH 10.5

4,000 to 7,000 ppm fluoride. This is slightly below the 8,500 to 17,000 ppm threshold range determined by Rynasiewicz.⁽⁸⁾

The addition of 345 ppm chlorides or 1270 ppm iodides (as lithium- or ammonium-salts) to pH 10 water at 360 C had no adverse effect on the corrosion behavior of Zircaloy-4.⁽¹⁴⁾ Suspensions of synthetic crud (Fe_3O_4) did not accelerate attack under these conditions.

Rozenfel'd, et. al.,⁽¹⁵⁾ have also studied the effect of halides on the corrosion behavior of zirconium alloys in high-temperature water. Zirconium-1 to 2.5 niobium alloys and Ozhennit-0.5 Zr + 0.2 Sn, 0.1 Fe, 0.1 Ni, 0.1 Nb) began to exhibit severe corrosion in 360 C water at greater than 100 mg fluoride/liter (as KF). Chloride ion (as NaCl) in the range of 1 to 10,000 mg/liter had no adverse effect on corrosion resistance. These authors related this behavior to the chemical affinity of zirconium for halides and oxygen which is $\text{F} > \text{O} > \text{Cl} > \text{Br} > \text{I}$. Thus, the fluoride ion was able to displace oxygen in competing reactions for zirconium, while the other halides were not able to do so.

OTHER SOURCES OF FLUORIDE

A rather unusual source of fluorides which resulted in Zircaloy failure has been related by Notley and Robertson⁽¹⁶⁾ who exposed defected Zircaloy clad UO_2 to high-temperature water under irradiation. Severe hydriding failures occurred within 22 hours' exposure in the Zircaloy cladding of fuel elements whose cores contained

340 to 560 ppm F (as CaF_2). On the other hand, no excessive hydriding was observed after 300 days' exposure in defected fuel elements containing UO_2 cores with less than 6 ppm fluoride.

DISCUSSION

The conditions have been pretty well defined for the effect of fluorides on the corrosion behavior of zirconium alloys in high-temperature water. Delay in transfer time from the HF-HNO_3 pickling solution to the rinse water can allow sufficient fluoride to remain on the surface to affect corrosion behavior. Fluoride analysis of oxide films after pickling and after pickling and corrosion testing range from 50 to 760 $\mu\text{g F/dm}^2$ on corrosion-resistant material. The wide range in results does not necessarily represent gross differences in analytical techniques among different laboratories. Rather, it could reflect a difference in transfer time from the pickle bath to the rinse solution. However, the results of Beg and Brown,⁽⁷⁾ which indicated the same surface concentration of fluoride in "good" and "poor" corrosion-resistant samples, can not be explained in this manner. In their experiments, the reduction in corrosion resistance was due to insufficient stirring of the solution during pickling rather than to transfer effects.

It is fairly well established that zirconium alloys begin to lose corrosion resistance at about 100 ppm fluoride (as a salt) in high-temperature water (343 to 360 C), although, Krenz⁽¹³⁾ observed accelerated corrosion in 300 C water containing only 10 ppm fluoride.

Krenz⁽¹⁰⁾ also observed similar results during the leaching of Viton "A" where the fluoride concentration of the water (at 300 C) ranged from 3 to 10 ppm with one excursion to 73 ppm. Chlorides and iodides, at 10,000 and 1270 ppm respectively, had no adverse effects on zirconium alloys in 360 C water.

Fluorocarbon plastics have been shown to contribute fluoride ions to high-temperature water. Teflon is more resistant to degradation than Viton A presumably because the latter contains unsaturated carbon atoms which provide an area of weakness in breaking down the molecule (Viton "A" is a copolymer of hexafluoropropylene and vinylidene fluoride while Teflon is polymerized tetrafluoroethylene).

Although the conditions which cause fluoride-accelerated attack of zirconium alloys are fairly well known, the mechanism of attack is not well defined.

Griggs and Shannon,⁽⁶⁾ citing Blumenthal,⁽¹⁷⁾ believed the following reactions probably occur:

Equation (1) represents the reaction during normal pickling. Equation (2) would account for fluoride contamination from delayed rinsing during pickling since H_2ZrOF_4 is only slowly soluble in acids and is insoluble in neutral or basic solutions. Equation (3) would represent the reaction upon exposure to high-temperature water.

Kass, et. al.,⁽⁴⁾ believed the white precipitate which formed during pickling was a hydrated fluoride whose composition was similar to that shown in equation (4).

Rynasiewicz,⁽⁸⁾ also believed equation (4) represents the contamination reaction during pickling. However, he proposed the following reaction upon exposure to high-temperature water:

These latter two reactions are analogous to those described by Ephraim⁽¹⁸⁾ for hydrolysis of SnCl_4 .

It is quite possible the high-temperature form of the oxyfluoride might be identified by X-ray diffraction techniques. According to Rynasiewicz,⁽⁸⁾ the fluoride contamination associated with the non-protective white oxide is 8,500 to 17,000 ppm. For a compound of the general formula ZrOF_2 , this would represent upwards of 6 per cent of the total weight of the film. This could well be within the limits of detection by X-ray diffraction for a mixture of this type.

CONCLUSIONS

1. Fluoride contamination of zirconium alloy surfaces or of the aqueous solution can cause accelerated corrosion in high-temperature water.

2. Delay in transfer from the HF pickle bath to the rinse solution is a major cause of fluoride contamination. Up to 7600 ppm fluoride have been found in the oxide on corrosion-resistant alloys. The threshold concentration for producing accelerated corrosion lies between 8,500 and 17,000 ppm fluoride in the oxide film.

3. Accelerated corrosion of zirconium alloys begins at about 100 ppm dissolved fluoride in 300 to 360 C water, although increased corrosion has been reported at 10 ppm fluoride at 300 C.

4. Chlorides (10,000 ppm) and iodides (1270 ppm) have no adverse effect on the corrosion behavior of zirconium alloys in high-temperature water presumably because zirconium has a higher affinity for oxygen than for chlorine or iodine. Zirconium has a greater affinity for fluorine than oxygen.

5. Fluorocarbon plastics affect the corrosion behavior of zirconium alloys by contributing fluoride ions to the high-temperature water or to the zirconium when in direct contact.

6. The mechanism of corrosion is not well understood, but apparently is related to the formation of zirconium oxyfluorides during the pickling operation and during exposure to fluoride-contaminated water.

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REFERENCES

1. Lustman, B. and Kerze, F., Jr., The Metallurgy of Zirconium, Vol. 4 Div. VII NNEs, McGraw-Hill, New York (1955).
2. Hoge, H. R. and Shapiro, Z. M., "Investigation of the Effect on Corrosion Resistance of Zr Crystal Bar, of Zr Iodides, and High Temperature Ceramics", USAEC Report WAPD-RM-52 (May 23, 1951).
3. Kass, Stanley, "Effect of Residual Etchant on the Corrosion Behavior of Zircaloy-2", Corrosion 17 (12) 566t-570t (December, 1961).
4. Kass, S., Fontanese, D. J., Oaks, A. E., and Scott, D. C., "Pickling of the Zircaloys Prior to Corrosion Exposure", USAEC Report WAPD-TM-141 (September, 1958).
5. Kass, Stanley, "Corrosion Testing of Two Zirconium Alloys", Corrosion, 16 (2), 96t-99t (February, 1960).
6. Shannon, D. W., and Griggs, B., "Preparing Zircaloy-2 for Autoclave Testing", USAEC Report HW-60433 (July 1, 1959).
7. Beg, K. and Brown, F., "Unpublished work, Atomic Energy of Canada, Limited.
8. Rynasiewicz, J., Reactor Technology Report No. 22, Chemistry, pp V.15-V.27, USAEC Report, KAPL-2000-19 (September, 1962).
9. Friedl, E. Burt, Berry, Warren E., Miller, Paul D., and Fink, Frederick W., "The Nitric-Hydrofluoric Acid Pickling of Zircaloy-2", USAEC Report BMI-1270 (June 11, 1958).
10. Krens, F. H., "Unpublished work, Atomic Energy of Canada, Limited.

11. Tolstaya, M. A., Gradusov, G. N., and Bogatyreva, S. V., "Investigation of the Corrosion-Resistance of Zirconium Alloy Tubes in Water at High Temperatures", Corrosion of Reactor Materials: A Collection of Articles, USAEC Translation AEC-tr-5219, pp 280-290 (October, 1962).
12. Moore, R. E. and Rau, E., "Evaluation of Viton and Other Non-metallic Gasketing Materials in Contact with Structural Alloys", USAEC Report WAPD-BT-22, pp 71-77 (March, 1961).
13. Krenz, F. H., "A Preliminary Study of the Effect of Added Fluoride on the Corrosion of Zr-2 in Water at 300 C", Canadian Report CRGM-1082 (March, 1962).
14. Berry, Warren E., White, Earl L., and Fink, Frederick W., "Zircaloy-4 Corrosion in Halide Solutions and at Crevices in High-Temperature Water", USAEC Report BMI-1571 (March 19, 1962) and Corrosion 19 (7), 253t-259t (July, 1963).
15. Rozenfel'd, I. L., Ol'Khovnikov, Yu. P., Sudarikova, A. A., "The Effect of Composition of Water on Corrosion of Zirconium Alloys at High Temperatures and Pressures", translation of paper presented at IAEA Conference at Salzburg, June 4-9, 1962, AEC-tr-5374 (December 5, 1962).
16. Notley, M.J.F., and Robertson, J.A.L., "Zircaloy-UO₂ Failures Tied to Fluorides", Nucleonics, 19 (3), 77-79 (March, 1961).
17. Blumenthal, W. B., The Chemical Behavior of Zirconium, D. Van Nostrand Company, Inc., (1958).
18. Ephraim, Fritz, A Textbook of Inorganic Chemistry, English Edition by P.C.L. Thorne, Gurney and Jackson, London (1934) pp 293-299.

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