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TO: E. A. Smith
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EFFECT OF ZIRCONIUM JACKETED SLUGS ON THE REDOX PROCESS

Reference: Memorandum, "Effect of Zirconium Clad Slugs on Redox Separation", to R. B. Richards from E. A. Smith, August 3, 1950.

In the reference memorandum above, an inquiry was made concerning possible adverse effects on the Redox Separations process if Hanford Works uranium slugs were clad with zirconium instead of with aluminum as at present. Lower corrosion rates of zirconium would help permit higher pile operating levels. The present letter summarizes a survey of Project literature on the dissolution of zirconium metal, particularly with reference to dissolving the above mentioned zirconium-clad slugs in preparation of Redox process IAF feed.

Recent work at Argonne National Laboratory and Knolls Atomic Power Laboratory on processes to recover Uranium from the Uranium-Zirconium fuel elements to be used in the Naval Reactor has indicated that there are two processes that could possibly be adapted to dissolve zirconium-clad Hanford type slugs. Conclusions reached after a study of this work are summarized below.

SUMMARY AND CONCLUSIONS

It is considered possible that either the fluosilicic acid-nitric acid or the hydrofluoric acid-aluminum nitrate process for dissolving the zirconium cans might be adapted and used successfully in the Redox plant

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dissolving equipment as now designed. The only additional equipment required would appear to be facilities for adding another "cold" process solution to the dissolvers.

Although the dissolving cycle would probably be lengthened slightly, it is tentatively assumed that the presently planned 3 Redox dissolvers would have adequate capacity.

All studies reported to date on these zirconium dissolving processes have been on a laboratory scale and of a scouting nature. For these reasons, and because of differences between the Naval Reactor fuel elements and the proposed Hanford-type slugs, development of the following additional information is considered necessary to demonstrate one or both of the above processes for preparing Redox IAF feed by dissolving Hanford-type zirconium-clad slugs:

a. The minimum HF concentration required for dissolution of the Hanford-type zirconium-clad slugs should be determined for the hydrofluoric acid-aluminum nitrate process.

b. The optimum fluosilicic acid concentration for dissolving Hanford-type zirconium-clad slugs, and compatibility of this fluosilicic acid with the other ions in Redox IAF feed (i.e., precipitation with sodium), should be determined for the fluosilicic acid-nitric acid process.

c. Zr solubility in solutions containing 2.0 $\underline{M}$ U should be determined for both processes.

d. The effect of the added ions (0.11 $\underline{M}$ Zr, and Fluoride or Fluosilicate) on the solvent extraction of U and Pu and on the Decontamination Factor should be established.

e. The effect of Al-Si or other bonding layers on solvent extraction of U and Pu and on D.F. should be established.

f. Corrosion rates on the dissolver should be determined at boiling temperature.

g. Corrosion rates in the oxidizer should be determined at both ozonization conditions and dichromate oxidizing conditions.

h. Corrosion rates on the rest of the plant equipment, particularly the IAW concentrator, should be determined.

i. The time required for dissolution of the Zr jackets should be established by semiworks dissolution studies using "cold" zirconium-clad slugs.

DISCUSSION

Either process could possibly produce a satisfactory Redox feed that would not result in excessive corrosion rates in the Redox stainless-steel equipment. That either process can be handled at boiling temperatures in stainless has not been proven, however.

Of the two processes, the fluosilicic acid-nitric acid process appears to be the most advantageous as the hydrofluoric acid-aluminum nitrate process would require the handling of large volumes of hydrofluoric acid.

As discussed further below, a potential disadvantage of the fluosilicic-nitric process is the relatively low solubility of Zr in this solution. Available data on Zr solubility indicate that this process could not be adapted to Redox without possible changes in the Redox Flowsheet if the thickness of the Zr jackets is to be much over 10 mils on the sides and 100 mils on the ends. This low Zr solubility would also require that the dissolver be charged before each cut, instead of after every third cut which would probably lengthen the dissolver time cycle by several hours.

The time required to dissolve off the Zr jackets should not materially add to the time cycle for either process, as Zr is reported to dissolve quite readily in either process solution.

The available information on the various processes for the recovery of U from U-Zr fuel elements and possible applications of this information to handling Zr-clad slugs in the Redox process are as follows:

0.25 M Fluosilicic Acid and 15 M Nitric Acid

The minimum amount of this solution required to dissolve one gram of Zr (in the absence of Uranium) is approximately 65 ml. (making a 0.17 M solution of Zr). Two grams of Zr (crystal bar of unstated shape) treated with approximately 130 ml. of this solution at 75°C. was completely dissolved in 90 minutes. It was believed by A.N.L. personnel (ANL-4425) that this solution could possibly be contained in stainless-steel, so it is possible that it could be used in Redox dissolvers as presently designed. This would require experimental confirmation.

Assuming that the Zr jacket thickness is 10 mils on the sides and 100 mils on the ends of an 8 inch slug, the mole ratio of U to Zr is approximately 18 to 1. A 2.0 M U IAF solution would therefore contain 0.11 M Zr. Assuming that high U concentration would not effect the solubility of Zr, this concentration would be below the solubility of Zr (0.17 M) in this solution. The possible adverse effect of 2 M UNH concentration on Zr solubility should be determined.

No work has been done on the distribution of U and Zr between this solution and hexone.

In the TBP process for E.B.R. fuel recovery 0.01 M fluosilicate ion has been found to complex tracer quantities of Zr and provide higher Zr decontamination factors. It is possible that the 0.25 M fluosilicate ion in this process would complex both the 0.11 M "cold" Zr and the fission-product Zr in the same way and aid in Zr decontamination.

Further work on the fluosilicic acid-nitric acid process for Naval Reactor fuel recovery has been abandoned by A.N.L. in favor of the hydrofluoric acid-aluminum nitrate process because Zr is five times more soluble in the later solution. Higher Zr solubilities are desirable for the Naval Reactor process because the limiting Zr solubility actually determines the IAF feed volume for the Naval Reactor process. The mole ratio of Zr to U in the Naval Reactor fuel elements is approximately 100 compared to 1/13 = 0.056, calculated above for Redox.

Hydrofluoric Acid and Aluminum Nitrate

This solution, prepared by adding HF to a concentrated ANN solution, was found to dissolve U-Zr alloy containing 1% U readily. The ANN is added to complex the HF so that it does not attack stainless steel. Concentrations in the dissolver solution from the tentative A.N.L. dissolution procedure are approximately 0.86 M Zr, 0.01 M U, 0.78 M Al, and 5.4 M fluoride. Corrosion tests indicate that this solution at 70°C. corrodes Type 302 stainless steel at the rate of 0.008 inch per year. Further corrosion tests would be required at boiling temperature.

Distribution ratios for U in this solution with hexone, dibutyl carbitol, carbon tetrachloride with TBP and methylcyclohexone with TBP have been reported. E^{o}_{a} Zr this solution and hexone was found to be 0.14, which is about the same as would be expected with a nitrate solution 0.78 M in ANN. No work with higher ANN concentrations has been reported.

Other Processes

Both A.N.L. and K.A.P.L. have done work on dissolving Zr by electrolysis. A.N.L. made one test dissolving Zr anodically in a fluosilicic acid-nitric acid mixture. Rapid attack was found at 5 volts and a current of 5 amps. K.A.P.L. has worked on dissolving Zr by alternating-current electrolysis, using Zr as the electrodes. An appreciable current flows only when the impressed emf is of the order of 100 volts. Very little data on this method are available here.

References:

ANL-4425	Chemical Engineering Report for Oct., Nov., and December, 1949.
ANL-4463	Chemical Engineering Report for Jan., Feb., and March, 1950.
KAPL-264	Sect. I Progress Report for October, 1949.
ANL-4444	A.N.L. Combined Monthly Report for quarterly period ending April 31, 1950.

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