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CONTINUOUS DISSOLUTION OF ZIRCONIUM REACTOR FUELS IN TITANIUM EQUIPMENT: LABORATORY DEMONSTRATION

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ABSTRACT

Continuous dissolution of 2% U-Zr alloy fuel in a laboratory-scale titanium dissolver was demonstrated using refluxing 3 M HNO_3 --1.2 M HF --0.4 M HBF_4 --0.6 M Cr III --0.4 M Cr(VI) --0.46 M Zr as the dissolvent. Dissolution rates and solution corrosion rates were 8-16 $\text{mg/cm}^2\text{-min}$ and ~1 mil/mo, respectively. Reagent was added to the dissolver at the rate needed to maintain the potential measured by a gold vs calomel electrode in the product effluent as close to a preselected standard value as possible.

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1.0 INTRODUCTION

The utility of a Darex¹ titanium dissolver would be greatly extended if the titanium vessel could be used in dissolution of reactor fuels containing zirconium as well as stainless steel. On the basis of batch laboratory studies,² the continuous dissolution of zirconium fuels in fluoride-containing reagents, in which the attack of fluoride on titanium was inhibited by the presence of fluoboric acid and chromate ion, appeared possible. In this work, a simple and dependable method of process control was developed and the Zircaloy dissolution rate, titanium corrosion rates, and dissolvent stability during operation of the proposed continuous process were investigated and found to be essentially as predicted from earlier batch studies.

Two methods of controlling the reagent feed rate by measuring the hexavalent chromium concentration in the dissolver were investigated by T. M. Gayle of the Instrumentation and Controls Division at Oak Ridge National Laboratory. One method, using ultraviolet colorimetry, was less dependable and more costly than a second method, in which the potential of the Cr(VI)-Cr(III) couple was measured with gold vs calomel electrode. The latter method, which has been used in industrial waste treatments,³ was used in this work.

Corrosion tests were performed by L. Rice, P. Neumann and co-workers of the Reactor Chemistry Division. Analyses of a salt which coated and protected the titanium were performed by M. M. Murray and co-workers of the Analytical Chemistry Division.

2.0 FLOWSHEET

A flowsheet for the proposed process (Fig. 1), based on results of feed preparation studies, was previously published in Ref. 2. In the present work, only the continuous dissolution portion of the process was demonstrated.

The process involves continuous addition of a solution containing 5.5 M HNO₃, 0.4 M HBF₄, 0.5 M (NH₄)₂Cr₂O₇, and 1.2 M HF to the dissolver to maintain the dissolvent composition at 0.465 M Zr, 2.8 M F,

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Fig. 1. Process for dissolving zirconium reactor fuels in Darex titanium equipment.

3 M HNO_3 , 5.5 M NO_3 , 0.4 M B, 0.6 M Cr(III) and 0.4 M Cr(VI) as the zirconium-containing fuel dissolves. Reagent is added at the rate needed to maintain the potential of the Cr(III)-Cr(VI) couple in the dissolver effluent at a preselected value. The dissolver effluent flows by gravity through a water cooled condenser and into the electrode chamber (Fig.2).

The electrode potential measured in the effluent under flowsheet conditions is about 1.10 volts (Table 1), as compared to a measured value of 1.158 volts in the fresh reagent. The dissolver effluent is stirred rapidly to prevent polarization as the effluent passes through the electrode chamber. For the demonstration runs, the optimum electrode potential, i.e. Cr(VI) concentration, was determined by measuring the potential in a solution prepared by dissolving a weighed quantity of Zircaloy-2 batchwise in the proper amount of reagent to yield the flowsheet dissolvent concentrations. This potential is maintained as precisely as possible throughout the run by increasing or decreasing the reagent addition rate as the measured potential in the effluent decreased or increased, respectively. Maintenance of the Cr(VI) concentration, or potential, at the proper level insures that all other components of the dissolver effluent are at the proper concentrations (See Eq. 1 below).

Table 1. Flowsheet Demonstration Runs: Dissolution of 2% U-Zr Alloy in Darex Titanium Equipment

TIF Run	2% U-Zr Alloy charge, g	heel, g	Avg. Rate, mg/cm ² min	Range of Cr(III)-Cr(VI) Potential in Product, volt	Reagent used, ml	Excess reagent ^b used, %	Average Effluent ^b F/Zr molar ratio
2	37.5	5.3	3.3 ^a	1.020-1.125	1000	14.1	6.85
3	36.0	7.0	8.1	1.116-1.127	680	18.0	7.1
4a	23.0	0	--	---	--	--	--
4b	15.0	1.5	16.3	1.105-1.123	1020	19.4 ^c	7.2 ^c

^a Run 2 was a trial run. A small amount of precipitate, which formed because the F/Zr molar ratio in the dissolvent was allowed to decrease below 5.5 for part of the run, slowed the reaction.

^b Most of the excess reagent was introduced at the end of a run when the amount of dissolving Zircaloy was small. In continuous operation, reagent consumption would be more efficient.

^c Average after two continuous dissolvings.

3.0 DEMONSTRATION OF CONTINUOUS DISSOLUTION

The process operated satisfactorily during flowsheet demonstration runs (Table 1) in all respects, including control of reagent feed rates, fuel dissolution rates, effluent composition and stability, and dissolver corrosion as determined by visual observation.

One difficulty was encountered which was unavoidable and was expected because of the small scale of the experiments. This was the slow response of the electrodes to changes in the dissolver effluent composition because of the large holdup in the electrode chamber (Fig. 2) relative to the effluent flow rate. Since the electrode chamber is about as small as it can be conveniently made, the only remedy for this difficulty is to use a higher effluent flow rate, i.e., dissolve a greater quantity of fuel per unit time. Such large scale runs may be performed in future development work. This difficulty made it necessary to operate with an average F/Zr ratio in the product of 7, rather than the desired value of 6, to allow for more fluctuation in this ratio without falling below 5.5. It was shown in run 2 that precipitation, which was observed during the batch laboratory studies² when the F/Zr ratio was 5.5 or less, severely depressed the average dissolution rate throughout the remainder of the run, even though the F/Zr ratio in the dissolvent was returned to the proper level by increasing the reagent feed rate. Therefore in runs 3 and 4, the reagent was introduced rapidly enough to keep the potential above 1.1 volts at all times. No precipitation occurred in runs 3 and 4, a and b, and the average dissolution rates were 8 and 16 mg/cm²-min, respectively, compared to only 3.3 mg/cm²-min in run 2 where a small amount of precipitate was found in the dissolver after the run. Most of the dissolution in runs 3 and 4, a and b, occurred when the F/Zr ratio in the dissolvent was about 6.5, with a corresponding potential of 1.115 volts. The high overall average ratios in runs 3 and 4, a and b, of 7.1 and 7.2, respectively, were caused by the addition of excess reagent toward the end of the run when the specimen of reacting Zircaloy had become very small. The pretreated (see Sec 4.0) titanium vessel appeared to suffer no corrosion attack at these higher F/Zr ratios, although after run 3, where the potential rose as high as 1.127 volts and the F/Zr ratio

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Fig. 2. Photograph of continuous dissolver, reagent feed pot, and chromium monitoring system.

probably rose as high as 8 toward the end of the run, the protective coat had dissolved from part of the vessel wall. This observation is in agreement with batch studies² where corrosion of the titanium was observed only when the F/Zr ratio was 8 or higher.

The maximum operating range for the process is over the F/Zr ratio range of about 9 to 5.5 (Fig. 3). The data in Fig. 3, taken from ref. 2, agrees well with the results of the present work. At the upper limit, a F/Zr ratio of about 9, the protective coating on the titanium (Sec 4.0) dissolves and the corrosion rate increases. As this ratio increases above 9, the corrosion rate becomes even higher. The titanium corrosion data of Fig. 2 represent only results with coated titanium. Longer term corrosion tests with solution in which the F/Zr ratio was greater than 8 would show higher rates, since the corrosion rates increase after the protective coat is completely dissolved. Therefore, the process should not be operated for long periods with solutions in which the ratio is greater than 8, and treatment of the vessel to develop a new protective film (see Sec 4.0) is required whenever a ratio of 8 is exceeded. The lowest F/Zr ratio at which practical operation is possible is 5.5, since precipitation occurs at ratios below 5.5. Operation of the process at as low a F/Zr ratio as possible is desirable because the amount of the highly corrosive fluoride ion handled in solvent extraction and waste storage should be kept as small as is practical.

Fortunately, the process has automatic safety features which make operation outside of the recommended operating range unlikely under most conditions. As Fig. 3 indicates, and as the high average dissolution rate of runs 4a and b show, it would be difficult to cause the F/Zr ratio in the dissolvent to become high enough to corrode the vessel rapidly as long as actively dissolving Zircaloy is present, because the Zircaloy dissolution rate increases rapidly with the F/Zr ratio. As discussed in detail later, in connection with the possibility of using less Cr(VI), there is little danger of depleting Cr(VI) should the reagent flow be stopped, since the Zircaloy dissolving rate drops rapidly as the F/Zr ratio drops below the value of 6.0 recommended in the flowsheet. Results of run 2 in Table 1 show that this decrease in rate is more drastic than indicated in Fig. 3 if the F/Zr ratio drops below 5.5 and precipitation occurs.

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Fig. 3. Titanium corrosion rates and zirconium dissolution rates in 3 M HNO₃-0.4 M HBF₄-0.5 M (NH₄)₂Cr₂O₇-1.2 M HF.

It is necessary in the process either to prepare enough dissolvent to fill the dissolver before each run by a batch dissolution of unirradiated Zircaloy in separate equipment or to save this amount of dissolvent from one run to the next. An initial batchwise dissolution of Zircaloy to prepare dissolvent of the flowsheet composition should not be performed in the titanium vessel, since the high concentration of uncomplexed fluoride in the reagent containing no dissolved Zircaloy rapidly dissolves the protective coating which must be maintained on the titanium to ensure low corrosion rates (see Sec 4.0). This batchwise dissolution was carried out in the demonstration runs in glass equipment. The Zircaloy dissolved rapidly and complexed most of the fluoride in a short enough time that there was no noticeable attack of the glass by fluoride.

It is also possible to prepare the starting dissolvent synthetically using zirconyl nitrate, and this method was used several times in the laboratory work.

One objective of the continuous dissolution experiments was to determine if the films, which were observed to develop on dissolving Zircaloy in previous batch studies, would increase in thickness and slow the rate during continuous dissolution. The films did increase in thickness but they slowed the rate of dissolution only toward the end of a run. The effect of the heavy films can be seen from the pitting attack (Fig. 4) which had occurred on the surface of Zircaloy specimens which were almost completely dissolved. Most of the film has been scraped off the specimens in Fig. 4. Fortunately, the only bad effect of this film formation is that a small heel remains and is dissolved only slowly when the dissolver is recharged with a new fuel element. Apparently, the film and heel both go into solution as shown in runs 4 a and 4 b where a heel from run 4 b was found only when the dissolver was opened after the run. The heel from run 4 a had completely dissolved.

The dissolution reaction is thought to be:

The reactants, other than zirconium in this equation, on a molar basis, are equivalent to the total moles in 2 liters of reagent when it is con-

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Fig. 4. Photograph of Zircaloy-2 heels.

sidered that 2 liters of reagent contain 0.4 moles of HBF_4 and 0.33 moles of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ which will not participate in the reaction. The excess fluoroboric acid is necessary because excess fluoride must be present to achieve a satisfactory dissolution rate. The excess Cr(VI) is not necessary for the reaction but is required for corrosion protection. The large amount of boric acid produced probably caused the product solution to be nearly saturated with this slightly soluble material.

The simplest improvement which could be made in the process would be to decrease the amount of Cr(VI) in the dissolvent. The large excess over the stoichiometric quantity in the reagent is used for corrosion protection in case the flow of reagent is inadvertently shut off. If this happens, it is necessary, as dissolution continues, to ensure that some Cr(VI) remains to protect the vessel until essentially all of the fluoride is well complexed by the reaction with zirconium. Under the flowsheet conditions, (Fig. 1) if all of the Cr(VI) were reduced to Cr(III), by eq. 1 the F/Zr ratio would be only 3.66, a safe condition corrosion-wise. Actually, this safety margin in Cr(VI) concentration is greater than necessary, since, as mentioned above, the dissolution rate decreases rapidly when the F/Zr ratio is reduced to 5.5 or less. A more practical Cr(VI) concentration in the dissolvent might be 0.75 M, which would ensure the presence of Cr(VI) until the F/Zr ratio decreased to 5.0. Decreasing the amount of Cr(VI) present in the product might make it possible to increase the concentration of the other components.

Eq. 1 indicates that no off-gas is produced during dissolution, and in practice no off-gas was observed. This is an advantage in that no off-gas handling system is needed, but a disadvantage in that some method of stirring the dissolvent must be substituted for the stirring that would be provided by a product off-gas. The dissolvent has to be stirred vigorously to ensure that the effluent is a representative sample of the dissolvent, or the electrode monitors cannot react properly. Therefore it was necessary to stir the dissolvent with a stream of nitrogen introduced into the bottom of the dissolver.

4.0 CORROSION

After 40 to 50 hr of operation with boiling dissolvent, there was no solution phase corrosion evident in the dissolver. The lower portion of the dissolver was pretreated five times before use, alternately with boiling solution (10 mins) and with an air stream until dry. This cyclic treatment is necessary to produce the protective film, which is probably a mixed zirconium-titanium fluoride or oxyfluoride, and is discussed in detail below. The upper portion of the vessel, which was exposed only to the vapor phase during dissolution runs, was not given this pretreatment because preliminary corrosion tests had indicated that corrosion rates in the vapor phase were very low and that the vapor phase also develops a coat which probably protects the titanium. However, examination of the vessel after the dissolution runs were complete revealed many pits where the coat had been penetrated in this area where the vessel had not been pretreated. The pits were up to 100 mils deep.

Thus, it appears that pretreatment of the entire vessel is necessary. One cause of this corrosion in the vapor phase may be that in some runs the fresh reagent was allowed to trickle down the vessel wall. In later runs, the reagent was introduced in the middle of the top of the vessel where it fell into the dissolvent without contacting the walls. In the corrosion tests described below, the vapor phase corrosion rate was low.

To gain some understanding of the nature of the protective film, methods of producing the film, and corrosion beneath the film, a group of nine welded samples of titanium-60 were immersed in boiling dissolvent, removed periodically, air dried, and weighed. The first ten immersions lasted 10 mins, the 11th, 30 mins, and the 12th, 13th, and 14th, 1 hour each. The specimens lost weight rapidly at the average rate of $0.1 \text{ mg/cm}^2\text{-min}$ for the 1st 10 mins (Fig. 5), less rapidly at about $0.5 \text{ mg/cm}^2\text{-min}$ for the 2nd and 3rd exposure, and gained weight during all subsequent exposures. These results show the beneficial effect of the air exposure to produce a protective oxide coat, since without the exposure to air, the corrosion rate would be expected to remain at the rate observed after the first immersion, which was over 400 mils/mo. Four immersions were

Fig. 5. Initial corrosion followed by development of a protective coat on nine titanium samples in Zircaloy dissolvent. Surface areas, $\sim 5 \text{ cm}^2$.

sufficient to produce a rapid increase in weight and a white coat over the entire specimen. After the 10th immersion, the weight changes began decreasing and were approaching a weight change value of zero after fourteen exposures. One specimen was further exposed for 2 hr and the coat was scraped off. This specimen showed an average corrosion rate of 10 mils/mo over the entire 15 exposures, lasting 7.5 hours. However, the scraped specimen showed no measurable weight loss beyond that which had already occurred after 3 immersions, showing that the protective film had reduced corrosion rates to <1 mil/mo, which is about the lowest rate detectable by this test. Since exposure to air is necessary to achieve protection, periodic interruption of the continuous dissolution process would be necessary to replenish the oxide-containing film. Further tests in progress have indicated the films on the specimens used to gather the data in Fig. 5 begin to break down after 72 hr immersion in boiling dissolvent, when not periodically exposed to air.

Corrosion tests were also performed in which welded titanium-60 specimens were stacked in a glass basket between plates of actively dissolving Zircaloy-2, to determine if contacting dissolving Zircaloy would appreciably change the titanium corrosion rates. In a 2-hr continuous dissolution experiment at the boiling point, untreated titanium corroded at 1-2 in./mo, showing that contacting the dissolving Zircaloy had little or no effect on the corrosion rate. A pretreated titanium specimen, one of those used to gather the data in Fig. 5, showed a small weight gain. A titanium specimen in the vapor phase, in contact with Zircaloy, showed a small weight gain, caused by a thin white coat which developed during the run.

A sample of the protective film on the titanium was carefully scraped off and analysed. The analyses showed the film contained 28.6 wt % fluoride, 49.7 wt % zirconium and 0.45 wt % titanium, i.e. 2.75 moles of fluoride and 0.02 moles of titanium per mole of zirconium. The X-ray pattern matched quite well the pattern of ZrOF_2 , but the composition of the film is still uncertain.

4.0 CONCLUSIONS

These continuous dissolution experiments have demonstrated that it is possible to dissolve zirconium-containing fuels in a titanium vessel at satisfactory rates with low titanium corrosion rates (probably 1 mil/mo), to achieve the necessary control of the process by a simple, continuous monitoring of the hexavalent chromium content of the effluent, and to produce a solvent extraction feed which compares favorably with existing processes for Zircaloy alloy fuels. The major disadvantage in the process is that the low titanium corrosion rates are achieved by precoating or film formation techniques not well understood and that pretreatment of all titanium equipment is necessary and must be repeated at intervals to prevent excessive corrosion. Further study of the mechanism of corrosion protection would be desirable before use of the process in a fuel reprocessing plant.

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