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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Corrosion Studies, Fluoride Volatility Processing, Hydrolysis Studies on Uranium Carbides, Protactinium Studies, Shear-Leach Process, Solvent Extraction Studies, and UO_2 Dissolution Studies) and Chemistry Research (Chemical Applications of Nuclear Explosions, Chemical Engineering Research, Ion Exchange Technology, Mechanisms of Separations Processes, Solvent Extraction Research, and Volatility Studies).

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POWER REACTOR FUEL PROCESSING

Corrosion Studies. "A" nickel exposed to nitrogen-saturated CCl_4 (at room temperature) at approximately 770°C corroded at rates of 565 to 613 mils/month for 24-hr exposures. "A" nickel is the most corrosion-resistant metallic material thus far tested in this environment.

Pyroceram 9608 reacted with molten aluminum at approximately 700°C. Three of the four specimens tested fractured during a 24-hr test, and the fourth specimen cracked upon application of very slight stress. "A" nickel suffered extensive local attack in contact with molten aluminum, but some areas were covered with a black tenacious material that resisted further attack.

In glass corrosion studies no boron was leached from glass Raschig rings containing 3.79 wt % boron after five weeks of contact with solutions containing 100 g per liter of uranium, 0.2 to 5 g per liter of thorium, and 0.1 to 0.04 M HNO_3. Samples having 110 cm^2 of surface area were exposed to 150 ml of solution at room temperature or room temperature to 65°C. The boron content of the final solutions varied from 0.02 ppm less to 0.04 ppm more than control solutions which had not contacted the Raschig rings.

Fluoride Volatility Processing: Pilot Plant. The system is being decontaminated with aqueous solutions prior to a corrosion check and several plant modifications. The modifications are desirable before short-cooled fuel is processed.

The problem of salt recycle as a means of lowering overall salt cost was studied by a series of dissolutions of Zircaloy-2 with HF in molten $NaF-LiF-ZrF_4$; an INOR-8 bench-scale dissolver vessel was used. Ten tests were made with about 35 mole % ZrF_4 in the initial charge, with the addition of NaF-LiF to the product salt to bring the composition back to about 35 mole % ZrF_4 for the following test. Sampling of the product salt indicated practically no corrosion-product buildup. Dissolution rates were in the same range as would have been expected with fresh salt.

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Fluoride Volatility Processing: Corrosion. In an extension of tests conducted at Battelle Memorial Institute (BMI) and previously reported, the corrosion of various Ni-Fe-Mo experimental alloys was compared with that of INOR-8 and Alloy 79-4 during exposure to HF for 72 hr in 50.5-37.0-12.5 mole % $NaF-LiF-BeF_2$ at 650°C. For an undetermined reason, this particular melt was even more corrosive than previous ones of the same composition. Metallography showed that INOR-8 and the 85-5-10 wt % and 80-18-2 wt% Ni-Fe-Mo alloys had been attacked the least, contrasting to the excellent showing of Alloy 79-4 in the earlier tests:

Alloy	Composition (wt %)			Max. Rate of Interface Penetration (mils/month)		
	Ni	Fe	Mo	Wt.-Loss Data	Micrometer	Metallography
INOR-8	71	5	16[a]	27.5	115	100
79-4	80	16	4	30.0	380	375
2	85	5	10	18.2	60	100
31	85	13	2	18.0	80	125
32	80	18	2	20.9	75	100
33	80	5	15	17.9	110	135
34	75	15	10	19.1	75	135
35	75	20	5	26.2	260	293
36	80	12.5	7.5	20.6	205	185
37	80	16	4	21.3	170	188
38	85	10	5	19.9	105	115

[a] +7% Cr.

In simulation of conditions that would be encountered in the burning and fluorination of graphite-base fuels, for example, the HTGR and the PBR fuels, various nickel-base alloys were cyclically exposed at BMI for 1 hr to $CO-CO_2-O_2$ (5%-60%-35%) at 700°C, and for 1 hr to F_2 at 400°C, with 1-hr helium flushes during temperature transitions. After 20 cycles, maximum penetration rates in mils/month were: L nickel, 1.6; Duranickel, 3.8; Monel, 8.2; Alloy 79-4, 11.5; and INOR-8, 5.4. Inconel-X and Inconel results were 31.4 and 14.9 mils/month, respectively, after six cycles.

Hydrolysis Studies on Uranium Carbides. The heat-treatment of uranium-carbon alloys with a C/U gross atom ratio of 2 at 2000°C for 6 hr and at 1100 to 1260°C for 238 hr had little effect on the combined C/U atom ratio (1.84), x-ray powder pattern, or hydrolytic properties. Hydrolysis in water at 80°C yielded about 40 ml (STP) of gas per gram of samples; the off-gas contained approximately 40% hydrogen, 16% methane, 27% ethane, 6% C_3- to C_8-saturates, and 9% unsaturates. Of the total carbon in the alloys, about 35% was evolved as gaseous products, and 22% was converted to insoluble wax.

The microstructure of the as-cast UC_2 sample showed a principal dicarbide phase and flakes of graphite; both heat-treated specimens had an additional third phase of parallel plates throughout the dicarbide grains. Since heat treating did not affect the chemical properties, this phase was probably soluble in the dicarbide when quenched from the melt.

Protactinium Studies. Unfired Vycor glass powder was used to remove protactinium from solutions simulating those obtained in the dissolution of fully irradiated, 30-day-decayed, Consolidated Edison Thorium Reactor Fuel. This solution was 0.5 M in thorium, 11 M in HNO_3, approximately 0.2 M in aluminum, 0.04 to 0.1 M in F^-, and the Pa^{231} concentration was 120 mg/liter. More than 99% of the protactinium was adsorbed on passing 130 ml of solution at a flow rate of 1 ml cm^{-2} min^{-1} through a column about 0.6 cm in diameter and 25 cm long, containing 5 mg of 60 to 80 mesh unfired Vycor glass. In a similar column experiment, 10 mg of Pa^{231} was adsorbed on 1 g of unfired Vycor. After washing with 11 M HNO_3 the column was eluted with 0.5 M oxalic acid. More than 99% of the protactinium was recovered at a concentration 12 times the feed concentration; the decontamination factor from thorium was 6300.

There was no change in the concentration of a Pa^{231} solution after one week of contact with type 347 stainless steel (2 cm^2 of stainless steel per milliliter of solution). The solution was 0.5 M in thorium, 11 M in HNO_3, and contained a trace of fluoride; the Pa^{231} concentration was 75 mg/liter.

Shear-Leach Process. Three shear-leach runs were made with ORNL Mark I fuel elements (unirradiated stainless-steel-clad UO_2) to evaluate the leaching characteristics of fuel sheared to lengths of 1/2, 1, and 1-1/2 in., respectively. The first two runs employed eight batches of sheared fuel, each containing about 24.4 g-moles of UO_2; the last run used nine batches, each containing about 26.6 g-moles of UO_2. In the first two runs, each batch represented 8 in. of fuel assembly and, in the last, 9 in. One batch was fed to the rotary-screw leacher every hour and contacted countercurrently over a 4-hr period with 7 M HNO_3 at 90 to 95°C at an HNO_3/UO_2 mole ratio of 4.

These runs indicate that apparent steady state is obtained in the leacher in 5 to 6 hr, that 66% of the UO_2 dissolves in one hour, and that the remaining UO_2, introduced to the leacher as fines, tends to cake and dissolve very slowly. For fuel sheared to 1/2-, 1-, and 1-1/2-in. lengths, the steady-state dissolution rate was 20.8, 22.6, and 22.9 g-moles of UO_2 per hour, and the UO_2 fines accumulation rate was 3.6, 1.8, and 1.5 g-moles of UO_2 per hour, respectively. Since these runs show that UO_2 fines crust or cake, thereby blocking access of the leach acid to the fines beneath the crust, shearing to greater lengths, thus producing less fines, reduces but does not eliminate the amount of undissolved UO_2.

The steady-state uranium concentration in the leach-product solution was 500 to 520 g/liter, and the HNO_3 concentration was 1.4 to 1.5 M. Dilution of this product with the drain liquor from the leacher produced a satisfactory Purex solvent extraction feed.

Stainless-steel-cladding fines, $\leq$1000 μ in diameter, dissolved completely in the nitric acid; this represents about 0.06% of the cladding entering the leacher.

Solvent Extraction Studies. It was found possible to calculate the distribution coefficient of dilute uranium from acid-deficient aluminum nitrate solution into 2.5% DSBPP in DEB from pH data on the aqueous feed solution without knowing either the aluminum concentration or the acid deficiency of the solution. This relationship is:

$$\log (U\ dc) = 7.04 - 2.38\ (pH\ of\ feed)$$

No other single variable has been found to correlate with the distribution coefficient. This data indicated a first order dependence of uranium hydrolysis with the hydrogen ion concentration in the systems studied.

The efficiency of sieve-plate pulsed columns for a process utilizing di-sec-butyl-phenylphosphonate in diethylbenzene for the separation of uranium from thorium was, expressed as HETS, 2.1 ft at a pulse frequency of 70 cpm, and 4.0 ft at 50 cpm for uranium extraction; 4.1 ft at 70 cpm, and 4.6 ft at 50 cpm for thorium scrubbing; 4.2 ft at 70 cpm, and 6.7 ft at 50 cpm for uranium stripping.

UO_2 Dissolution Studies. The instantaneous dissolution rate of UO_2 in boiling nitric acid that contained sodium nitrate or lithium nitrate was the same as in nitric acid alone of the same nitrate concentration. Mixtures studied varied from 10 to 80% salt and from 2 to 13 N HNO_3. The addition of nitrite did not vary the dissolution rate, probably because the nitrite is lost from the boiling solution. The addition of 0.1 N HF decreased the dissolution rate when added to $\geq$5 N HNO_3 and increased the rate when the acid concentration was less than 5 N HNO_3.

CHEMISTRY RESEARCH

Chemical Applications of Nuclear Explosions. Studies of the thermal decomposition of $MgSO_3$ and of the reaction between MgO and SO_2 in the 750 to 800°C range showed that the following reactions occur:

$$MgSO_3 \longrightarrow MgO + SO_2,$$

$$MgO + 1.5SO_2 \longrightarrow MgSO_4 + 0.25S_2.$$

The solid reaction product of $MgSO_3$ decomposition contained more than 95% MgO, and the balance remaining was $MgSO_4$. The reaction between MgO and SO_2 is very slow, even at 800°C. Only 9% conversion of MgO to $MgSO_4$ was achieved after 1 hr, using a 1.2-g MgO sample and an SO_2 flow rate of 142 cc/min (mole ratio SO_2/MgO = 38). The absence of MgS in the reaction product indicates that any MgS formed is consumed by the following reaction:

$$MgS + 2SO_2 \longrightarrow MgSO_4 + 0.5S_2.$$

If thermal decomposition products of $MgSO_3$ were analogous to those of $CaSO_3$, the formation of MgS by the following reaction would be expected:

$$MgO + SO_2 \longrightarrow 0.75MgSO_4 + 0.25MgS.$$

Chemical Engineering Research: Foam Separation. The determination of HTU_x values for stripping of Sr^{89} from a dodecylbenzenesulfonate solution were continued. HTU_x values from 13 to 20 cm, using a single tube on the 6-in.-ID column centerline as a liquid feed distributor, show that very poor liquid-foam contact is obtained from 27-cm countercurrent lengths. For 52- and 57-cm countercurrent lengths, the HTU_x values indicate normal liquid-foam contact for the lower half of the countercurrent region at 100 gal ft^{-2} hr^{-1}, but channeling may persist throughout the entire length at higher flow rates. One liquid distributor gave distinctly lower HTU_x values than other distributors for flows below 120 gal ft^{-2} hr^{-1}, but four distributors all gave HTU_x values of 2-4 cm for flows over 140 gal ft^{-2} hr^{-1}. The differences in HTU_x values for the spinnerette gas spargers with 50- and 80-μ-diam holes are small, variable, and probably not significant. When the slurry formed by the addition of 5×10^{-3} M NaOH and 5×10^{-3} M Na_2CO_3 to process water was fed to a foam separation column, the $CaCO_3$ and $Mg(OH)_2$ precipitates were removed from the solution by the foam, and the strontium decontamination factor necessary for low-activity waste (about 200) was possible. When 10 ppm of "Fab" was added to simulate impurities in low-activity waste, precipitation was delayed, and the decontamination factor for strontium was reduced to 10 or less.

Ion Exchange Technology. The study of the effects of gamma-radiation on anion exchange resins was initiated, using the hydroxyl form of Dowex 1 X-10 (50 to 100 mesh). A sample of the resin was placed in a system of flowing demineralized water (less than 1 micromho/cm) and exposed in a 10,000-curie cobalt-60 source to a dose of 4.2×10^8 r (about 1.1 whr per gram of dry resin). The maximum specific conductance of the continuously monitored effluent was 130 micromho/cm; the corresponding pH maximum value was 10.7. The effluent solution had a strong odor characteristic of amines, the active group on the anion resin. At the end of the experiment, about 62% of the original resin volume was recovered. About 10% of the original resin was recovered as particles smaller than 200 mesh; the residual 28% apparently had been converted to water-soluble radiolysis products.

A cursory examination of the continuously recorded pH data indicated that a substantial fraction of the active sites on the resin had been lost to the effluent after an exposure of about 1.3×10^8 r (0.35 whr per gram of dry resin) — about 1/3 of the total dose. During this period, the pH decreased to 8.4; thereafter it slowly decreased to about 7.8 to 8.0.

Mechanisms of Separations Processes. Partial pressures of tributyl phosphate at 25°C over its HNO_3-H_2O solutions are being measured as part of a study of the thermodynamics of extraction of nitrates by TBP. For this purpose the transpiration technique with P^{32} labeled TBP is being used. Anhydrous TBP, water-saturated TBP, and TBP in equilibrium with 0.765, 2.29, 4.36, and 5.46 M HNO_3 exhibited partial pressures of 0.558 ± 0.060, 0.374 ± 0.060, 0.275, 0.161 ± 0.012, 0.0763 ± 0.0031, and 0.0456 ± 0.0020 μ, respectively. Standard deviations ranged from 0.060 to 0.0020 μ, as indicated above, on 3 to 12 measurements.

From the ratio of pressures of TBP over water-saturated and dry TBP, the rational activity of TBP saturated with water is 0.670 ± 0.085. The corresponding molar activity coefficient, y_T, of TBP in the water-saturated solution is, therefore,

$$y_T = (0.670 \pm 0.085)\,\frac{C_0}{C} = 0.716 \pm 0.091,$$

where C_0 is the concentration of TBP in the anhydrous state, 3.654 moles/liter, and C is the corresponding water-saturated value, 3.420 moles/liter. Based on this value of the activity coefficient of TBP and a previously reported value of $K_1 y_T = 1.47$, the thermodynamic equilibrium constant, K_1, for the extraction of nitric acid by TBP is 2.05. This value, which has a standard deviation of about 0.25 to 0.3, is based on the activities of the H^+ and NO_3^- ions corresponding to the extraction equation:

$$H^+_{aq} + NO_{3_{aq}}^- + TBP_{org} \rightleftharpoons TBP \cdot HNO_{3_{org}}.$$

In terms of the more probable mechanism of extraction represented by the equation

$$HNO_{3_{aq}} + TBP_{org} \rightleftharpoons TBP \cdot HNO_{3_{org}},$$

the thermodynamic equilibrium constant is $2.05 \times 1.17 \times 10^4 = 2.40 \times 10^4$,

where 1.17×10^4 is the thermodynamic equilibrium constant for the dissociation of HNO_3 into its ions.

Solvent Extraction Research. In further testing of alkylbenzenes for possible use as diluents for organophosphorus extractants several high-boiling-point (higher than 349°C) polymethylbenzenes were shown to be much more resistant than Amsco 125-82 to degradation by boiling 2 M HNO_3. In a test where degraded 1 M TBP-Amsco extracted 4000 counts/sec of $Zr\text{-}Nb^{95}$ from 2 M HNO_3, similarly degraded 1 M TBP solutions in hemimellitene (1,2,3-trimethylbenzene), in prehnitene (1,2,3,4-tetramethylbenzene), and in isodurene (1,2,3,5-tetramethylbenzene) extracted but 125, 175, and 1400 counts/sec, respectively.

In further studies on the extraction of metal ions from 0.5 to 10 M HCl and LiCl—0.2 M HCl mixtures (0.5 to 10 M total Cl^-), maximum extraction coefficients obtained with 0.1 M amine in diethylbenzene were about 2 for Ti(III), 3 for Ti(IV), 60 for Mn(II), 1000 for Co(II), 1000 for Zn(II), 100 for Cu(II), 2 for As(III) and As(V), 8000 for Ga(III), and 700 for Zr(IV). In general, extraction coefficients increased with the increase in chloride concentration and were higher with Aliquat 336 than with the other amines.

In connection with studies of alkaline earth extraction from sodium nitrate solutions by benzene solutions of di(2-ethylhexyl)phosphoric acid (HDEHP) and its sodium salt (NaDEHP), precise vapor-pressure-difference (Δp) measurements at 20°C confirmed the dimerization of HDEHP (0.06 to 0.5 M) and indicated increasing polymerization of mixtures of HDEHP and NaDEHP (total reagent concentration = 0.10 M) as the NaDEHP:HDEHP ratio increased. The polymerization of NaDEHP in benzene was indicated by $\Delta p = 55 \pm 5\ \mu$ to be 13 ± 1 monomers per polymer at 0.10 M and varied directly but not linearly with concentration. The strontium salt of HDEHP was also shown to be polymerized.

Batch extraction tests, directed toward explaining and correcting the poor decontamination encountered in the amine extraction of plutonium from Purex 1BP solution, showed that aged 1BP solution does contain a considerable amount of readily extractable gamma activity. Up to about 5% of the

gross gamma was extracted in single equal-volume contacts with diethylbenzene, Amsco 125-82, and n-dodecane. Suprisingly, the gamma extraction was about 10 times higher by the hydrocarbon alone than in the presence of alcohol or alcohol plus amine. However, gamma extraction by the amine solution after prescrubbing with diluent was still significant so that prescrubbing will not suffice to correct the poor decontamination.

Volatility Studies: $NaF-SbF_5$ Complex. Some laboratory data on the sorption of SbF_5 on NaF was obtained because Sb^{125} activity has been observed as a contaminant in UF_6 from the Volatility Pilot Plant. In two tests, NaF/SbF_5 mole ratios of 3.95 and 4.03 were secured at 200°C, using 12 to 20 mesh NaF and a pressure of less than 5 psig. Previous experience with similar complexes indicates that the actual stoichiometric ratio that could be achieved with fine material would probably be 2/1. Preliminary measurements with a helium transpiration method indicated that the dissociation pressure of the $NaF-SbF_5$ complex is less than 0.04 mm Hg in the range 210 to 305°C.

Volatility Studies: Al-U Hydrochlorination in Fluoride Salts. Tests have been conducted on the hydrochlorination of Al-U alloy fuel in fluoride salts to obtain dissolution rates of 5 to 9 mils/hr at 500 to 600°C. Little reaction appears to occur below the salt surface, possibly due to the low solubility of HCl in the melt employed, 31-24-45 mole % $LiF-NaF-ZrF_4$. The most rapid reaction appeared to occur just above the surface of the salt in tests in which the fuel element specimen was allowed to float in the melt.

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