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CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing, Fluoride Volatility Processing, Chemical Engineering Research, Mechanisms of Separations Processes, Solvent Extraction Research, and Chemical Applications of Nuclear Explosions.

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POWER REACTOR FUEL PROCESSING

Corrosion Studies. Unwelded Corronel 230 was corroded in boiling (~116°C) 10 M HNO_3—0.5 M HF at a maximum rate of 60 mils/mo in 96 hr exposure. Under similar conditions, Hastelloy F (36 hr) and experimental alloys EB-4358 and EB-5459 (8 hr each) were corroded at rates of 212, >500, and >500 mils/mo, respectively. At 60°C the maximum rate for Corronel was 2.83 mils/mo in 312 hr exposure.

Unwelded Corronel 230 was corroded at maximum rates of 5 mils/mo in 312 hr exposure at 60°C in 1 M HNO_3—3 M HF vs 2700 mils/mo in the boiling solution. Type 309 SNb stainless steel, Hastelloy F, and Haynes experimental alloys EB-4358 and EB-5459 were corroded at maximum rates of 463 (20 hr), 123 (8 hr), 165 (8 hr), and 190 (8 hr) mils/mo, respectively, in boiling 1 M HNO_3—3 M HF. All materials tested in the boiling solution suffered localized attack.

Ni-o-nel was corroded at maximum overall rates of 0.31, 0.43, and 0.59 mil/mo vs 0.19, 0.27, and 0.42 mil/mo for LCNA* in the vapor phase above refluxing 4 M HNO_3 in exposures of 360, 516, and 676 hr, respectively. Grain boundary attack became visible on specimens of both alloys between 192 and 360 hr exposure. Specimens exposed to the condensate showed negligible corrosion rates (<0.01 mil/mo) and no visible change in appearance.

Darex Process. Methods of eliminating silica and other insolubles in a continuous Darex process for APPR fuel, which contains 2 wt % Si, were investigated further. About 10% of the silica was solubilized by complexing with fluoboric acid at the standard fuel solution content of 60 g/liter of stainless steel. A fluoride-stabilized silica precipitate that also formed was removed by filtration at an average rate of 0.5 $ml/cm^2 \cdot min$ or passed directly through the chloride stripping column. About 87% of the total solids passed through the column and those held up were easily washed through with hot nitric acid or water. During chloride stripping, 17% of the total fluoride appeared in the HNO_3-HCl condensate. Efforts to complex this free fluoride with aluminum or boric

* A low-carbon nickel alloy with the same nominal composition as Ni-o-nel except that C = 0.005%.

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acid were unsuccessful. Hydrated silica was also stabilized by 24 hr boiling of the fuel solution at total reflux. Filtration of the resulting solution at 70°C at an average rate of 1.2 $ml/cm^2 \cdot min$ removed 99% of the precipitate and insoluble stainless steel carbides and oxides.

Treatment of APPR fuel solution with gelatin or molybdates to coagulate or solubilize the hydrated silica was unsuccessful. However, molybdate treatment of solutions of fuel containing $\leq$0.5% silicon was encouraging.

Mechanical. Particle size measurements of the fines produced in the shearing of Kanigen and Nicrobraze 50 brazed assemblies to 1-in. lengths indicate that the stainless steel fines are larger, in general, than the porcelain fines. For all fines, 90% were >9520 μ, 9% <2000 μ, and only 1% <44 μ. Of the last fraction 84% were <10 μ and 50% <3 μ.

Solvent Extraction Studies. The separation of uranium from thorium in aqueous solution by extraction with 2.5% TBP is strongly dependent on the salting strength and the saturation of the solvent with uranium. Varying the aluminum nitrate content of the 0.01 N acid-deficient scrub from 0.6 to 1.5 M decreased the solvent saturation at the feed plate from 43% to 23% by decreasing the reflux. The fission product decontamination at the feed plate decreased from 100 to 30 and after three scrub stages, from 13,000 to 80.

Batch equilibration of 50 ml of a solution containing ~1.8 g/liter U, 0.5 M HNO_3, 0.01 M $NaNO_2$, and 2.7×10^4 c/m·ml Pu for 17 hr with 0.5 g of a zirconium-silicon-phosphate exchanger removed 99% of the plutonium from solution. Approximately 12% of the plutonium was removed from a similar solution containing 4 M HNO_3. The exchange material was prepared with a $ZrO_2 : SiO_2 : P_2O_5$ ratio of 1 : 4.8 : 0.7.

Uranium Carbide. Hydrolysis of a 158-g batch of uranium carbide at 80°C yielded 3.11 mg-atoms of carbon per gram of specimen as gaseous hydrocarbons, about 0.80 as a water-insoluble yellow liquid, and 2.12 in the water-insoluble uranium residue. The sample contained 3.82 mg-atoms of uranium, 7.45 of total carbon, and 1.16 of free carbon per gram of sample. Gas chromatographic analysis of the yellow liquid showed the presence of C_6 to C_{11} hydrocarbons; about 60% of the carbon was C_8 hydrocarbons. The uranium residue, containing 1.82 g of combined carbon and 2.20 g of free

carbon, yielded a dark-red solution and brown solids when reacted with 9 M HNO_3 at 80°C. Leaching of these solids with acetone yielded 0.36 g of free carbon and 2.44 g of dark-red acetone-soluble solids which were 50% carbon. Since the specimen originally contained 2.2 g of free carbon, it appears that the finely divided carbon dispersed throughout the carbide is attacked by HNO_3 under milder conditions than are required for the reaction of massive graphite with HNO_3.

FLUORIDE VOLATILITY PROCESSING

Pilot Plant. In two runs (TU-11 and 12) with nonirradiated fully enriched zirconium-uranium alloy fuel, 40-kg charges were dissolved at 650-500°C at an HF flow rate of 150 g/min. Dissolution rates in the NaF-LiF-ZrF_4 salt were 2.4 and 3.3 kg/hr, respectively, based on 90% completion. Corresponding HF utilization efficiencies were 17.5 and 24%. After the usual dissolution time, HF was passed in at 40 g/min to solubilize any dissolver metal remaining in the salt. The dissolver off-gas system performed well during both runs at a recycle HF flow rate of ~350 g/min.

A dual fluorine flow rate of 6 slm (for 100 min) and 14 slm (for 20 min) at 500°C decreased the residual uranium in the salt to <10 ppm. A complete uranium balance was not made because of system holdup, but nonrecoverable uranium losses for runs TU-11 and 12 were 0.25 and 1.59 g, respectively.

The off-gas filter was replaced with a new Yorkmesh cartridge in anticipation of irradiated fuel processing. The discharged cartridge showed no increase in pressure drop for eight runs.

Corrosion Studies. Studies made at Battelle Memorial Institute (under subcontract) indicated that Alloy 79-4 (79 wt % Ni, 4% Mo, remainder Fe) is more resistant to fluorination conditions than either Inor-8 or L-nickel. The presence of beryllium in the fuel salt increased its corrosiveness:

	Maximum Penetration Rate (mils/month)						
	27.5-27.5-45 mole % NaF-LiF-ZrF_4				27.8-20.4-6.8-45 mole % NaF-LiF-BeF_2-ZrF_4		
	Inor-8 (by wt loss)	Alloy 79-4 (by wt loss)	L-Nickel (by wt loss)	L-Nickel (metallographic)	Inor-8 (metallographic exam.)	Alloy 79-4 (metallographic exam.)	L-Nickel (metallographic exam.)
Vapor	3	1	0.2	8	9	7	11
Liquid	11	4	3.8	25	38	13	31
Interface	11	2	1.3	28	6	5	22

The metal specimens were exposed at 500°C in both series; fluorine was passed through for 150 and 162 hr, respectively. UF_4 was added to both salts periodically. In contrast to L-nickel, there was no significant intergranular attack of the Inor-8 or Alloy 79-4.

The oxidation resistance of Alloy 79-4 in 2000 hr exposure to air at 700°C was equivalent to that of Inor-8 and L-nickel. The advantage of an adherent scale on L-nickel was offset by the extensive intergranular attack which occurred. The results showed that complete protection from oxidation could be provided by Chromallizing, a proprietary chromium coating process.

CHEMICAL ENGINEERING RESEARCH

Both the flow capacity and the stage efficiency of the Mark IV stacked cone contactor increased with increasing temperature from 29 to 45°C in the extraction of uranyl nitrate from 1 M $NaNO_3$ by 15% TBP-Amsco. The flow capacity was 3.3 liters/min at 41°C compared to 2.4 liters/min at 29°C. The improvement at higher temperature probably results from the decrease in viscosity.

HETS values for extraction and stripping, with uranium as a stand-in for plutonium, were determined as part of the amine extraction final cycle plutonium flowsheet studies. The uranium extraction HETS value for a sieve plate column (0.125-in.-dia holes, 23% free area, aqueous continuous operation) decreased from 6.6 to 4.2 ft as the pulse frequency increased from 50 to 70 cpm, and for a nozzle plate column (0.125-in.-dia nozzles, 10% free area, solvent continuous operation), was 4.2 ft at a pulse frequency of 70 cpm. HETS values for uranium stripping decreased from 9.8 to 3.2 ft as the pulse frequency increased from 50 to 90 cpm for aqueous continuous operation of a sieve plate column and was 3.0 ft for solvent continuous operation of a nozzle plate column at 50 cpm pulse frequency.

MECHANISMS OF SEPARATIONS PROCESSES

Foam Separation. A continuous calcium and magnesium precipitator was built and operated to produce an adequate feed to a foam column from simulated ORNL low-activity waste. Fast stirring and 30 min contact time in the mixer and a partially agitated sludge column produced a high

quality effluent. Coagulation of the sludge was greatly improved by the addition of 2 ppm of Fe^{3+}. Addition of NaOH (to 10^{-2} M) to the mixer removed 95% of the calcium and 80% of the tracer Sr-85 present. Addition of a mixture of NaOH and Na_2CO_3 gave about the same calcium removal but increased the strontium removal to about 95%.

Partial agitation of the sludge decreased the total hardness of the effluent, without filtration, to 1.8 ppm as $CaCO_3$ and the solids, as Ca plus Mg, to $\leq$0.1 ppm (as Ca).

Discontinuous addition of grundite clay to the flocculator (total 3 g to 48 liters) produced an effluent, after 48 hr of continuous operation, with decontamination factor from strontium of 40-90 and from cesium of 10-40. The grundite was retained in the sludge column. The agitated sludge column, besides improving the hardness and clarity of the water, classified the $CaCO_3$ and strontium at the bottom of the column, thereby producing a concentrated sludge with ~12% solids, corresponding to a volume reduction of about 1000. These values may be compared with those obtained in the present low-activity waste treatment plant, which gives a volume reduction of about 300 and an average decontamination factor from Sr-90 of 4 and from Cs-137 of 6.5.

The heights of transfer units in a 6-in.-i.d. foam-liquid column were 0.8-1.6 in. for stripping of Sr-89 during eight runs with 4-11 in. of countercurrent length and liquid flow rates of 40-100 gal hr^{-1} ft^{-2}. The HTU values were increased as channelling increased. This increase was particularly noticeable for poor distribution of the liquid feed and was noticeable for increased liquid feed rates or for decreased foam rates.

Thermodynamics of Solvent Extraction. Vapor pressures and activity coefficients of nitric acid were determined by a transpiration method in the concentration range 1-16 M. The relation between the logarithm of the nitric acid partial pressure and the logarithm of its mole fraction was linear. The results correlate well with those obtained by freezing point depression methods. At constant nitric acid molarity, the partial pressure of the acid increased as the uranyl nitrate concentration increased. However, for a given mole fraction of nitric acid, addition of uranyl nitrate did not alter its activity.

SOLVENT EXTRACTION RESEARCH

Sulfuric acid was recovered from Sulfex decladding solution, for recycle with attendant waste volume decrease, by amine extractants. Sterically hindered tertiary amines (alkyl branching close to the nitrogen) were the most useful since they are readily stripped with water. With the more efficient amines, such as N-benzyl di(2-ethylhexyl)amine, 1 M H_2SO_4 was recovered.

Degradation of commercial aliphatic Amsco 125-82 by boiling nitric acid was decreased by treating with an equal volume of boiling 2 M H_2SO_4 for 4 hr under total reflux. The treated material, made to 1 M in TBP and boiled for 4 hr under total reflux with 2 M HNO_3, extracted no more Zr^{95}-Nb^{95} from another 2 M HNO_3 solution containing 10^4 c/s·ml of Zr^{95}-Nb^{95} tracer than did fresh TBP-Amsco, i.e., <100 c/s·ml. A 1 M TBP-Amsco solution so degraded without preliminary sulfuric acid treatment, after the usual sodium carbonate-calcium hydroxide scrubbing, extracted 4000 c/s·ml. No sulfur compounds remained in the Amsco after treatment.

In continued study of tracer strontium extraction (ORNL-3256) from 4 M $NaNO_3$ by di(2-ethylhexyl)phosphoric acid (D2EHPA) in benzene, the extraction coefficient went through a maximum in the pH region where $[NaD2EHP]/\Sigma[D2EHPA] = 0.25$ (pH from 4.5 to 5.5 depending on $\Sigma[D2EHPA]$). Such maxima were not shown in strontium extraction from systems containing only Sr^{++} and H^+ as cations or in sodium extraction with or without Sr^{++} present. These results indicate that the observed maxima in strontium extractions are associated with systems containing gross amounts of sodium and with a particular organic phase composition, i.e., $[NaD2EHP]/\Sigma[D2EHPA] = 0.25$.

In Na^+ free systems the strontium extraction coefficient, E_{Sr}, was proportional to $[H^+]^{-2}$ up to loadings of ~1 mole Sr/8 moles D2EHPA. In Sr^{++} free systems and in the presence of gross quantities of strontium E_{Na} was proportional to $[H^+]^{-1}$ to within 90% of stoichiometric (1 to 1) loading, and in the presence of gross quantities of Sr, E_{Na} was proportional to $[H^+]^{-1}$, though only small quantities of sodium could be extracted under these conditions.

CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

Magnesium sulfate reacted with hydrogen to form MgO, H_2O, H_2S, SO_2, and S at 734°C; the mole percentages of the original sulfate converted to H_2S, SO_2, and S were 43.4, 31.4, and 25.2, respectively. At 784°C, the mole percentages of H_2, SO_2, and S were 14.7, 44.4, and 40.4, respectively. The apparent activation energy for the reaction was calculated to be 18 kcal/mole.

The stoichiometry of the reaction of $CaSO_4$ with hydrogen was reexamined by more accurate analytical techniques. At 900°C, the mole percentages of the sulfate converted to H_2S and SO_2 were 2.0 and 1.9, respectively. The other reaction products were CaS, CaO, H_2O, and traces of S. Previous studies that had indicated that 6-20% of the sulfate was converted to H_2S and about 0.1% to SO_2 are suspected to be in error due to reaction of the SO_2 and H_2S in the H_2S absorption trap.

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