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CHEMICAL TECHNOLOGY DIVISION
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ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing (Processing Studies on Uranium and Thorium Carbides, Shear and Leach Process, and Solvent Extraction Studies); Fluoride Volatility Processing (Pilot Plant); Foam Separation Studies; Chemical Engineering Research; Ion Exchange Technology; Solvent Extraction Research; and Chemical Applications of Nuclear Explosions.

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POWER REACTOR FUEL PROCESSING

Processing Studies on Uranium and Thorium Carbides. Hydrolysis of uranium sesquicarbide in water or 6 M H_2SO_4 at 80°C yielded 60 ml (STP) of gas per gram of carbide, consisting of 58% hydrogen, 25% ethane, 6% C_3 - to C_8 -saturates, and 6% unsaturates. Of the total carbon in the specimen, half was in the gas phase and 11% in the wax, leaving nearly 40% unaccounted for and presumably in the solution. Reaction of the uranium sesquicarbide with 6 M HCl resulted in slight increase in the gas volume, quantity of free hydrogen, and amount of wax produced; the amount of ethane and butane decreased slightly. These small changes in reaction products when 6 M HCl is substituted for water or 6 M H_2SO_4 are probably caused by the dicarbide impurity in the sample.

Hydrolysis of thorium monocarbide, like that of uranium monocarbide, yielded principally methane (82%) with some hydrogen and small quantities of the higher hydrocarbons. The gaseous products were independent of reagent— H_2O , 6 M H_2SO_4 , or 6 M HCl; virtually all the carbon was in the gas phase.

Shear and Leach Process. Particle size distribution measurements for a carburized (0.8% max carbon) ORNL Mark I fuel prototype assembly sheared into separate batches of 1/2, 1, and 1-1/2 in. lengths showed 26, 44, and 20% more particles, respectively, in the fraction < 9520 μ than for a noncarburized assembly. Particles in the smallest fraction measured, < 44 μ , were 16, 20, and 22% less, respectively, than for a noncarburized assembly. The total stainless steel in the fractions < 9520 μ was 18.5, 5.3, and 3.3% of the original weight, respectively, and compares to measurements of 2.7, 2.0, and 1.1% for noncarburized elements.

A Yankee type fuel assembly of 25 porcelain-filled tubes, 5/16 in. o.d. with 1/4-in.-o.d. spacer ferrules, sheared into 1/4, 1/2, 5/8, 3/4, and 1 in. lengths, had 81, 30, 18, 15, and 11 wt % of the particles < 9520 μ . The tubes of this assembly, which is smaller than the ORNL Mark I assembly, were compacted in cuts more than 1/4 in. length and there was ~38 wt % particles in the fractions < 4760 μ .



The center step of the Squarkeen No. 3 (American Shear Knife Co.) moving blade was chipped on the cutting edge during the 5894th cut of a porcelain-filled ORNL Mark I fuel assembly. Failure occurred while shearing through the solid steel end plugs. A replacement blade of Kleenkut, obtained from the Heppenstall Company as an equal to Squarkeen, failed at 320 cuts.

Solvent Extraction Studies. In laboratory countercurrent batch extraction experiments with stored full-activity level U-233 solutions, gross decontamination factors of the U-233 product were at least 200; the product contained no Th-228. Solutions containing up to 30 ppm of Pa-231 in 0.5 M Th-11 M HNO₃ showed no indication of instability two weeks after preparation. Adsorption of protactinium from the Th(NO₃)₄-HNO₃ system on unfired Vycor glass and elution with oxalic acid separated it from thorium, ruthenium, zirconium-niobium, and rare earths by factors of > 50, 4000, 3, and 4 x 10⁵, respectively.

The relation for the instantaneous dissolution rate of 96% theoretical density UO₂ pellets in boiling 2 to 15.6 M HNO₃ is: log rate = 2.116 log (M H⁺) - 0.684. The addition of 0.1 M HF-0.3 M Al(NO₃)₃ increased the rate in 2 M HNO₃ by 80% but in 14 M HNO₃ by only 15%.

FLUORIDE VOLATILITY PROCESSING

Pilot Plant. Four more successful runs (R-3 through R-6) were made with 5- to 6.5-yr-decayed high-burnup (> 15%) zirconium-uranium alloy fuel (~44 to 46 kg per run). Analytical data from runs R-3 and 4 indicated that the bulk of the uranium decontamination from fission products continued to occur during fluorination and sorption-desorption on NaF. Maximum d.f.'s from volatile fission products during dissolution ranged from ~5 to 8 for Sb-125, and specific fission product activities in the UF₆ product were below analytical limits of detection. In run R-3 on 5-yr-decayed fuel, the Ru-106 d.f. increased to ~10⁸ while all other specific decontamination factors remained essentially the same (~10⁸ to 10¹⁰ for Cs-137, Sr-90, and rare earths; ~10⁴ to 10⁷ for Sb-125 and Zr-Nb-95).

For the four runs, dissolution rates ranged from 2.4 to 5.4 kg/hr and HF utilization efficiencies from 27 to 55%. Fluorine utilization in conversion of UF_4 to UF_6 was only 2 to 5%. After the first run, uranium recovery was > 99.5%. The UF_6 product contained < 900 ppm impurities in runs R-1 to R-4, but in R-5 an unexplained increase in the molybdenum level occurred (560 ppm in R-4 and 4300 ppm in R-5). The plutonium level was < 1 ppb for runs R-1 through R-3.

Equipment performance was generally satisfactory. In run R-3 the hydrofluorinator off-gas line became plugged during dissolution and indirect cleaning through the fuel slug chute was required. The NaF pellet bed was re-formed with difficulty in this run, but agglomerated pellets were broken up by inserting a metal tape in a rod-out line. Excessive leakage of a fluorinator flange in run R-6 required above normal inert-gas buffering for UF_6 containment.

The molten salt portion of the dissolver was (Run T-11) partially decontaminated by dissolution of a Zircaloy-2 simulated fuel element following run R-6. Inert-gas buffering of the leaking vessel flange without excessive inleakage was demonstrated. The dissolver was partially decontaminated, with d.f.'s of ~3 to 40 in the vapor section and of ~1 to 3 in the salt section.

Metallographic examination of two 3/8-in. sch 40 INOR-8 pipes removed from inside the hydrofluorinator after Run TU-11 showed a maximum corrosion rate of 0.12 mil/hr of HF exposure at a point 1.5 in. above the HF distribution plate near the bottom of the vessel. The pipes had been exposed to 20/43-17/41-22/58 mole % NaF-LiF-ZrF₄ for 1359 hr, including 503.4 hr in HF exposure time. Temperatures were 380-620°C and 490-675°C in the vapor and salt regions, respectively. The accentuated interface attack noted during laboratory hydrofluorinator corrosion tests was not observed. Only slight intergranular attack was noted, on one pipe in the upper half of the vapor region.

FOAM SEPARATION STUDIES

Calcium precipitation is the first step in new ion exchange and foam separation processes for decontaminating waste water. Beaker tests showed that when precipitation is made from 0.01 M NaOH, then sodium hexameta-phosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium orthophosphate, Fab, and Turco 4234 in 1-2 ppm concentration strongly interfere; fluoride and oxalate ions do not interfere. Phosphate interference was nearly eliminated by making the water 0.005 M each in NaOH and Na_2CO_3 and 1-5 ppm in Fe^{3+} , pH 11.3. With 0.01 M NaOH instead of 0.005 M, the treatment was less effective. In a 100-hr continuous precipitation run with ORNL low-activity waste, containing ~3 ppm of phosphorus as PO_4^{3-} , the total average dissolved hardness was decreased from ~70 to 4.7 ppm, as CaCO_3 .

Beaker tests also showed that phosphate interference in calcium precipitation can be eliminated by using orthophosphate, 40-50 ppm, in 0.004 M NaOH as the precipitant. In a continuous run with precipitation from 0.004 M NaOH-50 ppm PO_4^{3-} , the hardness was decreased from ~70 to 5.8 ppm, as CaCO_3 .

HTU_x values for foam separation stripping of Sr-89 from a dodecyl-benzene-sulfonate solution varied from 2.2-2.6 cm at 130-160 $\text{gal ft}^2 \cdot \text{hr}^{-1}$ to 4-10 cm at 80-110 $\text{gal ft}^2 \cdot \text{hr}^{-1}$ with a weir type liquid feed distributor. Values were lower with a spider type distributor of seven capillary tubes, but the difference was small at the higher flow rates.

Application of the chi-square statistical test confirmed the fit of normal distributions for foam bubble diameters from spinnerettes with 50- or 80- μ -dia holes; however, normal distributions are rejected for the bubble diameters from porous fritted glass or sintered metal gas spargers. Correct average diameters for calculating the foam surface area were derived from these normal diameter distributions.

CHEMICAL ENGINEERING RESEARCH

The flow capacity of sieve plate extraction-scrub pulsed columns for a flowsheet using di-sec-butylphenylphosphonate in diethylbenzene to

separate uranium from thorium was 490 to 1340 gal ft⁻² hr⁻¹, increasing with decreasing pulse frequency from 90 to 35 cpm. The flow capacity for the stripping column increased from 380 to 730 gal ft⁻² hr⁻¹ as the pulse frequency was decreased from 70 to 35 cpm.

ION EXCHANGE TECHNOLOGY

pH and specific conductivity data obtained as a function of irradiation time for solution effluent from columns of Dowex 50W X-8, X-12, X-16, and X-20 resin exposed in a Co-60 γ -radiation source in a system of flowing demineralized water should be calculable from each other, if other, as yet unidentified, radiation products do not affect them. Identified radiation products in the effluent included sulfate, sulfonate, and oxalate ions in the acid form. Published specific conductivity data suggest that, in the concentration range of interest, 10^{-3} - 10^{-5} N, ionization of these acids is essentially complete. Experimental data indicate that the three acids found in the effluent constitute the majority of the ionizable radiolysis products. Maximum specific conductivity in each run was 400-500 μ mhos/cm, which corresponds to a calculated pH of \sim 3. The minimum pH was 2.7-2.8. Sulfur determinations on the resin samples and the effluent gave a G(-S) of 0.5-1.0 atom S/100 ev of energy absorbed. This corresponds to 50-100 μ mho/cm, or 10-25% of the maximum specific conductance to be accounted for. Thus organic radiation degradation products of the resin polymer appeared to contribute the major amount of acidity.

SOLVENT EXTRACTION RESEARCH

Preliminary tests indicated the possibility of separating transplutoniums from lanthanides by extraction with dialkylphosphoric acids from organic acid solutions. In extraction by di(2-ethylhexyl)phosphoric acid from tartaric acid, americium and curium were shifted from their usual similarity to the medium-weight lanthanides to positions below cerium. Neither transplutoniums nor lanthanides were extracted from K₂CO₃ and K₂CO₃-KHCO₃ solutions by amines or organophosphorus extractants. Hydrazine hydrochloride prevented oxidation of Ru(III) to Ru(IV) by air or H₂O₂ so that it was not extracted by tertiary amines from concentrated lithium chloride solutions.

In further studies on extraction of metal ions from 0.5 to 10 M HCl and LiCl-0.2 M HCl (0.5 to 10 M total Cl) solutions with typical primary, secondary, tertiary, and quaternary amines in diethylbenzene diluent, the extraction power was in the order quaternary > tertiary > secondary > primary. Maximum coefficients (0.1 M amine) were 1.5 for Tl(III), 3 for Tl(IV), 60 for Mn(II), 600 for Ca(II), 0.03 for Ni(II), 100 for Cu(II), 2500 for Zn(II), and 2 for As(III). Extraction coefficients generally increased with increased chloride concentration and were higher from the salt than from the pure acid system.

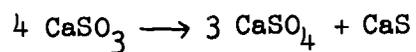
Continued studies of strontium extraction from sodium nitrate solutions by di(2-ethylhexyl)phosphoric acid (D2EHPA) and its sodium salt (NaD2EHP) in benzene confirmed that $E_{Sr} = [Sr]_{org}/[Sr]_{aq}$ is proportional to $[H^+]^{-2}$ with up to 15% of the reagent as NaD2EHP. At higher NaD2EHP concentrations, E_{Sr} was proportional at $a_{NaNO_3}^{-2}$ up to $a_{NaNO_3} = 1.5$ (~3.5 M NaNO₃), changing gradually to $a_{NaNO_3}^{-1}$ at higher NaNO₃ concentrations. These results suggest the general equation $Sr^{2+} + n/y(ZR)_y \rightarrow SrR_2 \cdot (Zr)_{n-2} + 2 Z^+$, where Z = H or Na and R = di(2-ethylhexyl)phosphate. Reagent dependence given by the slopes $[H^+]_{aq}^2 E_{Sr}$ vs [D2EHPA] plots at constant NaD2EHP varied from ~3 with 100% HD2EHP to 0.95 with 100% NaD2EHP. This suggests an initial reaction $Sr^{2+} + 3(HF)_2 \rightarrow SrR_2 \cdot 4HR + 2H^+$, since HD2EHP is a dimer, with diminishing values of n/y reflecting changes in n or y or both as more of the reagent is converted to the sodium salt.

CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

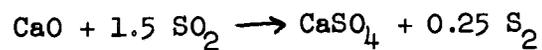
In further studies on the mechanism of the reduction of sulfates by hydrogen, thermal decomposition of CaSO₃ and MgSO₃ showed that these compounds were likely intermediates. Eighty to 90% of MgSO₃ formed MgO and SO₂ and the rest MgSO₄ and free sulfur. The large amount of SO₂ formed by decomposition of a MgSO₃ intermediate would lead to large quantities of free sulfur and H₂S in hydrogen reduction of MgSO₄, and such was observed.

Ten percent of CaSO₃ formed CaO and SO₂ and the remaining 90% CaSO₄ and CaS in 3/1 mole ratio. There was no free sulfur. When the CaSO₃ mole

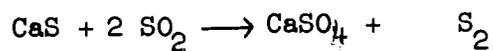
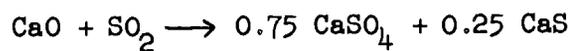
ratio of SO_2/CaO is 1, the compound undergoes autooxidation:



MgO was practically inert to SO_2 , but CaO was very reactive. When the SO_2/CaO mole ratio was 12, 90% of the CaO reacted according to



Free sulfur is formed from excess SO_2 :



MWG:mrh

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