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CHEMICAL TECHNOLOGY DIVISION

MONTHLY REPORT FOR NOVEMBER 1961

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## ABSTRACT

Process development studies are reported on Power Reactor Fuel Processing, Fluoride Volatility Processing, Ion Exchange Technology, Mechanisms of Separations Processes, Process Chemistry of Uranium and Thorium, Solvent Extraction Research, and Chemical Applications of Nuclear Explosions.

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POWER REACTOR FUEL PROCESSING

Beryllium- and Beryllium Oxide-containing Fuels. A simulated GCRE fuel element, containing 13 g of 66.5%  $UO_2$ -33.5% BeO pellets clad in 23.8 g of Hastelloy-X, was digested in about 400 ml of boiling 2 M  $HNO_3$ -4 M HCl. During 10 hr reaction, 77% of the Hastelloy, 99.6% of the  $UO_2$ , and 28% of the BeO were dissolved. Most of the undissolved Hastelloy-X was present as solid end caps.

Corrosion Studies. Welded specimens of Haynes 25 were corroded at a maximum rate of 0.36 mil/mo for the last half of a 408-hr exposure in refluxing 2 M HCl-5 M  $HNO_3$ . Attack was of an intergranular nature.

Nichrome V exposed for 19-24 hr in  $N_2$ - $CCl_4$  was corroded at rates of 2.62 mils/mo at 540°C, 5.1-5.3 at 570°C, 16.1 at 640°C, 41.6 at 670°C, and 14.9 mils/mo at 685°C.

Darex Process. The use of  $NO_2$  for low-temperature stripping of chloride from  $HNO_3$ -HCl mixtures, as an alternative to distillation, was studied with solutions containing dissolved stainless steel. Apparatus consisting of a 2-in.-dia stripping column, 36 in. long, packed with 1/4 in. Berl saddles, and a similar absorption column for aqua regia regeneration was assembled and scouting runs were made to determine the important variables. Chloride was removed to 0.084 M (3000 ppm) when feed solution (11.75 M  $HNO_3$ , 0.75 M  $Cl^-$ , 31 g stainless steel per liter, 2.8 g/liter U) was fed at 27 gal hr<sup>-1</sup> ft<sup>-2</sup> countercurrent to 549% excess  $NO_2$ . Chloride removal was improved by lower solution feed rates (longer residence times), lower stainless steel concentrations, and higher  $NO_2$  rates up to ~500% excess; above this rate, further increase in  $NO_2$  excess produced only marginal improvement. The nitric and hydrochloric acid concentrations of the feed solution in the ranges studied (9-12 M  $HNO_3$ , 0.2-1 M HCl) were of secondary importance, since the  $HNO_3$  in the stripped product, which may affect the final chloride concentration, approached a limiting value (~13.5 M) during  $NO_2$  sparging. The stainless steel concentration, probably the iron alone, became the controlling factor at low chloride concentrations.



Mechanical. Mechanical dejacketing of the SRE Core 1 fuel, burned to ~675 Mwd/ton and decayed about 2 years, was completed. Decontamination and equipment removal from the segmenting cell are approximately 90% complete. Samples of cladding dissolved completely in both 2 M HCl-5 M HNO<sub>3</sub> and 3 M HCl-4 M HNO<sub>3</sub>. Analysis of the solutions showed negligible uranium and plutonium: uranium from 0.001 to 0.0041 mg/ml (0.1 to 4.6 mg per mole of stainless steel) and plutonium from 108 to  $1.1 \times 10^3$  c min<sup>-1</sup> ml<sup>-1</sup>. A spectrophotometric scan of the dissolved jacket showed no fission products.

A satisfactory method of feeding and holding a fuel assembly during shearing was developed for use with the experimental chopper. A new gag (device for holding a fuel element while a cut is made) driving mechanism made possible shearing of a porcelain-filled stainless steel prototype fuel bundle to within 1.5 in. of the end. Other shearing tests with prototype fuel indicated that discrete pieces are produced when the flat side of a fuel assembly is sheared with a stepped blade. However, the sheared face of the bundle is not so compact as when shearing is across the diagonal, and drag back of tubes occurs when the blade is retracted. The force required to shear a Mark I assembly carburized to 1-2% carbon was ~25 tons as compared to ~50 tons for the ductile cladding.

Uranium and Thorium Carbides. Heat treatment of arc-melted UC<sub>1.5</sub> specimens for 60 hr at 1600°C had a marked effect on the products of water hydrolysis. A non-heat-treated specimen upon hydrolysis yielded 1.29 mmoles of methane, 0.88 of hydrogen, 0.44 of ethane, and small quantities of higher hydrocarbons per gram of sample. In contrast, a heat-treated specimen yielded 0.05 mmole of methane, 1.47 of hydrogen, and 0.67 of ethane as well as small quantities of higher hydrocarbons per gram.

Thorium monocarbide yielded about the same hydrolysis products as uranium monocarbide, principally methane (3.32 mmoles/g), with some hydrogen (0.64 mmole/g) and some higher hydrocarbons. Photomicrographs indicated that the thorium monocarbide was less pure than the uranium monocarbide, which probably explains the small decrease in methane concentration while the hydrogen and higher hydrocarbons increased slightly.

Uranium-Graphite Fuels. The reaction of uranium-free graphite with concentrated (60%) nitric acid is being studied. Reaction of 254 g of type GBF graphite for 211 hr with boiling HNO<sub>3</sub>, the acid volume being

maintained constant by daily addition of 90%  $\text{HNO}_3$ , yielded 33 g of water-soluble yellow solids. The solubility behavior of the solids indicated that they were a mixture of polycarboxylic acids. The mixture had a neutralization equivalent of 63 and contained 41.5% C, 2.0% H, and 0.5% N. It has not yet been determined whether the nitrogen is present as sorbed nitric acid or as organonitrogen compounds, but qualitative tests indicated that mellitic acid (benzene hexacarboxylic acid) is present.

In engineering-scale tests on semicontinuous leaching of graphite-2.6% U with 90%  $\text{HNO}_3$ , the uranium loss was 0.37%, corresponding to 100 ppm U in the graphite residue. The fuel was broken to -2 mesh and 73% was >12 mesh. It was batch-contacted for 2 hr with 90%  $\text{HNO}_3$ , then continuously leached with 90%  $\text{HNO}_3$  for 4 hr, and finally water washed. Uranium loss for -4 mesh fuel, 27% of which was >12 mesh, was 1.6% under identical treatment.

Solvent Extraction Studies. The amount of protactinium removed by adsorption on unfired Vycor glass from hydrochloric acid solutions containing  $7 \times 10^5 \text{ c min}^{-1} \text{ ml}^{-1} \text{ Pa}^{233}$  and  $\sim 0.05 \text{ M NO}_3$  was 81% from 0.1 M HCl, 65% from 1 M HCl, 75% from 4 M HCl, and 42% from 10 M HCl.

Preliminary experiments showed that  $\text{Pa}^{233}$  adsorbed on unfired Vycor from 6 M  $\text{HNO}_3$  may be eluted with 0.1 to 0.5 M oxalic acid.

#### FLUORIDE VOLATILITY PROCESSING

In a nonradioactive evaluation run in the Volatility Pilot Plant, the newly installed dissolver off-gas system prevented solids plugging of the dissolver off-gas valve during dissolution of dummy Zircaloy-2 fuel elements. Fifty-four kilograms of alloy was dissolved with HF feed rates of 162 and 350-370 g/min to the dissolver and flash cooler, respectively. The dissolution rate was 1.8 kg/hr and the HF utilization efficiency, 18.3%. Fully enriched zirconium-uranium alloy fuel, 40 kg, was processed with HF at an average flow rate of 128 g/min. The dissolution rate, 4.0 kg/hr, and HF utilization efficiency, 40.2%, were the highest of any run to date. No explanation is offered yet for the increase. Uranium was recovered as  $\text{UF}_6$  by fluorination at rates of 6 and then 16 slm for a total of 120 min. Non-recoverable uranium losses were only 0.1 wt %. There was no difficulty with either the dissolver off-gas system or molten salt transfer.

In laboratory studies hydrofluorination rates in various molten salt compositions were satisfactory with several types of fuel material. Zircaloy-2 dissolution rates were  $4.3-13.5 \text{ mg cm}^{-2} \text{ min}^{-1}$  in 37-50.5-12.5 mole % LiF-NaF-BeF<sub>2</sub> at 650°C with different ZrF<sub>4</sub> concentrations, the rate decreasing with ZrF<sub>4</sub> concentration in the range of 0-28 mole %. UO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-BeO tubular fuel elements dissolved in 40-49-11 mole % LiF-NaF-BeF<sub>2</sub> and in 63-37 mole % NaF-ZrF<sub>4</sub> at overall rates of 5-6 mil/hr at 650°C. ThO<sub>2</sub>-UO<sub>2</sub> (96-4 wt %) pellets clad in Zircaloy-2 were dissolved in 34-26-40 mole % LiF-NaF-ZrF<sub>4</sub> at 600°C at an estimated rate of about 20 mils/hr to give a final thorium concentration of 5%. In subsequent fluorination uranium volatilization was >99.6%.

#### ION EXCHANGE TECHNOLOGY

Amberlite 200 resin, after being exposed to cobalt-60 gamma for a total dose of  $0.97 \times 10^9$  r, lost 34% of its original capacity; Dowex 50W X-8 resin, after a dose of  $0.85 \times 10^9$  r, lost 30%. The radiolytic loss of sulfur, G(-S), for Amberlite 200 was calculated to be 1.2 atoms per 100 ev of Co  $\gamma$  radiation absorbed. The moisture content increased from its original 53% to 57%, median pore diameter from 250 Å to 315 Å, and surface area from 50 m<sup>2</sup>/g dry resin to 60 m<sup>2</sup>/g dry resin.

#### MECHANISMS OF SEPARATIONS PROCESSES

The surface chemistry and foaming properties of dodecylbenzene sulfonate were studied with respect to the use of this surfactant in a foam process for decontaminating ORNL low-activity waste. With tap water as a substitute for the waste, the saturated surface concentration of the sulfonate by both static and single-stage foam column methods was found to be  $3.1$  to  $3.4 \times 10^{-10}$  mole/cm<sup>2</sup>, the critical micelle concentration in the bulk phase  $2.2 \times 10^{-3}$  mole/liter, and foam stability  $<0.08 \times 10^{-3}$  mole/liter, i.e. at <4% of the CMC. At calcium concentrations of 0 to 4 ppm, sodium hydroxide concentrations of 5 or  $10 \times 10^{-3}$  M, and sulfonate concentrations of 62 to 250 mg/liter, the strontium distribution coefficient,  $\Gamma/x$  (foam/bulk solution), ranged from 1 to  $20 \times 10^{-3}$  cm. On the basis of a practical value of  $\Gamma/x = 2.5 \times 10^{-3}$  cm and a foam column of ~20 theoretical stages, the

calculated decontamination factor is  $>10^2$  for a volume reduction of  $10^2$ , a throughput of  $\sim 50 \text{ gal ft}^{-2} \text{ hr}^{-1}$ , and a bubble diameter of 0.5 mm.

#### PROCESS CHEMISTRY OF URANIUM AND THORIUM

Rice University (under subcontract) made a field survey during the past summer of the Conway granite formations in New Hampshire. Over 500 field spectroradiometric determinations were made on an extensive portion of the 400 square miles of outcrop area with a portable, single-channel, transistorized, gamma-ray pulse-height analyzer. Preliminary analysis of the data indicated that the accessible surface of the Conway granite averages at least 40 ppm thorium.

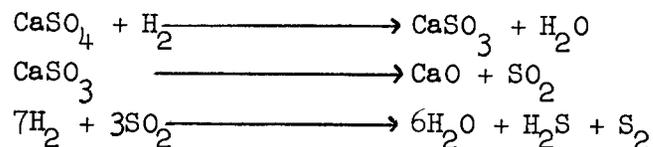
#### SOLVENT EXTRACTION RESEARCH

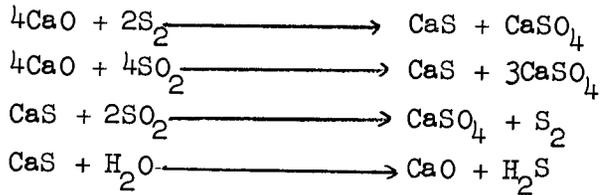
A method has been developed for removing diluent nitration products from spent Purex or Thorex solvent, TBP, and Amsco. Scrubbing with low-molecular-weight alkanol amines (e.g., ethanolamine) converts the offending nitroparaffins to their amine salts, which are preferentially removed by the amine phase. This method is the best liquid-liquid system thus far devised.

Tertiary amines have been shown to extract all the lanthanides preferentially to yttrium from concentrated chloride solutions. Relative extractabilities varied with composition of amine, diluent, and salting agent. Europium was always the most extractable of the series Ce, Eu, Tb, Ho, Tm, and Lu from  $11 \text{ N LiCl}-0.01 \text{ N HCl}$ . The maximum separation factor obtained between Eu and Y was  $\sim 10$ . Differences between the elements were smaller in extractions from  $8 \text{ N LiCl}-2 \text{ N AlCl}_3$ , with Lu sometimes more extractable than Eu.

#### CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS

Studies of the mechanism of the reduction of calcium sulfate by hydrogen showed the reduction to involve the reactions





The final products were CaS, CaO, H<sub>2</sub>O, and H<sub>2</sub>S; the solid reduction product contained 15-20 mole % CaO, the balance being CaS. SO<sub>2</sub> and S<sub>2</sub> were not observed in the off-gas and are intermediates only.

Deuterium readily exchanged with water at 10,000°K in a plasma jet. After injection of mixtures of 92 mole % D<sub>2</sub> and 8% H<sub>2</sub>O into the plasma jet, the water phase was found to contain 82.6 atom % D (0.775 g D<sub>2</sub>O/g of solution). The residence time for the mixture in the jet was approximately 40 msec. This result strongly suggests that tritium will exchange very rapidly with environmental water at nuclear explosion temperatures.

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