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ISOTOPES DEVELOPMENT CENTER

PROGRESS REPORT

CURIUM PROGRAM

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February 1963

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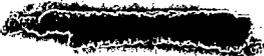
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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE NUCLEAR COMPANY
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1. IRRADIATION OF AMERICIUM-241

1.1. Irradiation Target Fabrication

Target Capsule Welding

Capsules welded at a speed of 2 rpm and 24-38 amp have been consistently sealed as indicated by vacuum leak test. The photomicrographs of weld sections show numerous gas bubbles in the weld zone which were attributed to the air in the capsule expanding from the welding heat. Additional investigation has shown that this expansion is responsible for only a small part of the trapped bubbles. Photomicrographs of weld sections made with vented capsules do not show a significant decrease in the number or size of trapped bubbles. Further studies will be made to determine if the trapped gas comes from oxide films or other contaminants on the aluminum metal which stronger cleaning agents could eliminate.

1.2. Americium-241 Fuel Element

Engineering calculations for irradiating gram quantities of Am^{241} in the ORR were completed. The 8-in.-long, 0.5-in.-OD, welded aluminum capsules will each contain 3 g of Am^{241} as pressed pellets of $\text{AmO}_2\text{-Al}$. The weight of aluminum in each capsule is 60 g. An ORR core piece has been designed and fabricated for irradiating up to 18 capsules. The calculations are based on an average perturbed thermal neutron flux of 3.0×10^{14} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ for the active target length, a maximum thermal flux in the target of 1.2 times the average flux, an irradiation time of 50 days, and an initial pellet to capsule radial gas gap of 1 mil. If all of the fission product gases are released, the maximum stress in the aluminum capsule would be 500 psi. Other features of the irradiation are found in Table 1.2.1.

Table 1.2.1. Calculated Am^{241} Capsule Heat Fluxes and Temperatures
At a Perturbed Flux of 3×10^{14} Neutrons $\text{Cm}^{-2} \text{Sec}^{-1}$

Conditions	Surface Heat Flux ($\text{Btu hr}^{-1} \text{ft}^{-2}$)	Surface Temperature ($^{\circ}\text{F}$)	Central Pellet Temperature	
			He Gap ($^{\circ}\text{F}$)	Air Gap ($^{\circ}\text{F}$)
Average Flux	438,000	192	682	789
Maximum Flux	526,000	205	793	922

2. CHEMICAL PROCESS DEVELOPMENT

2.1. Tramex Flowsheet Test at High Power Density

Effect of High Level Alpha Activity on Tramex Feed

Acid depletion G values were determined for two 10 M LiCl solutions containing 2.0 and 2.6 w/liter of Cm^{242} , respectively. Previously reported values of 4.07 and 5.5 molecules per 100 ev were averages for a wide range in acid concentration. Recent data show that the G values are dependent upon the acid concentration. In the range 0.4 to 1.0 M HCl, G values of 10 to 20 were measured. In the range from 0.01 to 0.4 M HCl, G values of 2.20 and 2.18 were obtained for activity levels of 2.0 and 2.6 w/liter, respectively. The acid loss mechanism is not known; however, the more rapid loss at higher acidities may result from radiolytic gas sweeping HCl from the solution.

If acid is not added to the high activity-level solutions, the curium will eventually precipitate as $\text{Cm}(\text{OH})_3$. Nickel present in one solution was precipitated along with the curium. After a period of time the nickel was oxidized to Ni^{3+} as evidenced by the color change from a greenish to a black precipitate.

Tramex Feed Adjustment Studies

Methods of replacing acid lost by radiolysis are being investigated. An equilibrium acid concentration of 1 M HCl was obtained when HCl gas was bubbled through 10 M LiCl at 25°C. This was reduced to 0.4 M HCl when HCl gas was bubbled through 10 M LiCl at 120°C. Preliminary results indicate an HCl partial pressure of ~ 14 mm Hg over 10 M LiCl-0.1 M HCl at 23°C.

Tramex Solvent Studies

Techniques for determining distribution coefficients of HCl between the hydrochloride salt of 0.6 M Alamine 336 in DEB and LiCl feeds were further refined and extended to include feeds containing AlCl_3 -LiCl mixtures. Americium distribution coefficients for feeds containing 9, 10, and 11 M LiCl were 0.34, 2.45, and 18.7, respectively, when the acid feed concentration was approximately 0.003 M.

Full Activity Level Tramex Flowsheet Test

A satisfactory joint between polyethylene tubing and glass has been obtained with Beckman Varigrip Teflon fittings. The glassware is being altered to provide stubs which will give a tighter seal.

Preliminary Testing of Cell 4 Equipment

An eight-stage mixer-settler was operated under Tramex flowsheet conditions with simulated feed. The total flow rate was 2 liters/hr with a scrub:feed:organic volume ration of 1:1:2. An improved set of impellers was designed and is being fabricated.

Actinide Extractability from NaHCO₃ Solutions

The relative extraction positions of the actinides in 30% Aliquat 336-DEB system from 0.5 M NaHCO₃ were determined and are listed in Table 2.1.1.

Table 2.1.1. Distribution Coefficients for Actinide Elements in 30% Aliquat 336-DEB from 0.5 M NaHCO₃

Element	Probable Valence	K _d (O/A)
U	6	13.6
Np	5	1.99
Pu	4	2.27
Am	3	0.52
Cm	3	0.65
Cf	3	2.03
Es	3	2.51
Ce	3	1.0
Eu	3	4.8

The actinide elements are shifted downward in relation in their lanthanide homologues, and it is possible to extract the rare earths from americium and curium. Group separation of actinides and lanthanides is not possible with this system. Similar results can be expected for the Dowex 21 K vs 0.5 M NaHCO₃ system.

Extraction of Actinides from α -Hydroxyisobutyrate Solutions

Tests were made to determine if Am-Cm and Cf-Es separation factors can be enhanced by the use of α -hydroxyisobutyric acid to form anionic complexes in the aqueous phase.

Actinide extraction into 30% Alamine 336-DEB from α -hydroxyisobutyric acid increases slightly with increasing acid concentration over the range 1 to 6 M. Distribution coefficients for Am, Cm, Cf, and Es from 4 M acid were 0.098, 0.05, 0.34, and 0.57, respectively. These represent separation factors of 1.94 for Am-Cm and 1.69 for Cf-Es.

Distribution coefficients between D2EHPA-DEB or 2-ethylhexylphenylphosphoric acid (2EH(ϕ P)A)-DEB and solutions of α -hydroxyisobutyric acid were approximately proportional to the inverse 1.5 power of the acid concentration. Separation factors also decreased with increasing acid concentration. For the system 0.1 M 2EH(ϕ P)A-DEB vs α -hydroxyisobutyric acid, Am-Cm separation factors decreased from 1.34 to 1.08 as the acid concentration decreased from 1.0 to 6 M.

2.2. Curium Recovery Facility (CRF)

The design of CRF Cell 4 is essentially complete. Comments have been made on various drawings and a review of the Critical Path Schedule was completed. Those jobs that could delay cold startup by May 10, 1963, will be expedited. A 3/8-in. tantalum disconnect has been successfully tested which has the surfaces of both the male and female portions burnished with a roller tool device. A mixer settler with ball bearings on the mixing shafts is now being tested. Impeller design will have to be modified to change its mixing characteristics. Heads of tanks T-402, T-406, and T-410 are being finished prior to shipment to Parma, Ohio, for plating. All coils and dip tubes for all vessels have been fabricated and are awaiting installation into their respective heads. Piping is being installed in the cell from rack-mounted disconnects to cell entry points. Fabrication of the sample transfer mechanism for the roof area will proceed upon receipt of final drawings from design.

3. CURIUM-242 SOURCE FABRICATION

3.1. Chemical Process Development

The Build-up of Noncondensable Gas Above a Curium Oxalate Slurry

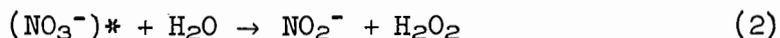
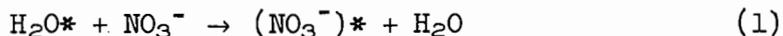
The rate of radiolytic gas evolution from process solutions containing Cm²⁴² was determined by measuring the pressure increase with time in a known contained volume above a solution or slurry at room temperature. In the case of an oxalate solution containing 1000 curies of Cm²⁴² as a curium oxalate precipitate, 94 cm³/hr is evolved. In a 4 N HNO₃ solution containing 1000 curies of Cm²⁴², the gas evolution rate is 28 cm³/hr.

An investigation of the effect of Co⁶⁰ gamma radiation on acid solutions of NaNO₃ was made by Lapik¹ and the yields of hydrogen, oxygen, peroxide, and nitrite were determined. The yield of hydrogen decreases with increasing concentration of NaNO₃, and is 0.03 molecule per 100 ev at 6.0 M NaNO₃. This yield of hydrogen represents a decrease by a factor of 70 compared to the radiolytic yield of hydrogen in pure water which

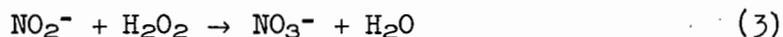
¹V. S. Lapik, et al., Proceedings of the Second All-Union Conference on Radiation Chemistry, Published by the Academy of Sciences, p. 137, Moscow, 1962

is about 2.0 molecules per 100 ev. This observation is in agreement with the low yield of noncondensable gas observed in our experiment with HNO₃ solution.

Sowden² states that excited water molecules react with nitrate ions to form nitrite ions by the following mechanism:



The nitrite ions can react with H₂O₂ which is a radiolytic product, to give the initial nitrate ion and water molecule as follows:



Thus, it can be seen that acid nitrate solutions have a high radiation stability.

According to V. S. Lapik¹, Table 3.1.1 shows the gas yields at various molarities of NaNO₃.

Table 3.1.1. Gas Yields as a Function of NaNO₃ Molarity

NaNO ₃ Molarity	Molecules per 100 ev		
	Oxygen	Nitrate	Hydrogen
2.0	0.18	0.30	<0.15
3.0	0.25	0.50	<0.15
4.0	0.30	0.70	<0.15
6.0	0.40	-	-

Hydrogen peroxide cannot be detected in greater than 0.1 M NaNO₃ solutions at a pH <1, because of the destruction of peroxide by nitrite according to reaction (3). Hence, an acid solution containing 1.0 to 2.0 N nitrate ions would have high radiation stability, and the principal noncondensable gas in this system would be oxygen. E. M. Nanobashvili³ shows that the nitrite yields are 40% less for irradiation with alpha particles from Pu²³⁹ than for irradiation with Co⁶⁰ gamma rays.

²R. Sowden, Trans. Faraday Soc., 55, 2084, 1959.

³E. M. Nanobashvili, et al., Proceedings of the Second All-Union Conference on Radiation Chemistry, Published by the Academy of Sciences, p. 155, Moscow, 1962.

Separation of Pu²³⁸ from Cm²⁴²

Samples of irradiated Am²⁴¹ that were discharged from the reactor several months ago will be processed to recover Cm²⁴² for oxalate precipitation and source pellet formation studies. The Pu²³⁸ formed by the decay of Cm²⁴² will be separated by ion exchange prior to the curium oxalate precipitation. Plutonium is readily adsorbed as Pu(NO₃)₆²⁻ on a Dowex 1 anion exchanger from an 8 to 10 N HNO₃ solution and the curium passes through the column into the effluent. Tracer experiments with a Pu²³⁸-Cm²⁴² mixture showed that about 90% of the plutonium was adsorbed by the anion exchanger from 8 N HNO₃, and the Cm²⁴² was found in the column effluent. The nitrite formed by the alpha radiation stabilizes plutonium as Pu(IV) without the use of a reducing agent. The separation should be improved at higher radiation levels and by the addition of a reducing agent.

Zirconium-Niobium Chemistry

The carrying of Zr⁹⁵-Nb⁹⁵ tracer on zirconium phosphate from 4 N HNO₃ was investigated to determine if excessive quantities of these elements can be removed from the product solution following the extraction procedure. It was found that 98.2% of the Zr⁹⁵-Nb⁹⁵ tracer is carried at 0.5 g/liter of zirconium carrier. The addition of 0.045 M H₂O₂ reduces the amount of Zr⁹⁵-Nb⁹⁵ tracer carried on the zirconium phosphate precipitate to only 41.9%. This behavior is due to the formation of a strong complex by niobium with peroxide, which is not carried on the zirconium phosphate precipitate. The volume of the zirconium phosphate precipitate is 20 to 40 cm³ per gram of isotopic zirconium.

The predominant species formed by alpha irradiation in nitrate solutions is the nitrite ion. Therefore, the Zr⁹⁵-Nb⁹⁵ tracer experiments will be repeated in the presence of 0.02 to 0.2 M NaNO₂. A zirconium phosphate precipitation to remove Zr⁹⁵-Nb⁹⁵ contamination from the product solution could be performed in the equipment presently designed for curium source compound production.

3.2. Source Fabrication Development

Curium Pellet Program

Preliminary work is underway on experiments to press a curium pellet, sinter the pellet, and measure the helium evolved due to alpha decay of Cm²⁴² in the pellet. Design has been completed on a sintering furnace which will be adaptable for melting-point determinations by an optical pyrometer.

The helium evolved from the pellet will be contained in a high vacuum system and the pressure will be gauged daily to measure the quantity evolved. At the end of a week a portion of the gas will be withdrawn and analyzed for He, N₂ and O₂. The gas sample will be placed in argon for handling purposes in order to increase the accuracy of the helium

analysis. These data will provide valuable information concerning helium pressure build-up inside a SNAP capsule.

The pellet pressing and sintering will provide experience in handling a hot pellet and aid in the equipment design for the full-size pellet experiments.

3.3. Source Fabrication Facility (SFF)

Final design criteria have been transmitted on the chemical process equipment and preliminary flow sheets have been approved.

The GPP modifications to Building 3028 are approximately 72% complete. The approval for equipment installation has been received and fabrication will start in March 1963. The estimated completion date for equipment installation is July 29, 1963.

The design status for the SFF and its equipment is listed in Table 3.3.1 and Table 3.3.2, respectively.

Table 3.3.1. SFF Design Status

Description	Percent Complete
Structural	95
Piping	85
Air Handling	90
Electrical	95
Civil	90
Chemical Process	75
Feed Station	20

Table 3.3.2 SFF Equipment Design Status

Description	Percent Complete
Bag out Port	98
Access Port	100
Waste Cask	98
Dolly	97
Sample Cask	100
Manipulator Decontamination	95
Welders	95
Doors and Inter-cell Transfers	98
Maintenance Enclosure	10
Chill Blocks	0
Cm ²⁴² Press	10

3.4. Encapsulation Development

Eight half-scale platinum capsules were welded, radiographed using a Co⁶⁰ source, and shipped to MND for SNAP-11 impact tests. The welds were performed by using argon shielding, 90-amp current, 9-v potential and a 2-rpm rotation speed. Two passes were made on each capsule.

Figure 3.4.1 illustrates that the poor detail obtainable in a radiograph of a thick-walled, spherical platinum capsule does not allow good definition of the weld penetration.

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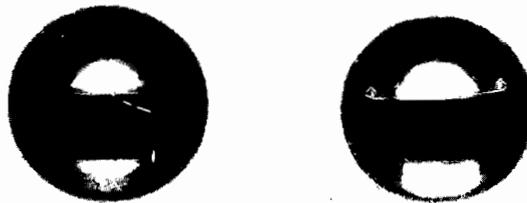


Fig. 3.4.1. Gamma Graph of SNAP-11 Impact Test Capsule

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