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FLWSHEET FOR AMERICIUM RECOVERY
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FLWSHEET FOR AMERICIUM RECOVERY AND PURIFICATION

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RESEARCH AND ENGINEERING OPERATION
CHEMICAL PROCESSING DEPARTMENT

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FLWSHEET FOR AMERICIUM RECOVERY AND PURIFICATION

Americium (atomic weight 241) grows into plutonium as a result of the 13-year half-life beta decay of Pu^{241} . An appreciable quantity of Am^{241} has grown into the scrap that accumulated following shut-down of the Recuplex facility, and which will be processed during the initial period of operation of the plutonium reclamation facility.⁽¹⁾ Current interests in trans-plutonium research and in isotopic heat sources make it desirable to consider the recovery of this Am^{241} .

The americium contained in scrap that is processed through the reclamation facility (Project CAC-880) should appear almost quantitatively in the aqueous waste stream (CAW). Subsequent processing of the CAW through the DBBP extraction column (CW) of the waste treatment facility (Project CGC-912) should result in further separation of plutonium and americium by extracting some of the plutonium while most of the americium remains in the aqueous waste stream (CWW). The fact that a low free nitric acid concentration will favor the extraction of americium into TBP-type solvents can be used to recover americium from the large volume, high salt concentration CWW stream. The flowsheets in this document present the chemical conditions for effecting this recovery.

The process consists of two main parts:

Part 1: Separation and Concentration

Part 2: Purification and Product Preparation.

The Part 1 process, shown in figure 1, separates the americium and remaining plutonium in the CWW from the large volume of aqueous waste by a DBBP solvent extraction step and physically concentrates these materials to a small volume for subsequent processing in small lab-scale equipment. This initial separation is accomplished in batch contact equipment which present conceptual design calls for installation in the new waste treatment facility (Project CGC-912).

After the initial separation, the americium is separated from plutonium and other impurities in a series of small ion exchange columns. The purified americium product solution is then concentrated, precipitated as the oxalate, and calcined to the oxide for shipment. This process, Part 2, is shown schematically in figure 2. At present, it is contemplated that the small lab-scale equipment required for these latter processing steps (ion exchange, etc.) will be installed in a new hood.

The ion exchange and final product preparation steps (Part 2) are simplified versions of flowsheet conditions already in use at Rocky Flats. Consequently, those portions of the flowsheet may be considered "firm" for design purposes.

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The initial part of the flowsheet (Part 1) has been developed using limited distribution ratio data. The specified process conditions are adaptable to a TBP flowsheet, where distribution ratios and equilibration data are better known; however, a somewhat lower yield might be expected. Additional laboratory data will be obtained during the next six months which may result in yield improvement and overall process simplification. Recent laboratory data indicate the DBBP flowsheet to be feasible with considerable advantage over TBP, however, final demonstrations have not yet been completed.

FLWSHEET - BASIS AND NOTES

Recovery

Americium is not extracted by TBP from aqueous solutions containing an excess of free (extractable) nitric acid and should appear almost quantitatively in the aqueous waste stream (CAW) of the reclamation facility (Project CAC-880).

It is assumed, but not necessary to the success of the recovery, that some purification of americium from plutonium is achieved by the DBBP extraction in the waste treatment facility (Project CGC-912).

Process conditions will be established to achieve a distribution coefficient ($E_{o/a}$) of 10 or greater, which will result in an americium recovery of 90 percent or better in one theoretical stage of extraction. Due to the fact that the height of a theoretical stage (HETS) may be excessive at low americium concentrations, batch contacting or mixer-settler operation with relatively long contact times is preferable to counter-current extraction and stripping columns. In the event that extraction coefficients considerably in excess of 10 prove to be attainable (which would allow a column design of less than one theoretical stage), batch contacting will allow greater volume reduction with subsequent process simplification in the purification steps. Expected distribution coefficients and stage heights from the DBBP system are such that packed column extractors of reasonable height (adaptable to existing building space limitations) will be possible and design may proceed along the path deemed most economical for this particular installation.

The extractant will be DBBP or TBP of relatively high concentration in a petroleum solvent or carbon tetrachloride. Ten to 30 percent DBBP in Soltrol is assumed for this flowsheet.

A concentration factor of about five times and decontamination from gross salt impurities will be achieved by solvent extraction. Further concentration will be achieved by loading the americium on a cation ion exchange resin. A loading of about 25 grams of americium is anticipated, which would result in approximately two loadings per month.

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Typical concentrations of americium will vary widely, depending upon the history of the source plutonium scrap.

Shielding will be necessary for personnel protection against the predominantly 60 kev gamma radiation associated with Am^{241} decay.

The flowsheet for recovery is presented in figure I.

Purification

Purification of Am^{241} will be accomplished by ion exchange, using an adaptation of the process used at the Rocky Flats Plant.⁽²⁾ The flowsheet is presented schematically in figure II. The product will be a purified americium oxide.

The americium production rate will vary between 25 to 100 grams per month, depending upon scrap processing rates and the history of the scrap. Assuming uniform processing over an 18-month period, the production rate will be about 55 grams per month.

Since the purification is essentially a laboratory operation, and will involve manipulations and decisions of a technical nature to optimize purification and yield, it is assumed that the purification hood will be outfitted and initial operations will be under the direction of a chemist or laboratory engineer.

A description of the purification process is as follows:

1. Receiving feed: On cation cartridge; unloaded by eluting with a high nitrate, low acid solution.
2. First anion column: Loaded directly by cation column effluent. Washed with high nitrate salts; this wash offers variable to remove cerium and rare earths as needed. Elution by dilute nitric acid.
3. Cation crossover column: Loaded directly with anion column effluent and uses water wash. Provides crossover from nitrate to chloride chemistry. Elution with a strong hydrochloric acid.
4. Second anion (chloride) column: This column allows americium to pass, but retains iron and plutonium when they are in the oxidized state.
5. Product concentration: A concentration to about 1/30 the column effluent volume drives off most of the hydrochloric acid. Acidity is then adjusted by dilution.

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6. Precipitation: The oxalate is precipitated, digested, and filtered out, and the filtrate disposed of as a chloride waste.
7. Calcination: The oxalate is calcined in a muffle furnace in the filter crucible used in the filtration.

The flowsheet details for these process steps are given in figures III through VII.

Americium will be collected on a cation resin in a cartridge containing lots of 25 grams. It will be eluted off by high nitrate salt solution. The high salt elutant will be used to directly load the next resin column, an anion column. The column will be washed with salt solution and the americium then eluted off with dilute nitric acid. This low acid elutant will be used as feed for the next cation column. On this column, the americium will be water-washed, then eluted with strong hydrochloric acid. The chloride stream will be oxidized by addition of nitrate and passed through an anion column, carrying the americium.

The product from the ion exchange treatment will be concentrated, with resultant removal of most of the hydrochloric acid, and then diluted. An oxalate precipitation will be followed by calcination to the oxide to give the final product.

Discussion - Purification

The entire purification flowsheet has not been demonstrated as an integrated process, but the individual steps have. The high salt anion column has been well explored (ORNL-3291). The last two columns, plus the following steps, are essentially the latest version of the flowsheet used by Rocky Flats for americium production (RFP-130). The hazardous thiocyanate portion of Rocky Flats flowsheet has been replaced by the more recently developed high salt flowsheet.

The processing after ion exchange will be on a scale that will best be accomplished in laboratory-type glassware. Also, purity requirements at this step indicate new, clean equipment may be frequently required.

Short-term storage may be on the ion exchange resins, reducing the need for tankage and permitting overnight standby. Solution movement may be by gravity or vacuum. With one exception, elution compositions of one column are loading compositions for subsequent columns, so that intercolumn adjustments and tanks are not required.

Variation of the wash conditions in the first anion column permit clean-up of a wide variety of impurities (ORNL-3153, page 88). Conversion from nitrate to chloride in this column has been demonstrated, and may be

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required if rare earth impurities are a problem. However, the chloride waste handling will be simpler if the crossover is in the next column, as shown on the flowsheet. Use of lithium salt will cause a neutron emission problem; the flowsheet is the worst case, and alternate salts will be used as conditions require.

Waste routings are made that permit recovery of unexpected losses without a large number of analyses or hold-ups. By routing all nitrate wastes back to the CWW neutralizer, the americium in the nitrate streams is automatically recovered. Any americium present in the chloride wastes will be precipitated on caustic neutralization, and thus easily detected and recovered.

Gamma instrumentation may be used advantageously for process control. Thus, the switch-over of effluent on unloading the cation resin could well be made on the basis of an in-line gamma determination. Column loadings, high waste losses, etc., may be followed by portable gamma sensitive instruments.

Shielding will be necessary for personnel protection of the predominantly 60 kev gamma radiation associated with Am^{241} decay.

Americium Nuclear Safety Considerations (s)

Am^{241} is safe in all configurations, concentrations, and H/Am ratios in sub-kilogram quantities. Quantities in excess of one kilogram are probably safe, but will require further evaluation if it should become desirable to handle such large quantities.

REFERENCES

1. HW-77765, "Americium Recovery Study", by P. H. Reinker, April 26, 1963.
2. RFP-130, "Preparation of Pure Americium", by V. A. Ryan, J. W. Pringle, January 8, 1960. Unclassified.
3. ORNL-3290, "Transuranium Quarterly Progress Report - Period Ending February 28, 1962", by D. E. Ferguson, June 13, 1962. Unclassified.
4. ORNL-3375, *ibid*, Period Ending August 31, 1962, by D. E. Ferguson, February 1, 1963. Unclassified.
5. ORNL-3408, *ibid*, Period Ending November 30, 1962, by D. E. Ferguson, June 7, 1963. Unclassified.
6. ORNL-3291, "Anion Exchange Recovery of Americium and Curium from Plutonium Process Wastes", by M. H. Lloyd. To be issued.

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7. ORNL-3314, "Chemical Technology Division Annual Progress Report for Period Ending June 30, 1962", September 22, 1962. Unclassified.
8. Private communication - R. L. Stevenson to M. J. Szulinski, July 11, 1963.

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FIGURE I

FLOWSHEET

AMERICIUM RECOVERY

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FIGURE II

AMERICIUM PURIFICATION

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FIGURE III - ISOLATION COLUMN
(Cation - Isolation, concentration, storage and transfer of Am)

Conditioning

1. Initial - treated with 0.1 M HNO_3 .
2. Between runs, back-flush with 24 liters of 0.1 M HNO_3 @ 1 liter/minute.
3. When not in use, keep unloaded column vented and covered with 0.1 M HNO_3 .

NOTES

- (1) Elution to be in 25-gram batches - loading may be greater.
- (2) Small volumes of wastes due to fractionation of elution.

Description

6" x 24", 8 liters Dowex 50 W-12, 50 - 100 mesh.
Provision for up-flow back wash.

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FIGURE IV - PURIFICATION COLUMN NO. 1

(Anion - nitrate - concentrate, store, purify)

Description

3" diameter x 30" high, glass.
Dowex 1 - 10 X (Permatit SK)
4 liters - 50 to 100 mesh.

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FIGURE V - PURIFICATION COLUMN NO. 2

(Cation - nitrate to chloride conversion)

Conditioning

1. Condition new resin with 4 liters of 0.1 M HNO₃.
2. Wash after elution with 12 liters of water (8 liters/hour). Discard to Cl⁻ waste.
3. Keep water on resin and keep column vented when not in use.
4. Keep system clean of metal ion impurities.

Description

3" diameter x 30" high.
Dowes 50 W, 4 liters.
Stream flow by gravity.

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FIGURE VI - PURIFICATION COLUMN NO. 3

(Anion - chloride, plutonium retention)

Conditioning

1. Wash new (clean) resin with 4 liters 7 N HCl.
2. Keep column under 7 N HCl when not in use. Keep vented.
3. When plutonium loading (dark brown) is high, elute with 0.2 N HCl. Follow with 7 N HCl.
4. Keep system clean of metal ion impurities.

Description

3" glass column, 24" long.
3 liters Dowex 1 - 4 (chloride form)
Stream flow by gravity.

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FIGURE VII - PRODUCT CONVERSION

All operations in clean glassware.
Laboratory-type operations.
CP reagents.

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