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Chemistry - Separation Processes
for Plutonium and Uranium
(TID-4500, 13th Ed.)

# PERFORMANCE OF A PLUTONIUM REFLUX SOLVENT EXTRACTION SYSTEM*

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By

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Advance Process Development
Research and Engineering Operation

March 27, 1957

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price 20 cents. Available from the
Office of Technical Services
U.S. Department of Commerce
Washington 25, D.C.

*Presented at the Aqueous Reprocessing Symposium in Brussels, Belgium, May 1957.

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# PERFORMANCE OF A PLUTONIUM REFLUX SOLVENT EXTRACTION SYSTEM

## I. INTRODUCTION

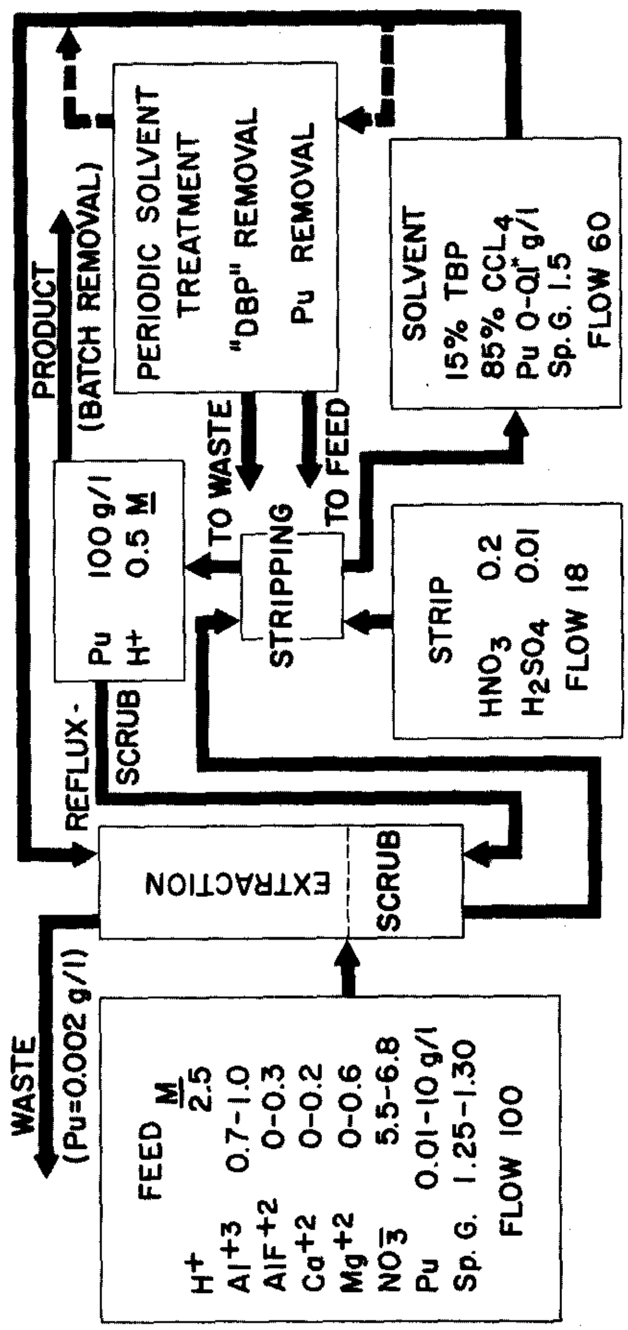
The operability of a product-refluxing flowsheet in a plutonium solvent extraction system was demonstrated during a six-month semi-works program to develop a plutonium purification process. The following paper describes briefly the semi-works performance of the reflux flowsheet, and summarizes the advantages and disadvantages of employing product refluxing as a solvent extraction technique.

## II. THE REFLUX FLOWSHEET

The semi-works reflux flowsheet, presented in Figure 1, is directed toward the recovery and purification of plutonium from sources that vary widely in plutonium content and chemical composition. The feed materials are variously pretreated to dissolve bulk solids and to eliminate or inactivate plutonium complexing agents (e.g., oxalate ion), surface active materials (e.g., colloidal silica), and excessively corrosive ions (e.g., fluoride ion). The treated materials are then subjected to extraction, scrubbing, and stripping operations that are intended primarily for the removal of chemical impurities, rather than the decontamination of fission products or the separation of uranium.

The solvent is a heavier-than-water mixture of 15 per cent tributyl phosphate in carbon tetrachloride. The salting strength of the feed is provided by aluminum nitrate, in addition to the calcium and magnesium nitrate salts that may be present from dissolved recovery materials. A low-acid-high-salt content feed is employed to obtain optimum distribution coefficients for mixtures of plutonium(IV) and (VI) valence states. No attempt is made to control the valence state of the plutonium in the feed. The stripping agent is a mixture of dilute nitric acid (which prevents the

TYPICAL REFLUX FLOWSHEET
FOR PLUTONIUM PURIFICATION




* ARBITRARY LIMIT FOR ACCUMULATION OF "UNSTRIPPABLE" Pu PRIOR TO PERIODIC SOLVENT TREATMENT

FIGURE 1

AEC-GE RICHLAND, WASH.

precipitation of plutonium polymer) and dilute sulfuric acid (which reduces the organic raffinate losses by a factor of 2 to 3). A short scrub section (approximately one theoretical stage) is employed between the extraction column feed point and the stripping column product-removal point. The scrubbing agent is product solution which is refluxed to produce the concentration effects shown in Figure 2.

## III. SEMI-WORKS PERFORMANCE

### A. Process

The reflux flowsheet was successfully employed for feeds varying from 0.01 to 10 grams plutonium per liter. Product concentrations of up to 110 g/l were readily attainable, despite marked changes in feed composition. Product purity in terms of ionic contaminants was excellent (even after stream-stripping and evaporating to 400 g/l plutonium, the product purity was 95-97 per cent). Good ruthenium decontamination (D. F. $\sim$ 100) was achieved with certain high-activity feeds. Zirconium-niobium decontamination was generally high (D. F. $\sim$ 60) when the off-standard feeds were first introduced into the system, but gradually decreased to a lower "equilibrium" level (D. F. 5-10) as activity accumulated in the refluxing product inventory.

The final waste losses from both aqueous and organic raffinate streams were 0.6 per cent of the feed. Attempts to reduce the losses were unsuccessful, due to a number of uncontrolled factors associated with plutonium valence distribution throughout the system and solvent degradation effects. Varying amounts of both plutonium(III) (0 to 51 per cent) and plutonium(VI) (0 to 67 per cent) were observed in the solvent extraction system (despite feed adjustments with ferrous ion and nitrite ion). The presence of the less desirable valence states presumably resulted from disproportionation of plutonium(IV) under conditions of high plutonium concentration and low acidity. Waste loss control difficulties, however, were not attributable to this factor alone, since large quantities of plutonium(III) were readily

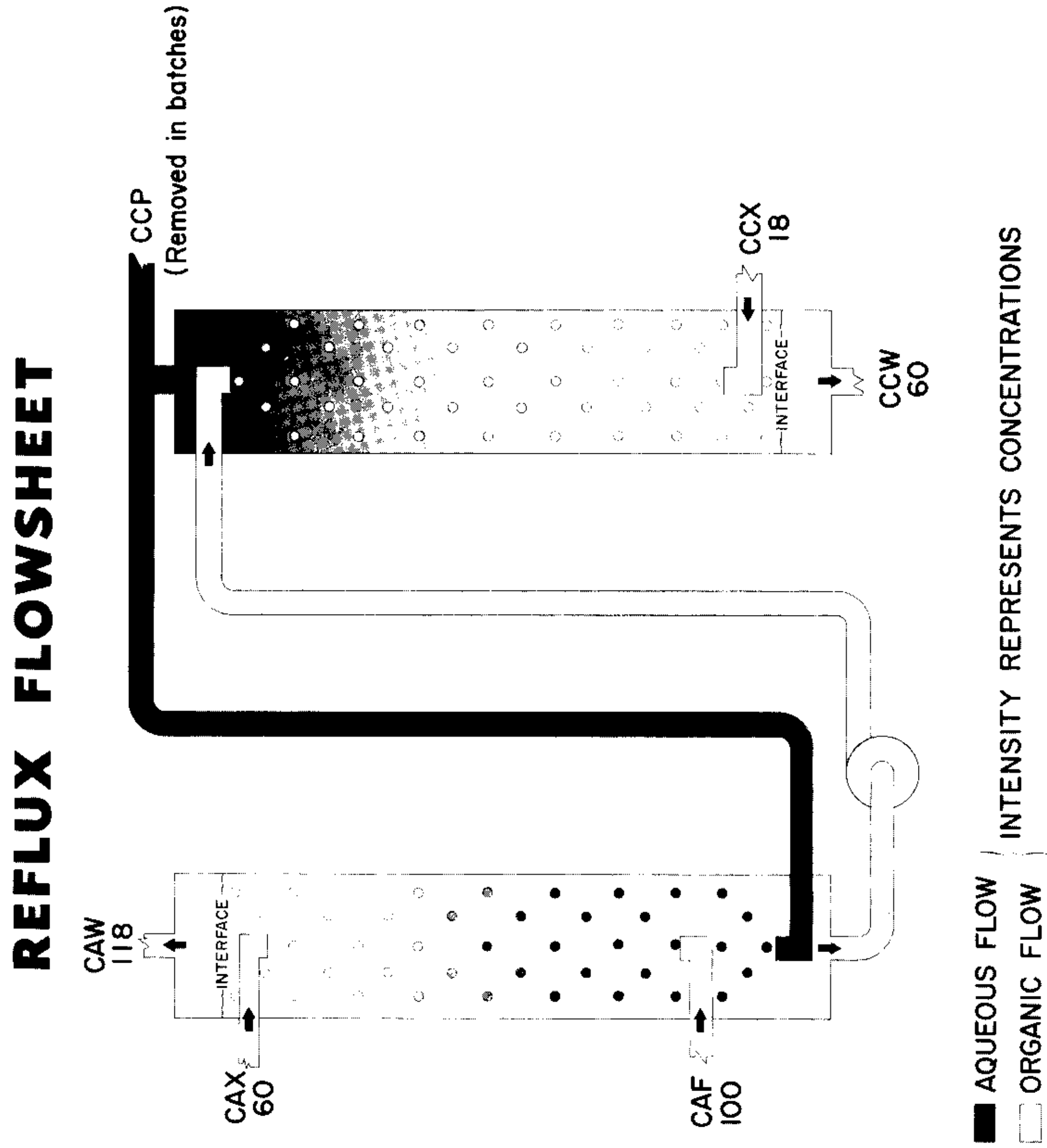

REFLUX FLOWSHEET
CCP
(Removed in batches)
CCX
18
CCW
60
INTERFACE
CAW
118
INTERFACE
CAX
60
CAF
100
AQUEOUS FLOW
ORGANIC FLOW
INTENSITY REPRESENTS CONCENTRATIONS

FIGURE 2

converted to plutonium(IV) under the acid and salt conditions in the extraction column. The rate of solvent degradation varied considerably and not in direct proportion to the plutonium content of the system. The effect of the solvent degradation was aggravated by the fact that the organic raffinate from the stripping column was recycled directly as the extractant feed to the extraction column, so that solvent degradation products accumulated within the system for periodic removal, rather than continuous removal as practiced in most solvent extraction plants. Furthermore, the "unstrippable" plutonium recycled in the extractant apparently has a low enough distribution coefficient (15-67) to affect extraction column performance. The relatively large amounts of "unstrippable" plutonium (approximately 0.9 per cent of the feed) accumulated in the solvent necessitated separation of the plutonium from the complexing solvent degradation products in the periodic solvent treatment step and recycle of the plutonium to the feed.

Although a complete understanding of all the mechanisms involved in a reflux system was not achieved, the process performance of the reflux flowsheet proved it acceptable for application to recovery operations and potentially capable of extension to mainline production operations.

B. Operational

Physical operation of the semi-works flowsheet was distinguished by the general stability of the system under widely varying feed conditions. Three adjuvants to reflux operation were important in controlling the process and maintaining operating stability: 1) a gamma absorptometer in the product stream, 2) glass columns, and 3) pulse perforated-plate columns and heavier-than-water solvent. A continuous knowledge of the product concentration, as provided by the gamma absorptometer, facilitated start-up operations, indicated the size (and abnormal shifts) of the plutonium operating inventory, and permitted control of the batch removal of product. The glass columns permitted early detection of column upsets due to flooding or emulsions, unfavorable pulse conditions, and increases in waste losses that resulted from shifts in the plutonium operating inventory (an in-line instrument serving as a qualitative plutonium waste monitor would be an effective substitute for the visibility of glass columns). The semi-works pulse columns (packed with nozzle plates spaced 4 inches apart, having 11.5 per cent free area, and perforated with 1/8-inch diameter holes and 0.04-inch nozzle protrusions) and the heavier-than-water solvent provided a sufficiently stable system during a column shutdown that the system could be operating essentially as a batch process; viz. the two phases in the columns did not separate (except on individual plates) during shutdowns of up to four days, so that intermittent start-up and shutdowns presented few difficulties. Moreover, stable throughput rates of up to 1100 gal/hr/ft$^2$ were readily attainable, while column upsets were generally characterized by total flooding, rather than emulsion formation on local-cyclic flooding. The extractant served as the continuous phase in both the extraction (organic) and stripping columns (aqueous), so that interfacial cruds and entrainment did not interfere with product quality.

## IV. ADVANTAGES OF REFLUX OPERATION

Product refluxing, in conjunction with a plutonium product monitor and a qualitative waste monitor, provides marked advantages to a plutonium solvent extraction system.

### A. Process

High plutonium concentrations are attainable with a reflux flowsheet, at least 110 g/l (the actual limit has not been determined). The product solutions are relatively low in acid concentration, which is a condition for plutonium polymer formation, but there has been no evidence of polymer precipitation at the higher plutonium concentrations. The low acidity of the product solutions presents an advantage, since adjustment to the particular acidity required for subsequent process steps is facilitated. Refluxing to such high concentrations eliminates the need for further concentration of the plutonium either by evaporation or ion exchange prior to subsequent processing. The high plutonium concentrations in the scrub section would also benefit fission product decontamination if secondary scrubbing would prevent build-up of activity in the refluxing inventory.

B. Operational

The actual operation of a solvent extraction system is rendered considerably more flexible by the use of a reflux flowsheet. A constant product concentration can be maintained despite wide variations in the plutonium content of the feed. There is a greater latitude in operating control techniques, such as rapid achievement of "equilibrium" after start-up by introducing the plutonium operating inventory through the reflux-scrub stream (although in the semi-works system, as mentioned above, it was not necessary to empty the columns for a shutdown). The product can be removed from the system in controlled batch quantities, thus easing the transition from continuous to batch operation and reducing product storage requirements.

## V. DISADVANTAGES OF REFLUX OPERATION

Product refluxing does present some disadvantages, most of which arise from the large concentrations of plutonium present in the system.

A. Design

The use of a reflux flowsheet to achieve high plutonium concentrations involves maintaining a rather large plutonium operating inventory, the size of which is dependent upon the product concentration, the dimensions of the equipment, and the efficiency of the columns (i.e., low "HTU" values contain the bulk of the inventory in shorter sections of the extraction, scrub, and stripping columns). The semi-works operating inventory was probably greater than the inventory that would have been required for a continuous evaporator or for an ion exchange system, but it was not excessive.

The reflux flowsheet necessitates either a greater extraction efficiency or a greater extraction column height than a non-reflux flowsheet, since the column contains plutonium at greater concentrations than the feed, and since there is a column operating inventory which tends to shift somewhat with flow changes, column upsets, etc. (backcycling of the aqueous raffinate to the preceding decontamination cycle has therefore been suggested for application of the reflux technique to the final plutonium cycle of a Purex-type system).

The large quantities of plutonium contained in a high product concentration solvent extraction system require careful vessel design and a fail-safe interlock system to prevent critical mass conditions. The need for a criticality control interlock system complicated the design of the semi-works installation considerably, but had little effect upon operating flexibility.

B. Process

The problem of plutonium fixation due to solvent degradation by alpha particle bombardment is enhanced by the presence of highly concentrated plutonium solutions. Although the "unstrippable" plutonium content of the organic raffinate is reduced considerably by the addition of sulfuric acid to the stripping agent, complete control has not as yet been achieved. It is therefore necessary to separate the "unstrippable" plutonium from the complexing degradation products in the solvent treatment operations and recycle the plutonium solution to the feed stream. In addition, the control of plutonium valence throughout the system is complicated by disproportionation effects to the point where methods for assuring optimum valence distribution are not yet available. These problems, however, are not severe enough to prevent the application of the reflux flowsheet to at least recovery operations.

## IV. SUMMARY AND CONCLUSIONS

The operability of product refluxing in a plutonium solvent extraction system has been demonstrated on a semi-works scale. Although the mechanisms involved are not completely understood, operating experience has shown that the refluxing technique presents definite advantages in terms of over-all processing flexibility and the reduction in the number of process steps required to attain plutonium concentrations of up to 100 grams per liter. The high plutonium concentrations present in a reflux system, however, result in certain equipment design problems and also accelerate solvent degradation with its associated problem of "unstrippable" plutonium. Despite these disadvantages, product refluxing may be considered as an efficient and practical technique for providing concentrated plutonium solutions.