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REMOTELY-OPERATED TRANS-PLUTONIUM

CHEMICAL PROCESS CELLS

M. S. Coops, C. L. Hanson, R. W. Hawk, and V. E. Scribner

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REMOTELY-OPERATED TRANS-PLUTONIUM
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ABSTRACT

Twenty-eight radioactive pile slugs containing gram quantities of plutonium, americium, and curium have been successfully processed in a heavily-shielded, remotely-operated chemical facility utilizing push button flow process control techniques. The chemical process, which is designed for trans-plutonium element processing, utilizes filtration, distillation, and ion-exchange techniques to separate the gamma active actinide elements from the gross quantities of fission products produced during irradiation. The equipment operates at kilocurie alpha activity levels in the presence of corrosive chemical reagents, is exposed to high beta and gamma radiation levels, and yet allows total confinement of the hazardous contaminants to the primary enclosures. Ventilation equipment includes refrigerated caustic scrubbers and multiple high-efficiency filters.

INTRODUCTION

The Livermore laboratory has been involved in the chemical processing and purification of large quantities of trans-plutonium elements for many years.⁽¹⁾ The first of several large scale processing operations took place in the fall of 1953,

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

and involved the isolation of gram quantities of Cm^{242} from fission products produced during reactor bombardment of several grams of Am^{241} . This operation, and subsequent similar runs, led to the evolution of the present techniques discussed in this paper. The facility described herein was extensively rebuilt in 1960-61, but retains the existing shielding wall and manipulator system designed into the original facility; in practice, the manipulators are used for replacement of broken or radiation damaged equipment and are not normally used during actual processing operations.

DESCRIPTION

General: Fig. 1 indicates the outline of the shielding and includes the ventilation schematic of the overall installation. Fig. 2 is a sectional view cutting through the shielding, process enclosure, incoming transfer system, solid waste disposal facility, and also indicates the relative position of the valving and some of the process glassware. Fig. 3 is a photograph of the actual cell taken from the operating face, and shows the position of the control consoles relative to the viewing windows, manipulators, and control valves. The basic cell construction is of interlocking six inch thick lead blocks on the front face; the side walls, ceiling and rear walls are constructed of standard concrete. The six inch front wall allows the use of through-the-wall manipulators. Castle manipulators, equipped with air tight booting, are the sole means of mechanical manipulation in this cell; the choice of this type of manipulator was dictated by the requirement of completely air tight enclosures. The enclosures or "cell boxes" are fabricated from mild steel and are corrosion-proofed with baked phenolic resins. Viewing windows are of 5009 series plexiglas as are the translucent panels in the rear of the enclosure. Lighting is by means of high intensity mercury lamps located above and forward of the enclosure and are directed into the enclosure by means of polished aluminum reflectors. External lighting was chosen to allow easy replacement of bulbs and to keep the internal box

temperature as low as possible; this arrangement has proven satisfactory, and has eliminated the requirement for cooling the box atmosphere. All gasketing has been kept above the floor level of the box to minimize the effect of chemical reagents on the organic seals. Polyvinyl bagging connects the box to the input chute and air lock as well as to the solid waste coffin located underneath the enclosure. Metal bag expanders, also resin coated, are used to protect the vinyl bagging from alpha and beta radiation and also serve to keep the plastic booting free from mechanical damage.

The ventilation system provides about an air change per minute of fresh, filtered air to each enclosure. The exhaust air is passed into special high efficiency refrigerated scrubbers followed by banks of high efficiency filters in series, electronic monitors sensitive to α , β^- and γ radiations, and then exhausted to a stack. The enclosures are maintained at about 0.2 inches water column negative to the room atmosphere by automatic control devices. The off-gas treatment is sufficient to remove virtually all radioactivity with the exception of the (short lived) noble gases. Provision is made to change the scrubbing solutions remotely when the activity level warrants such treatment. All electrical power for the cell system is supplied by power circuits backed up by an auxiliary generator.

The Chemical Process. An introduction to the chemical flow sheet used in transplutonium chemical processing work is necessary to allow one to appreciate fully the fundamental problems incurred in these operations. Figs. 4 and 5 show the general chemical scheme used at this laboratory to isolate plutonium, americium, curium and heavier actinide elements from reactor irradiated capsules. It should be noted that relatively concentrated solutions of hydrochloric and nitric acids appear throughout the flow sheet. No alternatives to these reagents were available at the time this process was developed. Very corrosion resistant materials are therefore required for construction of all equipment. In order to allow a small group of chemists to operate

this facility the equipment was kept at a minimum size. Volumes are limited to the 5 liter or less category with the inherent result that the radiation levels encountered in the process solutions is quite high. Alpha concentrations per liter of solution quite normally exceed 8×10^{14} dis/min, and have occasionally risen above 7×10^{13} dis/min per milliliter. The latter value corresponds to 35,000 curies per liter or 1200 thermal watts per liter of process solution. It is therefore understandable that radiolysis of the process solutions can be a major design problem; foaming and boiling of the process liquids have strongly influenced the design of process equipment.

However, we have not experienced any major deviations from expected chemical reactions; the prototype chemistry performed on tracer scale is directly applicable to that performed inside the cell. Certain minor deviations from tracer scale have been made to allow for the reactions due to the radiolysis products of the water solvent.

The Flow Process System. From past experience, it has been found that in order to maintain adequate process control of very high level solutions, it is necessary to use closed process equipment. Open top equipment allows the spray formed from the constantly forming gaseous decomposition products of water to spread massive contamination throughout the box and ventilation ducting leading to the scrubbers. In addition to contamination, the combination of the intense alpha sources and the corrosive nature of the reagents leads to very severe corrosion problems, even of the most resistant alloys. General corrosion and product loss has been reduced to acceptable levels by the adaption of a continuous flow system to what is basically a batch process. The basic flexibility of the batch process is maintained by use of a fully remote control process scheme to route the process solutions from one stage of the process to the next. This is accomplished by the scheme illustrated in Fig. 6. Primary solution containment is provided by closed containers, and the motive force for liquid transfer is accomplished by application of either vacuum or pressure to these units by remotely operated valves.

Fig. 7 represents the flow schematic used to control the dissolution and filtration processes carried out in the first stage of processing. Fig. 8 illustrates a similar unit that is used in other stages of the remote processing scheme. The latter flow system controls the operation of ion-exchange columns, stills, and filtration processes. By use of the block valves present in the upper and lower manifolds, one can perform three different types of operations in the same enclosure simultaneously. This feature compensates for the slightly extended time interval required to perform a chemical operation by this method.

The flow schematic is laid out in the form of a map on consoles convenient to the operator with illuminated push button controls at the indicated points. The chemist selects the path required to perform the desired chemical step by pressing the appropriate buttons on the console map, and then controls the rate of the process by adjusting the appropriate vacuum or pressure regulator to govern the pressure applied to the glass vessels inside the enclosure.

A chemist can master the technique of flow control in a few hours of instruction and practice. An individual can operate more than one console if the process step consumes a considerable period of time to perform (e.g. distillation, filtration).

Process Components and Materials. The major items in the remote process system are the reservoir containers ("Pots"), the oil-heated stills, the condensers, receivers, and feed flasks, the jacketed ion-exchange columns and the jacketed filters. All of these specially designed components are made of pyrex glass. The glassware is fitted with precision bore tubing connections so that it can be easily joined to the polyethylene tubing used for the manifolding between the glass components and the valves providing flow control.

Polyethylene tubing and valves are employed exclusively throughout the flow system. Polyethylene (or more recently polypropylene) fittings are used to join

the components to the manifold and provide simple disconnects to the glass components. Fig. 9 is a photograph taken through the lead glass viewing window of the first enclosure, and shows the general method of connecting the units together with polyethylene tubing and fittings. The heated-jacket glass container used for dissolving the aluminum slugs is also visible. The filter system shown in this photograph was fabricated from Kel-F and platinum frit. The strong sodium hydroxide solutions used for slug dissolution and the hydrofluoric acid used during the precipitate leaching process render glass frit to be an unsuitable construction material for the initial filtration step. Recent units have been fabricated entirely of platinum with a glass upper section for visibility. These have survived well under extreme alpha and beta bombardment and are also resistant to the thermal heat inherently present in very active alpha sources. Fig. 10 is a similar photograph taken through the viewing window of the third enclosure. The visible equipment includes the jacketed ion exchange column, a jacketed glass filter and an oil-heated glass still. The pumps are used to circulate hot and cold water to the various process components. The energy available from gram quantities of Cm^{242} would boil solutions to dryness if they are not chilled to low temperatures during storage periods. Many of the ion-exchange operations, and also the filtrations, must be carried out at elevated temperatures (85°C) to obtain maximum separation characteristics. Water is used as the heat exchanging fluid as it is the least complex liquid to handle if it is inadvertently mixed with the process materials due to equipment failure. The glass still is heated with Kel-F oil and is operated at temperatures up to 350°C . The advantages of the oil are twofold; it does not impair visibility during distillation (an important detail when reducing the volume of solutions to a specific value) and it does not char residues that appear on the inner surface of the flasks as the volume is reduced. The latter point is revelant as plutonium compounds are sparingly soluble

even in the strongest reagents after being heated above 400° C. Electrically heated units tend to raise the temperature of the vessel wall above the liquid level beyond that point and result in plutonium residues that redissolve with difficulty.

The circulation pumps are pneumatically driven and have been found to be more reliable than electrically powered units. In addition, they do not add heat to the enclosure and also allow adjustable delivery pressure or volume.

The chilled water heat exchangers are built into the metal enclosure but are insulated from it. These are operated from Freon compressors outside the main building that have been set so that the gas pressure in the refrigerant line is always positive with respect to the enclosure atmosphere. In this way, any possible refrigerant leaks are into the enclosure, and the possibility of contamination being drawn into the Freon system is minimized. The exchanger unit consists of two independent copper coils cast in a block of aluminum; there is no direct water contact with the Freon system. This feature is important as eventually the liquid exchanger inside the enclosure becomes contaminated from the box atmosphere and manipulator fingers.

High power-density resistance elements are used to heat the water for the jacketed filters and ion-exchange columns. Connections between components are made by means of glass to metal ball joints wherever moderate pressures and elevated temperatures are encountered simultaneously. The ion-exchange columns are of a design to prevent mixing of the bed while they are in operation. Fig. 11 shows a sectional view taken through the column assembly and its buffer piston assembly. The resin bed is restrained by means of two glass frits comprising the upper and lower limits of the bed. The upper frit, which is contained in the sliding glass plunger assembly, is free to move inside the barrel of the main jacket assembly. In this

way it is possible to compensate for the expansion and contraction of the resin bed which occurs with a change of reagent concentration passing through the resin.

The silicone rubber seal that maintains the liquid tightness of the expandable assembly is constructed to minimize the force required to extend or contract the upper plunger. The buffer piston provides a piston area equal to that of the plunger and thereby assures that the force required to move the plunger either way is only that which is required to overcome friction due to the silicone sealing ring. Travel of the plunger in either direction is accomplished by raising or lowering the pressure applied to the buffer piston and is controlled by the operator from the control console.

Radiolysis of the solutions by the intense alpha activity forms gaseous products that displace the solution passing through the bed. Therefore, the columns are normally run at a positive pressure on the feed side to prevent gas pockets from developing in the bed. These gases are displaced by the eluant and pass on through the resin and are released to the reservoir collecting the column eluate. The plunger of this column assembly is constructed with 3 tubing connections to the cavity above the restraining frit. One of these is used to apply the pressure or vacuum required for operation; the other tubes extend down to within a 1/16 of an inch of the frit surface.

To load the resin bed, the solution containing the material is fed through one of these tubes into the reservoir above the frit and passed through the bed. A small rinse is used to clear the line of remaining feed solution and this is also passed through the resin bed; then both of the feed tubes are thoroughly rinsed with the eluting solution to remove any feed material not already adsorbed on the resin. This rinse solution is retained and combined with the feed for the next successive batch to be run. In this way, tailing of the loading species is eliminated and the adsorbed ions are kept on a very sharp band of resin. It is very essential not to have tailing of the loading material when the species to be retained is the slowest moving ion

loaded on the column, as is the case in the lithium chloride separation of actinide elements from lanthanide (rare earth) elements.⁽²⁾ The illustration in the left side of Fig. 11 shows the relative positions of two different species being eluted from a resin bed as a function of volume. From this illustration it is readily seen that the separation obtainable from such an elution depends heavily on two major points: (1) the band must be loaded as perpendicular as possible to the vertical axis of the resin bed and (2) the band must be as sharply defined as is practicable under the prevailing conditions. Utilization of these special ion-exchange column loading techniques has permitted the achievement of separation factors normally only obtainable on tracer-level elutions during full scale processing operations. As such, it is reasonable to expect decontamination factors of several thousand on remotely operated units of this type.

Analytical Process Control. As indicated on Figs. 7 and 8, an assay device is installed in the manifold common to all the process equipment. This is a single bore plug valve rotating through a 90° angle that allows an accurately known volume of liquid to be withdrawn from the manifold and passed outside the cell to a gloved assay enclosure. The plug of the valve is remotely driven by pneumatic air cylinders. The volume of the bore, which is filled by passing solution through the lower manifold, is rotated to align with a reservoir of rinse solution; the resulting solution is flushed out to an analytical enclosure where further operations are performed manually. Large dilution factors are required to lower the concentrations of the cell solutions to an activity level suitable for radioanalysis; part of this dilution is provided by the method of process sampling. A further dilution by standard volumetric techniques is required before samples may be radiometrically analyzed. Bubbles are excluded from the solution by applying a partial vacuum to the solution to be assayed immediately prior to sampling; the solution is then forced through the valve bore by the application of moderate pressure.

Analytical results normally are reproducible to plus or minus 5 percent on routine process assays. This is satisfactory for the operation of the process.

Equipment Replacement and Maintenance. All functional equipment in the process enclosures has been designed and constructed so that it may be completely replaced by the use of the Castle manipulators. Although replacement of large items can prove to be a tedious chore under certain conditions, normal cell operation requires little mechanical manipulation during an actual process cycle. Maintenance work is performed between operations and has not seriously affected normal processing schedules. Actually, most maintenance work has been of a minor nature and has consisted primarily of the replacement of cracked or leaky tubing fittings. Glassware replacement (required because of the browning of pyrex glass components in the severe radiation environment) has been performed on a routine basis between processing operations.

The replacement of valves has been far lower than anticipated for such operations. The valves are constructed so that replacement is quite simple and rapid; they are easily disconnected from the manifold and unscrew directly from the actuator base by use of the manipulators. The main cause of the few valve failures to date has been due to the transfer of solutions from the still to other components in the system before they have cooled below 90°C . The excessive heat allows the seat to deform, with the result that the valves fail to seat as tightly as they normally would be expected to do.

The major difficulty with the present system has been the tendency of the polyethylene nuts on the manifold fittings to crack and allow leakage from or into the system. This has been greatly alleviated by gradual replacement of polyethylene fittings with polypropylene fittings which have recently become available.

Some difficulty has been experienced with the plugging of frits during column operations. This has been traced to the slow precipitation of zirconium oxychloride from near-neutral solutions. The problem has been solved by the addition of small

amounts of fluoride salts to keep the fission product zirconium in solution. Tar formations appear during leaching of the initial precipitate and seem to be polymerized compounds of ruthenium formed during irradiation.. Although these formations tend to slow down the operation somewhat they have not interfered with the leaching process, and are discarded to waste after leaching. The polyethylene tubing appears to be in satisfactory condition after 2 years intermittent service. All lines and valves are rinsed out first with weak acid and then with water after a process cycle is completed. Apparently this care has extended the life of the equipment substantially.

CONCLUSIONS

The process system described has performed up to and beyond expectations. The ability to replace individual components has been a most valuable asset, and has allowed minor process modifications to be performed during operations. Glass components have been satisfactory for the containment of very concentrated alpha active solutions for extended periods of time provided they are cooled and the liquid level maintained at original levels.

Polyethylene seems to be a satisfactory material for process components so long as it is rinsed free of major concentrations of activity during periods of inactivity. The plastic components have survived the corrosive conditions very well. It has been noted that the tubing sections give warning prior to failure from radiation effects by becoming chalky white instead of translucent to visual observation.

Although the polypropylene fittings have just come into use, it appears that this material will alleviate in large degree the problem of cracked or split ferrules and fittings.

The plexiglas used for construction of hardware throughout the enclosures has changed to an amber or red color in some locations but does not show any signs of mechanical failure.

The use of organic polymers for the highly corrosive process has been, in general, very satisfactory. One has to exercise care in the choice of components and materials and to anticipate the effects of environment on each item chosen. The experience gained in this continuing operation has demonstrated that if maintained within their limitations, plastic components can be very successfully used for the handling of very alpha active solutions.

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(2) E. K. Hulet, R. H. Gutmacher, and M. S. Coops, "Group Separation of the Actinides from the Lanthanides by Anion Exchange," Journal of Inorganic and Nuclear Chemistry 17, 350 (1961).

- Figure 1. Cell outline including ventilation schematic for primary alpha enclosures.
- Figure 2. Sectional view taken through shielding and alpha enclosure indicating relative position of components.
- Figure 3. Photograph of operating face of cell showing relative positions of consoles, manipulators, viewing windows and control valving.
- Figure 4. Chemical flow sheet - part one.
- Figure 5. Chemical flow sheet - part two.
- Figure 6. Diagram indicating method of process control and location of components.
- Figure 7. Process control schematic - Box I.
- Figure 8. Process control schematic - Box III.
- Figure 9. Interior View of Box I.
- Figure 10. Interior view of Box III.
- Figure 11. Cross-sectional view of ion-exchange column including elution sequence diagram.
- Figure 12. Rear view of alpha enclosures taken in place inside gamma shield.
- Figure 13. Partial view of ventilation manifolding showing filtration and activity monitoring equipment.

FIGURE 1

Figure 2

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FIGURE 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

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Figure 9

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Figure 10

Figure 11

Figure 12

Figure 13