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DR-000246
0072-8

I-15169

UCID--20016

DE84 012827

Evaluation of Nonaqueous Processes for Nuclear Materials

Task Report to the Long-Range
Planning Committee

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December 1983

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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I. EXECUTIVE SUMMARY

A working group was assigned the task of evaluating the status of nonaqueous processes for nuclear materials and the prospects for successful deployment of these technologies in the future. In the initial evaluation, we narrowed the study to the pyrochemical/pyrometallurgical processes closely related to the processes used for purification of plutonium and its conversion to metal. We reviewed the status of the chemistry and process hardware and evaluated the development needs in both chemistry and process equipment technology. Finally, we established the requirements for successful deployment of this technology.

We evaluated the status of the technology along three lines: (1) we first examined the current applications for completeness, (2) we then attempted to construct closed-cycle flow sheets for several proposed applications, (3) and finally we reviewed the status of technical development and future development needs for general applications. Using these three evaluations, we constructed three different perspectives that together present a clear picture of how complete the technical development of these processes is.

1. Current applications. The electrorefining and metal reduction steps work well,¹ although not 100% reliably. The metal rings pictured as the expected product are sometimes not produced, with the result that the plutonium is either in the starting impure anode "heel" or dispersed in the salt phase. In either case, there is a significant loss of time and process efficiency. On a systematic basis, however, these processes work satisfactorily most of the time. Salt extraction of americium from stockpile return plutonium generates purified plutonium as intended, but also produces a salt waste that contains significant quantities of plutonium.² Other currently unprocessable wastes are also produced at times.
2. Flow sheets. We examined three flow sheets to assess the completeness of their technical work. These were (a) the metal processing lines for special isotope separation (SIS) support at LLNL and for the Rocky Flats metal rework line, (b) a proposed process for Zero Power Plutonium Reactor (ZPPR) fuel return, and

(c) the rework of Pu-containing salts accumulated at the Rocky Flats Plant (RFP). While all flow sheets are extremely tentative, data are available for the major steps of the mainline processes. Few data are available for the side streams required to close the process loops, but reasonable assumptions have created possible flow sheets. Limited information is used to predict the behavior of trace components in recycled streams. Major additional components that might be introduced in salt or ash treatment are not considered to present serious problems. Nonaqueous recycle loops are at present being developed for salt and electrorefining heels to avoid buildup of massive quantities of these materials. Recycle is possible by aqueous means, but that choice would reduce the apparent advantages of nonaqueous processes resulting from low waste generation and reduced process steps.

3. Development needs. A summary of the development needs for the RFP applications is given below;³ a more detailed review is provided in Appendix A to this report. In general, development needs are indicated by the absence of data that are required to construct flow sheets for proposed process options. These development needs are extensions of the existing chemistry bases and include the following:
 - a. Determination of additional distribution coefficients
 - b. Extension of separation/reaction studies to additional binary and ternary salt systems
 - c. Determination of reaction rate data for process steps
 - d. Development of recycle and/or cleanup processes for byproducts and waste streams
 - e. Determination of the behavior of minor components on extensive recycle
 - f. Determination of the purity requirements for starting materials
 - g. Improvement of most hardware operations.

Eleven general conclusions are supported by the detailed study.

1. The chemistry of these processes is simple. Much of the needed technical development effort would be expended on basic chemistry.

2. The methodology is effective where it is applied with glovebox operations. For higher throughputs and working with highly radioactive materials, considerable hardware and operations development will be required.
3. Most mainline steps shown in the flow sheets have been demonstrated at laboratory scale or larger.
4. Additional chemical studies are required on solubilities, extraction into mixed molten salts, phase diagrams in complex systems, behavior of minor components (impurities), viscosities, densities, and kinetics in all process steps.
5. Process steps in current use are workable, but have not been optimized. The work needed for some improvements has been identified.
6. Comparison of the process waste generated by aqueous vs nonaqueous processes is exaggerated by looking only at the intermediate form. Most of the water in the aqueous streams will eventually be released as water vapor. All final materials from nonaqueous streams must be disposed of as transuranic or higher active wastes.
7. Line-generated wastes have not been completely defined for the proposed processes.
8. None of the processes in current usage is completely closed. Aqueous processes will be required for the indefinite future to support the pyro mainline systems to accommodate such problems as line-generated wastes and accident or spill cleanup wastes.
9. Applications of pyro technology to irradiated nuclear materials have not been demonstrated and will not be developed unless a significant technical requirement forces that development.
10. Process hardware (technology) development is required for both cold and highly radioactive process applications. This will include mixers for materials of greatly different densities, phase separation techniques, pumps, controls, valves, and sensors for temperature, density, composition, etc.
11. Comparison of the pyro flow sheets with purex flow sheets for current-generation LWR fuels shows no net advantage for pyro technology.

II. INTRODUCTION

Nonaqueous processes have been used to produce metals and ceramic materials from the earliest recorded history. To the present, these processes have dominated the ore processing, glass, and ceramics industries.

It has long been recognized that nonaqueous processes have four significant potential advantages over aqueous processing for nuclear materials.

1. Radiation damage would be greatly reduced or nonexistent.
Nonaqueous processes can provide for processing of highly irradiated and/or short cooled fuel and special targets.
2. Considerably fewer steps are generally involved in the processes so that smaller spaces and reduced operating costs should result.
3. Higher density streams should also lead to smaller facilities with potentially lower capital costs.
4. The absence of moderators allows larger masses of fissionable materials to be handled.

Our study group was chartered by the Nuclear Energy Subcommittee of the LRPC to evaluate the status and potential of nonaqueous technology for potential applications to nuclear materials processing. We have identified two areas that have major importance for the defense and nuclear energy communities: (1) near-term problems in weapons materials production and (2) potential processes for recovery of resource materials from spent nuclear reactor fuels that include Naval propulsion, test, and demonstration reactors and nuclear electric power plant fuels. A wide spectrum of technologies ranging from molten salts and molten metals to halide volatilization processes has been studied. Initial evaluations of the available technologies indicate that only those nonaqueous technologies collected under the general area of pyrochemical and pyrometallurgical processes hold significant potential for handling the problems of greatest near-term interest. Of these, the most successful applications have been processes used in the purification, refining, and conversion of plutonium oxides to weapons-grade plutonium metal. Because of the short time available for our study, we focused on these pyrochemistry steps as the basis for process flow sheets.

The use of nonaqueous processes for nuclear material dates to the earliest production of uranium or plutonium metal by reduction of the fluorides, oxides, or fused salts. This conversion cannot be done in aqueous

solution. The capabilities in nonaqueous processes for purification and conversion of plutonium from oxides or salts to final weapons-grade metal have gradually been expanded. The fundamental chemistry is as old as the bronze age; only the element being cast (Pu) is new.

Pyroprocesses have been proposed for all steps in the conversion of plutonium oxide and scrap to final weapons-grade plutonium metal. Several of these steps: calcination, calcium metal reduction, molten salt extraction, and electrorefining, have also been applied routinely at the Los Alamos National Laboratory.¹ A brief description of these processes will be given in Chapter III.

The tools used in the glovebox operations are quite basic, nearly all standard hardware store or chemistry laboratory equipment: hammers, wrenches, screwdrivers, spatulas, etc. The lack of any major effort to improve the technology is apparently justified by the fact that the processes work for most purposes and show clear advantages over the aqueous steps that they have displaced. At LANL, all pyro operations have been adapted to the same furnace design. This consistency may be helpful to operating personnel as they move from one operation to another. However, this uniformity may stifle attempts to improve equipment and operations.

We have examined the adequacy of the chemistry basis for the applications of pyrotechnology to all proposed processes. As an aid to this evaluation, we looked both at the technology as it is now applied and at the completeness of flow sheets for each application.

III. SUMMARY OF BASIC PROCESS STEPS

Three near-term applications of pyrochemical technology to the processing of nuclear materials are described in the flow sheets accompanying this report. These flow sheets have been constructed from six basic process steps:

1. Direct oxide reduction
2. Molten salt equilibration
3. Metal-metal equilibration
4. Metal distillation
5. Electrorefining
6. Pyroredox refining.

These six process steps can be combined into a large number of potential process flow sheets, all of which share the advantages of pyrochemistry over conventional aqueous systems: very compact equipment, resistance to radiation damage, high density, and high concentration of in-process materials and products. These steps do not represent the total array of pyrochemical techniques available to the process designer. The very powerful "salt transport" process is not required by these applications, and its description is omitted, although it allows very elegant nuclear fuel reprocessing schemes to be designed. (Pyroredox is actually a special case of salt transport processes in general.) Such operations are deferred to the realm of long-term applications.

Direct Oxide Reduction

The direct oxide reduction step employs the thermite reaction between PuO_2 (or UO_2) and Ca metal to produce Pu (or U). The reaction is carried out at 835°C in the presence of a CaCl_2 flux that dissolves the CaO product; excess Ca is added to drive the reaction to completion. Vigorous stirring is required to maintain intimate contact between the very dense actinide phases and the Ca and flux. This same density difference simplifies phase disengagement after the reaction is complete, when the actinides pass to the next step and the salt moves to processing for recycle.

Molten Salt Extraction

Separations based on the transport of one or more components of a single-phase mixture into a second, immiscible phase are common to many

chemical processes. The transfer may or may not involve chemical reaction, but in all cases, an equilibrium distribution is approached that is based on a minimum system free energy.

In the molten salt extraction step, the first phase is molten Pu with ^{241}Am contaminant, and the second phase is a NaCl-CaCl_2 salt with a few percent MgCl_2 added. Am is oxidized to AmCl_3 by the MgCl_2 , and partitions to the salt phase; two sequential extractions remove about 90% of the Am. Small amounts of PuCl_3 are also extracted, requiring a salt cleanup process to recover Pu from the salt phase. Mg metal from the reduction dissolves in the Pu and is removed by evaporation.

Metal-Metal Extraction

Separations can also be based on the partition of dissolved species between two immiscible alloys. Distributions between the phases are governed by the net free energy of the reactants involved; however, because solvation reactions are generally less energetic, the partition achieved per contact stage is less dramatic than in oxidation-reduction separations.

Metal Distillation

Metal distillation or vacuum evaporation is an effective pyrochemical process step because of the very large differences in vapor pressure available between many of the common metal solvents (zinc, calcium, magnesium) and actinide series elements at temperatures below about 800°C . At temperatures around 1200°C , separations such as Pu-Am become possible using fractional distillation techniques. While the vapor pressures of metals are well known, the activities of components of metallic solutions are often not available. Substantial work will be required if distillation is to be extended beyond simple binary systems.

Electrorefining

The electrorefining process step transports in-process metal through a salt phase under the influence of an electrical potential. The important feature in the process is the "buffering" of the salt phase with a substantial quantity of ions of the metal being purified. The excess of these ions forces the retention of impurities as metals and prevents their transport to the cathode and appearance in the product.

When this technique is used for Pu purification, the NaCl-KCl salt phase is doped with PuCl_3 , forcing impurities more electropositive than Pu into the salt and leaving those less electropositive than Pu as metals retained in the anode.

Additional processing of both residual anodes ("heels") and the Pu-containing salt is necessary for a closed cycle. This processing is currently being practiced at LANL.

Pyroredox Refining

Pyroredox (and indeed, electrorefining) is a special case of the general class of pyrochemical operations termed "salt transport" processes. Pyroredox is considered an alternative to electrorefining as a final purification step in Pu recovery from scrap or material rework and is an appropriate technique for recycle of severely contaminated anode heels from electrorefining.

The pyroredox step for Pu occurs in two separate stages. The first is the oxidation of impure Pu with ZnCl_2 to form PuCl_3 and Zn metal. Impurities not oxidized by ZnCl_2 are left in the Zn metal stream and are concentrated by evaporation of the Zn. The PuCl_3 is taken up by the salt phase.

In the second step, the PuCl_3 is reduced with Ca metal, leaving additional impurities as chloride salts. Salt and metal phase separations are accomplished by density differences, which are, as in the other salt-metal operations, quite large.

The general class of salt transport process steps is too extensive to be covered here in any detail,* but all of the steps involve the selective oxidation of one or more components of a metal solution into a salt phase and subsequent reduction into a second alloy. These techniques find application in proposed commercial nuclear fuel cycles and are beyond the scope of the near-term uses of pyrochemistry considered next.

Near-Term Applications of Process Flow Sheets

We have selected three near-term applications of pyrochemical processing of nuclear materials as a part of this study. They may provide some larger scale experience in pyrochemistry and point to additional development needs

* A more extensive description is contained in Appendix A.

that have not become apparent in bench scale work. Aqueous processing of nuclear material currently enjoys an experience advantage of literally thousands of man-years over pyrochemistry. To become truly competitive as a processing alternative, pyrochemistry must develop a proven history in applications for which it has been selected because it has unique and very economically favorable advantages over conventional methods.

We selected three applications:

1. Processing of Pu scrap and parts requiring rework
2. Processing of ZPPR fuel
3. Processing of salt residues.

In the balance of this section, we will discuss how the basic steps are combined into process flow sheets for these applications, as well as the developments needed to implement each at pilot or larger scale.

Processing of Pu Scrap and Parts Requiring Rework

This application of pyrochemistry is in operation on a small scale at LANL and is being set up as a metal production line (MPL) for Triton parts at LLNL. Use of such processing at RFP would be attractive economically and should be seriously considered as a major pyrochemical demonstration.

In Fig. 1, which is drawn for Pu scrap fed as oxide, the feed stream is sized and calcined in air at 800°C to provide input to the direct oxide reduction (DOR) step. Because scrap Pu is quite pyrophoric, it is normally burned in air to the oxide for safety and convenience in handling.

The DOR step is conducted as a batch operation in current bench-scale applications, and the maximum charge of Pu is limited to about 4 kg by criticality considerations. A difficulty here is the fact that the batch is cooled and the phases separated mechanically as solids using hand tools, a slow procedure that also necessitates the breakage of the MgO crucible.

Development work is required to move the process to a fast-cycle batch type, with phase separations accomplished on molten materials in relatively long-lived containers.

Both tantalum and tungsten show promise as crucible materials, but they may require doping the $\text{CaCl}_2\text{-CaO}$ flux with CaF_2 to lower the melting temperature to reduce corrosion and product contamination. Techniques for controlling the phase separation are also required.

- Material
foundry scrap, site returns, etc.
- Process

FIG. 1. Metal production line.

Continuing research is necessary on the chemistry of the salt phase, particularly on the salt regeneration shown in the flow sheet that rechlorinates the CaO-CaCl_2 to CaCl_2 with CCl_4 or HCl and adsorbs the off gas in a NaOH scrubber. Some impurity buildup in the CaCl_2 recycle can be expected, and the entire area of salt regeneration and recycle will require attention if salt wastes are to be minimized. Although Ca recycle by electrorefining the CaCl_2 is not shown on the flow sheet, it could reduce the amount of salt waste by closing the reagent system around the DOR step.

The Pu from the DOR step moves forward to the molten salt extraction, where a $\text{CaCl}_2\text{-MgCl}_2\text{-NaCl}$ extractant removes Am that has grown into the Pu during storage. The extraction, as previously described, is quite effective for Am removal, but also removes some Pu from the main stream.

This step must be studied further to refine the distribution coefficients as functions of salt composition and to determine the behavior of insoluble impurities and oxy-chlorides, as well as possible double salts.

Salt recycle is also a development task for this step, because the salt product must be cleaned of Am and Pu and, as much as possible, regenerated for reuse. A second flow sheet, Fig. 2, shows the Pu recovery/salt cleanup operation for the metal production line.

The first step in this process is another DOR step using Ca to reduce Am, Pu, Mg, and some Na. The Na distills off during the reaction, while the Mg and any excess Ca are removed in a moderate-temperature distillation step at 800°C and the Pu and Am proceed to the third step, a metal distillation at 1200°C . This step is shown on Fig. 2 as two batch distillations in series, with bottoms (Pu) recycled to the feed of the molten salt extraction step in the main process flow sheet.

Development work will be required on a recycle step to return the salt, stripped of Am and Pu, to the extraction step of the main process. A chlorination step, such as that used in DOR salt cleanup, will be necessary, and Ca must be bled off to maintain the proper salt ratio.

The Pu product from the salt extraction is then cast into anodes for electrorefining. The electrorefining step produces a high-purity Pu ready for alloying and fabrication. Unfortunately, the electrorefining process also produces an anode residue or "heel" with an unacceptably high level of

FIG. 2. Salt regeneration.

impurities, largely Ga.* The heel represents 10-15% of the Pu feed to the electrorefining step.

The anode residues may be processed either by conventional aqueous means or pyrochemically. The pyroredox step described above has been proposed as a method of purification; this would allow return of essentially all of the Pu from the anode residues to the feed of the electrorefining step.

Large-scale application of pyroredox as an integral step in a process flow sheet will require additional development work. The current level of operation is a 2-kg batch, and although the basic chemistry of the purification (oxidation with ZnCl_2 followed by reduction with Ga) has been thoroughly demonstrated, problems routinely occur in the disengagement of the PuCl_3 phase from the Zn alloy. The problem is the formation of a third, "black salt" phase. In the laboratory, it is broken away from the salt in solid form and recycled. In production, it would be returned to rework, but in a semicontinuous production process it could cause blurring of the phase boundary with resulting contamination. Study of the salt/Zn/Pu system may provide a solution, as may clever equipment design that allows for recycle of an indeterminate phase.

In production operation, the amount of impurities carried in this "black salt" is small. Impurities in feed can be decreased by a factor of 10 as the process now stands and are adequate for meeting present Category I metal specifications. Solving the "black salt" problem would produce ER quality metal.

The final steps of pyroredox are Zn recovery by evaporation and cleanup of the CaCl_2 product. The CaCl_2 cleanup is similar to that required following the molten salt extraction of Am from Pu metal, and the same comments apply.

Processing of ZPPR Fuel

The second flow sheet, Fig. 3, concerns recovery of plutonium from zero power plutonium reactor fuel. It is quite compact in comparison with an equivalent aqueous process and, if side loops for salt reprocessing can be kept small in size, produces a minimal quantity of waste material.

* Delta Plutonium, a common alloy, contains approximately 1% gallium and may constitute a substantial portion of the feed.

FIG. 3. ZPPR fuel processing--simplified process flow diagram.

Simple mechanical decanning of the fuel is envisioned as this fuel does not contain fission products.

The deacid fuel, a U-Pu-Mo alloy, moves to the first pyrochemical process step, a metal-metal extraction as described previously.

The critical process step in this ZPPR fuel processing flow sheet is the partitioning of Pu from U. This is accomplished by co-melting the U with Fe (to lower the melting point, 725°C) and contacting it with liquid Mg. The Pu partitions to the Mg phase while the U-Fe does not. Four or more counter-current contact stages are needed to achieve the required degree of separation. The Mg is evaporated to recover Pu from the extractant. The U-Fe alloy could be processed by salt transport or pyroreodox for U recovery and Fe recycle, but the relatively low value of D-38 dictates that it is more economic to discard the U fraction to waste.

Process equipment for this operation exists only conceptually, but could be designed with a major development effort. Research will be required to determine distribution coefficients more accurately than they are now known, and kinetic data are lacking that will be necessary for equipment design. An additional development requirement will be the determination of possible buildup of metals in the cover salt used to reduce Mg vapor losses.

The Mg-Pu alloy is stripped of Mg in a vacuum evaporation step, actually a single-stage distillation.

The Pu, together with any Am daughter, then moves forward to an Am extraction into molten salt and a final purification by electrowinning, exactly as it is processed in the first flow sheet for reclamation of Pu scrap material. These steps have already been described and are rather well developed. The requirements for processing salts for recycle and treatment of anode residues are the same as in the salt recycle case.

Processing of RFP Salt Wastes

Salt waste from ²⁴¹Am extraction from stockpile Pu is accumulating at RFP; Pu (as PuCl₃) is contained in this material, along with the ²⁴¹Am.

The material was originally KCl-NaCl-MgCl₂, but it has degraded during extended storage in 55-gal drums and is partially hydrolyzed. The first proposed process step should be rechlorination (for example, with Cl₂, HCl, or COCl₂ (carbonyl chloride)) to provide starting material free of water and oxides. This step is well-founded chemically, but has not been tested for

this salt mixture because salt-contacting equipment, even at pilot scale, that would be suitable for this operation does not now exist. Some technology development will be required to implement this step.

Rechlorinated salts from the first step would proceed to a Ca reduction step, which is the same as the reduction shown for extraction salt recycle in Fig. 2. The reduction product is a Ca-Mg-Pu-Am alloy that is partitioned to Ca-Mg and Pu-Am by vacuum evaporation at $\sim 800^{\circ}\text{C}$.

Because this particular application of pyrochemistry deals with a manageable amount of existing waste and can recover pure Pu, the economic benefits are very great. The experience gained in addressing a problem even of this limited size would be of great value in demonstrating the potential of pyrochemistry in other, larger scale applications.

Process Summary - Development Requirements

Pyrochemical methods have three benefits: large separation factors in some cases, high density and concentration of in-process materials, and radiation resistance of salts and metals. There are also three disadvantages: high temperatures, exotic materials of construction, and in some cases excessively dilute in-process streams. Each particular application must be considered separately.

The three near-term applications we have discussed for pyrochemical processing of unirradiated nuclear materials demonstrate the potential of pyrochemistry as a process option. The major factor inhibiting its use for other than Pu processing is lack of experience in its large-scale application in shielded, remote facilities.

While the basic chemistry of each of the processes described in this report is known and has been applied at laboratory or small production scale, the descriptions of the process steps and flow sheets have pointed out four areas where basic research and development work is necessary:

1. Construction materials need extensive improvement.
2. Process equipment for remote maintenance pyrochemistry must be developed.
3. Instrumentation for process control and for optimum reagent use must be developed.
4. The available data base will need to be expanded by research in three areas:

- a. Distribution coefficients for salt-metal, metal-metal, and ternary, etc., systems
- b. Vapor liquid equilibrium data for metal distillations
- c. Kinetics of reactions and interphase transport data for salt-metal, metal-metal, gas-salt, etc., systems.

None of the requirements for development presents an overwhelming problem, and in fact some pyroprocessing at ton/year rates has been used since 1967. What is necessary is that one or more of the most advantageous pyrochemical applications actually be designed and built as an integrated process, so that a foundation of experience can be laid that will eventually place pyrochemistry in a more competitive position with respect to traditional techniques.

IV. EVALUATION OF PYROPROCESSING TECHNOLOGY

Introduction

The principles of pyrometallurgical treatment of ores remain unchanged from early historic times, although refinements in operating methods and changes in scale have been achieved. The applications considered for materials of interest here pose six difficulties over more conventional ore refining.

1. Plutonium is extremely valuable, reactive, and toxic.
2. Nuclear criticality limits quantities of materials handled at one time. (The absence of water is highly advantageous.)
3. The chemical reactivity of these materials requires inert atmosphere operations.
4. Separations from quite similar chemical elements are often required.
5. Separations from a large number of chemical elements simultaneously may be required.
6. Final products of very high purity are usually desired.

Extensions of the existing operations to include all steps potentially applicable to plutonium recycle and production will not require major changes in the nature of the operations. However, extensions to large-scale shielded operations necessary for spent nuclear fuel reprocessing with uranium and plutonium separation and decontamination would necessitate major technology development. Some issues related to spent-fuel processing will be discussed later.

The nature of Pu production processes discourages changes from the current batch concept. The process steps are each carried to completion; no continuous operations are involved. Scale-up to large or continuous processes offers no major advantage because of criticality considerations, the high density of liquid plutonium, and the great differences in density between molten salts and molten plutonium. The high densities imply that continuous operations with flow between steps must involve small streams or very heavy weights; mass limits imposed by criticality constraints require that plutonium inventories remain small; therefore, flow systems would be restricted to quite small volumes. There may be no net advantages in truly continuous operations

for these processes. However, continuous operation without the need for long heat-up and cool-down times could lead to large increases in throughput while still retaining the batch process and inventory control aspects of the current procedures.

Electrorefining is inherently a batch process, and a cell, once charged, runs theoretically at no net throughput. The principles of electrorefining require that a batch heel must be removed with the impurities. To avoid contaminant carryover, a significant quantity of plutonium must be left in the anode heel to be reworked. Replacement of the electrorefining process with pyroredox (when developed) will have the potential of semicontinuous operation. At present, the pyroredox option consists of two steps that require substantial additional chemical development to perfect the process. Initial experience at Rocky Flats Plant³ was limited by poorly engineered and installed equipment. Further development must be carried out on the chemistry of this system, and questions still remain regarding the required purity of the process salts and the fate of minor constituents in recycle streams. All of these issues must be resolved before attempts to operate in a semicontinuous mode can be undertaken.

The optimum pyroprocess may vary according to the application. Capacity requirements appear to be adequate in the batch mode for scrap and weapons plutonium rework if the complete system is in place. Support for the Hanford plant plutonium isotope separation may require semicontinuous operations to handle process internal recycle streams. This application may introduce bulk impurities into recycle streams that have not been considered in the chemistry process research.

Operation of the metal processing line at LLNL will initially produce byproduct streams for which no recycle capability is currently available. Plans have been laid out by LLNL plutonium technology scientists to complete the chemistry experiments necessary to develop these processes. Conceptual processes do exist, as described above in Chapter III. These new processes create new material problems and new off-gas cleanup problems that have not yet been evaluated. Line-generated wastes will be treated off-site. That work is directly supportive of the equivalent needs of the RFP processing and would be applicable to a plant-scale isotope separation process.

Comparison with the chemistry research and development that was done for the purex process flow sheet is of interest. It has been estimated that more

than 1000 man-years were expended to measure all of the chemical parameters for all of the elements of importance to that application. More nearly 100 man-years have been expended on the detailed chemistry of pyroprocessing. It is estimated that another 50 man-years will be required to sort through the chemistry issues that revolve around the metal processing line and Rocky Flats Plant applications. Because of the lack of pyrochemical data, it is impossible to do a direct comparison of pyro versus aqueous processes for all applications. It is also very clear that once one is working with metallic plutonium or plutonium oxide, there is a major advantage in staying in the nonaqueous system, if at all possible. A comparative analysis done for RFP applications shows an advantage in going to a nonaqueous process even if it is necessary to expend 50-75 man-year development costs up front.² The process that is eventually targeted retains an approximate 10 percent aqueous stream capacity for miscellaneous support operations. That 10 percent, on a fraction of plutonium inventory throughput basis, represents equivalent floor space requirements because of the dilute nature of the waste, scrap, or byproduct streams that are reconcentrated by aqueous routes.⁴

This requirement for aqueous processes to support the mainline pyroprocess approximately doubles the minimum floor space (increasing the direct capital cost accordingly). Analysis of the conceptual flow sheets for side-stream rework of a complete pyro line indicates at least a doubling of the number of process steps; in addition, there will be an increase of a few percent in the load to the mainstream processes. These conceptual processes for the side streams produce much more waste per kg of plutonium throughput than does the main process; however, the net waste produced for the total process is increased only on the order of 5% by these side streams.

Processes such as purex also generate side-stream waste, and comparisons with pyrochemistry require an equal basis. The important point is that side streams and support processes are often neglected, particularly in conceptual processes, which tends to make conventional, well-understood techniques appear much more complex than less well-understood competitors. We have attempted to remove this bias in our comparisons.

Spent Nuclear Reactor Fuel Processing

Commercial scale reprocessing of spent fuel has been conducted worldwide. Conceptual pyroprocesses have been proposed for recovery of uranium and plutonium from spent nuclear reactor fuel, but these have not been defined in

the detail required for development of plant designs and flow sheets.⁵ We can only estimate such factors as chemical consumption, the mass transported in process, heating requirements, side stream rework, and amounts of waste produced.

Figure 4 presents a block diagram of the major operations in a spent nuclear fuel processing plant. Figure 5 provides a schematic flow sheet for a pyro separation process for irradiated fuels. Figure 6 is a comparable sketch of the purex separation process.

From these simple sketches of the nuclear reprocessing plant, we can develop a clear impression of the fraction of the facility that will be replaced or significantly altered by a nonaqueous process. Special accommodations in the conventional parts of the plant to couple pyrochemical operations to the nonaqueous support systems will sharply decrease the apparent advantages of pyro's reduced size and number of steps.

We will review the operations shown in Fig. 4 and compare these operations in the aqueous plants and in the conceptual pyro plant. Reference numbers refer to major blocks outlined on Fig. 4.

1. Fuel Receiving and Storage

These operations are highly dependent on the specific fuel design and its operating history, but are independent of what is to be done with the fuel in processing. Fuel can be processed in nonaqueous systems that are cooled for shorter times than is acceptable for aqueous/organic systems. Therefore, a nonaqueous system needs less storage for fuel cooling in the total cycle; the plant requires only onsite feed inventory quantities. If cooling times are too short, a new problem arises with containment of short-lived fission products; that is not a consideration for the backlog of unprocessed fuel existing today.

2. Mechanical Headend

The mechanical headend cell must allow for movement of the fuel from storage, through cleaning, to the mechanical preparation room. As much surplus hardware as possible should be removed from any fuel type. This removed hardware requires further handling for waste disposal. That disposal problem is simpler from the headend cell in all cases than is providing for separation and disposal at a later stage in the process.

Chop-leach as now used for light water reactor (LWR) type fuels requires a large high-power shear plus special baskets to remove the hulls from the dissolver and packaging for disposal. Conceptual aqueous

FIG. 4. Block diagram of operations.

FIG. 5. Conceptual pyroprocess for $\text{UO}_2\text{-PuO}_2$ fuel.

FIG. 6. Conceptual aqueous (Purex) process for $\text{PuO}_2\text{-UO}_2$ fuel.

flow sheets for liquid metal fast breeder reactor (LMFBR) type fuels also generally assume chop-leach operations with cladding hulls being removed from the dissolver. These combined operations, excess hardware removal, shearing of whole fuel bundles, and spent-hull removal dictate the size of the headend mechanical cell.

For the high-temperature gas-cooled reactor (HTGR) graphite, handling and size reduction are necessary to prepare the fuel for burning. No fuel element materials are diverted to waste disposal at this first mechanical step.

Mechanical removal of excess hardware should be accomplished before the dissolution step for both processes. If the proposed zinc dissolution decladding process works satisfactorily for LWR and LMFBR fuels, the space required for shearing could be eliminated from the pyro plant design. Removal of the cladding sponge from zinc solvent for the pyroprocess will be equivalent to hull handling from the aqueous leaching. Following removal from the dissolver, the sponge or hulls must be compacted, packaged, and stored for shipment to disposal. These operations are essentially equivalent for the two processes. The net difference in mechanical operations is the absence of the shear in the conceptual pyroprocess. That shear is the most difficult mechanical operation in the purex process.

3. Decladding and Dissolution

Shearing of whole-fuel bundles is followed by dissolution of the fuel meat in aqueous nitric acid. This aqueous stream is transferred to accountability and feed adjust tanks and then fed to a series of extraction steps for separation of the uranium and plutonium and the decontamination of both of these from fission products.

The decladding and preparation for dissolution steps for the HTGR involves burning of the crushed material in at least two separate stages. Silicon carbide hulls on the fuel pellets are then cracked or crushed, and this product is finally fed to an acid dissolver. Beyond this stage, separation and purification of the thorium and uranium are similar to the aqueous process for plutonium and uranium. Therefore, we will not separately discuss the HTGR process further.

In the conceptual pyroprocess for LWR/LMFBR fuels, the decladding is a disintegration of the metal clad by molten zinc or other suitable material as described above.

This melt is separated from the (UO_2 , PuO_2 , fission products) fuel meat, and the zinc metal is distilled away from the cladding. The residual metal cladding sponge is then compacted for storage. The solid oxide fuel is reduced by calcium with the uranium and plutonium being taken up in a copper-magnesium (or other) alloy. Some fission products are separated into the salt at this stage. As in the aqueous process, provision must be made for the required safeguards accountability measurement at this stage. Following the calcium reduction step, the U, Pu, and fission products are separated and decontaminated through a series of steps similar to those required for the aqueous system.

The chemistry, the operating conditions, and the process hardware are quite different for the two approaches, but when we look more closely at the steps in the two processes, we see a great similarity. This should not be surprising. There are four requirements:

- a. Separate the cladding from the fuel
- b. Separate the U and Pu from fission products
- c. Separate the Pu from the uranium
- d. Purify the U and Pu as required.

In the purex process, shown in Fig. 6, the uranium and plutonium are separated from most of the fission products in the first-cycle extraction column; the Pu and U are then separated in the first-cycle separation column. The uranium and plutonium are then separately put through one additional cleanup cycle to further remove fission products.

The operations for the pyroprocess are similar following the decladding; the dissolved fuel is put through a process in which plutonium is separated from uranium by extraction into a salt and back extraction to another alloy. The uranium then goes through an extraction cycle. Additional cycles will be required for adequate decontamination of both the Pu and U; much of the research and development manpower that was expended on the purex process (as mentioned earlier) was spent on developing multistage contacting equipment to enhance separations in each cycle. This same area should be a major focus of pyroprocess development work.

The two processes again are seen to require similar processes and roughly equivalent numbers of steps. In terms of difficulty, the aqueous system has advantages because the low temperature and conventional equipment made from readily worked stainless steel give a very big "familiarity" edge to the

aqueous system. When the chemistry is completely known and acceptable materials, process equipment, and instrument and control systems are fully identified, the pyroprocess will still be at a disadvantage because of the high temperatures and inert atmospheres required.

Off-Gas Cleaning

Off-gas cleaning from fuel processing is required to retain fission products Kr and I and to prevent other volatilized fission products (e.g., Cs and Ru) from escaping to the environment. The inert atmosphere required for the pyroprocess should work very well in off-gas cleaning systems; capture of ^3H , Kr, and I should be readily accomplished. The chemical load transported to the off gas because of the high temperatures remains unspecified.

The systems for cleaning off gas from the aqueous systems have been designed on the basis of pilot plant tests. The required retention of krypton, tritium, and carbon-14 for HTGR remain unproven.

Final Product

The product will be either a metal or an oxide depending on the process and the use intended for the product. Because of the high capital investment needed for plutonium or uranium nitrate conversion to oxide, serious consideration should be given to the intended application. The pyroprocesses are currently designed to produce plutonium metal as the final step in purification; conversion of the purified metal to pure oxide would be required for return to conventional LWR fuels. These are process and application specific. This part of the plant process is not a major part of the total plant costs.

Waste Production

Wastes produced by aqueous and nonaqueous processes are in different chemical form, but are otherwise similar in content, as shown in the flow sheet in Fig. 4. In both aqueous and nonaqueous systems, the major chemical contents of the process streams are proposed for recycle. In the aqueous streams, the major component is water; the eventual fate of all of this water will be uncontrolled release. Nitric acid is recoverable; most other waste chemicals are eventually incorporated into one of the waste

fractions: high-level waste (HLW), intermediate-level waste (ILW), or low-level waste (LLW). These wastes will eventually be converted to a stabilized form suitable for disposal according to the applicable criteria.

The total wastes that would be produced per ton of fuel from an optimized pyroprocess have not been established. The flow sheet shown in Fig. 5 and used for discussion might initially be operated by discarding or storing all salts and alloys carrying products. An actual plant operation would expect to recycle much of these streams with the minimum possible discarded as carriers for the fission products. The total salts or alloys discarded will be transuranic or higher level wastes. No general release will be possible, in contrast to the case with water from the aqueous system. It is difficult to imagine that the total final form HL wastes produced by pyroprocessing would be less than the currently projected <80%/MTU final glass waste form for the LWR-purex process.

Intercycle or Interprocess Storage Requirements

Aqueous plants rely on intercycle storage capacity for the accumulation of the product from one process, appropriate process chemical adjustments, and feed to the next process at an appropriate rate. Because of lack of detail for the pyrochemical-based flow sheet, an evaluation of the intercycle storage and process adjust steps cannot be made. From the information available on feed compositions and concentrations, the streams can be estimated to be fairly large for managing the total stream from LWR fuel dissolution. Uranium solubility in these alloy/salt systems appears to be a limiting factor in good flow sheet development.

Current pyro applications are for small batches; the interprocess storage requirement is only a piece-count problem. In a full-scale, remote, radioactive application, considerable thought must be given to product and byproduct handling from each stage. Because these materials solidify at well above normal working temperatures, allowance must be made for keeping them hot and/or for storing them in reheatable tanks. Such equipment requires increased complexity and maintenance. Adequate space must be provided for operations and for remote recovery from failed equipment and abnormal operations.

The lack of detail for the possible pyrochemistry-based flow sheets precludes the evaluation of mismatches between process steps and the impact of

process upsets. Allowance must be made both for chemical rework of process upsets and for the mechanical maintenance problems referred to above. Decontamination and final cleanup of equipment for maintenance will be done at least in part with aqueous solutions. Contaminated scrap and some line-generated wastes will be leached, if appropriate, and recycled as is now done at the LANL scrap recovery.⁴

The total intercycle storage (tankage) and waste volumes have not been estimated with any accuracy because of lack of flow sheet chemistry detail. It can be seen from the generalized discussion above that many of the chemical side stream rework problems are similar to the aqueous plant problems.

1. Low-level and trace residual chemical materials often are best removed with aqueous cleaning.
2. Any of the pyrochemical operations that require movement of process equipment will require extra room for manipulators and connect/disconnect jigs.
3. All high-maintenance equipment will need to be accessed for remote replacement.
4. Feedthroughs for electrical equipment, rotating feedthroughs for stirrers and pump rotors, and mechanically operating valves or diverters will require access for maintenance.
5. Major design and operational issues remain open before the final layout and operational evaluation can be completed for the pyrochemical processes.

It is apparent from the above brief evaluation that a totally nonaqueous facility for spent-fuel reprocessing is not possible at present without a major development effort. Aqueous systems for support of the main process probably will always be required. The mechanical manipulations and expected high maintenance of the pyrochemical process equipment will increase the in-cell space requirements far beyond those apparently indicated by the high density of the process streams.

Relative Stream Volumes and Weights

Although the process streams are high density and plutonium is very soluble in some of the proposed salts and alloys, uranium is not nearly so soluble in the alloys and salts identified. Dissolution of the equivalent of

1000 kg of U metal requires about 9000 kg (~1500 liter) of Cu-Mg alloy in the pyrochemical process applied to pressurized water reactor (PWR)/boiling water reactor (BWR) fuels; the same process requires 6000 kg (~6000 liter) of 3M nitric acid leachant in conventional processes. While the aqueous liquid occupies at least four times the volume of the alloy solution, it can be handled at room temperature while the alloy must be handled at 700°C. While the entire 1000 kg of U may not be in solution at any one time, the relative weights and volumes still move between process steps. Further, it is not necessary that the entire ton of U-Pu fuel be dissolved simultaneously in the aqueous process. What is required in both cases is that the minimum unit that can be identified be dissolved and measured for safeguards accountability reasons. That unit can be a single fuel element in either the aqueous or the pyroprocess. Each will require that the minimum batch be homogenized adequately to provide a representative sample for uranium and plutonium analyses. The dissolver product, therefore, shows no advantage for pyrochemistry.

The dissolver itself is another point for comparison. In aqueous processing, it rejects cladding hulls and volatile fission products/gases. In the pyrochemical method, the dissolver rejects these items, plus almost 12,000 kg of CaO/CaCl₂/CaF flux contaminated with several kg of fission products. The reprocessing of the waste flux and CaO is a large task, but must be accomplished because this waste would otherwise occupy essentially the same volume as the entire aqueous dissolver product.

During the decontamination and separation processes, pyrochemistry enjoys a volume reduction, particularly over U in organic phases, where 1000 kg of metal require about 16,000 liter of aqueous solvent, while the minimum alloy volume is 4000 liter. The total mass of in-process material is, however, about equal, and again the pyrochemical system must be maintained at 700°C.

Products are weight equivalent: nitrate solutions, about 3500 liter per MT for aqueous, Zn solutions/intermetallics, about 3500 kg or 500 liter for pyrochemistry; the volume reduction is a factor of 7.

Wastes are difficult to evaluate: with total internal recycle and waste volumes reduced by evaporation/combustion/electro-winning from solution, net waste should be equivalent for either process. Any comparison would have to be based on actual purex vs conceptual pyro, and would have little meaning without far greater detail than is now available for pyroprocessing.

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APPENDIX A. CHEMICAL PROCESSES

The purpose of this appendix is to provide a more detailed description of the chemical processes involved in process steps than was given in the body of the text.

It draws heavily on the published work of M. S. Coops and J. B. Knighton, which has been included in edited form with their consent.

A bibliography of recent survey articles on pyrochemical techniques applied to nuclear materials can be used by the reader to obtain further information.

Reduction of Plutonium Oxide to Metal

All actinide metals are pyrophoric, and it is common practice to burn metallic scrap to oxide as a safety precaution. Plutonium is typically stored as PuO_2 and must be chemically reduced to metal prior to component manufacture. This has traditionally been done by precipitating $\text{Pu}_2(\text{C}_2\text{O}_4)_3$, $\text{Pu}(\text{O}_2)_2$, $\text{Pu}(\text{OH})_3$, or PuF_3 from solution and converting it to PuF_4 for bomb reduction to metal. This method is now being replaced by direct reduction techniques.

The first successful reduction of PuO_2 to metal with calcium was reported in 1958. The process was carried out in two stages: an initial thermit reaction between PuO_2 and Ca, followed by a leaching step with CaCl_2 to dissolve the CaO reaction product and any unreacted Ca. The fluid flux permitted finely divided plutonium to coalesce into a pool of metal. Rotation of the inclined reaction vessel was used to promote slag dissolution and metal consolidation. The original process has since been significantly improved by workers at several DOE sites.

The DOR process now used for production work utilizes a CaCl_2 (or $\text{CaCl}_2\text{-CaF}_2$) flux both to dissolve the CaO reaction product at the reaction site and to provide a fresh supply of Ca reductant to keep the reaction going. This process exploits the solubility of Ca and CaO in CaCl_2 while utilizing the insolubility of plutonium metal in the Ca-CaO- CaCl_2 reaction flux to permit metal consolidation. Vigorous stirring is used to keep the reactants in intimate contact so that the reaction is driven to completion. Recent development work at LANL has increased the batch size to one kilogram of oxide feed. It appears that the limitation on DOR batch size will be from criticality safety constraints.

This direct oxide reduction process is replacing fluoride reduction as it eliminates neutron exposure to operating personnel (alpha particles from plutonium decay have sufficient energy to eject neutrons from fluorine by the α, n reaction) and eliminates reduction residues that require subsequent treatment for Pu recovery.

In the LANL application, the reaction is carried out under an inert atmosphere in an open crucible at approximately 830°C. Vitrified magnesium oxide ceramic is commonly used as a container material, but tungsten and tantalum can also be used. If the latter are used, CaF_2 is added to lower the temperature needed to liquefy the flux, thereby decreasing the corrosion of the crucible and subsequent contamination of the metal product. Intense stirring is required to keep all of the reactants in contact as the very dense PuO_2 sinks and Ca metal floats in the melt. The reaction is exothermic, and a temperature rise occurs after initiation. The overall chemical reaction is:

The mechanism for the reaction is not fully understood at present, but is believed to take place in several steps. Several of the possible reaction species and their free energy of formation are listed below:

<u>Compound</u>	<u>KCal/mole</u>	<u>ΔG @ 1000 K</u> <u>KCal/gr-ATM oxygen</u>
PuO_2	-210.130	-1 5.065
$\alpha\text{-Pu}_2\text{O}_3$	-367.696	-122.565
$\beta\text{-Pu}_2\text{O}_3$	-343.942	-114.647
PuO	-113.057	-113.057
CaO	-127.200	-127.200

One possible reaction mechanism is

<u>Reaction</u>	<u>ΔG @ 1000 K</u>
$2\text{PuO}_2 + \text{Ca} + \beta\text{Pu}_2\text{O}_3 + \text{CaO}$	-50.882 KCal
$\beta\text{Pu}_2\text{O}_3 + 3\text{Ca} + 2\text{Pu} + 3\text{CaO}$	-37.658 KCal

It is also feasible to assume the following mechanism:

<u>Reaction</u>	<u>ΔG @ 1000 K</u>
$\text{PuO}_2 + \text{Ca} \rightarrow \text{PuO} + \text{CaO}$	-30.127 KCal
$\text{PuO} + \text{PuO}_2 \rightarrow \beta\text{Pu}_2\text{O}_3$	-20.755 KCal
$\beta\text{Pu}_2\text{O}_3 + \text{Ca} \rightarrow 2\text{PuO} + \text{CaO}$	- 9.372 KCal
$3\text{PuO} + \text{Pu} \rightarrow \beta\text{Pu}_2\text{O}_3$	- 4.771 KCal
$\text{PuO} + \text{Ca} \rightarrow \text{Pu} + \text{CaO}$	-14.143 KCal
$3\text{PuO}_2 + \text{Pu} \rightarrow 2\beta\text{Pu}_2\text{O}_3$	-57.497 KCal

An additional back reaction can occur between $\beta\text{Pu}_2\text{O}_3$ and PuO_2 to form $\alpha\text{Pu}_2\text{O}_3$. Conditions leading to the formation of $\alpha\text{Pu}_2\text{O}_3$ are to be avoided as the reaction between a single atom of Ca and $\alpha\text{Pu}_2\text{O}_3$ is not thermodynamically favorable:

$\alpha\text{Pu}_2\text{O}_3 + \text{Ca} \rightarrow 2\text{PuO} + \text{CaO}$	+14.382 KCal
$\alpha\text{Pu}_2\text{O}_3 + 2\text{Ca} \rightarrow \text{Pu} + \text{CaO}$	+ 0.239 KCal
$\alpha\text{Pu}_2\text{O}_3 + 3\text{Ca} \rightarrow 2\text{Pu} + \text{CaO}$	-13.904 KCal

Although the exact chemical mechanism for the direct oxide reduction reaction has not yet been fully characterized, it has been well established that the reaction goes to completion when excess calcium is present, sufficient CaCl_2 is available to dissolve the CaO produced, and adequate stirring is used. As calcium metal is soluble to about 1 wt% in CaCl_2 at 835°C, excess Ca ensures that the reaction is driven to completion by mass-action effects.

The CaCl_2 -rich end of the CaO - CaCl_2 phase diagram has been worked out and is shown in Fig. A-1. The phase diagrams indicate that CaO is soluble to 18.5 mole % in CaCl_2 at 835°C, but if the loading of CaO rises much above 14 mole % the increased viscosity of the melt retards consolidation of the droplets of plutonium into a single pool. The 700-gr PuO_2 reduction process at LANL used 50 mole % excess calcium reductant and a CaO loading in CaCl_2 of about 14 mole %, to give product yields in excess of 99.5%. After the melt is allowed to cool, an ingot of plutonium metal can be readily cleaved from the solidified flux. The salt phase contains negligible unreacted PuO_2 .

FIG. A-1. Partial ternary phase diagram for the CaCl_2 -rich side of the CaCl_2 - CaF_2 - CaO system. Source: D. Wenz, I. Johnson, and R. Wolson, *J. of Chem. and Eng. Data*, 14(2) (April 1969).

Extraction of Americium with Molten Salt

All reactor-produced plutonium contains a mixture of several plutonium isotopes. The continuous decay of ^{241}Pu (14.8-y half-life) is the source of ^{241}Am . This isotope decays by alpha emission with the simultaneous emission of 60-kV gamma rays in 80% abundance. In order to minimize personnel exposure, this element is removed from the metal prior to fabrication.

Early experimental work in electrorefining demonstrated that americium could be partitioned between molten plutonium and a molten NaCl-KCl salt containing Pu^{+3} ions. It was also demonstrated that americium could be extracted from Mg-Zn-Pu-Am alloys with immiscible molten magnesium chloride salts. Work was undertaken at Rocky Flats to study the extraction of americium from molten plutonium by contacting with molten NaCl-KCl salt containing a few percent of MgCl_2 .

A production process has evolved from this original work and is now used for extracting americium from kilogram amounts of plutonium metal. This process is based upon equilibrium partitioning (by oxidation-reduction reactions) of americium and plutonium between the molten chloride salt and the molten plutonium phase. The chemistry of this process is shown by the following reactions:

The free energies of formation for the actinide compounds above are given by the following:

<u>Compound</u>	<u>ΔG @ 1000 K (KCal per gram-atom of chlorine)</u>
AmCl_3	-67.0
PuCl_3	-58.4
MgCl_2	-57.6

The thermodynamic activity equilibrium constant (K_a) is expressed in terms of mole fraction (X) and activity coefficient (γ) by the following equation:

$$K_a = \frac{(X_{AmCl_3})(\gamma_{AmCl_3})(X_{Mg})^{3/2}(\gamma_{Mg})^{3/2}}{(X_{Am})(\gamma_{Am})(X_{MgCl_2})^{3/2}(\gamma_{MgCl_2})^{3/2}}$$

The term $\frac{X_{AmCl_3}}{X_{Am}}$ is defined as the distribution coefficient (D_{Am})

and is simply the ratio of the mole fraction of $AmCl_3$ in the salt to the atom fraction of Am in the metal.

The activity coefficients in the above equation may be determined by obtaining experimental data for D_{Am} , and relating K_a to the free energy change for the reaction using the equation $\Delta G_f = -RT \ln K$.

In laboratory work, the following closely related, but not identical, relationship is used to determine the partition value between phases:

$$K_d = \frac{\text{conc. of } AmCl_3 \text{ in salt phase}}{\text{conc. of } Am \text{ in metal phase}}$$

By convention, the above ratio is usually expressed in weight percent instead of mole fractions. For extraction work, the term α is used for the extraction factor and is related to K_d in the following manner:

$$\alpha = (K_d)\left(\frac{s}{m}\right)(F)(\beta)$$

where

α = extraction factor = $\frac{\text{Wt. of solute in salt phase}}{\text{Wt. of solute in metal phase}}$

K_d = distribution coefficient (as defined above)

s/m = salt-to-metal ratio by weight

F = fraction of equilibrium attained

β = effects of side reactions

For a multistage countercurrent extraction operated in true equilibrium without side reactions, the partitioning of a solute into the metal phase (f_m) and the salt phase (f_s) is defined as follows:

$$f_m = \frac{(c - 1)}{(a^{n+1}) - 1}$$

$$f_s = 1 - f_m$$

where n = number of countercurrent stages.

Present production processes use two-stage countercurrent extraction to remove americium from molten plutonium with magnesium chloride-based salts. Both 35 mole % NaCl - 35 mole % KCl - 30 mole % $MgCl_2$ and 50 mole % NaCl-26 mole % $CaCl_2$ - 24 mole % $MgCl_2$ are used for americium extraction. The above salt will extract 90% of the americium present when a salt-to-metal mass-ratio of 0.06 is used in a two-stage countercurrent extraction.

The Am and Pu are recovered from the NaCl- $CaCl_2$ - $MgCl_2$ salt by contact with liquid calcium metal at approximately 850°C in a batch extractor. The calcium reduces $AmCl_3$, $PuCl_3$, and $MgCl_2$ to form a 50/50 mole % NaCl- $CaCl_2$ salt phase and a molten Am-Pu-Mg-Ca alloy that is immiscible in the above salt. After cooling, the metal phase is cleaved away from the salt phase and the salt phase is analyzed. Little, if any, Am or Pu remains in the salt phase, and the salt residues can be discarded to waste. Metal recovery begins by evaporating magnesium and calcium from the residual metal button at about 800°C in vacuum. The americium can then be distilled away from the plutonium in a vacuum still operated at 1200°C, using yttria ceramic vessels to contain the molten metal fraction. The bottom fraction contains the plutonium that is recycled back into the main plutonium stream.

Plutonium Electrorefining

The first publication related to plutonium electrochemistry dates back to Manhattan Project work at Los Alamos. Improvements have continued, and in 1962 a production process (3-kg scale) for routine production of >99.9% pure metal was reported. Recent developments at Los Alamos have expanded the capacity of the electrorefining cells to about 6 kg per batch, with a cycle time of five days.

The principle of the electrorefining process is basically simple: plutonium is oxidized at a liquid metal anode containing impure metal feed and the resulting Pu^{+3} ions are transported through molten salt to a cathode where pure metal is produced. The transport salt is usually eutectic NaCl-KCl, but NaCl- $CaCl_2$ can also be used. As liquid plutonium metal builds

up on the cathode, it drips off into an annular channel surrounding the anode cup where it coalesces into a pool of metal and is recovered after the cell is cooled. The entire chemical process is performed in a molten salt bath.

The basic chemistry of the electrorefining technique is as follows:

PuCl_3 must be added to the cell prior to operation to maintain a high concentration of Pu^{+3} ions in the salt phase. This PuCl_3 also acts as a salt-phase buffer to prevent dissolution of trace impurities in the metal feed by forcing the anode equilibrium to favor production (retention) of trace impurities as metals, instead of permitting oxidation of the impurities to ions. Metallic impurities in the feed fall into two classes, those more electropositive and those less electropositive than plutonium. Because the cell is operated at temperatures above the melting point of all feed components, and both the liquid anode and salt are well mixed by a mechanical stirrer, chemical equilibrium is established between all impurities and the plutonium in the salt even before current is applied to the cell. Thus, impurities more electropositive than the liquid plutonium anode will be oxidized by Pu^{+3} and taken up by the salt phase, while impurities in the electrolyte salt less electropositive than plutonium will be reduced by plutonium metal and collected in the anode. Those impurities less electropositive than plutonium that are already present in the molten anode will remain in the anode. The extent of these reactions will be determined by the reaction-free energy and concentration for each of the impurities in the molten anode/electrolyte salt system. Americium can be used as an example of a very electropositive impurity:

When current is passed through the cell, the concentration of impurities in the product obtained at the cathode will depend upon their concentration in the salt. If equilibrium conditions exist in the cell, the following equation applies:

$$\frac{(Am)}{(Pu)} \text{ metal product} = \frac{1}{K} \frac{(AmCl_3)}{(PuCl_3)}$$

Where the parenthesis refer to the chemical activities of the reactants and K is the equilibrium constant for the previous equation. Similar considerations apply to the oxidation of less electropositive impurities from the anode when a current is passed through the cell. Thus, for the case of iron impurity in the anode, the reaction

favors the production of iron metal instead of ferrous ion because the free-energy change for the reaction is +96 kCal (+96 KCal is equivalent to an equilibrium constant of 1×10^{21} at 1000 K).

The composition of the salt electrolyte in the cell does not change during the electrorefining cycle so long as the driving potential of the cell is kept below the decomposition voltage of the electrolyte. The following gives the decomposition potential of normal components of the electrolyte:

<u>Chloride salt</u>	<u>Decomposition potential at 800°C</u>
CaCl_2	3.32
KCl	3.44
NaCl	3.25
MgCl_2	2.46
PuCl_3	2.40

Because the energy required to strip the electrons from plutonium metal at the anode is exactly matched by the energy returned at the cathode, the potential required by the process is only that required to overcome time-invariant (I^2R) losses in the cell circuit and time-dependent resistance (electrode polarization).

Polarization of the anode occurs after most of the plutonium is transferred across the cell, and impurities constitute a large percentage of the anode. The reason for this can be demonstrated by using the case of delta plutonium alloy feed. Delta alloy contains ~1 wt.% gallium. The normal operating temperature of the electrorefining cell is 750°C, and at this temperature the delta alloy melts to form a liquid phase.

As electrorefining proceeds, plutonium is selectively removed from the anode and the composition of the anode becomes enriched in gallium. At approximately 18 mole % gallium, the lower density eta phase Pu begins to form (at 750°C) and a mixture of solid eta phase and liquid is formed at the anode surface (eta phase floats on the liquid plutonium phase). The back-EMF of the cell gradually increases as the eta phase is formed. Vigorous stirring exposes liquid plutonium and permits oxidation to proceed at the anode surface, but at 25 mole % gallium, the anode solidifies. Continued operation of the cell oxidizes gallium in the ratio of the composition of the solid anode.

To prevent the passage of impurities, the back-EMF of the cell is monitored at frequent intervals. The current to the electrodes is turned off, and the voltage of the cell is measured. When the back-EMF reaches a predetermined value, operation of the cell is terminated, and the cell is allowed to cool. The cathode product, which consists of very pure plutonium metal, is recovered from the solidified salt mass by breaking the ceramic vessel and brushing the ring free of adhering salt. The product ring typically amounts to about 85% of the original mass of the anode feed metal. The impurity level of the cathode product from electrorefining is usually below normal spectroscopic detectability levels if the cell is run at anode current densities of 0.60 amps per sq. cm. or less.

The level of purification that can be achieved from impurities by the electrorefining process is directly related to the free-energy formation of the chloride salt and of each impurity present in the feed metal, as discussed above.

The basic electrorefining process is now being used on a production scale for the purification of nonspecification plutonium metal. The technology is sufficiently well developed to permit 24-h unattended operation of the electrorefining cells, and the quality of the product metal is highly consistent. This technology is rapidly replacing aqueous chemistry for plutonium metal purification.

Salt Transport Processes

The term "salt transport" refers to a technique whereby a metallic solute is transferred selectively from one liquid alloy (donor) to another liquid alloy (acceptor) by circulating a molten salt between the two alloys. The transfer takes place through oxidation of the solute by the salt at the donor alloy and its subsequent reduction by the acceptor alloy.

A salt transport procedure for uranium is illustrated schematically in Fig. A-2. Metallic uranium, which is initially present in the donor alloy, is oxidized and extracted into the transport salt.

Zirconium and all the elements below it in Table A-1 should be separated readily from uranium and plutonium by a process in which the uranium and plutonium are extracted into a molten salt.

The difference in the distribution behavior of two elements, M_a and M_b , is expressed as a separation factor, α :

$$\alpha = \frac{D_{M_a}}{D_{M_b}}$$

where D_M is the distribution of M between the metal and salt phases:

$$D = \frac{X_{\text{MCl}_n}}{X_M}$$

The equilibrium constant, K_a , is related to the standard free-energy change, ΔG^0 , for Reaction 1 by the equation:

$$-RT \ln K_a - \Delta G^0 = \Delta G_{\text{MgCl}_2}^0$$

Uranium in solution in the acceptor and donor alloys is equal to the ratio of the distribution coefficients of uranium for each alloy and the salt. The separation factor is strongly dependent on the composition of the liquid alloy and, to a lesser extent, on the temperature and on the composition of the molten salt.

FIG. A-2. Salt transport.

Table A-1. Standard free energies of formation of chlorides at 1000°K.*

MCl_n	$-\Delta G_f$ (kCal/g-equiv. Cl)	MCl_n	$-\Delta G_f$ (kCal/g-equiv. Cl)
BaCl ₂	83.6	MgCl ₂	57.7
CsCl	82.6	UCl ₃	54.0
RbCl	82.5	MnCl ₂	42.2
LiCl	78.8	ZrCl ₂	34.2
KCl	81.6	ZnCl ₂	34.1
SrCl ₂	80.8	CrCl ₂	32.8
SmCl ₂	80.0	CdCl ₂	30.4
EuCl ₂	79.0	FeCl ₂	26.3
CaCl ₂	76.7	CuCl	22.0
NaCl	76.2	NiCl ₂	18.6
LaCl ₃	67.0	NbCl ₅	11.4
PrCl ₃	66.3	MoCl ₂	8.0
CdCl ₃	66.3	TcCl ₃	7.4
NdCl ₃	64.2	PdCl ₂	5.3
YCl ₃	61.2	RhCl	1.4
PuCl ₃	58.4	RuCl ₃	0.3

* Source: J. B. Knighton, "Pyrochemical Processing of LWR and LMFBR Fuels by the Salt Transport Method," Akademische Verlagsgesellschaft, Wiesbaden, 1978.

When the transport salt containing the UCl_3 is contacted with the acceptor alloy, the reverse reaction takes place:

Therefore, the net reaction is:

Magnesium chloride consumed at the donor alloy by oxidation of uranium and plutonium is regenerated at the acceptor alloy by magnesium reduction of UCl_3 or $PuCl_3$. Thus, the beginning and end salt composition is constant in the salt transport operation. For each mole of uranium transferred from the donor alloy to the acceptor alloy, 1.5 moles of magnesium are transferred in the opposite direction. The increasing concentration of magnesium in the donor alloy and magnesium depletion in the acceptor alloy must be taken into account in the design of a practical process.

When the reduction reaction has reached equilibrium, both alloys are in equilibrium with the transport salt, and the ratio, R , of uranium in solution in the acceptor and donor alloys is equal to the ratio of the distribution coefficients of uranium for each alloy and the salt.

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