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ABSTRACT

An accelerator-driven subcritical nuclear system is briefly described that transmutes actinides and selected long-lived fission products. An application of this accelerator transmutation of nuclear waste (ATW) concept to spent fuel from a commercial nuclear power plant is presented as an example. The emphasis here is on a possible aqueous processing flowsheet to separate the actinides and selected long-lived fission products from the remaining fission products within the transmutation system. In the proposed system, the actinides circulate through the thermal neutron flux as a slurry of oxide particles in heavy water in two loops with different average residence times: one loop for neptunium and plutonium and one for americium and curium. Material from the Np-Pu loop is processed with a short cooling time [illegible] days because of the need to keep the total actinide inventory low for this particular ATW application. The high radiation and thermal load from the irradiated material places severe constraints on the separation processes that can be used. The oxide particles are dissolved in nitric acid and a quaternary ammonium anion exchanger is used to extract neptunium, plutonium, technetium, and palladium. After [illegible] the Am-Cm and higher actinides are extracted using a TALSPEAK-type process. [illegible] proposed operations were chosen because the [illegible] processing [illegible] [illegible] [illegible] processing [illegible]

[illegible]

[illegible]

strikes a heavy metal target. For transmutation applications, the actinides and long-lived fission products are circulated through a blanket region surrounding the target. The stable and short-lived transmutation products are removed from the circulating loops using advanced separation processes to remove neutron poisons and to minimize production of undesirable radionuclides. The thermal power resulting from fissioning the actinides may be converted into electricity. A portion of this electrical power is used to drive the accelerator with the remainder used in the commercial power grid.

A key feature of the accelerator transmutation of nuclear waste (ATW) concept is the use of an intense thermal neutron flux. This allows significant transmutation rates with small blanket inventories of the isotopes to be transmuted. We currently estimate that ATW systems can achieve neutron fluxes in the range of 10^{15} - 10^{16} neutrons/cm²-sec. Fluxes in standard thermal reactors are typically one or two orders of magnitude lower. Fast reactors attain about the same flux as an ATW system, but cross sections for transmutation are generally an order of magnitude smaller in the fast neutron spectrum. Consequently, for a given transmutation rate, ATW systems require an order of magnitude smaller inventories. This in turn permits the use of a smaller capacity chemical processing facility and results in smaller end-of-life residues in the overall system.

Both aqueous and nonaqueous carrier and cooling media are being considered for use in various ATW designs. Nonaqueous media such as molten salts allow the system to operate at high temperatures and near ambient pressure, giving more efficient conversion of thermal power to electrical power. However, the chemical separations for these systems will require significant development work. [illegible] aqueous systems can draw upon a wealth of [illegible] processing [illegible] developed [illegible] This paper will [illegible]

[illegible]

target designs are being evaluated, but the particular design used in this example consists of a heavy water cooled tungsten target surrounded by a lead annulus. A heavy water moderator blanket surrounds the target area. The heavy water system has some similarities to a CANDU reactor type design. An array of tubes in the blanket carry the materials to be transmuted by the thermal neutron flux. Some tubes carry actinides as an oxide slurry or suspension in heavy water. The suspension is recirculated in the blanket for a period of time until a desired burnup is achieved. A slipstream is routed to separation operations for actinide and selected fission product recovery, followed by reintroduction of these elements into the neutron flux. Fission products are contained in other tubes in forms suitable for transmutation. Initial estimates indicate that the ATW system could transmute the transuranic elements and key long-lived fission products (technetium and iodine) discharged from eight 3000 MWt light water reactors.

The excess neutrons generated in the spallation target allow any number of long-lived fission products to be transmuted. However, as more fission products are addressed, a greater fraction of the generated power is required to run the accelerator. Thus, the choice of which fission products to transmute must be based on analyses of costs and benefits. In this system, strontium and cesium have extremely small neutron absorption cross sections and are not considered for transmutation. We envision a nuclear waste management strategy in which these radionuclides would be placed in engineered storage for more than 10 half-lives to allow them to decay to stable materials. It is generally agreed that of the remaining long lived fission products, ^{99}Tc and ^{129}I represent the greatest risk to the biosphere.[illegible] We have chosen in this model system to transmute only these two fission products. The system transmutes both the fission products from the LWR spent fuel as well as those created from actinide burning in the neutron flux. The system must transmute 2400 kg/yr of actinides, 250 kg/yr of technetium, and 70 kg/yr of iodine to support eight LWRs. For the technetium and iodine, about 80% of the material transmuted comes from the LWR waste while 20% is generated from actinide burning. The actinide burning produces about 90 kg/yr of other long-lived fission products that are not transmuted in this version of the ATW system, primarily ^{107}Pd and ^{135}Cs with smaller amounts of [illegible] and [illegible]. The actinide transmutation also produces [illegible] kg/yr of stable and short lived (half life < 30 years) radioactive fission products. These include [illegible] kg/yr of [illegible] and [illegible] kg/yr of [illegible].

The americium and curium are fissioned more slowly than the plutonium and neptunium and are also more difficult to separate from the fission products. Therefore using separate recirculating loops with Am and Cm in one and Np and Pu in the other [illegible] times [illegible] better optimized [illegible] irradiated material; therefore, the Am and Cm loop can be processed less frequently and [illegible] before processing. This approach [illegible] actinide inventory [illegible] system [illegible].

The [illegible] processing needed [illegible]

irradiated material from the Np/Pu loop is processed after 5–10 days of cooling time and the material from the Am/Cm loop is processed after about [illegible] days of cooling time. Without the benefit of long periods for decay, a variety of short lived isotopes [illegible] radiation induced decomposition of solvents and chemical reagents is a major concern and is an important consideration in selecting separation approaches. Because our goal is transmutation and not fuel fabrication, the purity specifications of the material that is sent to the transmuter are less stringent,[4] requiring different criteria for metal ion separation factors. The fission product impurities are maintained at a level where they do not interfere substantially with the neutron economy of the transmuter. The overall goal of the processing system is to minimize TRU waste streams and return all actinides to the transmuter.

We have also been guided by the need to propose separation technologies that have been used at a significant scale. The proposed operations were chosen because they have been successfully tested for processing high-level radioactive fuels or wastes in gram to kilogram quantities. Such technologies were chosen so that overall material balances could be estimated. The system has not been optimized and there are numerous avenues for improvement. The details of the flow sheet are discussed below.

ACTINIDE OXIDE SLURRY LOOPS

The baseline actinide blanket feed consists of a low fired mixed oxide slurry in heavy water. The transmutation system uses D_2O rather than normal water to more efficiently thermalize the neutron flux and minimize neutron absorption. Slurry feeds allow easy removal of actinides and most fission products from the D_2O carrier. Using oxide slurries avoids using acid solutions in the transmuter eliminating the production of neutron activation products and radiolysis products of the acid anion. An oxide slurry concentration of about [illegible] g/L was found to give satisfactory system performance in the neutronics calculations. This slurry concentration is more readily handled than the [illegible] g/L [illegible] slurries used by ORNL researchers on early thorium breeder fuel cycles.[5] The oxide preparation uses spray calcining for particle size control and slurry stability.[illegible] Further optimization of the oxide particle properties, if warranted, could be accomplished with a sol-gel process. However, more waste will be generated from this operation.

After a residence time of [illegible] days in the transmuter for the Np/Pu loop, the oxide slurry is removed and processed after cooling for about five days to recover the plutonium, neptunium, and technetium for return to the transmuter. This process may also be done as a [illegible] per day slipstream on the blanket slurry. The raffinate containing the remaining radionuclides is stored for [illegible] days before it is further processed for trivalent actinide recovery, mostly [illegible] Am, which are then returned to the transmuter. The Am/Cm [illegible] longer residence time of [illegible] days in the [illegible] and allows a [illegible] time of about [illegible] days before processing. The [illegible] slurry loop contains [illegible] kg of actinides.

[illegible]

There are [illegible]

to the transmuter. The concentrated slurry is evaporated several times after addition of fresh D_2O and helium sparged for complete tritium removal. At periodic intervals during the lifetime of the transmuter, the D_2O will have to be replaced or be processed to reduce the tritium level. There is a transition from a D_2O slurry system to H_2O solution processing at this point. The wet slurry is dissolved in concentrated HNO_3 without the aid of HF.[10-12] Further out gassing is expected and these gases are vented to the gas handling system. Ruthenium volatilization will be enhanced by ozone sparging during dissolution and the RuO_4 collected.[4,15] The majority of the irradiated material is expected to dissolve easily, because of the low-fired nature of the mixed actinide oxides. Any residue will be filtered and saved for more stringent dissolution techniques.[14,15]

NEPTUNIUM, PLUTONIUM, AND TECHNETIUM RECOVERY

The initial separation operations must be robust and selective for plutonium and neptunium. A liquid-liquid anion exchange separation using a quaternary amine is proposed to accomplish this separation. The liquid anion exchanger Aliquat 336 was chosen because of its stability in the presence of the high radiation fields. This extraction system has high extraction values and selectivities for tetravalent Pu and Np over fission products.[16-19] Aliquat 336 has higher radiation stability than tributylphosphate (TBP), which is used in the PUREX process.[20] Since little uranium is produced in the transmuter, Aliquat 336 can replace TBP when only Np and Pu require selective removal. The degradation products of Aliquat 336 are weaker extractants than the original compound and therefore they don't degrade the selectivity of the system significantly. Another advantage of this system relative to systems using phosphorus containing extractants, is that the thermal decomposition products of Aliquat 336 are non radioactive gases and do not add to the waste. A further advantage of this process is that the technetium fission product is well extracted and can be easily sent to the technetium transmutation loop. Fission product palladium will also be extracted in this process.

The Pu/Np/Tc recovery system employs centrifugal contactors or possibly pulse columns as the equipment for the first extraction step. Centrifugal contactors minimize solvent contact time with the highly radioactive aqueous phase, thus extending the extraction solution lifetime. However, potential third phase or solids formation would reduce their effectiveness. The back extraction processes use pulse columns as they allow for longer contact times which facilitate the separations.

The acid solution from the oxide dissolution is adjusted to 2 M HNO_3, and the plutonium valence is adjusted to Pu(IV) with $NaNO_2$. The neptunium remains largely in the pentavalent state at this stage and is reduced and extracted in a second set of contactors after Pu and Tc are extracted. The total volume of the solution is scaled to approximately 10 watts/L to allow manageable heat loadings for the solutions. Processing experience at the [illegible] processing facility and recent Los Alamos experience with concentrated ^{238}Pu solutions support the heat loading value [illegible]. In recent Los Alamos tests, a [illegible] solution of ^{238}Pu in 2 M HNO_3 was prepared. The acid concentration and Pu valence were checked [illegible]

[illegible]

with ascorbic acid to reduce neptunium to the tetravalent state. Ascorbic acid seems a good choice because it rapidly reduces neptunium and excess ascorbic acid and its degradation products are converted to carbon dioxide and water in subsequent calcining operations. Assuming that Np and Pu behave similarly, [illegible] of the Np can be extracted in the shorter second set of contactors. Figure 1 illustrates some extraction data obtained at Los Alamos for Pu(IV) and Tc(VII) so that we could have a set of distribution coefficients determined under similar conditions.[21] These values are in good general agreement with the literature data.

Sizing the first extraction bank based on the least extractable component ensures that enough stages are available to properly extract the elements for return to the transmuter. To calculate the required number of stages for the liquid anion exchange extraction portion of the flowsheet, technetium is used as the "key" component. Plutonium and neptunium have higher distribution coefficients than Tc. Therefore, using Tc extraction behavior to calculate the number of stages and phase ratios produces a conservative design. The Tc distribution coefficients are reasonably sensitive to acidity and total organic phase loading. Actual experimental data was used in the design and this was consistent with literature values.

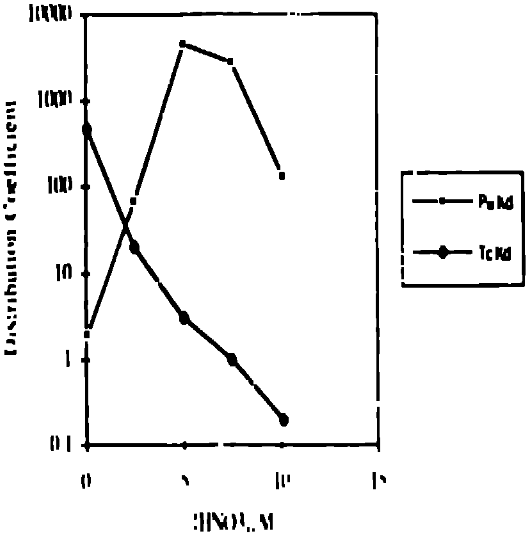

Figure 1. Distribution Coefficients for Pu and Tc Extraction with 0.2 M Aliquat 336 in Diisopropylbenzene

The Pu and Np are back extracted with 0.1 M HNO_3, leaving Tc and Pd in the organic phase. A controlled thermal denitration process is used on the aqueous strip solution to produce mixed oxide powders of Np and Pu suitable for return to the transmuter. Thermal denitration [illegible]

[illegible]

external cooling for 90 days to allow for further decay to facilitate the separation of the higher actinides.

The spray calcination design is based on experience with spray calcination of PUREX waste streams at the Idaho Chemical Processing Plant (ICPP). High recoveries of nitric acid have been demonstrated with proper engineering of the off gas handling systems.

The Tc and Pd are stripped with 1 M ammonia solution. This stripping also serves as a extractant cleaning step to remove some organic degradation products. It is expected that substantial degradation will occur at these high radiation fields.[27] An additional filtration step for the organic extract may be required as solid polymers have been observed. The aqueous strip is denitrated with volatilization of Tc_2O_7 which is collected for Tc recycle to the transmuter.[illegible] [28] Palladium oxide is the major solid product from this step. This material can be combined with other wastes for immobilization or kept for separate disposal. The organic phase will be recycled for reuse in the next batch. Solvent makeup from degradation losses will be necessary. It is also possible that there will be such high losses that extraction solutions will be used for only one contact.

AMERICIUM AND CURIUM RECOVERY

After 90 days to allow for further decay of short lived radionuclides, the aqueous stream from the Np–Pu separation is processed to recover Am, Cm, and higher actinides. The baseline process (TALSPEAK) for separation of Am, Cm and the higher actinides from the fission products was chosen because it is the best system currently demonstrated for radioactive waste treatment.[illegible] It has been demonstrated that Am and Cm can be separated from the lanthanide fission products with sufficient purity for reentry into the transmuter. The first step, extraction of the trivalent actinides and lanthanides from the rest of the fission products with 1M HDEHP (di-2-ethylhexylphosphoric acid), is critical because it determines if the aqueous raffinate stream is TRU or non-TRU. It is this aqueous raffinate stream that can be further treated for Cs and Sr recovery if required. This waste stream contains the majority of the fission products that make up the HLW for short term on site storage (about 300 years) in the Swedish [illegible] process. [illegible] reasonable separations were accomplished [illegible] they were not sufficient to make this waste stream non-TRU. [illegible] The conditions used in this step were not those that have been reported in other processes that use HDEHP [illegible] separating trivalent actinides, such as the TALSPEAK process used at Oak Ridge National Laboratory. [illegible] It has been demonstrated that at equilibrium [illegible] concentrations of [illegible] M instead of 1 M [illegible] coefficients are greatly improved. A [illegible] pH [illegible] is required for proper extraction [illegible] TALSPEAK [illegible] step. The acid concentration [illegible] accomplished in the proposed system by [illegible]. The [illegible] optimized in the [illegible] TALSPEAK [illegible]

[illegible]

literature. Calculations for the formic acid denitration process are based on actual experience with denitrating waste solutions at Los Alamos National Laboratory.

After the HDEHP is loaded with actinides and lanthanides, the actinides are selectively back extracted from the organic phase with an aqueous phase containing 1.0 M lactic acid and [illegible] M diethylenetriaminepentaacetic acid (DTPA). Because the radiation levels are quite high from the presence of Cm isotopes, it is likely that the DTPA and lactic acid will be severely degraded and will not be available for recycle.[34] This aqueous back extraction stream is sent directly to thermal denitration to give CmO_2, AmO_2, and higher actinide oxides for recycle to the transmuter. The 1 M HDEHP organic stream from which the actinides have been stripped is contacted with 6 M nitric acid to recover the lanthanide fraction. The acid stream containing the lanthanide fission products is sent to spray calcination which yields an oxide suitable for storage or preparation of an immobilized waste form. Nitric acid is recovered from the off gas stream from the spray calcination because of the high acid concentration. The HDEHP solvent will be washed with 0.5 M ammonium carbonate and recycled after makeup for degradation. The waste stream from the organic wash will be spray calcined.

The slurry in the Am–Cm loop resides in the transmuter for 90 days to allow more efficient transmutation of these elements. Irradiated oxide from the Am–Cm loop is dissolved in nitric acid as described above after cooling for 90 days. This feed has low levels of Np and Pu and enters the baseline process at the liquid anion exchange step for processing primarily to remove Tc. The total material balance for the baseline process is given in Figures 2–7 below. It is reported on an elemental weight basis as opposed to an oxide weight basis. After the majority of the material is returned to the transmuter, the remainder of the wastes consists of TRU solids and non-TRU liquid or gaseous wastes with the majority being water. The need for rapid processing after transmutation will generate a larger volume of aqueous waste. Water will be recycled after distillation to various points within the reprocessing plant. Gaseous products of thermal denitration (CO_2, NO_x) will be filtered and scrubbed as necessary before release.

Material control and accountability (MC&A) is integrated into the process. Fissile material amounts at all points in the entire system at any time should be known for both MC&A and criticality purposes. For an aqueous based process system this is straightforward to accomplish. The current determinations for reactor systems uses manual isotope dilution mass spectrometry (IDMS) techniques. At a variety of points in the processing, online verification of actinide materials will be developed as advanced concepts. Development of advanced process diagnostics is also desirable.

The final waste forms are yet to be determined since there are no licensed waste forms at this time and the current licensing concepts are based on longer term underground storage requirements (10,000 years) as contrasted to short term storage (300–1000 years). It is desirable to consider other forms besides vitrification. [illegible] form currently used at the Idaho National Engineering Laboratory (INEL) may be acceptable. Further waste form development is required and should be [illegible] to the concept of short term on site engineered storage facilities.

[illegible]

[illegible]

[illegible]

decreased neutron capture and reduced structural requirements on the present design of the ATW blanket system. Less tritium would be produced and the requirements for such rapid recycle time might be relaxed, lessening the severe demands on shielding and processing. This concept would enhance the energy production aspects of the transmuter.

Many of the actinide oxides are insoluble in molten salts.[5] Development work is required to establish that the nongaseous fission products remain intact in the original oxide particles. Then a ready separation of the oxide particles from the molten salt could be accomplished through filtration or centrifugation techniques. Though such separations have been accomplished, improved technology for separation of solids from molten salts at high temperature is desirable. The molten salt would be recirculated to the blanket after addition of actinide oxide feed material. The actinide oxide solids would be dissolved in acid and could be processed using the baseline technology described above.

TRAMEX WITH HIGH NITRATE SOLUTIONS

If all the actinides could be recovered simultaneously using one solvent system, the baseline flow sheet could be greatly simplified. In extraction systems for actinides from solutions containing high chloride concentrations with liquid anion exchangers such as trialkylamines or tetraalkylammonium salts (TRAMEX), both the tetravalent and trivalent actinides can be extracted and separated from most other fission products including the trivalent lanthanides. Processing in chloride medium is undesirable because of corrosion problems and neutron absorption problems from chloride impurities in the blanket. Studies have indicated separations of actinides from fission products could be accomplished from solutions with high nitrate concentrations.[6] This idea would require further verification as there is conflicting data in the literature. The advantages are the use of one solvent system that has high stability, elimination of phosphorus containing extractants from the flowsheet that give difficulty in waste management, and reduction in the number of required processing steps. The disadvantage is the use and subsequent disposal or recovery of high concentrations of nitrate salts.

DIRECT TRIVALENT ACTINIDE EXTRACTION

Another advanced approach relative to the baseline flowsheet is to find high stability solvent extraction systems that can directly remove trivalent actinides from the trivalent lanthanides and other fission products with high specificity to replace the TALSPEAK process. A number of studies have demonstrated the potential of this actinide lanthanide separation approach.[7] Though these extractants give the desired specificity, they have not had extensive testing for stability or to scale. The advantages of replacing the TALSPEAK process would be a decrease in the number of processing steps with increasing waste reduction, especially if the phosphorus containing extractants could be replaced.

CARBONATE FLOWSHEET

An alternate flowsheet might be based on selective precipitation of actinide and [illegible] tively removed, the actinides could be recovered as a group or individually by selective carbonate or hydroxide precipitations under different conditions leaving the remaining fission products in solution. The advantages would be more rapid turnaround of processing streams with less complex processing steps and without the accompanying organic solvent degradation and the ease of redissolving the carbonate precipitates. The rapid return of the actinides would allow for lower process inventories for the actinides. Disadvantages include the need for extensive solid liquid separations in a high radiation environment and further processing of fission product streams would be required to obtain the high TRU decontamination factors needed to meet class C or better waste criteria. However, these wastes would contain low levels of actinides and could be more processed after much longer cooling times.

CONCLUSION AND SUMMARY

The current baseline flowsheet is feasible and can be achieved with available technology. It has performance factors that make it attractive for supporting transmutation options for waste treatment. Judicious use of spray calcination reduces solid waste volumes and the selective nature of the ion exchange extractants allow for efficient recovery of the targeted radionuclides. The flowsheet has the flexibility to be adapted for spent fuel recovery or processing of some defense wastes. We have begun the experimental validation of some portions of the separation chemistry. Significant improvements in the flowsheet seem possible with technologies that require fairly modest development efforts.

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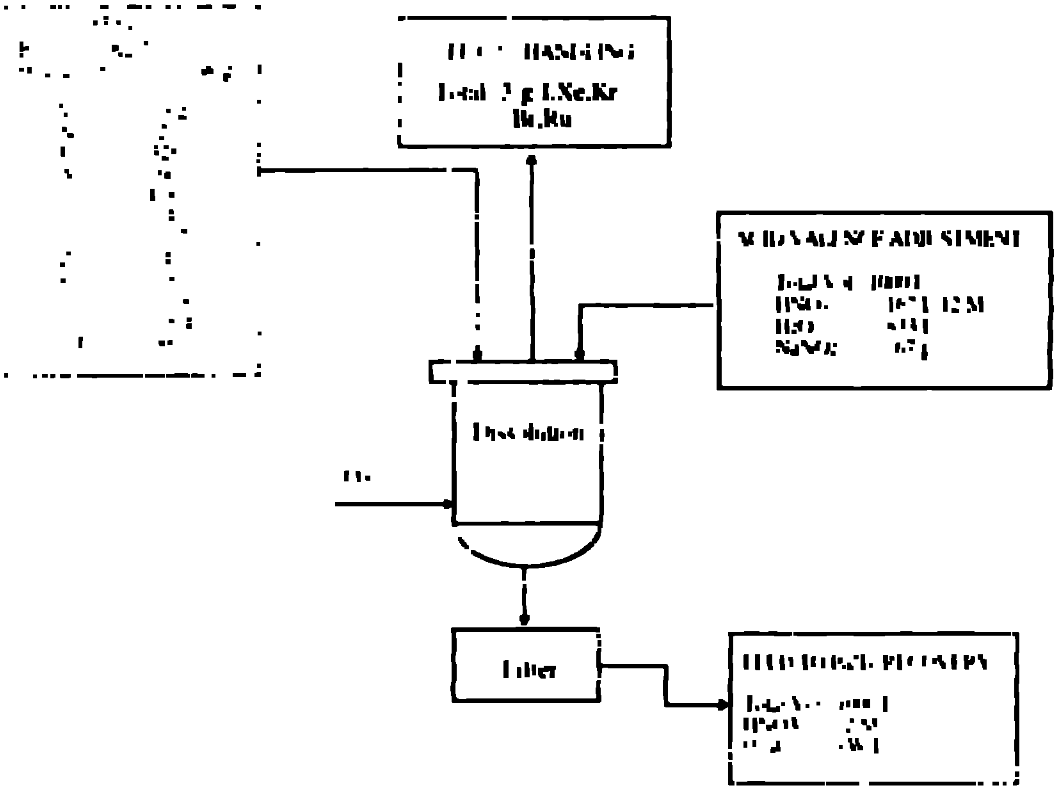


Figure 2 Material Balance for Head end Dissolution for Np/Pu Recovery

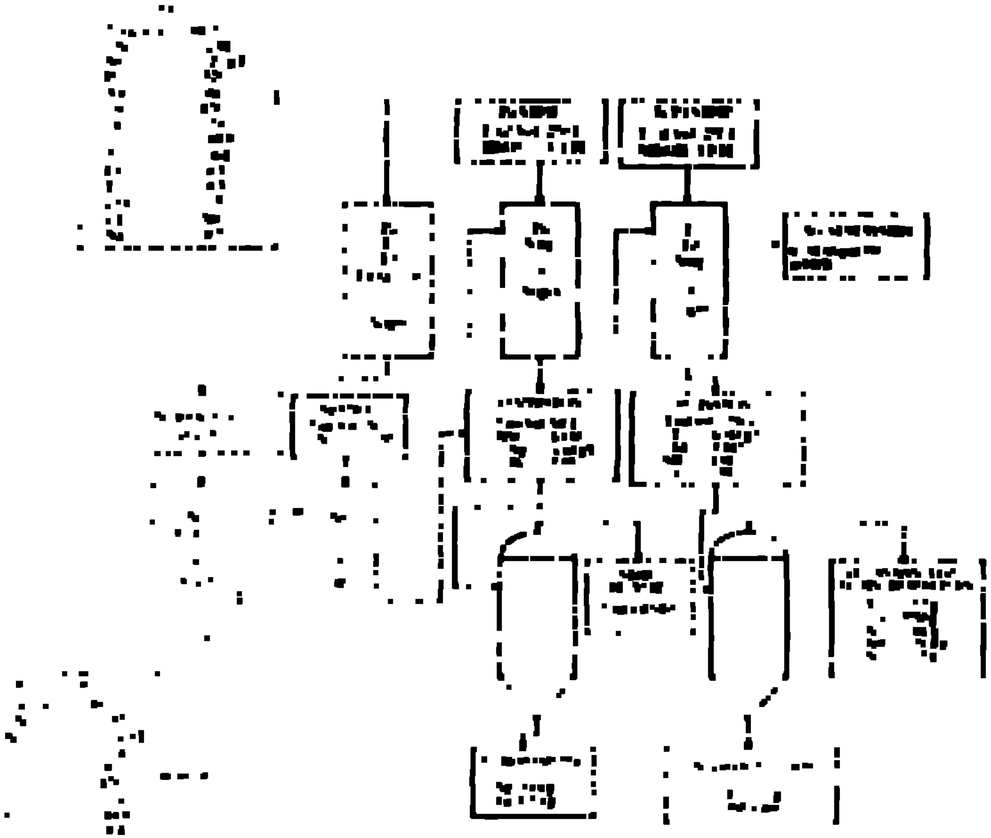


Figure 3 Material Balance for Np/Pu/Tc Recovery

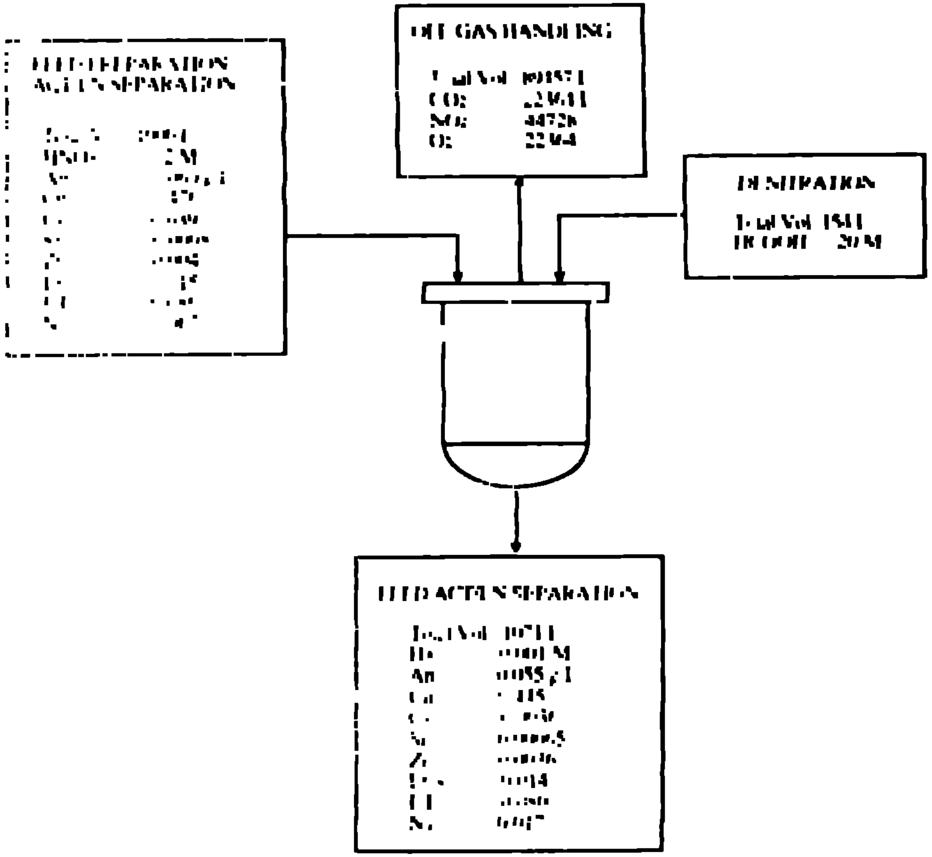
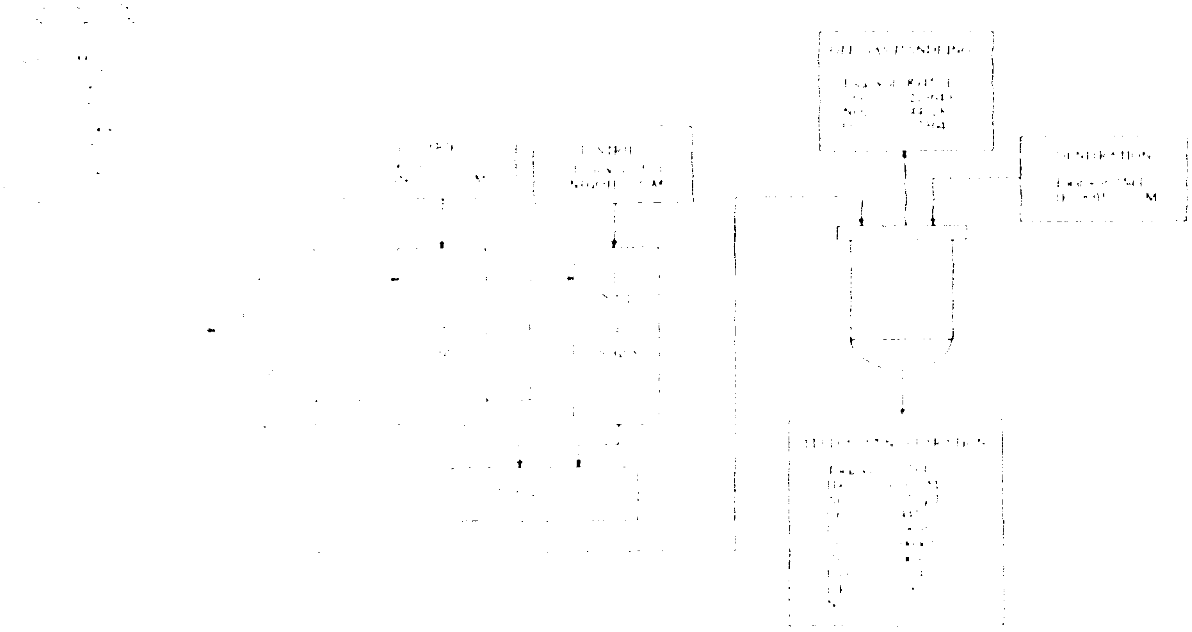


Figure 4. Material Balance for Feed Preparation from Np-Pu Recovery to Am-Cm Recovery



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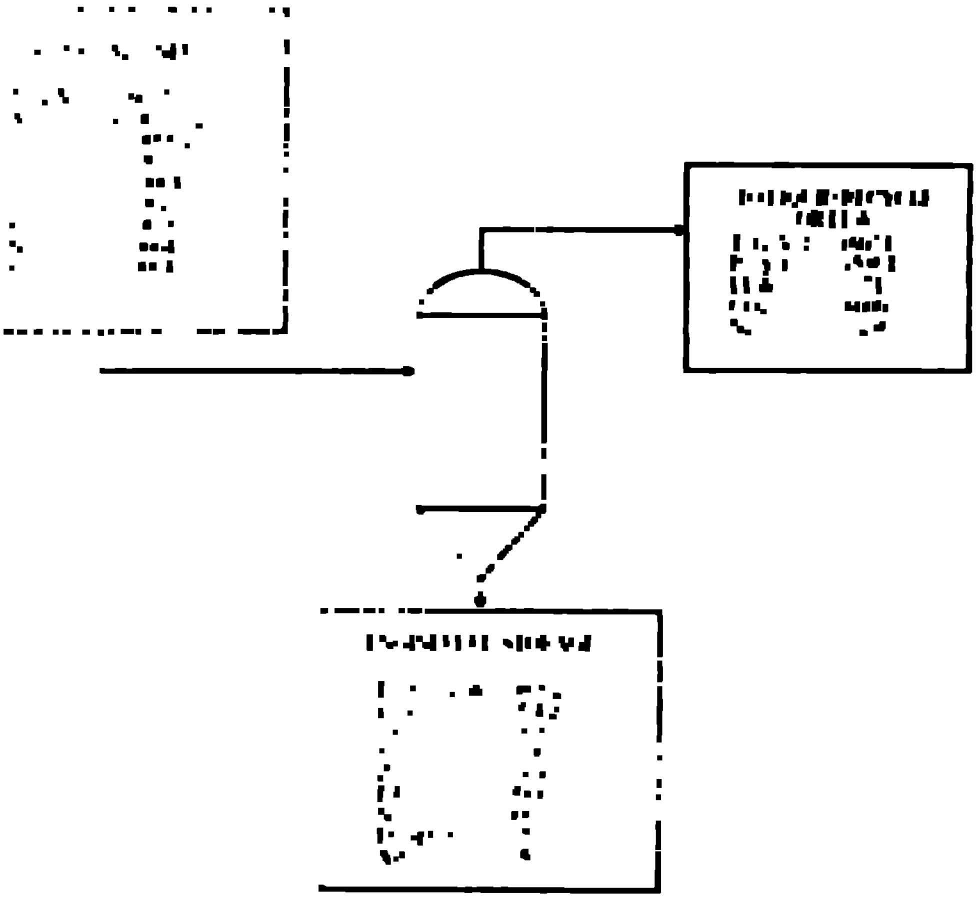

Figure [illegible] Material Balance for Spray Calcination Process