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TITLE

PYROCHEMICAL SEPARATIONS PROCESSES OF POTENTIAL HAPO INTEREST

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GENERAL ELECTRIC

February 28, 1957

W. H. Reas
Manager, Chemical Research
Chemical Research & Development Operation
HANFORD LABORATORIES OPERATION

References: (1) HW-47650, "A Proposed Pyrochemical Dissolution and Head-End Method for Zirconium Clad Fuel Elements", R. H. Moore, January, 1957.

(2) HW-48503, "Pyrochemical Separations Processes of Potential HAPO Interest", R. H. Moore, February 18, 1957.

In reference (1), Mr. Moore reviewed the status of development of pyrochemical processing and suggested a method of adapting this technique to processing fuels of potential interest to HAPO. While the specific process suggested by Mr. Moore at this time included features which required a definite extrapolation of today's technology, this process was felt to have sufficient potential value to warrant your consideration for research effort. I understand that your personnel are considering this proposal at the present time.

In reference (2), Mr. Moore has extended his theoretical calculations and correlations and has suggested ways of greatly increasing the process' versatility while simultaneously greatly reducing the extrapolation of technology required to make the operations successful. It is hoped that you will consider this second reference very seriously in reaching any conclusion as to the advisability of your organization undertaking research work in this field in the near future.

As you well understand, the division of reactor development is quite interested in developing a versatile and economical reprocessing technique for irradiated fuels. As Mr. Moore describes in reference (2), his suggested process potentially meets these criteria. If HAPO is to retain an active part in the atomic energy program of the future, the reprocessing of power fuels will almost certainly be included. The development and application of a versatile and economical separations process during the early 1960's is regarded as a necessity in reaching this goal. In view of this premise, I trust that you will seriously consider adding pyrochemical processing to your research agenda.

ORIGINAL SIGNED BY
R. E. TOMLINSON

Manager, Advance Process Development
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PYROCHEMICAL SEPARATIONS PROCESSES OF POTENTIAL HAPO INTEREST

R. H. Moore

Advance Process Development
Research and Engineering Operation
CHEMICAL PROCESSING DEPARTMENT

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I. INTRODUCTION

A survey of the literature of pyrochemical processing has been made with the intent to present the theory, status, and application to future HAPO technology. It has been found that most pyrochemical processes under investigation today are direct extrapolations of early Ames work on fission product volatility and molten metal extraction[1], or the results of efforts to confirm Brewer's predictions[2] as regards the scavenging power of oxides, nitrides, carbides, and halides.

In general, the promise or predictions of these earlier investigations have been substantially confirmed. Unfortunately, the results do not lead to confidence that these processes are of potential value to HAPO.

The writer finds, in the majority of pyrochemical processes, molten uranium metal is almost invariably one of the phases. Thus, operating temperatures are in the range 1150-1200 C, or higher. Materials required to contain the reacting system are few in number and never ideal for construction of large scale equipment. In the writer's opinion, an indefinite period of development of suitable refractory and chemically inert materials must be awaited before these processes can be applied on a large scale.

An area of pyrochemical processing which seems to have been entirely ignored by laboratories engaged in this work concerns the pyrochemistry of fused halides. The writer is aware of only one proposed process involving the pyrochemistry of fused salts. This is the result of studies by Gibson, et. al.,[3] in England, who proposes to dissolve uranium in molten $PbCl_2$ and then reduce back to metal with magnesium. Following this work, Feder, et. al.[4] have shown that $ZnCl_2$ also dissolves uranium.

There is a substantial amount of fundamental information on the properties of uranium and plutonium halides available[5,6] and a wealth of information on halide pyrometallurgical processes in general, by Kroll[7,8]. From this information, the writer has found it possible to devise several processes of potential or, possibly, immediate interest to HAPO. These are presented here for the purpose of stimulating interest in the pyrochemistry of molten halides as applied to HAPO separations problems.

In an earlier report[9], it was proposed that laboratory research be initiated to develop a pyrochemical dissolution and head-end process to be coupled with solvent extraction decontamination cycles. It is the purpose of this report to show that the previous proposal is merely a specific example of a very general process.

II. SUMMARY

Pyrochemical processes can be limited to dissolution only, or extended to complete pyrochemical processing with fully decontaminated UF_6 and partially decontaminated plutonium nitrate the products. As a dissolution and head-end process, the proposed process is believed to be applicable

to the dissolution of all fuel element and cladding materials which are available today, except those high in molybdenum, to yield an aqueous nitrate solution suitable for solvent extraction processing. A maximum operating temperature of 500 C can be achieved in the head-end process, so that operation in equipment fabricated from molybdenum or its alloys is possible without excessive corrosion.

(1) A pyrochemical dissolution and head-end process to be coupled with conventional solvent extraction decontamination cycles is outlined in detail. In brief, the process consists of the dissolution of fuel and cladding in molten $BiBr_3$, with separation of bismuth metal containing Ru, Rh, Pd, Mo, and Te fission products. In the initial phase of the dissolution, where essentially only the cladding is dissolving, an assist from free bromine will probably be required to attain a high rate of dissolution on refractory cladding. Free bromine also assures formation of the higher and most volatile halides of the cladding elements facilitating their removal in the dissolution step. The salt phase containing the fuel constituents is distilled to recover excess solvent for recycle, and the resulting UBr_3 (and UBr_4) containing plutonium and fission product bromides is oxidized with oxygen gas to liberate bromine and yield nitric acid soluble U_3O_8, etc. The liberated bromine is employed to convert bismuth metal back to $BiBr_3$ for recycle.

This process is considered to have the following advantages over the similar process proposed earlier:(9)

(a) Bismuth metal is less corrosive than cadmium or zinc metals. In this process, bismuth metal does not require distillation.

(b) Operating temperatures attain a maximum of about 500 C, approximately 300-400 C lower than in the preceding process. This results in marked reduction in energy requirements and substantially reduces the corrosion problem.

(c) The kinetics of gas-solid phase oxidation are almost certain to be better than solid-solid phase oxidation.

(d) All other advantages of the previous process are retained.

In this process, all but one to five per cent of the bismuth metal recycles. This small loss is accepted to permit the confinement of Ru, Rh, Pd, Mo, and Te fission products in compact solidified bismuth metal. Halogen is consumed in irrecoverable form as cladding element halides. Oxygen is consumed to convert uranium to U_3O_8 and regenerate halide combined with uranium for recycle (after reaction with bismuth metal to form $BiBr_3$). Nitric acid is consumed to convert U_3O_8 to uranyl nitrate.

The cladding elements are separated from the fuel elements as volatile halides which can be condensed and solidified for storage in compact form. With stainless steel cladding, non-volatile nickel and chromium halides accompany uranium and are converted to innocuous nitrates.

(2) It is shown that the dissolution and head-end process can be extended to produce UF_6 with decontamination anticipated to meet diffusion plant specifications. Plutonium is separated and recovered in aqueous nitric acid solution for further decontamination by solvent extraction.

This process is summarized as follows:

(a) Dissolution as above with partial decontamination.

(b) Conversion of UBr_3 to UBr_4 by bromination at 400 C.

(c) Distillation of UBr_4 at 766 C. Non-volatile $PuBr_3$ is collected in $BaBr_2$ for criticality control. Substantial decontamination of the uranium phase is anticipated.

(d) Metathesis of UBr_4 to UF_4 with BiF_3 obtained by reaction of HF with bismuth metal separated during dissolution. Volatile $BiBr_3$ is generated at 453 C to drive the reaction to completion. The latter recycles to the dissolver.

(e) Fluorination of UF_4 to UF_6 and distillation of the latter to effect final decontamination and yield a specification product.

(f) Oxidation of $PuBr_3$ and $BaBr_2$ mixture with oxygen.

(g) Solution of plutonium and barium oxides in nitric acid to provide feed for solvent extraction decontamination cycles. Note that this solution has a "built in" Redox type salting agent, $Ba(NO_3)_2$.

The process possesses advantages over solvent extraction enumerated below:

(a) It is more compact, leading to low capital investment.

(b) It is simple in concept. The number of steps leading to fully decontaminated UF_6 is approximately equal to the number required to produce fully decontaminated 60 per cent uranyl nitrate.

(c) Criticality calculations will probably show that the process is much less sensitive to criticality hazards than conventional solvent extraction.

(d) The fission products, Mo, Te, Ru, Rh, and Pd, are retained in and confined by solidified bismuth. Zirconium and niobium, as well as the cladding elements, are stored as solidified halides. Long lived fission products, the alkali metals, alkaline earths, and rare earths, accompany plutonium and are isolated in smaller volumes of neutralized wastes than currently attained by solvent extraction where these elements are separated from the combined uranium and plutonium stream.

(e) The inherent capacity for recycle of process chemicals is probably high enough to keep chemical costs as low as is presently achieved.

(3) Possible variations on these processes are indicated briefly to illustrate the general nature of the process itself and the concepts behind it.

(4) Pertinent pyrchemistry, basic to these processes, is outlined in some detail.

(5) Although initially conceived as a process for dissolution (and subsequent processing) of zirconium clad uranium metal fuels, for which it is ideal, it has been shown that, with minor changes in the nature of and order of addition of reagents, uranium oxide fuels and zircalloy and, probably, stainless steel cladding can be handled in the same equipment with a high probability of success. Highly enriched fuels present no problem to the dissolution and head-end process itself, but present the usual problem when the process is coupled with conventional solvent extraction processing.

III. FUNDAMENTAL PYROCHEMISTRY

Dissolution in a fused salt has an advantage over pyrometallurgical processes, wherein uranium is handled throughout as metal, in that the choice of solvent salt automatically determines the range of operating temperatures. In the example chosen to illustrate the processes of concern here, $BiBr_3$ (M.P. - 218 C, B.P. - 453 C) was selected with $BiCl_3$ (M.P. - 232 C, B.P. - 447 C) the alternate. Fortunately, the volatility of the higher bromides and chlorides of cladding elements to be dissolved, in the main, is greater than that of these solvents, while the bromides and chlorides of uranium and plutonium are much less volatile than the solvent. These physical properties of the system, outlined in Table 1, set the stage for a process which permits separation of cladding elements, solvent, and fuel elements providing all can be converted to chlorides or bromides. The probability that this can be achieved is dependent, in turn, upon the chemical properties of the system, and presented below are the documented chemical reactions which show that the chemical properties are indeed such as to predict the success of the process, as conceived.

(1) Dissolution Reactions:

(a) With free halogens: All free halogens convert uranium (and, indeed, most metals) to halide salts.(5) Mo, W, the platinum metals, Cu, and Ni are resistant, with the degree of resistance a function of temperature. With free halogen, molybdenum is unattacked below 300 C, with the rate of attack increasing above this temperature.(12) Note that the range of fluidity of $BiBr_3$ and $BiCl_3$ conveniently overlaps this temperature. Further, the use of these solvents would not preclude simultaneous use of free halogens to supplement their solvent power as needed.

Reaction of free halogens with zirconium yields the tetrahalide, with iron, FeX_3, with nickel, NiX_2, with chromium, CrX_3 (unless oxygen is also present when $CrOX_2$ may form), with tin, SnX_4, with aluminum, AlX_3, with niobium (as with tantalum, NbX_5.(8) All are volatile with respect to BiX_3, with the exception of NiX_2 and CrX_3.

Free halogens form monovalent alkali metal halides, divalent alkaline earth metal halides, and, predominantly, trivalent rare earth halides which are non-volatile with respect to BiX_3.

Uranium forms volatile UF_6 (B.P. - 56 C) with fluorine, UCl_6 (B.P. - 277 C), UCl_5 (B.P. - 427 C), and UCl_4 (B.P.- 787C) with chlorine, UBr_3 (B.P. - 1567 C) and UBr_4 (B.P.- 766 C) with bromine.(5)

Significantly, plutonium forms only $PuBr_3$ (B.P. - 1512 C). $PuBr_4$ is unknown and believed too unstable to exist even in the vapor phase.(14) This affords a basis for the distillation separation of uranium and plutonium by distillation of UBr_4. Similarly, with chlorine, plutonium forms $PuCl_3$ (B.P. - 1767 C). $PuCl_4$ is unknown in the solid phase, but moderate pressures of $PuCl_4$ are calculated to exist when chlorine is passed over heated $PuCl_3$.(14)

In general, reactions of free halogens with metals are characterized by what amounts to ignition followed by an exothermic reaction. Unfortunately, data do not appear to be available on the ignition temperatures of concern. This point is of process interest, however, and it should be noted that, while free halogens may have to be employed occasionally to achieve a desired reaction product or suitable dissolution rate, this is done in BiX_3 media which serves as a heat control device as well as solvent.

Fluorine converts UO_2 to UF_6, whereas chlorine reacts to form UO_2Cl_2.[5] The writer has been unable to find direct evidence that bromine reacts with UO_2 to form UO_2Br_2; however, it is not unreasonable to assume that the reaction occurs at sufficiently high temperatures.

(b) With anhydrous halogen acids: Anhydrous halogen acids can also be used to supplement the solvent power of the fused salt or alter the nature of the dissolution products. Hydrogen is, of course, a hazardous byproduct of metal dissolution.

In general, the behavior of the halogen acids is similar to that of the free halogen except that the oxidizing power is not as great and the highest oxidation state is not formed in many cases. With HCl, zirconium forms $ZrCl_4$ and uranium forms UCl_4.[5] Plutonium doubtless forms $PuCl_3$.

With oxides, the following equilibria must be considered:

$$UO_2 + 4\ HX \rightleftharpoons UX_4 + 2\ H_2O. \qquad (1)$$

When the halogen is fluorine, the equilibria favors the right below 700 C and the left side above 800 C.[5,7] Other halogen acids are reported not to attack UO_2[5] which doubtless means that the left side of the equilibria is favored at even lower temperatures with these acids.

Halogen acids are, therefore, not likely to be employed in the process considered here. They are ineffective (HF excepted) in dissolution of UO_2, and present a hydrogen hazard upon dissolution of metals.

(c) Reduction halogenation: Should direct halogenation of oxide fuels fail to yield an adequately soluble uranium oxyhalide, reduction halogenation can be resorted to.[7,8]

By pre-reduction with carbon, it would be possible to liberate uranium so it can be halogenated:

$$UO_2 + C + 2\ X_2 \rightleftharpoons UX_4 + CO_2. \qquad (2)$$

Bromine has been shown to dissolve UO_2 in accordance with the above equation.[5]

The carbon can just as well be employed in a mixture with the free halogen, e.g., as CO, or as a halogenated compound, e.g., $COCl_2$ or CCl_4.[5,7,8] These reactions and some in section III-1-a lead to confidence that oxide fuels will not constitute an insoluble dissolution problem.

(d) Fused salt dissolution: Evidence has been presented in a prior report[9] that zirconium and uranium are adequately soluble in the salts of a number of more noble metals, including BiX_3. Dissolution usually results, however, in formation of the lower (and least volatile) halides which will require further halogenation to permit removal by distillation. W. J. Kroll cites numerous instances of molten salt dissolution reactions and their applications.[8]

Many metal oxides are appreciably soluble in the fused chloride of the metal. For example, 20 per cent by weight of CaO will dissolve in molten $CaCl_2$.[8] It is interesting to speculate on the possibility that UO_2 might have appreciable solubility in BiX_3 solutions containing UX_3 or UX_4.

Many metals dissolve in the halides of other metals, possibly forming sub-halides or dissolved metal with powerful reducing potential. Metals such as Ba, Sr, Ca, Na, K, Mg, Zn, Cu, Cd, and Pb behave in this way.[7] The behavior of bismuth in this respect will be of primary interest.

(e) Summary of dissolution reactions: From the reactions outlined in (a), (b), (c), and (d), it is possible to conclude:

1. Aluminum clad uranium metal fuels are best dissolved in molten BiX_3 alone.

2. Zirconium-clad, zircalloy-clad, and (with certainty) stainless steel-clad fuel elements can best be dissolved with assistance of free halogen to ensure formation and volatilization of the higher halides, ZrX_4, SnX_4, FeX_3, and CrX_3. With stainless steel cladding, the free halogen may be required to permit an adequate dissolution rate. With zirconium-clad or zircalloy-clad elements, free halogen may best be employed only during initial stages of dissolution, as in a cladding removal step.

3. Oxide fuel elements can probably be dissolved, with free halogen assistance, providing the resulting oxyhalide has sufficient solubility in the melt. Reduction halogenation might also be employed, following removal of the cladding as above. Considerable solubilization of UO_2 or UO_2Cl_2 might be achieved by dissolving uranium simultaneously to yield UX_3 or UX_4 in solution.

(2) Oxidation Reactions:

Following solution of the fuel element, separation of the cladding elements, and isolation of fuel constituents as halides, a method is needed to convert the fuel constituents to nitric acid soluble form. Of course, the anydrous chlorides or bromides are appreciably soluble in water and, if desired, could be dissolved directly in nitric acid. The halogens could then be distilled off as nitrosyl halide. This method results in a net consumption of halogen in the stoichiometric quantities required to combine with uranium, etc., since the nitrosyl halide would have to be reduced to the anhydrous halogen for recycle.

Oxygen is about the cheapest reagent that could be found to substitute for halogen so as to permit halogen recycle. Further, the oxides of the fuel constituents should be readily soluble in nitric acid. For the oxidation of halogens, the following reactions are available:

(a) With water vapor: Water vapor oxidizes hot halides by the equilibrium reaction:(5,7)

$$MX_4 + 2\ H_2O \rightleftharpoons MO_2 + 4\ HX \qquad (3)$$

This reaction goes to the right at temperatures above 800 C with fluorides. The same is probably true at still lower temperatures with chlorides and bromides. The reaction is the basis for an analytical method for determination of halogens in metal halides.(10)

(b) With oxygen: Oxygen displaces iodine, bromine, chlorine, and sometimes fluorine from metal halides with a facility in the order listed.(7) The multivalency of uranium and the variable stability of its halides combine to make the reaction more complex than with many elements:

With UF_4 (the lowest fluoride which can readily be formed), the oxidation proceeds as indicated by the following equations:

$$2\ UF_4 + O_2 \xrightarrow{800\ C} UF_6 + UO_2F_2. \qquad (4)$$

$$2\ UO_2F_2 \longrightarrow UO_2 + UF_4 + O_2. \qquad (5)$$

$$UO_2F_2 \longrightarrow UO_2 + F_2. \qquad (6)$$

$$4\ UO_2F_2 \longrightarrow U_3O_8 + UF_4 + 2\ F_2. \qquad (7)$$

The major products with oxygen in excess are, therefore, UF_6 and U_3O_8, plus fluorine. For the process envisioned here, the volatile UF_6 byproduct would be lost (similarly with plutonium); hence, the fluoride system cannot be regarded as suitable.

In the chloride system, both UCl_3 and UCl_4 must be considered. UCl_4 reacts with oxygen as follows:(5)

$$UCl_4 + O_2 \xrightarrow{>250\ C} UO_2Cl_2 + Cl_2, \quad (8)$$

$$3\ UO_2Cl_2 + O_2 \xrightarrow{>250\ C} U_3O_8 + 3\ Cl_2. \quad (9)$$

The chloride system would appear to be satisfactory; however, at temperatures in excess of 250 C, side reactions such as (10) and (11) can occur:

$$2\ UCl_4 + Cl_2 \xrightarrow{>250\ C} 2\ UCl_5, \quad (10)$$

$$2\ UCl_5 + Cl_2 \xrightarrow{>250\ C} 2\ UCl_6. \quad (11)$$

Small losses of uranium may occur in this manner. Plutonium would not behave analogously due to the instability of $PuCl_5$ and $PuCl_6$.(14) Its oxidation would probably lead directly to oxide and free halogen.

With UCl_3, oxidation starts according to the equation:(5)

$$2\ UCl_3 + O_2 \longrightarrow UO_2Cl_2 + UCl_4 \quad (12)$$

Whereupon, the same sequence of reactions may be assumed as with UCl_4.

Inasmuch as the higher bromides of uranium are unknown and believed to be too unstable to exist(5,6), the oxidation of uranium bromides (and iodides) is comparatively simple and yields the oxide and halogen in two steps. With UBr_4, e.g.:

$$UBr_4 + O_2 \longrightarrow UO_2\ Br_2 + Br_2, \quad (13)$$

and

$$3\ UO_2Br_2 + O_2 \longrightarrow U_3O_8 + Br_2. \quad (14)$$

Similarly, with UBr_3:

$$2\ UBr_3 + O_2 \longrightarrow UO_2Br_2 + UBr_4, \quad (15)$$

and this reaction is followed by the same sequence as with UBr_4.

(c) With metal oxides: As indicated in an earlier report,[9] the oxygen carrier may be a metal oxide.[7] The reactions may be represented by the following equilibria:

$$UX_4 + MO \rightleftharpoons UOX_2 + MX_2 \quad (16)$$

$$UOX_2 + MO \rightleftharpoons UO_2 + MX_2 \quad (17)$$

Clearly, where the halide MX_2 is volatile at the reaction temperature employed, the equilibria will be displaced markedly to the right.

(d) Selection of optimum oxidation reactions: The oxidation of UBr_3 begins at room temperature[5] and proceeds in a straightforward manner. In the bromide system, oxygen (or air) is the preferred oxidant. Any of the reactions mentioned should, however, be satisfactory.

In the chloride system, oxygen may not be satisfactory as a result of volatile UCl_6 formation. Either steam or metal oxides should be satisfactory alternates.

IV. DESCRIPTION OF POTENTIAL PYROCHEMICAL PROCESSES

In an earlier report,[9] a pyrochemical dissolution and head-end process was proposed which was based on the criteria:

(1) The solvent must be less volatile than cladding element halides, but more volatile than uranium and plutonium halides.

(2) The solvent must be more volatile than its oxide, so that distillation of the solvent drives the reaction.

(3) The metal (zinc or cadmium) must be sufficiently volatile to permit decontamination by distillation.

It is now recognized that only the first of these criteria is necessary to a successful process. Thus, a much wider choice of conditions is allowed.

A. Discussion of Dissolution and Head-End Process

For this example, $BiBr_3$ is chosen as the solvent. $BiCl_3$ is, of course, a suitable alternate. A schematic flow diagram of the process is shown in Figure 1. The dissolver design suggested earlier[9] may be satisfactory. It could be constructed of molybdenum which is resistant to bismuth metal to 1010 C[11] and very resistant to halogens.[12]

The molten solvent containing UBr_3 could be distilled as shown in a fluidized bed using nitrogen or argon as a fluidizing gas. In case removal of $ZrBr_4$ or $NbBr_5$ was incomplete during dissolution, a trace of

bromine could be added to the fluidizing gas to complete conversion of lower halides to volatile higher halides. These would distill and recycle to the dissolver and then volatilize to waste.

The fluidized bed still would operate at about 500 C. The effluent $BiBr_3$ vapor would be condensed at about 400 C to permit recycle of the fluidizing gas.

Solid UBr_3 would be discharged to a reactor where it is burned in oxygen (or air) to U_3O_8 with liberation of bromine. The bromine effluent is condensed to permit oxygen recycle and is then vaporized over molten bismuth coming from the dissolver to regenerate $BiBr_3$ for recycle. A heel of bismuth metal is always retained in this reactor to contain Mo, Te, Ru, Rh, and Pd fission products. Periodically, this heel is sent to waste where it solidifies to provide safe, low volume storage for these fission products.

A scrubbing tower (possibly a spray tower) is inserted between the dissolver and the bismuth-bromine reactor. Molten $BiBr_3$ coming from its condenser passes through this tower enroute to the dissolver and removes any entrained uranium and plutonium from the bismuth metal.

Finally, U_3O_8, etc., is dissolved in nitric acid. Residual halogen, if any, is removed by distillation.

It is intriguing to speculate on the possibility that oxidation of UBr_3 and distillation of $BiBr_3$ (including the excess) could be done in the same reactor. $BiBr_3$ should be markedly more resistant to oxidation than the other compounds present. If this could be done, oxygen (or air) would be substituted for the inert fluidizing gas, and U_3O_8 would discharge from the fluidized bed still. Two condensers in series, one for $BiBr_3$ and one for bromine, would permit recycle of the oxygen fluidizing gas. With air, recycle might not be required.

As outlined here, this process has certain advantages over the process proposed earlier:[9]

(1) Bismuth is less corrosive than cadmium or zinc.[11]

(2) Operating temperatures are 300 to 400 C lower, with consequent reduced corrosion and energy requirements.

(3) The kinetics of gas-solid phase oxidation will probably be better than those of solid-solid phase oxidation.

The process retains all the advantages of that previously proposed over aqueous methods. It is compact, provides safe, low volume storage of solid wastes, and yields substantial decontamination from Zr, Nb, Mo, Te, Ru, Rh, and Pd.

B. Complete Pyrochemical Process

The process described in the preceding section is essentially a dissolution and head-end process. Decontamination is completed after conversion to an aqueous phase using conventional solvent extraction processing. An alternate path is to go all the way to UF_6, the most logical HAPO uranium bearing product, and to use solvent extraction only for the low volume plutonium cycles.

A schematic flow diagram of a proposed process to achieve this objective is shown in Figure 2. The dissolver is identical to that described previously, and $BiBr_3$ is again the solvent. The salt phase leaving the dissolver is, as before, distilled in a fluidized bed, but here, sufficient bromine is employed in the fluidizing gas to ensure conversion of UBr_3 to UBr_4 (M.P. - 519 C). The distillation temperature must be carefully controlled between 453 C and 510 C to prevent melting of UBr_4.

UBr_4 leaving the bottom of the fluidized bed still is fed to a heat exchanger where it melts and flows to a bed of $BaBr_2$ fluidized by an inert gas containing a trace of bromine. UBr_4 (B.P. - 766 C) distills, leaving a deposit of $PuBr_3$ (B.P. - 1512 C) on the $BaBr_2$ (M.P. - 847 C) particles. The $BaBr_2$ bed is necessary as a diluent for plutonium from a criticality standpoint and as a collector for $PuBr_3$ (M.P. - 681 C) which is molten at these temperatures.

The UBr_4 effluent from the plutonium separation step is substantially decontaminated from alkali, alkaline earth, and rare earth bromides which are non-volatile and accompany plutonium. As such, UBr_4 is an undesirable product and may require additional decontamination.

The fluidizing gas containing UBr_4 vapor is allowed to cool below, e.g., 600 C, and passed into a bed of BiF_3 (M.P. - 727 C) where conversion to UF_4 and distillation of $BiBr_3$ results. $BiBr_3$ is recycled to the dissolver, and the UF_4-BiF_3 mixture emerging from this reactor is fluorinated to UF_6, the BiF_3 remains unchanged and is permitted to recycle. Final distillation of UF_6 completes its decontamination and separation from fluorine, wereupon it may be shipped to the diffusion batteries.

It should be noted that the reaction:

$$3\ UBr_4 + 4\ BiF_3 \xrightarrow{500\text{-}600\ C} 3\ UF_4 + 4\ BiBr_3\uparrow \qquad (18)$$

has a "built in" driving force, in that volatile $BiBr_3$ is formed. Further, BiF_3 is furnished by reaction of anhydrous HF vapor with molten Bi emerging from the dissolver. As with the previous process, a heel of molten bismuth is maintained as a repository for Mo, Te, Ru, Rh, and Pd fission elements. Unfortunately, the BiF_3

(M.P. - 727 C) must be transferred as a molten phase from this reactor and cooled and solidified before being fed to the reactor where conversion of UBr_4 occurs.

Returning now to the $PuBr_3$-$BaBr_2$ phase, this is reacted with oxygen to liberate bromine for process use and convert the bromides to oxides soluble in nitric acid. $Ba(NO_3)_2$ formed in this way serves as a portion of the required salting strength in a Redox or TTA type series of solvent extraction cycles. An ion exchange process could also be used.

As in the preceding process, all bismuth is recycled except the discarded heel. Anhydrous HF is consumed at the rate of four moles/mole of uranium (with HF at $0.20/lb, this is $128/ton of uranium). Fluorine requirements are identical with those of the present process. Aside from the initial inventory (as $BiBr_3$), all bromine requirements to make up losses of cladding element bromides are furnished by bromine recovered from $BaBr_2$ (currently quoted at $0.53/lb in 100 lb drums)[13] or free bromine (at $0.30/lb). A portion of this cost can be charged to aqueous decontamination cycles as cost of salting agent. Other chemical costs include the cost of fluidizing (inert) gases and small amounts of nitric acid and hexone. On the whole, the writer doubts that chemical costs will greatly exceed those of combined aqueous processing and UF_6 production.

The path of fission products in this process differs markedly from that of present processes. Cladding elements and fission product zirconium-niobium are stored as solid bromides. Solid bismuth metal (one to five per cent of the total) is used to confine Mo, Te, Ru, Rh, and Pd. Any of these, plus Zr-Nb, reaching the fluoride volatility stage will be accommodated as neutralized wastes.

Alkali metals, alkaline earths, and rare earths stay in low volume plutonium cycles. These will eventually appear as neutralized waste, but of smaller volume than presently obtained.

In comparing this process with an all fluoride volatility process, note that a substantially better decontamination potential exists. Decontamination from about 99 to 99.9 per cent of Zr, Nb, Mo, Te, Ru, Rh, and Pd is obtained during dissolution. Decontamination of uranium from alkali metals (Cs, Rb), alkaline earths (Sr, Ba), and rare earths during distillation of UBr_4 should be very substantial ($>10^3$). Additional decontamination of UBr_4 from Zr, Nb, Ru, Rh, Pd, Mo, and Te is also possible at this point. The final UF_6 distillation step would have to achieve a decontamination factor of only 10^3 to 10^4 to yield a specification product. This is readily attainable.

Mo and Te are troublesome elements in the all fluoride volatility process. Here the concentration of these elements is markedly reduced in advance of UF_6 distillation. In addition, troublesome plutonium is separated prior to conversion to fluoride. This is done to avoid problems of PuF_4 and PuF_6 instability.

The process offers advantages over conventional solvent extraction as follows:

(1) Due to the high density of process streams, the process is more compact, leading to low capital investment.

(2) It is simple in concept. The number of processing steps leading to UF_6 production is approximately equal to the number required to produce decontaminated uranyl nitrate by solvent extraction. Thus, UO_3 production and conversion to UF_6 is entirely eliminated.

(3) The process is less sensitive to criticality considerations in view of the absence of water (hydrogen). The plutonium cycles (solvent extraction), if designed "always safe", would permit this type plant to process natural or enriched fuels at will.

(4) Fission products, e.g., Ru, Rh, Pd, Mo, and Te, are, in the main, confined within compact, solid metal. Zirconium and niobium, along with the cladding elements, are stored as solid halides. Wastes from low volume plutonium cycles contain long lived fission products, but these will constitute substantially smaller volume than similar wastes currently stored.

(5) Recycle of process chemicals can probably keep chemical costs about as low as in the present solvent extraction process.

C. Process Variations of Interest

Alternate processes can be devised using oxygen or steam or metal oxides as oxidants. Solvents such as $CdBr_2$, $CdCl_2$, $ZnBr_2$, $ZnCl_2$, or other salts can be used.

Metal separating in the dissolver can be distilled for deentrainment or decontamination or can be reacted with either free halogen or halogen acids, produced in the process, to regenerate the solvent.

V. CONCLUSIONS

The processes outlined here appear to have a sound theoretical and chemical basis. They appear to have four singular advantages over presently conceived pyrochemical processes elsewhere considered:

(1) Moderate operating temperatures can be employed permitting use of metal equipment.

(2) The process can be integrated rather simply with existing solvent extraction facilities.

(3) The process is potentially capable of processing all or most of the fuel elements and cladding materials of any significance.

(4) As a complete pyrochemical process, the decontamination potential for the uranium product exceeds that of any pyrochemical process proposed to date. Plutonium separation from uranium is simultaneously achieved.

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TABLE I

VOLATILITY DATA OF PROCESS INTEREST

Compound	Melting Point, °C	Boiling Point, °C
$BiBr_3$	218	453
$BiCl_3$	229	441
UBr_3	752	1567
UCl_3	835	1727
UBr_4	519	766
UCl_4	590	787
$PuBr_3$	681	1512
$PuCl_3$	760	1767
$ZrBr_2$	627	1227
$ZrCl_2$	727	1477
$ZrBr_4$	---	357 (sublimes)
$ZrCl_4$	---	331 (sublimes)
$NbBr_2$	---	non-volatile
$NbCl_2$	---	non-volatile
$NbBr_5$	227	272
$NbCl_5$	210	246
$AlBr_3$	97.5	263.3
$AlCl_3$	---	180 (sublimes)
$SnBr_2$	215	620
$SnCl_2$	247	652
$SnBr_4$	30	207
$SnCl_4$	-33	113
$SiBr_4$	3	153
$SiCl_4$	-68	57
$NiBr_2$	---	977 (sublimes)
$NiCl_2$	---	987 (sublimes)
$FeBr_3$	227	627
$FeCl_3$	304	319
$CrBr_3$	---	927 (sublimes)
$CrCl_3$	---	947 (sublimes)

FIGURE 1
SCHEMATIC FLOW DIAGRAM FOR DISSOLUTION AND HEAD-END PROCESS WITH NO METAL DISTILLATION

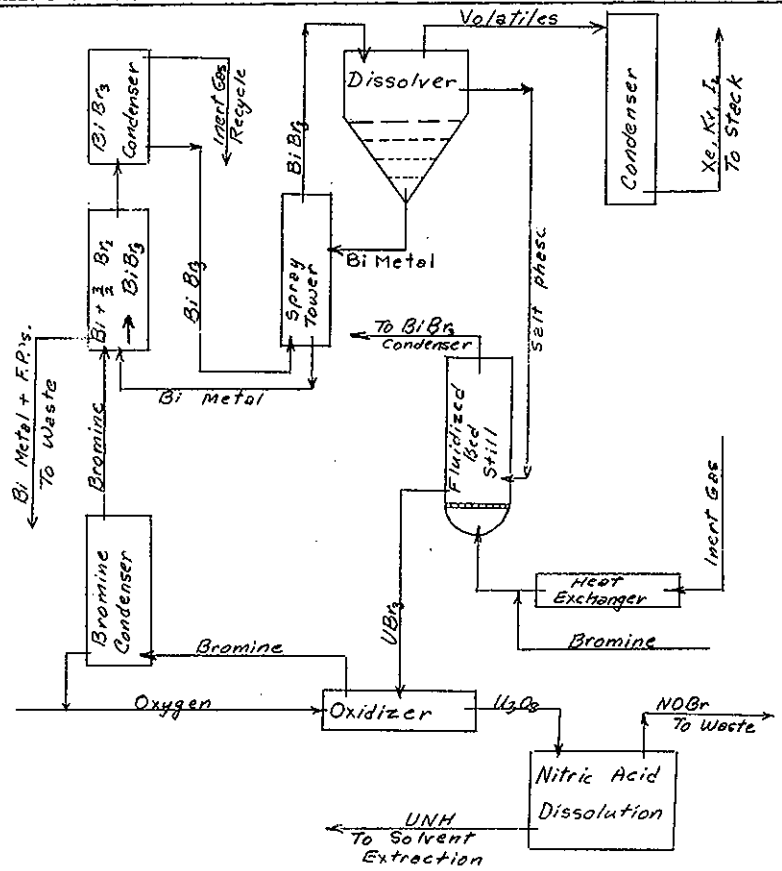
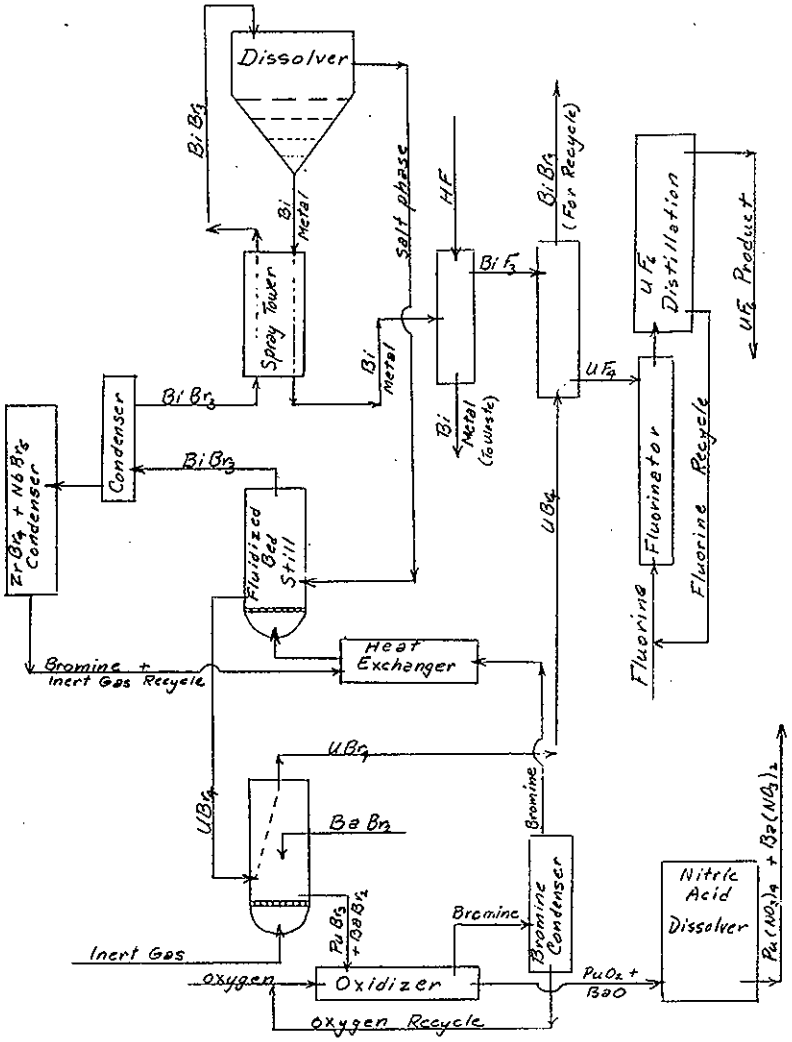


FIGURE 2

SCHEMATIC FLOW DIAGRAM FOR COMPLETE PYROCHEMICAL PROCESS TO UF_6 AND $Pu(NO_3)_4$



APPENDIX

PROBLEMS IN HANDLING SUBLIMATES IN PYROCHEMICAL PROCESSING

In the pyrochemical dissolution and head-end process proposed here, problems may arise in the handling and disposal of cladding element halides which sublime from the dissolver. These will be accompanied by volatile fission product halides and fission product permanent gases. In addition, free halogen gases of appreciable value may be present, if necessary for control of oxidation state or dissolution rate.

The subliming cladding element and fission product halides must be removed from the dissolver off-gases to permit iodine removal prior to dispersion of permanent gases in the atmosphere via the stack. It is proposed here to utilize a fluidized bed as a condenser and collector for the subliming materials. Air could be used as the fluidizing gas.

The bed medium could be varied to suit the circumstances. If zirconium is the cladding element and its eventual recovery is desired, the bed can be the zirconium halide issuing from the dissolver.

The bed must be cycled through a heat exchanger so that the particles of the bed rather than the wall of the unit serve as a heat transfer surface. Operated in this way, the fluidized bed avoids difficulties with clogging and variable heat transfer in condensers of more conventional design. Its operability, using $ZrCl_4$, has been demonstrated.(15)

A portion of the bed can be continuously discharged to waste containers to be sealed and stored. Radioactive heating during storage can be controlled by varying the ratio of non-radioactive bed make-up material to radioactive material condensing.