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POSSIBLE PROCESS ALTERNATIVES FOR CONVERTING RECOVERED URANYL NITRATE TO URANIUM HEXAFLUORIDE

SPECIAL RE-REVIEW
FINAL DETERMINATION
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INTRODUCTION

The uranium recovery processes which are in operation or under construction at the present time — TBP, Redox and Purex — yield an aqueous uranyl nitrate solution as the recovered uranium product. For conversion of this recovered uranium to UF_6 for feed to the gaseous diffusion plants, the uranyl nitrate in the solution is concentrated with or without prior organic stripping, calcined to UO_3, reduced to UO_2 with hydrogen, hydrofluorinated to UF_4 with HF, and finally fluorinated to UF_6 with elemental fluorine.

In practice, the above series of reactions has encountered three principal operating difficulties. They are:

1) Metal contamination of the uranium (principally due to corrosion in the concentrators) which necessitates a repurification step.

2) Foaming during calcination of UNH produced by a solvent extraction process employing TBP solvent. When this difficulty is encountered the calcining time cycle is greatly increased and production capacity is seriously curtailed.

3) Poor reactivity of the UO_3 in the reduction and hydrofluorination reactions, thereby limiting the capacity of the equipment for converting UO_3 to UF_6.

The present memorandum, without intending to be in any way an exhaustive study of the subject, has been prepared for the purpose of reviewing some processing alternatives which would alleviate these difficulties and perhaps provide other benefits in addition. These alternatives may serve as suggestions for future development of improvements for the particular portion of the uranium processing cycle in question; they have arisen during laboratory studies of means of eliminating the above noted difficulties. Without detailed consideration of economic or engineering implications of the alternatives, the following summary lists recognized reactions or operations which have been demonstrated in the laboratory to be chemically feasible.

The advantages offered by these alternatives make them worthy of thorough economic and process comparisons to place them on a quantitative rather than qualitative basis, and the request is herewith submitted for such an evaluation to be undertaken by the Process Studies group of the Chemical Development Unit.

SUMMARY

Some possible alternative operating procedures may be summarized as follows:

1) Precipitation of UO_4 from the aqueous UNH solution without prior concentration, followed by reduction, by hydrofluorination, then fluorination. The peruranic acid is produced as an indefinite hydrate. Indication of the water of hydration is omitted in this memorandum.

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2) Uranyl oxalate precipitation followed by reduction. hydrofluorination, then fluorination.

3) Ammonium diuranate precipitation followed by the same sequence of reduction, hydrofluorination, and fluorination.

4) Electrolytic precipitation of UO_3 from the aqueous solution followed by the presently used series of reactions for conversion of UO_3 to UF_6.

5) Precipitation of UO_2F_2 from the organic extract stream followed by reaction with fluorine to produce UF_6.

6) Adsorption of UNH in an ion-exchange column, elution with excess HF to form UO_2F_2, and electrolysis of the UO_2F_2 to form a slurry of UF_4.

7) Reduction of the UO_2^{+2} to U^{+4} by chemical means, e.g. stannous ion, and precipitation of UF_4 with a fluoride.

DISCUSSION

The means are already at hand for alleviating, if not completely removing, all three of the difficulties noted for the present series of operations for converting solvent extraction recovered uranium to diffusion plant feed. 1) The metal contamination resulting from concentrator corrosion can probably be reduced by use of different materials of construction, a different type of concentrator, or by altering operating procedures. 2) Foaming of TBP-produced solutions during calcination can at least be kept under control if not completely prevented, by adequate phase separation (decantation), by stripping to remove dissolved or entrained organic, and by limiting storage time prior to concentration and calcination. 3) The reactivity of UO_3 in the reduction and hydrofluorination reactions can be improved by hydration of the oxide to form the mono- or dihydrate. Whatever advantages there may be in the processing alternatives listed in the summary arise from the fact that on a laboratory scale they do a far superior job of eliminating the present basic difficulties. Furthermore, they present the possibility of lowering 1) over-all cost, 2) metal contamination (in addition to eliminating corrosion contamination), and 3) fission product contamination. The achievement of additional fission product decontamination in the course of the coupling process could effect savings in the solvent extraction recovery of uranium. The possible advantages and disadvantages of each alternative coupling process are briefly discussed below.

1. The disadvantages of precipitating UO_4 from aqueous uranyl nitrate solution include the relatively high cost of the hydrogen peroxide required, and the difficulty associated with handling a highly bulky precipitate.

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There is also the possibility of increased consumption of hydrogen during the reduction operation unless the UO_4 is first heated to drive off the additional oxygen; this occurs above about 150°C. Advantages include 1) the reduction of metal contamination of the uranium, 2) elimination of concentrator corrosion, 3) elimination of calcination foaming, and 4) the production of UO_3 which is at least twice as reactive as the UO_3 produced by UNH calcination followed by hydration. Some fission product decontamination is achieved by UO_4 precipitation.

2. Uranyl oxalate is appreciably more aqueous-soluble than UO_4, but is otherwise a potentially better intermediate than UO_4. Costs for oxalic acid are less than for hydrogen peroxide, metal contamination is reduced, good fission product decontamination is achieved, the foam problem is eliminated, and the product is extremely reactive in the reduction and hydrofluorination operations. It is reported in the literature (Bull. Soc. Chim., France, 11, 531 (1912)) that simple heating of uranyl oxalate in the absence of air produces UO_2 without the use of hydrogen.

3. Ammonium diuranate precipitation eliminates corrosion contamination from the concentrators, but is otherwise relatively ineffective in metal impurity removal. The cost is less than either the oxalate or peroxide precipitations. Foaming is eliminated, and the product is extremely reactive in the reduction and hydrofluorination operations. The possibility of fission product decontamination is uncertain.

4. Electrolytic precipitation of UO_3 is relatively cheap; the literature (K-600, Part I) reports that the energy cost is less than one cent per pound of uranium which is only possible by virtue of the fact that the uranium is transported rather than reduced by the electric current. Concentrator corrosion and foaming are eliminated by this operation. Fission product and metal decontamination are uncertain. Since the lower reactivity of UO_3 produced by UNH calcination is definitely associated with the calcining step as well as with the presence of metallic impurities, it could be expected that UO_3 produced by electrolytic deposition would be about as reactive as uranyl oxalate, UO_4, or ammonium diuranate, in the reduction and hydrofluorination operations. It may be noted in this connection that UO_3 produced by heating UO_4 at 370°C. for one hour is almost as reactive as the original UO_4, which shows about twice the reactivity of any trioxide produced by UNH calcination and subsequent hydration.

5. Chemically, the coupling of uranium recovery to the UF_6 diffusion process, could be greatly simplified by precipitating uranyl fluoride directly from the organic extract stream, then fluorinating the product to yield UF_6. The reactions would be as follows:

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a) $UO_2(NO_3)_2 + 2HF \longrightarrow UO_2F_2 + 2HNO_3$,
b) $UO_2F_2 + 4F_2 \longrightarrow UF_6 + 2F_2O$.

The first reaction has been demonstrated in the laboratory to precipitate the uranium essentially completely. Although the second reaction is reported in the literature, it was not demonstrated in the Process Chemistry Laboratories due to the non-availability of elemental fluorine at HAPO. In this procedure uranium could be transferred in the form of solid UO_2F_2 from one site to another.

Obviously the procedure outlined would eliminate the reactivity, foaming, and corrosion problems, but would introduce many others. The organic stripping column would be eliminated. The heat energy consumption involved in the concentration, calcination, reduction, and hydrofluorination reactions would be eliminated. Consumption of HF would be theoretically half as much, but the consumption ' fluorine would be twice as great (allowing for the recovery of fluorine from fluorine oxide). The consumption of hydrogen for reduction would be eliminated. The effect of the UO_2F_2 precipitation on metal impurity and fission product decontamination is unknown at this time. A number of modifications of this procedure are possible.

6. Although nothing has been done in our laboratories on the ion-exchange-electrochemical reduction method, it has been studied at Oak Ridge with definitely encouraging results. Preliminary cost estimates indicated that uranium can be converted to UF_4 at a cost of 20 to 25 cents per pound, which is considerably cheaper than the present method.(1,2) The decontamination from fission products and metallic impurities is not known but is under study.

   NOTE: In view of present plans for a pilot plant (fiscal 1954 and 1955) to be built at ORNL to study this process further, it would seem desirable to take urgent action to review the entire problem, with the thought in mind that this pilot plant (and associated studies) should more logically be located at HAPO.

7. Little is known here regarding the suitability of chemical reduction of UO_2^{+2} to U^{+4} with stannous or ferrous ion, with H_2 or NH_3 gas at elevated temperature, or with zinc. These have been shown by workers at Oak Ridge to be feasible but much less desirable than 6), above.(1)

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In conclusion, it may be noted that the chemical operations now in use were developed for the preparation of diffusion plant feed from natural uranium which was purified by batch ether extraction. These reactions had already been defined prior to the undertaking of the atomic energy program. With the recovery of irradiated uranium by continuous solvent extraction utilizing other solvents and with the expanded knowledge of the chemistry of uranium now available, it is <u>inconceivable</u> that a cheaper method cannot be developed for coupling the recovery of irradiated uranium to the enrichment or separation of U^{235} by gaseous diffusion.

The purpose of this brief review is simply to point up a few of the many possible avenues of approach to a more satisfactory process, and to suggest that intensive development studies be initiated for those which hold out the greatest promise of achieving reduced unit costs.

M K Harmon
M. K. Harmon, Process Chemistry

(1) ORNL - 1494, Chemical Technology Division Quarterly Progress Report, for Period Ending 2-20-53.

(2) HW-28665, Report on Visits to KAPL and ORNL, [illegible] B. Barton, 7-10-53.

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