LETTER TO THE EDITOR

COMMENTS ON "NUCLEAR FUEL REPROCESSING OF (U,Pu)O_2 FUEL"

Reference 1 proposes a method for reprocessing of uranium and plutonium mixed-oxide (MOX) fuel. The technique adopts the following steps: a voloxidation process to oxidize the fuel, selective dissolution of uranium and its purification by solvent extraction, and reductive dissolution of plutonium dioxide using uranous nitrate.

The author of Ref. 1 appears to have oversimplified many aspects and has assumed several things by taking them for granted. Based on these assumptions, which are in practice far from the truth, he lists several advantages, particularly related to the economics of the industrial process. These claims, in our opinion, will be difficult to attain in practice.

First, consider the application of this process to natural uranium oxide thermal reactor fuel (according to Ref. 1, because of the 1% plutonium formed in the fuel, this fuel also belongs to the category as defined there). Reference 1 does not bring out specifically how this method is superior or economical compared with conventional methods. The author of Ref. 1 wants to claim higher decontamination because of the voloxidation process and thereby states that the purification step of solvent extraction is not necessary. As thermal reactor fuels are normally cooled a long time, decontamination from fission products, particularly gaseous fission products, is marginal by voloxidation, and it cannot make the fuel free from radioactivity and suitable for direct refabrication. The author also suggests that the solvent extraction process be used to purify uranium. Since he is advocating that uranium and plutonium not be separated, we are unable to understand the use of reductive dissolution. If there is no need to separate plutonium from uranium, we see no purpose being served by this process. We are also sure that this process is not necessary for the purpose of dissolution of plutonium dioxide, as plutonium dioxide to the 20% range in MOX fuel is easily soluble in nitric acid if proper care is taken to ensure that the plutonium is in the solid solution phase. In fact, there are references where solubility is claimed for a wide range.[2]

Thus, we see that this process neither decontaminates to the degree needed nor is it necessary for the dissolution of plutonium; it is an unwarranted complication. The additional problems associated with this process when applying it to industrial reprocessing are not realized. Normally, thermal reactor fuels in industrial plants are processed at the rate of 1 to 5 tonne/day. To carry out the suggested process for this large volume of fuel, using a high-temperature operation is technically complicated and economically not encouraging for the following reasons:

1. At the highly active head-end step, a process for handling solids at a high temperature is being used.

2. The choice of a suitably corrosion-resistant material and problems of maintenance are involved.

3. The off-gas from the voloxidation process has to be specifically filtered and treated using high-temperature-resistant filters to prevent carryover of particulate matter bearing plutonium.

Problems are involved in transferring calcined fuels from the calciners to the dissolver as *in situ* dissolution in a calciner cannot be done because the material used for calcination will not be corrosion-resistant to nitric acid. Such nitric acid-resistant material is very costly.

Hence, the process cannot avoid transfer of solids or powder bearing plutonium. The process of transferring such material from the calciner to the dissolver without loss is difficult.

4. It is assumed that, while dissolving the oxidized fuel, no plutonium will go into solution; whereas in practice, plutonium will dissolve in sufficient quantity and will be associated with uranium, which will make it difficult to handle this uranium without proper precautions, particularly without providing alpha containment.

5. The process assumes that the oxidation will leave the plutonium dioxide in a state that will not dissolve in nitric acid. After dissolving uranium in nitric acid, if the uranium solution has to be taken out for purification as mentioned, a filtration step must be introduced to separate plutonium. Otherwise, the insoluble plutonium will be lost in the raffinate solution. The process assumes that after oxidation, no plutonium will dissolve but only uranium will dissolve.

6. But the uranium solution taken after dissolution will always contain sufficient plutonium, and hence, the process of reducing the U(VI) solution to U(IV) must be carried out within an alpha containment after the solution is purified by solvent extraction in a shielded containment; shielding will be necessary because voloxidation alone cannot remove all fission products. We do not find the need for all these processes to put plutonium and uranium back in solution.

7. The author assumes one uranium purification cycle alone is sufficient to make it fit for direct refabrication. In the case of uranium decontamination, plutonium resulting

from direct dissolution of the fuel without voloxidation will also be suitable for refabrication. Highly effective decontamination processes have recently been demonstrated.[3]

We suggest a simpler process for this fuel under the conditions assumed in Ref. 1, namely, natural uranium fuel bearing 1% plutonium, sufficiently cooled so that direct fabrication can be attempted with one cycle of solvent extraction. Direct denitration of codecontaminated solution results in the formation of oxides. This process is shown in Fig. 1.

To summarize, if the process proposed in Ref. 1 is adopted for thermal reactor fuel as suggested, it will involve handling large volumes of high-activity solids in a high-temperature process. The uranium must be filtered using large volumes, and solvent extraction of uranium must be carried out in a shielded cell with alpha containment, as the uranium will not be free of fission product activity or plutonium. Since fission products would not have been fully decontaminated from the fuel, refabrication must be carried out from behind a shield, i.e., remotely. This is in no way better than the conventional process from an operational point of view, and it may not be economical as a whole as more steps are involved and remote refabrication is necessary.

Here, for the simple case, the fuel is assumed to be CANDU-type natural uranium oxide irradiated to 9000 MWd/tonne U and cooled for at least 2 yr. (It may be mentioned that none of these parameters is defined in Ref. 1.) The uranium purified by one cycle of solvent extraction cannot be discarded as mentioned, because of its plutonium content. It must be stored until it is cooled and refabricated; this has cost implications.

Considering application of the proposed process for other fuels containing up to 20% plutonium, it has been demonstrated in an industrial plant that fuel can be dissolved directly in nitric acid, if proper care is taken during fabrication. Hence, this method is not necessary for the purpose of dissolution of the plutonium dioxide. Voloxidation alone cannot decontaminate the fuel sufficiently to avoid solvent extraction or purification to make it suitable for direct fabrication. Hence, refabrication must be done remotely. All the other disadvantages mentioned with respect to thermal reactor fuel such as filtration steps, shielding, and alpha containment for reduction of U(VI) to U(IV), etc., are also applicable here. A simpler scenario that has been experimentally tested is given separately. Incidentally, no mention was made in Ref. 1 of whether or not this process was carried out experimentally and tested on a pilot scale.

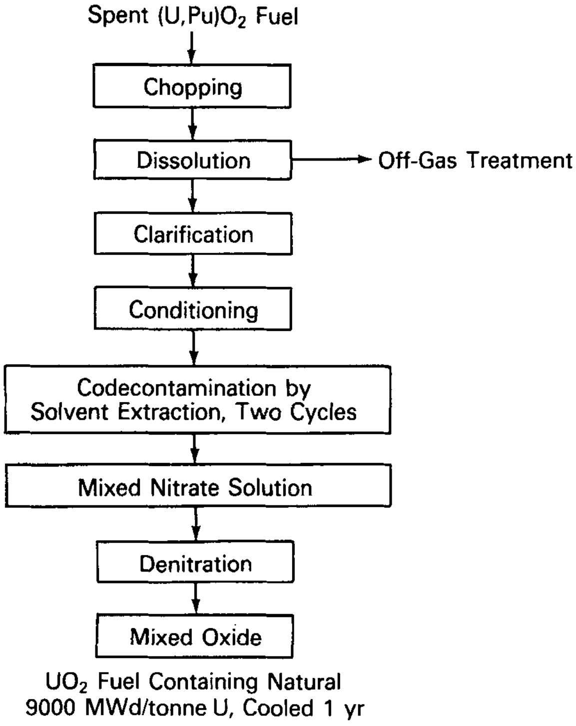

Fig. 1. Scheme for reprocessing of thermal reactor fuel.

The dissolution process using U(IV) as a reductive step is less efficient, needing U(IV) in quantities greater than a stoichiometric amount with the use of the holding reductant, namely, hydrazine. This method, if adopted for fast reactor fuel, will be more cumbersome than the usual method and will not be economical.

We propose a method that has been tested in our laboratory; it is described in the Appendix. It is proposed that it be used on an industrial scale. This method also has the advantages of being applicable to other advanced fuels such as mixed carbide or uranium and plutonium nitride.

The scenario for reprocessing fast reactor and advanced fast reactor fuel is given in Fig. 2. If the plutonium content is <20% in MOX fuel, an electrooxidation step is not necessary. The process currently followed at Dounrey or Marcoule can be adopted. For a higher percentage of plutonium or for mixed-carbide fuel, our process will have the advantage. In the process we suggest, the handling of solids at the active end using voloxidation is avoided, as the fuel is directly chopped into the electrolytic-type dissolver. The electrooxidative dissolution technique (EODT) enhances the dissolution of plutonium dioxide or mixed-carbide fuel. It also destroys the organic acids formed during the dissolution of mixed-carbide fuel in nitric acid almost quantitatively.

The merits and demerits of the reductive dissolution suggested in Ref. 1 and the EODT we propose are compared as follows:

1. Electrolytically reduced U(IV) (0.2 *M*) must be stabilized by 0.5 *M* hydrazine. Hydrazine is a potential explosion hazard, especially when used at high temperature. Use of hydrazine is avoided in the EODT.

2. The reductive dissolution process is carried out at 90°C for 2 to 3 h, whereas the EODT process in the presence of a silver catalyst is a room-temperature operation.

3. Noble metal fission products such as molybdenum, technetium, ruthenium, rhodium, and palladium exist not only in metallic phases, but also in intermetallic alloys of the composition $U,Pu(Ru,Rh,Pd)_3$. In the reductive dissolution process, that alloy is present along with the metallic fission product residue. In the EODT process, the uranium and plutonium will be leached from that alloy because uranium and plutonium are baser metals as compared with palladium, ruthenium, and rhodium. This has the advantage that (a) the valuable plutonium is recovered by leaching from the solid waste, (b) the disposal of the insoluble waste becomes easier, as the alpha-emitting plutonium is removed from waste, and (c) the introduction of 0.2 *M* U(IV) from the electrolytic reduction step into the reductive dissolution process increases the liquid waste volume, because in our process after the EODT, U(VI), if needed to make up a particular composition of fuel for refabrication, can be introduced from a concentrated solution of 1.26 *M* or more.

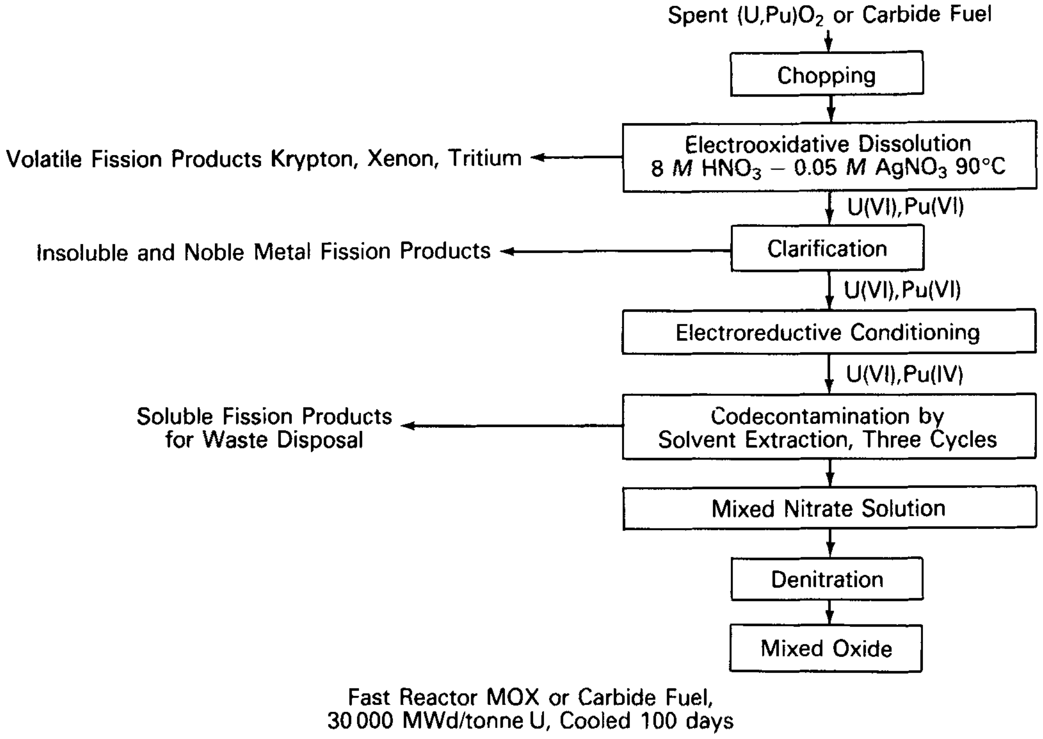

Fig. 2. Scheme for reprocessing of fast reactor fuel.

Because of these advantages, it is recommended that voloxidation and the last two steps of the proposed process, namely, electrolytic reduction and reductive dissolution, may be replaced by the EODT.

Thus, for MOX fuels bearing <20% plutonium, the present process itself is simpler. If refabrication could be remotely carried out, the processing steps also could be reduced. It appears that the field of specialization of the author of Ref. 1 is in the area of oxidation kinetics of uranium oxides. Using some of his ideas, he has extended it to the area of fuel reprocessing, and he is probably not familiar with problems associated with industrial fuel reprocessing. Even in the oxidation kinetics of uranium oxides, attention is drawn to the conclusion in Ref. 2.

APPENDIX

Description of the Electrooxidative Dissolution Technique

In this technique, electrooxidation is carried out in 8 M HNO_3-0.05 M $AgNO_3$. Both compartments are separated by a porcelain diaphragm. About 6 V is required to sustain a 3-A current through the cell. The anode is platinum-plated titanium gauge, and the cathode is a 1-mm-thick × 10-mm-diam coil of titanium wire.

When this method is applied to advanced fast reactor fuels such as mixed carbide, the electrooxidation enhances the rate of dissolution of the fuels and oxidatively destroys the soluble organic acids formed from the dissolution of the carbide in nitric acid, such as oxalic acid, mellitic acid, and some unidentified ones, within 6 h of electrolysis. This technique enhances the rate of dissolution of plutonium dioxide. Hence, it is also applicable to MOX fuels. This method works in the presence of 1% ruthenium, and thus this method is also applicable to irradiated fuels, unlike the 4 M HNO_3 – 0.1 M U(IV) dissolvent. The latter method has been found to fail for irradiated fuels because of the presence of ruthenium, a fission product.

This method eliminates the use of corrosive hydrogen fluoride. Also, in this method, uranium and plutonium present in the intermetallic alloy with noble metal fission products such as ruthenium, rhodium, and palladium are leached.

The entire plutonium after EODT will be present in the hexavalent state. Then conditioning involves adjustment of free acidity to 4 M HNO_3 and reduction of Pu(VI). This reduction can be carried out electrolytically. This avoids use of $NaNO_2$ or NO_2 gas for reducing Pu(VI) to Pu(IV). By choosing the correct initial acidity for dissolution, one may not be required to adjust the free acidity. The acidity of 4 M can be obtained after EODT itself.

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