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Chemistry-Separation Processes for Plutonium

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HIGH TEMPERATURE DECONTAMINATION AND SEPARATION PROCESSES

Leo Brewer

May 6, 1949

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High Temperature Decontamination and Separation Processes

by

Leo Brewer

This paper is based on thermodynamics calculations performed in 1945.

It would be very desirable to have a separation and decontamination procedure which would separate the uranium, plutonium, and fission products without introducing any large amounts of new material and which, if possible, would keep the uranium in the same state as it is used in the pile. The following high temperature procedures were considered from this viewpoint, using available thermodynamic data to calculate the feasability of the proposed procedure.

I. Decontamination in the Metal State

A. Decontamination by Vaporization: A possible decontamination procedure would be the hydriding of uranium metal to the powdered hydride and then dehydriding at 500°C. with removal of volatile fission products with the hydrogen. If we assume that all rates of diffusion are rapid and that no intermetallic compounds or solid solutions are formed, then Xe, which comprises about 9% of the fission products, and Cs, which comprises about 6% of the fission products, could be removed. No other main fission product could be removed and no uranium nor plutonium would be removed. If the uranium were heated up to its melting point, Ba and Sr, which together comprise 13% of the fission products, could also be removed. Thus only a total of 28% of the fission products could be removed as gaseous Xe, Cs, Ba, and Sr. In addition to these, one would also expect to vaporize Rb, I, Kr, Br, Sn, Cd, and Sb, but these altogether do not comprise 5% of the fission

products. Some Te, which comprises less than 5% of the fission products, might also vaporize, but one would expect a relatively stable uranium telluride to be formed which would greatly reduce the volatility of Te. Thus under optimum conditions at the melting point of uranium, one could not remove as much as 38% of the fission products. Since elements like Mo, Zr, the rare earth metals, Ru, and Cb would not be removed to any appreciable extent, it is clear that it would not be worth the trouble of heating up the uranium to remove the volatile fission products.

B. Decontamination by High Temperature Scavengers: A possible procedure of great value would be the treatment of uranium metal with some material which would remove the plutonium and fission products leaving uranium metal which could be returned to the pile if one were working with enriched material or which could be used as a pile reflector or for other purposes if too highly depleted. A number of possible materials which could be added to molten uranium will be considered. It will be assumed that the melting of the uranium has removed the volatile fission products Xe, Ba, Sr, Cs, Rb, I, Kr, Br, Sn, Cd, and Sb.

If a small amount of carbon were added to the molten uranium, it is possible that the zirconium and columbium might separate as a light scum and could thus be removed from the uranium. It might even be conceivable for some of the rare earth metals to also be removed with the Zr and Cb. If all of these elements were actually removed by this process plus the elements removed by vaporization, one would have removed all of the important fission products except Mo which amounts to almost 13% of the fission products and Ru which amounts to almost 10% of the

fission products. However, it would be necessary to check the solubilities of these carbides in uranium. By adding somewhat of an excess of carbon so that UC would also be formed, one might get better removal of the fission product carbides as a mixture with or a solution in UC. The plutonium would, however, remain with the uranium. Without removal of the plutonium, it would probably not be worth the trouble of handling of molten uranium just to remove the fission products.

Addition of nitrogen would be much less effective than addition of carbon for removal of the fission products and although PuN is believed to be more stable than UN, there is not likely to be any appreciable separation of the small amount of Pu present.

Addition of oxygen as the gas or in the form of solid UO_3 would probably remove all the rare earth metals including Y and possibly also plutonium in an oxide scum which could be removed. However, Mo, Zr, Ru, and Cb which comprise 43% of the fission products would not be removed. The value of this step would depend upon the removal of plutonium. If effective removal of plutonium from uranium metal by addition of UO_3 can be obtained, this might be a valuable step. If successful, the oxide treatment could be followed by a carbon treatment which could remove Zr and Cb and thus the plutonium, and all major fission products but Mo, Ru, and probably Te would have been removed from the uranium by a vacuum heating, followed by treatment with UO_3 and removal of the oxide scum, and then treatment with carbon and removal of the carbide scum.

The use of US_2 instead of UO_3 would produce essentially the same results except that removal of plutonium would probably be more effective. Since this is a critical point, it would be important to check the distribution of plutonium between uranium metal and US solid as well as the distribution of plutonium between uranium metal and UO solid as suggested above. Mo and Ru would remain in the uranium as in the oxide case.

The addition of UI_3, UBr_3, or UCl_3 offers the possibility of removal of plutonium and fission products as either a halide scum or as gases. In either case, the separation would be essentially the same as for the oxide or sulfide systems although the plutonium separation might be more effective with the use of the halides. Addition of UF_3 would give one a fluoride scum which would also contain plutonium and the rare earth elements as in the case of the other halides.

Thus, one would conclude that there is a possibility that a procedure which involved vacuum casting of uranium metal, treatment with a halide, oxide, or sulfide of uranium and removal of the scum, and treatment with carbon and removal of the scum would result in separation of plutonium and all of the major fission products from the uranium except for Mo and Ru. The possibility appears promising enough to warrant experiments to check the results of the thermodynamic calculations.

II. Decontamination of Uranium as a Carbide

We might consider the possibility of using uranium carbide in the pile or converting uranium metal from a pile to a carbide

by reacting with carbon to obtain UC for example and then heating this carbide in order to vaporize volatile fission products. Since the carbide is high melting, one could use a much higher temperature and thus vaporize less volatile elements that could not be vaporized from the metal. However, the thermodynamic calculations indicate that the volatilities of many of the elements are decreased due to carbide formation. If the carbide UC is heated to 2000°C. and rapid diffusion assumed, Xe, Ba, Sr, Cs, Te, Rb, I, Kr, Se, Br, Sn, and Sb would vaporize, but this amounts to less than 37% of the fission products. Except for the increased volatility of Se and Te, the heating of the carbide does not remove volatile impurities any better than does the heating of the metal. There is some possibility of vaporization of Pu under these conditions, but it would be too small to be used for separation with the large excess of UC present. Therefore, heating of uranium carbide shows no promise as a decontamination or separation procedure.

III. Decontamination of Uranium as a Nitride

The calculations for the nitride indicate the same behavior as for the heating of the carbide. No satisfactory decontamination or separation would be obtained upon heating the nitride.

IV. Decontamination of Uranium as an Oxide

If the uranium from the pile were heated to a high temperature in oxygen, we could obtain removal of Mo, Ru, Cb, Te, Se, Sn, Sb, and Rh as gaseous oxides as well as removal of Xe, Cs, Rb, I, Kr, and Br as gaseous elements. However, this would result in removal of not much over 50% of the fission products and such

important fission products such as Zr, the rare earth elements, and Ba and Sr would not be removed at 2000°C., for example. Plutonium would not be separated from uranium by this process; so it does not appear to be promising.

V. Decontamination of Uranium as a Sulfide

The calculation for the sulfide indicates the same behavior as for the nitride and carbide and would not be promising.

VI. Decontamination of Uranium as a Halide.

If the pile uranium were heated with excess of chlorine, the uranium could be vaporized off along with Mo, Zr, Ru, Cb, Te, Se, Sn, Sb, and Rh as volatile halides together with Xe, I, Kr, and Br as gaseous elements. The residue would contain plutonium, the rare earth elements, Ba, Sr, Cs, and Rb. Temperatures of 700 - 1000°K. would suffice for this process although even lower temperatures might be satisfactory. If a vacuum casting had preceeded the treatment with chlorine, the Ba, Sr, Cs, and Rb could have been removed then leaving only the rare earth elements with Pu.

Use of fluorine instead of chlorine would give similar results except that Zr might be only incompletely removed unless rather high temperatures were used and there is some possibility of loss of Pu as PuF_6 along with the uranium.

In the chlorine process the uranium will vaporize largely as UCl_4 while in the fluorine process the uranium will vaporize as UF_6 or UF_5 depending upon the temperature and the amount of fluorine added. Counter current continuous processes could be set up in both cases, so that metal would be fed in at one end and

plutonium and rare earth halides removed at the other end where the halogen is being introduced and the uranium could be removed at the point along the length of the apparatus where it had the desired oxidation state. The halide going beyond that point would completely react with the entering metal. The uranium could be removed from the fission products by reduction with H_2 to UCl_3 and then treatment with I_2 to vaporize UCl_3I leaving most of the fission products behind.

Summary

A consideration of possible high temperature decontamination and separation processes that could be applied to a uranium pile indicates two possible procedures which appear promising enough to warrant investigation.

The first process would consist of three steps. First the uranium slug from the pile would be heated inductively or in a resistance furnace by remote control and cast under reduced pressures to remove volatile fission products. Then the molten uranium would be treated with a very small amount of an oxide, sulfide, or halide of uranium which would separate as a floating layer or on the walls of the container after having extracted the plutonium and the rare earth elements. The floating layer would be scraped off by remote control or the uranium cast away from the scum into another crucible where the Zr and Cb could possibly be removed by treatment with carbon. The fission products and plutonium which have been removed would be in a very small volume of material and the uranium could be cast in a new slug and reintroduced into the pile after enrichment or could be used as a reflector and absorber on the outside of piles to prevent loss of neutrons.

This process has the advantage that it might well be incorporated with a high temperature pile so as to provide continuous decontamination and separation. If the above treatment were effective, 67 h. Mo, 42 d. Ru, and ly. Ru would be the main sources of activity in the uranium. It would be difficult to remove the Mo and Ru from the uranium although it might be

possible by extracting the molten uranium with some metal like Ce which could possibly remove the Ru as an insoluble phase or with some metal like Ge which might remove the Mo. As containers for the molten uranium, it might be possible to get tungsten, ThS, CeS, UC, TiC, ZrC, Ta_2C, and similar materials to last long enough to be practical.

The second method has the disadvantage compared to the first that the uranium would not remain in the metal form. This method involves a continuous counter current halogenation of the uranium from the pile which would leave plutonium and the rare earth elements remaining as solid halides and which would remove most of the other fission products along with uranium as volatile halides. Relatively low temperatures might suffice for this process and the container problem might be a relatively simple one. By proper arrangement of oxidizing conditions, it might be possible to fractionate the volatile halides so as to obtain fairly good purification of the fission products from the uranium. If the uranium were then to be used in the pile again, it would have to be reduced to the metal which would make this method somewhat disadvantageous compared to the first suggested, but if the uranium were to be stored, it would be relatively compact.

This work was performed under the auspices of the Atomic Energy Commission.

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