Super High Temperature Method
(Reprocessing)-Separation-Conditioning-(Disposal)

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Summary

Research and development of a simplest process of disposing of high-level radioactive waste, Super High Temperature Method, has been carried out. Batch pouring process of continually supplied fused and molten raw material of calcinated waste has been investigated. This process has successfully delivered two good products of platinum group element alloys and solidified HAW of highly reduced volume which may contain actinide elements.

1. Introduction

Two lines of research and development have been carried out as to HLLW Management. One way is to obtain solidification of HLLW to store it for several tens of years and then bring it to underground disposal.A second is that by transmutation. Namely, partitioning long-lived nuclides out of HLLW and transmuting them into nuclides of shorter lives (Research and development of retrieving useful elements out of HLLW has also been carried out and put to practical use too. Effective utilization of elements contained in HLLW is acknowledged to be an important subject. It will, however, be left out of this paper, because the principal subject here is to present the trend of HLLW management simply and clearly).

There have often been disputes between two lines of research and development. Selection of the nuclides to be put to transmutation was one of subjects of disputes. Prof. Pigford has pointed out, "Minor actinides that are thought to be highly toxic will be stably maintained under the environment of the underground disposal. In selecting the objects of transmutation, they should be fission product nuclides of relatively high mobility." There has been no true technical discussion as regards this suggestion.

Another subject of a dispute is that about the accountability. A transmutation facility will have to be operated in order to carry out transmutation of the nuclides. Operation of the facility will require energy. This energy will be supplied by nuclear power generation. Nuclear fission products will be produced by operating nuclear power plant. The total amount of toxicity of the nuclear fission products is required to be less than the amount of nuclides that is put to transmutation. Furthermore, there is another problem of the total amount of wastes generated in the whole nuclear fuel cycle mainly involved in nuclear power generation for operating the facility. Also the facilities and the installations will become wastes. The facilities to be used for transmutation of specific kinds of nuclides are bound to be contaminated. This issue either has not been put to relevant discussion.Other concerns are related to social acceptability of the under-ground disposal and realizability of transmutation. Political and generic measures to cope with these problems are being investigated in France.[1]

Apart from these discussions, technology aiming at reasonable HLLW management is subjected to research and development recently.

It is the concept of "Reprocessing-Separation-Conditioning-Disposal" together with research and development of industrial technology that makes the concept feasible. Super High Temperature Method by Japan, Partitioning-solidification technology by former USSR, proposal of Separation-Conditioning (S-C) concept by France, SYNROC Solidification of partitioned actinides by Australia are included. Waste Minimization by U.S. also may be in the same line.[2]

The method by former USSR is in partitioning HLLW into several groups of fission products by means of extraction or ion exchange and solidifying each group separately. In one of these processes HLLW is partitioned into fission products and transition metal elements (Zr, Mo,Pd etc.). FPs are vitrified. Transition metals are cemented. Other than vitrification, Synroc Solidification by melting has also been developed. Cold crucible method has been developed as for solidifica-tion technique. 1996, the First Committee of Nuclear Ministry of Russia(MINATOM) decided to extend this method further.

France established a law in order to proceed research and develop-ment concerning High Level Waste Management with centralized concern about waste management including P/T. An annual report of each organization which checks and reviews the research and development activities is published in accordance with this law. The first report in 1995 describes the concept of Separation-Conditioning(S-C). France considers the reprocessing process a unified process of reprocessing andwaste management. (They are not necessarily treated in the same way in other countries. Reprocessing plants are closed in those countries and management of HLLW in hand is a subject of concern). France is making an effort to reduce the output of radioactive wastes to an utmostlimit in reprocessing process based on the above mentioned concept.

Development of a cold crucible is being carried out in order to cope with obsolescence of the melting furnace. This technique is in the stage of technical completion.

In Australia, Research of Synroc solidification of actinides separated from HLLW is being carried out. Development of the above mentioned solidification technique by Russia and development of the oxide solidification technique by Super High Temperature Processing Method by Japan that will be described later are both in the line leading toward the method of solidification unexpectedly similar to Synroc Concept created by Prof. Ringwood.

In the United States research and development is being carried out based on the idea of minimizing the waste generated in the reprocessing plant for military purposes. However, this idea is not carried through HLLW management. A huge vitrification plant is being brought into operation. At INEL, on the other hand, research and development ofSeparation-Conditioning is just being carried out. Structuring of the overall concept of Waste Minimization of HLLW may be required.

As to S-C in Japan, partitioning by wet method and solidificationof each group was proposed by JAERI. Development of partitioning technique is being mainly carried out at JAERI, while development of vitrification technique is not being carried out.

Super High Temperature Method in Japan is a new S-C technique by metallurgical procedure. In the beginning, this method was started aiming at solidification of HLLW without addition of matrix material like glass. It was discovered in the stage of research that highly exothermic FP, cesium, is vaporized and separated, that elements of the platinum group are reduced by adding reducing agents and separated as alloys, and that other FP oxides (including actinides) are melted and solidified.

Selection of the reductant is an important subject in Super High Temperature Method. Platinum group elements are those which can be easily reduced among HLLW FPs. Insoluble materials in spent fuels are small particles of alloys formed by the platinum group elements in FP under the condition of oxygen shortage.

Platinum group elements are reduced when the calcine is heated in the inactive atmosphere, and small particles of alloys are formed. Small particles of alloys are dispersed in the calcine of oxides of FP elements which are not reduced under this condition. When the calcine is heated with addition of reductant, the whole system is melted and themetal and the oxide phases are separated into upper and lower layers. The principal action of the reductant consists of reduction of the transition metal elements included in FP. As the results of reaction, the transition metal elements including platinum group elements form alloys of relatively low melting points. And also, the reductant produced by reaction is an oxide itself. This oxide forms a composite oxide of relatively low melting point.

The reductants are selected from elements with intermediate value of the standard free energy of oxide phase formation and that of metal phase formation. Also, it is chosen to be one of elements which bring about the phenomenon of lowering of melting point. Results of selection of favorable candidate elements are boron, aluminum, silicon, and titanium.

When boron is adopted the oxide phase is of poor water resistance. When aluminum is adopted lowering phenomenon of melting point is relatively weak, thus the temperature of treatment is required to be brought up. When silicon is used, the oxide phase becomes glassy. Namely, vitrification is attained within Super High Temperature Method. When titanium is used, separation of two phases is effective, and the oxide phase is water resistant also. Therefore, at this time, silicon and titanium are favorable as reductant.

Processing with titanium compounds were adopted for current experiments. Titanium alloys, titanium carbide, and titanium nitride are applicable as reductant of titanium compounds. Since titanium alloyis in the form of particle, it is feared that homogeneity of mixing with calcine might be insufficient. Since titanium carbide and titanium nitride are in stable powder form, mixing with calcine will be easy. Titanium nitride has been chosen this time.

Reductants are titanium or reducing titanium compounds.Titanium is turned into titanium oxide as the result of reaction and introduced into the oxide phase. Titanium constitutes composite oxides with rare earths, alkaline earths, zirconium, etc. that constitutes oxide phase. By this method, separation of cesium, retrieval of elements of the platinum group, and high volume reduction and solidification are achieved through simple procedures.

In this report, results of experiments concerning continuous supplyof simulated calcine-retrieval of the platinum group elements by batch flow down process-preparation of solidification of highly reduced volumewill be presented.

2. Process of Super High Temperature Method

The Process of Super High Temperature Method is as follows:

HLLW → Calcination → Sublimation → Reduction → Melting → Pouring → Separation → Storage

High level liquid waste is brought into composite oxides of fissionproducts through calcining process. Cs etc. are separated through vaporization of the calcine.

Oxides of platinum group elements are reduced into metallic phase and partitioned from the oxide phase of rare earth elements and other elements by processing at 1000 C with the reductant of titanium nitride.The system is then processed by melting at 1600 C in order to be partitioned into two phases of metal and oxide.

3. Objectives of the experiments

Up to this stage, experiments have been carried out using 20 g of simulated calcine and a crucible of 30 ml in order to determine the conditions of reduction and fusion-separation of the platinum group elements. Next stage will be developing the technological facilities. A cold crucible technology is presumed for the melting facility. As a preliminary experiment for this process, a method of heating the crucible for melting by high frequency induction and subsequently melting the calcine by conduction heating from it has been investigated. In the process of melting, the calcine is continually supplied. As to crucibles, there are two ways of methods one of which is using the same crucible for melting and also for solidifying, and another is to provide these two sorts of crucibles separately. By the former method the surface portion of the solidification will not be melted homogeneously. It is required to establish a method of obtaining a satisfactory solidification by the latter. Two procedures were examined in comparison.

4. Experiments

Sample material:

Calcine of equivalent composition to that after sublimation was prepared by blending commercially available oxides of reagent grade. The amount of the reagent is several hundreds of grams.

Heating:

The melting temperature is 1600C. The apparatus is shown in Fig. 1.

Three ways of heating were carried out.

1. A carbon crucible was heated by high frequency induction method.
2. A boron nitride crucible placed in a carbon crucible which was heated by high frequency induction was in turn heated by conduction method.
3. A method to pour the melt from the nitride crucible as above into the receptacle installed underneath (Fig.2).

Melting:

The sample material was melted by continuously feeding it into the crucible in terms of a vibration feeder.

Pouring:

In the three methods as mentioned above, molten sample material was poured into the receiving crucibles (kept at protection temperature) through a bottom hole of the melting crucible.

Solidification:

Sample material was released to be solidified by deenergizing the protective heating of the melting crucible or the receiving crucible.

5. Results and discussion

(1). The method of high frequency induction heating the carbon crucible.

In this case the metal and the oxide phases are separated into the upper and the lower layers. However, the state of separation is not clear-cut. Also there are voids in the oxide phase. This is thought tobe attributed to the reduction reaction caused by the crucible material, carbon.

(2). The method of conduction heating the nitride crucible which is placed in a carbon crucible heated by high frequency induction.

In this case the metal phase and the oxide phase are separated into upper and lower phases. Separation of the metal ingot is appreciable also. No void is observed in the oxide phase. It is thought because the crucible material, boron nitride does not generate reduction reaction that gives out bubbling action. However, the surface of the oxide phase is not clean.

(3). The method of pouring down into the receiving crucible installed underneath from the boron nitride crucible in the procedure (2).

In this procedure, the metal phase and the oxide phase are separated cleanly. The metal ingot is also separated well. There is no void observed in the oxide phase. The surface of the oxide phase is clean (Fig.3).

I has been confirmed that normal metal and oxide layers can be constituted by the process of continuous feed and batch pouring. Feasibility of formation of normal products has been demonstrated by making it possible to melt the calcine at high temperature in terms of the cold crucible process,although the melting in this experiment was carried out by thermal conduction method.

References:

[1] The first report, National Evaluation Commission, France, 1995

[2] Misato Horie, High Level Radioactive Waste Treatment: State of Current Research and Development, (PNC TN9420 94-0190, 1995)

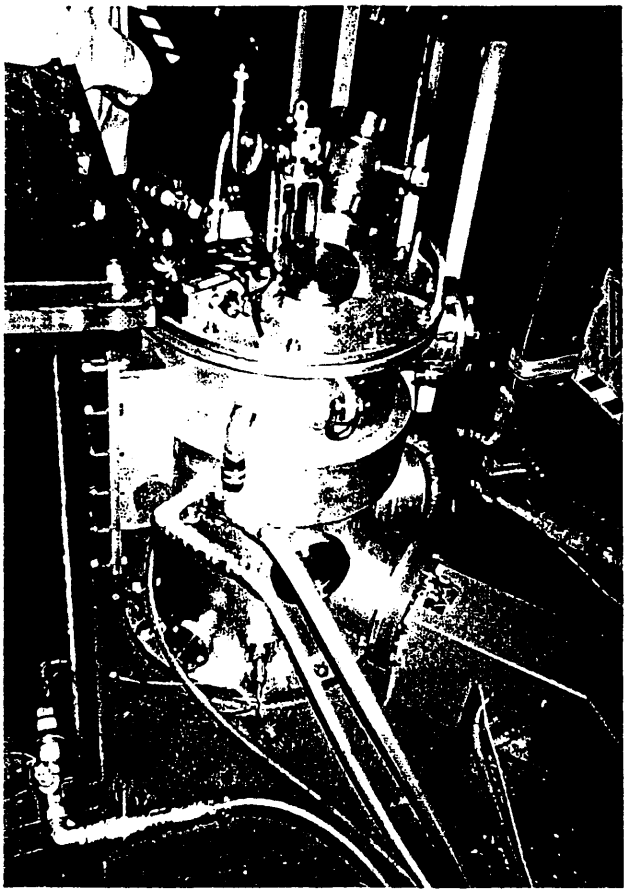

Fig.1 The experimental apparatus

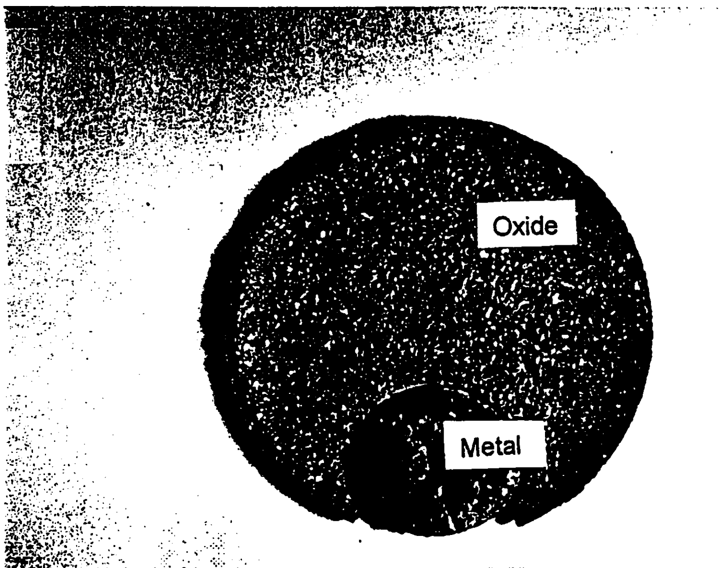

Fig.3 Oxide and Metal obtained by the method of pouring down

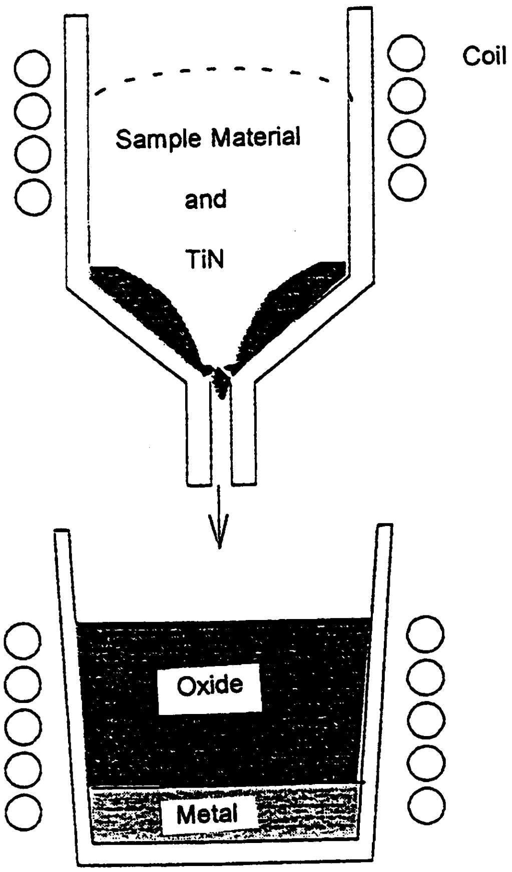

Fig.2 Crucibles of the method of pouring down