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ADVANCED TECHNOLOGY FOR HIGH-LEVEL LIQUID WASTE MANAGEMENT SUPER HIGH TEMPERATURE METHOD

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ABSTRACT

To rationalize waste management, R&D was conducted on the Super High Temperature Method, the simplest process for high-level liquid waste management, based on the concept of Separation-Conditioning. This process is shown as:

HLLW -> Calcination -> Cs Sublimation -> Reduction -> Melting -> Solidification
700°C 1000°C 1000°C 1600°C

In the process, cesium with 40% of the thermal power of the fission products (FP) is separated, and approximately half of the FP (platinum elements–Ru, Rh, Pd–and other transition elements) in the calcined HLLW is reduced with titanium nitride (TiN). The material is melted at 1600°C. Reduced platinum elements in the FP form a metal ingot, while unreduced residue forms an oxide ingot. Very compact HAW, composed of FP titanates (titanates of alkali earths, rare earths, zirconium and actinide elements), is achieved and the product serves as its own matrix. Conventionally, solidification (conditioning) has been conducted by introducing matrix materials (such as glass). However, the FP metal ingot and oxide ingot are solid without matrix materials.

The quantity of waste is referred to by weight, volume and number of HAW canisters of solidified HLLW. (Conventionally, an 800-t reprocessing plant, generates approximately 1000 canisters of HAW each year.) From the viewpoint of determining the facility size and handling frequency, the quantity of generated HAW is important. In order to determine the quantity of HAW, the oxide was characterized. Factors considered were density, thermal conductivity, coefficient of expansion, EPMA, X-ray diffraction, etc. The following dimensions and quantity-related information were calculated on the basis of obtained data:

Dimensions: Height: 1.1 m. Diameter: 25.7 cm
Quantity: Weight: 45.23 kg/t-U, Volume: 8,565 cm^3/t-U
Number of canisters: 0.15/t-U

The HAW generated by an 800-t reprocessing plant is just 120 canisters/year, or about one tenth (10%) of that generated by conventional vitrification technology.

INTRODUCTION

Three concepts of managing HLLW (High-Level Liquid Waste from the Purex Reprocessing Process) have been developed: vitrification of all fission products (FP) and their disposal; partitioning and transmutation (P-T); and separation and conditioning (S-C). The S-C concept aims to rationalize HLLW management. The S-C concept is not as widely known as the two former concepts. However, S-C has been introduced in the USA; in Russia, S-C has been developed in the field of HLLW, while France mentioned it in a CNE (National Evaluation Committee) report.

The Super High Temperature Method (SHTM) is the simplest S-C technology. It has been developed with the aim of achieving very compact HAW (solid High Active Waste containing actinides) by separation of cesium (high thermal power FP) and noble-metal FP through addition of a small amount of a titanium compound.

The HAW serves as its own matrix. Researchers have long maintained that solidification (conditioning) is optimized by introducing a matrix material (such as glass, bitumen, or cement). However, metal and oxide FP are already solid and introduction of a matrix material is not necessary for solidification of HLLW.

The quantity of waste is referred to by weight, volume and number of HAW canisters. Weight and volume affect the size of the treatment facility. Large weight and volume require large apparatus, such as a melter for the HAW, and more melters must be used. Thus, the size of the treatment facility inevitably increases, and the cost of HLLW management rises. Vitrification requires addition of glass at ten (10) times the volume of FP. SHTM achieves reduced weight and volume of HAW by treating HLLW with only small amounts of additives.

From the viewpoint of handling frequency and facility size, the quantity of HAW is an important factor. If the quantity of HAW is reduced to one tenth (10%), HAW handling frequency is reduced to 10% at the treatment, storage and disposal facilities. Moreover, these facilities will be smaller than those required when vitrification technology is used.

In order to determine the quantity of HAW, the oxide was characterized. The factors considered included coefficient of expansion, X-ray diffraction, density, and thermal conductivity. The temperature of the HAW at the center must remain below its transition or melting temperature. The thermal stabilization of HAW was proven by X-ray diffraction and the coefficient of expansion at 1000°C. Thermal conductivity was used to calculate the HAW center temperature. On the basis of these data, the dimensions and quantity of HAW were calculated:

Dimensions: Height: 1.1 m; Diameter: 25.7 cm
Quantity: Weight: 45.23 kg/t-U; Volume: 8565 cm^3/t-U
Number of canisters: 0.15/t-U

The HAW generated by an 800-t reprocessing plant is just 120 canisters/year or about one tenth (10%) that of vitrification technology. Thus, SHTM rationalizes HLLW management.

SHTM PROCESS

This process is shown as:

HLLW -> Calcination -> Cs Sublimation -> Reduction -> Melting -> Solidification
700°C 1000°C 1000°C 1600°C

In the process, cesium with 40% of the thermal power of the FP is separated by sublimation. In the reduction, about half of the FP (platinum elements–Ru, Rh, Pd–and other transition elements) in the calcined HLLW is reduced with titanium nitride (TiN):

$$MOx + TiN = M + TiOy + zN_2 \qquad (M: \text{ Ru, Rh, Pd and others})$$

The obtained metal forms many small particles and is dispersed in the unreduced FP oxide.

The materials are melted at 1600°C, forming two layers. The reduced platinum elements in FP form a metal ingot in the lower layer. The unreduced residue forms an oxide ingot in the upper layer. This product is the very compact HAW composed of FP titanates (titanates of alkali earths, rare earths, zirconium and actinide elements) with its own matrix.

RESULTS AND DISCUSSION

Calculation of HLLW composition

The composition of HLLW was calculated for spent fuel with a burn-up of 45.000 Mwd/t-U and a cooling period of 5 years. The total activity, thermal power and weight of FP in HLLW were 7.5^5 Ci, 2.5^3 W and 47.5 kg/t-U.

Preparation of simulated calcined HLLW

Three kinds of simulated calcined HLLW were used: (a) for cesium sublimation, (b) for reduction and melting, and (c) for characterization of HAW.

(a) Mixed oxide of almost all FP and corrosion products (CP)
(b) Mixed oxide of almost all FP without cesium and rubidium, and CP
(c) mixed oxide of limited FP (alkali earths, rare earths and zirconium) and uranium dioxide.

Cesium Sublimation

Of the major FP, cesium has a very low boiling point (bp) of 668°C. Cesium oxide in calcined HLLW decomposes at high temperature and cesium sublimates. The treatment time for 90% cesium sublimation was 5 h at 800°C, 2 h at 900°C and 1 h at 1000°C.

The thermal power of cesium (Cs-Ba) is 1.1 kw/t-U and accounts for approximately 40% of the FP thermal power. The thermal power of HAW is discussed from the viewpoint of the FP content in HAW, the storage period of HAW in the storage facility, and the volume of the HAW disposal site.

Based on conventional vitrification technology, the FP content is limited to 10wt%, the storage period is 50 years, and a large volume disposal site is needed in proportion to the HAW thermal power. Cesium separation eliminates these restrictions and reduces the cost of HLLW management.

In addition, SHTM based on the S-C concept and minimum additives enables further cost reductions by mitigating other restrictions.

Reduction

In terms of ΔG (standard free energy of oxide formation), FP, CP and actinides form two groups: platinum and transition elements, and alkali earths, rare earths, zirconium and actinide elements.

The former group has a high .G, and the latter has a low .G. Elements with intermediate.G values are boron, aluminum, silicon and titanium (these are not contained in FP). These elements, nitrides and carbides function as reductants of the former oxides. Thus, the former group are separated as metals from the latter group. The reductant is oxidized and forms a mixed oxide of the latter oxides. Oxide formation lowers the melting point reducing the treatment temperature of the melting process.

Nitrides are very useful because they resist air and moisture, are in the form of a fine powder and can be mixed easily with the calcined HLLW powder.

Titanium nitride was selected in this experiment because boron nitride caused a low leach rate of HAW, silicon nitride produced glass-like materials, and aluminium nitride did not lower the melting point. The use of nitrides must be discussed in more detail.

In the reduction process, about half of the FP (platinum elements–Ru, Rh, Pd–and other transition elements) in calcined HLLW was reduced with TiN in an argon gas atmosphere.

$$MOx + TiN = M + TiOy + zN_2 \qquad (M: \text{ Ru, Rh, Pd and others})$$

The obtained metal formed many small particles dispersed in the unreduced FP oxide. The amount of TiN was equimolar to the oxides of platinum and other elements. The amount of TiN was only 22.55 to 100 calcined HLLW. The titanium oxide formed was 29.11 to 100 calcined HLLW.

The reduced elements were analyzed; with the exception of strontium, yttrium and zirconium, low-atomic-number elements were contained in the metal. The recovery ratios were as follows: ruthenium 102%; rhodium 83%; palladium 100%; and molybdenum 95%.

The remaining oxides were alkali earths, rare earths and zirconium oxides. The amount of oxides (remaining oxide + titanium oxide) was 45.23 kg/t-U by calculation.

Melting

To separate the metals and oxides, all the materials must be melted. In the melting, two layers are formed: a metal layer, and an oxide layer. The density of metals is higher than that of oxides. So the former was deposited under the latter, rather like mercury (Hg) under water.

The metals of platinum elements and the oxides of rare earths, etc., in FP have a high melting point. However, due to lowered melting point caused by CP and titanium oxide, the two layers melted at 1600°C.

Melting was performed in a 10-g scale experiment with a carbon heater melter, and in a kg scale experiment with a cold crucible induction melter (CCIM). In the small-scale experiment, a button-like metal ingot was obtained. In the CCIM experiment, a large rock-like oxide and a large ingot of platinum metals were obtained. The success of kg-scale melting showed the possibility of SHTM, not only at a scientific level but also at a technical level.

Characterization and Calculation of HAW Dimensions

As mentioned above, the quantity of HAW is very important from the standpoint of cost reduction of the operation and construction of facilities. With SHTM, the weight and volume of HAW are very small. To reduce the number of HAW canisters, a large diameter HAW may be considered but as with cesium (Cs-Ba), the high thermal power of strontium (Sr-Y) is a limiting factor. Accordingly, the thermal stability must be maintained and the diameter limited to control the temperature at the center.

The diameter is calculated as follows:

T (center) -- T (surface) = Linear Heat Density/4.* Thermal conductivity

Linear Heat Density * Height = Volume Heat Density *.R^2 * Height

The most important factors are T (center) and thermal conductivity. To determine the HAW quantity, the oxide was characterized. Factors considered were thermal conductivity, coefficient of expansion, X-ray diffraction, density, EPMA, etc. The dimensions and quantity of HAW were calculated based on these data.

The thermal conductivity (.800°C) and coefficient of expansion (.1000°C) showed a smooth increase with temperature. The X-ray diffraction pattern showed that the HAW had a rock-like structure and retained the same pattern in the measured temperature range (.1000°C). Thus, the HAW is stable at high temperatures and T (center) can be set at 800°C.

The data from the calculations and experiments enabled the dimensions and number of HAW canisters to be calculated.

HAW of Super High Temperature Method:

Temp. of HAW center:	800°C
Temp. of HAW surface:	400°C
Thermal conductivity:	1.19 w/mK
Linear heat density:	5979 w/m
HAW Height:	1.1 m
Volume heat density:	0.1155 w/cm^3
Weight:	45.23 kg/t-U
Volume:	8,565 cm^3/t-U
Density:	5.28 t/m^3
HAW Diameter:	25.7 cm
Thermal power:	6,576 w/HAW
HAW canisters generated:	120/year from 800-t plant
FP Contained:	FP in 6.65t-U/HAW

In connection with the quantity of HAW generated, a comparison between SHTM and vitrification follows:

	SHTM	Vitrification	Unit
Weight	45	500	t-U
Volume	8.6	185	t-U
Number of canisters	120	1000	800-t plant

For SHTM, the amounts of platinum elements and cesium must be considered. These elements are valuable as materials for jewelry and as a (gamma) source. In the non-ferrous metals industry, many hazardous elements have been released into the environment and it was only the use of these elements that saved the industry.

Cost Effects of HLLW Management by SHTM Concept

In the treatment phase, handling of materials is decreased, a small melter can be used, and the frequency of HAW canister handling is decreased. However, SHTM also produces cesium, platinum elements and HAW, so the cost reduction may be small.

From the storage viewpoint, the number of HAW canisters is reduced, so the storage facility can be smaller, achieving a large cost reduction.

The disposal cost is estimated at 3 trillion yen for 40,000 HAW canisters. This cost, which is proportional to the quantity of HAW, is about half the conventional total disposal cost. Use of SHTM reduces the quantity of HAW, so the disposal cost is reduced dramatically. Therefore, SHTM is a potential technology for cost reduction of HLLW management. The technology reduces the quantity of waste in comparison to that associated with direct disposal of spent fuel. With the development of the salt-free process and SHTM, the Purex process is the most rational process.

CONCLUSION

The author has developed the SHTM concept and shown that an 800-t reprocessing plant would generate only 120 HAW canisters per year by SHTM compared to 1000 canisters for conventional vitrification technology.

REFERENCE

Misato HORIE, 'Super High Temperature Method of High Level Liquid Waste Treatment' ANS 90 Winter Meeting (Trans. of ANS, Vol. 62, p.111, 1990)

NOTE

The number of tables and figures was restricted for inclusion of this document in the proceedings. However, persons interested in SHTM can obtain them from the author at:

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