

**MULTI-LAYERED DISTRIBUTED WASTE-FORM OF I-129 - STUDY ON IODINE
FIXATION OF IODINE ADSORBED ZEOLITE BY SILICA CVD**

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ABSTRACT

A new waste-form concept for I-129, multi-layered distributed waste-form, has been proposed and studied. The purpose of this research is to realize a practical waste-form that has an extremely low leaching property for a long period (approximately a million years). The proposed waste form is composed of three components such as iodine bearing material (zeolite), coating layer (silica and apatite) and low solubility matrix (apatite). With a screening test of inorganic iodine adsorbents, Ca-Ag-A type zeolite (Ca-Ag-A) was selected as iodine bearing material because of its large chemisorption amount of iodine. The coating method for the zeolite was examined and the result showed that silica and hydroxy-apatite coating was successful. As the next step, we are now investigating the matrix forming.

INTRODUCTION

Because of its long half-life (17 million years) and little retardation effect expected by engineered and natural barriers, I-129 is the most influential nuclide in the exposure dose evaluation at TRU waste disposal in Japan. On this background, we have been developing a multi-layered distributed waste forms of I-129. The goal of this waste-form development is to realize a low releasing rate of I-129 for a long period of more than hundreds thousands years. In this paper we will describe the concept of multi-layered distributed waste-form of I-129 and the experimental results we obtained so far mainly paying attention to the development of inorganic iodine adsorbents.

CONCEPT OF MULTI-LAYERED WASTE-FORM FOR IODINE 129

Figure 1 shows the concept of the multi-layered distributed waste-form for I-129. The aim of this concept is to realize a practical waste-form, that has an extremely low leaching property for a long period (approximately a million years), by combining different functional materials, such as iodine bearing material and low leaching material. Considering the long half-life of I-129, it seems unpractical to confine iodine till most of them will be decayed. Therefore our approach is not to realize “confinement ” but to realize “controlled release”. The demonstrability of the long-term performance is also our major concern .

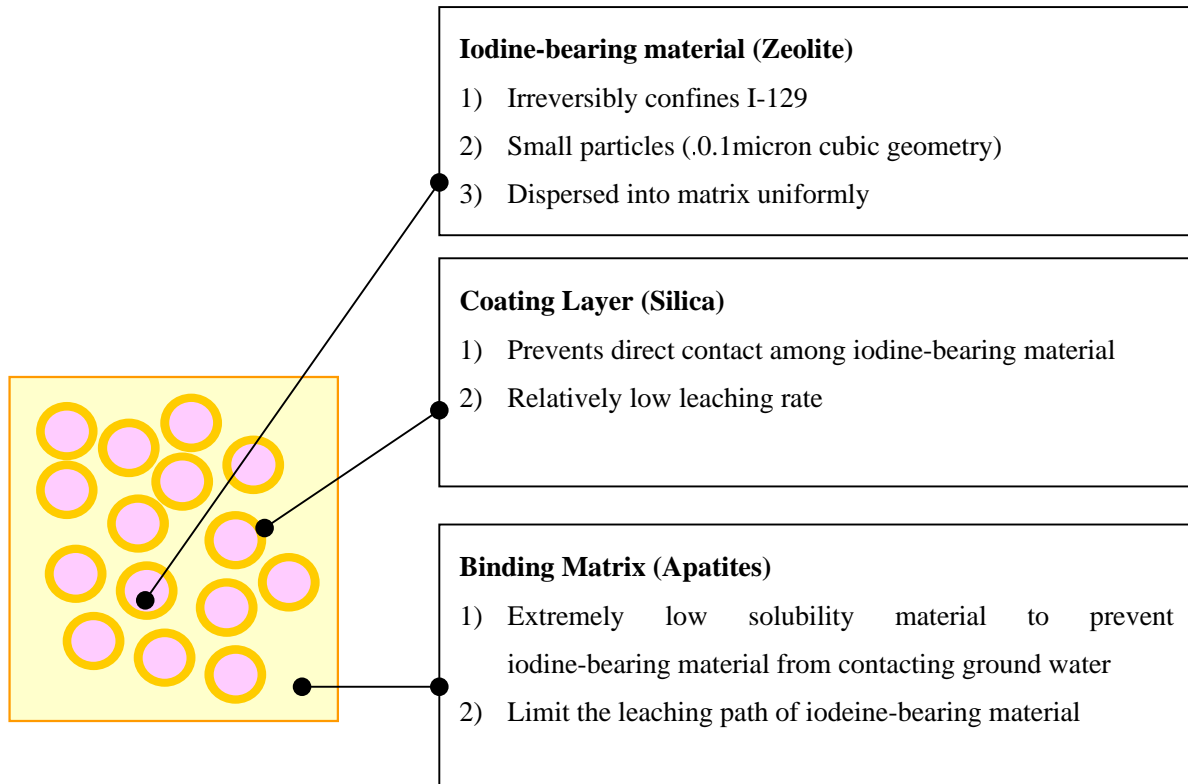


Figure 1 Concept of multi-layered distributed waste-form for I-129

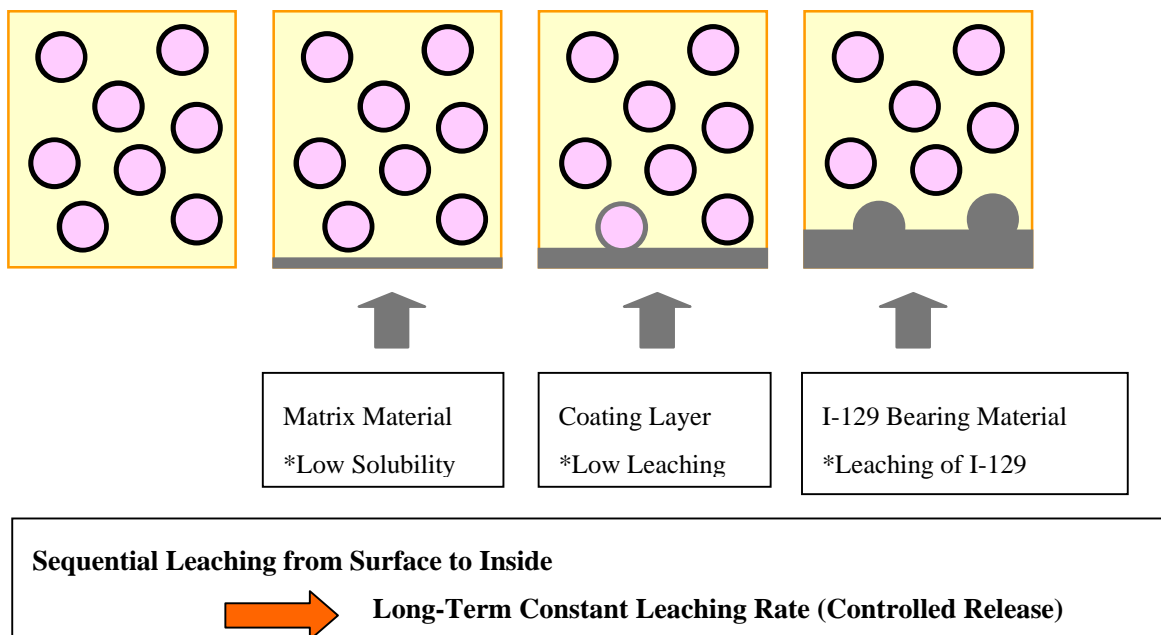


Figure 2 Leaching Scenario for the multi-layered distributed waste-form

The proposed waste-form is composed of three components such as (1) iodine bearing material, (2) coating layer and (3) matrix material. The iodine bearing material should be small particles which are dispersed in the waste-matrix in order to assure the uniformity in the matrix material. The coating layer acts as a barrier to prevent the direct contact among iodine bearing material particles and, as a result, to prevent the formation of direct leaching path through the connection of iodine bearing particles. The coating layer can also act as a barrier for iodine leaching if extremely low leaching rate material is used as the coating material. In addition to that, the coating layer has a function to prevent iodine release during the process of matrix formation. The matrix material must have the lowest leaching rate among the three components.

Figure 2 shows the “leaching scenario” of this waste-form. After disposed at underground site, underground water will invade and come into contact with the surface of the waste-form at first. It is expected that the low solubility matrix material can well retard the contact of groundwater with particles. However, sooner or later, the groundwater will contact a particle. If the coating layer of the particle is intact, the release of iodine-129 will also be retarded according to the barrier function of the coating layer. If the coating layer will be leached by the groundwater, iodine will be resolved into the groundwater and then be released outside the waste-form.

The following consideration shows the easiness of the demonstrability of this concept.

Here, we assume that particles within the matrix are in contact with other particle(s) and low solubility matrix works only to limit the leaching path, that is, the leaching of particles occurs sequentially from surface to inside and never occurs at once. This assumption, where the retarding effect of matrix material is not directly expected, is obviously the conservative assumption. In this case, if the lifetime of each particle is t years and the number of the sequence which is necessary for leaching all particles in the waste-form is N , then the releasing period of the waste-form will be $t \times N$ years.

For example, let the size of the particles to be 0.1 micrometers and the dimension of the waste-form to be 10 cm, then the number of the sequence (N) will be 10^6 . If the lifetime of each particle is demonstrated as 1 year, this means that it takes a million years to release all iodine from the waste-form. This means that the leaching rate of this waste-form is 10^{-6} . If we consider the retarding effect of the matrix material, the leaching rate will be even lowered. The important point of this scenario is that it is enough to show the lifetime of particles and the low solubility of matrix material in order to demonstrate the performance. Since the expected lifetime of particles is relatively short (1 year), it seems easier to demonstrate the lifetime of particles by experiments.

The above mentioned scenario hold good if the followings are satisfied:

- a. Relation among the leaching rate of each component:
Iodine bearing material $>$ Coating layer \geq Matrix material
- b. Compactness of the matrix material
- c. Intact of the interface between matrix and particles

In this study, we have selected the following composition as the candidate for the multi-layered distributed waste-form:

- a. Iodine bearing material: Zeolite
- b. Coating layer: Silica and hydroxyapatite
- c. Matrix: Apatite (hydroxyapatite or fluoroapatite)

Here, apatite is a mineral with extremely low solubility [1] under a wide range of pH conditions.

EXPERIMENTAL STUDY

In this chapter, our experimental study is described. We have developed a candidate of “particles” that is iodine adsorbed zeolite crystal, which was first coated with a silica-network as an inner layer and then coated with apatite as an outer layer to facilitate extremely long-term iodine fixation. Here, we will describe the experimental results concerning the optimization of iodine adsorbent and coating techniques (silica and hydroxyapatite coating), at first. Then, our process for apatite matrix forming, which is not completed yet, is described.

Iodine Adsorption on Zeolite

Iodine bearing material has a function to confine I-129. The long-term stability is not always a necessary condition for the material selection. Here we selected the optimum iodine bearing material considering the following conditions.

- a. Amount of adsorbed iodine
- b. Large irreversible, chemi-sorption amount
- c. Easiness of coating

Iodine crystals, for which the temperature was set at 100 deg-C and then subjected to vaporization with helium gas, was supplied to an adsorption column. The total amount of adsorbed iodine was measured by comparing the weight increase between before and after iodine adsorption on a fresh sample. When iodine adsorption was saturated, the stream line was changed and helium gas was supplied as a counter purge flow, and the pressure reversible amount (physical adsorption amount) was removed. Then, iodine gas was re-supplied from the inlet to the regenerated sample and the pressure reversible adsorption amount was measured with after the second adsorption. The pressure irreversible amount (chemi-sorption) was calculated by the difference between the total and the reversible amount.

The amount of adsorbed iodine of (1) Na-X type zeolite (SiO₂/Al₂O₃ ratio 2.5), (2) Ag-Na-X type zeolite, (3) Ag-Ca-A type zeolite, (4) ALPO, (5) SAPO, and (6) apatite were evaluated using the above-noted apparatus. Silver ion exchange was undertaken as follows:

- (1) Zeolite powder was cleansed with pure water several times for chlorine removal.
- (2) Powder was dispersed in pure water and silver nitrate was added and stirred for several hours.

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(3) Powder was filtered, cleansed, and dried.

(4) Samples were formed as granules and finally calcined at 450 deg-C to remove crystal water.

The amounts of adsorbed iodine of these samples were shown in Table 1 and these results can be summarized as follows:

(1) Apatite indicated little iodine adsorption.

(2) The iodine adsorbed amounts of ALPO and SAPO were small and most of these consisted of physical adsorption.

(3) Ag-Ca-A type zeolite (Ag-Ca-A) showed the maximum amount of adsorbed iodine at a silver ion exchange ratio of 20 mol%, and its adsorbed amount was 47 w% at an iodine concentration of 1,000 ppm, room temperature.

(4) Samples, for which the calcination temperatures were 450 deg-C and 650 deg-C respectively, were compared; the sample calcined at 450 deg-C showed a larger amount of adsorbed iodine.

(5) Samples, for which calcination was undertaken in air and nitrogen atmospheres respectively, were compared; the sample calcined in air showed a larger amount of adsorbed iodine.

As the result, Ag-Ca-A (silver exchange ratio of 20mol%) was chosen as the adsorbent for iodine fixation.

Table 1 Sample list and results of iodine adsorbed amounts measurement

.Preparation..24hrs×200ml/min.absorption .24hrs×200ml/min.He purge

Adsorbent	Preparation	Iodine adsorbed amounts.%. Chemisorption Physisorption Chemisorption + Physisorption		
		Na-X	Granule . Air (450.)	43.8
Ca-A	Granule . Air (450.)	27.3	7.5	34.8
Apatite	Granule . Air (450.)	0.2	0.3	0.6
ALPO	Granule . Air (450.)	0.1	17.9	18.0
SAPO	Granule . Air (450.)	0.9	13.1	14.0
Ag-X.	Ag 100. exchanged . Granule . Air (450.)	33.4	1.0	34.5
Ag-A.	Ag 100. exchanged . Granule. Air (450.)	6.1	0.1	6.2
Ag-A.	Ag 60. exchanged . Granule. Air (450.)	11.5	0.2	11.7
Ag-A.	Ag 40. exchanged . Granule. Air (450.)	31.3	0.0	31.3
Ag-A.	Ag 20. exchanged . Granule. Air (450.)	41.3	0.6	41.9
Ag-A.	Ag 10. exchanged . Granule. Air (450.)	20.7	4.6	25.3
Ag-A.	Ag 100. exchanged . Granule. Air (450.)	0.6	0.0	0.6
Ag-A.	Ag 100. exchanged . Granule. Air (450.)	5.3	0.0	5.3

Silica coat on zeolite

Granular iodine adsorbed Ag-Ca-A was loaded into a small column, for which the temperature was set at 100 deg-C. When tetra methoxy ortho silicate (TMOS) gas was supplied, TMOS was adsorbed on the surface of the zeolite crystals. Following TMOS adsorption, 10 vol% water vapor containing ammonium (1vol%) was supplied to the crystals.

TMOS was hydrated, silicic acid formed on the surface of the crystals, and methanol was transferred to the gas phase. Following several repetitions of TMOS adsorption treatment and hydration with water vapor for silicic acid deposition on the zeolite surface, the temperature was raised to 350 deg-C to dehydrate the silicic acid to promote silica network formation. The enhancement of iodine fixation by silica coating was evaluated by observing the amount of adsorbed iodine before and after calcination.

Figure 3 shows the amount of adsorbed iodine before and after silica coating. It was confirmed that iodine loss through silica coating remained at about 5 w%. Figure 4 shows the relationship between the coating times and the amount of adsorbed iodine. As the amount declined to less than 10 w% at three coatings, it was insufficient for iodine fixation. On the other hand, there was no loss at six or more coatings, and it was understood that iodine was completely fixed to Ag-Ca-A crystals by six or more coating repetitions.

Hydroxyapatite Coating Procedure by Sol-Gel Method

An apatite-gel was obtained from $\text{Ca}(\text{OC}_2\text{H}_5)_2$ and H_3PO_4 in ethylene glycol-ethanol solution [2]. For the characterization of the coated-zeolite samples, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were employed. SEM micrographs of silica-apatite coated Ag-A zeolites after two coatings and one heat treatment showed that the silica-covered iodine adsorbed Ag-A was then coated with amorphous hydroxyapatite, which had a diameter of about 0.05-0.2 μm . Furthermore, the amorphous apatite bound the cubic Ag-A grain.

The TGA profile shows total weight losses of non-coated, silica coated, and silica-apatite coated Ag-A from room temperature to 1200°. In the case of non-coated Ag-A, the weight loss occurring from room temperature to 350° was due to the release of iodine. No weight loss was observed at temperatures greater than 350°. On the other hand, silica coated Ag-A showed a profile including two steps: an initial weight loss (21%) that occurred from room temperature to 320°, and the another one (10%) that occurred from 320° to 900°. Furthermore, in the TGA profile of silica-apatite coated Ag-A, the weight loss occurred more slowly. From these results, it is concluded that the iodine fixation capacity of Ag-A was enhanced by the silica-apatite coatings.

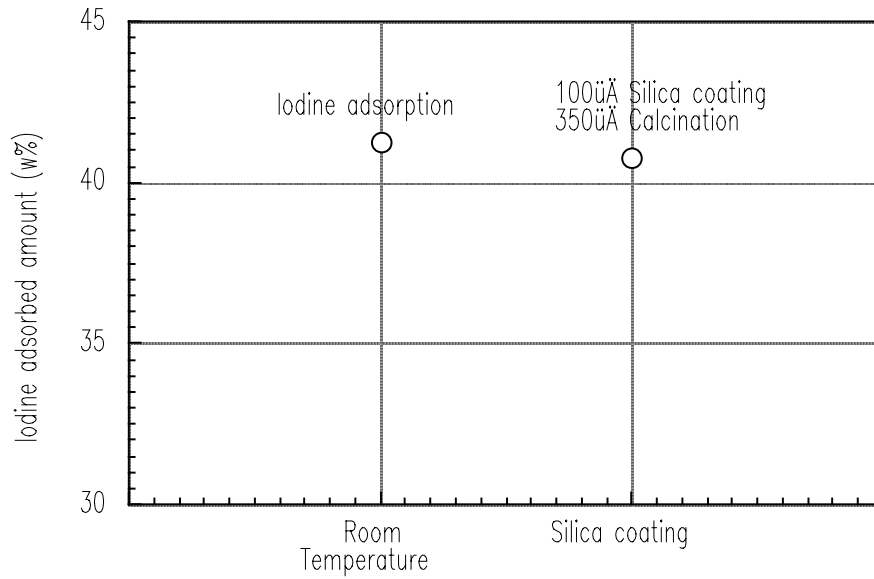


Figure.3 Iodine fixation inside Ag-Ca-A(20mol%)

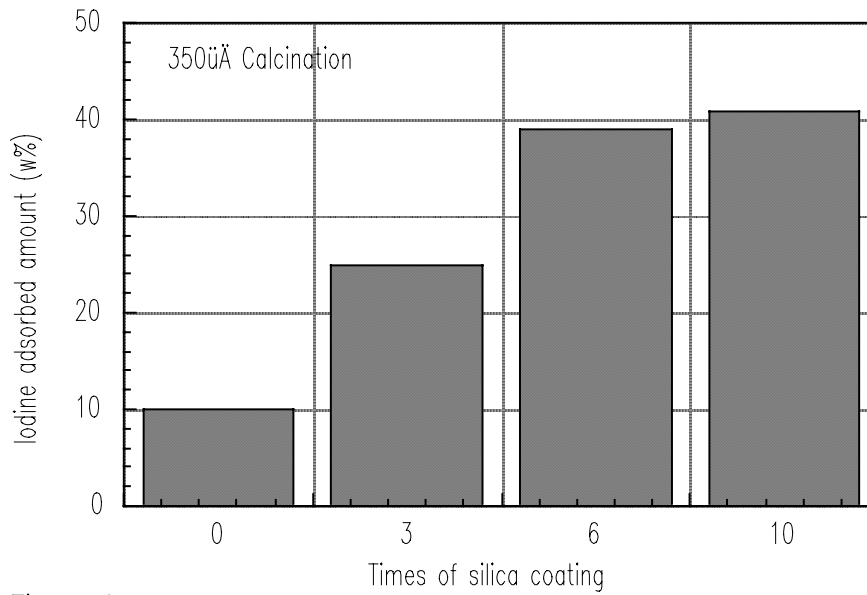


Figure.4 Relationship between the silica coating times and the iodine adsorbed amount

Forming of apatite matrix

As for the matrix material, we are now studying the forming of hydroxy-apatite (HAP). Here we describe the outline of our approach to forming matrix material.

Synthesis of HAP will be done by the same procedure described in the previous section. Iodine adsorbed zeolite crystal, of which the surface is coated with silica as an inner layer and HAP as an outer layer, is dispersed into HAP powder and compressed at 200 kg/cm² for the forming. The formed medium is calcined at 1,000 deg-C for a few hours and volatile materials are removed, allowing the removal of micro pores and the formation of high density iodine fixation material (95% or greater). As this iodine fixation medium contains HAP, which is one of the lowest solubility inorganic compounds and is used as a matrix material, it can be expected to fix iodine for a few million years. Furthermore, when the OH group of HAP is substituted with fluorine ions, this fluoro-apatite (FAP) is thought to show even lower solubility and it can be expected to serve as a more desirable matrix material.

CONCLUSIONS

In this paper, we have proposed a new idea of I-129 waste-form. With a screening test of inorganic iodine adsorbents, it was found that Ca-Ag-A type zeolite (Ca-Ag-A) showed large chemisorption amount of iodine. Next, the coating method for the adsorbent was examined and the result showed that silica and hydroxy-apatite coating was successful.

In order to complete the development of this waste-form the following study will be necessary.

- The leaching experiments for iodine-bearing particles (silica and apatite-coated zeolite)

- The leaching experiment for apatite

- Confirmation of matrix forming

- Engineering design for the waste-form (dimension of the waste-form, size of particles, filling ratio of I-129, thickness of coating layer)

- Process design and cost evaluation

[REFERENCES]

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[2] P. Layrolle, et. al., J. Am. Ceram. Soc., 81 [6] 1421-28 (1998)