

Difficulties in Treatment of Contaminated Water in Fukushima-1 Nuclear Power Plant and Disposal of its Secondary Waste

–Proposal of Countermeasures with Focus on Disposal–

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The completion of a cold shutdown state (step 2), in response to the efforts to resolve the Fukushima Daiichi Nuclear Power Plant Accident, was declared in December 2011. The temporarily installed water treatment system is being operated for circulating water cooling, which supports the cold shutdown state of the nuclear reactors. However, the installation of the permanent water treatment system, and efforts to deal with the storage, processing, and disposal of secondary wastes generated by the contaminated water treatment are also required. In this commentary, we outline the current status of contaminated water treatment, and explain the adsorbent performance as well as technical issues regarding future processing and disposal.

I. Issues of Contaminated Water Treatment

When the accident occurred at the Fukushima Daiichi Nuclear Power Plant, several hundred tons/day of water was continuously poured into the plant to cool the reactor core, and large amounts of contaminated water containing high concentrations ($\sim 10^6$ Bq/cm³) of radionuclides such as cesium were produced in a short period, making it difficult to secure a storage location. However, there are no examples of previous measures taken for dealing with large volumes of highly radioactive water containing seawater. In step 1 of the path for resolving the accident, the water treatment system for decontaminating water by removing radionuclides such as cesium (Cs) and iodine (I) was installed, and the circulating water cooling (**Figure 1**), which reuses the decontaminated water as cooling water, was initiated in June 2011^{1, 2)}. Through this, stable cooling of the nuclear reactor became possible, and in December of the same year, a cold shutdown state (step 2) of the nuclear reactor was achieved³⁾.

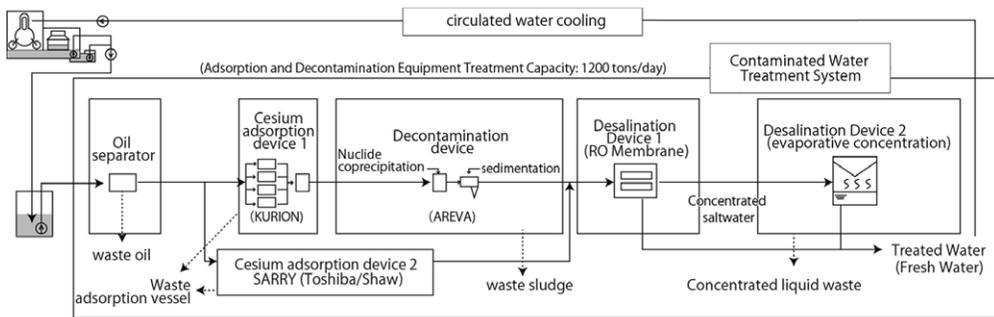


Figure 1 Contaminated water treatment system supporting circulating water cooling^{1,2)}

1. Contaminated Water Treatment System¹⁻³⁾

(1) Oil Separation Device

Highly contaminated water is transferred from No. 1–4 reactor turbine buildings, etc., to a centralized waste treatment facility, and is treated by the water treatment system. Turbine oil that was mixed owing to the tsunami hinders decontamination, and is therefore removed by an initial oil separator.

(2) Radionuclide Removal Device

The nuclides subject to decontamination include Cs-134 (half-life of two years) and Cs-137 (half-life of 30 years), which emit strong gamma rays. Serial operation of a cesium adsorption device from U.S.-based KURION with a treatment capacity of 1,200 tons/day and a decontamination device from France-based AREVA was started on June 17, 2011, and the Cs-137 concentration was reduced from $1/10^5$ to $1/10^6$ of the concentration before decontamination. The KURION adsorption device sends contaminated water into adsorption vessels (4 series) filled with herschelite, which is a kind of zeolite with a high Cs^+ ion-exchange capacity, and removes 99% or more of the radioactive Cs. The AREVA decontamination device is based on a sedimentation method that adds chemicals and adsorbs Cs^+ in a fine powder of ferrocyanide, which is then bonded to grains of sand with an organic polymer and rapidly precipitated. The sand is reused, and therefore, waste sludge (precipitate) containing Cs is generated as secondary waste. However, owing to the problems associated with the handling of the waste sludge and device corrosion by the chemicals, the AREVA decontamination device was shut down on September 13, 2011.

SARRY, the second cesium adsorption device from Toshiba/Shaw, has two series of adsorption vessels, and was added in August 18, 2011. After Cs is roughly removed with synthetic zeolite, it can be decontaminated with titanium silicate to at or below the Cs detection limit ($1/10^6$). With the KURION and SARRY devices, the waste adsorption vessels become high-dose secondary waste.

(3) Desalination Device

Contaminated water from which Cs has been removed is first separated into fresh water and concentrated saltwater by using a reverse osmosis (RO) membrane, and the concentrated saltwater is further subjected to evaporative concentration and separated into fresh water and concentrated liquid waste (secondary waste).

2. Contaminated Water Treatment Results and Secondary Waste Generation Amount⁴⁾

The cumulative treatment amount by the radionuclide removal device has reached 195,860 m³, and following operation of the SARRY device, the storage amount (contaminated water level) in each building has been undergoing a decreasing trend. As of January 3, 2012, the injection amount of treated water (fresh water) into the No. 1–3 reactors is 588 m³/day, and thus, a margin remains with respect to the actual treatment amount of approximately 1,000 m³/day over a period of 6.5 months by the water treatment system.

The amount of secondary waste generated is shown in **Figure 2**. The graph shows waste sludge of 581 m³, the number of waste adsorption vessels (290 KURION vessels and 28 SARRY vessels), and concentrated liquid waste of 5,452 m³. The SARRY device has treated a volume of 77,210 m³, and the generation amount thereof is one digit less than that by KURION.

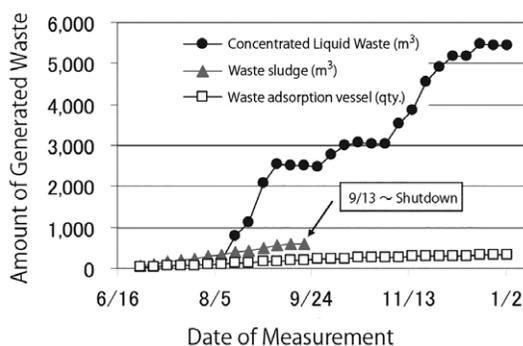


Figure 2 Amount of waste generated in contaminated water treatment (through Jan. 3, 2012)⁴⁾

3. Issues with Contaminated Water Treatment

(1) Increase in the Volume of Contaminated Water due to Groundwater Inflow

Table 1 shows the water volume, including that of contaminated water, in the treatment. After RO membrane desalination, the concentrated saltwater that has not yet been subjected to evaporative concentration is the largest, with the total volume reaching 44% of the total 200,000 m³. The inflow of groundwater into the buildings has been indicated as a primary cause for the increase of 80,000 m³ compared to 120,000 m³ immediately before the operation of the water treatment system³⁾. The system is operated to maintain a water level that is lower than the level of ground water so that contaminated water does not leak externally, and therefore, urgent groundwater countermeasures are being sought.

(2) Long-Term Stable Storage of Secondary Waste

Almost all radioactive Cs is concentrated in the waste adsorption vessels, and therefore, evaluations and countermeasures from a safety perspective, such as the generation of hydrogen through water radiolysis, are desired. Stabilization of waste sludge and evaluation of the corrosion of waste adsorption vessels and concentrated liquid waste storage tanks owing to salt content, are also important.

Table 1 Total Volume Including that of Contaminated Water in Treatment (As of Jan. 3, 2012)⁴⁾

Contaminated Water, Treated Water	Water Volume (m ³)	(%)
No. 1-4 Reactor Buildings	80,250	40
Centralized Waste Treatment Facility	15,540	8
Saltwater (After Cs Decontamination)	2,474	1
Concentrated Saltwater (After RO Membrane)	87,029	44
Concentrated liquid waste (after evaporation)	5,452	3
Treated Water (Fresh Water)	8,552	4
Total Volume	199,297	100

(3) Contaminated Water Treatment Moving Forward

Through the operation of desalination devices, the removal of calcium and other such seawater salt content is advancing; therefore, a water treatment system that takes the removal of Sr-90 (half-life of 30 years) contamination, which has been difficult thus far, is now desired.

II. Decontamination Adsorbents

1. Adsorbent Selectivity

In the area of selective adsorbents for radionuclide decontamination, there are numerous reports on primarily inorganic ion exchangers⁵⁾. Highly contaminated radioactive water is limited to the use of highly radiation-resistant inorganic ion exchangers. The Cs ion exchange and adsorption characteristics of many inorganic ion exchangers are being examined, and an indicator (ion-exchange free-energy change, ΔG°) that indicates the selectivity of ion-exchange adsorption has been reported. This value serves as a significant standard when comparing Cs adsorption capacities. With regard to the ΔG° value for inorganic ion exchangers that exhibit high selectivity for Cs, the selectivity for Cs increases as the negative value increases, and therefore, inorganic ion exchangers can be ranked as insoluble ferrocyanides > heteropoly acid salts > zeolite groups. When the Cs partition (distribution) coefficient values (K_d (cm³/g), the concentration ratio of Cs in a solid phase and a liquid phase) from a high-concentration (5M) Na salt solution and a high-concentration (3M) nitric acid solution are measured, insoluble ferrocyanide (KNiFC, KCoFC) and heteropoly acid salts (AMP, AWP) exhibit K_d values of 10³ cm³/g or higher (90% or higher as an adsorption rate). However, these highly selective adsorbents are fine powder particles as is, and are difficult to handle, and therefore, a granulation method must be developed and numerous inorganic porous body (silica gel, zeolite, etc.)-bearing composites are being researched⁵⁾. However, zeolites exhibit a high adsorption characteristic toward Cs even from a Na salt solution (seawater-based), are abundantly produced in Japan, and can be used as a packed column, and therefore, they excel as adsorbents for Cs decontamination at the local site.

2. Adsorbent Structure

Adsorbents having high selectivity for ¹³⁷Cs have channels with openings that are close to that of the ionic radius of Cs, the structure is stabilized by ion exchange with exchangeable cations, and many exhibit an “ion sieve action” of removing other cations having large

hydrated ion radii. For example, all high decontamination adsorbents (crystalline silicotitanate (CST), Ni-based insoluble ferrocyanides, **Figure 3**) used to treat highly contaminated water at the Fukushima Daiichi Nuclear Power Plant have narrow channels with openings that are close to that of the ionic radius of Cs. Within the nuclear plant sites, CST is used as a packed column and insoluble ferrocyanides are used for sedimentation treatment.

The zeolite group can be classified into zeolites having a three-dimensional basket structure and those having a “beehive”-type tunnel structure. The Si/Al ratio is from $1\sim\infty$, and the Cs and Sr adsorption characteristics vary significantly. In particular, “lantern-shaped” chabazite and “beehive”-shaped mordenite exchange, adsorb, and stabilize Cs inside narrow fine holes (**Figure 4**). Note that with regard to Sr adsorption, A and X types, which have three-dimensional basket structures, a small Si/Al ratio, and a large cavity (super cage) internally, exhibit high selectivity⁶⁾.

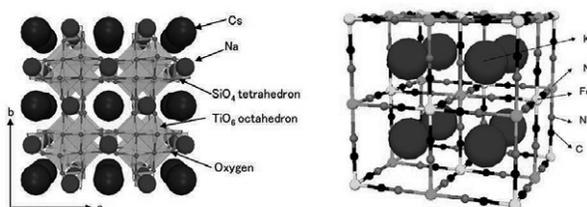


Figure 3 Structures of Adsorbents for High Cs Decontamination (CST (left), KNiFC (right), provided by the JAEA Center for Computational Science & e-Systems)

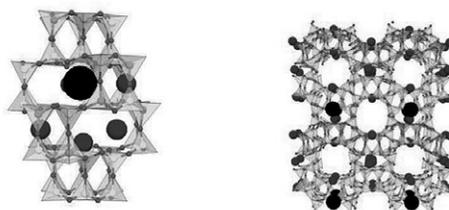


Figure 4 Schematic of Zeolite Structure (chabazite (left), mordenite (right), provided by the JAEA Center for Computational Science & e-Systems)

3. Selective Removal of Cs and Sr from Seawater

After the TMI Accident, the necessity for building a system for treating highly contaminated water was advocated in Japan, and the decontamination of radioactive Cs and Sr through inorganic ion exchangers was evaluated⁷⁾. Examples of selective removal of Cs from seawater through each type of zeolite powder are shown in **Figure 5**. Chabazite, mordenite, and clinoptilolite exhibit K_d values that are close to 10^3 cm³/g (around 90% as an adsorption rate). In addition, the selective removal of Cs and Sr from simulated highly contaminated water using a mixed zeolite column was evaluated⁸⁾.

Following the Fukushima Daiichi Nuclear Power Plant Accident, the characteristics of granular inorganic ion exchangers for adsorbing Cs and Sr from seawater were evaluated by a voluntary team from the Atomic Energy Society of Japan (including Hokkaido University, Tohoku University, Tokyo Institute of Technology, Kyoto University, Kyushu University, and JAEA), and adsorption evaluation data on over 600 points were disclosed with regard to data

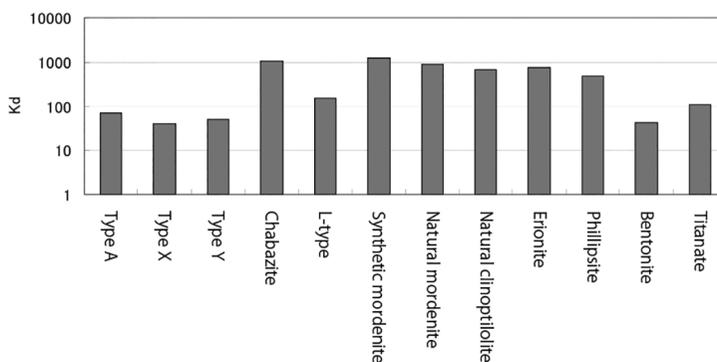


Figure 5 Comparison of K_d Values of Cs from Seawater through Various Zeolite Powders

such as adsorption rate, adsorption characteristics from concentrated seawater, and adsorption volume⁹⁾. In the tests, Cs was added to actual seawater in a reaction vessel, a liquid phase was sampled after every certain amount of time, the concentration was measured, and the change over time in Cs adsorption (K_d value) was examined.

The K_d values exhibit an increasing trend with the passage of time, and a near-equilibrium state is approached with the zeolites after 24 h. The ranking of the adsorptivity (ranking of the K_d value for Cs) is insoluble ferrocyanides > mordenite, chabazite > clinoptilolite > A, X, and thus, corresponds closely to the ranking of Cs selectivity. Of the zeolites, mordenite and chabazite have a K_d value of around 800 cm³/g (approximately 90% adsorption) after 24 h and approach the value of powdered zeolite. The ¹³⁷Cs radiation concentration in actual seawater does not change after filtration by a Millipore filter (0.45 μm), and even when the pH is adjusted with hydrochloric acid (to 2.4), there is almost no change in the adsorption results; therefore, as a chemical species, the ion-exchange adsorption as Cs⁺ is dominant. With Cs adsorption into mordenite from concentrated seawater (double and triple concentrations), compared to actual seawater, the K_d value exhibits a decreasing trend in accordance with the concentration of seawater at double concentration, $K_d = 197$, and at triple concentration, $K_d = 146$.

On the other hand, in the case of insoluble ferrocyanide-carrying resin and CST resin, high K_d values of 10³ or greater are maintained even in concentrated seawater. The adsorption isotherm of Cs into zeolite from seawater is an upward projection, and suggests high selectivity of Cs. The adsorption form was Langmuir-type adsorption and the saturated adsorption amount was 0.72 meq/g (9.5 wt%). Note that the Cs content percentage at the Cs concentration region (around 1.5 ppm) anticipated for seawater is estimated to be 0.0845 wt%. **Figure 6** shows the relation between the partition coefficient and adsorption rate constant (relative value) of Cs for various adsorbents in a seawater system. As is clear from the graph, the adsorbents are generally classified into highly selective insoluble ferrocyanides and CST and a zeolite group. The zeolite group has partition coefficient values in the range of 10²–10³, but a large difference in the adsorption rate is observed. As is observed in mordenite produced in Ayashi, Japan, the difference in the particle diameter significantly impacts the adsorption rate.

Figure 7 shows the relation between the partition coefficient and the adsorption rate constant (relative value) of Sr for various Sr adsorbents in a seawater system. The partition coefficient is lower than the case for Cs, but the type A and type X zeolites having a three-dimensional basket structure exhibit a K_d value of 10² or greater. Note that the ranking of divalent

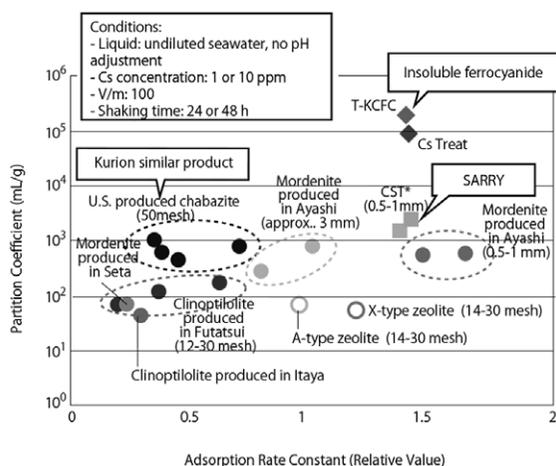


Figure 6 Relation between the Partition Coefficient and Adsorption Rate Constant (Relative Value) of Cs of Various Cs Adsorbents

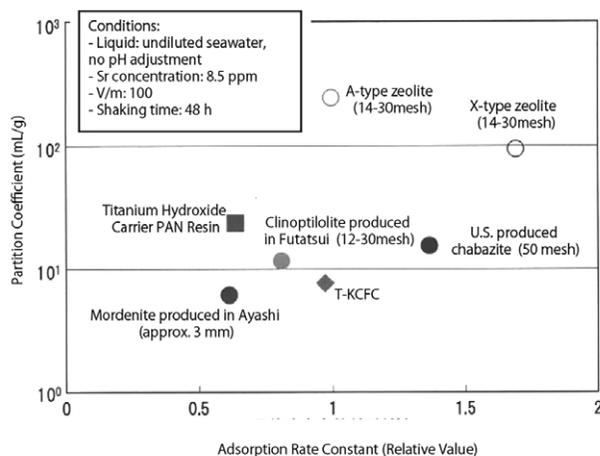


Figure 7 Relation between the Partition Coefficient and Adsorption Rate Constant (Relative Value) of Sr for Various Sr Adsorbents

cation selectivity in A-type zeolites is as follows.



Moving forward, the construction of a Sr decontamination system based on these zeolites is conceivable.

4. Adsorbent Evaluations and Issues

The partition coefficient and adsorption rate of the adsorbents are significantly affected by physical and chemical properties such as purity, cationic form, surface form, and macro

cavities, and therefore, the characterization must be carefully evaluated. When selecting and using an adsorbent, the adsorbent must be determined through a comprehensive evaluation that includes not only these adsorbent properties but also factors such as stability and solidification treatment.

III. Disposal of Solid Waste Generated by Contaminated Water Treatment

1. Definition of Disposal

Methods for treating and disposing of not only radioactive materials but also toxic substances can be summarized as the following two types. If waste can be diluted to a safe concentration or less, it can be diluted and discharged into the environment. If dilution is not possible, the volume of the waste is reduced as much as possible and the waste is then isolated into tight containers. Both methods are designed to eliminate any negative impact on the environment. Disposal is an act of making the wastes safe without any type of treatment after the act (after disposal), and treatment is the act of processing waste into a form that is suited for disposal and storage. The above-described adsorption treatment reduces high-concentration liquid waste to a concentration that can be discharged into the environment, and is a method of trapping radioactive substances and transferring them to durable solids.

Radionuclides have a half-life, and if the toxicity can be reduced to a safe level during the period in which the radionuclides are fully isolated, safety can be ensured. However, if the radionuclides have a very long half-life, a fully sealed state cannot be maintained until the toxicity is reduced to a safe level.

In this case, a restriction method is used so that the discharged concentration can be diluted. For example, methods of solidifying waste in concrete and melting waste and forming it into glass are used to treat waste and convert it into a chemical form that is not easily dissolved in water to thereby dissolve the waste slightly at a time until it is at or below an amount that can be dissolved or is at or below a safe concentration. In addition, providing a barrier material such as clay around the solid body and delaying the translocation thereof is a technique for reducing the concentration that is discharged into the environment. Rocks and soil also have a retardation effect on the translocation of radionuclides, and therefore, the depth of the disposal site also has an effect of reducing the concentration discharged into the environment.

2. Classification of Disposal Methods

The Specified Radioactive Waste Final Disposal Act of Japan classifies disposal methods into the following four types (**Figure 8**).

- (1) Trench disposal (simple landfill near the ground surface)
- (2) Pit disposal (burying underground in a concrete structure)
- (3) Subsurface disposal (disposal at a depth of 50 m or greater with the use of barrier materials)
- (4) Geological disposal (disposal at a depth of 300 m or greater with the use of barrier materials)

The type of disposal method to be used for disposing different types of wastes is determined by performing a safety evaluation so that public radiation exposure becomes 10 μ Sv or

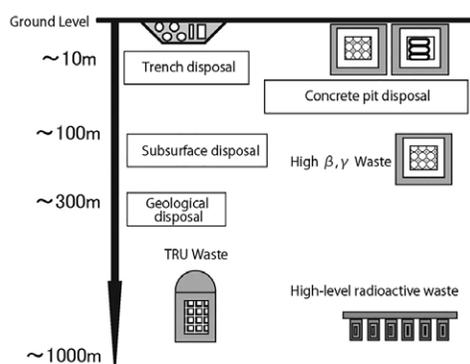


Figure 8 Classification of Underground Burial Disposal Methods

Table 2 Upper Limit Recommended Values According to Disposal Method⁸⁾ (Bq/t)

Nuclide	Trench Disposal		Pit Disposal		Subsurface Disposal and Geological Disposal Classification Value
	Recommended Upper Limit Concentration	Evaluation Value of Classification Value Dependency	Recommended Upper Limit Concentration	Evaluation Value of Classification Value Dependency	
C-14	-	$10^{10^{11}}$	10^{11}	-	10^{16}
Cl-36	-	10^7-10^8	-	$10^{11^{11}}$	10^{13}
Co-60	10^{10}	-	10^{15}	-	-
Ni-63	-	-	10^{13}	-	-
Sr-90	10^7	-	10^{13}	-	-
Tc-99	-	$10^5-10^6-10^{11}$ $10^4-10^5-10^{12}$	10^9	-	10^{14}
I-129	-	10^4	-	$10^{10^{12}}$	10^{12}
Cs-137	10^8	-	10^{14}	-	-
α -nuclide	-	10^9	10^{10}	-	10^{11}

¹¹: Value estimated from relative concentration with respect to Co-60.

¹²: Value estimated from relative concentration with respect to Cs-137.

less per year. However, waste can be generally classified by the concentration of radioactive substances contained in the waste (**Table 2**)⁸⁾. The values shown in the table indicate the maximum concentration at which disposal is possible with each of the disposal methods, and are set 10 to 100 times higher than the concentration that satisfies the yearly 10 μ Sv amount (10 times for α nuclides and trench disposal, 100 times for all others). Therefore, the average concentration in the waste to be disposed becomes 1/10th to 1/100th or less than the figures shown in the table.

3. Issues with Contaminated Water Treatment Waste Disposal

The following points must be considered with regard to the disposal of solid waste generated from the treatment of contaminated water in the Fukushima Daiichi Nuclear Power Plant.

- (1) Contained nuclides (radiation amount, half-life)
- (2) Amount of heat generated
- (3) Solidification form

(4) Accompanying substances

The type and concentration of the contained nuclides are important when determining which disposal method (depth) to use for disposal. This time, the waste contains an overwhelmingly large amount of cesium, but ^{137}Cs has a half-life of 30 years, and because this is relatively short, subsurface disposal and geological disposal classifications are not mentioned for cesium. Therefore, when determining the disposal depth, the concentrations of nuclides other than ^{137}Cs become important. Measurement is easy with γ -ray nuclides, but with regard to other nuclides, the concentration measurements or information for estimating the concentration is necessary.

Information regarding the amount of heat generated is necessary at the design stage of the disposal site. When the amount of heat generated is large, the removal of heat underground becomes a problem when waste is disposed, and to maintain the temperature at or below the heat resistance temperature of the barrier material, considerations such as leaving an interval between the wastes must be made. Nuclides that generate considerable heat have a relatively short half-life, and therefore, intermediate storage until disposal is also conceivable.

Another important issue is processing the adsorbing material into a form that is suited for disposal. With regard to ferrocyanide sedimentation in particular, there is a possibility of chemical degradation in a reducing environment; therefore, the material must be changed into a suitable form. It is thought that disposal sites can be designed for the disposal of zeolites in their current form. If converted into glass or compressed bodies, a unique treatment facility becomes necessary. In the case of high-temperature treatment, the adsorbed cesium might undergo volatilization and move into exhaust gas, and additional waste is then generated in the exhaust gas treatment system. From the perspectives of the heat resistance temperature of concrete and the generation of hydrogen through radiation decomposition of the contained moisture, the concrete solidification method cannot be easily selected for cases in which the concentration is high.

Ample consideration must also be given to accompanying substances. When contaminated water is treated, the water contains oil content and salt content, and therefore, the interaction between these and the barrier materials must be examined. There is a concern that the salt content can cause issues such as corrosion of metal vessels, a decrease in the strength of concrete structures, and a decrease in the swelling force/water cutoff performance of clay. When oil (organic substance) is contained, there is a concern about the generation of hydrogen or other gases through radiation decomposition, and therefore, incineration, acid digestion, or other such treatment becomes necessary.

Therefore, the disposal method is determined according to each solidified body while paying attention to the abovementioned points.

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