

Chapter 7 Evaluation of alternative technologies for the TRU waste disposal facility

7.1 Basic concepts for alternative technologies

The performance assessment of the basic design for the disposal facility and the engineered barriers presented in Chapter 4 revealed that the key nuclides in a geological repository for TRU waste are I-129 and C-14. These nuclides are long-lived, soluble and have very little sorption properties. In the groundwater migration scenario, it was also shown that the performance of the disposal facility and the engineered barriers is highly sensitive to parameters such as the hydraulic conductivity of the geological environment and sorption coefficients for I-129 and C-14. In future, more reliable data on these parameters will be obtained for specific geological environmental conditions. However, at this point in time neither a systematic approach to TRU waste disposal nor an actual disposal site has been specified. Consequently, it is considered appropriate to evaluate high-performance engineered barriers that are predicted to be safe in a wide range of geological environments. It is considered that this approach will result in wide safety margins for the disposal facility.

In addition, the specific characteristics of TRU waste disposal are evaluated in detail using the latest available information. Alkaline alteration of bentonite and long-term effects of nitrates are still controversial problems. These problems are being discussed internationally and evaluations are continuing (e.g. NUMO, 2004). Model validation and verification based on ongoing research and development will help to improve confidence. In addition, to mitigate the effects of these problems and to find innovative solutions, alternative engineered barrier designs, alternative technologies for waste treatment are considered appropriate.

In this chapter, two alternative concepts currently being developed are briefly described:

1. Improving safety margins for a wide range of geological environments by developing alternative engineered barrier technologies for:
 - Immobilizing I-129
 - Confining C-14 on the long term;
2. Minimizing uncertainties by:
 - Developing low-pH cement to reduce the alkaline alteration of bentonite
 - Developing nitrate decomposition techniques to reduce the long-term effects of nitrate/bituminized waste

It should be noted that the various alternative engineered barrier technologies described in this chapter have not been integrated into the basic concept. The reason is that these technologies are still in the early stages of development. Remaining issues concerning long-term reliability and the possibility of cost increases have been identified and associated research and development should be performed over an appropriate time period.

7.1.1 Alternative engineered barrier technologies

Since I-129 and C-14 are soluble and show little sorption, their release from the waste needs to be restricted in order to decrease their effects on performance assessment results. As the half-life of I-129 is 15.7 million years, it would be difficult to prevent the release of this nuclide from the waste and ensure its isolation from the surrounding environment for such long times. Hence, the evaluation assumes that release of I-129 will occur. On the other hand, the half-life of C-14 is 5,730 years and the time required for the activity of C-14 to decrease to about 1/1,000 of its initial value will be around 60,000 years, which is around 10 times its half-life. Over this timescale, it is considered that C-14 will be sufficiently contained by the waste package.

Alternative technologies for the engineered barriers of a geological repository for TRU are classified into the following two types:

- Iodine immobilization: a solidified body is used to control release
- Long-term confinement of C-14: containment of C-14 by a sealed waste package for 60,000 years.

7.1.1.1 Iodine immobilization technologies

For a geological repository of I-129 as a form of the spent silver-sorbent coming from reprocessing by private sector plants in Japan, safety is improved by developing iodine immobilization techniques and by considering and improving the performance of candidate immobilization solids in a wide range of geological conditions.

Iodine immobilization and preprocessing technologies are currently being developed (RWMC, 2005). Continuous management processes, the physical properties of the solids obtained and the upgrading of long-term performance assessment models are also being considered. A technical evaluation of the results will be undertaken from the perspectives of ensuring safety and economic efficiency for treatment and disposal in TRU waste disposal. Moreover, fundamental research on the properties for spent silver-sorbent will be used to develop tests on actual waste. Since complete retention of I-129 in solid phases is not possible, models are used to predict long-term safety by assuming release mechanisms from the solid phases.

7.1.1.2 Long-term C-14 confinement technologies

In order to reduce C-14 release, waste confinement packages are being developed. The aim is to develop waste packages that can effectively optimize the geological disposal system. For the canisters for compressed hulls and endpieces, disposal packages made of high-strength and ultra-low-permeable concrete (UHPC) or titanium alloy-carbon steel composites are considered. The decomposition of organic C-14 into inorganic form using self- β -ray-catalyst is also being evaluated.

The aim is to ensure that the waste package is able to contain the C-14 for a period of 60,000 years, which is about 10 times the half-life of C-14 (5,730 years). In the case of concrete containers, this goal is achieved by using the UHPC package without placing joints. In the case of the metal containers, the required retention period can be achieved by using disposal packages made of titanium alloy, which have high corrosion resistance.

Hence, assuring the long-term integrity of packages is necessary for the long-term confinement of C-14. For the UHPC concrete package, it is necessary to evaluate several phenomena such as fracturing, permeability and chemical degradation and to establish the assessment method of the long term stability of UHPC and its manufacturability. For titanium alloy-carbon steel composite containers, it will also be necessary to evaluate the mechanisms of titanium corrosion and material degradation under the reducing conditions occurring underground. Investigations of other long-term immobilization technologies for C-14, such as immobilization of inorganic carbon by oxidized TiO_2 -catalyzed, self- β -ray catalysis is also being carried out. Clarification of the decomposition mechanisms and modeling and evaluation of the long-term integrity of the catalytic agent are considered to be important issues.

7.1.2 Alternative approaches for reducing remaining uncertainties

7.1.2.1 Development of low-alkaline cement

It has been shown that the alteration of buffer material is greatly reduced if the pH remains below 11 (Kubo et al., 1998). Hence, it is considered that the performance of a disposal facility will be considerably improved if the pH of the solution that leaches from the cement is low. In order to decrease the effect of alkaline components from cementitious material on repository performance, several organizations have been considering modified cements. These modifications involve adjusting the cement components by adding pozzolanic material to Portland cement to produce relatively low-alkaline conditions. The development of low-pH cement such as LAC-S has been investigated (Hironaga and Tanaka, 2000).

Addition of pozzolanic materials such as silica fume or fly ash to Ordinary Portland Cement (OPC) creates cement with low-pH properties and Erwin hydrates (high fly ash content, silica fume cement (HFSC)). In the latter, the generation of soluble alkaline salts such as $\text{Ca}(\text{OH})_2$ is decreased (Owada et al., 2000a). Low-pH cement produced by adding silica powder (low heat, high performance concrete (LHHPC)) has also

been developed (Gray and Shenton, 1998).

OPC is a relatively low-cost material and is widely used in engineering applications. The alkaline characteristics of OPC would decrease the solubility of actinides and prevent the corrosion of steel reinforcements and the sorption distribution coefficients for major elements are such that this cement is useful for engineered barrier and backfill materials. Mixed cement such as fly ash cement and furnace cement are also considered to be potentially suitable as engineered barrier materials because of their greater chemical stability than OPC. In the development of low-pH cement, the effects of a decrease in pH, understanding and modeling strength, construction features and long-term behaviour, acquisition of sorption data and improvement of economic efficiency are considered to be important future issues.

7.1.2.2 Development of nitrate decomposition technologies

Large amounts of low-level enriched liquid waste which contains soluble or insoluble salts such as NaNO_3 , NaNO_2 , Na_2CO_3 and Na_2HPO_4 are generated during PUREX reprocessing as large volumes of nitric acid and TBP are used. It was proposed in Chapter 3 that, in order to prevent adverse effects of nitrate ions, Group 3 waste should be emplaced downstream of the facility and far from the other waste groups, with tunnels arranged in a horizontal direction to groundwater flow. As described in Section 4.4.11, the behaviour of nitrate in the deep geological environment has been investigated in recent years. However, model validation and confirmation is required in order to improve reliability.

In the JAEA Tokai reprocessing plant, bitumen solidification was initially adopted for ocean disposal of low-level enriched liquid waste and about 30,000 200L drums were manufactured between 1982 and 1997. In accordance with a partial revision of Japanese fire regulations in May 1988, a safety evaluation of the bitumen solidification process was carried out between 1989 and 1991. In particular, it was found that bitumen complexes with high concentration of nitrate salts and nitrites with no flame-retardant additives were classified as primary hazardous materials under the revised regulations (Ochiai et al., 1997a-d).

It is important to understand that there is still uncertainty regarding the behaviour of NO_3 in the deep geological environment or the chemical activity of bitumen solidification. Investigation of these uncertainties through laboratory or in situ experiments should be performed in order to improve the reliability of the evaluation of the disposal system. Additionally, alternative technology such as decomposition of nitrate salt and combustion treatment of bitumen components should be evaluated from the viewpoint of engineering feasibility, waste volumes/features of secondary waste and economic efficiency. It is also important to consider adopting such alternative technology as a treatment method for low-level enriched liquid waste.

7.2 Iodine immobilization technologies

Techniques for development of I-129 disposal are classified into the following 3 types.

- Leaching model (intergranular diffusion, congruent dissolution)
- Distribution equilibrium model
- Solubility equilibrium model

In the leaching model, I-129 is physically sealed into intergranular solids and is released from the solid by diffusion due to infiltrated groundwater. The iodine also leaches due to surface dissolution of the solid. In the distribution equilibrium model, iodine is released depending on its sorption/desorption property onto solid hydrates. In the solubility equilibrium model, iodine is fixed in an insoluble mineral as its component element.

Eight iodine immobilization techniques and their performance assessment models are summarized in Table 7.2-1. These are considered to be promising techniques for immobilizing iodine over a wide range of geological environments.

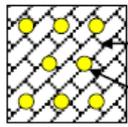
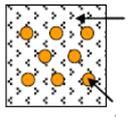
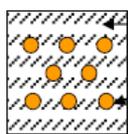
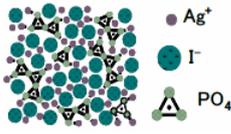
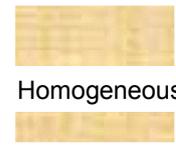
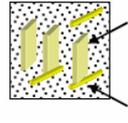
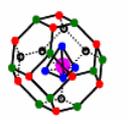
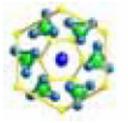
Table 7.2-1 Iodine immobilization techniques and performance assessment models

Solidification technique	Immobilization mechanism	Performance assessment model (assumption)
Rock solidification	AgI is fixed in SiO ₂ (quartz) grain boundaries	Diffusion through intergranular quartz
AgI glass	Immobilizing I as a glass-forming component (3AgI-2Ag ₂ O-P ₂ O ₅)	Leaching model
BPI glass	Fixing I in a glass (6.5PbO-3B ₂ O ₃ -0.5ZnO) matrix	Leaching model
Apatite solid	I adsorbed zeolite into fluor-apatite (Ca ₁₀ (PO ₄) ₆ F ₂) matrix	Leaching model
Hardened cement	Sorption of IO ₃ ⁻ onto ettringite and monosulphate	Distribution equilibrium model
Insoluble mineralization/ synthetic sodalite	Immobilizing I in synthetic sodalite (Na ₈ (AlSiO ₄) ₆ I ₂)	Solubility limit model
Insoluble mineralization/ synthetic lead apatite	Immobilizing I in synthetic apatite (Pb ₁₀ (VO ₄) ₆ I ₂)	Sorption model (ion exchange)
Copper matrix solid*	Immobilizing spent silver-sorbent in a copper matrix	Leaching model

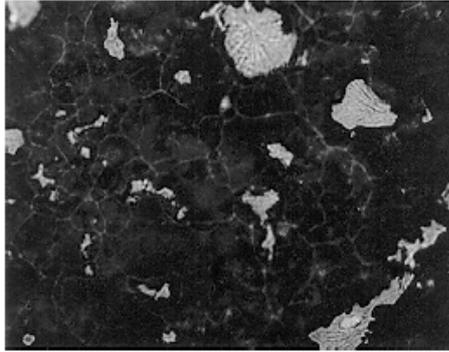
* Honda et al. (2005)

The schematic chemical compositions (raw materials and solids) and immobilization mechanisms for eight solids are shown in Table 7.2-2. Diffusion coefficient, leach rates and distribution coefficient for rocks, AgI vitrified waste, copper matrix solid and hardened cement are also listed.

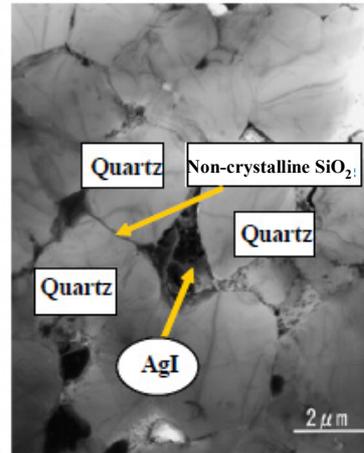
Table 7.2-2 Structure and chemical composition of iodine immobilization solids

Iodine immobilization techniques		Chemical composition		Conceptual diagrams of iodine confinement/immobilization	Iodine release parameter
		Raw material	Waste form		
Crystalline matrix	Rock	Spent silver-sorbent (=silica gel, AgI)	SiO ₂ (quartz), AgI (I content: 14wt%)	 Quartz AgI	Diffusion coefficient : 1.0×10 ⁻²⁰ (m ² /s)
	Apatite	Fluor-apatite (Ca ₁₀ (PO ₄) ₆ F ₂): Zeolite (I sorption) =85 : 15 (weight ratio)	Fluor-apatite (Ca ₁₀ (PO ₄) ₆ F ₂) : Zeolite (I sorption) (I content: 2wt%)	 Fluoro-apatite Zeolite absorbent with iodine	-
	Copper matrix	Cu powder: Spent silver-sorbent =50:50 (vol%)	Cu powder : Spent silver-sorbent (I content: 0.7wt%)	 Cu matrix Silver absorbent	Leach rate : 9.0×10 ⁸ (Bq/y)
Glass	AgI glass	AgI : Ag ₄ P ₂ O ₇ =3:1(mol ratio)	3AgI-2Ag ₂ O-P ₂ O ₅ glass (I content: 30wt%)	 Ag ⁺ I ⁻ PO ₄	Leach flux : 1.0×10 ⁻⁸ - 10 ⁻⁷ (g/cm ² /d)
	BPI glass	• Glass frit : BPI =91 : 9 (wt%) • Glass frit PbO : B ₂ O ₃ : ZnO =65 : 30 : 5 (mol%) • BPI ; BiPbO ₂ I	6.5PbO-3B ₂ O ₃ -0.5ZnO Glass, BiPbO ₂ I (I content: 2wt%)	 Homogeneous matrix	-
Cement	Hardened cement	• Alumina cement / CaSO ₄ ·2H ₂ O =100/15.5 • NaIO ₃ conc. 0.4 mol/dm ³ • NaIO ₃ sol./cement =0.56	AFm:10wt% AFt:46wt% Al(OH) ₃ :44wt% (I content: 1.85wt%)	 AFm or IO ₃ -AFm AFt or IO ₃ -AFt	Distribution coefficient : >100 ml/g
Synthetic mineral	Synthetic sodalite	NaAlO ₂ : SiO ₂ : NaI =3 : 3 : 1 (mol ratio)	Na ₈ (AlSiO ₄) ₆ I ₂ (I content : 11wt%) (measured value)	 Na Si Al I	-
	Synthetic lead apatite	PbO : V ₂ O ₅ : PbI ₂ =9 : 3 : 1(mol ratio)	Pb ₁₀ (VO ₄) ₆ I ₂ (I content 7.2wt%) (measured value)	 Pb V O I	-

As an example in Table 7.2-2, a brief description for the rock immobilization is shown here. Figure 7.2-1 shows an optical microscope image (left) and a TEM image (right) of AgI immobilized in the rock.



Optical microscope image of a thin section of rock (x 1000). Black: SiO₂; Grey/White: AgI



TEM image showing the rock surrounding AgI

Figure 7.2-1 Micrographs of AgI in rock

Based on TEM observations, it is found that SiO₂ in the matrix forms quartz crystals (a few μm -10 μm in diameter) covered by a thin layer (30 – 50 nm) of amorphous SiO₂. Iodine exists as AgI crystals which is sealed into the matrix pore as ca. 20 nm aggregates. Since the compressive strength of the rock is over 100 MPa, it is considered that fracturing is unlikely after disposal. Permeability was shown to be low.

Leaching of I and Si was evaluated in long-term experiments where rock was immersed in conditions envisaged in the TRU waste disposal environment, i.e. high pH and reducing conditions (artificial seawater equilibrated with a cementitious material, O₂ < 1 ppm, Na₂S (3×10⁻³ mol/dm³), pH 12.5 and 35°C), for 300 days. The temporal change in I and Si leach rates is shown in Figure 7.2-2.

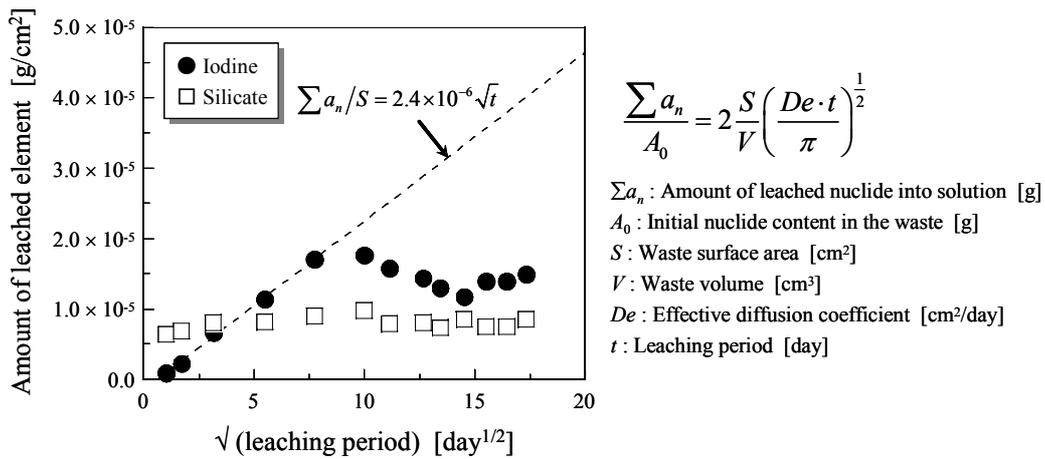


Figure 7.2-2 Relationship between amount of iodine and silicate leached and $\sqrt{(\text{leaching period})}$ for long-term leaching experiments

It is considered that the release of I from rock occurs through (1) the dissolution of amorphous SiO_2 forming approximately 50 nm cavities, (2) the dissolution of AgI by some reducing agents in solution which enters the cavities, and (3) diffusion of dissolved I out of the solid. The conceptual behaviour of I released from the rock over 60 days is shown in Figure 7.2-3. A linear trend can be seen up till about 60 days in Figure 7.2-2, indicating diffusion. However, this trend decreases with time after 60 days.

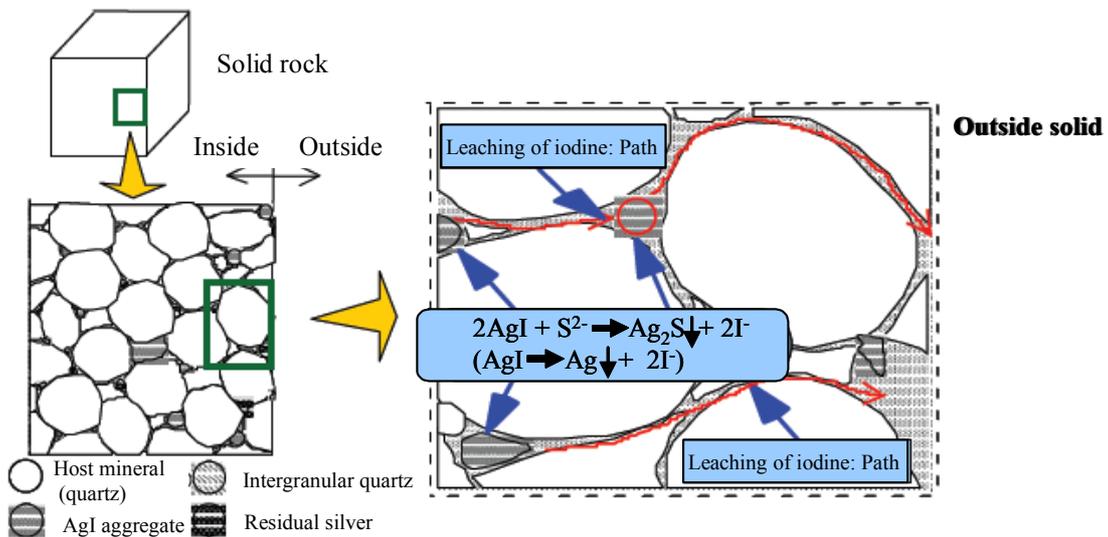


Figure 7.2-3 Schematic diagram of iodine leaching in rock

From the results above, it can be suggested that the iodine retention is maintained over the long term through high compressive strength, low permeability and the low solubility of the quartz matrix in a reducing environment.

From the I-129 release data and formula in Figure 7.2-2, the diffusion coefficient is found to be extremely low ($D_e = 4.1 \times 10^{-20} \text{ m}^2/\text{s}$), verifying that the solid has a strong inhibition for iodine release.

Using the iodine release data in Table 7.2-2 for an evaluation on a practical scale (rock: $\phi 25.5 \times 24(\text{cm})$, AgI glass: $\phi 43 \times 32.5(\text{cm})$, copper matrix solid: $\phi 82 \times 173(\text{cm})$), the release period of iodine from these solids is estimated to be about 100,000 years or more. In the analyses in Section 4.5.4, if a leaching period of 100,000 years is assumed for I-129 (without degradation of the engineered barriers), the maximum dose is $2 \mu\text{Sv/y}$ irrespective of the hydraulic conditions of geological environment. This is as low as the Reference Case.

7.3 Long-term C-14 confinement technology

In this section, long-term confining technology for C-14 (in Group 2 waste) developed by the Radioactive Waste Management Funding and Research Center is described.

Two types of packages were developed for confining C-14 over the long-term: (1) a package using high-strength and ultra-low-permeable concrete and (2) a metal package with Ti-Pd alloys (RWMC, 2005) (Table 7.3-1).

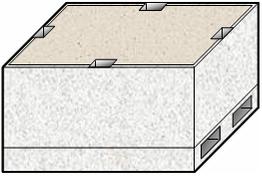
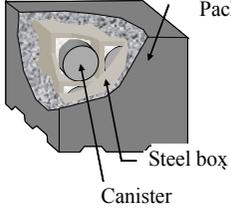
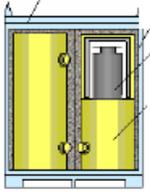
The concrete package is a casting mold made of high-strength and ultra-low-permeable concrete (UHPC) and is used for preventing the infiltration of groundwater. The packages were manufactured by the continuous placing method with heat-stress analysis performed as a countermeasure against crack formation during production. Small-scale packages ($60 \text{ cm} \times 60 \text{ cm} \times 60 \text{ cm}$) have already been successfully manufactured using this method. For long-term sealing, water infiltration characteristics of UHPC are estimated by a coupled permeability-chemical degradation analysis which considers Ca leaching and retention by ettringite generation based on its hydraulic conductivity ($4 \times 10^{-19} \text{ m s}^{-1}$), which is measured by cold isostatic pressing method (hereafter CIP). It was shown that water migration after 60,000 years would be about 14 cm and the loss in thickness due to chemical degradation about 4 cm. This is considered sufficient in terms of performance (Figure 7.3-2).

The sealing properties of the metal package made from Ti-Pd alloy for containment over 60,000 years were also evaluated (Table 7.3-2). In the initial oxidizing conditions immediately after closure of the disposal facility, it was shown that the metal alloy packages are immune to depassivation and crevice corrosion (Figures 7.3-3 and 7.3-4). In the reducing atmosphere that forms some time after closure, the growth of a hydrate layer resulting from hydrogen absorption and the progress of stress corrosion cracking (SCC) were

modeled. Assuming that the temperature in the disposal facility remains at 80°C, the thickness of the hydrate layer is about 35 µm and fracture depth about 17 µm. Again this is considered to be sufficient for the purposes of C-14 containment.

Although not a sealing technique, another approach being developed for reducing the effects of C-14 is to decompose organic C-14 to an inorganic form through use of photocatalysts. This is achieved through decomposition of organic C-14 using self-β-ray catalized excitation. However, there are many future issues that need to be dealt with, including clarification and modeling of the decomposition mechanism and evaluation of catalysts over the long-term.

Table 7.3-1 Characteristics of different types of packages for the long-term containment of C-14

Waste package		Reference	Package for long-term C-14 retention	
Specification and function		Package B	Concrete package for long-term C-14 retention	Metal package for long-term C-14 retention
Basic concept				
Purpose/concept		Canister storage package	<ul style="list-style-type: none"> Package sealed with high-strength and ultra-low-permeable concrete C-14 in Group 2 is retained for 60,000 years 	<ul style="list-style-type: none"> Package sealed by composite with titanium alloy C-14 in Group 2 is retained for 60,000 years
Basic specification	Size	1.50 m×1.50 m×1.10 m	1.8 m×1.8 m×1.6 m	1.038 m×1.038 m×1.726 m
	Material	Main body: carbon steel, filling: cement mortar	high-strength and ultra-low-permeable concrete	Handling package: carbon steel, main body: titanium alloy / carbon steel composite, filling: silica sand
	Weight	About 7 tonnes	About 13 tonnes	About 6.5 tonnes
	Number of stored waste	4 (canister)	6 (canister)	4 (canister)
Function	Mechanical stability	Considered	Considered	Considered
	• Storage efficiency			
	• Filling material	Cement mortar	None	Only retention of content
	• Mechanical evaluation	Stack considered	Consideration of stack and dropping	Consideration of stack and dropping
	• Pressure resistance	Not considered	Ground and lateral pressure considered	Ground and lateral pressure considered
	• Heat characteristics	Guaranteed below 80°C	Guaranteed below 80°C	Guaranteed below 80°C
	Containment		60,000 years (by prevention of water infiltration)	60,000 years (by corrosion prevention)
	• Chemical degradation		Consideration of leaching and Aft formation	Evaluation of corrosion mechanism and hydrogen embrittlement stress corrosion cracking
	• Nuclide diffusion coefficient	Not considered	× (from sealing concept)	× (from sealing concept)
	• Water density / permeability		Retention evaluation	Evaluation of corrosion behaviour and SCC
	• Corrosion resistance		Evaluation as chemical degradation	Sealing evaluation
	Produceability	Possible to design using existing techniques	Prevention of cracking during construction and placing joint	Plausible materials and design using existing welding techniques
	Confirmation of produceability	Unconfirmed	Confirmed with models up to 60 cm×60 cm×60 cm	
	• Demonstration with scale model			
Emplacement / handling	Assumed to be by forklift and crane	Assumed to be by forklift	Assumed to be by forklift and crane	
Dropping	Not evaluated	Evaluation of dropping on a corner from 4.5 m (maximum height of handling)	Evaluation of vertical drop from 5.5 m (during vertical loading)	
Gas effect	Not considered	Inner pressure is guaranteed by material strength because of sufficient internal space.		
Radiation shielding	Not expected	Additional shielding is necessary during handling	Surface: 1 mSv/h, 1 m: 50 μSv/h	
Others		Containment of C-14 by sealing for 60,000 years		

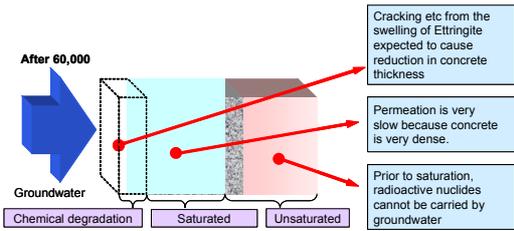
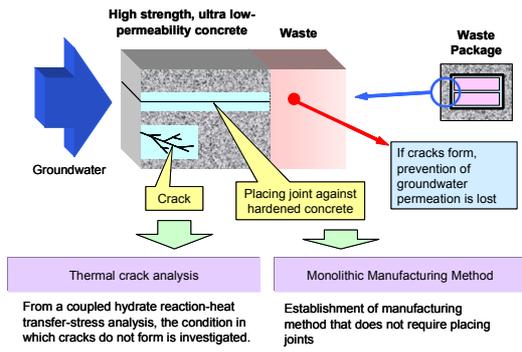


Figure 7.3-1 Concrete packages for containment of C-14

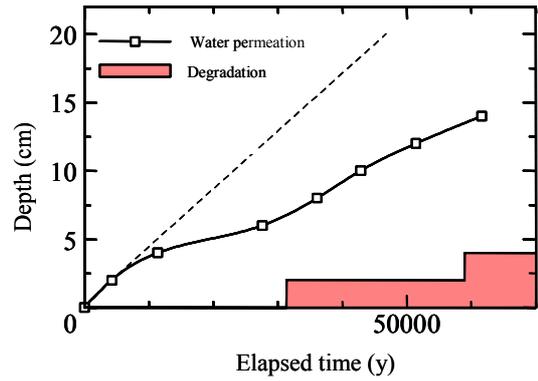


Figure 7.3-2 Result of coupled water permeation-chemical degradation analysis

Table 7.3-2 Metal packages for containment of C-14

Corrosion style	Required performance	Selection of basis
De-passivation	No sensitivity	Electric potential evaluation
Crevice corrosion	No sensitivity	$E_{SP} < E_{R,CREV}$
SCC resulted from hydrogen absorption	Not produced during target period	Production-evolution model

E_{SP} : Natural corrosion potential

$E_{SP} < E_{R,CREV}$: Critical electric potential of crack corrosion occurrence

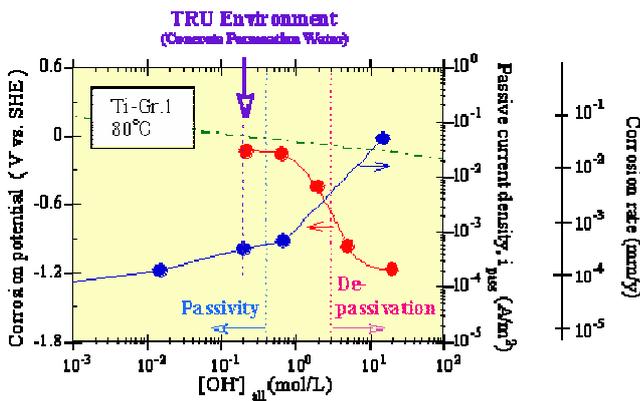


Figure 7.3-3 Passivation-depassivation transition of Ti-Gr.1 at 80°C

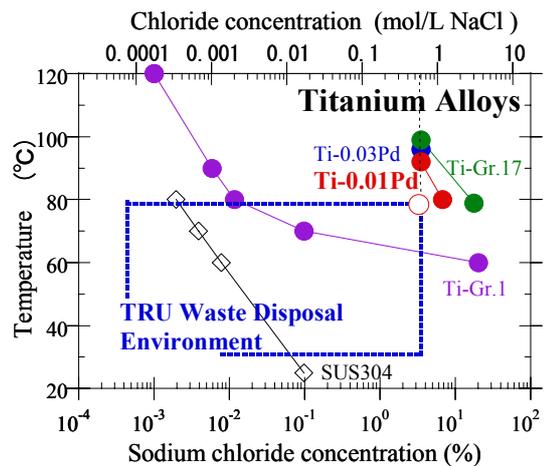


Figure 7.3-4 Initial corrosion sensitivity of titanium alloy in a TRU waste disposal environment

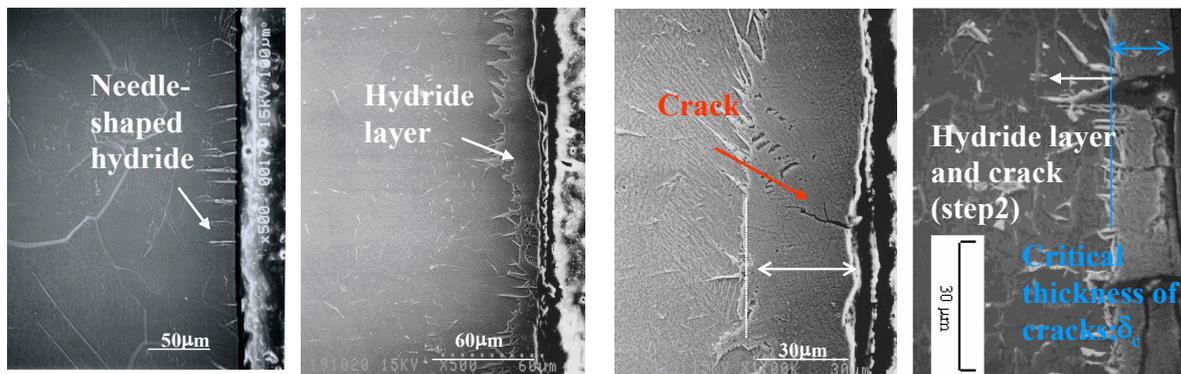


Figure 7.3-5 Result of SCC progress evaluation test of Ti alloy

7.4 Development of low-alkaline cement

The change in performance of the disposal facility due to alteration of barrier components is described in Section 4.4.2. In particular, it is well known that alkaline components (Na, K, Ca) leached from cementitious material increase the pH in the disposal facility and surrounding groundwater, resulting in alteration of the buffer material and host rock. Repository performance is thus affected by temporal changes to permeability and/or sorption properties (e.g. Aoyagi et al., 1998; Bateman et al., 1998). Since buffer material is not greatly altered if $\text{pH} < 11$ (Kubo et al., 1998), reducing the pH of leachates from cementitious material by developing low-pH cement has been a key area of research.

In Japan, two types of low-pH cement are being developed (1) by adjusting the components of cementitious materials and (2) by adding large amount of pozzolans to Ordinary Portland Cement (OPC). These two areas of research are summarized briefly here.

7.4.1 Adjusting the composition of raw materials and cement additives

This type of low-pH cement is created by adjusting the composition of raw materials and the heating conditions used to produce clinker and the mineral composition of hydrates added to clinker to produce hardened cement. $\text{Ca}(\text{OH})_2$, C-S-H, monosulfate (AFm), ettringite (Aft) and hydrogarnet (C_3AH_6) are alkaline metals that leach into groundwater from hardened cement. It is therefore considered possible to control the alkaline content of leachate by changing the composition of hydrates used during cement hardening.

Cement with gypsum added to Erwin-pyrite-ferrite type clinker was evaluated (Takuma et al., 1996; Sakamoto et al., 1996) and it was found that leachate from the hardened solid was reduced to pH 10.3 (Fujita et al., 1998). This cement is called Low Alkaline Cement (LAC). The main hardened component in OPC is C-S-H, while that of LAC is ettringite. The strength of LAC was found to be almost the same as OPC (Fujita et al., 2005) (Figure 7.4-2). Hence, LAC creates a low-pH leachate while, at the same time, has the same strength as OPC. Due to the time needed for hardening and high heat generation, a full-scale demonstration has yet to be performed. This is a future task for demonstrating the practical feasibility of this cement. Since the mineral type in the hardened LAC is different from that of OPC, large-scale demonstration of reactions with groundwater should also be considered.

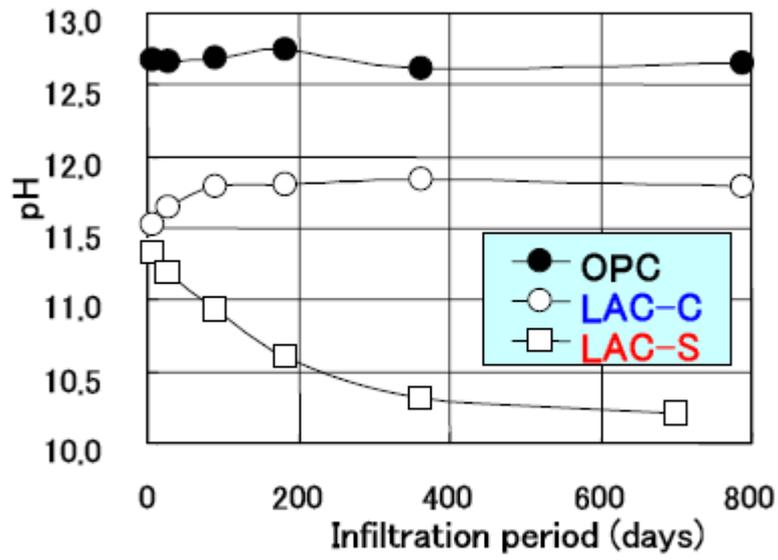


Figure 7.4-1 Comparison of pH of leachates from LAC and OPC

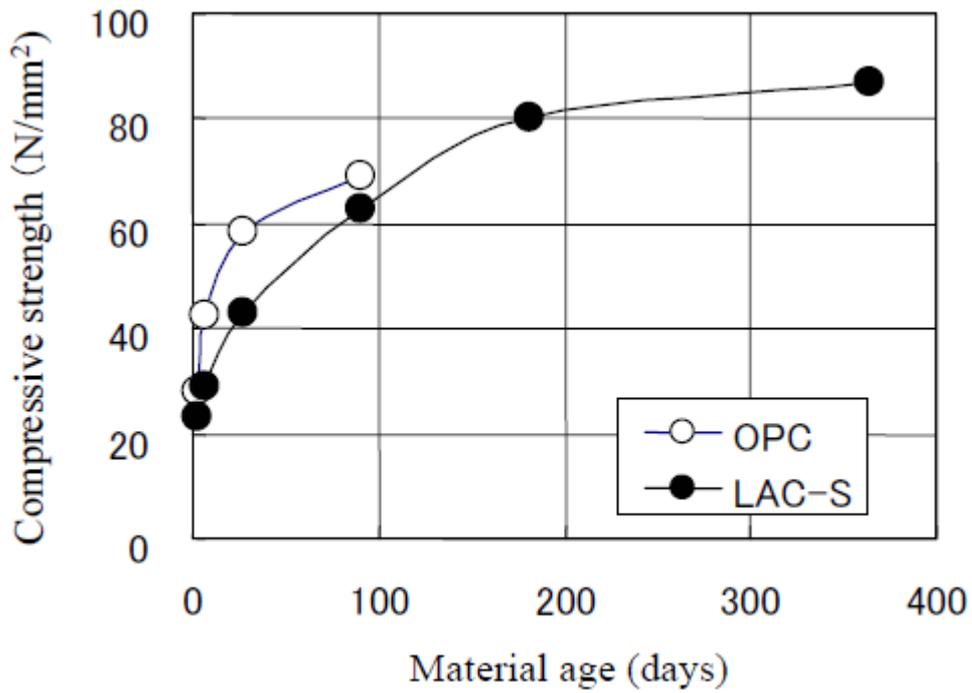


Figure 7.4-2 Comparison of the compressive strength of LAC and OPC

7.4.2 Adding large quantities of pozzolans

It is considered that Ca(OH)_2 which is contained in hardened cement, forms from Ca that is not completely consumed by hydrated hardening reactions (Berner, 1992). However, SiO_2 or Al_2O_3 in pozzolans generate C-S-H or calcium-aluminate-hydrate (C-A-H) by pozzolanic reaction with Ca (Arai, 1991); these have a solubility that is lower than that of Ca(OH)_2 and hence can potentially reduce Ca ion concentration in the leachate. Based on this concept, low-pH cement was developed by adding large amounts of fly ash and silica fume to high-volume silica fume cement to produce high-volume fly ash silica fume cement (HFSC) (Mihara et al., 1997; Owada et al., 2000a).

Figure 7.4-3 shows the variation in pH of leachate from OSF cement, which is a type of HFSC made by adding fly ash and silica fume to OPC. The pH of the leachate from OPC exceeds 12.5 (Ca(OH)_2 equilibrium), while that of OSF does not exceed 11. Also, the Ca ion concentration in leachate increases in OPC up to about 20 mmol (Ca(OH)_2 equilibrium), but for OSF it is only several mmol (Owada et al., 2000a).

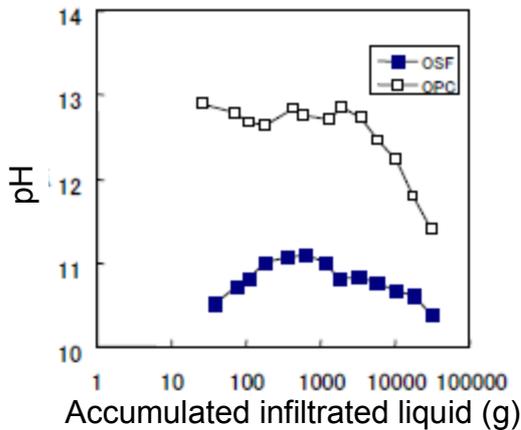


Figure 7.4-3 pH variation of leachate from OPC and HFSC

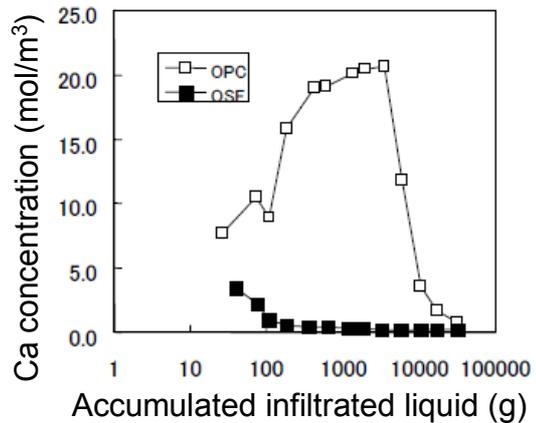


Figure 7.4-4 Variation of Ca concentration of leachate from OPC and HFSC

Table 7.4-1 Solidification time of HFSC mortar and compressive strength

Cement	Solidification time (hours – minutes)		Compressive strength (MPa)				
	Start	Finish	Material Age 2 days	Material Age 3 days	Material Age 7 days	Material Age 28 days	Material Age 91 days
HSF	28-20	32-10	5.7	8.2	12.3	26.4	39.8
OSF	26-50	31-40	5.1	8.5	16.7	37.7	50

The flow properties and mechanical strength of HFSC were also investigated and it was shown that this cement had sufficient workability for filling small spaces. It was also shown that the hardening time and compressive strength (Table 7.4-1) were appropriate for practical application (Owada et al., 2000b). Concerning the evaluation of the long-term alteration of HFSC, since the mineralogy of hardened HFSC is not different from that of hardened OPC, it was shown that the relationship between the Ca/Si ratio and pH of leachate could be illustrated using existing models for OPC leaching (e.g. Atkinson, 1987; Berner, 1988).

7.5 Development of nitrate decomposition technologies

The methods for removing nitrates from liquid waste are divided into decomposition of nitrate into other materials and the removal of nitrates from the liquid waste. These methods are further sub-divided as shown in Figure 7.5-1. They are used for processing liquid wastes or radioactive liquid wastes in the general industrial field.

The decomposition processes employed are reduction processes using electrolysis, oxidation-reduction reactions and bioprocessing using microbes to decompose the nitrates. Membrane disposal (dialysis) and ion exchange are classified as removal processes.

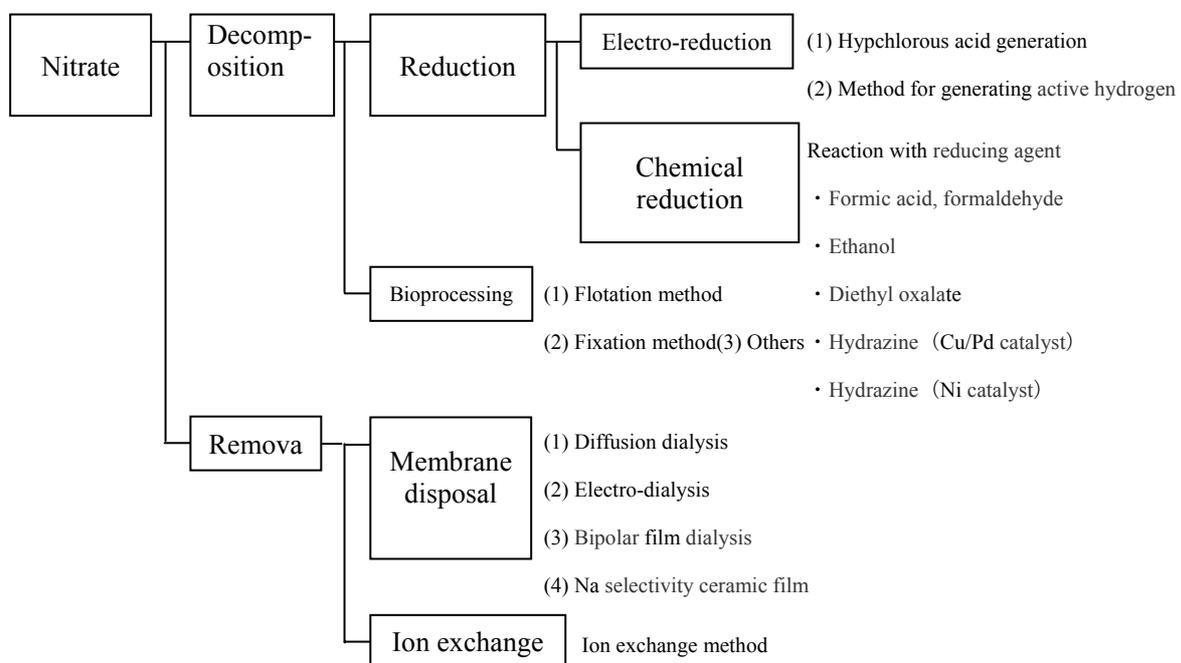


Figure 7.5-1 Methods for decomposing and removing nitrates

Among the decomposition methods based on chemical reduction, the one using reduction by formic acid and formaldehyde decreases the concentration of nitrates and nitric acid in solutions by catalyzing reactions of these reagents. The method was developed for denitrification of nitric acid by Broudic et al. (2000). This reducing reaction is complex and it has been shown to depend on many factors, such as acidity and temperature. For the stable progress of reactions, it is necessary to add NaNO_3 , maintain the solution at boiling point and strictly control the flow velocity of the reagents. A future issue to be considered is the intense reaction that occurs if conditions are inappropriate.

The processing technique for nitrates that uses amide sulphuric acid has already been used in the JAEA Ningyotoge Works to treat nitric acid waste in the form of NaNO_3 . The method has actually achieved decreased concentrations of nitrogen and uranium in liquid wastes that are suitable for discharging into a river. In this example application, the only radionuclide in the nitrate salt solution is U and the behaviour of Pu and fission products in solutions of nitrate are considered to be issues for future investigation.

In each case where a decomposition process is to be employed, the treatment of byproducts from the decomposition, including the remaining cations (especially Na), the behaviour of radionuclides, the economic implications of secondary waste and comprehensive treatment should be considered.

There are already more than about 30,000 200L drums of bituminized waste and preprocessing of the waste to separate nitrates is necessary in order to decompose the contained nitrates.

Although there are no examples of experiments or other research concerning the preprocessing, tests of nuclide and salt leaching by water were performed using samples from actual solids from JAEA. It was found that about 8% of salt infiltration at 25°C was increased to 70% at 40°C for 400 days (Hida et al., 1999). Further evaluations are needed to determine the optimum conditions.

A plasma incinerator (Hoffelner et al., 1996) is used in the ZWILAG centralized interim storage facility in Switzerland to decompose various types of mixed radioactive waste and organic materials using a high-temperature plasma arc. Although it is expected that this method will result in gasification and mineralization of the nitrate and bitumen components, an evaluation of the applicability of the method and the safety of its operating conditions must be considered in future.

References

- Aoyagi, T., Maeda, M., Mihara, M. and Tanaka, M. (1998): Evaluation of Permeability and Swelling Pressure of Compacted Bentonite Using a Calcium Hydroxide Solution, Japan Nuclear Cycle Development Institute, JNC TN8400 98-002. [written in Japanese]
- Arai, Y. (1991): Semento no Zairyo-Kagaku (in Japanese) (Material Chemistry of Cement, Second Edition, translated by JAEA), Dainippon-Tosho. [written in Japanese]
- Atkinson, A., Heare, J.A. and Knights, C.F. (1987): Aqueous chemistry and thermodynamic modelling of CaO-SiO₂-H₂O gels, United Kingdom Atomic Energy Authority HARWELL Approved for Publication, AERE R 12548.
- Bateman, K., Coombs, P., Noy, D.J., Pearce, J.M. and Wetton, P.D. (1998): Numerical modeling and column experiments to simulate the alkaline disturbed zone around a cementitious radioactive waste repository, Mat. Res. Soc. Symp. Proc., 506, pp. 605.
- Berner, U.R. (1988): Modelling the Incongruent Dissolution of Hydrated Cement Minerals, Radiochimica Acta, 44/45, 387.
- Berner, U.R. (1992): Evaluation of Pore Water Chemistry during Degradation of Cement in a Radioactive Waste Repository Environment, Waste Management, 12.
- Broudic, J.C., Brossard, P. and Ananiev, A., et al. (2000): Method for reducing nitrate and/or nitric acid concentration in an aqueous solution, PCT/WO 00/06503.
- Fujita, H., Noguchi, S. and Hironaga, M. (1998): Development of Low Alkalinity Cement Containing Häüyne –Effect of the Mixing of Silica Fume on the pH Behavior–, 1998 Fall Meeting of the Atomic Energy Society of Japan (III), September, 1998, p. 755. [written in Japanese]
- Fujita, H., Hironaga, M., Komatsu, S. and Inatsugu, S. (2005): Physical Properties of Concrete and Mortar Using Low Alkalinity Cement Containing Häüyne, 2005 Annual Meeting of the Atomic Energy Society of Japan (III), March, 2005, p. 655.
- Gray, M.N. and Shenton, B.S. (1998): Design and Development of Low-Heat, High-Performance, Reactive Power Concrete, The International Symposium on High-Performance and Reactive Power Concrete, Sherbrooke PQ, Canada.
- Hida, S., Furukawa, N., Murayama, Y., Ito, Y., Ishii, T. and Akimoto, F. (1999): Asufaruto-Kokatai no Shinseki Shiken (in Japanese) (Leaching Experiment of Asphalt Waste, translated by JAEA), Japan Nuclear Cycle Development Institute, JNC TN8430 99-007. [written in Japanese]
- Hironaga, M. and Tanaka, Y. (2000): Development of Low alkaline Cement, Central Research Institute of Electric Power Industry, CRIEPI Annual Research Report 2000. [written in Japanese]
- Hoffelner, W., Mueller, T., Fuenfschilling, M.R., Jacobi, A., Eschenbach, R.C., Lutz, H.R. and Vuilleumier, C. (1996): New incineration and melting facility for treatment of low level radioactive waste in Switzerland, International Workshop on Therm Plasmas Hazard Waste Treatment, Verenna, 1996, pp. 126-145.
- Honda, A., Suguro, T. and Sasaki, R. (2005): An Estimation of the Release of Radioactive Iodine from the Waste Package Solidified by Copper Matrix, Japan Nuclear Cycle Development Institute, JNC

- TN8400 2004-029. [written in Japanese]
- Kubo, H., Kuroki, Y. and Mihara, M. (1998): Experimental Investigation on Alteration of Bentonite by Concrete Pore Fluids, *Tsuchi-to-Kiso*, Vol. 46, No. 10, pp. 31-34. [written in Japanese]
- Mihara, M., Iriya, K., Neyama, A. and Ito, M. (1997): Experimental and Modelling Studies on the Interaction between Cement Paste with Silica Fume and Distilled Water, *Radioactive Waste Research*, Vol. 3, No. 2, pp. 71-80.
- NUMO (2004): Proceedings of the International Workshop on Bentonite–Cement Interaction in Repository Environments, Nuclear Waste Management Organization of Japan, NUMO-TR-04-05.
- Ochiai, K., Fujita, H., Murayama, S. and Takeda, K. (1997a): Asufaruto-Kokatai no Kikenbutsu Hantei Shiken (in Japanese) (Hazard Judgment Test of Asphalt Waste, translated by JAEA), Power Reactor and Nuclear Fuel Development Corporation, PNC TN8410 97-115. [written in Japanese]
- Ochiai, K., Fujita, H., Murayama, S. and Takeda, K. (1997b): Asufaruto-Kokatai no Kikenbutsu Hantei Shiken II (in Japanese) (Hazard Judgment Test of Asphalt Waste II, translated by JAEA), Power Reactor and Nuclear Fuel Development Corporation, PNC TN8410 97-116. [written in Japanese]
- Ochiai, K., Fujita, H. and Murayama, S. (1997c): Asufaruto-Kokatai no Kikenbutsu Hantei Shiken III (in Japanese) (Hazard Judgment Test of Asphalt Waste III, translated by JAEA), Power Reactor and Nuclear Fuel Development Corporation, PNC TN8410 97-117. [written in Japanese]
- Ochiai, K., Fujita, H. and Murayama, S. (1997d): Asufaruto-Kokatai no Kikenbutsu Hantei Shiken IV (in Japanese) (Hazard Judgment Test of Asphalt Waste IV, translated by JAEA), Power Reactor and Nuclear Fuel Development Corporation, PNC TN8410 97-118. [written in Japanese]
- Owada, H., Mihara, M., Iriya, K. and Matsui, J. (2000a): An Investigation of Cementitious Materials for Radioactive Waste Repository –Mechanic Properties of Low Alkalinity Cementitious Materials–, Japan Nuclear Cycle Development Institute, JNC TN8400 99-057. [written in Japanese]
- Owada, H., Mihara, M., Iriya, K. and Matsui, J. (2000b): A Study on the Practicability of Highly Containing Fly Ash and Silica Fume Cement, Japan Nuclear Cycle Development Institute, JNC Technical Review, Vol. 6., pp. 43-52. [written in Japanese]
- RWMC (2005): Development of packages for TRU wastes (H16), Radioactive Waste Management Funding and Research Center. [written in Japanese]
- Sakamoto, H., Haga, K., Shibata, M., Fujita, H. and Kobayashi, K. (1996): pH Control of Cement for Engineered Barrier, *Journal of the Atomic Energy Society of Japan*, Vol. 38, No. 4, pp. 51-53. [written in Japanese]
- Takuma, Y., Fujita, H., Sakamoto, H., Kobayashi, K., Haga, K. and Uchida, S. (1996): Hydration and pH Behavior of the Cement Prepared from the Mixture of Häüyne-Containing Clinker, Anhydrite and Blastfurnace Slag, *Journal of the Ceramic Society of Japan*, Vol. 104, No. 11 (1215), pp. 1040-1047. [written in Japanese]