

## **Cement Based Encapsulation Experiments for Low-Radioactive Liquid Waste at Tokai Reprocessing Plant - 11078**

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### **Abstract**

Development work has been carried out for several years on cement based encapsulation techniques for low-level radioactive liquid waste generated from Tokai Reprocessing Plant (TRP). The newly developed processes will be installed in the liquid waste treatment process at the Low-level radioactive Waste Treatment Facility (LWTF) that was constructed to provide safe, effective and economic treatment of Low-Level radioactive Waste (LLW). There are two main liquid effluents that will be treated in the LWTF: the first contains mainly sodium nitrate and the second contains principally monosodium phosphate. Both effluent streams will undergo chemical treatment processing and cement immobilization prior to disposal.

The essential technologies of the LWTF liquid waste treatment and encapsulation processes for each of the waste streams for the nitrate-ion decomposition and cement based encapsulation technology are described. In addition, recent development work for the encapsulation of sodium carbonate is described.

### **INTRODUCTION**

The LWTF was constructed to treat a number of wastes and has been undergoing non-radioactive commissioning since 2006. Two liquid wastes will be treated in the LWTF: a sodium nitrate based liquid waste and monosodium phosphate based liquid waste that is referred to here as simply “phosphate effluent”.

The sodium nitrate based liquid wastes arise from processes such as solvent washing effluent, radionuclide analysis waste, off-gas scrubber waste, and decontamination waste, while the phosphate effluent is generated from the Solvent waste Treatment demonstration facility during recycling of dodecane. Currently, the two effluent streams are being stored in the low-level radioactive waste storage facility but will subsequently be treated in LWTF and encapsulated in cement for interim storage and disposal.

The sodium nitrate containing effluent will be treated by a radionuclides separation process that has been developed by Japan Atomic Energy Agency (JAEA) to reduce the cost of deep geological disposal. This process partitions the waste into two waste streams; the first is a “slurry effluent” containing the majority of the activity from the parent effluent but has only ~1/10 the volume and will be disposed of by deep burial, the second is referred to here as “nitrate effluent” and has a very low radioactivity content that is acceptable for shallow burial. This process reduces the overall disposal cost since only the higher activity, but smaller volume stream requires deep disposal, whereas the untreated parent effluent would have all required deep disposal.

The nitrate effluent has an acceptable activity level for shallow burial, but there are concerns that leaching of high levels of nitrates could affect the environment surrounding a disposal site. For this reason, JAEA is developing technology to decompose nitrate ions. Small-scale trials using hydrazine, formic acid and a Pu-Cu catalyst have shown that over 90% of the sodium nitrate can be converted to sodium carbonate and nitrogen gas. Alternatively, some of the waste stream can be converted to NaOH for reuse in the nuclide separation process by adjusting the reactant in the decomposition reaction.

The phosphate effluent is not treated using the radionuclide separation process because it is not cost-effective. Instead, the phosphate effluent will be encapsulated in cement following pre-treatment with lime that ensures it is compatible with the immobilization process.

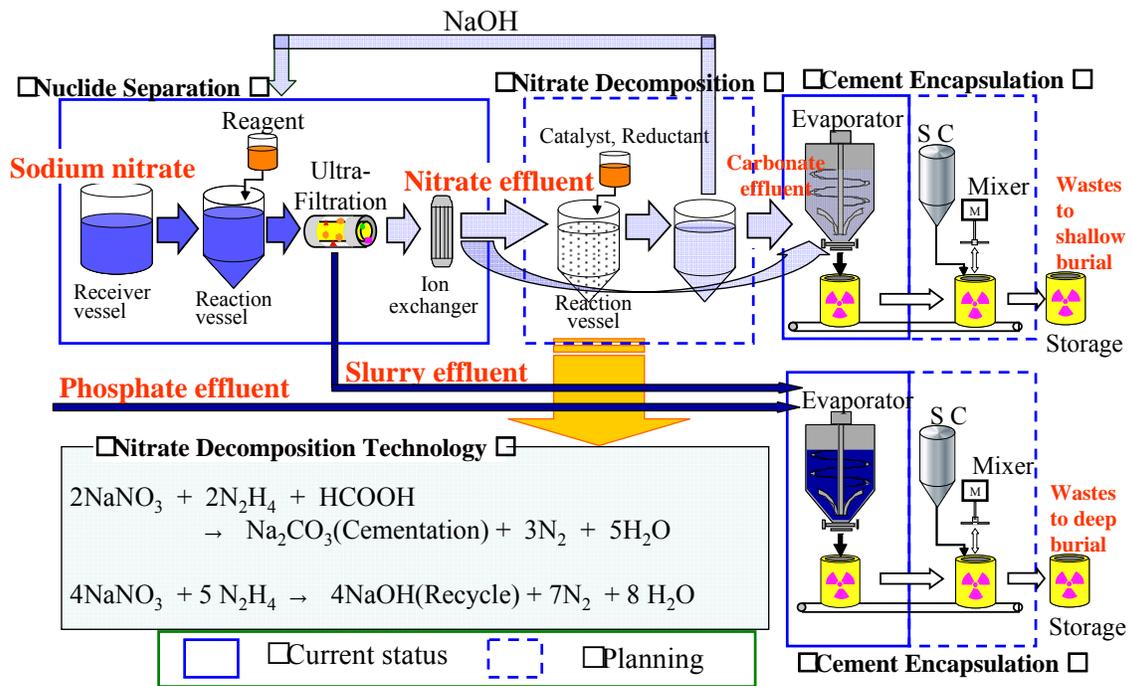
The proposed treatment methods for each of the wastes have required the development of new engineering and technical solutions. Particular challenges include minimising the volume of waste for geological disposal

and the development of robust cement encapsulation systems. In the first part of this presentation technical development of the LWTF liquid treatment process, cement based encapsulation for a sodium nitrate based liquid waste and phosphate effluent, and nitrate-ion decomposition technology are summarized. The second part of the presentation focuses on recent research for cement based immobilization of the sodium carbonate based liquid waste which will be generated from the nitrate-ion decomposition process.

**OUTLINE OF WASTE TREATMENT IN THE LWTF**

The basic flowsheet of the radioactive liquid waste treatment process in the LWTF is shown in Figure I. As described above, there are five main waste treatment processes that will be carried in the LWTF:

- (i) nuclide separation for sodium nitrate liquid waste treatment to generate slurry effluent and nitrate effluent;
- (ii) encapsulation of slurry and nitrate effluent;
- (iii) phosphate effluent pre-treatment and encapsulation.
- (iv) nitrate decomposition of nitrate effluent to form sodium carbonate effluent;
- (v) encapsulation of sodium carbonate containing effluent.



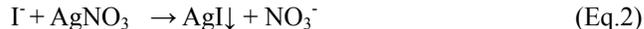
**Figure I. Basic flow of the radioactive waste treatment in LWTF**

**ESSENTIAL TECHNOLOGIES OF THE LWTF**

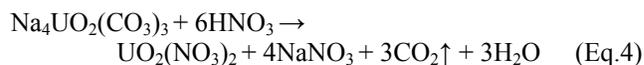
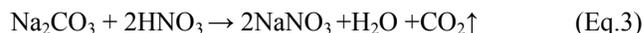
**Sodium nitrate liquid waste treatment process - Radionuclide separation process<sup>(1) (2)</sup>**

The removal process for the radionuclides consists of precipitation, co-precipitation, and ion exchange. In the first precipitation process iodine is separated from the liquid wastes by precipitation with silver nitrate (following Eq.2)) followed by removal of this solid phase by ultra-filtration. Iodine exists in various oxidation states in the solution, therefore to produce silver iodide any iodate ions need to be reduced. This can be achieved using sodium sulfite (following Eq.1)). The optimum pH of the precipitation reaction is pH 6.5-7.0.

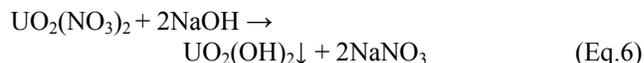
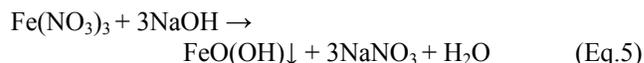




The next step uses co-precipitation with ferric hydroxide floc to remove alpha nuclides (Pu, U, etc.) and beta/gamma nuclides (Ru, Ce, etc.). Uranium forms a soluble uranyl-carbonate complex with carbonate ions and this reduces the effectiveness of uranyl-carbonate separation by ferric hydroxide co-precipitation and ultra-filtration. Consequently it is necessary to remove the carbonate ions from solution before the co-precipitation process. This is achieved by converting uranyl-carbonate to uranyl-nitrate by adding nitric acid to adjust to pH 1, also the temperature of the liquid waste is kept at 80°C. As a result, the carbonate ion is driven out from the liquid waste in the form of CO<sub>2</sub> gas. This reaction is represented by following (Eq.3) and (Eq.4).



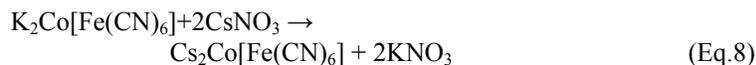
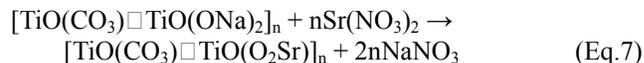
In the case of uranyl-nitrate, the co-precipitation reaction is represented simplistically by (Eq.5) and (Eq.6)



The amphoteric nuclides are not removed under the alkaline conditions, but can be removed under neutral conditions with a ferric hydroxide floc. The procedure is the same as that of the preceding stage, excluding the pH condition. The amount of co-precipitant added is 150 mgL<sup>-1</sup> ferric nitrate. In this case the decontamination factor of alpha nuclides is over 1E+6 and the decontamination factor of beta/gamma nuclides is over 1E+2.<sup>(3)</sup>

Since the liquid waste contains a large quantity of sludge a cross flow-type ultrafilter has been adopted to remove it from the stream. The liquid phase crosses and permeates through the filter elements while the sludge is concentrated on the interior surface. By using the cross flow-type of ultrafilter the accumulation of sludge on the filter is prevented and clogging is considerably reduced as concentrated sludge is washed away by the circulation flow.

The final step involves ion exchange. This is used because cesium and strontium have high solubilities and removal by co-precipitation is ineffective. Cesium is removed from the nitrate effluent using a potassium cobalt ferrocyanide resin, while strontium is removed using a sodium titanate resin. The binder in these resins is polyacrylonitrile. These reactions are represented by the following (Eq.7) and (Eq.8).



### **Sodium nitrate liquid waste treatment process - Cement based Encapsulation Technology**<sup>(4) (5) (6)</sup>

Slurry and nitrate effluent will be immobilized in the LWTF using an in-drum mixing process. Following separation of the nitrate containing waste into two types of waste effluents (nitrate and slurry effluents), water is evaporated from the liquid waste to minimize its volume. The total salt content of the effluent after evaporation is about 70 wt% and the approximate slurry effluent and nitrate effluent salt composition is given in Table I.

Table I. Typical Salt Composition of Nitrate, Slurry and Phosphate Effluents

Waste	NaNO <sub>3</sub>	NaNO <sub>2</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Fe(OH) <sub>3</sub>
Nitrate effluent (wt%)	98	-	-	2	-
Slurry effluent (wt%)	75.5	10	12	1	0.5

Initial development work focused on identifying the optimum cement type for immobilizing the simpler waste composition of nitrate effluent. A comparison of three cement types to immobilize sodium nitrate solution was first undertaken; this involved 100% ordinary Portland cement (OPC; conforming to JIS (Japanese Industrial Standard (JIS)5210)), a blast furnace slag (BFS)/OPC mixture in a ratio 70:30 (conforming to JIS 5211), and 100% ‘Super Cement’ (SC). Super Cement is the commercial name of a proprietary formulation blended cement manufactured by JGC Corporation (Japan) and is an alkali activated slag cement with various minor additives to enhance process and product performance. These small-scale trials identified that for this waste type SC showed lower sensitivity of setting time to the sodium nitrate concentration of the waste and superior strength development (exceeding 28 day compressive strength of 10 MPa), even up to 70 wt% NaNO<sub>3</sub> in the cemented product. Subsequent development work for immobilizing sodium nitrate containing wastes has therefore focused on optimizing immobilization using SC.

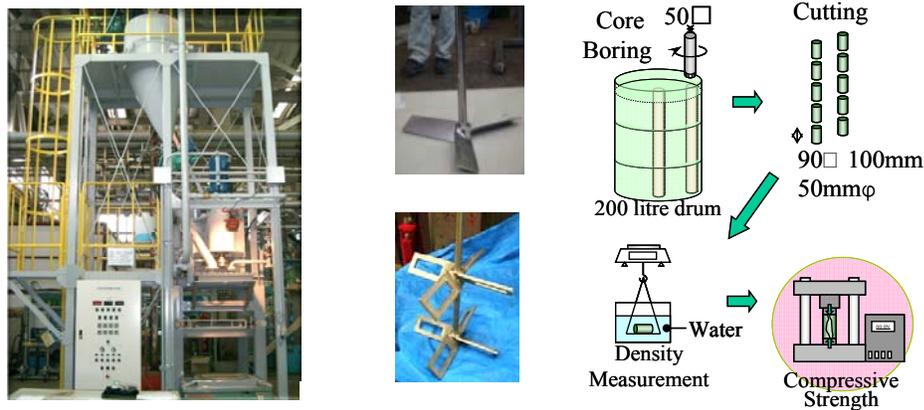
At small scale, trials using SC to immobilize nitrate effluent simulant have shown acceptable performance for a formulation range of:

Water-to-cement ratio            0.67 – 1.00  
 NaNO<sub>3</sub>wt%                        40 – 55%

At water-to-cement ratios above 1.0 the compressive strength was below the JAEA requirement of 10 MPa,<sup>(5)</sup> while below w/c 0.7 the fluidity of the grout mix was too low for mixing and handling. Note that the w/c ratio is much higher than is typical for OPC based grout mixes (~0.35). This may be important because there is a limit to the salt concentration that can be achieved by the evaporator, and so the higher w/c ratio used with SC minimizes the amount of cement required and hence increase the sodium nitrate loading of the encapsulated waste.

Full-scale 200-litre trials have been performed using SC to immobilize nitrate effluent simulant using formulation of 50 wt% total waste salts loading with a w/c 0.67. (See Figure II). The waste simulants were prepared by mixing the salt solutions in 200-litre drums using a propeller mixing paddle. Mixing was continued for a further five minutes once the addition of cement powders had been completed.

After 28 days of curing cores were bored from the 200-litre drums and tested for compressive strength and density. Homogeneity of the sample was demonstrated by assessing by the variation in strength and density along the length of the cores (at 10 different points) to give an indication of the performance of the mixing paddle and operating conditions.



Full-scale mixing equipment Propeller type paddle Full-scale mixing trials

Figure II. Full-scale mixing equipment and summary of trials

Slurry effluent contains additional species to those in the nitrate effluent, as shown in Table I. The effect of these species on the properties of cemented waste has been investigated. In particular, small-scale trials using simulants containing  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Fe}(\text{OH})_3$  were used to determine sensitivity of the encapsulation process to the sodium bicarbonate concentration, which causes a substantial retardation of setting, reduction in fluidity and reduction in strength. This has allowed limits on the sodium bicarbonate concentration to be specified to ensure acceptable wasteform properties. Full-scale 200 litre trials using slurry effluent simulant have been performed to confirm implementation of the encapsulation process using formulation of 50 wt% total waste salts loading with w/c 0.67.

Finally, consideration has been given to the effect of minor component species in the slurry effluent waste. It is predicted that slurry effluent contains low concentration of a number of chemical species as shown in Table II. Although these “minor species” are present in much lower concentrations than the main waste component they can, in some cases, still affect the physical properties of the waste, such as the rheology or adversely affect the hydration chemistry of the cement during encapsulation. Small-scale trials have indicated that in practice these minor species do not significantly affect the process.

Table II. Predicted Minor Species in the Slurry Effluent

Minor species	TBP +DBP	Al	B	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	V	Zn
/ ppm	1000	1167	913	350	21	42	255	127	4754	1231	647	764	2494	95	106	170

Demonstration of full-scale 200-litre trials has now also been performed using SC to immobilize slurry effluent simulant also containing the minor species listed in Table II. Water-to-cement ratios of 0.56 and 1.08 with a total salts waste loading of 50 wt% were investigated, based on the results of small-scale trials. Measurement of the strength of a core sample showed that the simulated wasteform with w/c 1.08 varied in strength along its cylindrical axis, falling below the 10 MPa requirement at the top and bottom of the wasteform. In contrast, at w/c 0.56 the wasteform strength exceeded 20 MPa throughout. These results confirm that slurry effluent can be encapsulated using SC and further work is being undertaken to optimize the cement formulation at full 200 litre scale.

#### Phosphate Effluent treatment process – Pre-treatment and Cement based Encapsulation Technology <sup>(7)</sup> <sup>(8)</sup>

Phosphate effluent consists principally of an aqueous solution of monosodium phosphate with a typical concentration of  $440\text{gL}^{-1}$ . The waste will be immobilized in the LWTF using an in-drum mixing cement encapsulation process.

Phosphate effluent has a pH of  $\approx 4$ , therefore, it is necessary to ‘pre-treat’ the waste before mixing to increase the pH to make it compatible with the cement powder. In addition, phosphates are well known to cause severe retardation in cement systems.

A pretreatment process based on precipitation of calcium phosphate has been developed. This approach was selected because calcium phosphates are generally highly insoluble and do not interact significantly with cement during its hydration. The most thermodynamically stable precipitation product is hydroxyapatite (following (Eq.9)), but the precise composition of the precipitate depends upon the reaction conditions used and generally amorphous material is precipitated first that may subsequently convert to a crystalline phase.



The neutralization process is carefully controlled by managing the operating temperature ( $\sim 50^\circ\text{C}$ ) and concentration of reagents used to avoid the formation of hydrated disodium phosphate during the neutralization process, which could cause serious processing difficulties. The pre-treatment formulation is expressed as the molar ratio of calcium hydroxide to monosodium phosphate (in the untreated waste). The optimum molar ratio has been demonstrated to be  $\sim 2.4$ .

Below this ratio hydrated sodium phosphate crystals are formed, causing a severe increase in the waste viscosity, while above 2.4 the excess lime decreases the fluidity waste during mixing with cement.

Grout formulations based on BFS and SC formulations have been investigated using non-active waste simulants. Trials performed at small-scale show that both cements can successfully encapsulated the pre-treated waste. The wasteform compressive strength depends mainly on the w/c cement ratio, with the waste loading having a smaller effect on the strength but significant effect on the viscosity of the mix. The JAEA requirement of 28 day compressive strength  $\geq 10$  MPa was exceeded for formulations:

BFS: w/c < 0.75 (waste loading NaNO<sub>3</sub> 12-14.5 wt%)

SC: w/c < 1.65 (waste loading NaNO<sub>3</sub> 13-16 wt%)

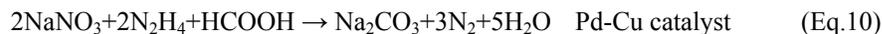
Where the water-to-cement ratio was defined by assuming that during pre-treatment each H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ion was neutralised to produce two H<sub>2</sub>O molecules. The waste loading was defined as the mass of NaH<sub>2</sub>PO<sub>4</sub> from the untreated waste simulant that was immobilized in the cement, given as a weight percentage of the wasteform.

Full-scale 200-litre trials have demonstrated both pre-treatment and encapsulation of phosphate effluent simulant using SC. Pre-treatment used a calcium hydroxide to monosodium phosphate molar ratio of 2.4 and encapsulation used a w/c ratio of 1.51. Compressive strength of the cores extracted from the trial drums were about 10 MPa (9.02 to 10.32 respectively). These trials suggested that the phosphate effluent is expected to be encapsulated with acceptable strength by further optimization of in the cement formulation.

#### Nitrate-ion Decomposition Technology <sup>(9)</sup>

JAEA are developing a nitrate-ion decomposition technology to treat sodium nitrate as the major constituent in the low level liquid waste. This is of interest because in order to dispose of the encapsulated waste by shallow land burial it will be necessary to minimize nitrate leaching to the surrounding environment to meet the environmental acceptance criteria.

To investigate methods for decomposing nitrate-ion several small-scale trials were performed using a reductant and catalyst in sodium nitrate solutions. Solutions for the test were kept at 80°C. Experimental results have shown that combinations of a Pd-Cu catalyst and the reductants hydrazine with formic acid or just hydrazine can decompose the nitrate-ion to nitrogen gas and sodium carbonate or sodium hydroxide respectively. The main reaction is described by following (Eq.10) and (Eq.11). The converted sodium carbonate is planned to be immobilized by cement materials.



In a further study, it was found that sodium hydroxide produced from the nitrate and hydrazine reaction could be reused as a reagent for pH adjustment in LWTF. This could reduce the waste volume and cost for disposal.

These small-scale trials have shown that over 90% of the nitrate ion can be decomposed. These results suggest that this combination of catalyst and reductant is suitable for the treatment of nitrate solution generated from the reprocessing plant.

If nitrate-ion decomposition is implemented then;

- All of the very low radioactivity nitrate effluent, with the majority of nuclides removed, and which formed the bulk of the original waste stream, can be disposed of by shallow land burial.
- It is possible to reduce by 30% the quantity of cement products which need to be disposed of by shallow land burial by recycling the sodium hydroxide that is a product of the nitrate-ion decomposition process.

#### CEMENT BASED ENCAPSLATION TRIALS FOR SODIUM CARBONATE <sup>(10)</sup>

This section summarizes recent development work to immobilize the carbonate effluent arising from the nitrate-ion decomposition process. It is intended that this waste stream will be encapsulated using an in-drum mixing cement encapsulation process in the LWTF.

Following decomposition of the nitrate-ion, water is evaporated from the liquid waste to minimize its

volume and the total salt content of the effluent after evaporation is about 50 wt%. At temperatures below 35.4°C and carbonate concentration about 50 wt%,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$  is formed in the carbonate effluent. Hence, if the waste cools below the melting points of hydrated sodium carbonate then solidification of the waste can occur as the hydrated crystals are capable of incorporating all the free water originally present in solution. This has the potential to cause problems during encapsulation because water is needed for the cement hydration reaction. The low melting point for the hydrated crystals may also affect the stability of the cement encapsulated waste through dimensional instability and the potential mobilization of activity whenever the melting point is crossed.

Another consideration for disposal is the pH of the grout wasteform: the carbonate effluent has a pH of  $\approx 11.5$ , but once cement material is added the pH of the grout mix increase due to reaction of carbonate with calcium hydroxide in the cement releasing sodium hydroxide. High alkalinity of the wasteform can affect the cement hydration rate but also, following wasteform disposal, may damage the bentonite barrier that is planned to surround the disposal site by generating hyperalkaline water flows.

To investigate methods for encapsulating this effluent waste non-radioactive trials were performed using waste simulants prepared as solutions of sodium carbonate. The work presented here gives some of the results from our study of two cement types to encapsulate the waste simulants: SC and BFS. Small-scale trials were used to investigate the optimum cement type and the effect of the water-to-cement ratio and waste loading on encapsulating the simulants. The optimum formulation have been demonstrated at 200 litre scale.

## Experimental

Waste simulant was prepared as a solution of sodium carbonate (Takasugi Pharmaceutical Co., Ltd, Food Additives grade) at the concentration required for subsequent encapsulation. In some cases sodium nitrate was included in the simulant to represent incomplete destruction of nitrate. These solutions were prepared at 50°C to emulate the anticipated temperature of the waste following evaporation.

SC is a proprietary cement formulation and was supplied by JGC (Japan) and BFS conforming to JIS 5211 was obtained from HITACHI CEMENT CO., LTD. Cemented samples were prepared by adding the cement powders (held at ambient room temperature) to the waste simulant prepared at 50°C.

Small-scale trials were performed at  $\sim 0.5$  litre scale using hand mixing with a spatula until the mix was homogenous and at 2 litre scale using a low-shear mixer (described in the JIS R 5201) at 160 rpm for 1 minute and 250 rpm for 1 minute following addition of the cement powder. Full-scale trials were performed using 200-litre drums and a propeller type paddle operating at 160 to 250 rpm (See Figure II).

500ml size small scale trials investigated a series water-to-cement ratios: 0.8, 1.5, 1.8 and 1.94 and sodium carbonate loadings: 30, 40, and 50 wt%  $\text{Na}_2\text{CO}_3$  (given as the percentage weight of sodium carbonate in the cemented product). Thus, in total 12 trials were performed for each cement type.

2 litre trials were performed to confirm the operating conditions for encapsulation prior to full-scale trials. Both the 2 litre trials and full-scale trials used the formulation: w/c 0.8,  $\text{Na}_2\text{CO}_3$  loading 30 wt%.

Grout mixes were monitored for:

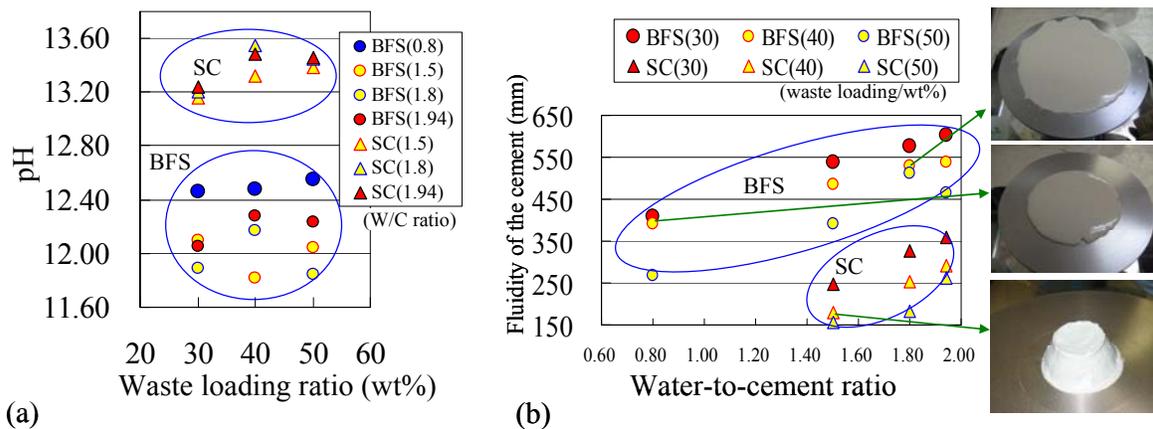
- pH using an pH meter with glass electrode.
- Fluidity of the cement – the cone flow table test was used: 344  $\text{cm}^3$  grout is poured into a flow cone on a table; the cone is lifted and the cement allowed to flow from its base across the table. The diameter of the resulting circle of grout in two perpendicular directions is averaged to give a measurement of the fluidity. The acceptance criterion for fluidity is a minimum diameter of 250 mm, which is determined from performance constraints of full-scale mixing equipment.
- Time for the cement to set – the acceptance criterion is within one day, which is required because of the restricted curing space available.
- Presence of bleed – the acceptance criterion is no bleed present, because the presence of bleed can indicate insufficient cement hydration. In addition, it is undesirable to have free liquid present in a waste package.
- Compressive strength – the acceptance criterion is over 10 MPa after 28 days curing. This gives a significant margin over the waste transportation requirement of approximately 8 MPa.

Static leaching tests were performed for the 500 ml scale samples with w/c 0.8 and  $\text{Na}_2\text{CO}_3$  waste loading 30, 40 and 50 wt%  $\text{Na}_2\text{CO}_3$  to collect data that will be used to assess compatibility with final disposal.

The samples were cured for 365 days before the leach test. The static leaching procedure was a simplified and modified method of the American Nuclear Society for solidified low-level radioactive wastes in standard. The size of the samples is 15\*15\*20mm. The surface area to water ratio is 10. 165ml of deionised water was placed in a 250ml polypropylene container. The pH of leachate was measured on the 1st, 2nd, 5th, 7th, 14th and 28th days.

**Results and discussion**

The pH of the grout mixes and waste loadings for the cementation trials performed using SC and BFS are shown in Figure III (a) for the small-scale 500 ml trials, with the fluidity of the cement as a function of water-to-cement ratio is shown in Figure III (b).



**Figure III. (a) pH of the grout mix and waste loading ratio for the cementation trials performed using SC and BFS and (b) the fluidity of the cement as a function of water-to-cement ratio**

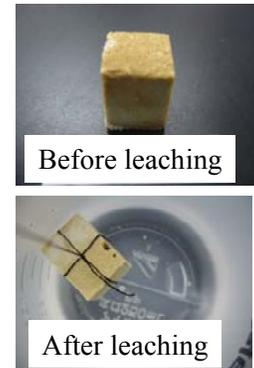
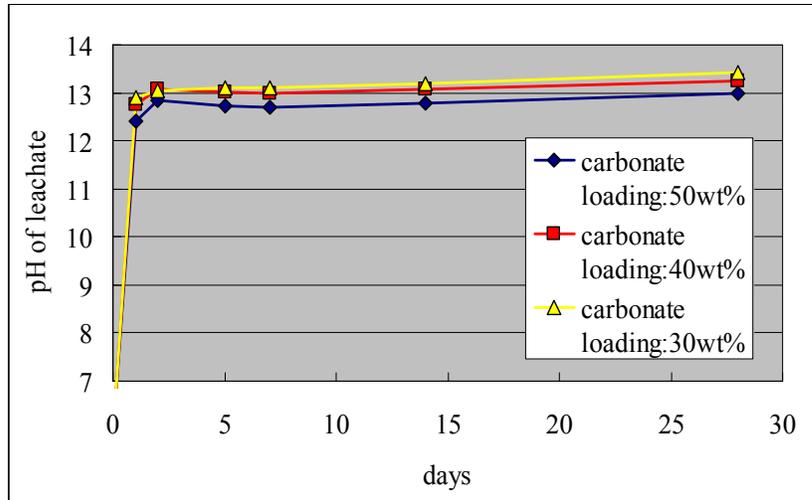
On the whole, the grout mix pH of the SC trials is higher than BFS trials. This is caused by the reaction of carbonate with calcium hydroxide present as one of the components of the SC blend, causing precipitation of calcium carbonate and formation of sodium hydroxide. Further, the pH of the grout mix is approximately constant with waste loading ratio, which is expected since the reaction is limited by the calcium hydroxide derived from the cement and this remains unchanged with the Na<sub>2</sub>CO<sub>3</sub> loading.

Figure III (b) shows a strong correlation of the water-to-cement ratio with the flow measurements (for a fixed waste simulant loading) and also shows reduced flow at higher sodium carbonate loadings. The lower fluidity of the cement results from the increasing solid content of the mix, as expected. The lower fluidity of SC than the BFS mixes may be due to its higher fineness, which increases the water demand for surface wetting; this is similar to the result of encapsulation trials for nitrate effluent and phosphate waste where SC must be used at a higher water-to-cement ratio than conventional OPC or BFS cement.

In the small scale trials performed using SC the fluidity of the cement and compressive strength did not meet the criteria of 250 mm and 10 MPa for any formulation. In contrast, the trials performed using BFS found acceptable fluidity for mixing, and a compressive strength of 12.4 MPa after 28 days for the lowest w/c ratio and waste loading only (w/c=0.8 with waste loadings 30 wt%). Consequently this latter formulation has been investigated in subsequent trials.

Leaching trials were performed for the BFS samples for waste loadings of 30, 40 and 50 wt% Na<sub>2</sub>CO<sub>3</sub> with water to cement ratio of 0.8. An example of the leaching test results is given in Figure IV, together with pictures of specimens. The pH increased to ~13 after 1-2 days leaching and thereafter showed only a moderate further increase. The pH of leachates are almost same across the range of waste loading investigated; this result is consistent with the result in Figure III that showed the pH of the grout mix is approximately constant with the waste loading. The leaching tests also showed that the carbonate at loadings of 30 wt% was stable after 28 days leaching test, but the specimens containing carbonate at loadings of 40 and 50 wt% showed

significant structural degradation. This further demonstrated that the maximum loading of carbonate to make a robust product is 30 wt%.



The picture of specimen of carbonate loading 30wt%

**Figure IV. The leaching test result of cement encapsulated carbonate together with the picture of specimen of carbonate loading 30wt%.**

Owing to the superior performance of BFS in the small-scale trials this cement powder was selected to confirm the formulation for carbonate effluent encapsulation using a low-shear mixer at 2 l scale before the same formulation was implemented at full 200 litre scale. A water-to-cement ratio of 0.8 with waste loadings 30 wt% was investigated based on the results of 500ml small-scale trials. The wasteform formulations and results of these trials are summarized in Tables III and IV.

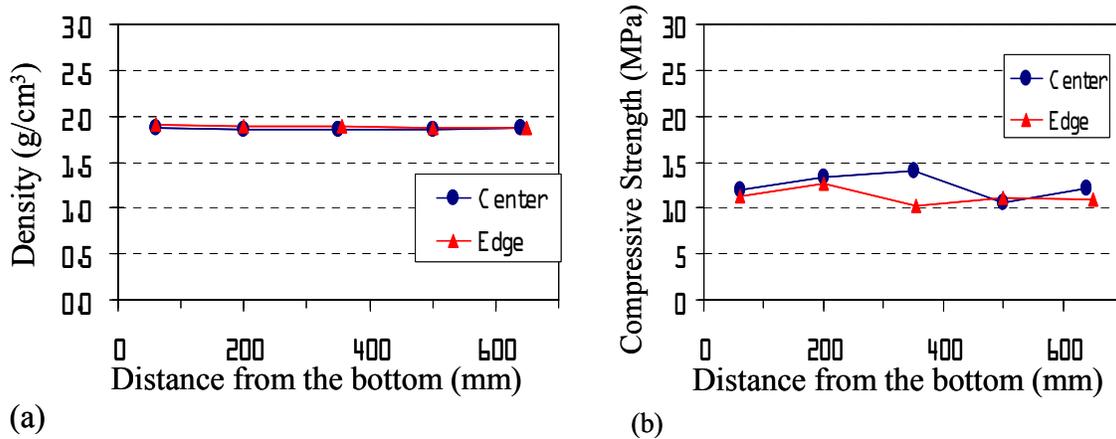
The result indicate that incomplete conversion of the nitrate (98 wt% conversion) does not adversely affect the wasteform strength, with the compressive strength in the 2 litre mix slightly higher than for the 500 ml hand mixed sample (15.9 MPa compared with to 12.4 MPa).

**Table III. The Formulation of Full-Scale Carbonate Effluent Encapsulation Trials**

Waste loading	30wt%	
Cement	BFS#4000	
Water-to-cement ratio	0.8	
Simulant temperature	50°C	
	wt%	kg
Na <sub>2</sub> CO <sub>3</sub>	29.5	100
NaNO <sub>3</sub>	0.6	1.9
H <sub>2</sub> O	31.1	105
Cement	38.9	132
total	100	339

**Table IV. A Summary of the Full-Scale Trial Results Together with Low-Shear Mixer Trial Results**

	low-shear mixer trials (2 litres)	Full-scale trials (200 litres)
simulant pH	11.76(53°C)	11.30(50°C)
grout mix pH	13.01(37°C)	12.94(43.6°C)
Fluidity of cement/mm	300	184
Setting time/days	1	1
Compressive strength/MPa	15.9	11.8 □ average □



**Figure V. (a) Specific gravities measurements and (b) Compressive strength measurements after 28 days curing.**

The compressive strength results and density measurements of core samples taken from the 200 litre sample are shown in Figure V. The small range of measurements along the length of the core samples demonstrate that a homogeneous wasteform was produced using the chosen mixing method and that the JAEA strength requirement of 10 MPa was exceeded throughout. However, comparison of the trials performed at 2 litre and 200 litre scale shows a lower fluidity and compressive strength was observed in the larger trials. This is thought to be caused by differences of scale and effectiveness of mixing.

The sample from the 2 litre scale mix showed a significant dimensional change, with expansion observed over 7 days for the sample with 30wt% Na<sub>2</sub>CO<sub>3</sub> loading. For example, a sample with initial dimensions 160\*40\*40mm when demoulded subsequently expanded to 165\*41\*41mm over 7 days. However, on full-scale trials, such expansion of simulants wasn't observed. A possible cause of this instability may be re-crystallisation of the hydrated sodium carbonate which may have formed during the more rapid cooling of the 2 litre sample. Further trials to understand the underlying cause of expansion and inhibit this effect will be executed in the future.

**CONCLUSIONS**

The LWTF has been constructed to provide safe, effective and economic treatment of low-level radioactive waste from the Tokai reprocessing plant.

The radionuclide separation process for the low level radioactive liquid sodium nitrate containing waste has been developed to reduce the volume of wastes, which must be disposed in the deep geological repository at high cost.

The non-radioactive development work of cement based encapsulation has been performed at both small and full-scale (up to 200 litres) to investigate the optimum cement formulation for nitrate, slurry and phosphate effluents. The results from these studies demonstrate that these effluents can be successfully

encapsulated. The cement based encapsulation equipment is being designed and is going to be installed in the LWTF liquid waste treatment process.

The non-radioactive development work of nitrate-ion decomposition has been performed at small-scale to investigate the optimum decomposition conditions. These small-scale trials have shown that over 90% of the nitrate ion can be decomposed. BFS cement have been demonstrated to be capable of encapsulating the resulting carbonate effluent up to sodium carbonate loading of 30 wt% at full-scale 200-litre. In this cases, adequate compressive strength, setting time and an absence of bleed is achieved.

JAEA will continue research and development work on nitrate-ion decomposition and cement based encapsulation technology. This technology will be implemented in the LWTF in the near future.

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