

Development of New Treatment Processes for Low-Level Radioactive Waste at Tokai Reprocessing Plant - 10403

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Abstract

The Low-level radioactive Waste Treatment Facility (LWTF) constructed at the Tokai Reprocessing Plant has been undergoing non-radioactive commissioning since 2006. The aims of the LWTF are to provide safe, effective and economic treatment of Low-Level radioactive solid and liquid waste generated from the Tokai Reprocessing Plant (TRP).

The solid waste is going to be incinerated in the solid waste treatment process. For liquid wastes the sodium nitrate based effluent is going to be treated by a radionuclides removal process before encapsulation in cement and phosphate based waste is going to be encapsulated in cement following pre-treatment with lime.

The cement based encapsulation process has been investigated since 2002 to reduce the volume of waste for geological disposal. In addition, nitrate ion decomposition technology is under development to allow disposal of nitrate based waste by shallow burial underground while protecting the environment around the disposal site from the potential leaching of nitrate.

The essential technologies of the LWTF and results of R&D work for cement based encapsulation and the nitrate-ion decomposition technology are described.

INTRODUCTION

The Low-level radioactive Waste Treatment Facility (LWTF) has been constructed to treat a number of solid and liquid wastes. The novel technologies and method developed for this waste treatment plant are described here.

In Japan solid wastes are categorized into combustible materials that readily burn, non-combustible wastes that cannot be burned, and a third category termed "incombustible wastes" which describes hard to incinerate materials waste that are intermediate between combustible and non-combustible wastes. The combustible and incombustible waste are going to be incinerated in the solid waste treatment process.

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, such as solvent washing effluent, radionuclide analysis waste, off-gas scrubber waste, and decontamination waste, were historically concentrated by evaporation and then immobilized with the phosphate effluent in bitumin. However, this process was discontinued in 1997 after a fire in the bituminization facility. Currently, the above liquid waste and phosphate effluent are being stored in the Low-level radioactive Waste Storage Facility (LWSF) but will subsequently be treated in LWTF liquid waste treatment process and encapsulated in cement.

The phosphate effluent is generated from the Solvent waste Treatment demonstration facility (ST) to allow reuse of the dodecane. This phosphate effluent will be treated in LWTF and encapsulated in cement.

The proposed treatment methods for each of these wastes has required the development of new engineering and technical solutions. Particular challenges include management of chloride generated during incineration of incombustible wastes which can exacerbate corrosion, minimising the volume of waste for geological disposal, and the development of robust cement encapsulation systems. Engineering developments of the LWTF solid and liquid treatment processes are described in the first part of this presentation, and in the last part, technical research for cement based encapsulation and the nitrate-ion decomposition technology are described.

OUTLINE OF WASTE TREATMENT IN THE LWTF

The basic flow of the radioactive waste treatment process in the LWTF is shown in Fig. I.

There are three main waste treatment processes that will be carried in the LWTF: (i) solid waste incineration; (ii) sodium nitrate liquid waste treatment and encapsulation; and (iii) phosphate effluent treatment and encapsulation.

The solid waste is brought into the LWTF in drums. Solid waste items less than 5 kg are thrown into the incinerator by an automated system. The ash from the incinerator is then packed in a drum and stored. The maximum capacity of the incinerator is about 400 kg/day and processing about 3,600 drums/year is possible, with a volume reduction ratio for the waste of about 1/50 (ash / original solid wastes) achieved.

For the low-level radioactive sodium nitrate liquid waste the first treatment step involves removal of nuclides. This process consists of precipitation, co-precipitation, ultra-filtration and ion exchange. The products of this process are (i) a highly radioactive liquid waste (smaller portion) named “slurry effluent” and (ii) a very low level radioactive liquid waste (larger portion) named “nitrate effluent”. After being concentrated using evaporators both of the effluents will be encapsulated in cement.

The radionuclides removal process contributes to the reduction in volume of the liquid waste by creating a smaller volume of slurry effluent to be solidified and which must be disposed in the deep geological repository at high cost. This volume reduction will reduce the cost for the final disposal of the liquid waste stream. The slurry effluent solidified wastes are expected to be 1/10 of the total amount of the solidified nitrate wastes.

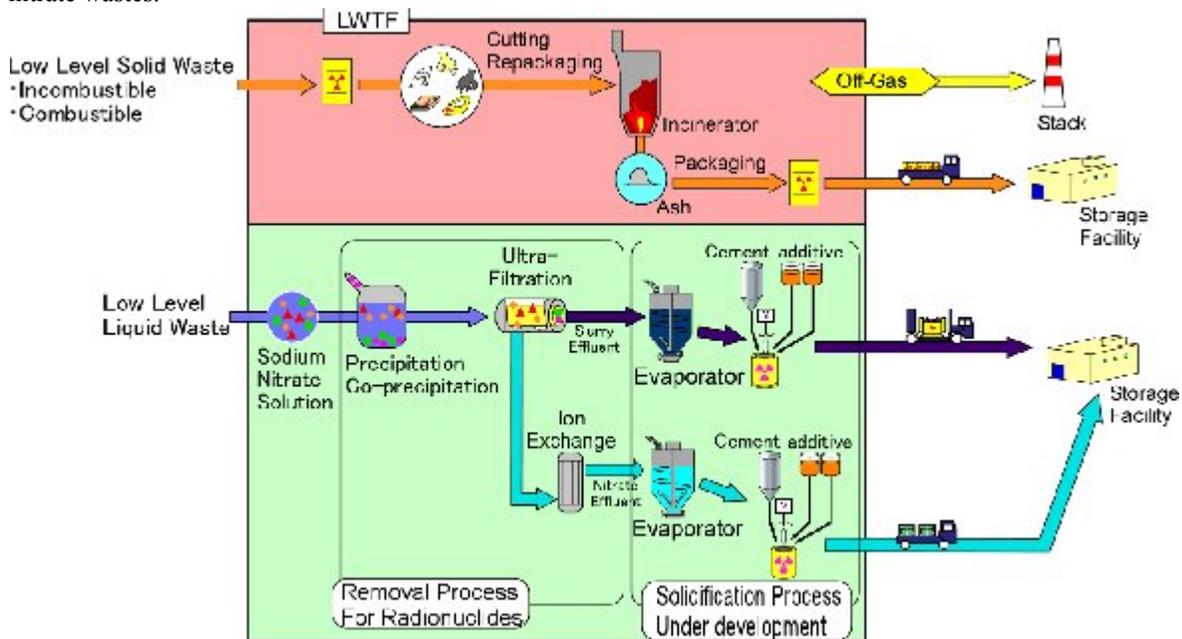


Fig. I Basic flow of the radioactive waste treatment in LWTF

ESSENTIAL TECHNOLOGIES OF THE LWTF

Solid waste treatment process - Incineration process⁽¹⁾

The objective of the waste incineration process is to accomplish a large volume reduction of solid waste in order to minimize the amount of final waste products for storage and disposal. Incineration is being adopted to treat incombustible solid wastes which include chlorinated organics such as PVC and chloroprene. The problem of burning incombustible solid waste is the generation of chlorine gas which exacerbates corrosion of materials. To solve the problems this causes the incinerator is made of corrosion resistant metal and uses cooling water to control the temperature of the incinerator. Also, many air nozzles supply air to prevent soot generation and incomplete combustion. The whole system consists of an incinerator, second burner, and an off-gas treatment unit.

The incinerator consists of a vertical metal cylinder in the upper region and firebrick in the lower region, as illustrated in Fig. II (Vertical Cross-section View of incinerator). The vertical cylinder is made of Hastelloy™ (Ni-Cr-Mo alloy), which resists corrosion by hydrogen chloride gas. Using metal instead of firebricks also keeps the incinerator small. Cooling water circulates through the water jacket surrounding the cylinder to control the incinerator temperature and to prevent over heating which can promote corrosion.

The wastes fed into the incinerator will be burned at about 800°C. There are many air nozzles on the interior wall to supply plenty of air. The nozzles supply a uniform high velocity air supply that mixes with the waste and decomposed gas. This prevents soot or black smoke generation by preventing incomplete combustion and maintains stable operation.

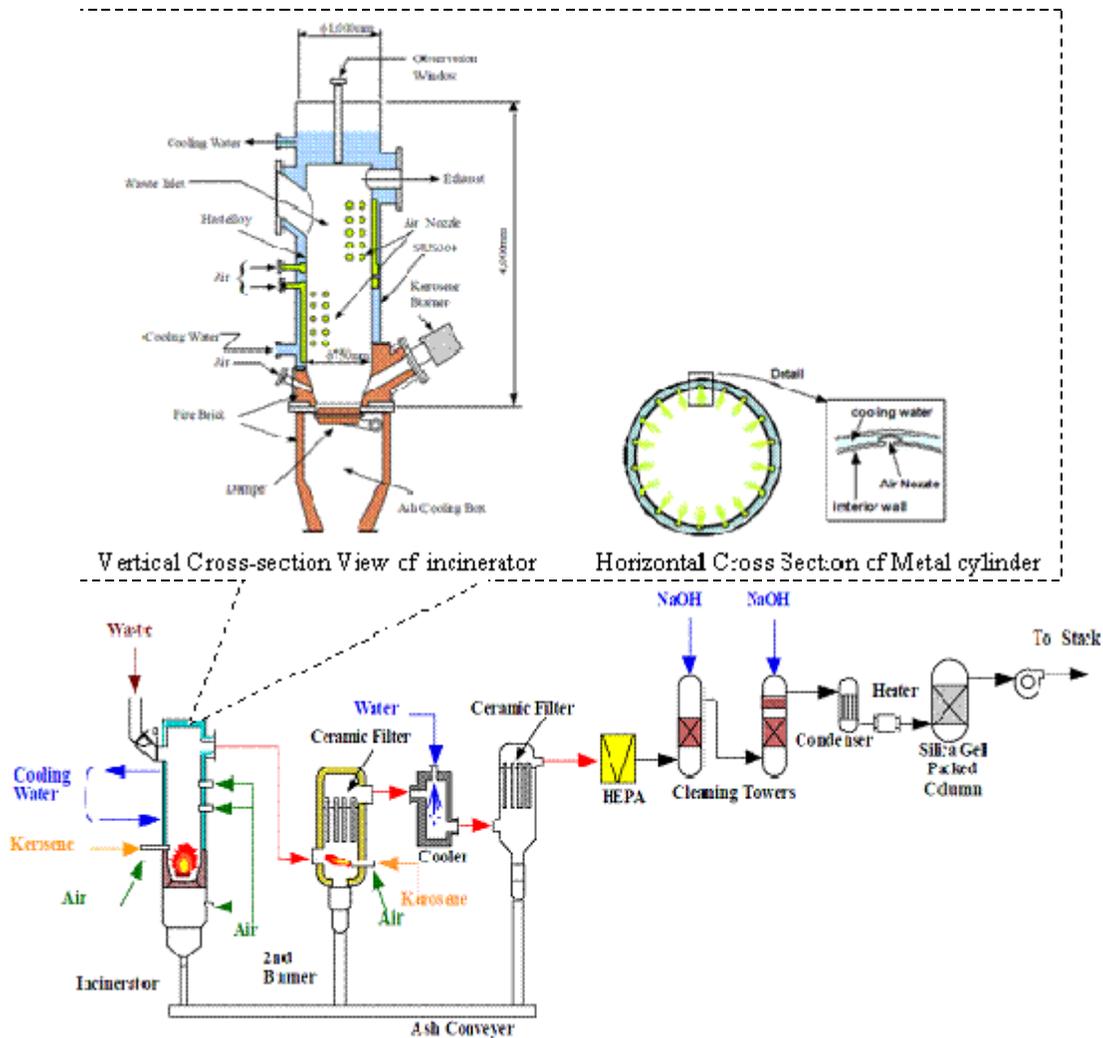


Fig. II Schematic Diagram of Off-Gas Treatment Unit

The second burner is equipped with a high temperature ceramic filter and the kerosene burner. The kerosene burner heats the high temperature ceramic filter, which captures the fines and burns them on the filter surface.

The off-gas treatment system is schematically illustrated in Fig. II. Initially, the off-gas flows to the water spray cooler where it is cooled by water spray to about 225°C and flows onward to the ceramic filter. At this temperature most of the vaporized low boiling point metals (lead, zinc, etc.) and metal chloride gases (generated during the incineration) condense to the solid phase. The ceramic filter removes most of these as

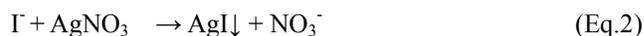
well as other entrained particles. This ceramic filter also removes radionuclides (Co, Cs etc.) from the off-gas. From the ceramic filter the off-gas flow to the HEPA-filter, which filters the remaining radionuclides (Se, Ru etc.), and then to the cleaning towers. Cleaning towers wash out the hydrogen chloride gas and other pollutants such as nitrogen oxide and sulfur dioxide. The liquor in the cleaning towers (wash water) is neutralized with sodium hydroxide solution to form a sodium chloride solution. The wash water used in the cleaning towers is maintained at pH neutral by the addition of sodium hydroxide to prevent absorption of carbon dioxide. After use the wash water is dehydrated in a drum dryer and the resultant sodium chloride powder will be loaded into drums and transported to the storage facility. Finally, the treated off-gas will be discharged to the atmosphere through the stack.

Ash generated by incineration is cooled in the cooling box installed in the bottom of incinerator (see Fig. II). Cooled ash is transported to drums by means of a vibration conveyor (See Fig. II). Ash captured in the ceramic filter is also transferred to drums. Filled drums are then transported to the storage facility.

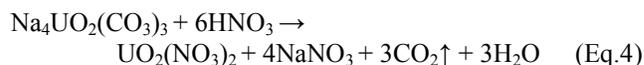
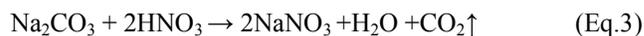
Sodium nitrate liquid waste treatment process - Radionuclide removal process⁽²⁾⁽³⁾

The removal process for the radionuclides consists of precipitation, co-precipitation, and ion exchange.

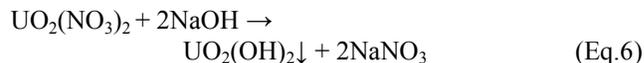
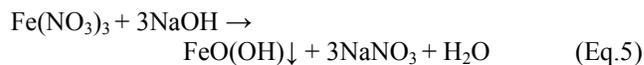
In the precipitation process iodine is separated from the liquid wastes by precipitation with silver nitrate (following Eq.2) followed by removal of this solid phase by ultra-filtration. Iodine exists in various oxidation states in the solution, therefore to produce silver iodide any iodate ions need 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 the result, the carbonate ion is driven out from the liquid waste in the form of CO₂ gas. This reaction is represented by following (Eq.3) and (Eq.4).



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

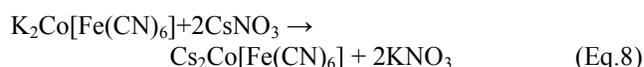
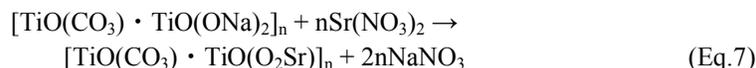


The amphoteric nuclides are not removed under the alkaline conditions, but can be removed under neutral conditions with a ferric hydroxide floc. The procedure is the same as that of the preceding stage, excluding the pH condition. The amount of co-precipitant is 150 mgL⁻¹ for iron nitrate. In this case the decontamination factor of alpha nuclides is over 1E+6 and the decontamination factor of beta/ gamma nuclides is over 1E+2.⁽⁴⁾

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 waste circulates through the reaction tank and filter (tube inside) by a pump. The liquid phase crosses and permeates through the filter elements while the sludge is concentrated on the interior surface. Concentrated sludge is washed away along with the circulation flow. By using the cross flow-type of ultrafilter the accumulation of sludge on the filter is prevented and clogging is considerably reduced.

The final step involves ion exchange. This is used because caesium 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).



CEMENT BASED ENCAPSLATION TRIALS⁽⁵⁾⁽⁶⁾

This section summarizes the development work to immobilize the low-level radioactive liquid waste. The low-level radioactive liquid wastes that will be immobilized are the nitrate and slurry effluent from Radionuclide Removal Process and the low-radioactive phosphate effluent generated from Solvent waste treatment demonstration facility. A cement based encapsulation process has been adopted in the LWTF to immobilize these effluents.

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 70wt %). The phosphate effluent is not evaporated but has to be 'pre-treated' to neutralize the pH to make it compatible with the cement powder because the phosphate effluent has a pH of ~4.

Table I. Typical salt composition of nitrate, slurry and phosphate effluents

Waste	NaNO ₃	NaNO ₂	NaHCO ₃	Na ₂ SO ₄	Fe(OH) ₃	NaH ₂ PO ₄
Nitrate effluent (wt%)	98	-	-	2	-	-
Slurry effluent (wt%)	75.5	10	12	1	0.5	-
Phosphate effluent (wt%)	-	-	-	-	-	100

The slurry effluent contains sodium hydrogen carbonate and the phosphate effluent consists mainly of sodium dihydrogen phosphate (See Table I). As the concentration of the sodium salt in the effluent increases, adverse effects for the encapsulation of the waste become more significant. For instance, low fluidity, low compressive strength and increase in the setting time.

To investigate methods for encapsulating these three effluent wastes non-radioactive trials were performed using 'waste simulants'; for the nitrate effluent a solution of sodium nitrate was used while for the slurry and phosphate effluents the appropriate salt ratios (Table I) in solution were used.

The work presented here gives some of the results from our study of three cement types to encapsulate these three waste simulants.

Experimental

The cements used were ordinary Portland cement (OPC) (conforming to JIS (Japanese Industrial Standard) 5210), a blast furnace slag (BFS) and OPC mixture (conforming to JIS 5211), and '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. The importance of the water-to-cement ratio used to immobilise the waste effluent has also been analysed, and the effect of the bicarbonate ion concentration in the slurry effluent and of the

sodium dihydrogen phosphate in the phosphate effluent have been investigated. In these trials the optimum conditions for encapsulation have been determined by small-scale trials and then demonstrated at full 200-litre scale.

Small-scale trials were used to investigate the optimum cement type and the effect of the water-to-cement ratio on encapsulating the simulants. Small-scale trials (~2 litres) were performed using a low-shear mixer (described in the JIS R 5201). Waste simulant was mixed with a hardener (aqueous sodium hydroxide), disperser ('WORK500' that is produced by the Zeon Corporation) and antifoamer ('NS-DEFOAMER 171' that is produced by the San Nopco Limited) at low speed, followed by the addition of cement powders. Once all powders had been fed into the mixer high speed mixing was performed for a further five minutes. The mixing paddle was removed and the cement was sealed in a container to prevent loss of water and cured at ambient temperatures.

Each sample was tested to assess:

- Fluidity of the cement – the cone flow table test was used: 344 cm³ 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.

Full-scale trials were performed using 200-litre drums. The waste simulants were prepared by mixing the salt solutions in 200-litre drums using a mixing paddle. Sodium hydroxide, disperser and antifoam were added before feeding the cement powders into the drum while mixing. Mixing was continued for a further five minutes once the addition of cement powders had been completed.

Fluidity measurements, setting time and bleed observations were performed as described for the small-scale trials, and after 28 days of curing cores were bored from the 200-litre drums and tested for compressive strength tests and density. Homogeneity of the sample was assessed by the difference 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.

Results and Discussion:Nitrate Effluent

Three cement types were used in these trials: 100% OPC, BFS/OPC mixture in a ratio 70:30, and 100% SC; in each case a water-to-cement ratio was chosen so that a fluidity of about 280 mm was achieved. For each cement type a series of different nitrate loadings were prepared: 30, 40, 50, 60 and 70 wt% NaNO₃ (given as the percentage weight of sodium nitrate in the cemented product). Thus, in total 15 trials were performed.

In the cases of OPC and 70:30 BFS/OPC, bleed was present in all trials, with this bleed remaining after 4 or 5 days of curing. This compares with no bleed present for the SC trials. For all three cements a decrease in compressive strength was observed with increasing nitrate salt loadings. In the case of OPC and BFS/OPC 70:30 cements, with a nitrate loading of 70 wt% the compressive strength fell below the acceptance criterion of 10 MPa. In contrast, the SC trials still showed acceptable compressive strength even for the highest nitrate salt loading, for which its strength was 20 MPa.

Owing to the superior performance of SC in these trials, this cement powder has been chosen to be investigated further for the encapsulation of nitrate, slurry and phosphate effluent at JAEA.

Water-to-cement (w/c) ratios in the range 0.43 to 1.22 were investigated using a sodium nitrate loading of 50 wt% and effluent temperature 50°C to reflect the typical nitrate concentration and temperature that will be obtained after evaporation. The details of the trials and results are summarised in Table II.

Table II. The effect of water-to-cement ratio for SC and nitrate effluent simulant; nitrate loading 50wt%.

	Water-to-cement ratio					
	0.43	0.61	0.70	0.79	1.00	1.22
NaNO ₃ / wt%	50	50	50	50	50	50
Water / wt%	15.0	19.0	20.6	22.0	25.0	27.5
SC / wt%	35.0	31.0	29.4	28.0	25.0	22.5
Fluidity test / mm	155	225	269	321	388	443
Bleed present (yes/no)	No	No	No	No	No	No
Setting time / days	1	1	1	1	1	1
Compressive strength / MPa	25.4	19.6	17.3	14.7	11.1	8.8

As expected, a reduction in fluidity was observed as the w/c ratio was reduced, but this was associated with an increase in compressive strength. For a water-to-cement ratio of 0.43 and 0.61 the fluidity fails the acceptance criterion of 250 mm, however at the higher ratios of 0.70 to 1.00 acceptable compressive strength was achieved after 28 days and no bleed was present. The acceptable range of the w/c ratio for SC is high compared to the usual value for OPC of 0.35⁽⁶⁾. 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 will minimize the amount of cement required and hence increase the sodium nitrate loading of the encapsulated waste.

Full-scale 200-litre trials were performed using SC to immobilize nitrate effluent stimulant. These trials demonstrated that homogeneous samples were achieved using the chosen mixing method to produce the encapsulated nitrate effluents because only a small range of compressive strengths and specific gravities were measured along the length of the cores extracted from the trial drums.

Results and Discussion: Slurry Effluent⁽⁷⁾⁽⁸⁾

A further set of trials investigated the effect of the bicarbonate concentration and of minor species addition in the slurry effluent waste on the properties of cemented waste.

First the effect of the bicarbonate concentration in the slurry was tested. In this case the minor species in the slurry effluent were not added. The salt loading, w/c ratio, and the NaHCO₃ concentration prior to evaporation used in these trials are given in Table III together with the results. As the sodium bicarbonate concentration is increased there is a significant reduction in the fluidity and compressive strength and an undesirable increase in the setting time for the cement. These results suggest that the NaHCO₃ concentration must be below 10 g/l (prior to evaporation) in order to achieve the required strength, fluidity and setting time.

Table III. Effect of NaHCO₃ on the slurry effluent encapsulation.

	NaHCO ₃ Concentration before evaporation (g/l)			
	10	49	85.7	
NaNO ₃ / wt%	41	41	38	37
Other salts / wt%	9	9	12	13
Water / wt%	20	26	25	23
SC / wt%	30	24	25	27
w/c	0.67	1.08	1.00	0.85
Fluidity test / mm	301	380	276	209
Bleed present (yes/no)	No	No	No	No
Setting time / days	1	1	2	4
Compressive strength / MPa	18.6	17.7	12.6	10.9

Full-scale 200-litre trials were performed using SC to immobilise slurry effluent simulant. Similar to nitrate effluent encapsulation trials, these results demonstrate that homogeneous samples were achieved using the chosen mixing method to encapsulate the slurry effluent. However, as the concentration of NaHCO₃ was

increased it was found that the compressive strength decreased and setting time was retarded, which is consistent with the small scale trials undertaken. It was also confirmed that adequate compressive strength and setting time are achieved provided the NaHCO_3 concentration does not exceed 10 g/l (prior to evaporation) with a total salt loading of 50 wt% at full 200-litre scale.

Next the effect of the addition of minor species in the slurry effluent waste was tested. It is predicted that low level radioactive liquid waste contains some small amount of chemical species as shown in table IV. 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, and may also adversely affect the hydration chemistry of the cement during encapsulation.

Table IV. 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

Two water-to-cement (w/c) ratios (0.75 and 1.08) were investigated using a slurry simulant containing the minor species at an effluent temperature of 50°C. The results were compared with trials using slurry simulant without the minor species.

The salt loading, w/c ratio are given in Table V together with the results. When the slurry simulant contained the minor species there was a significant reduction in the fluidity, however compressive strength was increased and there were no differences with bleed present or retarded setting times. Furthermore, in the case of w/c ratio 1.08 all assessment criteria were satisfied. These results infer that minor species significantly influence the fluidity, but it is possible to encapsulate the slurry containing minor species with acceptable properties.

Full-scale 200-litre trials were performed using SC to immobilise slurry effluent simulant containing minor species. A summary of the results are given in Figure III together with the picture of full-scale mixing equipment. A water-to-cement (w/c) ratio of 1.08 was investigated based on the results of small-scale trials. The compressive strength was determined to vary with the height of the wasteform. The reason thought to account for variability in compressive strength is precipitation of salts, because as the greater the distance from the bottom, the more the compressive strength tends to decrease. And frailty of the bottom sample was thought to be attributed to the effect of the mixing paddle in the low fluidity condition caused by the precipitation.

Table V. Effect of minor species on the slurry effluent encapsulation.

	Water-to-cement ratio			
	0.75		1.08	
NaNO ₃ / wt%	41	31	41	31
Other salts / wt%	9	9	9	9
Minor species / wt%	0	10	0	10
Water / wt%	21.5	21.5	26	26
SC / wt%	28.5	28.5	24	24
Fluidity test / mm	250	170	380	250
Bleed present (yes/no)	No	No	No	No
Setting time / days	1	1	1	1
Compressive strength / MPa	24.3	28.6	17.7	18.9

In order to solve this problem, a lower water-to-cement (w/c) ratio of 0.56 was chosen to reduce the fluidity with the aim of preventing the precipitation. Also, the double-banked mixing paddle for highly viscous liquid was applied in this equipment. In this trial adequate compressive strength was achieved and variation of the compressive strength with height of the wasteform was minimal.

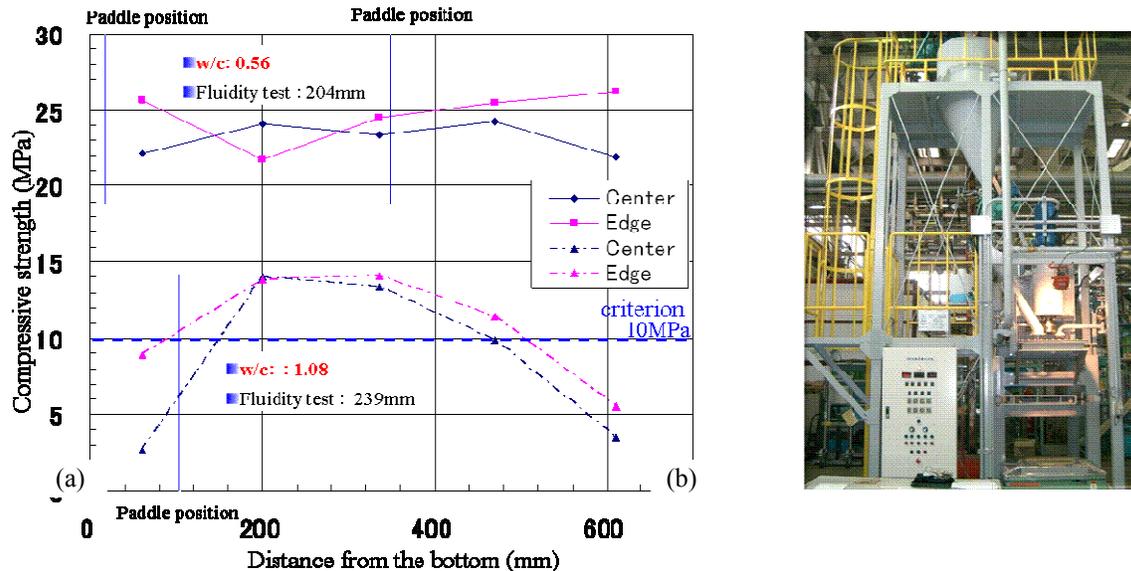


Fig. III (a) Compressive strength measurements after 28 days curing. (b) picture of Full-scale mixing equipment

Results and Discussion: Phosphate Effluent⁽⁸⁾⁽⁹⁾

The phosphate effluent consists principally of an aqueous solution of sodium dihydrogen phosphate with a typical concentration of 440gL^{-1} , with additional very minor species present.

The phosphate effluent has a pH of ~ 4 . Therefore, it is necessary to 'pre-treat' the waste before mixing to increase the pH to make it compatible with the cement powder. A 1:1 neutralization with NaOH produces hydrated Na_2HPO_4 crystals. Generally these have a low melting point. The principal product is $\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ with a melting temperature of 34.6°C , but $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ with melting point of 48.1°C may also form. Hence, if the waste cools below the melting points of hydrated disodium phosphate then, at the high concentration of hydrogen phosphate in the waste, solidification of the waste occurs owing to the hydrated crystals being 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. Moreover, the low melting point for the crystals, which releases water, is anticipated to affect the stability of the cement encapsulated waste through dimensional instability and the potential mobilization of activity whenever the melting/solidification point is crossed.

To remove the difficulty of hydrated disodium phosphate crystals forming in the phosphate waste, treatment with calcium hydroxide to produce a precipitate of calcium phosphate has been investigated. It is possible that several types of calcium phosphate may be precipitated. The most thermodynamically stable precipitation product is hydroxyapatite, 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.

Experiments were performed by preparing a solution of monosodium phosphate dihydrate of the appropriate concentration for the trial. The solution temperature was increased to 60°C , and then the required quantity of calcium hydroxide was added under continuous stirring.

Stirring was maintained until the temperature of the slurry fell to $\sim 35^\circ\text{C}$. After cooling, any water lost by evaporation (determined by the change in mass) was replaced. 79.4 g monosodium phosphate dihydrate per 100 g water was used for the waste simulant.

The pre-treatment formulation is expressed as the molar ratio of sodium hydroxide to monosodium phosphate (in the untreated waste) and the molar ratio of calcium hydroxide to monosodium phosphate (in the untreated waste). A key observation from the trials was that if insufficient calcium hydroxide was added

during pretreatment then small needle shaped crystals formed that were visible under an optical microscope (typical length 0.25-0.5 mm). In these cases the viscosity of the simulant was initially very high, although it was found to decrease significantly during the following weeks of storage; this behaviour was undesirable owing to the initial high viscosity that may prevent mixing of the treated waste. However, if visible crystals were not formed then the viscosity remained unchanged over time. The precise identity of the crystals formed was not determined in these trials, although the low melting point of these needle crystals $\sim 30^{\circ}\text{C}$ and observed removal of free water when they form is consistent with $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ crystallisation.

The minimum calcium hydroxide addition needed to prevent the formation of crystals was a calcium hydroxide to monosodium phosphate molar ratio of ~ 2.4 . The level of calcium hydroxide addition also affected the rheology of the phosphate waste following pre-treatment, and a minimum viscosity of the pre-treated waste coincides with a $\text{Ca}(\text{OH})_2/\text{NaH}_2\text{PO}_4$ molar ratio of ~ 2.4 that was just sufficient to prevent the formation of crystals in the pre-treated waste. Future work will investigate further the importance of temperature control on the pre-treatment process.

An investigation of the encapsulation of the pre-treated waste was conducted using the identified optimum pre-treatment formulation and Super Cement. In order to quantify the availability of water in the pre-treated waste a nominal water to cement ratio (w/c) was defined by assuming that during pre-treatment each H_2PO_4^- ion was neutralised to produce two H_2O molecules. The waste loading (L) was defined as the mass of NaH_2PO_4 from the untreated waste simulant that was immobilized in the cement, given as a weight percentage of the immobilised waste.

For trials investigating encapsulation of waste using Super Cement the range of formulations tested is shown in Figure IV (a), with the corresponding compressive strength of the samples shown in Figure IV (b).

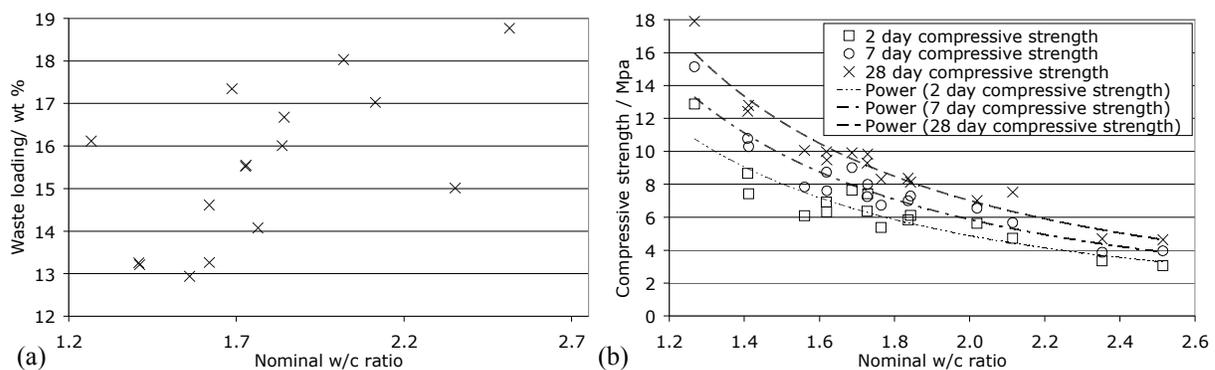


Figure IV: (a) Waste loading and nominal w/c ratio for the cementation trials performed using Super Cement. (b) Compressive strength after 2, 7 and 28 days curing as a function of the nominal w/c ratio for the cementation trials using Super Cement. The dashed lines are power law fits of the data points to guide the eye.

In all cases setting of the grout occurred within 24 hours, without bleed water being present at this time. It was found that the compressive strength of the cemented waste is largely determined by the w/c ratio, whilst the waste loading has a much smaller, secondary effect over the ranges investigated. Unfortunately, the waste loading has a strong effect on the viscosity of the grout, which increases significantly as the waste loading is increased for a fixed w/c ratio, and this is the limiting factor for the waste loading.

A compressive strength of 10 MPa after 28 days was achieved up to $w/c=1.65$ with waste loadings exceeding 13 wt%.

Pre-treatment of phosphate effluent using calcium hydroxide to precipitate calcium phosphate can be used to stabilize phosphate waste for encapsulation in cement. Encapsulation was successfully performed with Super Cement, with the encapsulated waste exceeding the JAEA requirement of 10 MPa after 28 days curing at waste loadings of up to 16.1 wt%.

Full-scale 200-litre trials were performed using SC to immobilize pre-treated phosphate effluent simulant.

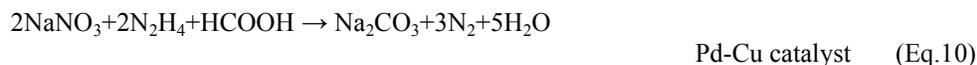
Compressive strength of the cores extracted from the trial drums was about 10 Mpa (9.09 to 10.32). These

trials suggested that the phosphate effluent is expected to be encapsulated properly by making small improvements in mixing formulation.

Nitrate-ion Decomposition Technology ⁽¹⁰⁾

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 a reduction of nitrate-ion concentration in the solidified waste will be required to achieve the environmental acceptance criterion.

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 hydrazine reductant with formic acid can decompose the nitrate-ion to nitrogen gas and sodium carbonate. The main reaction is described by following (Eq.10). 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. The encapsulation trials at small-scale showed that SC gives the best encapsulation performance and adequate compressive strength to encapsulate by-products.

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.

CONCLUSIONS

To provide safe, effective and economic treatment of low-level radioactive waste the Low-level radioactive Waste Treatment Facility (LWTF) was constructed. In order to incinerate the incombustible solid waste the incinerator that is made of corrosion resistant metal and uses cooling water to control the temperature of the incinerator was adopted. The anticipated volume reduction ratio (ash / original wastes) of wastes will be about 1/50 depending upon original waste compositions.

The radionuclide removal process for the low level radioactive liquid sodium nitrate containing waste which is composed of chemical precipitation for removal of iodine, co-precipitation of ferric hydroxide, ultrafiltration, ion exchange using sodium titanate resin and potassium cobalt ferrocyanide resin, is adopted to reduce the volume of slurry effluent solidified liquid wastes, which must be disposed in the deep geological repository at high cost.. This reduction in volume will reduce the cost for the final disposal of the liquid waste stream.

The non-radioactive development work of cement based encapsulation has been performed at both small and large-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.

JAEA has a plan to start radioactive commissioning of the LWTF after completing installation of

encapsulation equipment and non-radioactive commissioning. JAEA will continue R&D work on nitrate-ion decomposition technology. This technology will be adopted in the LWTF in the near future.

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