The Pretreatment and Immobilization Test on The Greater Than Class C Spent Ion Exchange Resins from Taiwan Research Reactor– 17177

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ABSTRACT

In this work, the experience on the removal of greater than Class C bead ion exchange resins from Taiwan Research Reactor spent fuel pool was reported. All of the spent ion exchange resins had been flushed, dewatered, and packed into lead-shield containers for 60 drums and pending for stabilization.

The metakaolin type of geopolymer was selected to immobilize the ion exchange resin. According to the “Regulations on Final Disposal of Low Level Radioactive Waste and Safety Management of the Facilities” Act in Taiwan, the immobilization waste form shall meet seven testing items. Herein, several immobilize samples were prepared with the following amounts of ion exchange resin, 6, 12 and 18 wt.%. The compressive strength of the samples ranged from 2.9 to 18.2 MPa. The Cs and Sr ions were effectively trapped by ion exchange resins. After the resins incorporated with the geopolymer matrix, the captured ions were expected difficult to leach out.

However, it is found that at the higher contents of ion exchange resins in the immobilize samples exhibited poor water resistance due to the swelling effect. Several parameters such as the ratios of SiO_2/Na_2O and powder/solution also the blast furnace slag dosage were investigated to improve processibility and improve performance.

INTRODUCTION

Ion-exchange resins (IERs) are employed to treat radioactive liquids in nuclear industry. Spent IERs become high activity radwastes and pose special handling and treatment problems due to binding of various radioisotopes. Generally, IERs are used to control the quality of coolant, minimize corrosion or degradation of system components, and remove radioactive contaminants in nuclear power plants. The major radioisotopes of these spent IERs are ^{60}Co and small amount of ^{137}Cs. However, spent IERs produced from the decommissioning nuclear facilities may contain a variety of radioisotopes including fission products (i.e. ^{137}Cs, ^{90}Sr, etc.), actinides, and transuranics (TRU) [1].

Sludge containing fine particles of used fuel is spread over the spent fuel pool in the Taiwan Research Reactor (TRR) due to the rupture of several fuel rods. Hence, approximately 13 m^3 and 2210 Ci of spent cation and mixbed exchange bead resins were generated from the water treatment processes. The major radionuclides exchanged on the spent resins are fission products (i.e. ^{137}Cs and ^{90}Sr) and TRU, so according to the radioactive wastes classification criteria, these spent resins should be classified as greater than Class C (GTCC) waste. In our previous work, the spent resins were mechanically flushed to eliminate the loose contaminants, but the major radioactivity was contributed by ion-exchange mechanism and regeneration process would not be performed due to liquid wastes produced again. Up to 2014, all of the spent resins were removed from the TRR spent fuel pool after dewatering, and then loaded into the lead-shield drums for temporary storage. However, according to the regulation, the spent resins have to be stabilized to produce a physically and chemically stable waste form. In this work, the pretreatment and immobilization test on the GTCC resins from TRR spent fuel pool was proposed.

Properties of the Spent Resins from TRR Spent Fuel Pool

The cation and anion exchange resins which were employed to treat the water in the TRR spent fuel pool are strong acid and strong base forms (see TABLE I). There were 7800 kg of spent resins withdrawn from the TRR spent fuel pool; part of spent cation exchange resins was separately packed and the remainder was mixed and packed in the containers. The specific radioactivities of the radionuclides were listed in TABLE II.

TABLE I. Properties of NRW-100 and NRW-400 Ion Exchange Resins.

Item	Cation	Anion
Spec	NRW-100	NRW-400
Form	Strong acid	Strong base
Functional group	SO_3^-	$N(CH_3)_3^+$
Total Capacity (eq./L)	1.8	1.0
Moisture Retention (%)	51-55	48-54
Specific Gravity (g/mL)	1.20	1.07

TABLE II. Radionuclides and Activities of TRR Spent IERs.

Item	Quantity
^{137}Cs(Bq/g)	2.5 x10^{7}
^{90}Sr (Bq/g)	3.5 x 10^{5}
Grossα	4.6 x 10^{5}
Dose rate (mSv/h)[1]	80~200
Gross weight (kg)	7,800
Volume (m^{3})	13

[1] About 42 kg of TRR spent resins in a basket

OVERVIEW THE TREATMENT OF SPENT IONEXCHANGE RESINS

The treatment of radioactive spent IERs is one of the most complex problems for nuclear industries in world. Since 1970s, IAEA focused on the management of spent IERs (LLW) which are produced by nuclear power plant operation, but there has been less discussion about the high activity and TRU-contaminated spent resins up to now. During the decades, the available and developing treatment approaches including direct solidification, oxidative decomposition[2-5], packing into high integrity containers [6] and super compaction [7]have been discussed as alternatives.

However, every treatment method for spent IERs encounters different drawbacks. The major problem of using cementation to treat IERs is swelling that leads to micro cracks and failure of waste form in long term storage or disposal. Especially for high surface radiation dose rate IERs, dry oxidation processes or incineration for the treatment of radioactive IERs encounter the challenge of off-gas treatment (e.g. ^{137}Cs, SOx, NOx), and wet oxidation processes would result in a secondary liquid radioactive waste stream that would pose further radioactive liquid wastes treatment problems.

By comparison of these treatment processes, direct solidification is still considered as a feasible way due to simple operation and equipment. Recently, many efforts attempted to develop new solidification reagents or modified cement like alkali activated cement and geopolymerization technology [8-12]. Wherein, geopolymer is considered to be an innovative material, it exhibits not only higher strength than conventional cement but also excellent heat and chemical resistance [13]. Geopolymer is a type of amorphous alumino-silicate cementitious material and it can be synthesized by polycondensation reaction of geopolymeric precursor and alkali polysilicates. The SIAL® matrix has been successfully employed to encapsulate radioactive spent IERs [8]. Furthermore, many papers also indicated that geopolymer material is zeolite-like three dimensional structure which is able to fix the organic beads and effectively capture the Cs and some heavy metal ions [14, 15].

PRETREATMENTON THE SPENT IRES FROM TRRSPENT FUEL POOL

Mechanical Decontamination Process

After water treatment processes, wet spent IERs were poured from the canister into the tank. The spent resins were flushed by ultrasonic cleaning processes to eliminate the deposited contaminants on the surface of resins (see Fig. 1). Unfortunately, the removal efficiency of radionuclides (^{137}Cs, ^{90}Sr, and Gross α) was ineffective. Less than 1 wt.% of sludge was removed from the surface of resins. The radioactive hot spots were still present in the resins rather than the sludge. As expected, since the highly soluble radioactive ions (i.e. Cs and Sr) were embedded in the resins via ion-exchange process, the removal efficiency of mechanical decontamination methods were limited. Otherwise, alpha-emitters such as uranium and TRU radionuclides may be present as particles and perhaps firmly deposit on the resins. Consequently, a highly dispersive mechanical decontamination may be able to further remove them.

Fig. 1. The Decontamination of the Spent IERs in Tank of the Spent Fuel Pool.

Dewatering and Packaging Process

In order to meet the schedule of the TRR decommissioning project, these spent IERs must to be removed and stored safely. Before temporary storage, the free water should be removed first. Hence, a stainless steel basket with screen mesh in the bottom was employed to load the spent IERs during processing the dewatering. The loading process was performed underwater in the TRR spent fuel pool to prevent people from radiation. A cone lead-shield was designed for dewatering and packaging processes. When the basket loaded with spent IERs was removed from the water, it was instantly covered by the cone lead-shield and placed on a water collection base (see Fig. 2). The base is part of a dewatering system which connects to a suction pump for free water removal. A vacuum drying system equipped with a heat plate was employed to further dewater at 200 ºC and 13000 to 16000 Pa. The whole dewatering system was operating for few hours and about 10 to 15 Kg of free water was removed. The final water content of spent IERs were estimated to be around 45 to 55%. After dewatering process, 180 baskets loaded with spent IERs were produced.

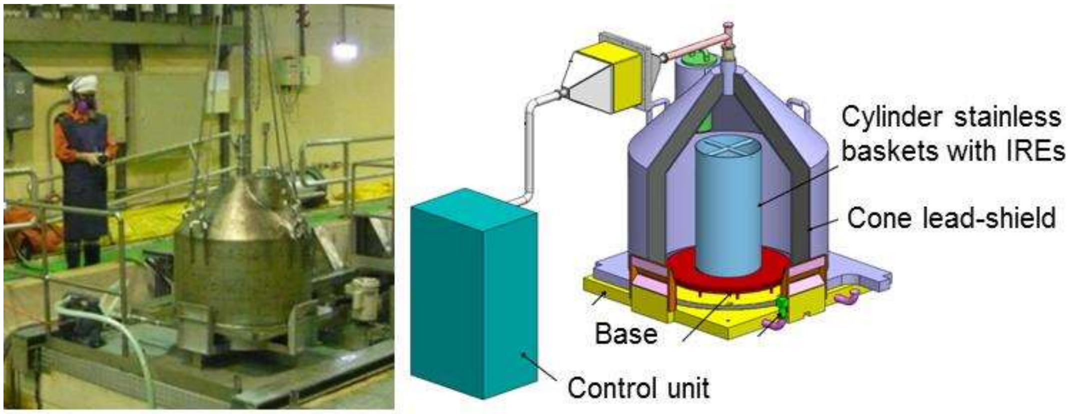

Fig. 2. Dewatering System for Wet Spent IERs.

A storage container had been licensed by the authority in Taiwan; it was constructed with lead shielding 5 cm thick around the drum and lid. Each lid was equipped with a ventilation filter. In the packaging process, an inner stainless steel drum coated with fiber reinforced plastic was first placed into the licensed container, and then three baskets with spent resins were packed into the drum (see Fig. 3). Hence, there were 60 drums of spent IERs with average surface radiation dose rate 40 to 100 μSv/h temporarily stored in the warehouse.

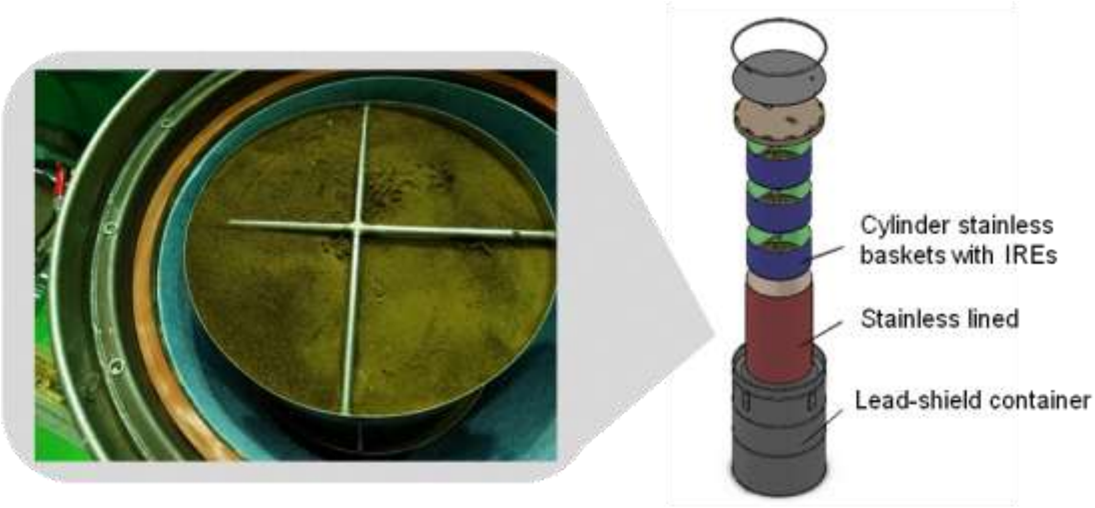

Fig. 3. The Packing Diagram of the Lead-shield Container.

IMMOBILIZATION TEST

Experimental Approach

The researchers at the Institute of Nuclear Energy Research (INER) had developed thermal pyrolysis and wet oxidation processes for the treatment of spent IERs, but the operation risks were still an issue. Therefore, the metakaolin type of geopolymer was selected to immobilize the IERs. Some additives like blast furnace slag also added to improve the workability of immobilization. The powder reagents of geopolymer were composed by the metakaolin and blast furnace slag. Several parameters such as SiO_2/Na_2O ratio of alkali-activation solution, powder/alkali-activation solution ratio were investigated to optimize the workability and the performance during preparation and immobilization stages, respectively. Those parameters show that the workability of geopolymer is significant; too sticky is not suit for workability, and too dilute may cause the resins float on the top of geopolymer samples. The workability is mainly dominated by the ratios of powder/alkali-activation solution and affected by the SiO_2/Na_2O ratio. The parameters also affect the compressive strength, which ranged from 6.1 to 71.4 MPa for the blank geopolymers were produced in this work. The workability of geopolymerization and mechanical strength of geoplymer sample are usually opposite in the preparation conditions. In order to select a proper condition during geopolymerization, the highest compressive strength condition of the blank geopolymer was not adopted to immobilize the IERs. Herein, we choose one parameter from those conditions that not only not too sticky but the compressive strength was good enough to prepare immobilize samples with contents of IERs such as 6, 12 and 18 wt.% (see Fig. 4).

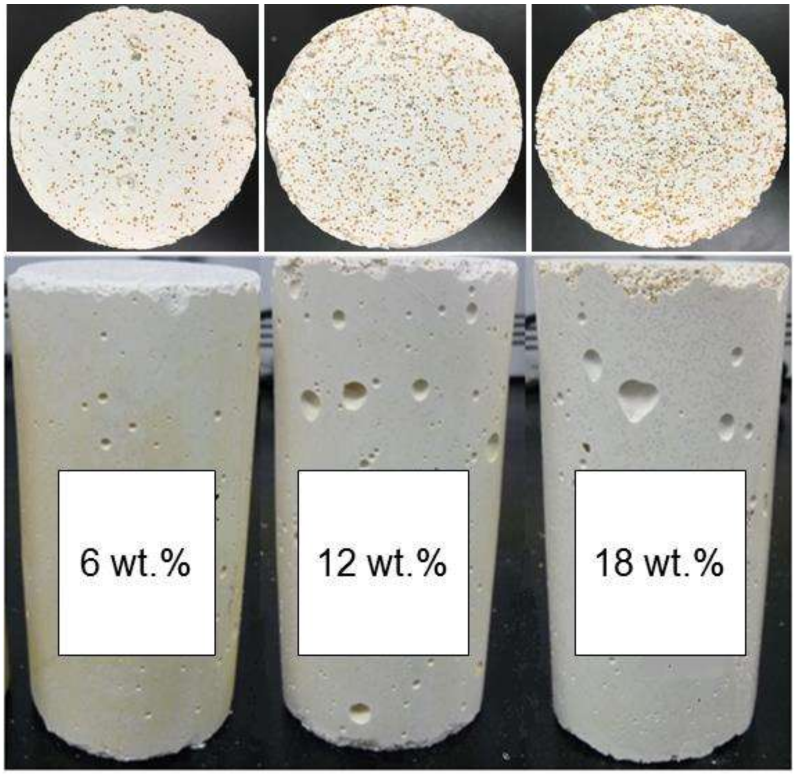

Fig. 4.Geopolymer Samples with Different contents of IERs.

According to the regulation mentioned above, the seven testing items including free standing water test, the mechanical strength, leaching rate index, water resistance, weather resistance, radiation resistance and bacteria resistance tests. The testing items were listed in TABLE III. All tests were going after curing 28 days of samples.

TABLE III. The Testing Items of the Regulations.

S/N	Test item	Test method	Standards
1	Free standing water	ANSI/ANS 55.1	1. The content of free standing water shall be less than 0.5% of the volume of the solidified waste. 2. The pH of free standing waste shall between 4 and 11, for cement-solidified waste which shall be larger than 6.
2	Mechanical strength	1. Common solidified waste except bituminous waste shall employ the ASTM-C39 or CNS 1232 test. 2. The ASTM-D5 test shall be used to test the penetration of bituminous waste.	1. The compression strength of common solidified waste except bituminous shall be larger than 1.5 MPa. 2. The penetration of bituminous waste shall be less than 100. The weight percentage of asphalt in the bituminous waste shall not less than 50%.
3	Leaching rate	ANS 16.1 (cement-solidified waste may be tested for five days)	The leaching index of all kinds of nuclides in the solidified waste shall be greater than 6.
4	Water resistance	Immerse the solidified waste in water for 90 days, and then test the mechanical strength (under normal temperature)	The test result shall meet the standard of Item 2.
5	Weather resistance	Circularly change the temperature and humidity, and then test the mechanical strength.	The test result shall meet the standard of Item 2.
6	Radiation resistance	Irradiating the solidified waste by Co-60 Gamma radiation, and then test the mechanical strength after the absorbed dosage reaches 1MGy.	The test result of compression strength shall meet the standard of Item 2.
7	Bacteria resistance	Perform the ASTM G21, and then test the mechanical strength.	The test result shall meet the standard of Item 2.

Results

The testing results were listed in TABLE IV. Most samples were met the criteria after the testing. The data show that higher contents of IERs in the immobilize samples exhibit lower strength including compressive strength and water resistance due to overloading and swelling of the IERs, respectively. After the radiation resistance test, the compressive strength of samples is slightly increased due to the longer setting time; it also implied that the samples were not influenced by radiation.

Because of climate in Taiwan, water and weather resistance tests are relatively important to the final disposal. TABLE V shows the pictures of sample after water and weather resistance tests. The appearance of samples which contain 6 and 12 wt.% of IERs do not obviously change in comparison of the original samples. It can see that sample with 18 wt.% loading of IERs had obviously cracks on the sample surface, and fail in the water resistance test. In case for the final disposal in Taiwan, the content of IERs in immobilization samples may proper for 12 wt.% or it need more modify for geopolymer samples. The content of IERs in immobilization samples may proper for 12 wt.% or it need more modify for geopolymer samples.

TABLE IV. The Testing Results of Sample in Different IREs Content.

Test item	**Testing results**		
	6 wt.% IERs	**12wt.% IERs**	**18 wt.% IERs**
Free standing water	No free standing water.		
Mechanical strength (MPa)	14.3~21.6	8.1~15.5	4.8~13.2
Leaching rate index	9.2~10		
Water resistance (MPa)	11.8~23.4	2.9~10.3	Fail (<1.5)
Weather resistance (MPa)	12.3~20.5	3.7~11.4	1.7~9.5
Radiation resistance (MPa)	23.3~34.8	12.5~18.2	8.3~14.1
Bacteria resistance (MPa)	12.5~24.9	9.7~10.5	5.1~9.3

TABLE V. The Sample Picture Took after Water Resistance Tests.

Test item	6 wt.% IERs	12 wt.% IERs	18 wt.% IERs
Water resistance			

CONCLUSION

Due to the fixed contamination arising from the radionuclides which embedded in the resins, the flush by ultrasonic cleaning processes work ineffectively on decontamination.

The dewatering process is useful to wet spent IERs. This process let the final water content of resins about 50%, it was close to fresh IERs. It is good for temporary storage in the lead-shield containers.

In order to let the workability of geopolymer is proper for immobilization process, the experiment did not use best compressive strength condition of the blank gerpolymer to immobilize the IERs. Although the compressive strength was not good as well, most samples tested from the regulations in Taiwan all meet the criteria. The result show that samples has no free standing water, and the compressive strength were range from 2.9 to 34.8 MPa which were much greater than the requirement.

Because of climate in Taiwan, water and weather resistance tests are relatively important to the final disposal. However, it is found that at the higher content of IERs in the immobilize samples, the water resistance capability of samples are obviously decrease due to the water absorption and volume swelling of the ion exchange resin. The content of IERs in immobilization samples may proper for 12 wt.% or it need more modify for geopolymer samples.

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