Jurnal Sains Nuklear Malaysia, 2024, 36(No. 2): 46 – 56
ISSN: 2232-0946

OPTIMIZATION OF FLY ASH-BASED GEOPOLYMER FOR IMMOBILIZATION OF SPENT RESIN FROM LOW LEVEL EFFLUENT TREATMENT PLANT (LLETP), MALAYSIAN NUCLEAR AGENCY

Nurul Wahida A.K.[1*], Rafizi S.[1], Ahmad Khairulikram ***Z.[1], Muhammad Fathi S.[1], Nurul Syazwani Y.[1] and Nor Atiqah A.S.[2]***

[1]Malaysian Nuclear Agency, Bangi 43000 Kajang, Selangor
[2]University Kuala Lumpur
**Corresponding author: nwahida@nm.gov.my*

ABSTRACT

Radioactive waste management is an important element in ensuring the peaceful use of nuclear and its related technology. In Malaysia, Malaysian Nuclear Agency is solely responsible for the management of radioactive waste in the country and its responsibilities include collection, transportation, treatment, storage and disposal of the radioactive waste. Treatment process is crucial in immobilizing the radionuclides from leaching out from the waste form. This project aims at assessing the effectiveness of fly ash-based geopolymer in the immobilization of radioactive waste in particular spent resin. In this project, spent resin from the Low-Level Effluent Treatment Plant (LLETP) will be treated with geopolymer blended from fly ash obtained as a by-product from a coal power plant in Malaysia. The spent resin from the LLETP becomes unusable after several cycles of usage and thus needs to be replaced. The spent resin is considered to be problematic and, in many cases, requires special approaches and precautions during its treatment to meet the waste acceptance criteria for disposal. This investigation serves to support the pursuit for effective and viable option to immobilize spent ion exchange resin at WasTeC in ensuring long-term safety.

Keywords: geopolymer, spent resin, immobilization

INTRODUCTION

Radioactive waste is produced in various fields such as agriculture, medicine, industry, and others. Nuclear Malaysia's Waste Technology Development Center (WasTeC), is the only agency responsible for handling the management of radioactive waste generated from the use of nuclear technology in Malaysia. Radioactive waste management includes collection, treatment and conditioning, storage and disposal. The facilities and equipment at WasTeC were mostly developed since 1982 and became fully operational since 1984. One of the facilities available is the Low-Level Effluent Treatment Plant (LLETP) for treatment of low-level liquid waste and storage of organic liquid waste. The plant has 4 collection tanks with a total capacity of 80 m^3 for storage of radioactive liquid waste obtained from laboratories in Malaysian Nuclear Agency.

In 2019, Tank 3A has been added to the LLETP and this collection tank is designed to collect the effluent from the newly installed mineral processing plant under Thorium Project that is yet to start operation. Tank 3A is specialized for liquid waste containing alpha emitters anticipated to be produced from the mineral processing activity. The Thorium Project aims to recover thorium, uranium, and rare earth elements in the monazite and xenotime which are by-products of tin mining processing. Extraction processes include acid leaching and selective precipitation that resulted in thorium, uranium and rare earth recovery. In this process, secondary effluent will be produced. The effluent contains physical, chemical or biological pollutants that often exceed the limit that has been set by the authorities. Figure 1 shows the flowchart for treatment of aqueous waste containing alpha emitters at the LLETP.

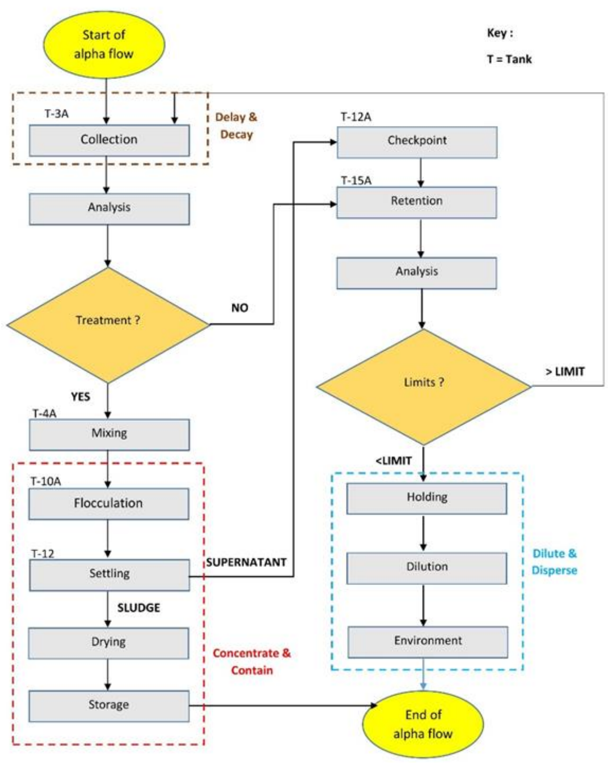

Fig. 1. Flowchart for Treatment of Aqueous Liquid Waste containing Alpha Emitters at Low Level Effluent Treatment Plant (LLETP), Nuclear Malaysia.

Treatment of effluent containing radioactive material is conducted using chemical flocculation-coagulation process. This process is commonly used in water and wastewater treatment in which compounds such as iron chloride and/or polymers are added to the wastewater to stabilize the colloidal material and cause small particles to accumulate into larger floats (Amuda et al., 2007; Tatsi et al., 2003; Abel- Shafy et al. 1991).

The effluent also contains physical, chemical or biological pollutants that often exceed the limit that has been set by the authorities. There are four parameters that usually exceed the limit: Chemical Oxygen Demand (COD), conductivity, total solid and the radioactivity for alpha emitters. The effluent discharge limit set by the regulator was successfully compiled by introducing an ion exchanger in the effluent treatment. Table 1 shows the analysis result for treatment of aqueous liquid waste containing alpha emitter.

Spent ion exchanger or spent resin requires special handling and treatment method due to its high radioactivity. This spent resin becomes no longer useful after several cycles of usage and needs to be replaced. Currently, approximately 640 kg spent resin from Nuclear Malaysia's research reactor were stored at WasTeC storage facility. Prolonged waste storage may pose risk to the human health and environmental due to potential leakage, which may contaminate the storage area. Currently, WasTeC is investigating treatment and disposal options for spent resin.

Table 1 Analysis Result for Treatment of Aqueous Liquid Waste containing Alpha Emitters.

Parameter	**Discharge Limit (DOE & SHE-MS)**	**Coagulation and flocculation treatment**	**After Treatment (ion exchanger)**
pH	6-9	<	<
Total Suspended Solid	50 mg/l	<	<
Temperature	40 ^{0}C	<	<
B.O.D	50mg/l	<	<
C.O.D	25 mg/l	> 25 mg/l (36 mg/l)	< 25 mg/l (6 mg/l)
Conductivity	1000 ⌠S/cm	>1000 ⌠S/cm (4392 ⌠S/cm)	< 1000 ⌠S/cm (103.7 ⌠S/cm)
Total Solid	1000mg/l	> 1000 mg/l (2843 mg/l)	< 1000mg/l
Radioactivity for alpha emitters	1.5 Bq/l	>1.5 Bq/l (27.7 Bq/l)	< 1.5 Bq/l (0.4 Bq/l)

*< = below discharges limit
*> = above discharges limit

Geopolymers are made by adding aluminosilicates to concentrated alkali solutions for dissolution and subsequent polymerization to form a solid (Perera et al., 2004). The advantage of this technology is that it can be performed at room temperature and does not require complex technology such as vitrification. The term 'geopolymer' was first introduced by Davidovits in 1978 to describe a family of mineral binders with a chemical composition similar to zeolites but with an amorphous microstructure (Rajamane et al., 2011).

Unlike ordinary Portland/pozzolanic cement, geopolymers do not form a calcium silicate-hydrates (CSHs) for matrix formation and strength but utilize the polycondensation of silica and alumina precursors to attain structural strength (Olawale et al., 2013). Two main constituents of geopolymers are source materials and alkaline liquids. Among hydraulic binders common in our modern world, Portland cement remains the most used. However, the production of Portland cement is a resource-exhausting, energy intensive process that releases large amounts of greenhouse gas CO_2 into the atmosphere (Guo et al., 2010).

The Geopolymer Institute in France recommended that rock based geopolymer cement as ideal for environmental applications, such as the permanent encapsulation of radioactive and other hazardous wastes, toxic metals, as well as sealants, capping, barriers, and other structures necessary for remedying toxic waste containment sites (Geopolymer Alliance, 2009). Geopolymer binder behaves similarly to Portland cement. It can set and harden in a room temperature and can gain reasonable strength in a short period. Some proportions of geopolymer binders have been tested and proved to be successful in the field of construction, transportation, and infrastructure applications. Any current building component such as bricks, ceramic tiles, and cement could be replaced by geopolymer.

Advantages of polymerization technology include (Jihui et al., 2021):

1. Fast hardening rate and high strength.
2. Good thermal stability and high temperature resistance
3. Strong material interface bonding ability.
4. Good corrosion resistance and durability

METHOD

Materials

Spent resin samples generated from the water treatment process of LLETP were prepared. The spent resins were scooped and filled in clean 3L sealed plastic containers for characterization. Direct immobilization and encapsulation of spent resin was used in this study. The fly ash used in this study was obtained from Sultan Salahuddin Abdul Aziz Power Plant, Kapar Selangor. To activate silica and alumina elements contains in fly ash, sodium hydroxide and sodium silicate were added. Super plasticizer was also added on the geopolymer mixture to obtain a good workability.

Particle Distribution, Morphological Imaging and Phase Identification.

Particle size analysis was performed using a PCScope PCS 81x digital microscope and Microtrac X-100 particle size analyzer. Phase identification was done by X-Ray Diffraction analysis using PANalytical X’Pert PRO MPD.

Analysis of Radionuclide Content

The fly ash samples were packed into 350 ml cylindrical plastic containers and measured using Ortec hyper-pure germanium (HpGe) gamma spectrometer system with 30% relative efficiency and a resolution of 1.74 keV at 1.33 meV of ^{60}Co. The detector efficiency calibration was performed using a multinuclides standard source in 350 ml plastic container (containing certified concentrations of ^{241}Am, ^{109}Cd, ^{57}Co, ^{123m}Te, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y, and ^{60}Co), purchased from Isotopes Product Laboratories (IPL, USA). Gamma Vision analysis software was used to analyze the samples. Gamma-ray energies of 1460Kev (K-40) for 40K, 1764.5 Kev (Bi214) and 351.9 Kev (Pb-214) were used to determine the concentration of ^{226}Ra. The activity of ^{226}Ra was assumed to be in equilibrium as its parent ^{238}U. Gamma-ray energies of 911.2, 964.6, and 969.0 KeV (Ac-228), were used to determine the concentration of ^{232}Th. While for spent resin, the samples were also packed into 320 ml cylindrical plastic container and were sent to Radiochemistry and Environmental Technology Group (RAS) for analysis of radionuclide content.

Mixture Proportions

A number of experiments were designed to test the influence of the variables on the workability and the strength of monolith geopolymer. The variables include workability, method of concentration and ratio of NaOH and Na_2SiO_3 and the effect of water and superplasticizer on strength. Based on this, the optimum geopolymer mixture was determined by casting pervious geopolymer monolith cube in order to obtain optimum ratios of fly ash to alkaline activator, sodium hydroxide (NaOH) to sodium silicate to solution (Na_2SiO_3), concentration of NaOH in molar, volume of superplasticizer, water and spent resin. The materials were prepared according to the given ratio and mixed in the Hobart mixer for 2 minutes. The slurry was poured into a 50 mm x 50 mm x 50 mm stainless steel cube mould. The samples were then vibrated to release any residual air bubbles and compact the sample. During the hardening of the geopolymer cement paste, the samples were covered with a thin film of polyethylene to avoid water evaporation and then kept for 24h in ambient condition of the laboratory before demoulding. Each sample were prepared in duplicates. The compressive strength determination of the sample was based on BS 1881-116:1993 standard. A total of 9 cube samples (50 mm x 50 mm x 50 mm) were prepared and tested at 3 different curing times (7, 14 and 28 days).

RESULTS AND DISCUSSION

Physical and Chemical Properties of Fly Ash.

The particle distribution of the samples was determined with a laser diffraction analyzer (Microtrac-X100). Table 2.0 shows that Kapar fly ash has a particle size range between 1.06-209.3 µm and the median particle size of 20.64 µm (Nurul Wahida et al.2021). Particle size of fly ash needs to be 80-90% lower than 45 µm to obtain the optimum binding effect (Fernandez-Jimenez et al., 2003).

Table 2. Granulometric Data for Fly Ashes

Samples	**Percentages % of particles with diameter**			**Mean Diameter (µm)**
	d_{10}	d_{50}	d_{90}	
Kapar fly ash	3.75	20.64	73.29	20.64

Mineralogy composition

There are two classes of fly ash which is defined by the ATM C618 which is Class F fly ash and Class C fly ash. The main difference between the classes is based on the amount of calcium, silica, alumina, and iron content in the ash. Based on the XRF result (Table 3.0), showed that the Kapar fly ash had a class C fly ash due to the total percentage of SiO_2, Al_2O_3 and Fe_2O_3 is less than 70% and the SO_3 content is less than 5% (Nurul Wahida et al., 2021). To obtain the optimum properties for binding, fly ash as source material should have a low calcium content, and material that does not burn less than 5%. In addition, Fe_2O_3 content should not be more than 10% and silica content should be between 40-50% (Suhana et al., 2015).

Table 3. Chemical Composition of Fly Ash

Oxide	**Kapar fly ash**	**ASTM C618 Class C**	**ASTM C618 Class F**
SiO_2	44.39	-	-
Al_2O_3	19.90	-	-
Fe_2O_3	3.75	-	-
Total SiO_2, Al_2O_3 & Fe_2O_3	68.04	Min. 50%	Min. 70%
CaO	5.44	-	-
SO_3	0.49	Max. 5%	Max. 5%

Radionuclides Content

The average radionuclide activity concentrations for fly ash are reported in Table 4.0 (Nurul Wahida et al., 2021). Activity concentration ranges from 96.5 to 338.5 Bq/kg, 139 to 422.7 Bq/kg, and 251.8 to 422 Bq/kg for ^{226}Ra, ^{232}Th, and ^{40}K, respectively. Coal that contains natural uranium and thorium is classified as Naturally Occurring Radioactivity Material (NORM) (Suhana et al., 2015). In the Second Schedule of Atomic Energy Licensing (Radioactive Waste Management) Regulations 2011 (P.U(A)274), the clearance limit set for activity concentration of radionuclides of natural origin for ^{226}Ra, ^{232}Th and ^{40}K shall not exceed 1000 Bq/kg, 1000 Bq/kg and 10,000 Bq/kg, respectively. The activity concentrations for sample fly ash from Kapar are below than the regulatory limit set by legislation.

Table 4. The Activity Concentration of ^{226}Ra, ^{232}Th, ^{40}K in Bq/kg for Kapar Fly Ash

Sample	**Activity Concentration (Bq/kg) (Nurul Wahida et al., 2021)**		
	^{226}Ra	**^{232}Th**	**^{40}K**
Kapar fly ash	338.5±9	422.7±24	251.8±9
P.U(A) 274	1000	1000	10000

The results of the gamma spectrometric analysis of spent ion exchange resins are shown in Table 5.0. The result shows the highest activity concentration value for spent resins was found for ^{228}Th (6.24±0.45 Bq/kg) and the lowest was for ^{234}U (2.49±0.09 Bq/kg) respectively. The activity concentrations of this spent resin are below than the clearance level set in the Second Schedule Radioactive Waste Clearance Level.

Table 5. The Activity Concentration for Spent Resin

Element	**Activity Concentration (Bq/kg)**
^{228}Th	6.24±0.45
^{230}Th	4.89±0.36
^{232}Th	5.42±0.39
^{234}U	2.49±0.09
^{235}U	< 0.2
^{238}U	< 0.2

*< = minimum detection activity

Optimum Mix Design for Immobilization of Spent Resin using Geopolymer Based Fly Ash

Table 6.0 shows the optimum value obtained for mix proportions based on the work that has been carried out in which the parameters such as the ratio of fly ash to alkaline solution, the ratio of Na_2SiO_3 to NaOH, NaOH molarity, volume of superplasticizer, water and waste loading has been considered for each of these parameters.

Jurnal Sains Nuklear Malaysia, 2024, 36(No. 2): 46 – 56
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The highest compressive strength on day 7 was 15.4 MPa compared to the previous study 6.1 MPa (Nurul Wahida et al.2015). According to International Atomic Energy Agency (IAEA), (1983) the minimum standard for compressive strength for monolithic radioactive waste immobilization after reaching the age of 28 days was 3.2-70 MPa and while Comissão Nacional De Energia Nuclear (CERN-NN), (2002) the compressive strength at age of 28 days must be greater than or equal to 10 MPa. Based on the result, the values obtained are within the recommended value by the IAEA and CERN-NN. Higher molar concentration of NaOH promotes the dissolution of aluminosilicate in early age, which lead to the increase of strength in early stage (Wei et al., 2019). The composition of the spent resin made up of the monolithic geopolymer was 14 % (wt). According to Natsuda et al., (1992) and Brookhaven National Laboratory, (1981) the solidification of spent resin into Ordinary Portland Cement (OPC) should be restricted to less than 20% to prevent the formation of cracks at higher loadings, which will result in an unstable waste product that tends to deteriorate in water when the waste loading is higher.

Table 6. The Optimum Mix Design for Immobilization of Spent Resin using Geopolymer Based Fly Ash

Details of Mix Proportion		
Parameter	**(Nurul Wahida et al., 2015)**	**Current study**
Ration fly ash to alkaline activator	2.0	2.5
Ratio Na_2SiO_3 to NaOH	2.5	3.0
NaOH (M)	12	14
Distilled water (%)	-	8
Superplasticizer (%)	6.0	2.0
Spent resin (%)	10	14
Curing Temperature	Room temperature	Room temperature
Curing time (hrs)	24	24
Compressive strength (MPa) on 7^{th} day	6.1	15.4

A new parameter, water was added compared to the previous study. Based on table 6.0, shows an increase in compressive strength compared to the study conducted by Nurul Wahida et al., 2015. The workability of the geopolymer concrete mixture can be enhanced and improved by adding more water (Subhash et al., 2013). However, an excessive amount of water will result in reduction of compressive strength. Sagoe-Crentsil et al., (2013) revealed that water takes part in the dissolution, hydrolysis and polycondensation reactions during geopolymer synthesis. It offers a medium for the dissolution of aluminosilicates and the transfer of various ions, hydrolysis of $Al^{3+}$and Si^{4+} compounds and polycondensation of different aluminate- and silicate-hydroxyl species. As a result, water has great effects on the geopolymer formation, structure of the geopolymer gels and properties of the products. According to Chindaprasirt et al., (2007) using extra water to improve workability of fly ash geopolymer had higher compressive strength than adding superplasticizer. In this study, the optimum water percentage obtained was 8%. Superplasticizer was added to improved and enhanced workability properties, strength and durability of the monolith geopolymer (Potluri et al., 2024). The inclusion of superplasticizer more than 2% resulted in bleeding as well as segregation of fresh geopolymer mixture. It also reduced the compressive strength of the monolith geopolymer

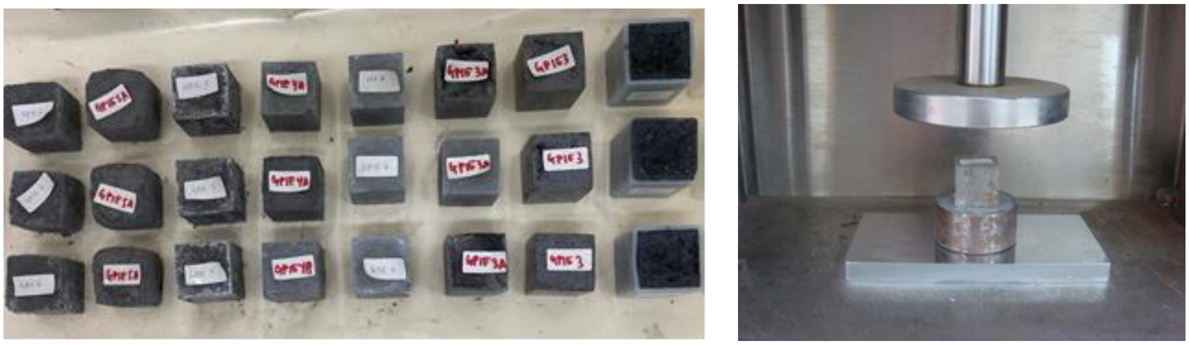

Fig. 2. Samples of Monolith Geopolymer

CONCLUSION

Results from the study shows that conditioning of the spent resin together with fly ash at room temperature can produce geopolymer with reasonable strength properties. The composition of the spent resin that make up the monolith geopolymer was 14 % (wt.), with the monolith geopolymer compressive strength of 15.4 MPa is well within the internationally acceptable value. Adding water in the geopolymer mixture can increase the compressive strength of the monolith geopolymer. This research should be put in a continuous effort in other method of testing such as leaching and durability test. In this way, more reliable data could be produced to support the use of geopolymer technology as an option for immobilization of radioactive waste. Furthermore, immobilization could enhance the handling and transportation of radioactive waste. Solidified waste is less prone to leakage, spillage, or accidental release during handling and transport operations, could reduce the risks to the workers and environment

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