

## Recycle Glass Waste as a Host for Solidification of Oil Sludge (Sisa Kaca Kitar Semula sebagai Perumah untuk Pemejalan Enap Cemar Minyak)

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### ABSTRACT

The production of oil sludge per year is more than 1 billion tonne that mainly generated from the production, refinery, storage, and transportation of petroleum. Disposal of oil sludge had been a great issue since the waste consists of highly concentrated of Natural Occurring Radioactive Material (NORM). Therefore, to overcome this problem, this study aims to investigate used and recycle borosilicate glass as a host for solidification of oil sludge. The oil sludge and glass host were mixed into different compositions, melted at high temperature (1,100 °C -1,200 °C) for 1 h in alumina crucible and rapidly cooling in the room temperature, by reducing the radioactivity levels of NORM. This study found out that, the optimum waste loading was obtained at a range of 20-25 wt% of oil sludge and 75-80 wt% of the glass host at 1,200 °C. All the glass waste was produced as an amorphous phase material with small amount of crystalline phase such as SiO<sub>2</sub>, Ba<sub>4</sub>-Al<sub>2</sub>-O<sub>7</sub>, AlPO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>Zn<sub>10</sub>, which observed to be appeared during the cooling process. The major elements of the glass waste were found to be distributed uniformly based on energy dispersive X-ray spectroscopy (EDX) mapping. Furthermore, the dissolution rate of indicator element increased due to the increase of pH solution, while the normalized releases of B, Si, and Na during product consistency tests were low and below the standard glass limit, which shows high durability of the glass due to lower release of glass elements. Therefore, this study emphasized the suitability of recycle borosilicate glass as a host for immobilization of oil sludge prior for disposal, while deploying high temperature technology.

**Keywords:** Borosilicate glass; hazardous waste; naturally occurring radioactive material (NORM); oil sludge; vitrification process

### ABSTRAK

Penghasilan enap cemar minyak daripada industri petroleum adalah melebihi 1 bilion tan pada setiap tahun semasa proses penghasilan, penyulingan, penyimpanan dan pengangkutan. Pelupusan enap cemar minyak telah menjadi isu besar kerana sisa enap cemar mengandungi unsur yang berbahaya. Oleh itu, bagi mengatasi masalah ini, enap cemar minyak dan sisa kaca dicampur menerusi beberapa komposisi yang berbeza dan dipanaskan pada suhu yang tinggi (1,100 °C -1,200 °C) selama 1 jam dan disejukkan pada suhu bilik bagi mengurangkan bahan berbahaya seperti radionuklid tabii (NORM). Keputusan kajian mendapati muatan sisa yang optimum adalah dalam julat 20-25 bt% enap cemar dan 75-80 bt% perumah kaca yang dipanaskan pada suhu 1,200 °C. Kesemua bentuk sisa kaca akhir mempunyai fasa amorfus dengan fasa hablur yang kecil seperti SiO<sub>2</sub>, Ba<sub>4</sub>-Al<sub>2</sub>-O<sub>7</sub>, AlPO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> dan Fe<sub>3</sub>Zn<sub>10</sub>, yang mungkin terhasil semasa proses penyejukan. Unsur utama tertabur dengan sekata menerusi pemetaan spektroskopi sinar-X penyebaran tenaga (EDX). Selain itu, kadar larutan unsur penunjuk meningkat dengan peningkatan pH larutan, manakala pembebasan ternormal oleh

B, Si, dan Na semasa ujian larut lesap adalah rendah dan di bawah had piawaian kaca, yang menunjukkan ketahanan kaca yang tinggi disebabkan pelepasan unsur kaca yang rendah. Oleh itu, kajian ini menekankan kesesuaian kaca borosilikat yang dikitar semula untuk digunakan sebagai perumah untuk memegunkan sisa enap cemar minyak sebelum dilupuskan dengan menggunakan teknologi bersuhu tinggi.

Kata kunci: Enap cemar minyak; kaca borosilikat; proses pengacaan; radionuklid tabii (NORM); sisa berbahaya

## INTRODUCTION

Oil sludge is a semi-solid waste and listed under the Resources Conservation and Recovery Act 1976 (RCRA) as hazardous waste (Johnson & Affam 2019). It has a very complex composition, consists of a mixture of oil, sediment, and water that contain radioactive elements as well as high hydrocarbon concentrations, including naphthalene (Canoba et al. 2007; Gopang et al. 2016) which may cause harm to the human and environment when exposed to it (Misra & Pandey 2005). Naturally occurring radioactive material (NORM) is identified as one of the materials in the oil sludge that composed of long-lived isotopes of uranium and thorium, can be concentrated and accumulated in tubing and surface of equipment due to the physical and chemical processes associated with oil and gas industry (Awwad et al. 2015). These isotopes then decay into radium-226 and radium-228, which they are relatively more soluble and become mobile in the fluid phase of the formation compared to its parent (Awwad et al. 2015). The decay process releases energy in the form of ionizing radiation that can be exposed to human and environment through direct exposure, through aqueous phase, inhalation, and ingestion (USEPA 2021). As it enters the human body, the radiant energy is sufficient to cause biological damage which increases the risk of cancer (Zakariya & Kahn 2014) and disturb the physical and chemical properties of contaminated soil such as nutrient deficiency, inhibit seed germination and cause restricted growth or demise of plants on contact (Hu et al. 2013).

The presence of NORM in the oil sludge had been recognized since the 1930s (Allam & Bakr 2015). Since then, petroleum industries and regulators have increased an awareness towards the presence of NORM on the implementation to reduce, recover, recycle, and dispose of this waste. However, the output of sludge is increased every year due to the high global demand for oil production (Hui et al. 2020) and caused the reduction of storage capacity and contributed to the one of corrosion factor on process equipment (Johnson et al. 2015).

There are a few treatments that have been developed for managing and disposing of this waste such as

incineration, solidification/stabilization, pyrolysis, and biodegradation (Johnson & Affam 2019), but it still and remains a challenging as a global problem for long-term. In Malaysia, the radioactive waste is either stored in the container or is incorporated into the surface soil using the landfarming method; and require large storage areas (Aja et al. 2016). Furthermore, geological and hydrological parameters must also be monitored to control the movement of hazardous waste into the environment for the long term. Since treatment options are limited and the volume of waste continues to increase, finding adequate space for waste storage is not practical in the long-term (Puad & Noor 2003). So, according to the previous studies, the vitrification process had been conducted using various types of waste especially in high level waste such as an asbestos-cement waste (ACW) was melted at 1,400 °C (Iwaszko et al. 2018). Their experiment showed that the vitrification is an effective method to neutralize hazardous waste, effectively binds the components of ACW in the glass structure and converts ACW into harmless product. Then, different concentration of uranium (0-50,000 µg/g) in the contaminated soil also being studied using the vitrification process (Chen et al. 2019; Shu et al. 2020). The results showed no crystallization phase was observed as the uranium addition amount gradually increased from 0 - 5,000 µg/g, but crystal diffraction peaks appeared when uranium amount reached 50,000 µg/g and the crystalline regions also evenly distributed in fracture surface due to their high homogeneity. The leaching rate of uranium was stable after 42 days which is  $5.73 \times 10^{-6}$  g/m<sup>2</sup> (Shu et al. 2020) and below  $5.09 \times 10^{-6}$  g/m<sup>2</sup> (Chen et al. 2019) in vitrified form.

Thus, vitrification technique is selected as a conditioning treatment in this study to overcome the limited storage of waste and reduce the exposure to the human and environment. This technique used recycled glass as a host due to the glass matrix capabilities to solidify radioactive waste through chemical bonding or incorporation with very high chemical resistance (Oniki et al. 2018). This technique is more relevant in various aspects including low level radioactive waste because

it has corrosion resistance to various environmental conditions and excellent stability (fixed range of post-vitrification composition), high usability for various types of industries and waste, waste management cost savings and high reduction in waste volume (up to a reduction of 90% compared to common alternatives) (Meegoda et al. 2003; Oniki et al. 2018; Ojovan & Batyukhnova 2007).

Therefore, the aim of this study was to incorporate the oil sludge containing NORM inside a glass-ceramic structure and to evaluate the properties of glass waste formed from physical and chemical aspects after vitrification process. This study will provide an alternative method for handling radioactive waste efficiently in the current storage facilities.

## MATERIALS AND METHODS

### PREPARATION OF SAMPLES

Low-level waste of oil sludge was obtained from the Malaysian Nuclear Agency, Selangor. The sample was produced by the petroleum industry in 2017 and was stored since then. On the other hand, recycle borosilicate glass as a host was collected, washed and prepared in the laboratory (mainly from laboratory apparatus). Semi-solid, blackish, and oily of oil sludge was dried for several days in a conventional oven at 80 °C to ensure significant moisture content was removed. Then, the samples (oil sludge and host) were homogenized by being crushed to a fine powder using pestle and mortar, then sieved through a 500 µm sieve for further analysis. The element composition in all raw samples were analysed using inductively coupled plasma-mass spectrometry (ICP-MS). Meanwhile, the concentration of uranium-238 ( $^{238}\text{U}$ ), thorium-232 ( $^{232}\text{Th}$ ) and potassium-40 ( $^{40}\text{K}$ ) in oil sludge were determined for 12 h of counting time using gamma spectrometry system with a High-purity Germanium (HPGe) detector couples to multi-channel analyser.

### NATURAL RADIOACTIVITY ANALYSIS

The dried oil sludge residue sample was packed into an airtight acrylic counting bottle and kept for 30 days to attain secular equilibrium with the parent's radionuclide

( $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ ) and their progenies (Bakr 2010). After 30 days, the oil sludge residue sample was counted for 12 h using a gamma spectrometer system to determine the concentrations of the natural radionuclides in the sample. Each sample was prepared, packed, and replicated thrice in accordance with the guideline (IAEA 1996). HPGe detector (GC3018) was used with a relative efficiency of 30% and a resolution of 1.8 keV at 1.33 MeV and the analysis of photo peaks was performed using Genie-2000 software (Canberra Inc). The activity concentration of  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$  were determined at peak energies of 352 keV of  $^{214}\text{Pb}$  and 1760 keV of  $^{214}\text{Bi}$ , 583 and 911 of  $^{228}\text{Ac}$  and 2,614 keV of  $^{208}\text{Tl}$ , and 1,460 keV, respectively. Quality control and quality assurance of the measurements were tested using IAEA Soil-375 as standard reference material (SRM) with known activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ .

### DETERMINATION OF ELEMENTS IN OIL SLUDGE AND GLASS HOST

EPA 3052 method was used to measure trace element and heavy metal in the raw samples (USEPA 1996). The sample was weighed and mixed with hydrochloric acid (HCl) and nitric acid ( $\text{HNO}_3$ ). The mixture was heated at  $180 \pm 5^\circ\text{C}$  in the microwave digester for 45 min and cooled to the room temperature. Then, the volume of distilled water was added to dissolve the metal sulphate and filtered to produce a clear solution. The concentration of elements in the clear solutions were determine by using ICP-MS (ELAN 9000 - PerkinElmer SCIEX). A standard solution was prepared using PerkinElmer Pre Plus (multi-element calibration standard 2).

### VITRIFICATION PROCESS

Various compositions of oil sludge mixtures with glass host were weighed and labelled according to its composition as summarized in Table 1 and placed into a 50 mL alumina crucible. The mixtures were melted in a furnace at 1,100 °C - 1,200 °C for 1 h, then cooled down to 500 °C for 2-3 h before removing and allowing them to cool at room temperature to evaluate their properties. The similar composition as G5 was not carried out at 1,100 °C due to inhomogeneous result of product of G2.

TABLE 1. Composition of glass waste form at different temperature

Oil sludge	Composition, wt%		Id/Temperature, °C	
	Oil sludge	Recycle glass	1,100	1,200
20		80	G1	G3
25		75	G2	G4
30		70	-	G5

#### EVALUATION OF GLASS WASTE FORM

The physical and chemical properties of the glass waste form after the vitrification process were investigated and evaluated using different analysis approaches, such as observation through an optical microscope, X-ray diffraction (XRD), field emission scanning electron microscopy with energy dispersive x-ray (FESEM-EDX) and product consistency test (PCT) analysis.

The XRD pattern was recorded using Bruker XRD D8 advance X-ray diffractometer with a Cu K $\alpha$  source ( $\lambda = 0.1542$  nm). The scans were performed at a speed of  $0.02^\circ/1.2$  s ranging from  $2\theta = 5 - 80^\circ$  at 40 kV and 40 mA. A piece of glass waste form was crushed and mixed with titanium oxide (TiO<sub>2</sub>) that used as a standard to determine the crystalline phase. The XRD spectrum was analysed using Diffrac Eva software.

Another piece of glass waste form was polished and coated with iridium to eliminate the charging effect in order to obtain the clearest images using FESEM-EDX (Merlin, Zeiss). The data were recorded on FESEM Merlin with energy of the electron beam being 30 kV.

The remaining pieces of glass waste form was crushed and sieved following standard PCT designated as ASTM C1285-14 (ASTM 2002) sieve -100 to + 200 mesh (0.149 - 0.074 mm). The glass was washed using ethanol and distilled water before drying in the oven at 50 °C. Then, dried glass waste was placed into the PFA TFE-fluorocarbon vessel. Type I deionized water was added at ratio 10:1 (liquid-to-solid), sealed and placed in an oven at a constant temperature of  $90 \pm 2^\circ\text{C}$  for 7 days.

After 7 days, the solution of glass waste form was retrieved and cooled to the room temperature. The solutions were filtered with a 0.45  $\mu\text{m}$  syringe filter and stored in a clean container. pH and temperature were also recorded after removing the leachates from the vessels. The clear solutions were analysed using ICP-MS to measure B, Si and Na elements and estimation for normalized releases was discussed elsewhere (Ruzali et al. 2021).

#### RESULTS AND DISCUSSION

##### RADIOACTIVITY CONCENTRATION OF <sup>232</sup>Th, <sup>238</sup>U, and <sup>40</sup>K IN OIL SLUDGE WASTE

As mentioned previously, the activity concentration of <sup>238</sup>U, <sup>232</sup>Th, and <sup>40</sup>K of the IAEA Soil-375 was measured experimentally and compared with the SRM certificate, as tabulated in Table 2. Table 3 summarizes and compares the activity concentration of <sup>232</sup>Th, <sup>238</sup>U, and <sup>40</sup>K that obtained from oil sludge in this research with other

studies. The average activity concentration of <sup>232</sup>Th, <sup>238</sup>U, and <sup>40</sup>K in this study were  $148.2 \pm 8.7$ ,  $200.5 \pm 18.6$ , and  $399.3 \pm 15.4$  Bq/kg, respectively.

Table 3 shows the activity concentrations of <sup>238</sup>U, <sup>232</sup>Th, and <sup>40</sup>K in oil sludge were different in each country due to several factors such as geological location, formation conditions, type of production wells and age of production wells (Abdel-Sabour 2015). These activities came mainly from the precipitates of hard insoluble radium sulphate as well as the radioactive silts and clays (Hasanuzzaman et al. 2016). In addition, these activities were more soluble in oil sludge and more easily released into the environment as well as a higher risk of exposure to humans especially to workers in oil and gas industries, who worked in cutting and replacing oilfield pipeline areas, removing solids from tanks and pits, and repairing gas processing equipment. They may be exposed to particles containing alpha and beta emitting radionuclide levels that could pose a health risk if inhaled or swallowed (Abdel-Sabour 2015).

##### DETERMINATION OF ELEMENTS IN OIL SLUDGE AND THE GLASS HOST

Concentrations of elements in the oil sludge residue and host of borosilicate glass are shown in Table 4. Oil sludge residue has a higher concentration of Ba, Pb, and Zn compared with previous studies (Aida et al. 2012; Ali et al. 2017a; Philemon et al. 2016), but concentrations of other heavy metals (such as Cr, Ti, and Zr) are lower in this study might be caused by different methods of wastewater treatment (Bakr 2010). However, according to the API 1989 report for metal concentration (Bakr et al. 2018), the level of Fe in oil sludge is quite high with lower concentrations of Ca and Al. This might indicate a chemical issue in the treatment of crude oil and an additional source of Fe besides the corrosion of pipelines which is attributed to the use of Al compounds of flocculants (Nuha 2012). The other elements were quite high because of several factors such as a rapid pressure drop, a loss of CO<sub>2</sub> from the solution, and a consequent rise in pH leading to very rapid scale formation at the specific locations (Nuha 2012).

According to Table 4, the host of B glass was categorized as sodium-borosilicate glass, which is most often used as laboratory glassware, while Ca was used as a property modifying component that helps accelerate the phase separation of the host and reduces the evaporation of highly volatile Na and K by limiting the amount of Ca during high temperature treatment (Ojovan et al. 2004). In addition, Al was used as a modifying oxide

that acts a balancing component to facilitate high levels of Ca in the host. It also prevents the cracks during the leaching test and improves moldability by minimizing the viscosity change relative to the change in the temperature (Ojovan et al. 2004). The small amount of Si plays an important role in the glass, forming the strong covalent

bonds involving  $\text{SiO}_4$ ,  $\text{AlO}_4$  and  $\text{BO}_4$  tetrahedral, and  $\text{BO}_3$  triangles (Stefan et al. 2012). The Si content from oil sludge could be benefit to the whole composition to form very durable waste glass formation. It made the glass most durable waste form and suitable matrix to capture the radioactive element in the range of temperature between 1,100 °C and 1,200 °C (Manaktala 1992).

TABLE 2. Validation result of SRM IAEA Soil-375

Radionuclide	Certificate values (Bq/kg)	Experimental values (Bq/kg)
$^{238}\text{U}$	24.4	$23.2 \pm 3.8$
$^{232}\text{Th}$	20.5	$20.9 \pm 1.8$
$^{40}\text{K}$	424	$391 \pm 16.1$

TABLE 3. Activity concentration of oil sludge waste (Bq/kg)

Location	Activity concentration in oil sludge			References
	$^{238}\text{U}$	$^{232}\text{Th}$	$^{40}\text{K}$	
This study	$200.5 \pm 18.6$	$148.2 \pm 8.7$	$399.3 \pm 15.4$	-
Indonesia	12.4 - 98.0	4.0 - 148.0	105.0 - 268.0	(Bakri & Siregar 2003)
Malaysia	13.0 - 40.0	37.0 - 48.0	-	(Puad & Noor 2003)
Ghana	2.8 - 36.1	2.6 - 55.9	26.8 - 189.9	(Darko et al. 2012)
Libya	5.0 - 19.0	2.0 - 12.0	-	(Mykowska & Hupka 2014)
Sudan	23.3 - 655.4	16.2 - 396.3	16.1 - 238.7	(Abu-baker et al. 2016)
Iraq	35.0 - 700.0	15.2 - 281.9	15.2 - 149.0	(Ali et al. 2017b; Nada & Omer 2016)
Albania	18.0 - 20.0	21.0 - 22.0	175.0 - 348.0	(Xhixha et al. 2015)
United Kingdom	1.6 - 9.4	0.03 - 0.94	-	(Garner et al. 2017)
Egypt	12.3 - 29.6	14.6 - 28.2	789.4 - 1680.5	(Ali et al. 2019)



TABLE 4. Elemental concentrations of oil sludge and host glass (mg/kg) using ICP-MS

Element	Oil sludge	Recycle glass
Al	2855 ± 11.27	551.4 ± 9.13
B	-	359.9 ± 7.57
Ba	755.74 ± 10.35	12.84 ± 0.63
Ca	6458.7 ± 15.85	1063.8 ± 3.29
Cr	6.1300 ± 0.05	-
Fe	37377 ± 12.50	1441.4 ± 6.44
K	1247.6 ± 10.0	952.1 ± 5.28
Mg	2025 ± 5.06	165.1 ± 4.95
Na	1811.2 ± 5.58	2613.7 ± 6.65
Pb	53.21 ± 1.9	12.91 ± 0.55
Si	329.8 ± 8.13	191.9 ± 4.1
Sr	174.43 ± 5.29	4.60 ± 0.61
Ti	28.8 ± 3.1	8.69 ± 0.16
Zn	274.1 ± 9.47	193.9 ± 2.68
Zr	1.45 ± 0.41	0.54 ± 0.46

## XRD ANALYSIS FOR RAW SAMPLES

XRD analysis on oil sludge waste and the host of borosilicate glass are done and presented in Figure 1. The XRD spectra were analysed by search and match with the powder diffraction file (JPDF) database from Diffrac Eva software. The highlight of these spectrum was shown in Figure 1, where there is quartz ( $\text{SiO}_2$ ), calcium oxide (CaO), halite (NaCl), and alumina ( $\text{Al}_2\text{O}_3$ ) detected at angle  $2\theta$  between 5 and  $80^\circ$ .

Based on Figure 1, the host of borosilicate glass was completely amorphous, and no crystalline peaks was observed. Meanwhile, an obvious  $\text{SiO}_2$  peak and other mineral such as CaO,  $\text{Al}_2\text{O}_3$  and NaCl were shown on oil sludge residue.  $\text{SiO}_2$  is classified as a silicate mineral and presents due to the formation of sandstone or sand (Al-Ghamdi & Sitepu 2018). While, CaO is acted as a flux, which reduces the melting temperature, thereby using less energy and lower quantities of soda ash

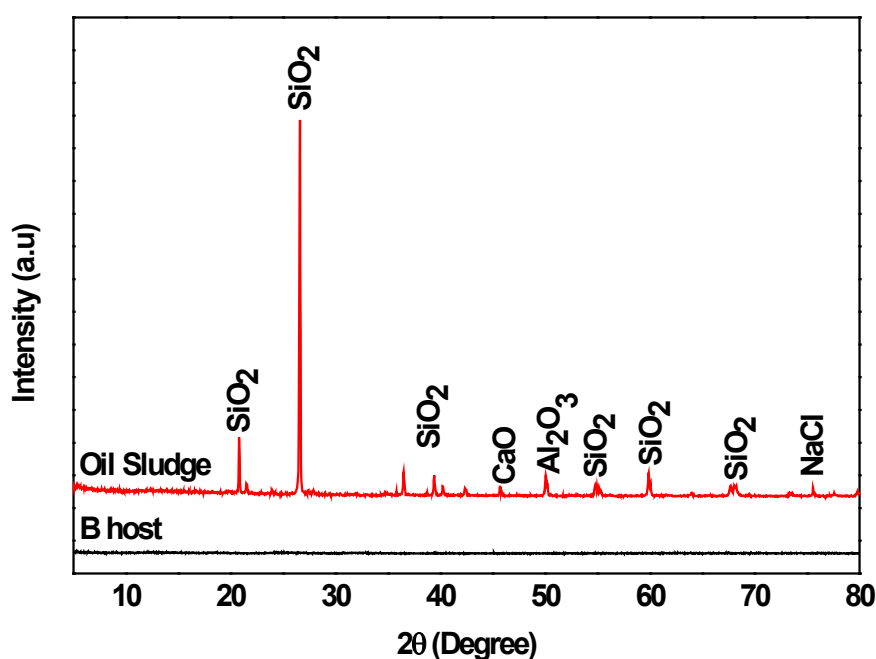


FIGURE 1. XRD patterns of oil sludge and borosilicate glass (B) host

(Shakhatreh 2015).  $\text{Al}_2\text{O}_3$  provides hardness, strength, and workability, and it is more resistant to the chemicals in useful materials like refractory bricks (Bednarek et al. 2016). NaCl (known as rock salt), which is present in the oil sludge due to the sediments source location in the sea (Meor et al. 2007).

#### PHYSICAL PROPERTIES OF GLASS WASTE FORM

Table 5 shows the sample information with various composition of mixtures between oil sludge and borosilicate glass, and observations of glass waste form at two different temperatures. At 1,100 °C, the glass waste forms of G1 and G2 were milky white in colour. These waste forms had rough and bumpy surfaces as well as black spot which refers to an inhomogeneous structure between the host and oil sludge. The waste forms were not dissolved completely during the melting process due to the high viscosity of the melt and perhaps the high waste loading (20 - 25 wt%) (Ruzali et al. 2021). These results also show that oil sludge is not uniformly mixed with the glass at this temperature, even though it is contained in the glass mixture between oil sludge and CRT glass (Ruzali et al. 2021).

To produce the glass waste form, samples G3, G4, and G5 were melted at 1,200 °C with various mixtures






of oil sludge and borosilicate glass as shown in Table 5. The G3 glass prepared with a mixture of borosilicate glass contained small bubbles and was a transparent green colour compared with G4, which had a cloudier green colour. These are due to the small amount of ZnO, which exhibits a fluxing effect when temperature is higher than 1,000 °C and increase the brightness of the glass surface (Karaahmet & Cicek 2019). Besides, the glasses had a smooth and shiny surface that influenced by the content of Ba in the sample, which is a very active alkaline element and facilitates the formation of glossy surface in the glass (Karaahmet & Cicek 2019). These observations indicate that the glass waste form melted at 1,200 °C was completely dissolved during the melting process. However, at high waste loading (30 wt%), undissolved particles are visible in G5. Based on the previous study, the increasing waste loading can affect the integrity of glass waste due to the presence of crystals (Fadzil et al. 2015). Even though, the crystalline phase also has positive effect as a shield to prevent the leaking of radioactive elements from the glass waste form (Ruzali et al. 2021) and can incorporate a large amount of waste elements (Ojovan et al. 2021).

So, 1,200 °C is the best temperature for melting process due to the homogeneity of glass waste form (G4

and G5) compared to 1,100 °C. This is also influenced by the suitable composition of host and waste to form the glass waste. Pei et al. (2020) found that the municipal solid waste through vitrification was greatly reduced the volume and weight, low leachability, and destructed organic composition due to the high temperature. The

optimum waste loading of 25 wt% melted at 1,200 °C in this study is the best candidate compared to other compositions. In addition, Stoyanova et al. (2019) found that the flexural strength of vitrified waste increased with temperature, achieving the maximum of 95 MPa.

TABLE 5. Physical observation with different composition of waste loading

Temperature, °C	
1,100	1,200
G1	G3
	
G2	G4
	
-	G5
-	



## EVALUATION TEST OF GLASS WASTE FORM

The different behaviours of waste forms with various oil sludge concentrations are attributed to specific glass/sludge structures during melting. The added of  $\text{TiO}_2$  with JPDF no. (00-021-1272) functioned as an internal standard that formed in XRD analysis (Fadzil et al. 2015). All the glass wastes prepared were mostly amorphous, but they contained small amounts of the crystalline phase as shown in Figure 2. Glass G1, which was prepared with a waste loading of 20 wt% at 1,100 °C, caused the nucleation of cristobalite ( $\text{SiO}_2$ ) phase (JPDF no. 01-082-0512) and berlinite ( $\text{Al-PO}_4$ ) phase (JPDF no. 01-073-26659) had been detected by XRD measurement. Berlinite is formed by a covalent network of oxygen-bridged alternating  $\text{H}_3\text{-PO}_4$  and Al that shares many chemical and physical properties of the dissolved Si in the sample (Bednarek et al. 2016). The intensity of the cristobalite and berlinite peaks are increased because of the rise in waste loading as showed in the prepared glass G2 prepared.

Increasing the melting temperature to 1,200 °C led to improve the crystallinity in the glass waste formed. The main crystal phases of quartz (JPDF no. 01-085-0930) and barium dialuminum oxide ( $\text{Ba}_4\text{-Al}_2\text{-O}_7$ ) (JPDF no. 01-073-2720) had formed in samples G3 and G4. Alumina ( $\text{Al}_2\text{-O}_3$ ) (JPDF no. 01-076-7774) was also formed and typically contained traces of Fe, Ti, V, and Cr in samples G3 and G4 because of the high content of Al in the oil sludge. Besides that, iron zinc ( $\text{Fe}_3\text{-Zn}_{10}$ ) appeared slowly in the G4 sample. However, G5 indicates that only an early stage of quartz crystallization was formed because the sample was incompletely homogenous between oil sludge and borosilicate glass. This might be attributed to a high concentration of oil sludge, as illustrated in Figure 2.

The image obtained from an optical microscope is shown in Figure 3. It shows the presence of tiny crystals (could incorporate a large amount of waste elements) (Ojovan et al. 2021) and bubbles in the glass waste. The morphology of the crystals is not clear because of their very low concentration and tiny size. This result also could be supported FESEM images through mapping and EDX analysis, and XRD pattern in Figure 2.

G3 of the glass waste form was selected for the FESEM-EDX analysis due to the homogeneity and completely melted at 1,200 °C. So, Figure 4 presents the FESEM micrograph and EDX spectra of G3, which has been magnified by 10,000x. The surface morphology analysis showed that glass waste formed had needle like shaped with a length of less than 2  $\mu\text{m}$ . However, these

needles could not be detected through XRD analysis due to the tiny size and not evenly distributed in the glass waste form.

The glass waste form also contained other elements and dispersed uniformly through EDX mapping with a magnification of 20,000x, as shown in Figure 5. While Table 6 showed that it had a high percentage of O (37.6 wt%), followed by Si (30.8 wt%), Ca (8.8 wt%), B (8.4 wt%), and Na (5.6 wt%), which are dominant elements found in the glass waste form. Other elements also detected with a small percentage (< 5 wt%) such as Pb, K, Al, Mg, Th, Co, U and Cs, with quite high deviation for several elements. Qualitatively, these results indicate that none of the detected phases enriched with a particular element.

Deionized water was used as a leaching solution in a PCT test. The pH of the solution before the leaching test was 7, then increased in range of 9.06 and 9.26 as shown in Table 7. This may be due to the glass composition, which contained alkali elements (such as Ca, Si, and Na); ions were released from the glass and underwent an ion exchange and inter-diffusion process with hydrogen in the deionized water (Lonergan & Neeway 2017). In a neutral solution, water reacts with alkaline ions at the non-bridging oxygen site to form hydroxyl bonds and releases alkaline ions into the solution resulting in an increase in the solution's pH (Lonergan & Neeway 2017).

When glass corrosion occurs in the form of glass waste, more alkali ions are released, which raises the pH of the solution. However, increase in pH is counteracted by the release of a weak acid (silicic acid). Previous study found that the elevated participation of the ion exchange process can lead to a release of elements; this is responsible for increasing the pH value of the leachates, particularly with a high surface-to-volume (S/V) ratio in the solution (Jain 2019).

Normalized release elements for B, Si and Na element were also summarized in Table 7. The normalized release elements (G1 & G2 at 1,100 °C) and (G5 at 1,200 °C) were high compared with the normalized releases from the glasses made (G3 & G4) at 1,200 °C. These can be influenced by factors such as homogeneity, different composition of glass and environmental tests (temperature, the change of pH solution) (Fadzil et al. 2015; Frankel et al. 2018; Rani et al. 2010). While the normalized released of homogeneous glass waste (G3 & G4) are lower and the formation of crystallinity does not threaten the integrity of the glass but increased the chemical durability of the glass waste. If normalized release ion of alkaline is higher in

the solution, so the ability of glass waste as a medium of radioactive waste storage is decreased. Kim et al. (2020) also showed that the different glass composition with low level radioactive solid waste can strongly affect the leaching behaviours and surface morphology of the glasses, which had high chemical stability through vitrification process.

The rate of normalized release elements in this study is slower compared with that of Farid et al. (2019)

because of the mass transport of  $H_2O$  or  $H_3O^+$  to the alkali sites and the removal of the alkali from the glass into the contact solution (Karaahmet & Cicek 2019). Compared to previous study using CRT glass as a host (Ruzali et al. 2021), similar waste loading of oil sludge was found to be optimum compositions at 1,200 °C while having lower normalized release of glass elements. Based on previous study, Fadzil et al. (2015) also recorded that the normalized release of B and Na from standard

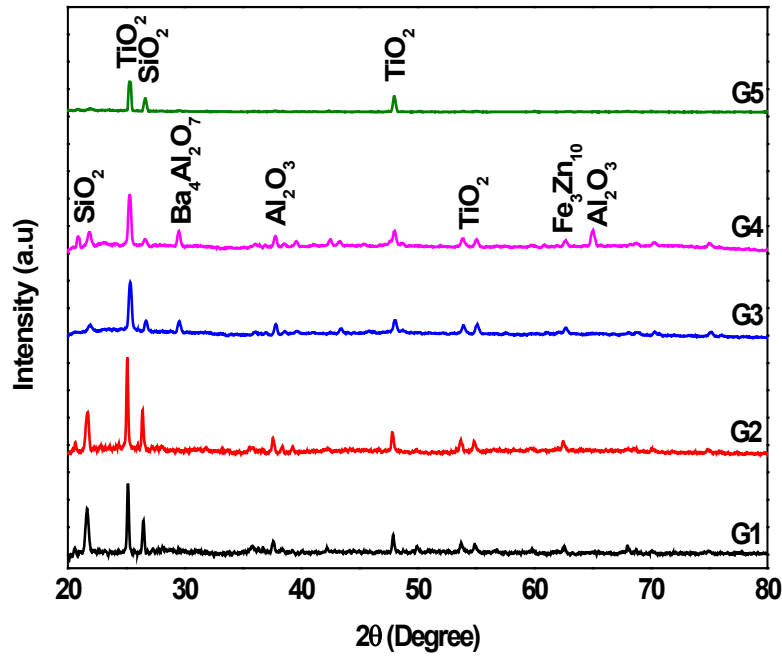


FIGURE 2. Crystalline phase formation presents in borosilicate glass at 1,100 °C and 1,200 °C

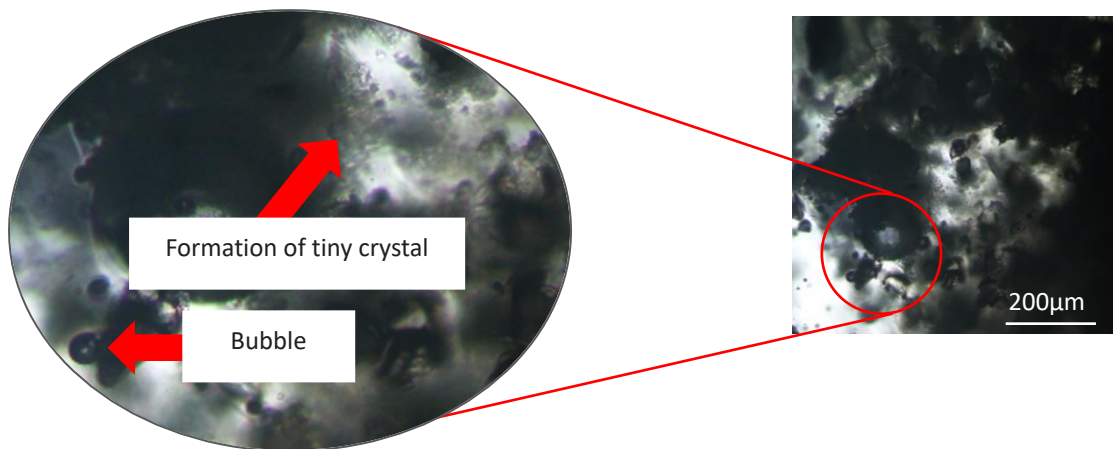


FIGURE 3. Image of bubbles and crystalline formation by an optical microscope

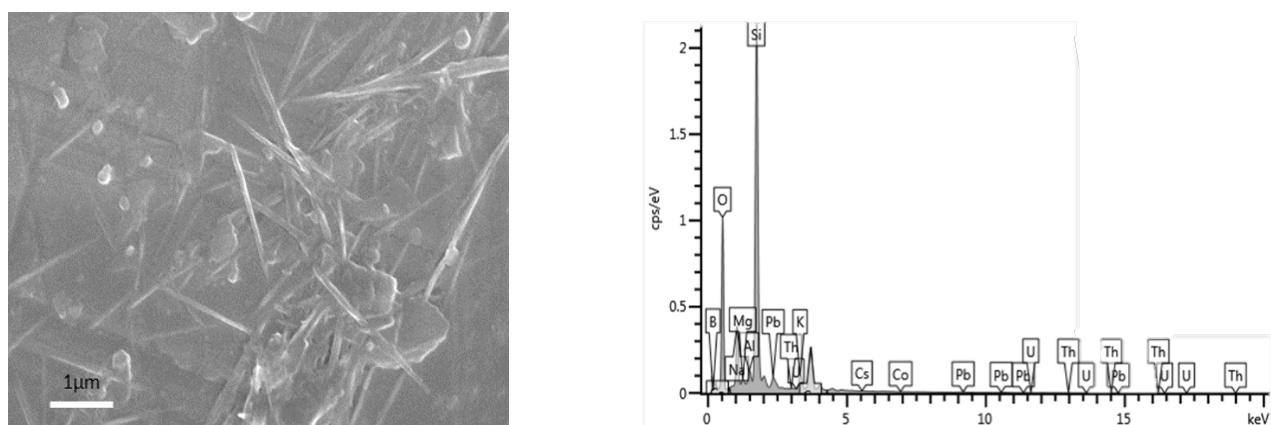


FIGURE 4. FESEM of glass waste form at high magnification and EDX spectra

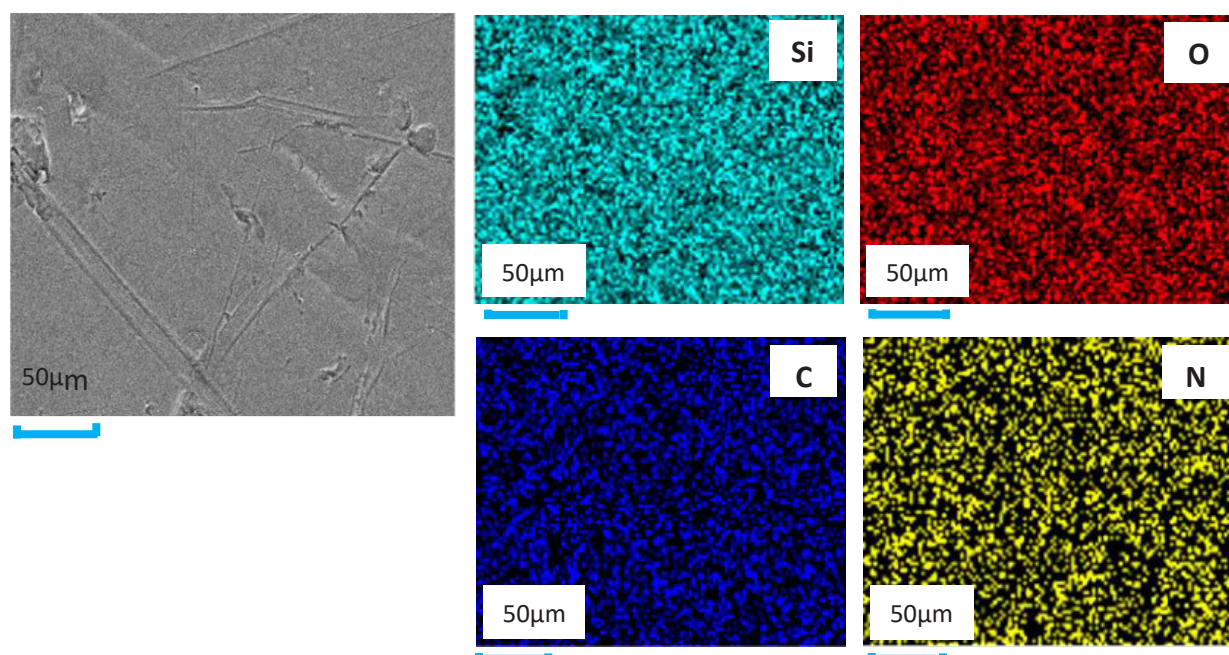


FIGURE 5. EDX mapping of glass waste form

environmental-assessment (EA) glass were 5.36-8.35 and 4.28-7.61  $\text{g}/\text{m}^2$ , respectively. The rate of these element releases is still below the EA standard glass limit and US criteria which are 6.68 and  $< 2 \text{ g}/\text{m}^2\cdot\text{d}$  (Kim et al. 2018; USEPA 2017; Vienna & Spearing 2003). So, the normalized release of U and Th are too small ( $< 0.0001 \text{ g}/$

$\text{m}^2$ ) and confirm that the glass waste forms in this research are suitable candidates for low-level waste of vitrification process, acceptable from an environmental perspective and can be used as an alternative to solve the problem of sludge waste in Malaysia.

TABLE 6. Distribution of element from EDX spectrum

Element	wt%
O	37.6 ± 1.6
Si	30.8 ± 1.3
Ca	8.8 ± 0.4
B	8.4 ± 3.7
Na	5.6 ± 0.3
Pb	3.8 ± 0.5
K	2.6 ± 0.2
Al	1.0 ± 0.1
Mg	0.5 ± 0.1
Th	0.3 ± 0.4
Co	0.1 ± 0.2
U	0.1 ± 0.4

TABLE 7. Normalized release and pH of glass elements (g/m<sup>2</sup>.d) during PCT

Sample	pH value	B	Na	Si
G1	9.20 ± 0.02	0.1949 ± 0.0008	0.2357 ± 0.0005	0.3066 ± 0.0002
G2	9.28 ± 0.01	0.1972 ± 0.0004	0.2415 ± 0.0001	0.3195 ± 0.0003
G3	9.16 ± 0.01	0.0044 ± 0.0005	0.0423 ± 0.0004	0.0023 ± 0.0002
G4	9.18 ± 0.02	0.0082 ± 0.0005	0.0485 ± 0.0001	0.0224 ± 0.0002
G5	9.23 ± 0.01	0.0116 ± 0.0004	0.0546 ± 0.0003	0.0457 ± 0.0002

#### CONCLUSION

This study found that vitrification technique using recycle borosilicate glass is suitable for immobilizing the sludge that contained NORM and harmful elements. Thus, the optimal waste loading of oil sludge is 25 wt% at 1200 °C with mostly amorphous phase but contain small amount of crystalline phase (such as SiO<sub>2</sub>, Ba<sub>4</sub>-Al<sub>2</sub>-O<sub>7</sub>, AlPO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>Zn<sub>10</sub>) and elements (Si, O,

Na and Ca) are evenly distributed through EDX analysis. The normalized release of glass elements was also lower than the standard limit and suitable to use as a host for waste immobilization prior for disposal due to high chemical durability of the glass waste form.

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