Evaluation of glass waste formed containing NORM

Nur Syuhada Izzati Ruzali¹, Syazwani Mohd Fadzil¹,a), Rohyiza Baan²

¹Nuclear Science Programme, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi Selangor, Malaysia.
²Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia.

a) syazwanimf@ukm.edu.my

Abstract. In oil and gas production, crude oil is an important ingredient in the manufacture industry. The sludge from the oil is semi-solid waste and classified as a low-level waste that consists of a mixture of oil, sediment and, water containing radioactive element (Naturally Occurring Radioactive Materials (NORM)); and high hydrocarbon concentration. It is categorized and considered as hazardous waste that required careful handling and treatment before disposal. Vitrification process was carried out in this study to immobilize the sludge containing radioactive waste. The objectives in this study is to optimize waste loading and to evaluate the glass waste formed after vitrification process. It is found that 20 wt% of oil sludge at 1200°C is the best optimize waste loading in the experiment because the glass waste formed are completely homogeneous phase.

1. Introduction

Naturally Occurring Radioactive Materials (NORM) can be found as abundant element in the earth. Uranium, thorium and potassium are radioactive elements that have long-lived and produced decay products such as radium and radon [5]. Normally, NORM can also found in a few industries including oil and gas and called as technologically enhanced naturally occurring radioactive material (TENORM) because it is produced by the human activities in the environment [5].

In oil and gas production, crude oil is an important ingredient in the manufacture industry. It is extracted from the bottom of the sea and transferred to the processing plant. It is refined and separated by boiling point to produce a large number of consumer products such as petrol and kerosene into asphalt and chemical reagents that used to make plastics and pharmaceuticals. This industry produces a variety of materials and consumed about 88 million barrels each day to the world [1]. However, it had serious concerns about the production of large amounts of oil sludge as a consequences of crude oil exploration, production and processing activities [2].

The sludge is semi-solid waste and classified as a low-level waste that consists of a mixture of oil, sediment and, water containing radioactive element; and high hydrocarbon concentration [3]. It is categorized and considered as hazardous waste that required careful handling and treatment before disposal because it can cause the most serious environmental problem and harmful to human health [1]. Due to high demand in the production of oil around the world, the annual output of sludge is estimated at around 1 billion tons per year [6]. Management and disposal of this hazardous waste remain challenging problem worldwide even as variety of treatments had been developed. Therefore, vitrification process was carried out in this study to immobilize the sludge containing radioactive waste. Vitrification is one of the processes that turns radioactive into the solid waste form which remain stable for many thousand years [4]. Besides
that, it also can reduce the volume of hazardous materials such as NORM. Thus, the objectives in this study are to optimize waste loading and to evaluate the glass waste formed after vitrification process.

2. Materials and methods
Oil sludge and glass pieces (host) were supplied from Malaysia Nuclear Agency (MNA). The sludge was thick, semi-solid form, dark brown lumps and in the wet condition. So, the sludge must first be dried in a conventional oven at 80°C for a few days. The aim of this drying process is to reduce the moisture content of waste until it less than 10 mf wt% (refers to the moisture free weight percentage). After that, the oil sludge and the glass host were homogenized by crushing to fine powders using mortar and pestle, then sieved through a 500 µm sieve. Then, the various composition of oil sludge and glass host were created and sealed in the container or plastic before vitrification process.

Table 1 shows the various composition contains 20-30 wt% of oil sludge and 70-80 wt% of glass host that were mixed together in the 50 ml alumina crucible and melted at 1100 °C -1200°C for an hour. Then, the glass waste form after vitrification process were observed and evaluated.

| Composition, wt% / Temperature, °C | 1100 | 1200 |
|-----------------------------------|------|------|
| 20 S + 80 H                      | S1   | S2   |
| 25 S + 75 H                      | S3   | S4   |
| 30 S + 70 H                      |      | S5   |

The glass waste form was evaluated using a few analysis such as observation through optical microscope, XRD and Field Emission Scanning Electron Microscopy (FESEM) (model Merlin, Zeiss). The optical microscope is used to investigate the formation of crystal, while XRD is used to identify the crystal phase, if formed. The FESEM is used to observe the morphology surface of sample and homogeneity. All instruments were analyzed at Centre for Research and Instrumentation Management (CRIM).

3. Result and discussion
3.1. Observation after melting process
Figure 1 showed the observation of various composition of samples after thermal process with different temperature. Fig. 1 (a) and (b) showed the samples of S1 and S2 that contained 20wt% and 25wt% of sludge and 75wt% and 80wt% of host respectively at 1100°C. Both samples were milky in white color and had rough and bumpy surfaces. The host was also not incompletely dissolved during the thermal process and had black spot obviously in the samples. This shows that oil sludge is not incompletely mixed with the host at this temperature.
Figure 1. Observation of sample after melting process.

Figure 1(c) and (d) showed the sample S3 and S4 that were melted at 1200°C with 20 and 25 wt% of oil sludge mixed with 75 and 80 wt% of host respectively. Fig. 1(c) had bubbled and transparent green color compared to Fig. 1(d) which is more cloudy and in green color. Both samples had smooth and shiny surface than the previous samples. This indicates that oil sludge and host were completely dissolved during the melting process in Fig. 1(c), but somehow contained undissolved particle at higher sludge content (Fig. 1(d)). The observation in Fig. 1 indicated that the glass waste formed that contained 20wt% of oil sludge at 1200°C was the best optimize waste loading in this study because the glass waste formed were homogenous phase. According to Singh and Chaturvedi study [7], the vitrification process of 15% waste, 35% Na2CO3 and clay started at 850°C and increased the temperature when increased the waste content.

3.2. Evaluation test

Figure 2 showed observation from optical microscope (OM). It revealed the presence of tiny crystals and bubbles in the sample. The morphology of the crystals is not clear due to very low concentration and small.
The different behavior of waste form with different concentration of oil sludge is attributed to specific glass/sludge interaction. At 1100°C, S1 presents with waste amount of 20wt%, as shown in Fig.3, indicates a high crystalline phase of cristobalite and berlinite at the early stage of crystallization. Berlinite is formed by covalent network of oxygen-bridged alternating phosphoric acid and alumina that shares many chemical and physical properties of silica dissolve in the sample. XRD spectrum for S2 in Fig. 3 shows the intensity of cristobalite and berlinite peaks are increase due to the increasing the concentration of waste.
Figure 4. Crystalline phase formation of glass waste formed at 1200°C.

XRD patterns in Fig. 4 that composed of 20wt%, 25wt% and 30wt% of oil sludge respectively at 1200°C. The main crystal phase in S3 and S4 are quartz (SiO$_2$) and tetrabarium dialuminum oxide (Ba$_4$Al$_2$O$_7$). Formation of corundum (Al$_2$O$_3$) typically containing traces of Fe, Ti, Vn and Cr in S3 and S4 due to the high content of Al in the oil sludge. Iron zinc (Fe$_3$Zn$_{10}$) is appears slowly in the S4. This can be attributed to the crystallization of the distinctive of iron and zinc-rich phase in the host and oil sludge. However, S5 indicates only early stage of crystallization of quartz is formed because the sample was incompletely homogenous between host and oil sludge and this might contributed by high concentration of oil sludge showed in Fig. 4. Cristobalite and quartz are present at all melting temperature, although the peaks intensity is lower with higher melting temperature due to its partial dissolution elements.

Figure 5. FESEM image of different composition at 1100°C (a) S1 (20 wt% sludge and 80 wt% host), (b) S2 (25wt% sludge and 75 wt% host).
Figure 5(a) and 5(b) showed FESEM image of different composition of waste which are magnified by 500x. S1 and S2 as shown in Fig. 5(a) and Fig. 5(b) respectively, indicates it had air bubbles and some corrosion formed in the sample might due to sample polishing before analysis. EDX analysis in Table 2 showed both sample had consistent homogeneous distribution throughout the sample. The crystal phases that were detected through the XRD and OM might be too small to be seen by FESEM.

| Element | Weight Percentage, wt% | σ |
|---------|------------------------|---|
| O       | 43.7                   | 0.6 |
| Si      | 38.0                   | 0.5 |
| Na      | 7.3                    | 0.2 |
| Ca      | 6.4                    | 0.3 |
| Al      | 1.9                    | 0.2 |
| P       | 1.7                    | 0.2 |
| K       | 0.6                    | 0.1 |
| U       | 0.4                    | 0.5 |
| Cs      | 0.1                    | 0.4 |

4. Conclusion
As a conclusion, 20 wt% of oil sludge at 1200°C is the best optimize waste loading in the experiment because the glass waste formed are completely homogeneous phase. SiO₂, Ba₄Al₂O₇ and a small formation of Al₂O₃ are the main crystalline phase that occurred in the both sample as shown in XRD analysis. The elements are distributed uniformly through EDX analysis and indicates these sample are almost amorphous because the size of crystal that can be seen in the FESEM are too tiny.

5. References
[1] Badrul I 2015 Petroleum sludge, its treatment and disposal: a review Int. J. of Chem. and Sci. 13(4): p 1584-1602.
[2] Bipin K, Raj M B 2013 Petroleum oily sludge and the prospects of microwave for its remediation. Int. J. of Eng. Res. and Tech. 2(11) p 359 – 370.
[3] Gopang I A, Mahar A S, Akhtar K S, Omer M, Azeem M S 2016 Characterization of the sludge deposits in crude oil storage tanks J. of Fac. of Eng.and Tech. 23(1) p 57-64.
[4] Harrison M T 2014 Vitrification of high level waste in the UK Procedia Mater. Sci. 7 p 10-15.
[5] Maria H P G, Andressa A D A, Yana B B, Clovis A H, Jose M D O G 2005 Radioactivity concentration in liquid and solid phases of scale and sludge generated in the petroleum industry J.of Env. Radioact. 81 p 47-54.
[6] Pazoki M, Hasandinarabadi B 2017 Management of toxic and hazardous contents of oil sludge in Siri Island Glob. J. of Env., Sci, and Manag., 3(1) p 33-42.
[7] Singh I B, Chatruvedi K 2015 Immobilization of toxic metals of industrial waste via low temperature vitrification Indian J. of Chem. Tech. 22 p 162-166.