



THE IMMOBILIZATION OF URANIUM RADIOACTIVE WASTE USING MATRIX MATERIAL OF SUPERCALCINE SILICO AND ZIRCONIO TITANATE SYNROCS

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ABSTRACT

The Uranium Concentrate Production Installation (UCPI) operation generates sludge radioactive waste containing uranium that must be immobilized by solidification process for preparation of disposal to ensure the environment safety in the present and future. This research aims to immobilize the radioactive sludge waste by solidification using coal fly-ash (CFA) as matrix material of supercalcine silico-titanate synroc compared to supercalcine zirconio-titanate synroc (standard synroc). The immobilization process was carried-out by mixing the radioactive sludge waste with CFA and precursor oxides namely BaO, CaO, and TiO₂ as addition of matrix materials. The matrix material composition of synroc using CFA (in weight %) i.e : Al₂O₃ (6.26); BaO (5.33); CaO (10.52); TiO₂ (68.02) ; and SiO₂ (6.07). The matrix material also contains oxides minor i.e : Fe₂O₃ (3.48), MnO₂ (0.04), K₂O (0.20) and Na₂O (0.08). Waste loading in the waste synroc block was 30 weight %. The mixture was dried at temperature of 100 °C, and calcined at 750 °C. The calcination powder resulted was pressed in the mold. Furthermore, the sintering process was carried-out at the temperature of 900 – 1300 °C for 1-4 hours to form the synroc block of solid multiphases ceramics. A comparison of immobilization process was done using matrix material of supercalcine zirconio-titanate synroc. The synroc block quality produced from immobilization was determined by testing density, compressive strength, and leach-rate of uranium. The test results showed that the best quality of waste supercalcine silico-titanate synroc block was obtained at the sintering temperature of 1100 °C for 3.5 hours with density 2.29 g/cm³, compressive strength 5.76 kN/cm², and leach-rate of uranium 1.05x10⁻⁶ g.cm⁻².day⁻¹. Whereas the immobilization process using the standard synroc obtained the optimum sintering condition at 1200 °C for 3 hours, with density 2.85 g/cm³, compressive strength 10.98 kN/cm², and leach-rate of uranium 1.17x10⁻⁵ g.cm⁻².day⁻¹. The quality of both synrocs by this sintering process conform with the quality of synroc block by the hot isostatic pressing process, and fulfill the quality recommended by the IAEA. By comparing the characteristic test results and economic aspects of both waste synroc blocks, the supercalcine silico-titanate synroc matrix using CFA can be utilized as alternative to replace the matrix material of standard synroc for immobilizing sludge radioactive waste containing uranium.

Keywords: immobilization of waste, uranium waste, long life alpha radioactive waste, synroc.

INTRODUCTION

Development and operation of Nuclear Power Plant (NPP) program in Indonesia requires the supporting of nuclear fuel supply and also treatment technologies of radioactive waste generated from the preparation and supply of nuclear fuel as well as from the operation of NPPs. The program must be prepared for independence and continuity of NPP operation in the future. The preparation to supply the nuclear fuel can be done through the mining of uranium ore then conducted a nuclear fuel fabrication through the stages of the process as follows: the processing of uranium ore, refining (purification), conversion, enrichment, reconversion, and fabrication [1]. The processing of uranium ore is the concentrating process of uranium from its ore (uranium content in the ore 0.1-0.5 %) to obtain uranium concentrate (yellow-cake) with a high uranium content (> 70 wt%). Followed the purification of uranium concentrate to obtain the high pure quality of uranium (nuclear grade uranium) in the form of uranium trioxide (UO₃). The conversion process is a process to convert UO₃ to UF₆ (gas) as a feed for the enrichment process, which is a process to increase content levels of ²³⁵U in uranium fuel. The enrichment processes

that have been established are gas diffusion and gas centrifugation processes. In the reactor using natural uranium fuel, the enrich process is not required. Reconversion process is the conversion process again the UF₆ (enriched) to UO₂ powder (enriched). The fabrication process is the manufacture process of fuel elements and nuclear fuel assemblies, started with the production of UO₂ ceramics pellets, the UO₂ pellets is then filled in the cladding (made from zircalloy or stainless steel), and then it is assembled into bundles of nuclear fuel which ready to be used as fuel in the nuclear reactor (NPP).

In Indonesia, the research and development (R & D) in uranium ore processing has been carried-out to obtain uranium concentrate (yellow cake) by researchers from the Mineral Nuclear Research Center -BATAN [2,3]. Then the R&D of purification process of yellow-cake have been carried-out by researchers at Yogyakarta Nuclear Research Center-BATAN and it have been successfully obtained the uranium dioxide powder (UO₂) with nuclear pure quality for nuclear fuel type of Heavy Water Reactor that uses uranium-natural fuel [4,5]. The preparation of nuclear fuel can be also carried-out by purification of phosphoric acid (produced from phosphate ore containing



uranium) as that was carried-out at the Uranium Concentrate Production Installation (UCPI). The facility of UCPI is an additional unit of phosphoric acid production using raw material of phosphate rock containing uranium. The UCPI has produced 8.810 tons of uranium concentrate (yellow-cake) with content 70 % U_3O_8 as a product that can be used to manufacture of nuclear fuel for NPPs through several stages of the processes as described above. The operation of UCPI generated the sludge radioactive waste containing uranium. The sludge radioactive waste has alpha activity 0.4 – 40.2 kBq/litre, beta activity 1173 – 4100 Bq/litre, and solid content total 40-50 wt% [6]. The sludge radioactive waste is included in the classification of long life alpha-low level radioactive waste containing natural uranium (99.274 atom% of $U-238$ isotope having half life 4.5×10^9 years) with the daughters of $U-238$ decaying i.e. : $Th-234$, $Po-234$, $U-234$, $Th-230$, $Ra-226$, $Rn-222$, $Po-218$, $Pb-214$, $Bi-214$, $Po-214$, and $Pb-206$ (stable) [7]. The sludge radioactive waste must be isolated to protect the radiation impact which danger to the peoples and environment. The sludge radioactive waste has to be immobilized through solidification process to become waste-form (waste block) which ready to be stored for long-term (many million of years) in the disposal facility (Deep Geological Disposal Facility).

Isolation of radioactive waste is done by immobilization of the radioactive waste through the solidification process using a matrix material, so that it is obtained waste form (radioactive waste block) which the radioactive elements are confined and isolated in the waste block. The matrix materials commonly used in radioactive waste immobilization process for long life alpha emitter-low and intermediate level radioactive wastes are asphalt (bitumen) and plastic polymers [8].

Current development of the immobilization was used synthetic rock of titanate (titanate synroc) as matrix material. The titanate synroc is a crystalline waste-form comprising a stable assemblage of titanate phases chosen for their geochemical stability and collective ability to immobilize all the radioactive elements present in high level radioactive wastes (HLW). The titanate synroc is very good for confine and isolate the radionuclide of fission products and actinide elements [9]. The immobilization technology using titanate synroc has been developed in Australia, United Kingdom, United State of America, and Japan [10]. The formation technique of titanate synroc have been developed by using the hot isostatic pressing (HIP) at high temperature. Based on the assessment results and consideration that the HIP equipment is not available, therefore in this research was carried out the formation technique of titanate synroc by sintering process at high temperature (900-1300 °C).

This research aims to obtain the process technology for immobilizing sludge radioactive waste containing uranium generated from operation of the UCPI by utilizing coal fly ash (CFA) to form the matrix material of supercaline silico-titanate synroc. The immobilization of radioactive waste using the high temperature sintering process was developed for replace the HIP process. The

immobilization by using matrix material of supercaline silico-titanate synroc is a development of matrix material that is relatively cheaper than the supercaline zirconio-titanate synroc (standard synroc for immobilization of radioactive waste). The quality of waste synroc block produced from immobilization process were determined by characteristic test of synroc block with parameters are : density, compressive strength, and leach-rate of uranium (leach-rate accelerated in pure water medium at temperature of 100 °C). This research is generally also aimed to obtain the immobilization process technology for radioactive waste containing uranium generated from the operation of nuclear fuel fabrication to support the nuclear fuel supply for nuclear research reactor and NPP operation program in Indonesia in the future.

METHODOLOGY

The materials and equipments

The materials utilized in this experiment were : synroc precursor oxides consisting of Al_2O_3 , BaO , CaO , ZrO_2 , TiO_2 , and coal fly ash (CFA), and the supporting chemical materials i.e. : uranyl nitrate hexahydrate (UNH), HNO_3 , $NaOH$, Na_2CO_3 , H_2O_2 , Arsenazo-III (all chemicals made from E.Merck with pro-quality analysis), demineralized water (pure water), and sludge radioactive waste containing uranium generated from operation of The Uranium Concentrate Production Installation (UCPI). The composition of CFA is shown in Table-1. Comparison of the composition precursor oxides in matrix material for standard synroc block and synroc block using CFA is shown in Table-2.

Tabel-1. Composition of coal fly ash (CFA) [11].

Content of Oxides	Concentration of oxides in CFA (wt%)
SiO_2	35.44
Al_2O_3	36.54
CaO	5.26
BaO	-
TiO_2	0.66
Fe_2O_3	20.32
MnO_2	0.20
K_2O	1.15
Na_2O	0.43

The equipments utilized in this experiment were : mold for waste block made from stainless steel, rolling equipment Gardco LabMill 8000, hot plate, oven Labtech LDO-080F Iwaki, furnace Vulcan A-550 1500 °C, test equipment for compressive strength (Carver Hydraulic Unit model 3012), equipment for test of leach-rate (Soxhlet), UV-VIS Spectrophotometer Lambda 35 Perkin Elmer, electric balance (digital), equipment for length measurement (Krisbow Digital), and laboratorium glassware equipments.



Table-2. Comparison of the composition of precursor oxides in matrix material for standard synroc block and synroc block using coal fly ash (CFA) [11,12].

Oxide	Composition of oxides	
	In matrix of standard synroc (supercalcine zirconio-titanate synroc) (wt%)	In matrix of synroc using CFA (supercalcine silico-titanate synroc) *) (wt%)
SiO ₂	-	6.07
Al ₂ O ₃	5.4	6.26
CaO	11.0	10.52
BaO	5.6	5.33
TiO ₂	71.4	68.02
ZrO ₂	6.6	-
Fe ₂ O ₃	-	3.48
MnO ₂	-	0.04
K ₂ O	-	0.20
Na ₂ O	-	0.08
Total	100.00	100.00
*) Composition (in wt %) : CFA (18) ; CaO (10.1); BaO (5.6); and TiO ₂ (71.3).		

Procedure of research

Analysis of uranium content in the sludge waste

A number of 200 ml of sludge radioactive waste containing uranium (generated from operation of The UCPI) was dried to obtain the sample of solid waste powder. The uranium content in sample was analyzed by the UV-VIS Spectrophotometry method. The analysis resulting uranium content in sludge radioactive waste was 25,977 ppm (equivalent to 2.85×10^5 Bq / liter or equal to 7.71×10^{-3} Ci / m³ thus included in the low level radioactive waste), while the results of the analysis of the content of uranium in powder resulted from drying of waste sludge was $59,080 \pm 209$ ppm.

Immobilization of uranium radioactive waste using coal fly ash (CFA) as matrix material of synroc

Preparation of the waste synroc block using CFA as matrix material of synroc (Table 2) with waste loading 30 wt%, was performed by mixing of 3.5 g the synroc matrix material with 1.5 g sludge waste containing uranium and stirred (using the rolling equipment) up to become the homogeneous slurry. The mixture (slurry) was dried at 100 oC and calcined at 750 °C in the furnace for 30 minutes. The powder of calcination result was pressed in the mold of waste block, and then the waste block resulted was conducted the sintering process at temperature of 900-1300 °C for 3 hours to form the solid multiphase of synroc monolite ceramics (waste synroc block). The experiment was repeated with varying the sintering time for 1- 4 hours (at the optimum sintering temperature).

Immobilization of uranium radioactive waste using matrix materials of the standard synroc

The same experiment (as mentioned on point 2) was conducted by using matrix materials of the standard

synroc (supercalcine zirconio-titanate synroc) with the composition of precursors oxides in matrix material for synroc standard as shown in Table-2.

The characteristic test for waste synroc block

The characteristic test for the waste synroc blocks (resulted from immobilization of waste using synroc matrix by sintering process as mentioned above) were carried-out with three parameters i.e.: density, compressive strength, and leach-rate of uranium. Test for density of waste synroc blocks were carried-out by measurement the weight and volume of the waste synroc blocks, then the density of waste synroc blocks can be calculated. Test for compressive strength of the waste synroc blocks were carried-out by using the compressive strength test equipment (Carver Hydraulic Unit model 3012). Test for leach-rate of uranium were carried-out according to the Japan Industrial Standard (JIS) method, namely the accelerated leach-rate method in medium of pure water (100 °C, for 12 hours) [13]. The JIS method is same as the method developed by the International Atomic Energy Agency (IAEA) [14]. Test for leach-rate of uranium was carried-out as follows : (a) the waste synroc blocks (5 g) was refluxed using Soxhlet equipment filled 500 ml of demineralized water (pure water) at temperature of 100 °C for 12 hours. (b) a number of 500 ml of leaching-water (containing of uranium) was concentrated by evaporation process until the volume of 10 ml (as sample of leaching-water for analysis of uranium). (c) the concentration of uranium leached in sample of leaching-water was analyzed by UV-VIS Spectrophotometry method (using Arsenazo-III reagent at pH 2.5) with detection limit is 0.057 µg/ml/1% absorbance). Further the leach-rate of uranium in water from the waste synroc blocks was calculated by equation : $L = (W_0 - W_t) / (A \cdot t)$. Where L = the leach-rate of uranium (g.cm⁻².day⁻¹), W₀ = the initial weight of uranium in the synroc block sample before leaching process (g), W_t = the weight of uranium in the synroc block sample after leaching process for t days (g), A = the surface area of the synroc block sample (cm²), and t = leaching time (day) [13,14].

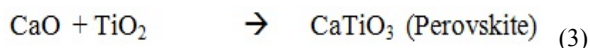
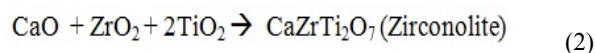
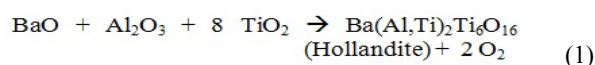
RESULTS AND DISCUSSION

Development of standard synroc

The first development of synroc matrix material was suggested as an alternative to replace the borosilicate glass for immobilization of high level radioactive liquid waste (HLLW), with the basic idea of incorporating the fission product elements of waste and associated actinides contained in the radioactive waste into the crystalline lattices of synthetic mineral, which were known to be very long life (many million of years) in nature. In 1978, Ringwood found synroc which is an assemblages of titanate minerals are much more water-resistant than the supercalcine suite of minerals [10]. The synroc production method is basically to first mix the liquid radioactive waste in nitric acid solution with the precursor oxides to make the synroc minerals. The standard matrix material of



titanate synroc precursor (supercalcine zirconio-titanate synroc) has the following composition (wt% oxides) : Al_2O_3 (5.4); BaO (5.6); CaO (11.0); TiO_2 (71.4); and ZrO_2 (6.6). The mixture is dried (at 100 °C), calcined (at 750 °C), and hot pressed under reducing condition at about 1200 °C and the pressure of 500-1000 bar to form a dense multiphase of synroc ceramics [12]. The major phases of minerals in titanate synroc are : hollandite $[\text{Ba}(\text{Al,Ti})_2\text{Ti}_6\text{O}_{16}]$, zirconolite $(\text{CaZrTi}_2\text{O}_7)$, and perovskite (CaTiO_3) , beside that are titan-oxides and alloy phases in small amount as minor phases. The formation of major phases in titanate synroc minerals occur at high temperature about 1200 °C by equations of reaction as follows:



According to the first goal of the synroc development, therefore it was developed the Synroc-C namely the kind of synroc developed to immobilize for high level radioactive waste (HLW) generated from reprocessing of spent nuclear fuel. The composition and mineralogy of Synroc-C (standard synroc) containing 20 wt% HLW, and radionuclide elements incorporated in lattices of the various mineral-analogue phases present is shown in Table-3.

Table-3. The composition and mineralogy of Synroc-C (standard synroc) containing 20 wt% HLW [9].

Phase of minerals	weight %	Radionuclides in lattices of mineral phases
a.Major phases :		
-Hollandite, $\text{Ba}(\text{Al,Ti})_2\text{Ti}_6\text{O}_{16}$	30	- Cs and Rb.
-Zirconolite, $\text{CaZrTi}_2\text{O}_7$	30	- Rare Earth(RE), actinides (An).
-Perovskite, CaTiO_3	20	- Sr, RE, and actinides (An).
b.Minor phases :		
Titan Oxides	10	
Alloy phases	5	- Tc, Pd, Rh, Ru, etc.
The other oxides	5	

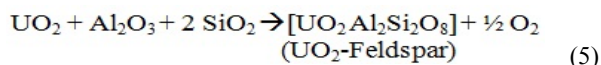
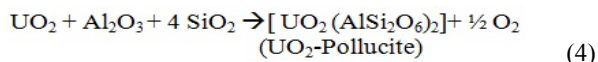
In the development of synroc for immobilization of radioactive waste containing uranium, plutonium, and the other actinides as well as the neutron absorbers (e.g. Hf and Gd), it are formed also some derivative phases from major phases reacted with the elements contained in the waste, i.e. : pyrochlore $(\text{CaATi}_2\text{O}_7, \text{A} = \text{Gd, Hf, Pu, and U})$ from derivative of zirconolite with additional of neutron absorber elements (Hf and Gd) for protect the criticality, brannerite $(\text{AnTi}_2\text{O}_6, \text{An} = \text{actinides})$, and freudenbergite $(\text{Na}_2\text{Fe}_2\text{Ti}_6\text{O}_{16})$ [9,12].

In ANSTO (Australia), the characteristic test results of waste titanate synroc block produced by hot-isostatic pressing (HIP) at 1200 oC was obtained the density of titanate synroc between 2.1-3.4 g/cm³. This density depend on kind of waste (content of radionuclides) and waste-loading [15]. The ability of titanate synroc to immobilize the heavy radioactive elements (e.g. uranium or actinides) is stronger than the light radioactive elements. Uranium contained in the waste synroc block is trapped into some phases such as zirconolite, perovskite, pyrochlore and brannerite. Therefore the titanate synroc waste-forms succeed particularly well in immobilizing the long life alpha-emitter of actinide elements [16].

The utilization of coal fly ash (CFA) as the matrix material of synroc

Based on the composition of CFA (Table 1), shows the presence of major oxides in the CFA namely SiO_2 , Al_2O_3 , and Fe_2O_3 . Beside that there are minor oxides i.e. : CaO , TiO_2 , MnO_2 , K_2O , and Na_2O . The content of elements or other oxides as an impurity in the order of ppm (parts per million) are : Ba, Cr, Hg, Ni, Sr, Cu, Pb, V and Zn (It is not included in Table-1).

In this research, the matrix of supercalcine silico-titanate synroc developed for immobilization of uranium sludge waste, does not use zirconium oxide (ZrO_2) as one component of precursor oxides and it is replaced by SiO_2 contained in the CFA as matrix material, so it is expected relatively cheaper than using the standard synroc matrix material. With additional the precursor oxides : BaO , CaO and TiO_2 into the matrix material of CFA, so the composition of the main precursor oxides to form supercalcine silico-titanate synroc are : Al_2O_3 , BaO , CaO , TiO_2 and SiO_2 . The main mineral phases are expected to occur at high temperatures of about 900-1300 oC with the above mentioned reactions (1), (2) and (3)[9]. The main mineral phases of zirconolite and perovskite reacted with the elements (U, Pu, the other actinides, and neutron absorbers e.g. Hf and Gd) contained in the waste to produce the derivative mineral phases, i.e. : AnTi_2O_6 ($\text{An} = \text{actinides}$), CaATi_2O_7 ($\text{A} = \text{Pu, U, Gd, Hf}$), and $\text{Na}_2\text{Fe}_2\text{Ti}_6\text{O}_{16}$. Beside that, it is also formed new mineral phases i.e.: the UO_2 -Pollucite, $[\text{UO}_2(\text{AlSi}_2\text{O}_6)_2]$ and UO_2 -Feldspar, $[\text{UO}_2\text{Al}_2\text{Si}_2\text{O}_8]$. These new mineral phases are produced from reaction of SiO_2 with UO_2 and Al_2O_3 as follow [9]:



Radionuclides in the waste will be trapped in lattices of mineral phases and even some radionuclides as a main constituent of derivative phases. The production technology of waste synroc block (waste synroc form) has been developed in Australia, the United States of America, United Kingdom, and Japan by the hot-isostatic pressing



(HIP). The HIP process requires hot-pressing equipment (at high temperature). One alternative of another process is through high temperature sintering process without hot-pressing, this process has been studied at the Lawrence Livermore National Laboratory [17]. In this research CFA as matrix material of supercaline silico titanate synroc was studied to immobilize the waste sludge containing uranium through a cold-pressing process, and then it is continued by sintering process at high temperatures (900-1300 °C). As the comparison is done also immobilization the uranium waste using standard synroc matrix.

Comparison of the composition between the both types of the precursor oxides as matrix material is shown in Table-2. Table-2 shows that the composition of the main precursor oxides (Al_2O_3 , BaO , CaO , and TiO_2) are relatively the same, except ZrO_2 in standard synroc was replaced by SiO_2 in the synroc using CFA, so this type of synroc using the CFA will be formed the supercaline silico-titanate synroc. The presence of SiO_2 in synroc using the CFA will be formed also derivative phases namely UO_2 -Pollucite: $[(\text{UO}_2)(\text{AlSi}_2\text{O}_6)_2]$ and UO_2 -Feldspar $[(\text{UO}_2)\text{Al}_2\text{Si}_2\text{O}_8]$ as shown in equation (4) and (6) [9]. The content of Na_2O and Fe_2O_3 in synroc using CFA will also possible to form freudenbergite phase ($\text{Na}_2\text{Fe}_2\text{Ti}_6\text{O}_{16}$). The content of K_2O and Na_2O can decrease the melting point and then it can decrease the sintering temperature [17].

Optimization of sintering temperature on immobilization of uranium radioactive waste using synroc matrix

The characteristic test results for density, compressive strength, and leach-rate of uranium to obtain the optimum temperature of sintering for the waste synroc blocks using the supercaline zirconio-titanate synroc (standard synroc) matrix and the supercaline silico-titanate synroc matrix (using CFA) are shown in Figure-1, Figure-2 and Figure-3. The condition of experiment is waste loading 30 wt%, sintering time 3 hours, and sintering temperature at 900-1300 °C.

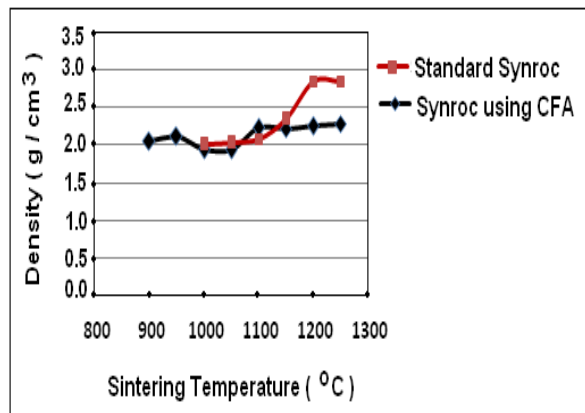


Figure-1. Effect of sintering temperature on the density for the both of waste synroc blocks (waste loading 30 wt% and sintering time 3 hours).

Figure-1 shows that the higher of the sintering temperature cause the higher the density values for the both types of waste synroc blocks. This case is caused the higher of temperature means the heat energy provided during the sintering process also increases. The energy provided at high temperature causes diffusion and formation of mineral phases of synroc, as well as the grains growth of mineral phases also faster and more perfect, so that the pores between grains decreases. After the sintering process of the block synroc waste occurs volume reduction due to formation the dense compact of multi-phases ceramics synroc so its density and compressive strength tends to increase. The experiment was stopped until the temperature of 1300 °C, because the temperature ≥ 1400 °C the synroc blocks melt and stick on the cup. Also according to Stewart (1994) [17] that the optimum condition of formation process for standard synroc can be reached at the temperature about 1200 °C. In Figure-1 it is shown also that the density of the waste standard synroc block relatively higher than the waste synroc block using CFA. The optimum conditions for the waste synroc block using CFA is reached at sintering temperature of 1100 °C with value of the density is 2.219 g/cm³. Whereas the optimum conditions for the waste standard synroc block is reached at sintering temperature 1200 °C with value of the density is 2.85 g/cm³.

Figure-2 shows also that the higher of the sintering temperature cause the higher compressive strength values for the both types of waste synroc blocks, and then reached to optimum value at 1200 °C for the waste standard synroc block, and at 1100 °C for the waste synroc block using CFA. This case shows the same phenomena with phenomena of increasing the density in Figure-1, that the higher of the sintering temperature cause the higher the density and also the compressive strength of the both waste synroc blocks. The optimum sintering temperature for the waste synroc block using CFA is lower than the optimum sintering temperature for the waste standard synroc block. This case is caused by the presence of K_2O and Na_2O contents that having the melting point lower than the main precursor oxides of synroc matrix, so that it can decrease the melting point of waste synroc block, while the sintering process was performed below the melting point of the waste synroc block. For the waste synroc block using CFA, decreasing of the compressive strength after sintering temperature higher than 1100 °C shows the presence some oxides especially the alkali metal oxides (K_2O and Na_2O) that are released and leave pores of the waste synroc block. The optimum conditions for the waste synroc block using CFA is reached at sintering temperature of 1100 °C with value of the compressive strength is 5.57 kN/cm². Whereas the optimum conditions for the waste standard synroc block is reached at sintering temperature 1200 °C with value of the compressive strength is 10.44 kN/cm².

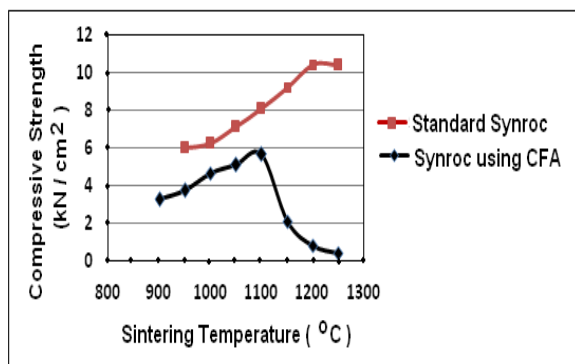


Figure-2. Effect of sintering temperature on compressive strength for the both of waste synroc blocks (waste loading 30 wt% and sintering time 3 hours)

Basic research result giving detail experiment data concerning the aqueous durability of synroc performance related to the leaching behavior of synroc in pure water at 95°C have been obtained [18,19]. The leach-rates of elements are not constant but fall rapidly in the first 10-30 days, after that they decrease asymptotically to the lowest value. The leach-rates of actinides from synroc are very low and decrease in the order of $U > Np > Pu > Am > Cm$. The leach-rates of actinides are typically 10-4 g/cm²day for the first few days, and they decrease asymptotically to values of $\sim 10^{-8}$ g/cm²day after 1000 days. It follows that synroc waste forms should succeed particularly well in immobilizing long-life alpha-emitter actinides elements [18, 19]. Further in this research, according to the IAEA and JIS methods, the standard test to find data rapidly for leach-rate of elements in synroc, it can be carried-out by accelerated leach-rate method in medium of pure water (100 °C) for 12 hours, namely the leach-rate in the first day [13, 14], Therefore the leaching times ($t = 12$ hours) are same for all samples. This standard test of leach-rate in the first day is necessary only to evaluate the immobilization process to find the best condition and the best quality of the waste synroc block. The leach-rate test results of uranium in the waste synroc blocks are shown in Figure-3.

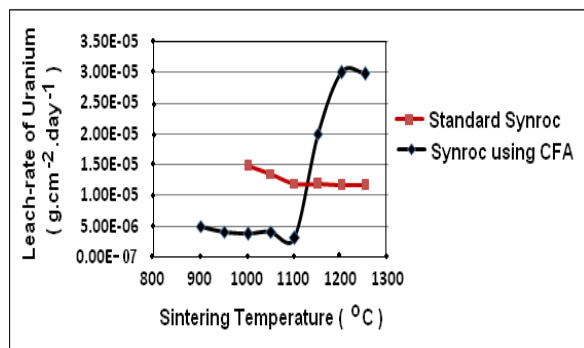


Figure-3. Effect of sintering temperature on the leach-rate of uranium for the both of waste synroc blocks (waste loading 30 wt% and sintering time 3 hours).

In Figure-3, it can be shown that the increasing of sintering temperature causes the leach-rate of uranium for the both of waste synroc blocks decreasing. The same phenomena shows that at high temperature the formation of mineral phases synroc more perfect to form a multi-phases ceramics which more dense and compact so that the radioactive elements are immobilized and isolated in the waste synroc block, and it is not easily leached by water. Whereas for the waste synroc block using CFA, the decreasing of leach-rate of uranium reaches the minimum value at the sintering temperature of 1100 °C, then increase after the sintering temperature higher than 1100 °C. This is accordance with the decreasing of the compressive strength (Figure-2) after sintering temperature > 1100 °C, this is due to several components (alkali metal oxides) released at the higher temperature thus decrease the synroc compactness and decrease the ability of immobilization and isolation of uranium. The leach-rate of uranium for the waste synroc block using CFA is relatively lower than the waste standard synroc, in the optimum condition shows the lowest leach-rate of uranium for the synroc block using CFA is reached at sintering temperature of 1100 °C and for the standard synroc block at 1200 °C. The value for the both of synroc block respectively are 3.09×10^{-6} g.cm⁻².day⁻¹ and 1.17×10^{-5} g.cm⁻².day⁻¹. This case is caused by the presence of K₂O and Na₂O contents in CFA that can reinforce the bond of uranium in synroc at temperature sintering ≤ 1100 °C. The leach-rate of uranium for the both waste synroc block is very low, this data shows that the both of synroc matrix is very excellent to immobilize and isolate the radionuclide of uranium. In this case the synroc matrix using CFA is better than the standard synroc matrix.

Based on the characteristic test results for the both of synroc blocks consisting of density, compressive strength, and the leach-rate mentioned above (Figure-1, Figure-2, and Figure-3) show that the optimum of sintering temperature for the waste synroc block using CFA is reached at sintering temperature of 1100 °C with the density value of 2.28 g/cm³, compressive strength of 5.57 kN/cm², and the leach-rate of uranium 1.05×10^{-6} g.cm⁻².day⁻¹. Whereas the optimum of sintering temperature for the waste standard synroc block at 1200 °C with the density value of 2.85 g/cm³, compressive strength of 10.98 kN/cm², and the leach-rate of uranium 1.17×10^{-5} g.cm⁻².day⁻¹.

Optimization of the sintering time on immobilization of uranium radioactive waste using synroc matrix

The characteristic test results for density, compressive strength, and leach-rate of uranium to obtain the optimum of sintering time for the waste synroc blocks using supercalcinic-zirconio titanate synroc (standard synroc) matrix and supercalcinic silico-titanate synroc matrix (using CFA) are shown in Figure-4, Figure-5 and Figure-6. The condition of experiment is waste loading 30 wt%, sintering temperature for the waste standard synroc block at 1200 °C and for the waste synroc block using CFA at 1100 °C, and sintering time between 1- 4 hours.



The phenomena occurring on the sintering time parameter is the same as in the sintering temperature parameter. The sintering process is needed energy which its quantity depend on temperature and sintering time, so that density and compressive strength of waste synroc block increase with the increasing the temperature and sintering time.

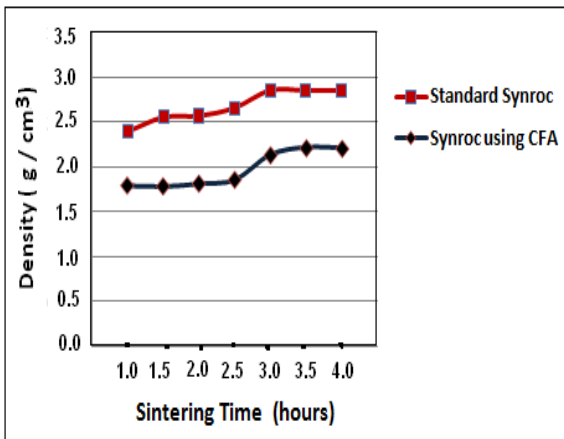


Figure-4. Effect of sintering time on the density for the waste standard synroc block at 1200 °C and for the waste synroc block using CFA at 1100 °C (waste loading of 30 wt%).

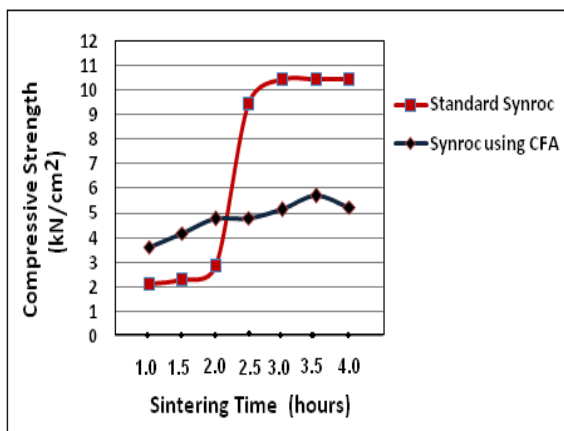


Figure-5. Effect of sintering time on the compressive strength for the waste standard synroc block at 1200 °C and for the waste synroc block using CFA at 1100 °C. (waste loading of 30 wt%).

Figure-4 and Figure-5 (the characteristic test results for density and compressive strength) show that the optimum condition of sintering process for the waste standard synroc block is reached at the sintering time for 3 hours, whereas for the waste synroc block using CFA is reached at the sintering time for 3.5 hours. In the optimum condition, the value of density and compressive strength for the waste standard synroc block are 2.85 g/cm³ and 10.98 kN/cm², whereas the value of density and

compressive strength for the waste synroc block using CFA are 2.29 g/cm³ and 5.76 kN/cm² respectively.

The phenomena mentioned above also effect the leach-rate (Figure-6). The addition of sintering time will give opportunity to allow the mineral phases formation of synroc were followed by the capture of the radioactive elements into the lattices of mineral phases in synroc blocks. The stronger of the bonds between the grains and the formation of the dense compact of multi-phases ceramics so that the leach-rate of uranium decreases. This case can be shown that the leach-rate of uranium decreases with increasing the sintering time, then after sintering time 2.5 hours sharply decreases and reaches the lowest value after sintering time 3 hours (for the waste standard synroc). Whereas the leach-rate of uranium for the waste synroc block using CFA is very low and the decreasing after sintering time for 3.5 hours is not significant. The lowest value of leach-rate of uranium is reached in sintering time of 3 hours with value 1.17×10^{-5} g.cm⁻².day⁻¹ for the waste standard synroc block, and 1.05×10^{-6} g.cm⁻².day⁻¹ for the waste synroc block using CFA. In the optimum condition, it is shown that the leach-rate of uranium for the both waste synroc block are very low, but the waste synroc block using CFA is lower than the waste standard synroc block.

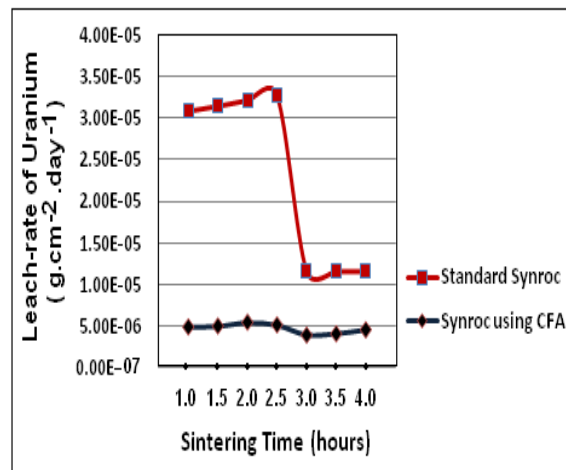


Figure-6. Effect of sintering time on the leach-rate of uranium for the waste standard synroc block at 1200 °C and for the waste synroc block using CFA at 1100 °C. (waste loading of 30 wt%)

The comparison based on characteristic test and economics aspect for the both synroc matrix

Based on the characteristics test results and economics aspect, comparison of the both waste synroc blocks can be made as shown in Table-4.



Table-4. The comparison between the waste supercaline silico-titanate synroc block (the waste synroc block using CFA) with the waste supercaline zirconio-titanate synroc block (standard synroc) by sintering process and standard synroc block by HIP proces.

Parameters	Synroc Block using CFA (by sintering)	Standard Synroc Block (by Sintering)	Standard Synroc Block (by HIP) [15,18,19,20]	Remarks For Synroc Block using CFA vs Standard Synroc by sintering
1. The optimum sintering process : a. Sintering Temperature (°C) b. Sintering Time (hours)	1100 3.5	1200 3	1200 ^{a)} -	lower (better) few longer
2. Characteristics synroc block in the optimum sintering process : a. Waste loading (wt%) b. Density (g/cm ³) c. Compressive strength (kN/cm ²) d. Leach-rate of Uranium (g.cm ⁻² .day ⁻¹)	30 2.29 g/cm ³ 5.76 kN/cm ² 1.05x10 ⁻⁶	30 2.85 10.98 1.17x10 ⁻⁵	9-44 2.1-3.4 ^{b)} - 10 ⁻⁷ - 10 ⁻⁸	- lower *) lower *) lower (better than standard synroc)
3. The economics aspect : a. Processing Cost b. Matrix material Cost	lower lower	higher higher	higher higher	- sintering temperature lower - utilization of CFA (cheaper)
^{a)} Temperature at the hot isostatic pressing (HIP) process. ^{b)} Depend on waste loading. ^{*)} Fulfill the quality recommended by the IAEA.				

The best sintering process for the both synroc blocks can be obtained, i.e : for the waste supercaline zirconio-titanate synroc block (standard synroc) at sintering temperature 1200 °C for 3 hours, and waste loading 30 wt%, with density 2.85 g/cm³, compressive strength 10.98 kN/cm², and leach-rate of uranium 1.17x10⁻⁵ g.cm⁻².day⁻¹, whereas for the waste supercaline silico-titanate synroc block (using CFA) at 1100 °C for 3.5 hours with waste loading 30 wt%, density 2.29 g/cm³, compressive strength 5.76 kN/cm², and leach-rate of uranium 1.05x10⁻⁶ g.cm⁻².day⁻¹. Based on the density and compressive strength, the quality of standard synroc block is better than the synroc block using CFA. Instead of leach-rate of uranium, quality of the synroc block using CFA is better than the standard synroc block, however the quality of both types of the waste synroc block with the sintering process in accordance with the quality of the waste synroc block with the hot pressing isostatic process having density between 2.1 - 3.4 g/cm³ [15] and the leach-rate of uranium between 5.0x10⁻⁴ – 6.0x10⁻⁶ g.cm⁻².day⁻¹ [14]. The quality of the waste synroc block also fulfill the quality recommended by the International Atomic Energy Agency (IAEA) that the value of compressive strength is 2 - 5 kN/cm² and the leach-rate is 1.7x10⁻¹ – 2.5x10⁻⁴ g. cm⁻².day⁻¹ [21]. In generally, the quality of the both synrocs by sintering process conform with quality of synroc block by the hot isostatic pressing (HIP) process.

Based on the sintering temperature and leach-rate of uranium shows that the waste synroc block using CFA are lower than the standard synroc, and also for the economics aspect namely the processing cost and matrix material cost for the waste synroc block using CFA is

lower (cheaper) than the waste standard synroc block, so the supercaline silico-titanate synroc matrix using CFA can be utilized as alternative for synroc material to replace the standard synroc material.

CONCLUSIONS

Immobilization process of sludge radioactive waste containing uranium using the supercaline silico-titanate synroc matrix using coal fly ash (CFA) by sintering process obtained the optimum condition on sintering temperature of 1100 °C and sintering time for 3.5 hours. For waste loading at 30 wt%, obtained density of waste synroc block is 2.29 g/cm³, compressive strength is 5.76 kN/cm², and leach-rate of uranium is 1.05x10⁻⁶ g. cm⁻².day⁻¹. Whereas the immobilization process of sludge radioactive waste containing uranium using the supercaline zirconio-titanate synroc matrix (standard synroc) obtained the optimum condition on sintering temperature of 1200 °C and sintering time for 3.0 hours. For waste loading at 30 wt%, obtained density of waste synroc block is 2.85 g/cm³, compressive strength is 10.98 kN/cm², and leach-rate of uranium is 1.17x10⁻⁵ g.cm⁻². day⁻¹. The quality of the both synrocs by sintering process conform with quality of synroc block by the hot isostatic pressing process, and also fulfill the quality recommended by the IAEA. Based on comparison of the characteristic test results and economics aspects for the both waste synroc blocks, the supercaline silico-titanate synroc matrix using CFA can be utilized as alternative for synroc material to replace the standard synroc material for immobilization of sludge radioactive waste containing uranium.



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