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Optimal treatment condition of solidification auxiliary agent for stable solidification of radioactive sludge

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1. Introduction

When various contaminated tanks treating radioactive waste fluid and pipe transport this radioactive waste fluid are exposed to fluid waste for a long time, the stainless steel material inside the tank or inside the pipe will corrode and sludge waste can be generated. Homogeneous powder waste as sludge should be solidified and disposed of according to the disposal criteria, which prevents the dispersion of radioactive nuclides from waste. When melt solidification cannot be performed due to the high melting point of the sludge waste, the sludge can be solidified adding a solidification auxiliary agent. It is important to determine which solidification auxiliary agent (SAA) to use. According to the type and the mixing ratio of SAA, the effect on the stability of the solidified sludge should be checked. By confirming which chemical reaction in SAA contribute to the stability of solidified sludge waste, it is possible to determine the type of solidified material, additive ratio, and heating temperature suitable for the characteristics of the sludge. Therefore, in this study, ferro frit 3195 that already showed stable solidification when it was used as SAA and new SAA (ferro frit 3110) was compared and it was also confirmed that what is dominant factor in SAA for making stable solidified sludge waste.

2. Methods and Results

2.1 Solidified Sludge Body Production

The composition of sludge waste was set to the main three oxides (Fe_2O_3, Cr_2O_3, NiO) generated by the corrosion of stainless steel. Since the generation ratio of each oxide can be different according to corrosion conditions (time, humidity, temperature, etc), the composition ratios of three oxides were set to those (Fe_2O_3 70 % Cr_2O_3 18 %, NiO 12 %) of Fe, Cr, Ni in stainless steel [1]. Cobalt powder was also added for leachability index evaluation. Before making production of the solidified sludge body, micro moisture in sludge waste should be removed by heating at temperature higher than 100 ℃. If solidified sludge body was made without the removal of micro moisture, when body is heated, the crack by the release of micro moisture can be generated. Ferro frit, glassy material including similar chemical compositions with borosilicate glass, was used as SAA in this study. Ferro frit is used as glaze to produce the stable pottery. Because ferro frit is mixed with water and used as a glaze, it is in the form of a powder processed into fine particles. Thanks to these fine particles, ferro frit can be easily mixed with sludge waste (powder) and homogeneously distributed in sludge particles. Table I shows two types of ferro frit used in this study.

Table I: Chemical composition ratio of each ferro frit

Composition	Ferro frit 3195	Ferro frit 3110
Na_2O	5.7	15.3
K_2O	-	2.3
CaO	11.3	6.3
Al_2O_3	12.1	3.7
B_2O_3	22.4	2.6
SiO_2	48.5	69.8
Total	100	100

After homogeneous mixing sludge and ferro frit, mixed powder was put in a pellet press die set and compressed by hydraulic compression press. By compression at room temperature, mixed powder can be shaped and densified. However, using only compression at room temperature, since stable solidification is impossible, the mixed powder after compression was heated. Table II shows the production conditions of each sample.

Table II: The production conditions of each sample

Sample	Used ferro frit	Mixing ratio (ferro frit:sludge)	Temperature (℃)
1	3110	10:90	800
2	3110	15:85	800
3	3110	20:80	800
4	3110	25:75	800
5	3110	10:90	950
6	3110	15:85	950
7	3110	20:80	950
8	3110	25:75	950
9	3195	10:90	950

In case of Ferro frit 3195, only using 10 % of ferro frit 3195, when mixed powder (10% ferro frit 3195, 90 % sludge waste) was heated at the temperature higher than 900 ℃, it was confirmed that stable solidified sludge body could be produced. Therefore, the sample produced by ferro frit 3195 was control group. However, in ferro frit 3110, since the composition ratios of such main components as SiO_2 and B_2O_3 are different with those of ferro frit 3195, other results may come out.

Since it was known that glass transition (softening) and carbonization of ferro frit contribute to stable solidification of sludge waste, considering the glass transition temperature (760 ~ 927 ℃) of ferro frit 3110, heating temperatures were set to 800, 950 ℃.

Although 800 ℃ is in glass transition temperature range, carbonization reaction is not generated. 950 ℃ is higher than glass transition temperature range and is known that carbonization reaction is also generated. However, although sample production conditions using ferro frit 3110 are 10:90 and 950 ℃, since stable solidified sludge body may not be produced, mixing ratio of sludge waste and ferro frit 3110 was set to four conditions (90:10, 85:15, 80:20, 75:25) to increase the stability of solidified sludge. Similarly, even if the carbonization reaction did not occur at 800 ℃, it was checked whether a stable solidified sludge body could be produced if the mixing ratio of ferro frit 3110 increased.

2.2 Chemical Analysis

Since it should be confirmed whether leaching resistance of sample is stable, each sample is immersed in leachate (DI water) and left for 24 hours. After 24 hours, the color change of leachate was checked by visual inspection. Using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), each leachate is analyzed to check the concentration of elements from sample to leachate for 24 hours. And using XPS (X-ray Photoelectron Spectroscopy), the chemical composition of each sample is confirmed. If there was a clear difference in leaching resistance for each sample, it was determined which chemical component was formed and caused the difference in leaching resistance.

2.3 Results

In ferro frit, such materials as B_2O_3 and SiO_2 may carbonized and changed to B_4C and SiC that contribute to high durability of solidified sludge. Although it was known that B_4C and SiC are formed at about 850 and 900 ℃, respectively, when Ni was used as catalyst [2-3], it was confirmed that leaching resistance of all samples made by ferro frit 3110 were low and the color of leachate was clearly changed. The color change of leachate means that the sludge material is easily dispersed from solidified sludge waste to leachate.

When visual inspection was conducted, there was no clear color change of leachate immersing sample 9 as Fig. 1. On the other hand, the color change of all leachates immersing samples made by ferro frit 3110 were clear. Sample 8, which was expected to be stable, also showed a distinct color change. Generally, it was known that the higher of SAA additive ratio, the more stable solidification. Therefore, it means that there is something dominantly contributing to stable solidification rather than the increase of SAA additive ratio. Currently, the components of each sample are under XPS analysis, and it is expected to know what difference contributes decisively to solidification stability through this analysis.

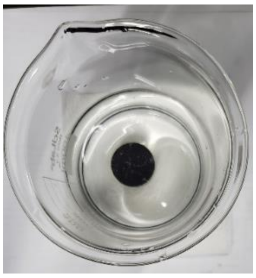

Fig. 1. Sample 9 after 24 hours in leachate.

Fig. 2. Sample 8 after 24 hours in leachate.

3. Conclusions

Ferro frit, which has a similar chemical composition with borosilicate, was used to stably solidify sludge oxides with high melting point. It was seen that the solidified sludge body made by ferro frit 3195 was stable while all samples made by ferro frit 3110 was unstable, which indicated the increase of ferro frit 3110 additive ratios could not always secure the leaching stability. It will be determined what chemical compositional differences between sample by ferro frit 3195 and sample by ferro frit 3110 caused these differences.

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