Requirements for the Application of Cement Solidification Process Control Program: Review on the Effects of Radioactive Waste, Cement, and Additive Composition

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1. Introduction

In nuclear facilities, radioactive liquid waste must be generated during operation or performing the experiments. During the storage of such radioactive liquid waste, various sludge waste can accumulate. In addition, even in cases where the radioactive liquid waste does not contain sludge, sludge waste can be generated during the evaporation process through treatments of the radioactive liquid waste. The sludge waste must be disposed permanently in a stable state, similar to solid radioactive waste. Therefore, it should be managed to meet the radioactive waste acceptance criteria in terms of radioactive properties, physical and chemical state, and other factors. Recently, the KORAD(Korea Radioactive Waste Agency) has established guidelines on applying the cement solidification PCP (Process Control Program) to dispose of sludge waste stably. Therefore, the requirements of the cement solidification PCP for sludge radioactive waste reviewed in this study. Additionally, it was investigated the characteristics of the radioactive waste, cement, and additives to meet the PCP requirements.

2. Guidelines on Cement Solidification Process Control Program

2.1 Raw waste characterization

Before the cement solidification of sludge, a investigation of the waste characteristics is necessary to be carried out, as shown in Table I[1]. Firstly, according to general characteristic requirements, investigation and management of the origin of sludge waste is need to be conducted. Among the physical characteristics, the percentage of moisture content in the sludge waste is important since it can affect the ratio of water and cement during the cement solidification. In terms of chemical characteristics, ions and salts in the sludge, which are the basic composition of solidified product, should be investigated as a basic requirement. Additionally, chelates and hazardous materials are important characteristics since they can affect the physicochemical properties of solidified product. The radioactive characteristics are also necessary to satisfy the acceptance criteria for the disposal similar to other radioactive wastes.

Table I: Survey contents of waste charactieristics[1]

characteristics	Content
General	Waste type Generation period Quantity
Physical	Moisture content Density
Chemical	Composition (ions, salts, etc.) pH Temperature Chelates and hazardous materials
Raidological	Nuclides (including concentration) Total activity

2.2 Solidification characterization

2.2.1 Cement

The cement used for solidification must be selected appropriately for the waste characteristics, such as Ordinary Portland Cement type 1 (OPC). The cement should be investigated for its chemical composition, density, particle size, and hydrolysis characteristics in advance. It should also be examined whether the sludge waste is stably integrated into the solidified form and does not adversely affect the performance of the solidified product. [1]

2.2.2 Additives

The additives used for solidification should be investigated for their chemical composition, chelating agents, and presence of hazardous materials. Additionally, an evaluation should be made regarding the benefits obtained from using additives. If the use of additives results in a degradation of the performance of the solidified product, the use of additives should be avoided. [1]

2.3 Acceptance criteria for solidified waste

The acceptance criteria for solidified product are shown in Table II, which includes standards for testing the structural stability and chemical stability of the

solidified waste [1]. These standards are same as those for accepting low and intermediate-level radioactive waste [2].

Table II: Test and standards of solidified product [1]

Content	Standard
Compressive strength test	500 psi
Immersion test (90days)	500 psi
After thermal cycling test (28 days)	500 psi
Irradiation test	500 psi
Leaching test (90 days)	Leaching index >6
Free standing liquids test	< 0.5 vol % of sample volume

3. Effects of composition

3.1 Radioactive waste

The components of radioactive waste sludge that mainly affect the stability of cementitious solids are organic compounds such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), oxalic acid, and citric acid. These can be present in liquid radioactive waste that has been used for decontamination, and may also be present in the sludge after treatment. According to NUREG report, the organic compounds can form radionuclide-chelate complexes that can enhance the movement of radioactive isotopes in disposal facilities [3]. In addition, the sulfates can also be reacted with the cement and generate the ettringite [4]. The enttringite can affect to the physical stability of solidified product [4]. Therefore, if organic matter or sulfate is present in radioactive sludge waste at concentrations above a certain value, the sludge should be excluded from solidification.

3.2 Cement

The major composition of OPC mentioned in PCP guidelines includes $3CaO{\cdot}SiO_2$ (C_3S), $2CaO{\cdot}SiO_2$ (C_2S), $3CaO{\cdot}Al_2O_3$ (C_3A), $4\ CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_3A), and the mixing ratios may vary depending on the manufacturer [5]. Therefore, in order to use cement of the level mentioned in the PCP guidelines, it is necessary to obtain the composition from the manufacturer or perform a chemical composition analysis

3.3 Additive

The additives used for cement solidification are water reduction agent and accelerators. As a water reduction agent, sodium silicate (Na_2SiO_4) can be mainly used. However, if the excessive concentration of Na_2SiO_4 is added, swelling or shrinkage of the solidified product may occur due to changes in humidity of the environment [4]. As a hydrolysis reaction accelerator, a Zn compound may be generally used. However, the effect is different depending on the concentration of the Zn compound. It was mentioned that ZnSO4 can be an accelerator of the hydrolysis reaction of cement at concentrations < 2.5%. On the other hand, $ZnSO_4$ is a retardant at concentrations between 2.5% and 5.5% [4]. Therefore, it can be better to add appropriate additives with certain concentration during the cement solidification, or not to use additives for stability of the solidified product.

3. Conclusions

In this study, in order to apply the cement solidification process control program guideline for radioactive sludge waste, preliminary research and literature research were conducted. As a result, it was confirmed that the composition and characteristics of radioactive waste had an effect on cement solidification. In addition, it was confirmed that additives can cause problems in the hydrolysis reaction and physical stability of solidified product. Therefore, it will be necessary to sufficiently investigate the target sludge waste and additives before cement solidification.

REFERENCES

[1] KORAD, 시멘트 고형화 공정관리프로그램 공정변수 개발 및 적용에 관한 지침 (2021).
[2] KORAD, 중저준위 방사성폐기물 동굴처분시설 인수기준 (2022).
[3] U.S. NRC, Characterization of Radionuclide-Chelating Agent Complexes Found in Low-Level Radioactive Decontamination Waste, NUREG/CR-6124 (1996).
[4] l. Luhar et al, Solidification/Stabilization Technology for Radioactive Wastes Using Cement: An Appraisal, Materials 2023, 16(3), 954 (2023).
[5] KS L 5201, Portland cement (2021)