Encapsulation of radioactive stainless-steel oxide sludge in aluminum using hot isostatic pressing process and treatment suitability assessment

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Abstract

Sludge powder with stainless-steel oxide generated from the long-term contaminated-waste fluid tank of a nuclear power plant was compressed into a cylindrical shape by a hydraulic press at room temperature. The cylindrical sludge was wrapped in molten Al in a carbon crucible and cooled and hardened at room temperature. Subsequently, the encapsulated sludge was heated and compressed by the hot isostatic pressing (HIP) process. The Al capsule was melted and separated from the cylindrical solidified sludge. In solidified sludge, the leachability indices of Co, Fe, Cr, and Ni were $17.5 \pm 0.0736$, $13.4 \pm 0.0952$, $11.2 \pm 0.0952$, and $16.9 \pm 0.0739$, respectively. This satisfies Korea’s criterion for the disposal of solidified radioactive waste, which is a leachability index of more than 6.

Keywords: Al, encapsulation, hot isostatic pressing treatment, oxide sludge, nuclear waste disposal
1 Introduction

Nuclear power plants have several drain tanks that treat fluid waste, including sludge. Although these metallic tanks are made of corrosion-resistant material such as stainless steel, they can still be corroded when the inner wall or a pipe of the tank is exposed to fluid waste for a long time [1]. After Fe, Cr (approximately 16% – 18%) and Ni (approximately 10% – 14%) occupy the second- and third-highest mass ratios in stainless steel [2]. As the generation ratio of each oxide material (based on Fe, Cr, Ni) in stainless steel can vary with the corrosion condition, the generation ratio of sludge in a contaminant tank cannot be calculated. Therefore, the simulated sludge is set to be composed of oxide materials in the mixing ratio of 70:18:12 (Fe : Cr : Ni) in stainless steel [3]. The oxides of Fe, Cr, and Ni have melting points of 1,565, 2,435, 1,955 °C, respectively [4–6]. The oxide material generated by corrosion is deposited to the outer surface of stainless steel. The sludge containing the oxide materials can be deposited inside the pipe or on the inner bottom surface of the drain tank. In accordance with the Notice of Article 11 of the Nuclear Safety and Security Commission (NSSC) of Korea—Intermediate and Low-level Radioactive Waste Delivery Regulations—powder sludge should be disposed in a solid form. Because the powder is radioactive, the most important objective of sludge solidification is to prevent it from dispersing into the environment. In general, melting or solidification methods using auxiliary materials (such as cement and glass) are employed for sludge solidification. However, heating oxide materials with high melting points to 2,500 °C increases the cost of waste treatment. Moreover, other hazardous materials present in the sludge could be vaporized and dispersed into the environment. The cement solidification method can solidify sludge without the application of heat. However, the main constituents of cement can be decomposed even at relatively low temperatures of 70–600 °C [7], which can damage the solidified waste and cause the materials to leak. The waste loading of cement solidification is approximately 60% – 70% [8]. In other words, 30% – 40% of cement is required for the disposal of 60% – 70% of waste, which will ultimately increase the total volume of disposed waste. Vitrification using glass is safer than cement solidification, but waste loading of vitrification method is also high (approximately 40% – 45%) [9].

Therefore, this study proposes a solidification method with lower waste loading. Theoretically, this method should have a high leaching resistance and should prevent the liberation of radioactive materials from the solidified mass. If neither melting of total sludge waste nor solidification with auxiliary materials are used, a sintering method, in which the powder is heated and pressed at a temperature marginally below its melting point, must be used for solidifying the powder. As compression plates made of metal can be damaged over time even at temperatures lower than their melting points, the hot press method using compression plates have a difficulty to sintering of sludge waste. Therefore, this study used the hot isostatic pressing method (HIP). The working principle of HIP is that the working fluid, an inert gas, expands when heated in a closed system [10]. The expansion of the inert gas compresses the material in the closed system and densify it. As the inert gas takes the shape of the closed system (container), it occupies the volume not occupied by the material and can simultaneously pressurize it isostatically when heated. In most HIP systems, N₂ or Ar are used as the inert gas to prevent chemical reactions with the material. However, if the material to be compressed is a powder, compression sintering cannot be performed because the inert gas can pass between its particles and the powder can be scattered in HIP. Therefore, the area (m²) of the sealed metal capsule (including sludge powder) needs to transfer the pressure of the expanding inert gas to the sludge powder in the capsule.

In this study, a molten Al metal capsule were employed to treat the powder sludge in the HIP process. This is essentially different from extant methods that utilize welding and degassing treatment. The stability of solidified sludge, i.e., the leaching resistance, was evaluated in terms of the leachability index of solidified radioactive sludge waste, satisfying the disposal criterion of the NSSC. The presence of contaminants due to material transfer from the mixed powder to Al in all stages, namely capsule packaging, HIP treatment, and capsule removal, was analyzed.

2 Methods

2.1 Molding of Sludge Powder

Ferro frit (a type of glass), a ceramic glaze, was employed as an auxiliary material for solidification. Its glass transition temperature varies with its main constituent, which can be SiO₂, B₂O₃, Na₂O, Al₂O₃, etc. The ferro frit used in this study has a glass transition temperature range of approximately 585–900 °C. To increase the volume reduction ratio compared to extant solidification processes (cement solidification or vitrification), the ferro frit was mixed with sludge in the ratio of 10:90. To verify the stability of solidified sludge, the leachability index of the leaching test target radionuclide was evaluated in the solidified sludge after HIP treatment. Because the literature does not contain data on oxide sludge and radionuclide concentration in contaminated tanks or pipes of domestic nuclear power plants, the radionuclide concentration data of the oxide layer in the primary system of Électricité de France was utilized [11]. In The Republic of Korea, if solidified radioactive sludge waste contain Cs, Sr, and Co, leachability indices of three radionuclides should be evaluated for solidification disposal. However, among those three radionuclides, only Co has been observed in the oxide layer of the primary cooling system of Électricité de France. Meanwhile, fission products such as Cs-137 and Sr-90 are typically found in spent nuclear fuel rather than solid waste. The possibility of their presence in the oxide layer of pipes or contaminated drain tanks is minor. Therefore, only Co was considered as the target radionuclide for the evaluation. Nonradioactive Co powder was used instead of radionuclide cobalt for safety reasons. As sludge + ferro frit + nonradioactive Co is a powder, it
should be homogeneously mixed and shaped at room temperature before sintering for best results. The molding process was also necessary to remove voids between the particles of the mixture. For molding, the powder mixture was compressed in a cylindrical pellet press die set (Fig. 1). However, because the mixture pressurized at room temperature was not in the sintered state, it could be easily damaged by external shock.

![Fig. 1 Mixed powder compressed at room temperature](image-url)

### 2.2 Encapsulation of sludge (before HIP)

A previous study packaged sludge powder in a stainless-steel capsule and pressurized it under inert gas in an HIP system [12]. This encapsulation method needs a complex capsule-production process. After heating the sludge to liberate fine moisture or gases generated by the chemical reaction, it is loaded in a stainless-steel container, which is then welded to a stainless-steel lid with an exhaust vent. The container must be sealed in a vacuum state by sucking out air from the vent and blocking it. If the seal fails under pressure during the HIP process, the inert gas will leak into the capsule, making it impossible to sinter the powder. In accordance with the Article 11 of NSSC Notice of Korea, Intermediate and Low-level Radioactive Waste Delivery Regulations, powdered sludge should be homogeneously solidified. As the stainless-steel capsule including sludge is double layer structure, the capsule should be removed after HIP treatment. In the encapsulation method of [12], the capsule becomes difficult to remove after being processed in the HIP system. The melting point of stainless steel is more than 1,400 °C; therefore, melting the capsule after HIP treatment is difficult [13]. Furthermore, the sludge containing traces of molten stainless-steel oxide may melt and stick to it. Cutting the stainless-steel capsule could also damage the sintered sludge within.

In the method, as the sludge is loaded in a stainless-steel container without pressurization, it may not be properly sintered due to the empty space inside the capsule. Moreover, even though other capsule-production methods exist, they require welding and degassing (for vacuum), which increase the complexity and cost of the process. Hence, the encapsulation method of sludge by directly melting the metal around it was used in this study.

The metal with a melting point lower than that of the sludge oxide material should be used as the capsule material so that it can be removed without melting the solidified sludge waste after HIP process. Al, which has a melting point of approximately 660 °C, was used as the capsule material [14]. When Al and the powder mixture were heated at approximately 800–900 °C, which is higher than the melting point of Al but lower than that of Fe₂O₃, only Al melted in the carbon crucible. As the sludge consisting of stainless-steel oxide did not melt, molten Al could encapsulate the mixed powder (Fig. 2).
To prevent a chemical reaction from occurring between molten Al and compressed powder, the latter was wrapped in a 0.1-mm SUS 304 film. When Al was melted in a carbon crucible, a square-shaped 5-mm SUS 304 plate was placed under the compressed powder in the crucible to prevent it from sinking to the bottom of the crucible and getting exposed to the outside environment. Fig. 3 illustrates the schematic of the encapsulation method.

When Al was melted, the 0.1-mm SUS 304 film and 5-mm SUS 304 plate protected the powder, preserving its cylindrical shape. Because molten Al can secure the surface of the compressed powder, the capsule can be sealed more easily than in the previous method that used welding and degassing.

2.3 HIP Treatment

The compressed powder packaged in the Al capsule should be treated with the HIP process. As the mixture compressed at room temperature is not a stable solidified body, the heat and pressure of the HIP process can be leveraged to reinforce the compressed powder and produce a stable solidified sludge. In the closed vessel of the HIP system, the material to be treated should not be melted or destroyed during the process. If it is melted or destroyed, the expanding inert gas can enter the powder and expand it. This will cause the sintering process to fail. As each material treated with HIP has a different melting point or fatigue strength, the HIP processing temperature and pressure conditions for each material must be considered. The fatigue strength of Al (Al 6061) is 100 MPa (approximately 14,500 psi) in the tensile strength range of 200–250 MPa [15]. Considering this and the melting point (approximately 660 °C), when the Al capsule (with the compressed powder) is treated in the HIP system, the heating and pressurization conditions should be lower than the melting point and fatigue strength. Therefore, we set the conditions to 13,000 psi and 620 °C, i.e., lower than the melting point and fatigue strength of Al. 620 °C is also in the range of glass transition temperature (585–900 °C) of ferro frit in this study. During HIP process, the softened ferro frit can act as a buffer so that the mixed powder in Al capsule is not damaged under high pressure.
2.4 Leachability Index Evaluation

The powder (sludge powder + nonradioactive Co + ferro frit powder as the solidification material) was packaged in molten Al. The solidified capsule was treated in the HIP system. After HIP treatment, the Al capsule was removed by re-melting it. To verify the stability of the compacted slag after separation from melted capsule, its leaching resistance was evaluated. It was confirmed that the leachability index of Co in the solidified sludge was more than 6, which is the solidified radioactive waste disposal criterion of Korea. Meanwhile, it was also confirmed that the sludge was stably solidified only when the main components (FeO, CrO, NiO) of stainless steel from the solidified sludge did not disperse into the leachate. Therefore, the leachability indices of the sludge’s main components, Fe, Cr, and Ni, were also evaluated. In South Korea, the leachability index evaluation of solidified radioactive waste is conducted according to the American National Standard (ANS)-16.1-2019 [16]. As stated earlier, because the main components of the sludge were not the target materials for the evaluation, there were not a criterion for the leachability indices of Fe, Cr, and Ni. The indices of these elements were only used to judge the stability of the solidified sludge.

The leaching resistance test duration was 5 days. Distilled water was used as leachate. The replacement period of the leachate was 24 h (± 0.5 h). The concentration of ions of Co, Fe, Cr, and Ni in each replaced leachate was analyzed by inductively coupled plasma mass spectrometry (ICP-MS). For the 5-days leaching resistance test, the effective diffusivity (D) from the solidified sludge to the leachate was compared in terms of a defined constant β (1.0 cm/s). The leachability indices (L) of Co, Fe, Cr, and Ni were calculated according to ANS-16.1-2019 as:

\[
L = \log \left( \frac{\beta}{D} \right) \tag{2}
\]

D: Effective diffusivity (cm²/s)

αᵢ: Leached mass of leaching target material (Co, Fe, Cr, and Ni) in leachate for ith leaching test interval (g)

A₀ᵢ: Initial total mass of leaching target material (Co, Fe, Cr, and Ni) in solidified sludge (g)

V/S: Volume of leachate (distilled water) (cm³) / surface area of solidified sludge (cm²), 10 cm (ANS-16.1-2019 recommendation)

t: Leaching time per leaching test interval (= Leachate replacement period: 24 ± 0.5 h, ANS-16.1-2019 recommendation)

β: Defined constant, 1.0 cm/s (ANS-16.1-2019 recommendation)

L: leachability index (unitless)

2.5 X-ray Diffraction (XRD) analysis

As the glass transition temperature (softening temperature) range of the ferro frit was approximately 585–900 °C, although Al did not melt during the HIP process, a certain amount of ferro frit of the powder in the Al capsule can be softened and deformed. The capsule was removed at 700–800 °C. Due to the deformation of the ferro frit, softened ferro frit may dispersed from the compressed powder to Al capsule. To verify this, the composition of the capsule was analyzed after removing it by melting. If the ferro frit or sludge constituents were homogeneously dispersed from the powder to the capsule, when the latter was melted, the constituents would be homogeneously mixed with Al. An X-ray diffraction (XRD) analysis of the Al capsule was used to confirm its final composition.

3 Results and Discussion

3.1 Leachability Index

The leachability index of Co after the HIP treatment of the solidified sludge was 17.5 ± 0.0736, which is more than 6. The effective diffusivity of Co was 3.52 × 10⁻¹⁸ cm²/s. Although there is no criterion related to effective diffusivity for the disposal of solidified radioactive waste in Korea, a low effective diffusivity means a low diffusion velocity from the solidified sludge to the leachate. A low diffusion velocity means that a small amount of material is dispersed from the solidified sludge to the leachate in the same leaching duration. If a large quantity of sludge is dispersed from solidified sludge to leachate, the sludge is unstable. Therefore, the lower the diffusion velocity, the more stable the solidified sludge. Moreover, no criterion exists for the leachability indices of Fe, Cr, and Ni for the disposal of solidified radioactive waste in the country. Therefore, although the leachability indices of the elements were higher than 6, only the indices of leaching-resistance target materials, namely Co, Ce, and Sr were used as indicators to judge the disposability of solidified radioactive waste.

However, to judge the stability of solidified sludge, the constituents of the solidified sludge, except Co, should not disperse into the leachate. Although the leachability index of solidified sludge’s Co is more than 6, if Fe, Cr, and Ni were easily dispersed into the leachate, the solidified sludge would be judged unstable. Therefore, the stability of the solidified sludge could be evaluated from the fact that the leachability indices of Fe, Cr, and Ni were all more than 6. The leachability indices of Fe, Cr, and Ni were 13.4 ± 0.0952, 11.2 ± 0.0952, and 16.9 ± 0.0739, respectively. As per Eq. (2), for the leachability index to be equal to 6, the effective diffusivity (D) should be 1 × 10⁻⁶ cm²/s. The effective diffusivities of Fe, Cr, and Ni
were $4.00 \times 10^{-14}$, $6.21 \times 10^{-12}$, and $1.23 \times 10^{-17}$ cm$^2$/s, respectively. The order of magnitude of these values is more than twice $10^{-6}$ cm$^2$/s.

### Table 1 The effective diffusivity and leachability index of Co, Fe, Cr, Ni from solidified sludge after HIP treatment

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective diffusivity (cm$^2$/s)</td>
<td>$3.52 \times 10^{-18}$</td>
<td>$4.00 \times 10^{-14}$</td>
<td>$6.21 \times 10^{-12}$</td>
<td>$1.23 \times 10^{-17}$</td>
</tr>
<tr>
<td>Leachability index</td>
<td>$17.5 \pm 0.0736$</td>
<td>$13.4 \pm 0.0952$</td>
<td>$11.2 \pm 0.0952$</td>
<td>$16.9 \pm 0.0739$</td>
</tr>
</tbody>
</table>

### 3.2 XRD Analysis

After the HIP treatment of solidified sludge and Al capsule, it was confirmed whether material was dispersed from the sludge powder to the capsule or not. The dispersion of sludge constituents, ferro frit, and Co can be observed using the XRD analysis of the molten Al capsule. Notably, the dispersion should not occur.

As illustrated in Fig. 4, the sludge and ferro frit constituents were originally oxide metals. No chemical reaction occurred in most of the constituents during the HIP process. However, SiO$_2$ and B$_2$O$_3$ underwent carbonization. SiC and B$_4$C can be synthesized at 900 and 850 $^\circ$C with Ni as the catalyst [17,18]. However, the powder consists of more Ni than ferro frit. Furthermore, SiO$_2$ and B$_2$O$_3$ account for approximately 50% and 20% of the trace products in ferro frit, respectively. Therefore, the powder consists of more Ni than SiO$_2$ and B$_2$O$_3$.

A certain amount of Co was oxidized and became CoO. The oxidation of Co to CoO occurs at approximately 900 $^\circ$C [19]. CoO is insoluble in water. During the HIP process, the softened ferro frit that was homogeneously distributed in the compressed powder would have stably fixed materials related to the sludge and nonradioactive Co. We assumed that this stable fixation of ferro frit caused the leachability indices of Co, Fe, Cr, and Ni to be more than 6.

![Fig. 4 XRD analysis of solidified sludge with HIP treatment](image)

Although ferro frit was softened during the HIP process, it was assumed that there was no material dispersion from the solidified sludge to the Al capsule. As illustrated in Fig. 5, when the Al capsule was melted after HIP treatment, the constituents of the compressed powder were not observed in the XRD analysis. In another study using radionuclides, when Al was exposed to Fe-59, Ni-63, and Co-60 at 359–629 $^\circ$C, the diffusivities of the three isotopes were as low as $10^{-14}$–$10^{-11}$ cm$^2$/s. They did not provide information on the dispersion of radioactive Cr in Al [20]. However, from the XRD analysis in Fig. 5, it was confirmed that Cr did not disperse in Al. This means that the capsule was not contaminated during the HIP process and can be recycled in the next HIP process for solidification of another sludge.
3.3 Comparison with Extant Encapsulation Techniques

This encapsulation method with molten Al simplifies the process of producing a canister and removing the capsule after the HIP process. In Table 2, it is compared with an extant encapsulation method using welding and degassing. The melting point of Al is markedly lower than that of stainless steel, and the proposed method can be used to manufacture capsules through a facile heating technique without complex processes such as welding, vacuum forming through degassing, and chimney sealing for vacuum sealed canister. Although the relatively low melting point of Al can limit the HIP treatment temperature under 660 °C, the sludge powder can be stably solidified using ferro frit with a softening temperature (glass transition temperature) of 585–900 °C. As stated earlier, considering that the melting temperature of stainless steel is higher than 1,400 °C and that the sludge consists of stainless-steel oxide, removing the stainless-steel capsule by melting and separating it from the sludge after the HIP treatment are difficult. As the capsule’s inner wall and the sludge within may coalesce during the HIP treatment under pressure, safely cutting and removing only the stainless-steel capsule without damaging the solid powder are also challenging. Conversely, the Al capsule can be easily removed by melting. After performing the HIP process and removing the capsule by melting, any damage to the solidified sludge was not observed. Furthermore, contamination of Al by the powder (sludge, ferro frit, non-radioactive Co) was also observed during the HIP process. The uncontaminated Al can be recycled for the next HIP process. This means that the disposal cost of radioactive sludge waste can be decreased by reducing the capsule production cost over successive HIP processes.

<table>
<thead>
<tr>
<th>Method</th>
<th>Previous</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Stainless-steel</td>
<td>Al</td>
</tr>
<tr>
<td>Process</td>
<td>Welding, degassing (for vacuum), chimney sealing</td>
<td>Compression (at room temperature), melting Al</td>
</tr>
<tr>
<td>Achievable temperature in HIP</td>
<td>Under about 1400 °C (Melting point of stainless-steel)</td>
<td>Under 660 °C (Melting point of Al)</td>
</tr>
<tr>
<td>Difficulty of removing after HIP treatment</td>
<td>Difficult to melt or cut</td>
<td>Relatively easy to melt (at the temperature higher than 660 °C)</td>
</tr>
</tbody>
</table>

4 Conclusions

The contribution of the study is an encapsulation technique to solidify radioactive waste for its safe disposal. The technique uses Al, which is easy to remove unlike stainless steel. Before HIP process, oxide sludge mixed with ferro frit was compressed at room temperature and encapsulating it in molten Al. A stable solidified sludge can be produced in HIP process. Compared to previous encapsulation methods, this method utilizes a facile process for the production and removal of the metal capsule. The leachability indices of Co and sludge constituents (Fe, Cr, and Ni) in solidified sludge after removing the Al capsule were more than 6, which is the lower threshold for the disposal of radioactive solidified sludge in Korea. XRD analysis revealed that material transfer from the powder to Al did not contaminate the latter throughout encapsulation by molten Al, HIP treatment, and capsule removal. It could be seen that this would contribute to the reduction of the treatment cost of the sludge solidification for disposal as the uncontaminated Al could be recycled for the next HIP process. It was thought that the treatment temperature of the HIP system limited to below 660 °C due to the melting point of Al could be increased by utilizing metals with a higher melting point than that of Al and lower than that of stainless steel.
5 Acknowledgment

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