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Original Article

Characteristics of Cement Solidification of Metal Hydroxide Waste

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A B S T R A C T

To perform the permanent disposal of metal hydroxide waste from electro-kinetic decontamination, it is necessary to secure the technology for its solidification. The integrity tests on the fabricated solidification should also meet the criteria of the Korea Radioactive Waste Agency. We carried out the solidification of metal hydroxide waste using cement solidification. The integrity tests such as the compressive strength, immersion, leach, and irradiation tests on the fabricated cement solidifications were performed. It was also confirmed that these requirements of the criteria of Korea Radioactive Waste Agency on these cement solidifications were met. The microstructures of all the cement solidifications were analyzed and discussed.

1. Introduction

A lot of uranium contaminated soil and concrete waste is generated from the dismantlement of uranium conversion facilities [1]. There are several disposal methods for radioactive waste such as regulation exemption, decontamination, and long-term storage [2]. It is necessary for us to achieve permanent disposal of radioactive waste. The methods for solidifying radioactive waste include cement solidification, asphalt solidification, and polymer solidification [3]. Cement solidification has several advantages such as well-known materials and technologies, various applications, and reasonable cost. On the contrary, it has certain disadvantages such as a large volume expansion of solidification for radioactive waste. Because cement solidification has excellent structural strength and a shielding effect, it is widely used for the permanent disposal of radioactive waste [3]. Cement solidification operates as a barrier against the leach of nuclides during radioactive waste disposal. To evaluate the criteria of Korea Radioactive Waste Agency (KORAD), integrity tests on the solidification of radioactive waste needs to be performed [4].

In this study, to inspect the criteria of KORAD, we carried out cement solidification of the metal hydroxide from

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radioactive waste. An integrity inspection such as the compressive strength, immersion, and leach tests on cement solidification were performed. We also analyzed the experimental results according to the criteria of KORAD. The calculation of the leachability index on the cement solidification (C-2.0) and cement solidification (C-1.5) for the leach detection of nuclides was carried out. The integrity of the cement solidification (C-2.0) and cement solidification (C-1.5) was also evaluated.

2. Materials and methods

2.1. Cement solidification

For the disposal of metal hydroxide in radioactive waste, we applied a cement solidification method [5–8]. The cement solidification was carried out according to the ratio of metal hydroxide from radioactive waste to cement. To mix the cement, water, and metal hydroxide powders, we used a mortar mixer according to the manual procedure. The equipment used for measuring the compressive strength of the cement solidification was also applied.

The ratio of metal hydroxide from radioactive waste to cement for cement solidification (C-2.0) was 2.0. At first, the powders were made from metal hydroxide waste using a bowl and a rod. Secondly, cement and water were mixed using a mortar mixer, and then the powders were added into the mortar mixer and mixed uniformly. Thirdly, the homogeneously mixed material was put into four polyethylene molds and then entirely covered with vinyl. Fourthly, after 4 weeks of cement solidification, a visual inspection of the cement solidifications was performed and it was then cut into 50-mm diameter and 100-mm height sections using a microcutter. The volume expansion of the primary cement solidification was about 150% in comparison with the volume of metal hydroxide from radioactive waste. Table 1 shows the chemical analysis of metal hydroxide waste, which consists of aluminum, potassium, calcium, iron, magnesium, sodium, uranium, etc. Table 2 shows the conditions of the cement solidification. The unit weight of the cement solidification decreases as the ratio of waste to cement increases.

The ratio of metal hydroxide from radioactive waste to cement for the cement solidification (C-1.5) was 1.5. The cement solidification (C-1.5) was made using an aluminum mold. Good solidification, such as primary cement solidification, was achieved. The volume expansion of cement solidification (C-1.5) was about 165% in comparison with the volume of metal hydroxide from radioactive waste. The ratio of metal hydroxide from radioactive waste to cement for the cement solidification (C-2.5) was 2.5. The third cement solidification was also made using an aluminum mold. After 1 week of cement solidification, a visual inspection of the cement solidification was performed, and all the cement solidifications were then fractured. It was determined that the ratio of metal hydroxide from radioactive waste to cement for cement solidification should be under 2.0.

Table 1 – Chemical analysis of metal hydroxide waste.

Element	wt%	Element	wt%	Element	μg/g
Al	21.0	U	0.87	Sr	177
K	6.86	Si	0.57	Li	275
Ca	6.66	Mn	0.24	Ni	177
Fe	5.60	Cu	0.10	Nd	164
Mg	2.33	Zn	0.10	Th	91
Na	1.62			Y	69

Al, aluminum; Ca, calcium; Cu, copper; Fe, iron; K, potassium; Li, lithium; Mg, magnesium; Mn, manganese; Na, sodium; Nd, neodymium; Ni, nickel; Si, silicon; Th, thorium; U, uranium; wt, weight; Y, yttrium; Zn, zinc.

2.2. Integrity tests on cement solidification

The integrity tests on cement solidification consisted of compressive strength, immersion, and leach tests. The compressive strength of the cement solidification was measured using compressive strength equipment (HCT-DC50 (Heungjin Company Model No.: HCT-DC50 Gimpo, Republic of Korea); Fig. 1). An immersion test was performed using the electric conductivity measurements and pH measurement of immersion water from the immersion exchange time (1 day, 3 days, 7 days, 14 days, 37 days, and 90 days). After an immersion test of 90 days, the compressive strength of the cement solidification was determined. The process of the leach test is as follows.

At first, the initial concentration of uranium on cement solidification was measured. The cement solidification is immersed in demineralized water for 90 days. Samplings of the demineralized water from the cumulative immersion time (2 hours, 7 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 19 days, 47 days, and 90 days) were made, and a chemical analysis of these samplings was carried out. Finally, the leachability index was calculated with the initial concentration of uranium, uranium concentration owing to the cumulative immersion time, the effective diffusivity, the volume of the specimen, the geometric surface area of the specimen, and the leach time.

$$L = \frac{1}{n}\sum_{1}^{n}[\log(1/D)]_n \quad (1)$$

$$D = \pi\left[\frac{a_n/A_0}{(\Delta t)_n}\right]^2\left[\frac{V}{S}\right]^2 T \quad (2)$$

$$T = \left[\frac{1}{2}\left(\sqrt{t_n} + \sqrt{t_{n-1}}\right)\right]^2 \quad (3)$$

Where L, leachability index; D, effective diffusivity (cm^2/s); T, leach time representing the "mean time" of the leach intervals (s); a_n, radioactivity during exchange time of immersion water (Bq or Ci); A_o, initial radiation rate of the specimen (Bq or Ci); S, geometric surface area of the specimen (cm^2); V, volume of the specimen (cm^3); and $\triangle t$, exchange time of immersion water (s).

Table 2 – Conditions of cement solidification.

Specimen No.	Cement/cement	Water/cement	Waste/cement	Total (g)	Unit weight (g/cm^3)
C-1.5	1.0	1.2	1.5	432.12	1.47
C-2.0	1.0	1.65	2.0	450.12	1.35
C-2.5[a]	1.0	2.2	2.5	471.11	-

[a] Cement solidification (C-2.5) is fractured.

2.3. *Scanning electron microscopy/energy-dispersive X-ray spectroscopy analysis on cement solidification*

A microstructure and element analyses on cement solidification (C-1.5, C-2.0, C-2.5) were conducted using scanning electron microscopy (SEM; Scanning Electron Microscope, JEOL (JEOL, Model: JSM-6610LV Tokyo, Japan), JSM-6610LV) and energy-dispersive X-ray spectroscopy (EDS; OXFORD (OXFORD Instruments, Model: X-MAX Abingdon, the United Kingdom), X-MAX). Fig. 2 shows a photograph of the SEM-EDS.

3. Results and discussion

3.1. *Compressive strength of cement solidification*

Table 3 shows the compressive strength of the cement solidification (C-2.0) and cement solidification (C-1.5) on the compressive strength criterion. The criteria of compressive strength is 34 kg·f/cm^2 [1]. The compressive strength of the cement solidification (C-2.0) was measured to be about 132 kg·f/cm^2. The compressive strength of the cement solidification (C-1.5) was also measured to be about 166 kg·f/cm^2. The compressive strength of the cement solidification (C-2.0) and cement solidification (C-1.5) was about four to five times bigger than the compressive strength criterion. The compressive strength of the cement solidification (C-2.0) with an immersion period of 90 days was measured to be about 115 kg·f/cm^2.

The compressive strength of the cement solidification (C-1.5) with an immersion time of 90 days was also measured to be about 97 kg·f/cm^2. The compressive strength of the cement solidification (C-2.0) and cement solidification (C-1.5) with immersion was about three times bigger than the compressive strength criterion. The compressive strength of the cement solidification (C-2.0) with an immersion period of 90 days was 87% of the compressive strength of the cement solidification (C-2.0) without immersion. The compressive strength of the cement solidification (C-1.5) with an immersion time of 90 days was 58% of the compressive strength of the cement solidification (C-1.5) without immersion.

To evaluate the radiation resistance of the primary cement solidification, the irradiation (10 MGy) of gamma rays of Co-60 on the cement solidification (C-2.0) was carried out. Before the cement solidification (C-2.0) was irradiated from gamma rays

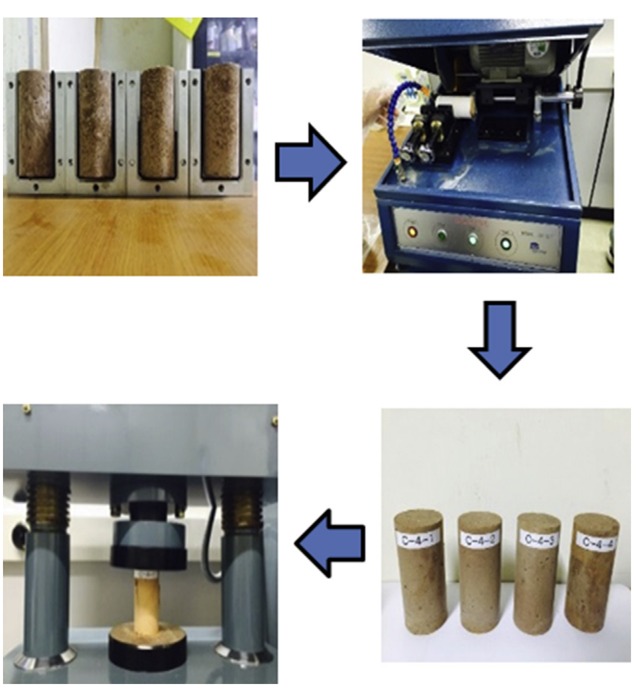

Fig. 1 – Process for measuring compressive strength.

Fig. 2 – A photograph of *scanning electron microscopy/energy-dispersive X-ray spectroscopy*.

Table 3 – Compressive strength of cement solidification(C-2.0) and cement solidification(C-1.5).

Sampling No.	Compressive strength (kg·f/cm^2)	Standard compressive strength (kg·f/cm^2)
C-1.5	165.51	34
C-1.5 (immersion)	96.63	34
C-2.0	131.55	34
C-2.0 (immersion)	115.1	34
C-2.0 (irradiation)	111.22	34

Table 4 – Cumulative leached index of cement solidified waste.

Element	Leach day				
	1	5	19	47	90
C-1.5	13.492	13.575	13.794	13.981	14.134
C-2.0	13.546	13.629	13.784	13.978	14.137

of Co-60, the compressive strength of the cement solidification (C-2.0) was measured to be about 132 kg·f/cm^2. After the cement solidification (C-2.0) was irradiated from gamma rays of Co-60, the compressive strength of the cement solidification (C-2.0) was measured to be about 111 kg·f/cm^2. The compressive strength was about three times bigger than the compressive strength criterion. The compressive strength was decreased by about 16% owing to irradiation of gamma rays of Co-60. It was confirmed that the fabricated cement solidification (C-2.0) and cement solidification (C-1.5) should meet the requirements of the criteria of KORAD.

3.2. *Leach test of cement solidification*

The initial concentrations of uranium in cement solidification (C-2.0) and cement solidification (C-1.5) were 2,904 μg/g and 2,729 μg/g, respectively. The uranium concentration of all the samplings of the demineralized water owing to the immersion cumulative time (2 hours, 7 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 19 days, 47 days, and 90 days) on the cement solidification (C-2.0) and cement solidification (C-1.5) were under 0.05 μg/mL. By calculating Eqs. (1–3) with Microsoft Excel (Microsoft Excel 2010), the leachability index on the cement solidification (C-2.0) and cement solidification (C-1.5) were 14.14 and 14.13, respectively [9]. Table 4 shows the cumulative leached index of cement solidified waste. These values were bigger than Criterion 6 of KORAD [10]. Fig. 3 shows the cumulative leach index of primary and secondary solidification. As the exchange time of the leach water increases, the cumulative leach index of the primary and secondary solidification shows an increasing trend.

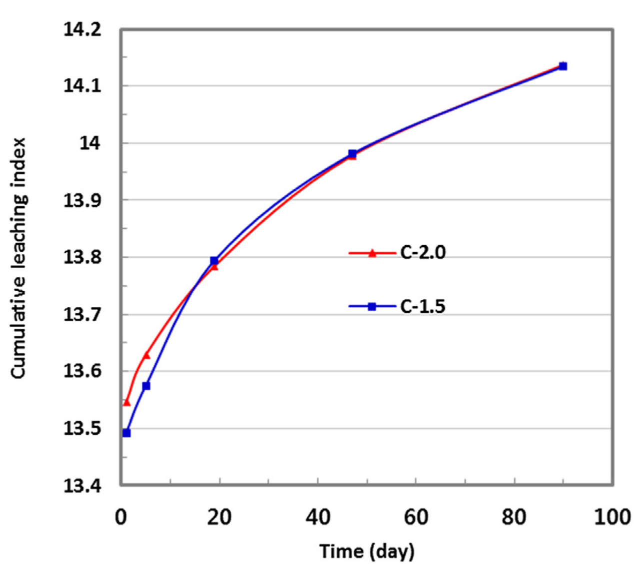

Fig. 3 – Cumulative leach index of primary and secondary solidification.

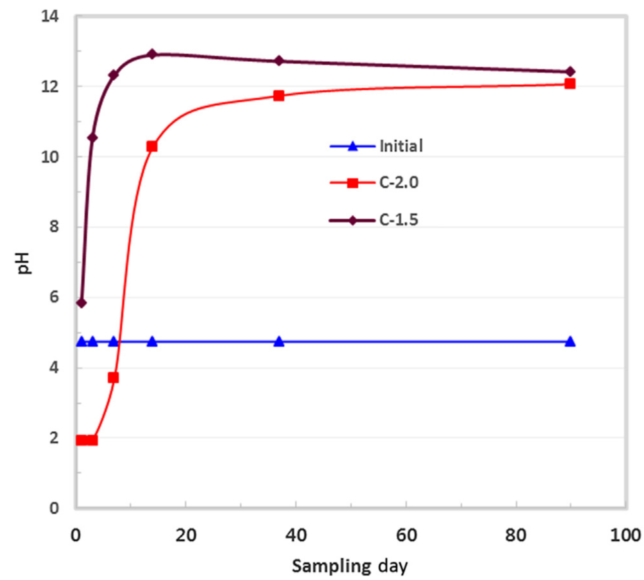

Fig. 4 – pH of primary and secondary solidification.

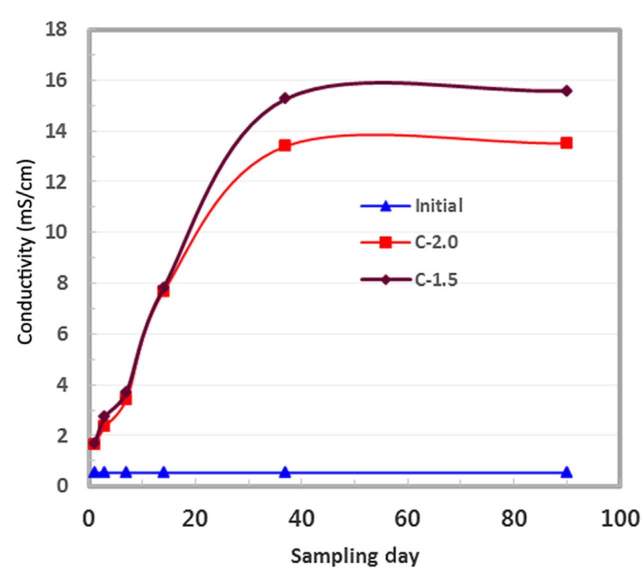

Fig. 5 – Conductivity of primary and secondary solidification.

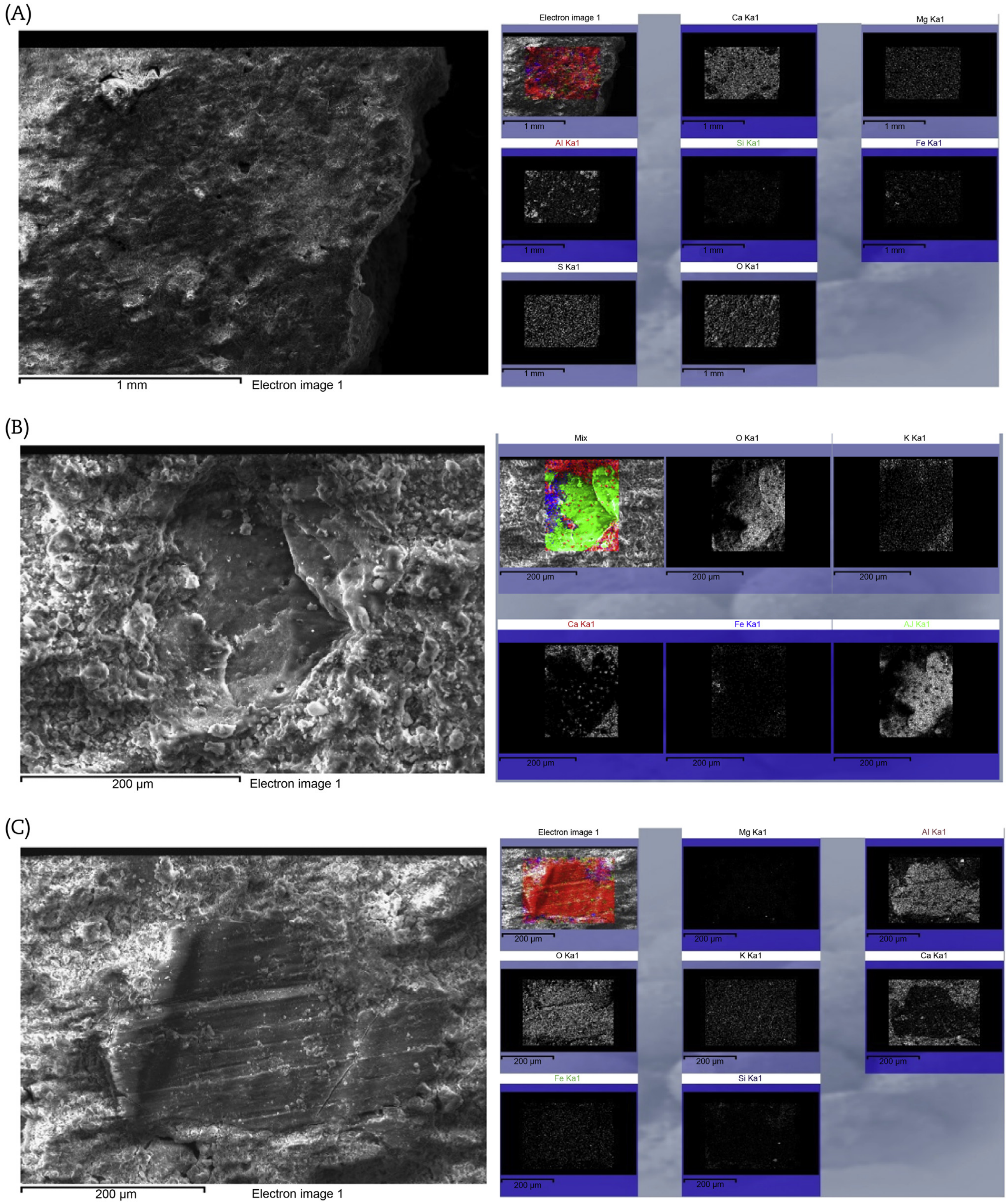

Fig. 6 – Microstructure of primary and secondary solidification. (A) C-1.5. (B) C-2.0. (C) C-2.5.

3.3. *pH of cement solidification*

Fig. 4 shows the measurement of pH of immersed cement solidification. As the number of sampling days of immersed cement solidification increases, the pH of the cement solidification (C-2.0) and cement solidification (C-1.5) shows an increasing trend. The pH of immersed cement solidification (C-1.5) was bigger than that of immersed cement solidification (C-2.0). This was due to the sufficient amount of cement used for the cement solidification (C-1.5) in comparison with the cement amount of the cement solidification (C-2.0). It was realized that the amount of calcium hydroxide from immersed cement solidification (C-1.5) was bigger than that from immersed cement solidification (C-2.0). During the immersion of cement solidification, it was realized that calcium hydroxide was released from the cement solidification. The cement solidification (C-1.5) rapidly approached 12 (pH) and then gradually maintained an equilibrium.

3.4. *Conductivity of cement solidification*

Fig. 5 shows the measurement of conductivity of immersed cement solidification. As the number of sampling days of immersed cement solidification increased, the conductivity of the cement solidification (C-2.0) and cement solidification (C-1.5) showed a similarly increasing trend. The conductivity of the cement solidification (C-2.0) and cement solidification (C-1.5) were bigger than the initial conductivity without the immersed cement solidification (C-2.0) and cement solidification (C-1.5). This was due to various metal ions from cement solidification. Thus, metal ions from immersed cement solidification (C-1.5) were bigger than those from immersed cement solidification (C-2.0). During the immersion of cement solidification, it was realized that various metal ions were released from the cement solidification.

The conductivity of the cement solidification (C-1.5) showed a rapidly increasing trend in comparison with that of the primary cement solidification. On the contrary, the conductivity of the cement solidification (C-2.0) showed a gradually increasing trend. This was due to the sufficient cement quantity of cement solidification (C-1.5) in comparison with the cement quantity of the cement solidification (C-2.0). Thus, various metal ions from immersed cement solidification (C-1.5) were bigger than those from the immersed cement solidification (C-2.0). During the immersion of cement solidification, it was realized that the ions of various metal hydroxides were released from the cement solidification.

3.5. *SEM-EDS on cement solidification*

Fig. 6 shows the microstructure and element analysis on cement solidification (C-1.5, C-2.0, C-2.5). According to the results of the SEM and EDS analysis of on all cement solidifications (C-1.5, C-2.0, C-2.5), the microstructures of all cement solidifications show a similar morphology. On the whole, the results of the element analysis on cement solidification (C-1.5) show a morphology in which soil containing an aluminum phase was united with cement. By contrast, the results of the element analysis on the cement solidification (C-2.0) show a morphology in which soil containing a calcium phase was not united with cement. It was realized that cement solidification (C-2.5) was fractured owing to a small amount of cement in contrast with that of soil.

4. Conclusion

We carried out cement solidification of metal hydroxide from radioactive waste. An integrity inspection of the compressive strength, immersion, leach, and irradiation tests on the cement solidification was performed. The compressive strength of cement solidifications (C-1.5, C-2.0) with immersion was about three times greater than the compressive strength criterion. Based on the analysis of the microstructure, the calcium phase in the soil does not chemically interact with the cement phase, which is one of the reasons for a fracture in solidification with a high waste loading (C-2.5). The leachability index by the American Nuclear Society 16.1 method on cement solidifications (C-1.5) and (C-2.0) was 14.13 and 14.14, respectively. These values are larger than Criterion 6 of KORAD. Therefore, it was confirmed that the requirements of the criteria of KORAD on these cement solidifications were met.

Conflicts of interest

All authors have no conflicts of interest to declare.

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