Arch. Metall. Mater. **71** (2026), 2, 617-620

DOI: https://doi.org/10.24425/amm.2026.158853

JAEWOONG HWANG[1,2], HYUNG-JU KIM[1], KEUNYOUNG LEE[1], SUNGJUNE SOHN[1*]

OPTIMIZATION OF CEMENTITIOUS WASTEFORM FOR IMMOBILIZING C-14 IN $CaCO_3$ RADIOACTIVE WASTE

This study examines the feasibility of immobilizing dispersive $CaCO_3$ radioactive waste containing C-14 carbonate based on ordinary Portland cement (OPC) hydration. Cementitious wasteforms were fabricated by incorporating $CaCO_3$ of waste loadings ranging from 20 to 60 wt.% by a conventional cement paste method. The performance of wasteform was evaluated in terms of mechanical and chemical durability specified in the waste acceptance criteria (WAC) for low- and intermediate-level radioactive waste disposal in the Republic of Korea. The compressive strength was evaluated under open and sealed curing conditions at curing periods of 7 and 28 days. As $CaCO_3$ content increased, the compressive strength was generally reduced, however, maximum value was obtained under 30 wt.% $CaCO_3$ with all curing conditions. Chemical durability was evaluated according to the ANSI/ANS-16.1 method. Linear cumulative leaching behavior of carbon was shown for all compositions. The leaching indices was derived with ranging of 12.0-12.7, corresponding to extremely low effective diffusion coefficients. Therefore, it was shown that OPC-based hydration provides an effective and acceptable immobilization strategy for dispersive $CaCO_3$ radioactive waste.

Keywords: $CaCO_3$; cementitious wasteform; compressive strength; C-14 leaching; waste acceptance criteria

1. Introduction

C-14, radioactive carbon, is generated by the neutron capture reaction of O-17 during nuclear power plant operation [1]. Since C-14 is classified as a radionuclide to determine intermediate level waste, an effective separation for C-14 is required. In nuclear power plants, C-14 is mainly captured by activated carbon in the air cleanup systems and separated as a gaseous waste treatment. Generally, spent activated carbon is considered as the primary C-14-bearing waste.

Korea Atomic Energy Research Institute has been developing a treatment process for C-14-contaminated spent activated carbon [2,3]. In this process, C-14 is desorbed from the spent activated carbon as a gaseous oxide form under high-temperature vacuum conditions. The resulting radioactive CO_2 is subsequently captured by alkaline-earth-metal-incorporated glass and converted into solid carbonate compounds such as $CaCO_3$. However, the carbonates formed in this step are highly dispersive, which can be easily scattered as fine particles. This characteristic increases the risk of inhalation exposure and environmental migration via groundwater. Therefore, the dispersive waste should be immobilized for geological disposal by satisfying the regulatory requirements [4-6].

Ordinary Portland cement (OPC)-based solidification has been widely recognized as a viable immobilization method for low-level radioactive waste [7-10]. By employing the cementitious matrix, wasteform can obtain appropriate mechanical integrity and chemical durability for long-term containment of radionuclides under geological disposal conditions. In addition, cement solidification provides practical advantages, including process simplicity and compatibility for various wastes with economic benefit.

Accordingly, this study examined the immobilization of the $CaCO_3$ glass by the cement hydration process using OPC to evaluate its suitability as a radioactive wasteform under the radioactive waste acceptance (WAC) criteria for low- and intermediate-level waste in the Republic of Korea [11,12]. The mechanical and chemical durability of the cementitious wasteform were evaluated by measuring the compressive strength and the leaching index in accordance with the standard test methods specified in the WAC of the Gyeongju repository.

[1] NUCLEAR FACILITY CLEANUP TECHNOLOGY DIVISION, KOREA ATOMIC ENERGY RESEARCH INSTITUTE, DAEJEON, REPUBLIC OF KOREA
[2] CHUNGNAM NATIONAL UNIVERSITY, DEPARTMENT OF ORGANIC APPLIED MATERIALS ENGINEERING, DAEJEON, REPUBLIC OF KOREA

* Corresponding author: sjsohn@kaeri.re.kr

2. Experimental

OPC (SAMPYO Cement) was used for synthesizing the cementitious matrix. To initiate cement hydration, deionized water was prepared in the laboratory. Because C-14 bearing $CaCO_3$ glass could not be utilized directly, $CaCO_3$ (Sigma Aldrich, ≥99.0%, powder) reagent was prepared as a simulated radioactive waste. The cementitious wasteforms were fabricated by a conventional cement paste preparation method. First, $CaCO_3$ and cement powder were blended to obtain homogeneity of the precursor and mixing water was added to the blended powder according to the prescribed mixing ratio to provide adequate workability for wasteform fabrication as shown in TABLE 1. The water ratio in the paste was determined as 30 wt.%, which could provide workability and prevent free water generation after wasteform curing. At this stage, sufficient mixing was performed to minimize agglomerated solid particles within the cement paste. Subsequently, the paste was poured into a plastic mold with a diameter of 23 mm. Cementitious wasteforms incorporating $CaCO_3$ were produced under various waste loadings of 20, 30, 40, 50 and 60 wt.%. The wasteform was cured at 24±2°C under a relative humidity exceeding 90% as a sealed curing condition. For open curing, the temperature and relative humidity were maintained at 24±2°C and 40-60%, respectively.

TABLE 1

Blending ratio for preparation of cementitious wasteform

ID	Composition (wt.%)			
	$CaCO_3$ (Waste)	OPC	Water	W/C
Ca-20	20	50	30	0.60
Ca-30	30	40	30	0.75
Ca-40	40	30	30	1.00
Ca-50	50	20	30	1.50
Ca-60	60	10	30	3.00

According to the WAC in the Republic of Korea, the evaluation of non-dispersibility treatment for dispersive waste is based on two requirements, a minimum compressive strength of 3.44 MPa and the absence of free water generation. Accordingly, this study measured the compressive strength of wasteform under two curing conditions, with the top surface exposed to air and under fully sealed. The curing periods of 7 and 28 days were determined to compare the compressive strength revealed in the early-age and standard period (28-day), respectively. The compressive strength tests were conducted under a loading rate of 0.3±0.1 MPa/s to satisfy both the Korean standard (KS F 2405) and the United States standard (ASTM C39) using a compression testing machine (Heungjin Testing Machine Company HCT-DC100) [13,14]. The fabricated wasteforms were analyzed by XRD to identify waste materials and hydration products. For the evaluation of chemical durability, leaching test was conducted using deionized water according to the ANSI/ANS-16.1 standard method [15]. The carbon concentration in leachate was measured by total carbon analysis using a total organic carbon analyzer (Shimadzu Corporation TOC-L). To ensure statistical reliability, all measurements for compressive strength and leaching behavior were performed in triplicate ($n = 3$), and the results are presented as the mean value with sample standard deviation.

A small amount of $CaCO_3$ formed during cement hydration can also contribute to carbon leaching. This results in higher carbon concentration in the leachate than the exact leaching fraction by initially added $CaCO_3$, potentially leading to an overestimation of the leaching index. However, this is considered as a conservative evaluation from the perspective of safety assessment for radioactive waste disposal. Therefore, the leaching index was determined by including all leached carbon associated with both $CaCO_3$ from waste materials and from cement hydration. X-ray diffraction (XRD, Bruker D2 Phaser) analysis was performed to assess phase identification varied with cement paste compositions. To enable a direct comparison of diffraction patterns obtained from mixtures with different $CaCO_3$ and cement contents, the raw XRD intensities were normalized by the total integrated intensity over the 2θ range of 10-60°. Each intensity was divided by the area under the corresponding diffraction curve, so that the integrated intensity of every pattern within this range was equivalent. This normalization minimized experimental variations such as sample mass and packing density in XRD sample holder preparation. Consequently, changes in relative peak intensities could be interpreted in terms of phase evolution regardless of absolute intensity differences.

3. Results and discussion

Fig. 1 presents the compressive strength of cementitious wasteforms under various curing conditions and periods. Compressive strength generally tends to decrease with an increase of $CaCO_3$ content. However, an exception is consistently observed under all curing periods and conditions that wasteforms of 30 wt.% $CaCO_3$ loading show higher compressive strength than those of 20 wt.% $CaCO_3$, despite the higher waste loading. The bulk densities of the wasteforms after 28 days of sealed curing support this observation, as the specimens with a waste loading of 30 wt.% present a slightly higher value than those with a waste loading of 20 wt.% which implies a denser internal structure. These results may be explained by the filler effect of $CaCO_3$ in balanced composition between $CaCO_3$ and cement [16]. The maximum compressive strength at 30 wt.% represents an optimal binder-to-filler ratio. At a lower waste loading of 20 wt.%, $CaCO_3$ content is insufficient to fully occupy the capillary pores within the cement matrix, resulting in an under-filled state. Conversely, at waste loadings exceeding 30 wt.%, the absolute volume of the cement binder becomes insufficient to effectively bond the $CaCO_3$ particles. This is attributed a dilution effect and weakened interfacial bonding between the particles that could cause mechanical strength decrease. The strength development observed at 30 wt.% is attributed to the filler effect, which is not limited to simple dilution or void filling, but is associated with improved particle packing and refinement of capillary porosity.

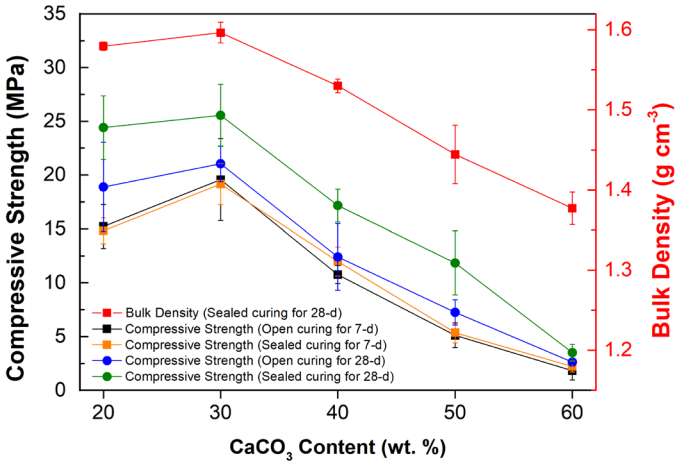

Fig. 1. Compressive strength of cementitious wasteforms with different curing periods (7-d and 28-d) and curing conditions (open and sealed), and bulk density of 28-d sealed cured wasteform depending on the $CaCO_3$ contents

After 7 days of curing no relationship was observed between the open and sealed curing conditions, indicating that exposure conditions of the wasteform did not significantly affect strength development in the early stages. However, a difference in compressive strength was identified even with exposure of the top surface after 28 days of curing. The compressive strength development in the longer curing period is influenced by whether the specimens are sealed during curing, which determines the degree of humidity maintained during the curing. The importance of sealed curing is clearly shown with consideration that cement hydration can contribute to strength improvement over the long-term period. The improvement in compressive strength under sealed curing at 28 days can be attributed to sustained internal humidity, which prevents premature self-desiccation and allows continued hydration of unreacted clinker phases. Under waste loading of 60 wt.%, the compressive strength exceeded the acceptance criterion of 3.44 MPa only in the case of 28-day sealed curing.

Fig. 2 shows XRD patterns of wasteforms after 28-day sealed curing depending on the cement paste composition presented in TABLE 1. The results revealed that with higher $CaCO_3$ contents, peaks of all cement-derived hydration products, including portlandite, ettringite, and monocarboaluminate disappeared, whereas the intensity of the calcite peaks increased. The increase in calcite peak intensity can be attributed not only to the initially added $CaCO_3$ but to secondary carbonation of CaO and $Ca(OH)_2$ originating from the cement and its hydration products.

In the Ca-20 specimen, although the initial cement content in the paste was as high as 50 wt.%, calcite appeared as the dominant phase in the XRD pattern. This behavior is attributed to the high crystallinity of calcite compared with cement hydration products, such as C-S-H gel, which are poorly crystalline. Nevertheless, hydration products such as ettringite and monocarboaluminate were clearly detected, together with residual clinker phases including larnite ($2CaO{\cdot}SiO_2$). The detection of monocarboaluminate in the XRD patterns indicates that $CaCO_3$ is not an inert filler but chemically participates in the hydration process. Carbonate ions react with the aluminate phases (C3A) to stabilize ettringite and form monocarboaluminate [17,18]. This reaction prevents the conversion of ettringite to monosulfate which negatively affects the mechanical strength. In addition, this chemical transformation increases the total volume of hydration products and refines the pore structure, potentially contributing to the enhanced mechanical strength observed at the optimal waste loading.

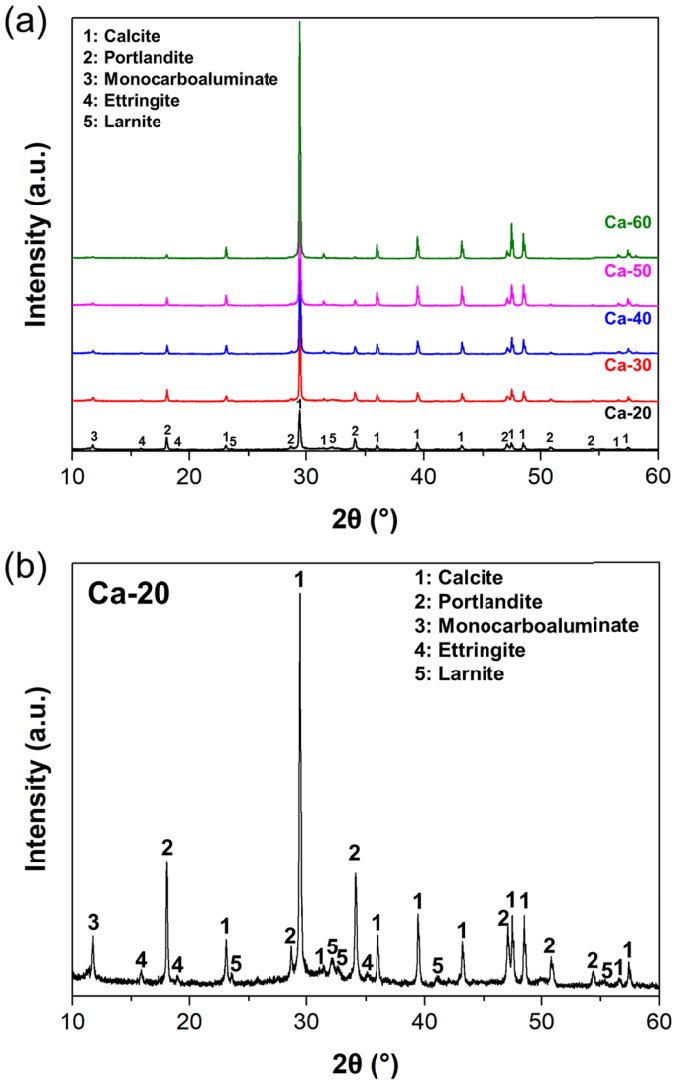

Fig. 2. (a) Normalized XRD patterns of 28-d sealed cured cementitious wasteforms depending on the $CaCO_3$ contents, (b) XRD pattern of 28-d sealed cured Ca-20 specimen

Fig. 3 presents cumulative fraction leached (CFL) of carbon during 5-day test. For all conditions, the CFL linearly increases with leaching time, and no abrupt acceleration behavior is observed. Although the cumulative fraction leached decreases with increasing $CaCO_3$ content, this trend is primarily attributed to the higher initial carbon inventory in the specimens rather than a substantial reduction in the carbon concentration in the leachate. In fact, the carbon concentrations measured in the leachate were comparable across all compositions. At a given

leaching time, the differences in CFL among the compositions are maintained from the early stage of the test, and the linearities from the CFL curves are shown to be parallel, indicating that the compositional differences do not diverge with time. The leaching indices of all specimens are calculated within the range of 11.15-11.75. Even if carbon is not specified as target element in ANSI-ANS-16.1 method, a leaching index of above 11 for carbon which corresponds to an effective diffusion coefficient on the order of 10^{-11} cm^2/s, indicates extremely low mobility and stable chemical durability of carbon in the cementitious wasteform.

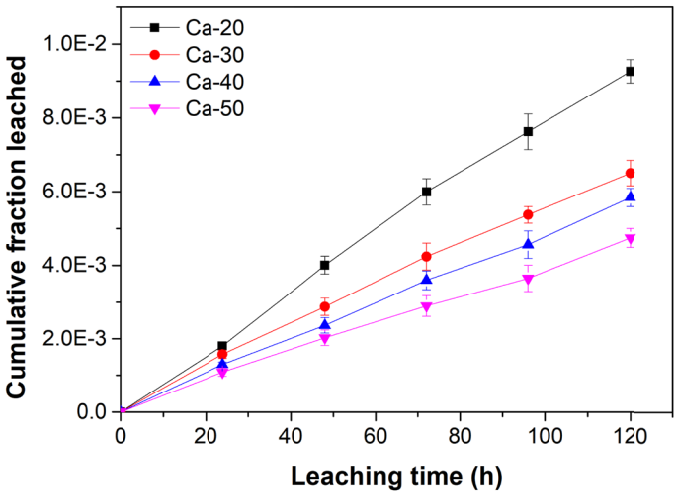

Fig. 3. Cumulated fraction leached of carbon for 5 days in 28-d sealed cured cementitious wasteforms depending on the $CaCO_3$ contents according to ANSI/ANS-16.1 leaching method

4. Conclusions

In this study, the immobilization of dispersive $CaCO_3$-based radioactive waste, representing C-14-bearing carbonate waste, as a cementitious wasteform was evaluated by the WAC for low- and intermediate-level radioactive waste disposal in the Republic of Korea. The wasteforms containing 20-60 wt.% $CaCO_3$ were successfully fabricated without free water generation at a fixed water content of 30 wt.%. While compressive strength was generally reduced with increasing $CaCO_3$ contents, the maximum value was shown at 30 wt.% $CaCO_3$ that the filler effect might affect. Sealed curing was shown to be favorable for long-term strength development. XRD analysis revealed that $CaCO_3$ chemically interacts with the cement matrix to form monocarboaluminate as a secondary phase, which can effectively stabilize ettringite and refines the microstructural density. The leaching tests conducted according to ANSI/ANS-16.1 presented linear cumulative leaching behavior with time for all compositions. The leaching characteristics of carbon revealed good chemical durability of cementitious wasteforms for $CaCO_3$ immobilization. These results suggest that cement hydration provides an effective immobilization approach for dispersive radioactive $CaCO_3$ waste within regulatory boundary that can provide a practical wasteform option for C-14 management during nuclear facility decommissioning.

Acknowledgments

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government Ministry of Science and ICT (RS-2025-02311305).

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