

Effects of inactive mineral fillers and fine aggregate on the strength and crack resistance of cementitious immobilization matrices

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Abstract

Cementitious matrices for radioactive-waste immobilization must satisfy mechanical and leaching requirements while maintaining macroscopic integrity without visible cracking. This study investigated the effects of ultrafine quartz and magnetite as inactive mineral fillers and standard sand as a fine aggregate on the strength, porosity, microstructure, and crack resistance of cementitious immobilization matrices. X-ray diffraction showed no detectable formation of additional crystalline reaction products associated with either filler. The aggregate-free quartz-containing matrix exhibited the highest calculated total porosity (32.5%) but also the highest 28-day compressive strength (46.3 MPa), indicating that its strength development could not be attributed to matrix densification alone and was consistent with a beneficial physical filler effect. Matrices 1–4 satisfied the numerical compressive-strength criterion of 3.44 MPa and exhibited cobalt leachability indices of 17.44–17.66, substantially above the criterion of 6. Nevertheless, matrices 2–4 developed visible cracks during drying or subsequent thermal and aqueous exposure and therefore failed to maintain the crack-free integrity required for wasteform acceptance. In contrast, all six sand-containing matrices remained free of visible cracks after 28-d curing and drying, 30 thermal cycles, and water immersion while maintaining compressive strengths above the acceptance criterion. At identical W/C ratios, the sand-containing matrices also exhibited lower calculated porosity and more continuous microstructures than their corresponding filler-only matrices. These results demonstrate that compressive strength and leaching resistance alone do not predict overall wasteform integrity and that incorporation of fine aggregate is effective for suppressing macroscopic cracking while retaining adequate mechanical performance.

1. Introduction

Cementation is one of the most widely applied processes for the immobilization of low- and intermediate-level radioactive waste (LILW), valued for its low cost, compatibility with diverse waste streams, radiation stability, and the mechanical strength and chemical durability of the resulting waste form [1–3]. Although the terms solidification and immobilization are often used interchangeably, solidification broadly denotes the conversion of a waste—including liquid streams—into a solid form, whereas immobilization emphasizes the physical fixation and containment of the waste within a stable matrix. The present study focuses on the immobilization function of the cementitious matrix itself, that is, on the integrity of the hardened waste form rather than on the incorporation of any specific waste stream.

For radioactive-waste immobilization, the cementitious matrix is frequently employed as a paste or fine mortar rather than as structural concrete, since coarse aggregates are often undesirable or impractical in conditioning operations. Matrices that lack a coarse-aggregate skeleton, however, are intrinsically more susceptible to shrinkage and cracking. It is well established that, upon drying, cement paste shrinks more than mortar and mortar more than concrete, because rigid aggregate particles restrain the volumetric contraction of the hydrating paste [4,5]. When this contraction is internally or externally restrained, tensile stresses develop, and cracking occurs once these stresses exceed the tensile strength

of the matrix [6]. Therefore, an aggregate-free cementitious immobilization matrix might be more susceptible to loss of macroscopic integrity through cracking during drying and after thermal or aqueous exposure. Representative domestic acceptance requirements include maintenance of wasteform integrity without visible cracking, a minimum compressive strength of 3.44 MPa after 28-d curing, thermal cycling and water immersion test, a leachability index of at least 6, and free water below 0.5 vol% of the wasteform [7,8].

Two compositional approaches were considered in this study. The first is the incorporation of fine mineral powders to modify the hydration and mechanical response of the cementitious matrix. Such fillers are not expected to form major new crystalline hydration products under ambient curing conditions, but their fine particle size can influence hydration and microstructure through physical effects such as heterogeneous nucleation, modification of the spatial conditions for C-S-H growth, and changes in particle packing [9–13]. Depending on the associated water demand, these effects may enhance mechanical performance without necessarily reducing the total porosity of the hardened matrix. The magnitude of these effects depends on the fineness and mineralogy of the filler, so inactive mineral fillers of different types can nonetheless produce distinct responses [12,13]. Accordingly, quartz was selected as a representative siliceous filler for evaluating the physical filler effect [14], whereas magnetite was selected as a high-density filler with potential relevance to radiation-shielding waste forms [15,16]. The second route is the incorporation of a fine aggregate fraction, which restrains the volumetric contraction of the paste directly rather than by densification [17,18]. The two routes act through different mechanisms and need not be mutually exclusive, yet they have rarely been compared within a single immobilization matrix system.

This study examines these two routes, both individually and in combination, in cementitious immobilization matrices. Quartz and magnetite were first evaluated separately as inactive fillers, after which standard sand was incorporated into each filler system at three proportions. The matrices were characterized by compression test, helium pycnometry, X-ray diffractometry (XRD), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS), and their durability was assessed by thermal cycling, water immersion, and leaching tests with reference to waste acceptance criteria (WAC) of the Korean LILW disposal facility [7,8]. This study aimed to examine how the incorporation of inactive fillers and fine aggregate affects compressive strength, density-based porosity, and cracking behavior, and to identify mixture compositions that combine adequate mechanical strength with resistance to visible cracking.

2. Materials and Methods

2.1 Materials

Ordinary Portland Cement (OPC) was used as a binder for all cementitious wasteforms. The standard sand (ISO 679) was used as a fine aggregate [19]. Two additives, quartz (SiO_2 , Junsei, 0.8 μm , 99.9%) and magnetite (Fe_3O_4 , Gojundo Korea, 1 μm , 99%) powders, were used as ultrafine mineral fillers to

examine filler-specific effects on the cementitious matrices, with magnetite additionally selected due to its high density and potential relevance to shielding-oriented wasteforms. 10 g of Cobalt powder (Daejung, 99.5%) was added into each wasteform of matrix 1–4 in fabrication stage for the leaching test as a non-radioactive surrogate for Co-60.

2.2 Specimen Preparation and Curing

Table 1 summarizes the compositions of the ten cementitious matrices, expressed as weight percentages of the total mixture. The sand and cement-only matrices (matrix 1 and 2) were prepared as reference systems. Quartz and magnetite were then incorporated separately as inactive fillers at a fixed cement-to-additive mass ratio (C/A) of 3.0. To evaluate the effect of fine aggregate addition, standard sand was introduced into each filler-containing system at three proportions while maintaining the same C/A ratio (matrix 5–10). The quartz-with-sand and magnetite-with-sand series represent progressively increasing paste fractions and decreasing standard sand fractions to examine the influence of fine aggregate content on the properties of each filler system.

The water-to-cement ratio (W/C) was 0.33 for the cement-only matrix, 0.50 for the magnetite matrix, and 0.60 for the quartz matrix. Among the sand-containing matrices (matrix 5–10), matrices 5 and 8 had slightly higher W/C ratios. The higher W/C of the quartz matrix reflects its greater water demand required to secure adequate workability. Each mixing proportion was selected to ensure adequate workability and integrity for the respective matrix.

Cement, filler, and mixing water were combined using a mechanical mixer. The mixing water was loaded first, followed by the cement and filler, which were added in several increments to ensure homogeneity, and the components were then mixed thoroughly. For fabricating wasteforms to evaluate compressive strength, the cement paste was cast into cylindrical molds ($\varnothing = 50$ mm, $H = 100$ mm) in three layers, each consolidated by tapping to remove entrapped air. All specimens were cured at $24 \pm 2^\circ\text{C}$ and $95 \pm 5\%$ relative humidity for 28 days. After the curing period, all wasteforms were demolded and dried at $24 \pm 2^\circ\text{C}$ and $45 \pm 15\%$ relative humidity.

Table 1
Mixing proportions of the ten cementitious matrices

Matrix name		Aggregate (Standard sand)	Cement (C) (wt%)	Additive (A) (wt%)	Water (W) (wt%)	C/A	W/C
1	Sand	66.7	22.2	-	11.1	-	0.50
2	Cement-only	-	75	-	25	-	0.33
3	Quartz	-	51.7	17.2	31.1	3.0	0.60
4	Magnetite	-	54.5	18.2	27.3		0.50
5	Quartz with sand	63.4	18	6	12.6		0.70
6		42	30	10	18		0.60
7		18.8	42	14	25.2		0.60
8	Magnetite with sand	63.4	18	6	12.6		0.70
9		45	30	10	15		0.50
10		23	42	14	21		0.50

2.3 Test Methods and Characterizations

The cementitious matrices were evaluated with reference to the Korean WAC and the corresponding test methods summarized in Table 2. In addition to the numerical performance criteria, the WAC requires the waste form to maintain macroscopic integrity without visible cracking. The compressive strength was measured according to KS F 2405 [20] at a loading rate of 0.4 ± 0.2 MPa/s. The thermal cycling test was performed in accordance with ASTM B553 [21] that each cycle held the specimen at 60 and -40°C for 1 h with heating and cooling rate of 10°C/h , and the cycle was repeated 30 times. The water immersion test followed the ratio of volume to surface area specified in ANSI/ANS 16.1 [22] method and conducted at 25°C for 90 days. After thermal cycling and immersion, the compressive strength was re-measured and compared with the 28-day strength. The leaching tests were conducted according to ANSI/ANS 16.1 [22,23] using cobalt added wasteforms. At the start of the leaching test, matrix 3 contained visible cracks that had developed during drying after 28-day curing, whereas matrices 1, 2, and 4 remained free of visible cracks. The leachate was sampled each day for 5 days and the cobalt concentrations were analyzed by ICP-MS. Free water was assessed by visual inspection with reference to EPA Method 9095B [24], and no free water was observed. Irradiation test was not conducted since the wasteforms contained no radiation-sensitive organic constituents, and cementitious matrices have generally been reported to retain their properties under irradiation conditions relevant to LILW immobilization [25,26].

Table 2
Waste acceptance criteria and corresponding test methods

Test	Method	Acceptance criterion
Compression test	KS F 2405	≥ 3.44 MPa (500 psi)
Water immersion test	NRC Technical Position on Waste Form Rev. 1	≥ 3.44 MPa (500 psi)
Thermal cycling test	ASTM B553	≥ 3.44 MPa (500 psi)
Irradiation test*	NRC Technical Position on Waste Form Rev. 1	≥ 3.44 MPa (500 psi)
Leaching test	ANS 16.1	Leachability index ≥ 6
Free standing water test	EPA Method 9095B	< 0.5 vol% of wasteform
* Not evaluated in this study		

The physical, mineralogical, and microstructural characteristics of the wasteforms were characterized using helium pycnometer (Quantachrome, UltraPycnometer 1200e), XRD (Bruker D2 PHASER), and SEM-EDS (Hitachi S4800) to investigate the effects of inactive fillers and standard sand on the wasteforms. The dry bulk density of each cylindrical wasteform was calculated from its measured mass and geometric volume, determined from the diameter and height. The specimens were then crushed and pulverized, and their powder density was measured by the pycnometer. The total porosity was derived from the dry bulk density and powder density as follows Eq. (1):

$$P = (1 - \rho_{\text{bulk}}/\rho_{\text{powder}}) \times 100 \text{ Eq. (1)}$$

, where P is calculated total porosity (%), ρ_{bulk} ($\text{g}\cdot\text{cm}^{-3}$) is the dry bulk density determined from specimen mass and geometric volume, and ρ_{powder} ($\text{g}\cdot\text{cm}^{-3}$) is the powder density measured by helium pycnometry.

XRD (Bruker D2 PHASER) analysis was performed to determine whether the incorporation of the filler additives induced the formation of new hydration phases during cement solidification. Because the analysis was intended to compare the crystalline phases present in each mixture and their corresponding peak positions, rather than their absolute or relative intensities, each diffraction pattern was normalized by dividing all intensity values by the maximum intensity of that pattern. SEM-EDS was conducted to examine differences in the microstructure of the matrices with and without standard sand. Fracture surfaces obtained after the compression test were utilized to preserve the original microstructural morphology of the hardened matrices.

3. Results and Discussions

3.1. Visual assessment of cracking behavior

The cracking behavior of the cementitious matrices was visually examined after curing and drying and following thermal cycling or water immersion test. Matrix 1, prepared as a conventional standard sand mortar, served as the reference case for macroscopic integrity. It remained free of visible cracks after 28-day curing and subsequent drying, after 30 thermal cycles or 90 days of water immersion. Because this behavior is expected for a conventional mortar containing a substantial fraction of fine aggregate in the wasteform, matrix 1 is not separately shown in Figs. 1 and 2.

The cement-only matrix (matrix 2) and magnetite-containing matrix (matrix 4) remained free of visible cracks during the initial drying period, whereas the quartz-containing matrix (matrix 3) developed visible surface cracks within one to two days after demolding as marked by red arrows shown in Fig. 1. Thus, among matrices 2–4, the quartz-containing matrix exhibited the greatest structural vulnerability to early drying-induced cracking.

Figure 2 presents visible cracks observed in the cement-only, quartz-containing, and magnetite-containing matrices after thermal cycling or water immersion test. The vulnerability of the aggregate-free matrices became more evident after thermal and aqueous exposure. Representative visible cracks are indicated by red arrows in Fig. 2. Matrix 3 entered these tests with pre-existing drying cracks, whereas matrices 2 and 4 had initially remained crack-free and developed visible cracking only after each test. Considering that the standard sand control (matrix 1) maintained its integrity under the same test conditions, these observations indicate that satisfactory integrity after initial curing and drying does not necessarily ensure resistance to cracking during thermal or aqueous exposure.

The incorporation of standard sand markedly changed this behavior. None of the six sand-blended matrices (matrices 5–10) exhibited visible cracking after 28-day curing and subsequent drying, and no visible cracks were observed after 30 thermal cycles or after 60 days of water immersion (Fig. 3). Particularly informative comparisons can be made at identical W/C ratios. Matrices 6 and 7 remained crack-free at W/C = 0.60, whereas the quartz-only matrix 3 cracked shortly after demolding at the same W/C ratio. Similarly, matrices 9 and 10 remained free of visible cracks at W/C = 0.50, whereas the magnetite-only matrix 4 developed cracks after thermal and aqueous exposure. These comparisons indicate that W/C alone cannot account for the observed cracking behavior and support the beneficial role of the fine-aggregate fraction in restraining macroscopic cracking. The results are consistent with the established restraining effect of aggregate on shrinkage of the cement paste [12,13].

3.2. Phase composition, porosity, and microstructure

Figure 4 shows the XRD patterns of the quartz- and magnetite-containing cementitious matrices after curing. The cement-only matrix (matrix 2) exhibited the characteristic crystalline phases of hydrated Portland cement, including portlandite (CH), ettringite (AFt), monocarboaluminate (Mc), and calcite (Cc), with residual unhydrated clinker phases assigned to alite and belite (C_3S/C_2S). The sand control (matrix 1) was dominated by α -quartz (Q), reflecting the quartz-rich composition of the standard sand, while the characteristic cement hydration phases remained detectable at lower relative intensities. In the quartz-

containing series as shown in Fig. 4(a), the characteristic Q peaks were observed in matrices 3 and 5–7, including the intense peak at approximately $2\theta = 26.6^\circ$, with the same OPC-related phases observed in the reference matrices. In the magnetite-containing series as shown in Fig. 4(b), the characteristic peaks of magnetite (M) were clearly observed in matrices 4 and 8–10, in addition to the quartz peaks originating from standard sand in matrices 8–10. CH, Cc, residual C_3S/C_2S , and minor AFt/Mc peaks were also observed depending on the relative cement content and peak overlap. A broad diffuse background was also observed in the low-angle region and over approximately $2\theta = 20\text{--}35^\circ$, which is characteristic of the amorphous C-S-H gel constituting the principal binding phase of hydrated Portland cement.

The incorporation of either quartz or magnetite did not produce additional crystalline phases that were absent from the reference cementitious matrices. The XRD patterns of the filler-containing matrices could be accounted for by the original filler phases (α -quartz or magnetite), the quartz originating from standard sand, and the crystalline hydration or residual clinker phases already present in the OPC system. Thus, no additional crystalline reaction products were detected as a consequence of quartz or magnetite addition under the curing conditions employed in this study. This observation is consistent with the fillers behaving predominantly as inactive mineral components rather than participating in the formation of new crystalline hydration products. Therefore, the differences in porosity and mechanical performance among the matrices are unlikely to arise from the formation of additional crystalline phases and should instead be considered primarily in terms of physical filler effects, mixture water demand, and the incorporation of fine aggregate. Although broad diffuse scattering attributable to poorly crystalline C-S-H was present in all cement-containing matrices, the XRD patterns do not permit quantitative comparison of the C-S-H content among the different formulations.

The calculated total porosities of the cementitious matrices are summarized in Table 3. The calculated porosities of the standard sand control (matrix 1), cement-only matrix (matrix 2), quartz-containing matrix (matrix 3), and magnetite-containing matrix (matrix 4) were 18.9, 21.8, 32.5, and 28.4%, respectively. Thus, incorporation of the fine mineral fillers did not result in a lower total porosity than that of the cement-only matrix. In particular, the quartz-containing matrix exhibited the highest porosity among the four reference formulations.

Table 3
W/C ratios and calculated total porosities of
the cementitious matrices

Matrix number and name		W/C	P (%)
1	Sand	0.50	18.9
2	Cement-only	0.33	21.8
3	Quartz	0.60	32.5
4	Magnetite	0.50	28.4
5	Quartz with sand	0.70	22.8
6		0.60	22.3
7		0.60	19.6
8	Magnetite with sand	0.70	17.2
9		0.50	15.6
10		0.50	21.4

The comparatively high porosities of the filler-containing matrices should be considered with the water required to obtain adequate workability. Matrix 3 was prepared at $W/C = 0.60$, substantially higher than $W/C = 0.33$ for the cement-only matrix, while matrix 4 was prepared at $W/C = 0.50$. The higher water contents provide a greater volume of initially water-filled space, part of which remains as capillary pore space after hydration and drying. Accordingly, the relatively high porosity of the quartz matrix is consistent with its greater water demand rather than with a filler-induced densification of the hardened matrix. Because filler type and W/C were varied simultaneously, however, the individual effects of filler mineralogy and water content cannot be quantitatively separated from the present dataset. The calculated porosities of the remaining sand-containing formulations are also reported in Table 3, but no general trend in porosity across the entire sand-containing series was inferred because their mixture proportions and W/C ratios varied among formulations.

An important implication of these results is that total porosity alone does not account for the subsequent mechanical response of the matrices [27]. As discussed in Section 3.3, the quartz-containing matrix developed the highest 28-day compressive strength despite having the highest calculated porosity. Therefore, its high compressive strength cannot be attributed to reduced total porosity or matrix densification. Combined with the XRD results, this observation provides a basis for considering physical filler effects when interpreting the strength development of the ultrafine quartz-containing matrix.

At the same W/C ratio of 0.60, matrix 7 exhibited a more spatially continuous distribution of the major matrix-forming elements than matrix 3, with fewer regions showing weak elemental signals as shown in

Fig. 5. This observation suggests a lower abundance of open voids on the fracture surface of matrix 7. This qualitative difference is consistent with the decrease in calculated total porosity from 32.5% for matrix 3 to 19.6% for matrix 7. Because both quartz powder and standard sand are SiO_2 -rich, however, their individual contributions could not be distinguished from the Si distribution alone. It should also be noted that the paste region immediately surrounding aggregate particles generally differs in porosity and hydrate morphology from the bulk paste [28], which may contribute to the local heterogeneity observed on the fracture surfaces.

Figure 6 presents a similar difference observed in the magnetite-containing system. Matrix 4 and 10 both contained magnetite and had the same W/C ratio of 0.50, allowing a direct comparison of the microstructural differences associated with incorporation of standard sand in the wasteform. SEM observations showed that matrix 10, which contained standard sand, exhibited comparatively broader and more continuous cementitious regions on the fracture surface, with fewer distinct open voids than matrix 4. EDS elemental mapping showed localized Si-rich regions in matrix 10, which is consistent with the presence of quartz-rich standard sand within the Fe-containing cementitious matrix. These SEM-EDS observations are consistent with both a more continuous local microstructure in the sand-containing matrix and the lower calculated total porosity of matrix 10 (21.4%) compared with matrix 4 (28.4%).

3.3. Compressive strength

Figure 7(a) presents the compressive strengths of matrices 1–4 after 28-day curing and drying, thermal cycling, and water immersion. All matrices exhibited compressive strengths sufficiently above the WAC minimum of 3.44 MPa. Thus, although all formulations satisfied the numerical compressive-strength criterion, compressive strength alone did not distinguish the matrices that exhibited visible cracking.

The most notable result was obtained for the quartz-containing matrix. Matrix 3 exhibited the highest 28-day compressive strength (46.3 MPa) despite its substantially higher W/C ratio (0.60) than the cement-only matrix (0.33). As shown in Section 3.2, matrix 3 also exhibited the highest calculated total porosity among matrices 1–4. Its comparatively high compressive strength therefore cannot be explained by reduced total porosity or matrix densification. Furthermore, XRD analysis revealed no additional crystalline reaction products associated with quartz incorporation. Previous studies have shown that finely divided inert particles, including quartz, can influence cement hydration through physical filler effects such as heterogeneous nucleation and changes in the spatial conditions for hydrate growth [9,11]. The high compressive strength of matrix 3 is therefore consistent with a beneficial physical filler effect of the ultrafine quartz, although the magnitude of this contribution cannot be quantitatively isolated from the effects of the other mixture variables. This interpretation is also consistent with the observations of Tavares et al. [14], who reported that quartz-containing cementitious composites could retain mechanical performance despite increased porosity.

The magnetite-containing matrix exhibited a different mechanical response. Matrix 4 developed a 28-day compressive strength of 22.5 MPa, lower than those of both the cement-only and quartz-containing

matrices but still well above the acceptance criterion. Thus, the incorporation of an inactive mineral filler did not produce a uniform strengthening response, and the resulting mechanical performance depended on the filler characteristics as well as the associated water demand and mixture proportions.

After thermal cycling, matrices 1, 2, 3, and 4 retained 84, 75, 39, and 92% of their respective 28-day compressive strengths. After 90 days of water immersion, the corresponding strength retentions were 99, 105, 50, and 102%. The maintenance or slight increase in compressive strength observed for the sand control, cement-only, and magnetite-containing matrices after immersion is consistent with continued hydration under sustained water availability. Residual C_3S/C_2S phases were detected by XRD after the initial curing period as shown in Fig. 4, providing a source for further hydration during prolonged immersion. In contrast, the quartz-containing matrix exhibited a substantial reduction in strength after both thermal cycling and immersion, consistent with the presence of pre-existing cracks, which likely contributed to the loss of load-bearing integrity. Nevertheless, its residual strengths of 18.1 and 23.1 MPa remained substantially above 3.44 MPa.

The post-exposure compressive strength results did not necessarily correspond to the macroscopic cracking behavior. As shown in Fig. 2, the cement-only and magnetite-containing matrices developed visible cracks after environmental exposure despite retaining substantial compressive strength, and their strengths after immersion were comparable to or slightly higher than their respective 28-day values. The quartz-containing matrix likewise remained well above the numerical strength criterion despite its pronounced visible cracking. These results suggest that satisfaction of the numerical compressive-strength requirement alone does not ensure compliance with the overall WAC, because the presence of visible cracking itself constitutes a failure of the wasteform integrity requirement.

The incorporation of standard sand into the quartz- and magnetite-containing systems produced the 28-day compressive strengths shown in Fig. 7(b). Matrices 7 and 10 exhibited the highest strengths within the quartz- and magnetite-containing sand-blended series, reaching 42.0 and 36.8 MPa, respectively, while the remaining compositions also maintained strengths above the WAC. Because the paste fraction, standard-sand fraction, and W/C ratio were varied simultaneously among matrices 5–10, the differences in compressive strength cannot be attributed solely to the standard-sand content. Importantly, however, adequate mechanical strength was maintained while all six sand-blended matrices remained free of visible cracks after drying and thermal cycling and, at the time of observation, after 60 days of water immersion as shown in Fig. 3. The addition of fine aggregate therefore improved resistance to macroscopic cracking without compromising the compressive strength required for WAC.

3.4. Leaching behavior

The leaching behavior of the cementitious matrices 1–4 was evaluated using cobalt powder as a non-radioactive surrogate for Co-60 incorporated at a conservatively high loading. Table 4 summarizes the cobalt concentrations measured in the leachates collected over five consecutive sampling intervals with the corresponding leachability indices calculated according to ANSI/ANS 16.1. Overall, cobalt release

from all four matrices was very limited. Most leachate samples contained cobalt at concentrations below the analytical detection limit of 1 ppb. For concentrations below the analytical detection limit, 1 ppb was conservatively used for calculation of the leachability index. Only a few measurable cobalt concentrations were observed. A concentration of 2 ppb was detected in the second-day leachate of matrix 1, while concentrations of 2 ppb and 1 ppb were detected in the first-day leachate of the magnetite-containing matrix and the fourth-day leachate of matrix 1, respectively. No persistent increase in cobalt concentration with leaching time was observed. For samples in which the cobalt concentration was below the detection limit, a concentration of 1 ppb was conservatively used for the leachability index calculation. Under this assumption, the calculated leachability indices ranged from 17.44 to 17.66, all well above the acceptance criterion of 6. The relatively narrow range of leachability indices indicates that the differences in matrix composition had no discernible effect on cobalt release under the test conditions [29]. Notably, matrix 3 exhibited visible cracks before the leaching test, whereas matrices 1, 2, and 4 remained crack-free at the start of the test. Nevertheless, the leachability index of matrix 3 was comparable to those of the other matrices, indicating that the visible cracking observed in matrix 3 did not produce a discernible increase in cobalt release under the present test conditions.

The leaching results should be considered with the mechanical and visual-integrity assessments rather than as an independent measure of overall wasteform performance. The uniformly high leachability indices indicate that cobalt retention was not the limiting performance criterion for the matrices. In contrast, substantial differences were observed in resistance to visible cracking and post-exposure mechanical behavior. The present results imply that sufficient compressive strength and leaching resistance do not necessarily ensure macroscopic structural integrity. Therefore, cracking behavior should be considered with conventional strength and leaching criteria when evaluating cementitious matrices.

Table 4
Cobalt concentration in leachates and calculated leachability indices of matrices 1–4

Matrix	Leachate concentration (ppb)					Leachability index
	1-Day	2-Day	3-Day	4-Day	5-Day	
Sand (Matrix 1)	< 1	2	< 1	1	< 1	17.49
Cement-only (Matrix 2)	< 1	< 1	< 1	< 1	< 1	17.66
Quartz (Matrix 3)	< 1	< 1	< 1	< 1	< 1	17.57
Magnetite (Matrix 4)	2	< 1	< 1	< 1	< 1	17.44

4. Conclusion

This study investigated the effects of ultrafine quartz and magnetite fillers and standard-sand incorporation on the performance of cementitious immobilization matrices. XRD analysis showed no detectable formation of additional crystalline reaction products associated with either filler, indicating

that quartz and magnetite behaved predominantly as inactive mineral components under the curing conditions examined. The aggregate-free filler-containing matrices (matrices 3 and 4) did not exhibit reduced total porosity relative to the cement-only matrix. Nevertheless, the quartz-containing matrix developed the highest 28-day compressive strength of 46.3 MPa, indicating that its strength development could not be explained by matrix densification alone and was consistent with a beneficial physical filler effect.

Although matrices 1–4 satisfied the numerical compressive-strength and cobalt-leachability criteria, matrices 2–4 developed visible cracks during drying or subsequent thermal and aqueous exposure and therefore failed to satisfy the crack-free integrity requirement. This suggests that numerical strength and leaching criteria alone do not ensure overall wasteform acceptance. This indicates that numerical strength and leaching criteria alone do not necessarily ensure preservation of macroscopic wasteform integrity. In contrast, all sand-containing matrices remained free of visible cracks after drying and thermal cycling and through 60 days of water immersion while maintaining adequate 28-day compressive strength. Comparisons at identical W/C ratios, together with SEM–EDS and porosity observations, support the beneficial role of fine aggregate in improving matrix continuity and restraining macroscopic cracking. Matrices 7 and 10 combined the highest strengths within their respective sand-containing filler series with crack-free behavior. Therefore, it is expected that fine-aggregate incorporation provides an effective approach for improving the structural integrity of filler-containing cementitious immobilization matrices without sacrificing the required compressive strength.

Declarations

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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Author Contributions

Writing – original draft: [Dong Seok Lim]; Writing – review and editing: [Sungjune Sohn, Min Ho Lee]; Analysis: [Sungjune Sohn]; Conceptualization: [Jihoon Kang, Dong Seok Lim, Woo Young Jung]; Supervision: [Hyun Chul Lee].

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Figures

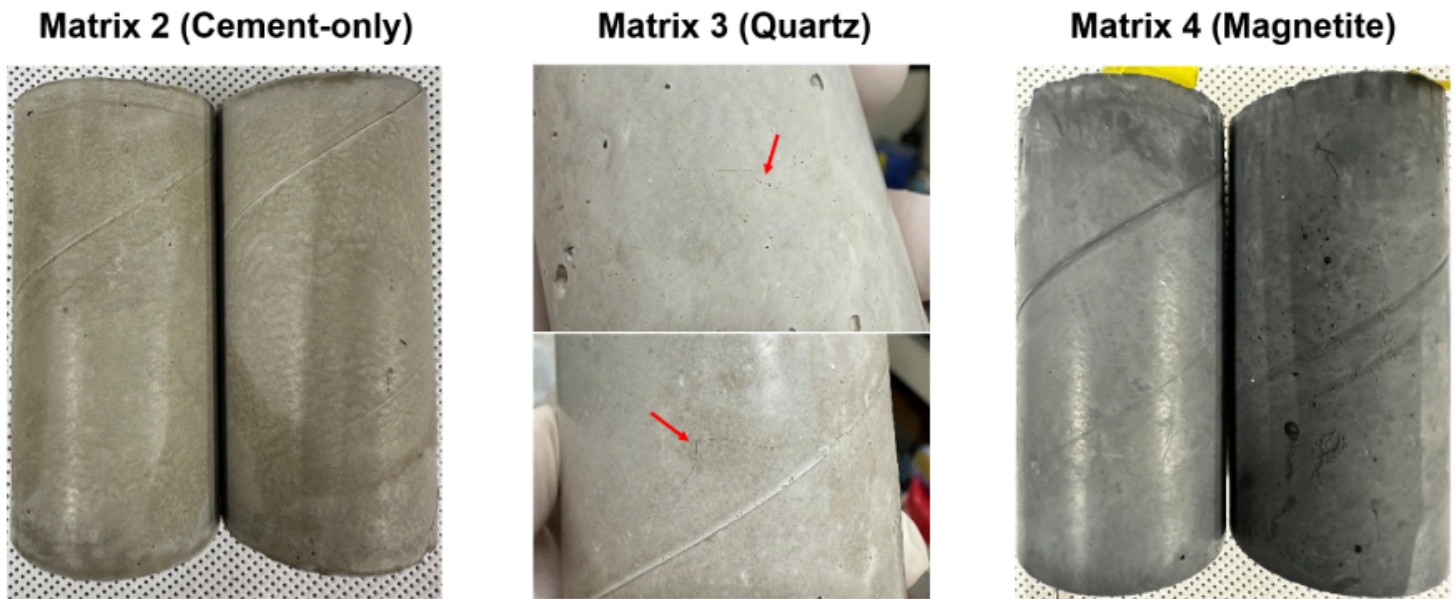


Figure 1

Visual appearance of the aggregate-free cementitious matrices after 28-day curing and drying

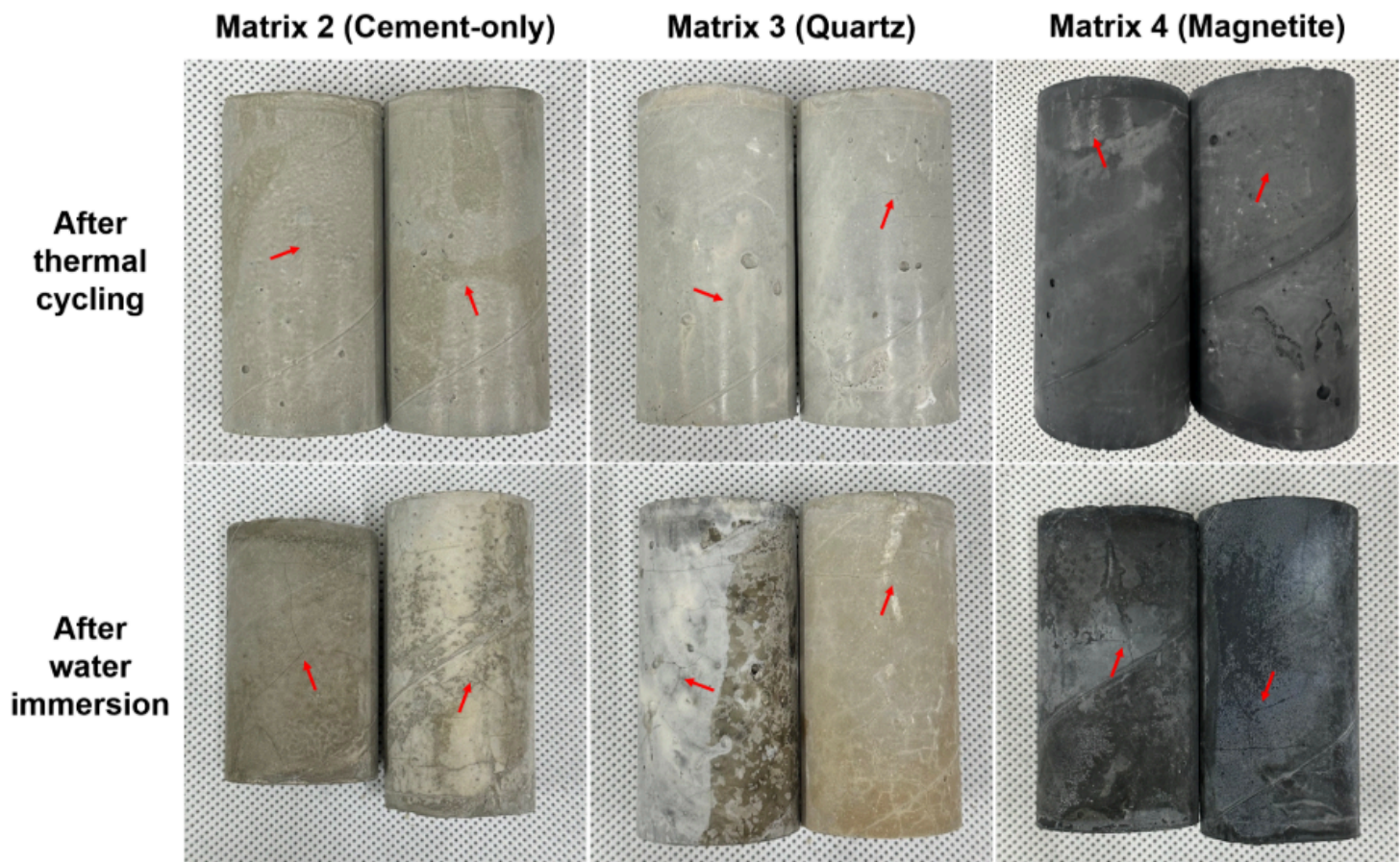


Figure 2

Visual appearance of matrices 2-4 after thermal cycling and 90-day water immersion tests

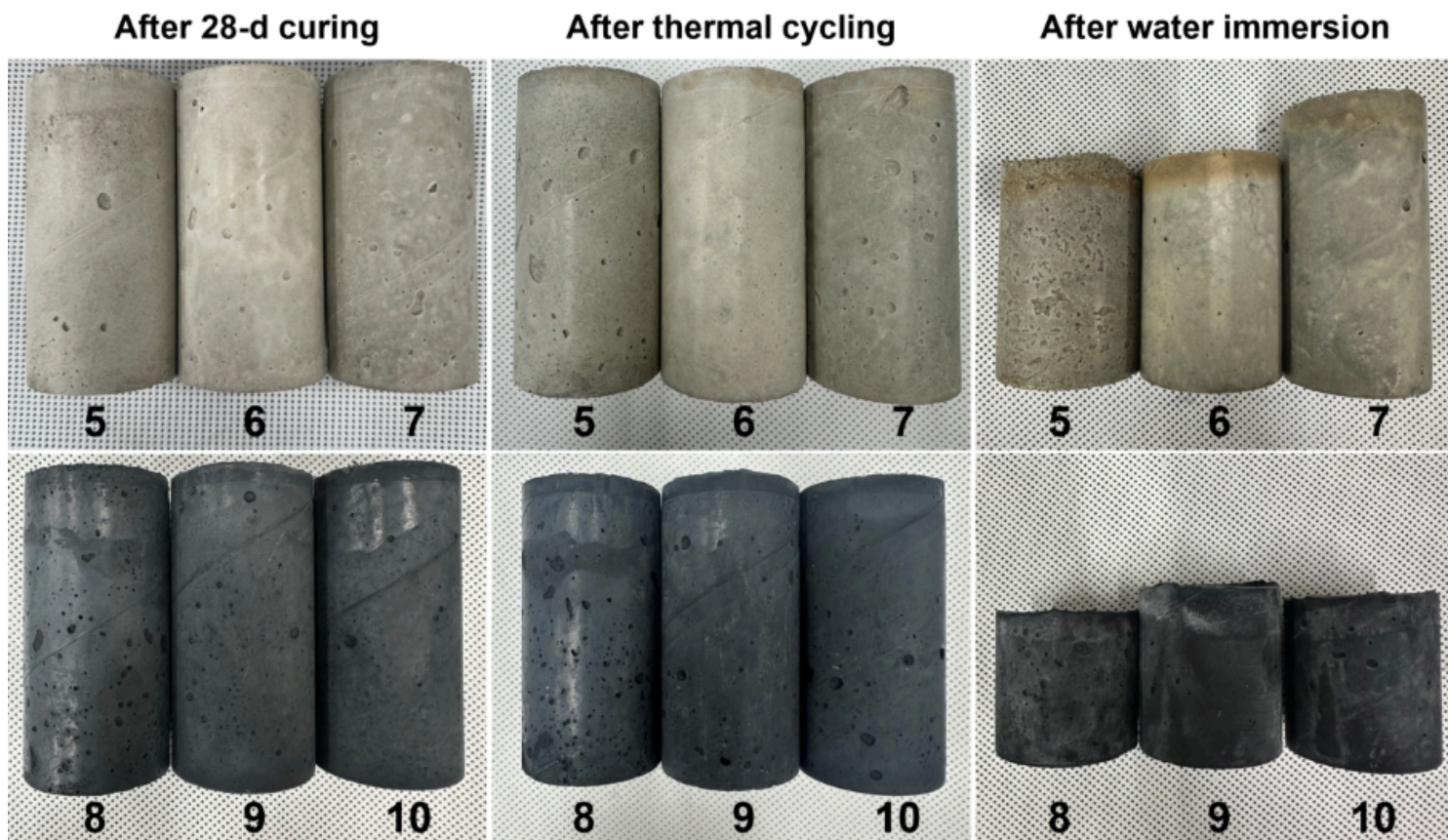


Figure 3

Visual appearance of the sand-blended matrices (5–10) after 28-day curing and drying (left), thermal cycling (middle), and 60-day water immersion (right)

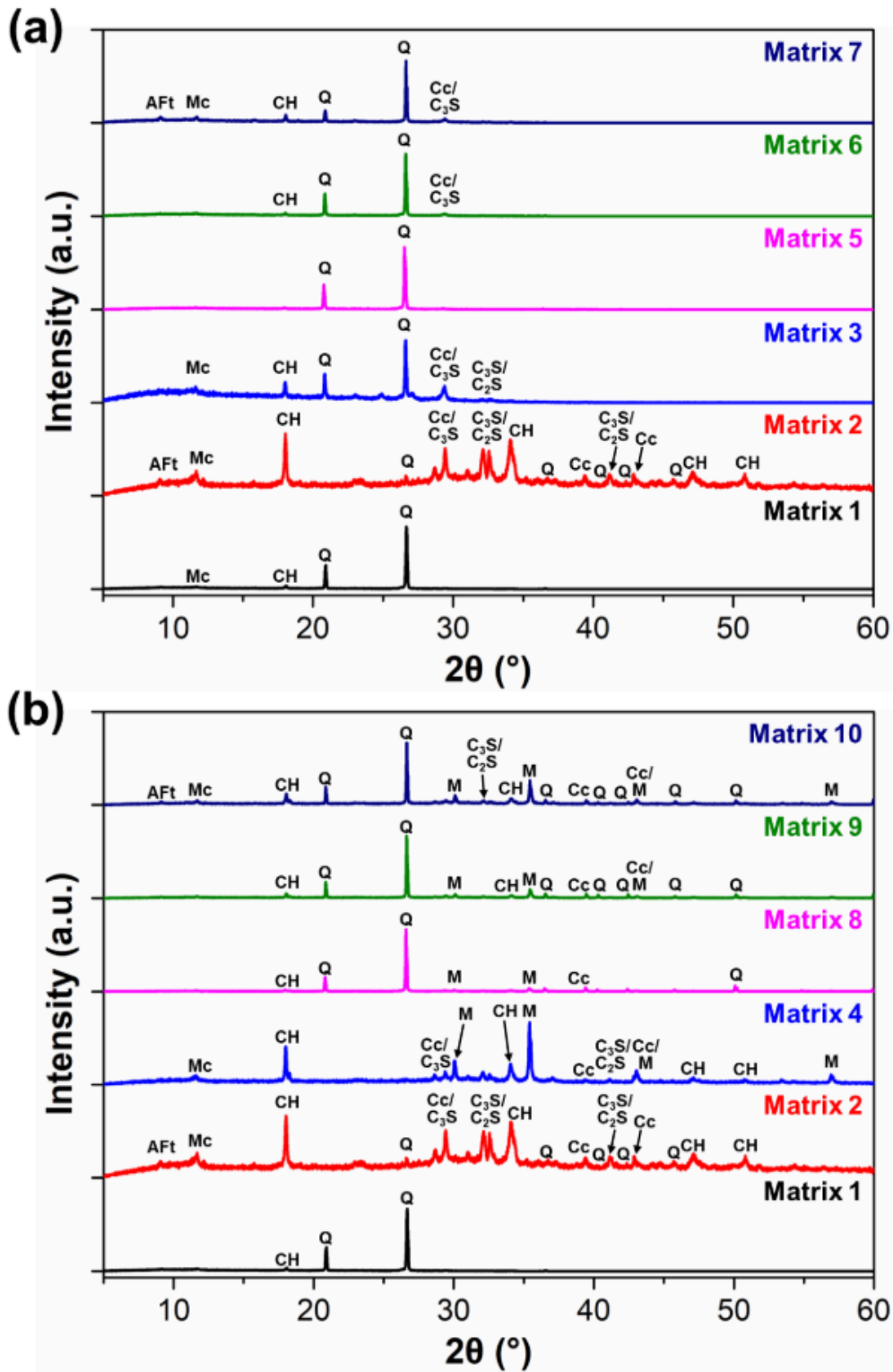


Figure 4

XRD patterns of the cementitious matrices after 28 days of curing: (a) quartz-containing matrices and (b) magnetite-containing matrices (Q: α -quartz; M: magnetite; CH: portlandite; AFt: ettringite; Mc: monocarboaluminate; Cc: calcite; C₃S/C₂S: residual clinkers)

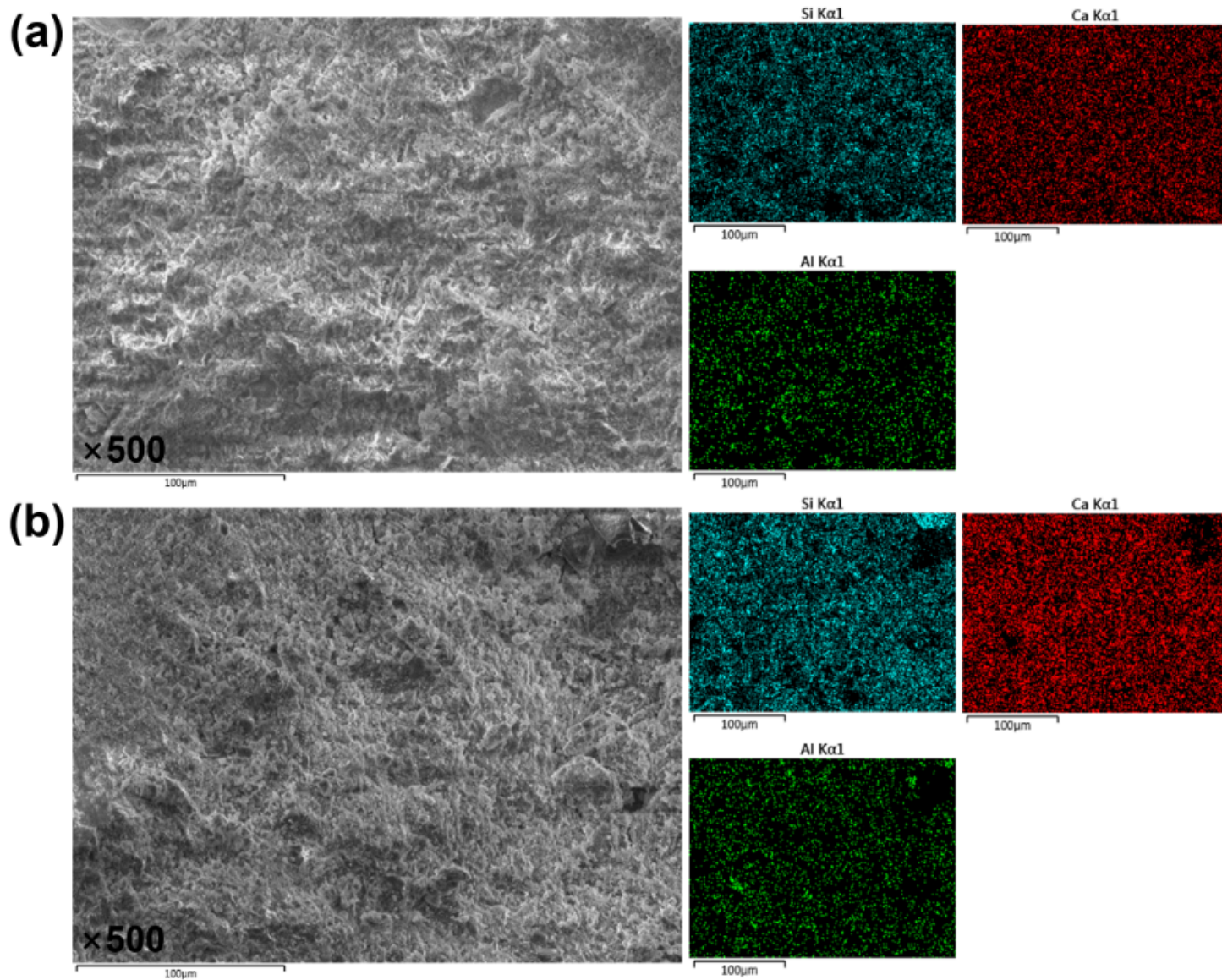


Figure 5

SEM-EDS analysis of the fracture surfaces of (a) matrix 3 and (b) matrix 7

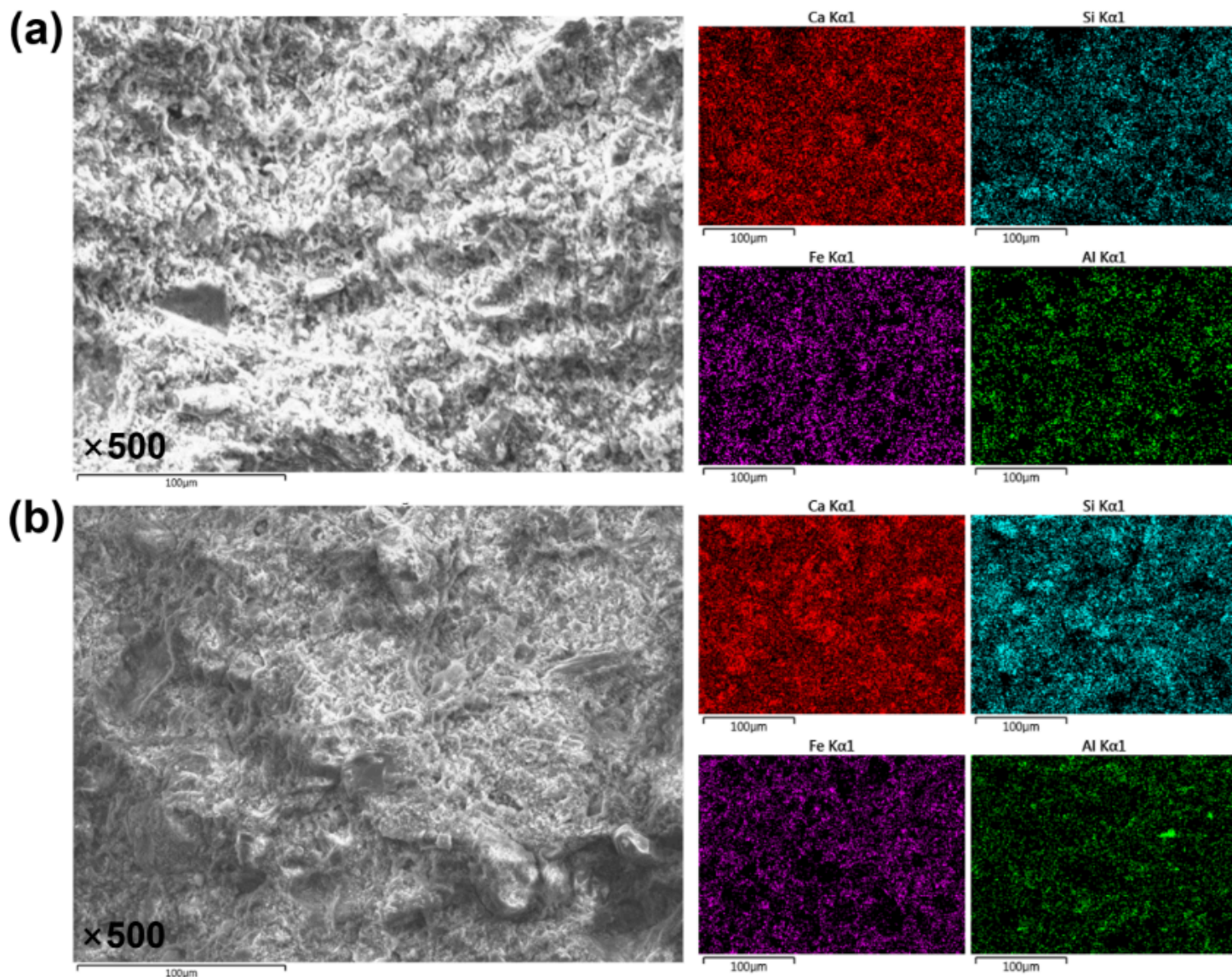


Figure 6

SEM-EDS analysis of the fracture surfaces of (a) matrix 4 and (b) matrix 10

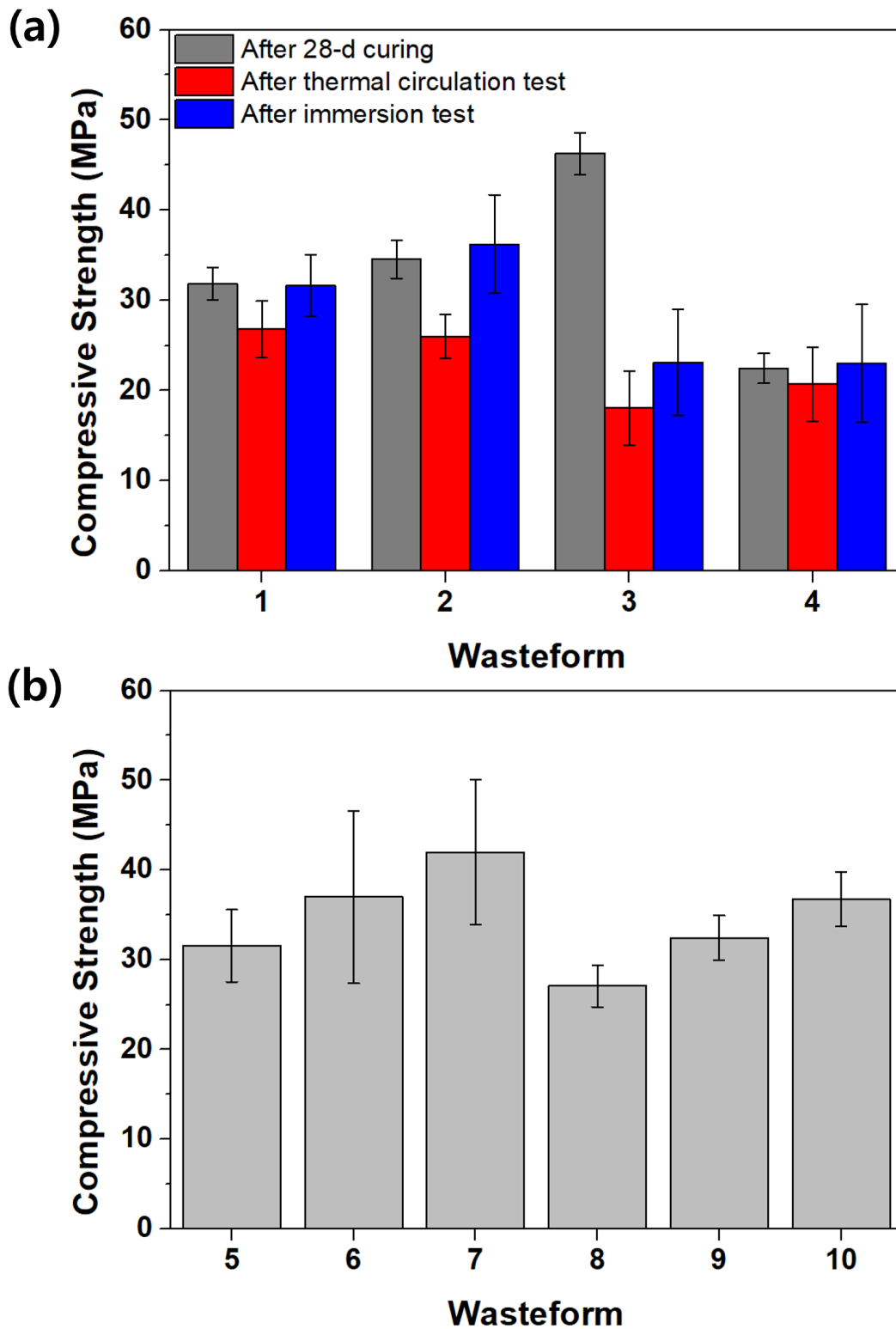


Figure 7

Compressive strength of (a) wasteforms (1–4) measured after 28-d curing, thermal cycling test, and water immersion test, and (b) cement wasteforms (5–10) measured after 28-d curing