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Immobilization of heavy metals in natural zeolite-blended cement pastes

Martin Vyšvařil*, Patrik Bayer

Brno University of Technology, Faculty of Civil Engineering, Institute of Chemistry, Žitkova 17, 602 00 Brno, Czech Republic

Abstract

The toxic wastes containing heavy metals are conducive to serious environmental problems at the contamination of water, air and soil. The ability of alumino-silicate systems to immobilize heavy metals from hazardous wastes by solidification process has been investigated since 1990s. Likewise, the efficiency of zeolites to fix heavy metals in their frameworks has relatively long been known. This paper deals with the investigation of efficiency of natural zeolite-blended cement pastes for the immobilization of heavy metals. Natural zeolite was used to partially replace ordinary Portland cement (OPC) at rates of 0% and 20% by weight of a binder and soluble heavy metal salts were added to a mixing water in an amount of 1% and 5% by weight of the binder. The flexural and compressive strength of the cement pastes were investigated, while the leachability of the heavy metals was determined. Additionally, scanning electron microscopy was performed to investigate the microstructure of the cement pastes, while the pore size distribution was analyzed with mercury intrusion porosimetry. The results indicated that the flexural and compressive strengths of the pastes containing 20 wt.% of natural zeolite were higher than those with OPC alone. It was also found out that the effectiveness in reducing the leachability of Ba, Cd, Cu, Ni and Pb was better for the natural zeolite-blended cement pastes.

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* Corresponding author. Tel.: +420-541-147-639; fax: +420-541-147-667.

E-mail address: vysvaril.m@fce.vutbr.cz

1. Introduction

With the increasing contamination of the natural environment, the problem of heavy metal immobilization becomes more and more significant. Various technologies have been developed to render a waste non-toxic or to reduce the potential for the release of toxic species into the environment. One of these technologies is solidification/stabilization (S/S) by cementitious binders. High pH of cement is effective in immobilizing many toxic metals by precipitation and sorption reactions and encapsulation of contaminated waste or soil [1,2]. Ordinary Portland cement (OPC) is widely used in these stabilization techniques due to its commercial availability and low cost. However, supplementary cementing materials such as granulated blast furnace slag, coal fly ash, condensed silica fume, rice husk ash and natural pozzolans are often used to replace OPC in S/S of wastes.

Slag-based cement effectively stabilizes chromates [3], which suggests that Cr^{VI} is reduced to Cr^{III} . The use of slag in cementitious binders can also greatly decrease the extracted amount of inorganic Hg compounds [3]. Many laboratory research projects and commercial applications have used Portland fly ash cement to stabilize/solidify hazardous, radioactive and mixed wastes [4,5]. A Portland cement/fly ash binder can be successfully used to solidify a heavy metal sludge containing Cd, Cr, Cs, Hg, Ni and Pb [5,6,7]. Other laboratory results [8] have indicated that the use of silica fume as an admixture in cement binder decreases the diffusion coefficient of contaminants very significantly, especially for organic contaminants, chromium and selenium [9,10]. Some results indicate that the use of silica fume is more effective than fly ash. Various investigators have used a cement-clay matrix to immobilize heavy metals in the composites, especially a cement-bentonite clay matrix [10,11], or a cement-kaolinite matrix [12]. Illite clay has proven to be an effective additive in cementitious waste forms for retarding the release of the soluble radioisotope ^{137}Cs [13].

Several natural pozzolans such as zeolites, calcined clays and volcanic ashes are used for production of natural pozzolan cements [14]. Only few publications can be identified on the direct use of blended or interground natural pozzolan cements for S/S. However, zeolites and several clay minerals have been widely used as sorbents for certain heavy metals [15–18]. Natural zeolites are microporous crystalline aluminosilicates containing clinoptilolite, with approximate empirical formula $(\text{Ca}, \text{Fe}, \text{K}, \text{Mg}, \text{Na})_{3-6}\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot 24\text{H}_2\text{O}$, as the main mineral component. The structure of clinoptilolite is based on a 3-dimensional skeleton made of silicon tetrahedrons interconnected by oxygen atoms with a part of silicon atoms replaced by aluminum atoms. It forms through the devitrification of volcanic ash in lake and marine waters. It is the most studied of all zeolites and is widely regarded as the most useful. Clinoptilolite has a particularly high cation exchange capacity which provides many useful properties, mainly in chemical engineering as catalyst support [19], molecular sieves [20], or sorbents [21]. In civil engineering, their utilization as pozzolans dates back already to ancient times when the mixture of zeolites containing tuff and lime was used as hydraulic binder [22].

Ch. Napia et al. investigated the properties of solidified waste using OPC containing synthesized zeolite ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$) and natural zeolite (clinoptilolite) as a binder [23]. They concluded that the use of zeolites to partially replace (20% and 40%) OPC as a solidification binder produced solidified waste with lower strength. However, it is more effectiveness in terms of leachability of Ni, Cr, Cu and Zn, than the use of OPC alone. The application of natural zeolite resulted in a better outcome than using synthesized zeolites.

Y.S. Ok et al. conducted studies to determine whether a granular material, formulated by mixing of zeolite with OPC, has a satisfactory efficiency for heavy metal removal from aqueous solutions [24]. Column experiments demonstrated that the material was more efficient and had a higher sorptive capacity than activated carbon for removing Cd, Cu, Pb and Zn from industrial wastewater.

W. Mozgawa et al. presented the results of application of natural clinoptilolite for immobilization of heavy metal cations (Ag^+ , Pb^{2+} , Cd^{2+} and Cr^{3+}) from aqueous solutions and used zeolite to prepare autoclaved new building composites with relatively low bulk density (about 1.35 g/cm^3) and with the compressive strength on maximum value about 40 MPa [25]. The influence of heavy metal cations on the compressive strength values was insignificant (except for the Cr^{3+} ions). Amounts of Ag^+ , Pb^{2+} and Cd^{2+} washed out with water from the prepared material were imperceptible.

The findings indicate that the natural zeolite (clinoptilolite) can be used as a cement replacement not only for its pozzolanic properties, but also as an effective adsorbent of heavy metals. This work presents applicability of natural zeolite to a mixture with OPC in order to immobilize heavy metals from a mixing water. In the work, tests of natural

clinoptilolite application for the sorption of Ba^{2+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Sr^{2+} cations have been conducted. The flexural and compressive strength were investigated for prepared cement pastes, while the leachability of the heavy metals was determined by inductively coupled plasma mass spectrometry (ICP-MS). Additionally, scanning electron microscopy (SEM) was performed to investigate the microstructure of the cement pastes, while the pore size distribution was analyzed with mercury intrusion porosimetry (MIP).

2. Materials and methods

The specimens ($20 \times 20 \times 100$ mm) were prepared from OPC (CEM I 42.5 R; specific surface area $360 \text{ m}^2 \cdot \text{kg}^{-1}$) as the main binder (OPC). In the second case (ZEO), a 20% part of cement was replaced by natural zeolite with a specific surface area $227 \text{ m}^2 \cdot \text{kg}^{-1}$. The chemical compositions of the initial materials are given in Table 1. The mineralogical composition of natural zeolite determined by XRD using the Rietveld method is presented in Table 2, its pozzolanic activity as measured by the Chapelle test was $0.7425 \text{ g CaO per 1 g of zeolite}$ and its average particle size was $35 \text{ }\mu\text{m}$. Dry mixture of cement and zeolite was taken as the binder and the cement pastes were prepared with the water to binder (w/b) ratio of 0.4. Heavy metals were added to the mixing water in the form of soluble salts ($\text{Ba}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$). Dosing of salts was carried out at rates of 1% and 5% of heavy metal by weight of the binder. The 5% addition of heavy metal was used only for those of heavy metals, for which positive results were achieved in the case of 1% addition.

The test specimens were demolded after 24 hours and placed on a grating above the water level in a plastic box for another 27 days. After this period, flexural strengths of the samples were determined using a standard three-point-bending test and compressive strengths were measured on the far edge of both residual pieces obtained from the flexural test according to CSN EN 196-1. The flexural and compressive strengths were obtained for 9 samples of each mixture. A study of pore structures of the samples included the determination of total porosity and pore size distribution via high pressure MIP using a Micromeritics PoreSizer 9310 that can generate a maximum pressure of 207 MPa and can evaluate a theoretical pore diameter of $0.006 \text{ }\mu\text{m}$. The microstructure of samples was observed using a MIRA3 (TESCAN) scanning electron microscope equipped with an EDX probe. The metal leaching from the samples was performed according to CSN EN 12457-2. The samples were crushed to reduce the particle size to less than 10 mm. The crushed sample was extracted using a deionized water in a volume with a weight equal to 10 times the weight of the sample. The extraction vessels were rotated in an end-over-end manner at 10 rpm for 24 h. The leachate was filtered through a $0.45 \text{ }\mu\text{m}$ membrane filter to remove suspended solids and then it was used for the determination of the metals present in the leachate by ICP-MS.

Table 1. The chemical composition of portland cement and natural zeolite (mass %).

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	LOI
cement	61.48	21.26	5.08	3.64	2.42	0.86	0.12	0.91	0.07	0.29	4.17
zeolite	3.24	67.30	11.97	1.40	0.11	0.75	0.43	3.28	0.04	0.14	11.44

Table 2. The mineralogical composition of natural zeolite (mass %).

	Clinoptilolite	Cristobalite	Quartz	Illite + Mica	Feldspar (albite)	Amorphous phase
zeolite	44.5	9.2	3.5	5.6	2.6	34.5

3. Results and discussion

3.1. Flexural and compressive strength

The metals may react with calcium hydroxide to produce insoluble compounds as a form of metal hydroxide; this mechanism inhibited the hydration and decreased the strength of the cement pastes, especially when the

concentration of metal was more than 0.3% by weight [26,27]. The strength of pastes with higher amount of heavy metals could be very low due to the inhibition of the cement reactions by the metal ions. Fig. 1. compares flexural and compressive strengths in the cement pastes in relation to the cement replacement by natural zeolite and a type of added heavy metal. Flexural strengths of the pastes with natural zeolite (ZEO) showed a slight improvement in comparison with OPC pastes except for the barium and mercury ions. The biggest difference in flexural strength was indicated in the pastes with 1% Cu addition. In this case, the ZEO sample achieved a double value of the strength than the OPC sample. The lowest flexural strength were detected in pastes with Cd^{2+} ions. The trend of compressive strengths was slightly different from the flexural one. The compressive strengths of the ZEO pastes were mostly similar to OPC pastes. But a large difference in strength was observed in pastes with Ba^{2+} ions. It was not possible to determine the strengths of pastes with 5% addition of Cr because of their disintegration during the storage. Generally, it was observed that the strength of cement paste decreased when the amount of added heavy metal increased, which is in agreement with the solidification/stabilization of plating waste [23].

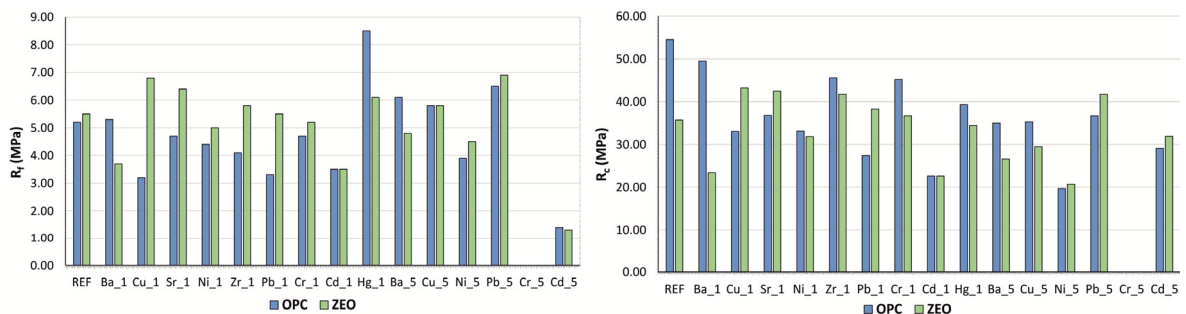


Fig. 1. Flexural and compressive strengths of cement pastes with the 1% and 5% addition of heavy metals.

3.2. Pore structure

The incorporation of natural zeolite decreased the total porosity of the cement pastes as compared with the OPC pastes, except for that of Ba and Cd addition, see Fig. 2. The variances in the total porosity was just infinitesimal, with exception of Cu^{2+} ions. This significant difference in total porosity between OPC and ZEO paste is reflected also in the flexural strength properties. It can be observed that the obtained strengths and porosities correlate with each other. The strength increased, while the total porosity of appropriate cement paste decreased.

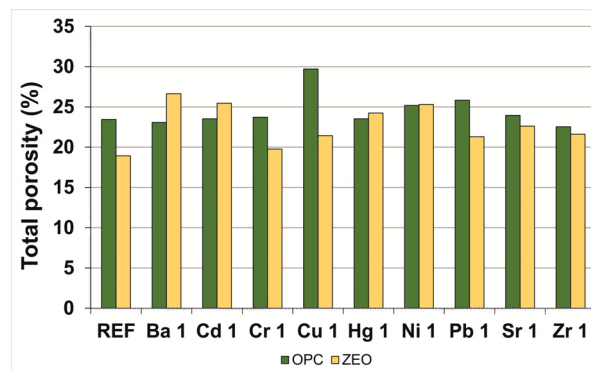


Fig. 2. Total porosity of cement pastes with the 1% addition of heavy metals.

The relationship between the pore diameter and incremental pore volume of the cement pastes at 28 days is depicted in Fig. 3. All investigated samples were represented by pores with a diameter of less than 1 μm . It was found that the OPC pastes with Cr^{3+} , Cu^{2+} , Ni^{2+} and Pb^{2+} ions contained pores with discrete diameters. The pores in OPC pastes with Cu^{2+} , Ni^{2+} and Pb^{2+} had a diameter of 1 μm and 0.1 μm , whereas the OPC paste with Cu^{2+} ions was the most porous paste. The OPC paste with Cr^{3+} ions contained the pores with a diameter of 1 μm and medium capillary pores with a diameter below 0.5 μm . Pore structures of the other OPC pastes were formed by pores with diameters mainly of 0.1–0.5 μm . Pore size distribution in ZEO pastes was slightly different. The ZEO pastes with Cu^{2+} , Zr^{2+} ions and without added heavy metal included only the pores with a diameter of 0.1 μm . The pore structure of ZEO paste with Ba^{2+} ions was represented by significantly higher proportion of pores with a diameter of 1 μm , which affected the strengths of this paste. The ZEO paste with Cr^{3+} ions contained again the smallest pores. The results showed that the blended cement paste containing zeolite presented a smaller pore size than the Portland cement paste.

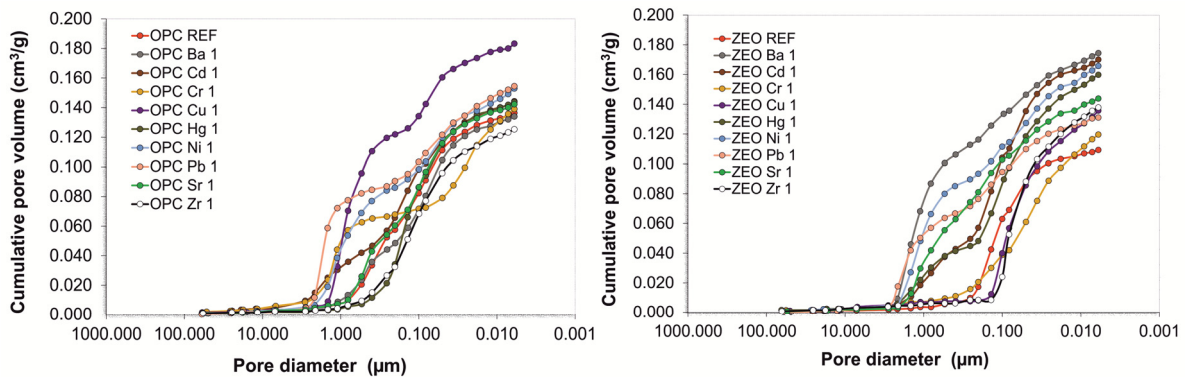


Fig. 3. Pore-size distribution of cement pastes with the 1% addition of heavy metals.

3.3. Microstructure analysis by scanning electron microscopy (SEM)

The microstructure morphology of the fractured surface was determined by SEM for all investigated samples at 28 days, but due to very similar microstructure of the samples, only 3 SEM images are presented in Fig. 4. Image A represents a microstructure of the reference sample with 20% of natural zeolite. In this image, the typical microstructure of cement paste can be observed – large crystals of portlandite, amorphous calcium silicate hydrates (C-S-H) and needle crystals of ettringite. Image B presents a microstructure of the ZEO paste with Cd^{2+} ions. Almost all investigated pastes with the addition of heavy metals showed similar microstructure represented in this image. The absence of ettringite was characteristic for these pastes. Image C illustrates a microstructure of the ZEO paste with Ni^{2+} ions, which was evidently different from the others. The enormous amount of calcite in untypical radial structures was observed here. By mapping the chemical-element distribution using EDX SEM, heavy metals were located in amorphous matrix and no crystalline structures with heavy metals were detected as well as the presence of the locations rich in particular heavy metal. It can be said that the incorporation of monitored heavy metal ions in natural zeolite-blended cement pastes reduces the amount of ettringite in these pastes but otherwise does not cause significant modifications in their microstructure, except for Ni^{2+} ions.

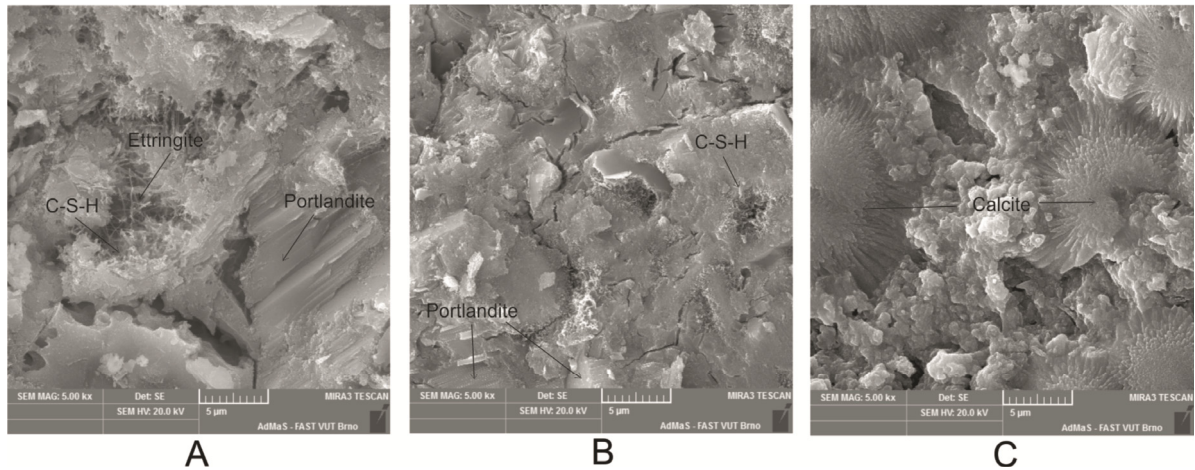


Fig. 4. SEM images of typical microstructure of investigated cement pastes; A – ZEO REF, B – ZEO Cd; C – ZEO Ni.

3.4. Leaching analysis

The concentrations of heavy metals leached from the cement pastes at 28 days are presented graphically in Fig. 5. It is obvious that natural zeolite-blended cement pastes are not suitable to immobilize Hg^{2+} , Sr^{2+} and Zr^{2+} ions as resulted from higher concentration of these metals in ZEO pastes leachates compared to OPC. On the other hand, the addition of natural zeolite effectively reduces the leaching amount of Ba, Cr, Cu, Ni and Pb from cement pastes containing 1% of heavy metals. Even in the case of 5% content of heavy metals, the effectiveness in reducing the leachability of Cd, Cu, Ni and Pb is better for the natural zeolite-blended cement pastes. The concentration of Cu, Ni and Pb in these leachates was lower than the limit in classification of leachability (IIa) specified by the regulation of Ministry of the Environment of the Czech Republic ($\text{Cu} < 5 \text{ mg} \cdot \text{l}^{-1}$, $\text{Ni} < 4 \text{ mg} \cdot \text{l}^{-1}$, $\text{Pb} < 10 \text{ mg} \cdot \text{l}^{-1}$). As it was already published [23], the leachability of heavy metals could be lower with a prolonged period of ageing of samples.

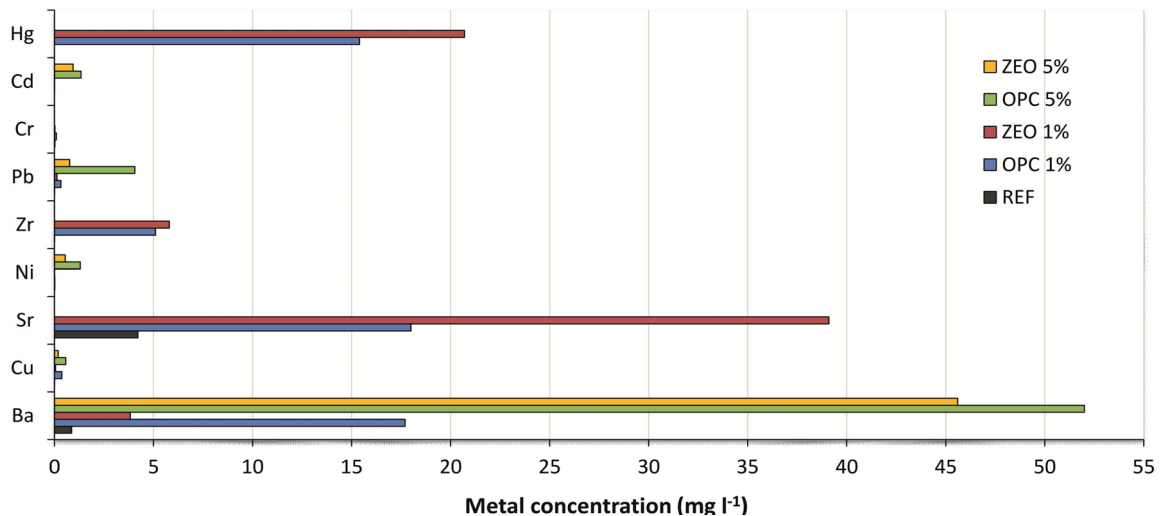


Fig. 5. Metal concentrations in cement pastes leachates.

4. Conclusions

On the basis of this study results, it has been concluded that:

- The use of natural zeolite as a partial replacement of cement does not very affect the strengths of cement pastes at the immobilization of heavy metals. The strength of cement paste decreases when the amount of added heavy metal increases.
- The natural zeolite-blended cement pastes exhibited ordinarily lower total porosity than those containing Portland cement alone. The blended cement pastes contain smaller pores than the Portland cement pastes, which impacted the flexural strengths.
- The microstructure of reference cement paste and paste with immobilized heavy metals differs only in the presence of ettringite. The addition of Ni^{2+} ions results in increasing content of calcite in untypical radial structures.
- The application of natural zeolite as a binder with Portland cement to reduce the leaching of heavy metals results in a better outcome than using ordinary Portland cement for Ba, Cr, Cu, Ni and Pb. The natural zeolite-blended cement pastes are not suitable to immobilize Hg^{2+} , Sr^{2+} and Zr^{2+} ions.
- The use of natural zeolite to a mixture with OPC achieves the best results at immobilization of Cu and Pb with regard to the effectiveness in reducing the leachability of these metals, low total porosities and relatively high strengths of this kind of cement pastes.

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