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Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials

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Abstract

Three cementitious materials were used to investigate solidifying and stabilizing hazardous wastes containing heavy metals. The cementitious materials were ordinary portland cement (OPC), clinker kiln dust (CKD) modified OPC, and CKD and quick setting agent (QSA) modified OPC. High alkalies in CKD accelerated the setting and hydration of cement, and QSA influenced quick setting and increased compressive strength of cement. For the solidification and stabilization of heavy metals in the steel industry, dust high alkali CKD modified cement reduced heavy metals leached from the waste form and increased compressive strength of the waste form. The CKD and QSA modified cement presented the least amount of heavy metals leached and the highest compressive strength due to a large number of formation of hydrates, and most effective stabilization of hazardous wastes containing multi-heavy metals. © 2000 Elsevier Science Inc. All rights reserved.

Keywords: Portland cement; Waste management; Calcium sulphoaluminate; Ettringite; Heavy metals

1. Introduction

Stabilization and solidification (S/S) is known as one of the most popular technologies for treating and disposing of hazardous wastes. This S/S technologies using cementitious materials have been used for decades as a final treatment step prior to the disposal of both radioactive and chemically hazardous wastes [1]. Stabilization alters hazardous wastes to more physically and chemically stable forms, resulting in better environmental acceptance. Physical stabilization refers to the process of solidification and improves engineering properties, such as bearing capacity, trafficability, and permeability of stabilized waste forms. Chemical stabilization is the alteration of the contaminants' chemical form so that leachability is eliminated or substantially reduced [1].

Solidification is the process of eliminating free water by hydration of a setting agent—generally cementitious materials. Portland cement is the most widely used for S/S as a binding material, which was originally from the solidification of nuclear wastes in the 1950s. Portland cement is not used alone but was used as major ingredient in a number of S/S process systems. Many formulations have been developed for the S/S process according to the kinds of wastes, heavy metals, etc. As a result, portland cement can be modified for suitable S/S process using fly ash, lime, slag, soluble silicates, clay, etc. [1–3].

One of the most difficult problems in this field is that the hydration of cementitious material is too retarded to set and harden enough due to the inhibition of hydration reaction of heavy metals in a landfill area. Some research results have been reported on accelerating hydration using kiln dust as an admixture to ordinary portland cement (OPC) for stabilizing and solidifying wastes [4–6].

In this study, OPC and two kinds of modified OPC—by clinker kiln dust (CKD) including high alkali sulfate salts, and quick-setting agent (QSA) containing calcium sulphoaluminate and anhydrite as major constituents—were used for S/S process. All specimens were cured in air, which was performed to closely simulate the conditions of landfill. The hydration and physicomechanical properties of the cementitious materials were investigated, and the degree of success in the S/S process of the cementitious materials was also studied, testing leachability of heavy metals and development of compressive strength of the waste forms.

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2. Experimental

Three cementitious materials used in the study were modified using CKD and QSA, as shown in Table 1. The specimen SS1 contains 20 wt.% CKD, and the specimen contains SS2 15 wt.% CKD and 10% QSA. QSA, which is commercially available in South Korea, is a cementitious materials with very fast setting time—less than 10 min of initial setting time. The chemical compositions and Blaine-specific surface areas of OPC, CKD and QSA are given in Table 2.

The CKD shows very high alkali contents, 10.5 wt.% K_2O and 0.7 wt.% Na_2O, and high sulfate content, 8.2 wt.%. The alkalies exist as alkali sulfates, such as K_2SO_4 and Na_2SO_4. CKD has also a very high Blaine-specific surface area of 7260 cm^2/g. QSA contains calcium sulphoaluminate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$) and anhydrite ($CaSO_4$) as main minerals, and a high Blaine-specific surface area of 5230 cm^2/g.

Physicomechanical properties of the modified cementitious materials by CKD and QSA were tested with ASTM C266 for setting time and with ASTM C109 for compressive strength. The specimens for the strength test were cured in air at 23 + 3°C with RH 70%. The waste forms were prepared with cementitious material/waste dust = 12.5% and water/cementitious material = 30%. The waste dust was collected from electrostatic precipitators (EP) in a steel plant. The waste dust and the cementitious material were mixed together and cast in 5 cm × 5 cm × 5 cm molds to test for compressive strength and underwent leaching test for heavy metal ions.

The hydration and the properties of waste forms were studied using SEM, XRD and BET. The specimens for studying hydration of cementitious materials were prepared with a water/cement ratio of 50% and cured in air at 23 + 3°C with RH 70%.

The S/S processes of heavy metals using experimental grade chemicals were first conducted in order to understand better the hydration and the S/S properties of three cementitious materials. The chemicals, $Cr(NO_3)_3{\cdot}9H_2O$ (Yakuri Pure Chemical, purity 98%), $Cd(NO_3)_2{\cdot}4H_2O$ (Junsei Chemical, purity 98%) and $Pb(NO_3)_2$ (Yakuri Pure Chemicals, Purity 99%), were used for heavy metal sources. The concentrations of Cr, Cd and Pb of solutions were all 2500 ppm, and they were prepared and mixed with three cementitious materials containing water/cementitious material = 30%. The pastes prepared with Cr, Cd, and Pb solutions were cast in a cylindrical plastic mold with 5 cm (ϕ) × 5 cm (h) and cured in air at 20°C with RH 70% for 28 days, and then solidified forms were used to conduct a leaching test.

Table 1
The mixture ratios of three cementitious materials

	Mixing ratio (wt.%)		
Specimens	OPC	CKD[a]	QSA[b]
OPC	100	–	–
SS1	80	20	–
SS2	75	15	10

[a] Clinker kiln dust containing high alkalis (Tonghae plant of Ssangyong Cement).

[b] Quick setting agent consisting of calcium sulphoaluminate and anhydrite (Ssangyong Cement).

Table 2
Chemical compositions and Blaine-specific surface areas of the three cementitious materials

	Chemical compositions (wt.%)									Blaine
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI	(cm^2/g)
OPC	20.7	6.8	3.1	62.4	3.3	0.2	0.7	1.7	0.9	3230
CKD	12.1	4.4	2.2	38.5	1.5	0.7	10.5	8.2	21.8	7260
QSA	5.3	19.1	0.5	48.7	1.2	0.2	0.2	18.1	6.7	5230

The S/S processes of the three cementitious materials, using real hazardous waste dusts that contain heavy metals from the steel industry, were studied. The waste forms were made by mixing waste, cementitious materials and water together (waste/cementitious material/water = 1.000:0.125:0.200) in a planetary mixer for 210 s. Then specimens of waste forms for testing compressive strength and leaching test were cast in a 5 cm × 5 cm × 5 cm mold and cured in air at 20 + 3°C with RH 70%.

The leaching tests of heavy metals were conducted on S/S waste forms based on the TCLP method. The waste forms were first crushed and the size selected was between 5 and 50 mm by sieving. The leaching solution used was distilled water pH-adjusted to 6.0. The crushed waste forms in the pH-adjusted water (solid/liquid = 1:10 by weight) were stirred for 6 h on a magnetic stirrer, and filtered using filter paper No. 5. Heavy metals in the filtered solution were measured using the ICP spectroscopy.

3. Results and discussions

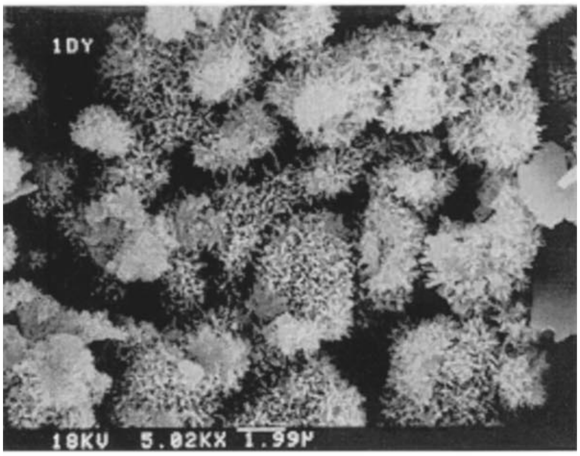
3.1. Physicomechanical properties and hydrates of cementitious materials

The setting time and compressive strength of cementitious materials are given in Table 3. SS1 and SS2 need more water due to their high Blaine-specific surface areas than

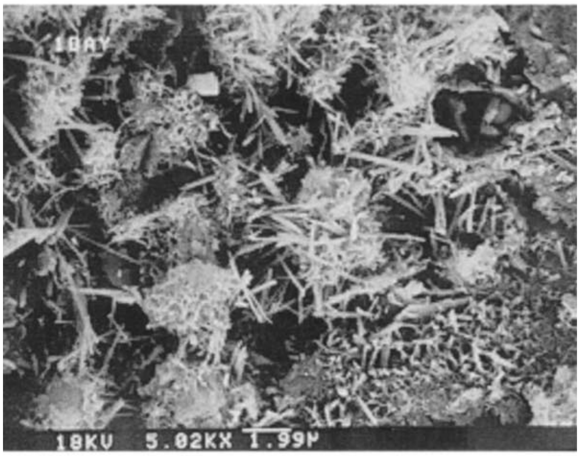
Table 3
Setting time and compressive strength development of cementitious materials used in the study

	Setting time (h:min)			Compressive strength (kg/cm^2)			
	W/C (%)	Initial	Final	1 Day	3 Days	7 Days	28 Days
OPC	26.0	4:00	8:20	65	182	234	339
SS1	28.6	3:05	6:30	81	195	239	332
SS2	28.2	2:00	4:40	98	236	325	363

(a) OPC



(b) SS1



(c) SS2

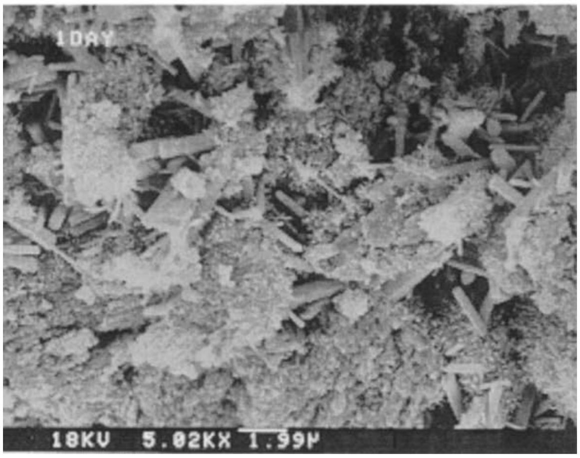


Fig. 1. SEM micrographs of three cementitious material pastes cured for 1 day in air at 23°C. (a) OPC, (b) SS1, (c) SS2.

OPC (additives, CKD and QSA consist of very fine particles as shown in Table 2), but the initial and final setting times of the SS1 and SS2 decreased by 1–2 and 3–4 h compared with OPC, respectively. The compressive strength developments of SS1 and SS2 show higher strength than that of OPC, especially at early hydration time. CKD contains high alkali sulfates, K_2SO_4 and Na_2SO_4. The alkali sulfates accelerate early hydration, resulting in fast setting and fast hardening in cementitious materials. When QSA is added to cementitious materials with CKD, the SS2 shows the fastest setting time and the highest compressive strength due to the activation of hydration by alkali sulfates and the formation of ettringite resulting from calcium sulphoaluminate and anhydrite in QSA.

Many studies show that alkalies accelerate early hydration, resulting in increasing the initial strength of portland cement, but decreasing compressive strength later [7–9]. In this study, the SS1, including CKD, presents high compressive strength up to 28 days because the specimens were cured in air. Generally, the compressive strength at 28 days is not so high after curing cementitious specimens in air, compared with those cured in water. Singh et al. [10] also reported that the addition of alkali by-pass kiln dust accelerated the hydration, causing decreased porosity in the hardened structure, and increased compressive strength for OPC and blast furnace slag-blended cement.

The SEM micrographs and XRD patterns of the three cementitious materials are given in Figs. 1 and 2, respec-

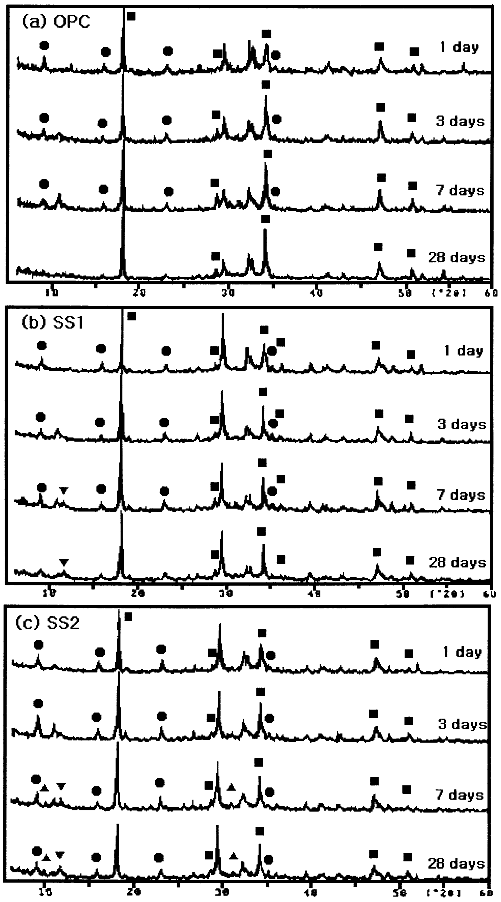


Fig. 2. XRD patterns of three cementitious material pastes cured for 1, 3, 7, 28 days in air at 23°C.

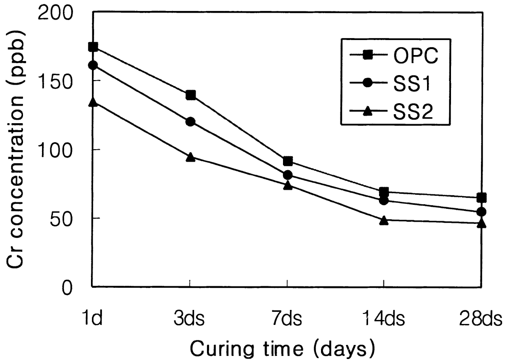


Fig. 3. Cr ion concentration leached from pastes of three cementitious materials as a function of curing time.

tively. In Figs. 1 and 2, the ettringite phase was detected at 1 day. The SS2 shows very well developed ettringite crystals because this binder includes $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ and $CaSO_4$, resulting in the creation and growth of ettringite at early hydration time. The ettringite formation is generally recognized as follows when C_3A and $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ coexist with SO_3^{2-}, Ca^{2+}, and H_2O [11]

$$C_3A + 3CaSO_4 \cdot 2H_2O + 26H \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H\,(\text{ettringite})$$

$$4CaO \cdot 3Al_2O_3 \cdot SO_3 + 8CaSO_4 + 4CH + 28H \rightarrow 3(C_3A \cdot 3CaSO_4 \cdot 32H)$$

where C = CaO, A = Al_2O_3, H = H_2O.

For SS1—since high alkalies from CKD accelerated the hydration of tricalcium silicate at early hydration time—calcium silicate hydrate (C-S-H) and portlandite ($Ca(OH)_2$) were formed much more than OPC. For SS2, well developed ettringite is formed at early hydration time due to addition of QSA consisting of $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ and $CaSO_4$, and C-S-H might be formed between the ettringite crystals at later hydration time. These hydration processes increase compressive strength continuously.

In the XRD patterns of OPC, SS1 and SS2, as shown in Fig. 2(a), (b) and (c), respectively, the hydrates, $Ca(OH)_2$, ettringite, monosulphate, tetracalcium aluminate carbonate 12-hydrate, C-S-H and C-A-H are shown. For SS1, the characteristic peaks of tetracalcium aluminate carbonate 12-hydrate ($C_3A{\cdot}CaCO_3{\cdot}12H_2O$) were detected in the samples of 7 and 28 days. It was considered that $CaCO_3$, not calcined, in CKD reacted with calcium aluminate hydrates. For SS2—including $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$—ettringite was detected from 1 day, and monosulphate, which was converted from ettringite, was also found from 7 days.

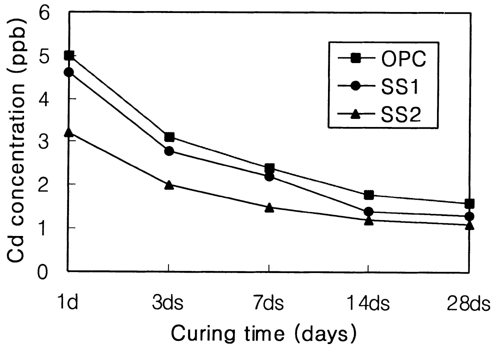


Fig. 4. Cd ion concentration leached from pastes of three cementitious materials as a function of curing time.

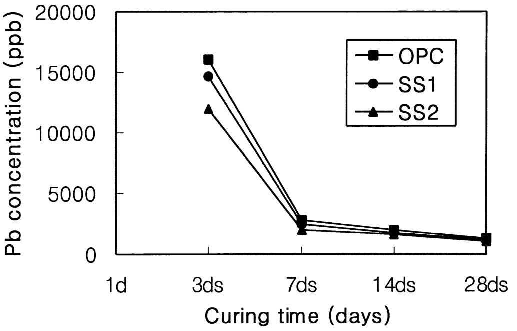


Fig. 5. Pb ion concentration leached from pastes of three cementitious materials as a function of curing time. (The cementitious materials were not hardened at 1 day.)

3.2. *Solidification/stabilization of heavy metals prepared from laboratory chemicals*

Figs. 3–5 show the results of TCLP leaching tests of Cr, Cd and Pb for the pastes made with three cementitious materials—OPC, SS1 and SS2. The concentrations of solutions for Cr, Cd and Pb using chemicals are 2500 ppm.

For SS1 including high alkali CKD, the heavy metal concentrations of Cr and Cd leached from solidified forms were lower than for OPC for all curing ages. These results were attributed to CKD, whose large surface area absorbed the heavy metal ions and high alkalies accelerated hydration, resulting in forming much hydration product, high specific surface area of C-S-H and calcium sulphoaluminate hydrates, which entrapped much heavy metal ions and stabilized them chemically. However, Pb content was higher than in OPC because of higher pH due to alkalies. Because of higher hydroxyl content, lead was dissolved from chemically bonded lead compounds, precipitated on the surface and was entrapped physically [12].

SS2 shows the best results for the S/S process due to QSA. Uchikawa [13] also reported that regulated set

Table 4
Chemical and heavy metal compositions of waste dust collected from an EP at a steel plant

Chemical composition (wt.%)								Heavy metal content (ppm)		
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Cr	Cd	Pb
5.1	12.1	67.5	1.1	2.6	0.63	1.57	3.3	3547	8	738

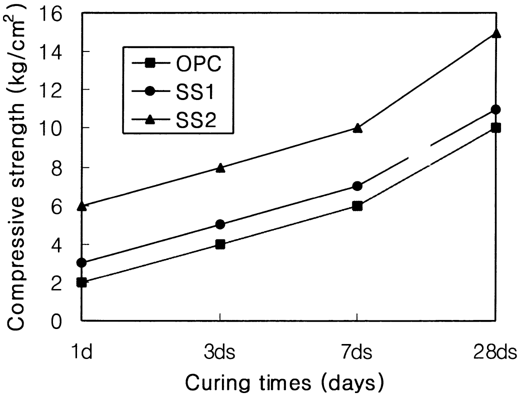


Fig. 6. Compressive strength developments of waste dust forms made with three cementitious materials.

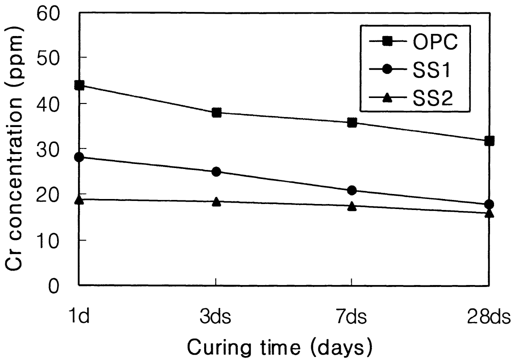


Fig. 8. Cr ion concentration leached from waste dust forms made with three cementitious materials as a function of curing time.

cement, consisting of calcium aluminate and anhydrite, had a better ability of solidifying hazardous heavy metals (Cr, Cd, Pb, etc.) than portland cement. He further suggested that calcium sulphoaluminate hydrate physically and chemically stabilized a greater proportion of hazardous heavy metals because of the high specific surface area of hydrates and not the increment of pH. The results of this study are very similar to Uchikawa's. The calcium sulphoaluminate and anhydrite in QSA, and alkalies in CKD accelerated the hydration and formed a lot of calcium sulphoaluminate hydrate, such as ettringite. As a result, fast and vigorous hydration created high specific surface areas of hydrated specimens, which were able to fix a lot more hazardous heavy metals during early hydration time. The S/S process of heavy metals continuously progressed since calcium silicates—such as tricalcium silicate and dicalcium silicate, formed C-S-H between prismatic ettringite, and densified the microstructure at later hydration time.

For S/S of Cr, Cd and Pb, the leached metal ions decreased with curing time (Figs. 3–5). For the S/S of Pb (Fig. 5), the Pb concentration could not be measured because the specimens were not hardened at 1 day. Many researchers studied the effects of heavy metals on cement hydration [14–16]. Tashiro [15] reported that the hydration of cement was retarded in the presence Zn, Pb and Cu. The inhibitory effects of Zn, Pb and Cu to cement hydration were related to the formation of double salts, which were formed between these heavy metals and calcium ions dissolved from cement. In this study, Pb (2500 ppm) retarded hydrations of all kinds of cementitious materials, resulting in not setting and hardening pastes until 1 day. After hardening pastes of specimens, the Pb concentration leached from the pastes dramatically dropped from about 15,000 to 3000 ppb as the curing time increased from 3 to 7 days. This result is considered in the change of pH according to curing time because the leachability of Pb is strongly dependent on pH [12].

3.3. Solidification/stabilization of heavy metals in the real waste

The S/S ability of cementitious material was studied using waste dust from a steel company, which contain Cr, Cd and Pb, as shown in Table 4. This waste dust consisted of fine powders collected from an EP of the steel plant. The waste dust was mixed with three cementitious materials with

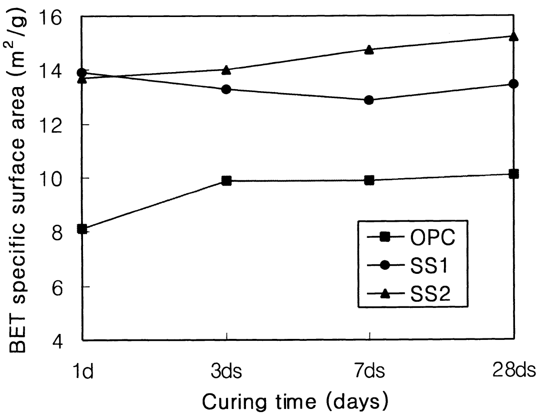


Fig. 7. BET-specific surface areas of waste dust forms made with three cementitious materials.

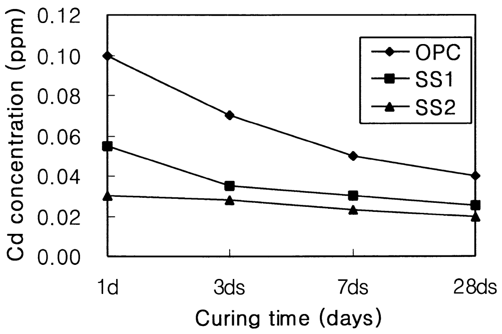


Fig. 9. Cd ion concentration leached from waste dust forms made with three cementitious materials as a function of curing time.

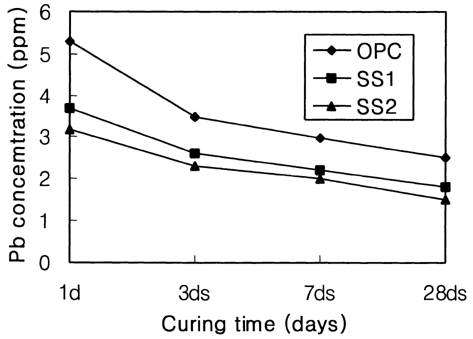


Fig. 10. Pb ion concentration leached from waste dust forms made with three cementitious materials as a function of curing time.

W/C = 20%, and cast in 5 cm × 5 cm × 5 cm molds. The specimens were cured in air atmosphere at 23 + 3°C with RH 70%.

Fig. 6 shows the compressive strength developments of waste forms made with three cementitious materials as a function of curing time. The results are similar to those of mortar for three cementitious materials shown in Table 3. SS1 developed compressive strength higher than OPC. SS2 developed the highest compressive strength, higher than any other cementitious materials at all curing days. SS1 and SS2 have higher BET-specific surface areas than OPC due to the addition of CKD and QSA. (Fig. 7) For SS1, alkalies in CKD accelerated the hydration of OPC at early hydration time, and its hydrates filled voids in the structure. It is also considered that the high specific surface area of had CKD contributed to the high development of compressive strength and better fixation of heavy metals because CKD acted as fillers for voids, resulting in the densification of the microstructure. For SS2, besides the role of CKD, QSA hydrated and formed calcium aluminosulphate hydrate, ettringite or monosulphate, etc., at an early hydration time.

Figs. 8–10 present the results of leaching tests of Cr, Cd and Pb for the solidified waste forms as a function of curing time. The results of leaching test for waste forms made with cementitious materials show very similar behavior to the previous results of leaching tests shown in Figs. 3–5, respectively. The results show that CKD is a good admixture for enhancing compressive strength of the waste form and significantly promotes the S/S process of heavy metals. Furthermore, QSA and CKD in SS2 produce much better qualities of S/S of heavy metals including pH-sensitive metals such as Pb.

Fig. 11 shows the proposed S/S mechanisms of heavy metals using portland cement [17]. Pb can be precipitated on the surface of hydrates, and Cr was incorporated in hydrates, especially C-S-H. Cd ion participated and incorporated into forming portlandite, $Ca(OH)_2$, resulting in substituting for Ca and creating the double compound $CdCa(OH)_4$. The effects of S/S of heavy metals are dependent on the amounts of hydrates created. Therefore, the addition of CKD in SS1 and both CKD and QSA in SS2 promote good fixation of hazardous wastes containing heavy metals.

4. Conclusions

The hydration and S/S effects of modified cementitious materials by addition of CKD (20% and 15%) and QSA (10%) to OPC were studied, and the following results were achieved.

1. High alkalies in CKD accelerate the hydration of cement at early hydration time, resulting in fast setting and hardening waste forms. The CKD-modified cementitious material developed high strength until 28 days—continuously when it was cured in air—and showed high specific surface area of hydrates as compared to OPC. The kiln dust-modified cementitious materials generated ettringite and Ca(OH)2 as major hydrates at early hydration time, and C3A·CaCO3·12H2O after 7 days' curing time. QSA also accelerated early hydration and formed many and well-crystallized ettringite.

2. Heavy metal ions leached from the pastes of modified cementitious materials are less than those of OPC. The modified cementitious materials rapidly set and hardened

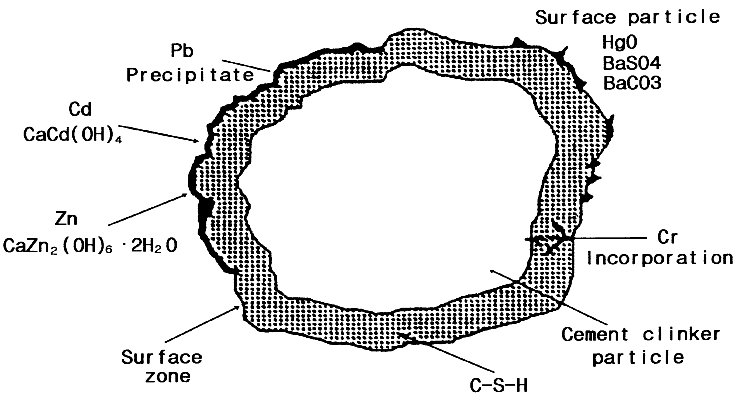


Fig. 11. Solidification and stabilization of heavy metals by hydrates of portland cement [17].

when 2500 ppm of Cr and Cd are added to them, and the effects of solidification and stabilization of Cr and Cd are significantly high at 1 day. When 2500 ppm of Pb are added to the modified cementitious materials, the cementitious materials did not set at 1 day, and the effects of stabilization of Pb are lower than Cr and Cd.

In the solidification and stabilization of waste dusts collected from EPs at steel plants, high alkalies in CKD accelerate the hydration of cementitious materials, resulting in development of higher strength. QSA, consisting of calcium sulphoaluminate and anhydrite, also promotes fast hydration and forms many ettringite at early hydration time. The QSA and CKD modified cementitious materials present the most effective contribution for fixation of heavy metals, especially wastes containing multi-heavy metals.

References

[1] T.E. Mayers, M.E. Eappi, Laboratory evaluation of stabilization/solidification technology for reducing the mobility of heavy metals in New Bedford Harbor superfund site sediment Stabilization of Hazardous Radioactive and Mixed Wastes, 2nd edn. ASTM publication, Philadelphia, PA, 1992, p. 304.

[2] W.S. Adaska, S.W. Tresouthick, P.B. West, Solidification and Stabilization of Wastes Using Portland Cement Portland Cement Association, Skokie IL, 1991, p. 4.

[3] F.P. Glasser, Chemistry of cement-solidified waste forms Chemistry and Microstructure of Solid Waste Forms Lewis Publishers, Chelsea, MI, 1993, p. 1.

[4] E.W. Stern, What is CKD? It is cement kiln dust — a by product about to become a valuable commodity, Rock Prod 82 (6) (1979) 84–88.

[5] D.S. Morgan, J.I. Nova, A.H. Halff, Oil sludge solidification using cement kiln dust, J Environ Eng 110 (5) (1984) 935–948.

[6] W.S. Adaska, S.W. Tresouthick, P.B. West, Solidification and Stabilization of Wastes Using Portland Cement, Portland Cement Association, Skokie, IL, 1991, p. 6.

[7] I. Jawed, J. Skalny, The influence of alkali sulfates on the properties of cement and concrete, World Cem 14 (9) (1983) 325–332.

[8] I. Odler, R. Wonnermann, Effect of alkalies on portland cement hydration: II. Alkalies present in form of sulfates, Cem Concr Res 13 (6) (1983) 771–777.

[9] N.B. Singh, M.P. Dwivedi, Effect of alkali carbonates M_2CO_3($M = Li$, Na, K) on the hydration of portland cement, Cemento 85 (4) (1988) 259–266.

[10] N.B. Singh, K.N. Bhattacharjee, A.K. Shukla, Effect of alkali bypass dust on the hydration of granulated blast furnace slag blended cement, Cem Concr Res 25 (4) (1995) 883–895.

[11] H.F.W. Taylor, Cement Chemistry Academic Press, New York, 1990, pp. 195–337.

[12] M.J. Cullinane, L.W. Jones Jr., P.G. Malone, Handbook for stabilization/solidification of hazardous waste Hazardous Waste Eng. Research Lab., USEPA, Washington, DC, 1986, p. 102.

[13] H. Uchikawa, Fixation of harmful element in industrial waste and sludge with cement, J Ceram Soc Jpn 12 (2) (1977) 103–117.

[14] W. Shively, P. Bishop, D. Gress, T. Brown, Leaching test of heavy metals stabilized with portland cement, J Water Pollut Control Fed 58 (3) (1986) 234–245.

[15] C. Tashiro, H. Takahashi, M. Kanaya, I. Hirakida, R. Yoshida, Hardening properties of cement mortar adding heavy metal compound and solubility of heavy metal from hardened mortar, Cem Concr Res 7 (3) (1977) 283–290.

[16] J.-H. Youn, B.-G. Jeong, H.-M. Lee, H.-S. Chung, C. Park, Immobilization of heavy metals using ordinary portland cement and lime–rice husk ash, J Korean Solid Wastes Eng Soc 12 (5) (1995) 645–653.

[17] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes Van Nostrand-Reinhold, New York, 1990, pp. 293–298.