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INFLUENCE OF CdO ON THE EARLY HYDRATION OF $3CaO.Al_2O_3$

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ABSTRACT

The influence of CdO on the hydration of $3CaO.Al_2O_3$ at 25°C was studied by X-ray diffraction, scanning electron microscopy, thermal gravimetry, and calorimetry for hydration times less than one day. The CdO had a small effect on the thermal characteristics of hydration. Slightly less heat was liberated when CdO was added to the $3CaO.Al_2O_3$. The presence of CdO increased the formation of the cubic hydrated phase. The cadmium was retained in the matrix as $Cd(OH)_2$.

Introduction

Cadmium is a toxic heavy metal. The prolonged exposure to cadmium and its compounds damages internal organs and causes cancer and hypertension. The U.S. produces approximately 700 metric tons of cadmium waste annually primarily from the electroplating, battery and paint industries (1). Cadmium waste immobilization in Portland cement concrete and subsequent shipment to landfill is a simple and cheap alternative to wet chemical remediation processes.

Portland cement hydration chemistry is complicated by the presence of cadmium. Cartledge and co-workers (2) observed that cadmium increased the degree of polymerization and the proportion of calcium-silicate-hydrate (C-S-H) gel phase in the hydrated Portland cement. The main cadmium species were $Cd(OH)_2$ encapsulated by C-S-H gel and/or $Ca(OH)_2$ which indicated that $Cd(OH)_2$ had nucleated the precipitation of the C-S-H gel and $Ca(OH)_2$. In consonance with these observations, Tamas et al (3) deduced that most cadmium was retained in the cement matrix as the hydroxide. Herrera (4) immobilized $Cd(OH)_2$ and $Cd(NO_3)_2$ in Portland cement. They concluded that $Cd(OH)_2$ was physically entrapped in the cement matrix. Furthermore, there appeared to be substitution of Ca^{2+} by Cd^{2+} in the cement hydration phases through a diffusion and/or dissolution mechanism. When $Cd(OH)_2$ was present, the $Ca(OH)_2$ and the C-S-H gel appeared earlier in the hydration sequence. Therefore, $Cd(OH)_2$ was likely a nucleation site. For $Cd(NO_3)_2$, the Cd^{2+} ions either formed the insoluble $Cd(OH)_2$ or reacted with $[Al(OH)_4]^-$ in solution and formed an octahedral coordinated Cd-Al complex. Cocke and co-workers (5,6) suggested that cadmium was retained in the cement matrix as a calcium hydroxycadmiate from the surface reaction of $[Ca(OH)_4]^{2-}$ with Cd^{2+}.

Investigations on systems containing the individual Portland cement components and cadmium are limited. Bhatty (7) reported inconclusively on the hydration of $3CaO.SiO_2$ with cadmium salt additives. Tashiro and Oba (8) concluded that $Cu(OH)_2$ retarded the formation of the cubic hydrated phase, $3CaO.Al_2O_3.6(H_2O)$. Zhao, Daugherty and Zhang (9) reported on the influence of lead compounds on the hydration of $3CaO.Al_2O_3$. The results indicated that the tetragonal PbO was the stable immobilized lead phase regardless of the lead compound originally added to the $3CaO.Al_2O_3$. To study the crystallochemical fixation of Cd^{2+} in the aluminate phase of cement, Auer and Pollmann (10) recently synthesized and characterized lamellar cadmium aluminum hydroxide compounds doped with SO_4^{2-}, CO_3^{2-}, Cl^- and NO_3^-. Previous work from this laboratory, showed that $Cd(NO_3)_2$ inhibited the hexagonal to cubic transition in the hydration products of $3CaO.Al_2O_3$ (11,12). But, it was not clear whether $Cd(NO_3)_2$ represented all cadmium compounds since the anionic portion of a metal salt can affect hydration. This paper reports, for the first time, on the influence of CdO on the hydration of $3CaO.Al_2O_3$. The thermal and calorimetric data, X-ray diffraction spectra and scanning electron photomicrographs provide insight into cadmium speciation and location in the hydrated products. The $3CaO.Al_2O_3$ phase pilot system represents a further contribution from this laboratory, and adds to the fundamental understanding of the mechanisms of waste immobilization in Portland cement systems (11-13).

Experimental

The $3CaO.Al_2O_3$ was obtained from Construction Technologies Laboratory (Skokie, Illinois) as powder ground to 3600 $cm^2\ g^{-1}$ fineness. The absence of residual CaO in the $3CaO.Al_2O_3$ was confirmed by differential thermal analysis (DTA) and X-ray diffraction (XRD). The CdO was Baker reagent grade (99.7% pure).

The rate of heat and total heat evolved during the first hour of hydration was measured with a specially constructed isothermal conduction calorimeter. The instrument consisted of a metal base plate on which a calorimeter was mounted surrounded by insulation. A heat flow meter located under the calorimeter cell measured heat production. The calorimeter cell was a chamber of teflon-coated aluminum into which a polyurethane insert was placed holding the sample. The instrument was closed water-tight with an aluminum cover and neoprene O-ring. A syringe containing the solution was inserted into the cell body through an opening in the septum. At the moment the solution was injected into the sample cup, the time was set to zero to mark the beginning of the reaction. The syringe was removed and the unit vibrated to ensure adequate mixing.. Additionally, the calorimeter was fitted to a cam assembly which thoroughly shook the sample. The calorimeter was placed in an isothermal water-bath. The voltage signals from the heat flow meters under the calorimeter cell were monitored by a Datataker DT100 Data Logger manufactured by Data Electronics. The rate of heat production, R, was calculated from the formula,

$$[1] \qquad R = \frac{V}{S \times M} \quad J \cdot s^{-1} \cdot kg^{-1}$$

where V was the voltage measured, S was the sensitivity of the heat flow meter determined from the instrument calibration ($V.W^{-1}$), and G was the mass of the sample (kg). The total heat evolved (Q) was determined by integration of Eq.[1] with time. The pertinent equation was,

$$[2] \qquad Q = \frac{1}{S \times M} \int V(t) \cdot dt \quad J.kg^{-1}$$

For the calorimetric experiments, a sample mass of 2.0 *g* (95 mol% C_3A and 5 mol% CdO) was placed in the sample cup of the calorimeter. A water to solid ratio of 0.40 was used and heat was recorded for 1 hour after the addition of the distilled water.

All other specimens were bottle hydrated, and subsequently examined. For these experiments, 5.0 *g* of C_3A or mixtures of C_3A and CdO (80 mol% C_3A + 20 mol% CdO) were reacted with 200 *ml* of distilled water in polypropylene bottles with continuous stirring at 25°C. To minimize carbonation, the bottles were sealed immediately after mixing. At 10 minutes, 30 minutes, 1 hour, 6 hours, 12 hours and 24 hours, the hydration products were vacuum filtered. Hydration in the solids was arrested by isopropanol immersion for one week and vacuum dehydration at 38°C. Specimens were stored in a desiccator over anhydrous $Ca(SO_4)_2$.

All the bottle hydrated solids were examined with powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and with the scanning electron microscope (SEM). For XRD, powdered samples were scanned from $2\theta = 2^\circ$ to $2\theta = 60^\circ$ at 2° min^{-1} with a Rigaku Geigerflex powder diffractometer fitted with a Cu Kα source and a monochrometer detector. TGA and DSC were performed with a DuPont TGA Model 951 and a DuPont DSC Model 2910, respectively. The temperature range was 25°C to 600°C at 20° min^{-1} and the N_2 gas flowed at 100 ml min^{-1}. Microscopy samples were observed with a Cambridge Stereoscan Model 250 SEM equipped for back scattered emission imaging (BSE) and energy dispersed X-ray (EDX) spectrometry.

Results and Discussion

The heats of mixing liberated during the hydration of $3CaO.Al_2O_3$ and $3CaO.Al_2O_3$ with CdO addition, are summarized in Table 1. The effects of CdO addition on the heats of hydration of $3CaO.Al_2O_3$ were subtle. The maximum heat rate decreased from 213 $W.kg^{-1}$ to 198 $W.kg^{-1}$, and the times to achieve the maximum heat rates were decreased from 212 *s* to 182 *s*. The total heat liberated during the first hour of hydration was slightly reduced by CdO from 0.206 $J.kg^{-1}$ to 0.204 $J.kg^{-1}$.

TABLE 1
Calorimetric Results for the Hydration of $3CaO.Al_2O_3$ and CdO.

Additive	Maximum Heat Rate ($W.kg^{-1}$)	Time at Maximum Heat Rate (*s*)	Total Heat at 1 Hour ($J.kg^{-1}$)
None	213	212	0.206
5 mol% CdO	198	182	0.204

TGA results for $3CaO.Al_2O_3$ and $3CaO.Al_2O_3$-CdO mixtures are presented in Figure 1 for 10 minutes, 1 hour and 1 day. At 10 minutes of hydration, there were two peaks for the $3CaO.Al_2O_3$ hydration. The peaks at 256°C and 282°C represented the hexagonal hydrated phase $4CaO.Al_2O_3.13H_2O$. When CdO was present at 10 minutes, the $4CaO.Al_2O_3.13H_2O$ peaks have broadened which indicated poorly formed hydrated structures. The DSC results for 10 minutes are given in Figure 2. In agreement with the TGA measurements, there were two endothermic

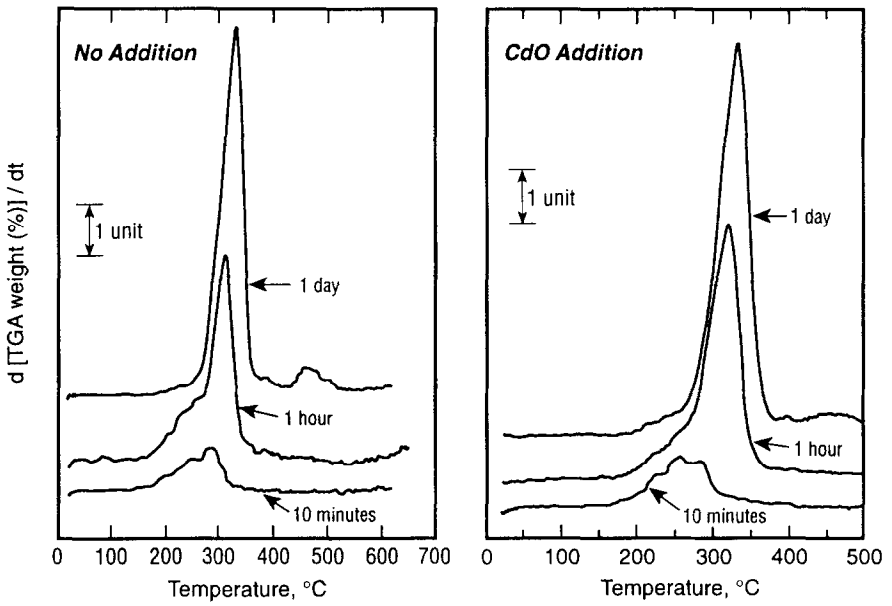

FIGURE 1
Thermal Gravimetric Analysis at 10 minutes, 1 hour and 1 day for (a) the $3CaO.Al_2O_3$ system and (b) for the $3CaO.Al_2O_3$-CdO system.

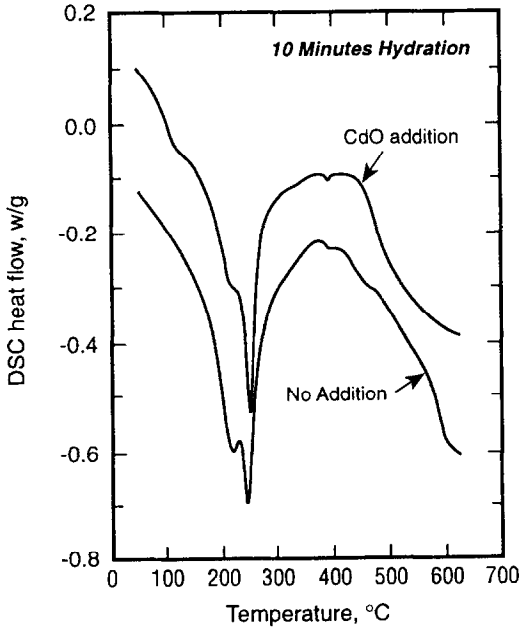

FIGURE 2
Differential Scanning Calorimetric Curve for 10 minutes hydration (a) the $3CaO.Al_2O_3$ system and (b) for the $3CaO.Al_2O_3$-CdO system.

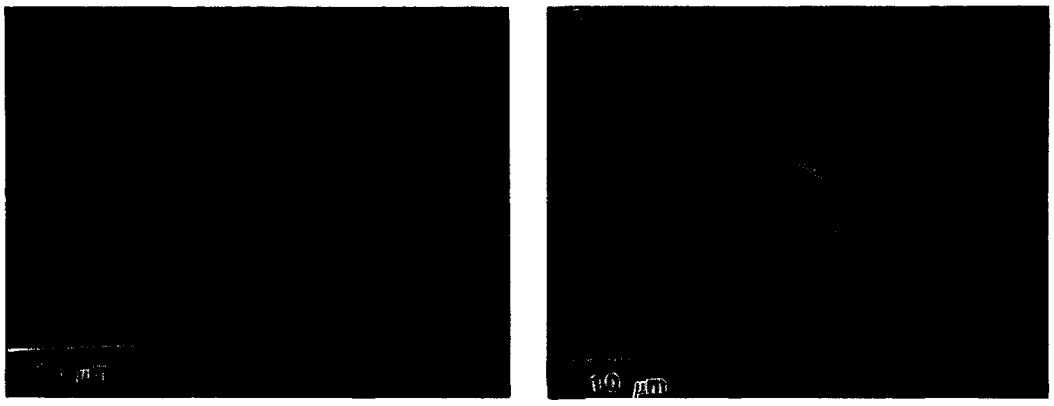

FIGURE 3
Scanning electron photomicrographs of $3CaO.Al_2O_3$ hydration products after 10 minutes. (a) $3CaO.Al_2O_3$ grain covered by early plates of hexagonal hydration products. (b) Hexagonal hydration product showing thin curved plates with curled edges.

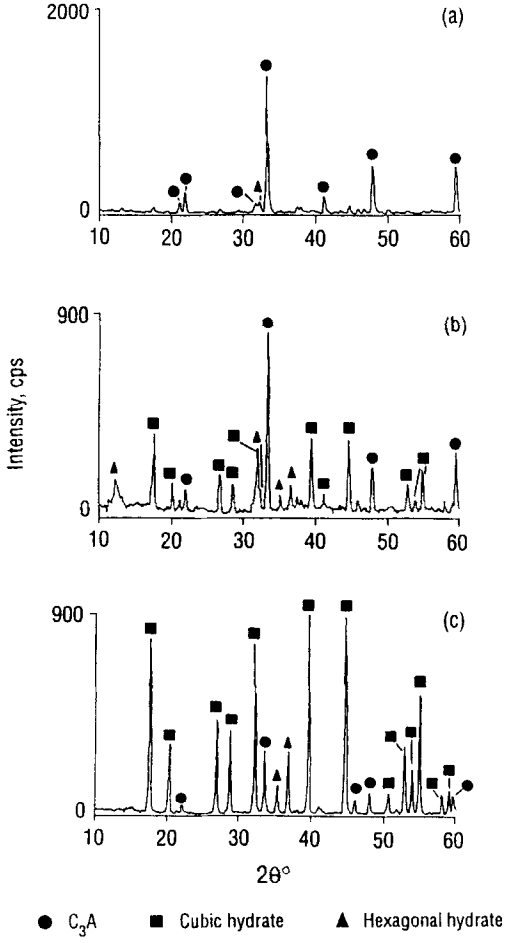

FIGURE 4
X-ray Diffractograms for $3CaO.Al_2O_3$ hydration products after (a) 10 minutes (b) 1 hour and (c) 1 day.

peaks between 200°C and 300°C. However, in the presence of CdO, the first peak was less pronounced and the second peak was sharper. Furthermore, there was a small endothermic peak at 375°C which cannot be readily associated with any hydrated phase. The peak probably represented the heat liberated as CdO reacted and formed $Cd(OH)_2$. Figure 3 is the SEM photomicrograph of $3CaO.Al_2O_3$ hydration corresponding to 10 minutes hydration. The unhydrated $3CaO.Al_2O_3$ grains formed a substrate to the plate-like hexagonal hydrate phase. Plate development was sparse. The plates were very thin, obliquely oriented with rolled edges, and generally equidimensional. The XRD diffractograms are presented in Figure 4 for $3CaO.Al_2O_3$ hydration. At 10 minutes, the XRD did not indicate which hexagonal hydrate predominated. The peaks for the hexagonal hydrates were broad and weak and consistent with the thin and poorly crystallized form observed in Figure 3. The cubic hydrogarnet phase, $3CaO.Al_2O_3.6H_2O$ was not present in either the XRD diffractograms or the SEM photomicrographs. Figure 5a is the SEM photomicrograph corresponding to 10 minutes hydration of $3CaO.Al_2O_3$ with CdO addition. In contrast to the undoped sample of Figure 3, there was a greater abundance of the hexagonal hydrate phases and the plates developed rosette-like clusters. However, many of hexagonal hydrates were poorly formed with curved and curled edges. The BSE image in Figure 5b suggested that cadmium occurred as a separate phase on the rosette edges. The XRD diffractograms for the CdO additions are given in Figure 6. At 10 minutes hydration, the CdO peaks at $2\theta=39^\circ$ and 55.5° were the only difference between the CdO doped and pure $3CaO.Al_2O_3$ systems.

At 1 hour hydration for $3CaO.Al_2O_3$, the TGA results in Figure 1 indicated a strong peak at 303°C and a weak 258°C shoulder which probably represented the $3CaO.Al_2O_3.6H_2O$ and the $4CaO.Al_2O_3.13H_2O$ phases, respectively. The XRD diffractogram in Figure 4b showed a well developed $3CaO.Al_2O_3.6H_2O$ phase and a minor presence of the hexagonal hydrated phases. The SEM photomicrograph at 1 hour is given in Figure 7. The $3CaO.Al_2O_3$ grains are covered by hydration products. The hexagonal hydrates exhibited two morphologies: shingled and euhedral

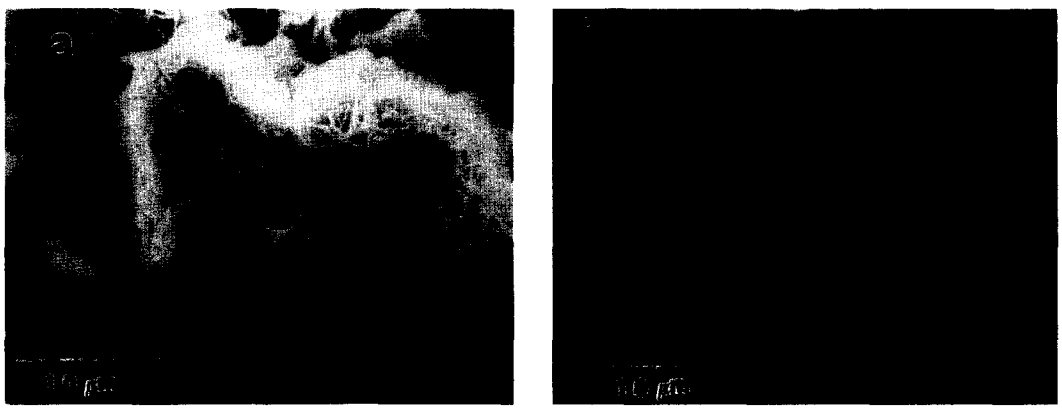

FIGURE 5
Scanning electron photomicrographs of $3CaO.Al_2O_3$ hydration products in the presence of CdO after 10 minutes. (a) Rosettes of hexagonal hydrate phase with sub-parallel edges and oblique interior. Note that the plates are very thin with a compromised hexagonal shape. (b) Back scatter photomicrograph of a rosette. Topography of grains is not apparent. The bright spots are cadmium rich phases. They form a filigreed texture consistent with the edges of the obliquely oriented hexagonal hydrate phase.

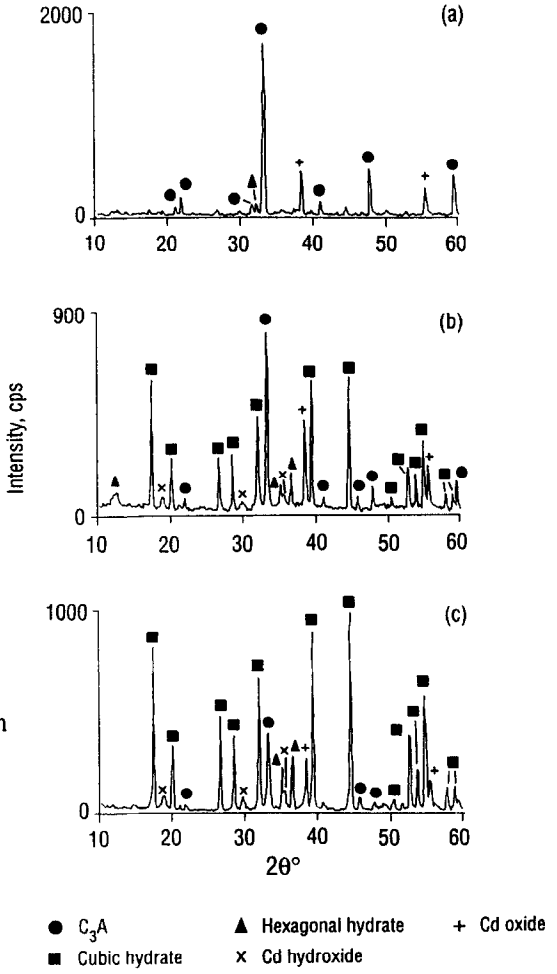

FIGURE 6
X-ray Diffractograms for $3CaO.Al_2O_3$ hydration products in the presence of CdO after (a) 10 minutes (b) 1 hour and (c) 1 day.

(2-6 μm). The $3CaO.Al_2O_3.6H_2O$ phase was fine-grained (0.25-1.0 μm diameter), and the grains were not clustered.

At 1 hour in the presence of CdO, there was a large endothermic peak at 318°C for the TGA results given in Figure 1. The peak was associated with the cubic phase $3CaO.Al_2O_3.6H_2O$. However, compared to the undoped $3CaO.Al_2O_3$, the peak has been displaced from 303°C. Furthermore, on the large endothermic peak, there was a very weak secondary shoulder peak at 268°C which corresponded to the hexagonal hydrates. It should be noted that the peak has been displaced from 258°C for the undoped system. The SEM photomicrographs are given in Figure 8. The hexagonal hydrates existed as rosettes and individual plates. The hexagonal plates of the rosette clusters remained very thin and curved, although some had an ideal hexagonal form (Figure 8a). Isolated hexagonal plates represented less than 20% of the specimen (Figure 8b). The $3CaO.Al_2O_3.6H_2O$ phase occurred as individual grains and represented 50% of the specimen. The $3CaO.Al_2O_3.6H_2O$ grains averaged 1 μm in diameter. The cadmium phase was a difficult to characterize spongy deposit (Figure 8b). The BSE image indicated that cadmium was located on the grain edges and as surface deposits. The XRD diffractogram in Figure 6b reflected the complexity of the system at 1 hour. The $3CaO.Al_2O_3.6H_2O$ phase dominated the diffractogram

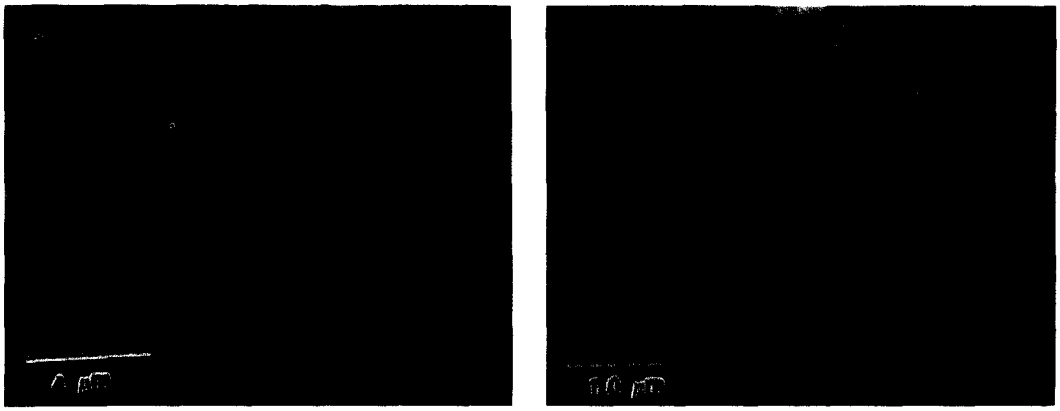

FIGURE 7
Scanning electron micrographs of $3CaO.Al_2O_3$ hydration products after 1 hour. (a) Poorly formed hexagonal hydrate phase with curved edges in contact with well formed hexagonal hydrate. The $3CaO.Al_2O_3.6H_2O$ grains are isolated and scattered throughout the microstructure. (b) Cluster of well formed hexagonal hydrate with $3CaO.Al_2O_3.6H_2O$ as individual grains.

which indicated its importance. The peak for the hexagonal hydrate phase $2\theta=12^\circ$ was much broader than for the undoped system. The broadened peaks confirmed the SEM observation that the hexagonal hydrates were compromised. A new cadmium phase, $Cd(OH)_2$, was present.

The TGA results for 1 day of hydration of $3CaO.Al_2O_3$ with and without CdO additions are presented Figure 1. For both systems, there were large endothermic peaks at 325°C which represented the expected abundance of the $3CaO.Al_2O_3.6H_2O$ phase. Interestingly, small exothermic peaks developed at 462°C and 442°C for the undoped and doped systems, respectively. In the former case, the peak probably represented a further manifestation of the $3CaO.Al_2O_3.6H_2O$ phase. For the cadmium additions, the peak at 442°C could be $Ca(OH)_2$ because it was possible that $Ca(OH)_2$ had formed by an exchange reaction of $Cd(OH)_2$ with calcium in the aluminate phase or in solution. The SEM photomicrographs for 1 day of hydration are given in Figure 9 for $3CaO.Al_2O_3$ and Figure 10 for $3CaO.Al_2O_3$ with CdO addition. In all cases, $3CaO.Al_2O_3.6H_2O$ was the dominant hydrated phase. The $3CaO.Al_2O_3.6H_2O$ grains were either weakly interlocked (1 μm diameter) or highly interlocked (5 μm diameter). Most hexagonal hydrates existed as well-formed individual grains generally attached to a $3CaO.Al_2O_3.6H_2O$ grain. The hexagonal plates were generally thicker than for 1 hour hydration. In Figure 10, the cadmium phase was difficult to distinguish in secondary imaging. However, cadmium phases formed encrustations on the hydrated phases (Figure 10b). In the BSE mode, the cadmium phases were found as deposits on the hydrate surfaces (Figure 10c). The presence of cadmium was confirmed by EDX semi-quantitative analysis (Figure 10d).

Conclusions

- The presence of CdO during the hydration of $3CaO.Al_2O_3$ had a minor influence on the heat of hydration and microstructural development. Furthermore, in comparison with previous

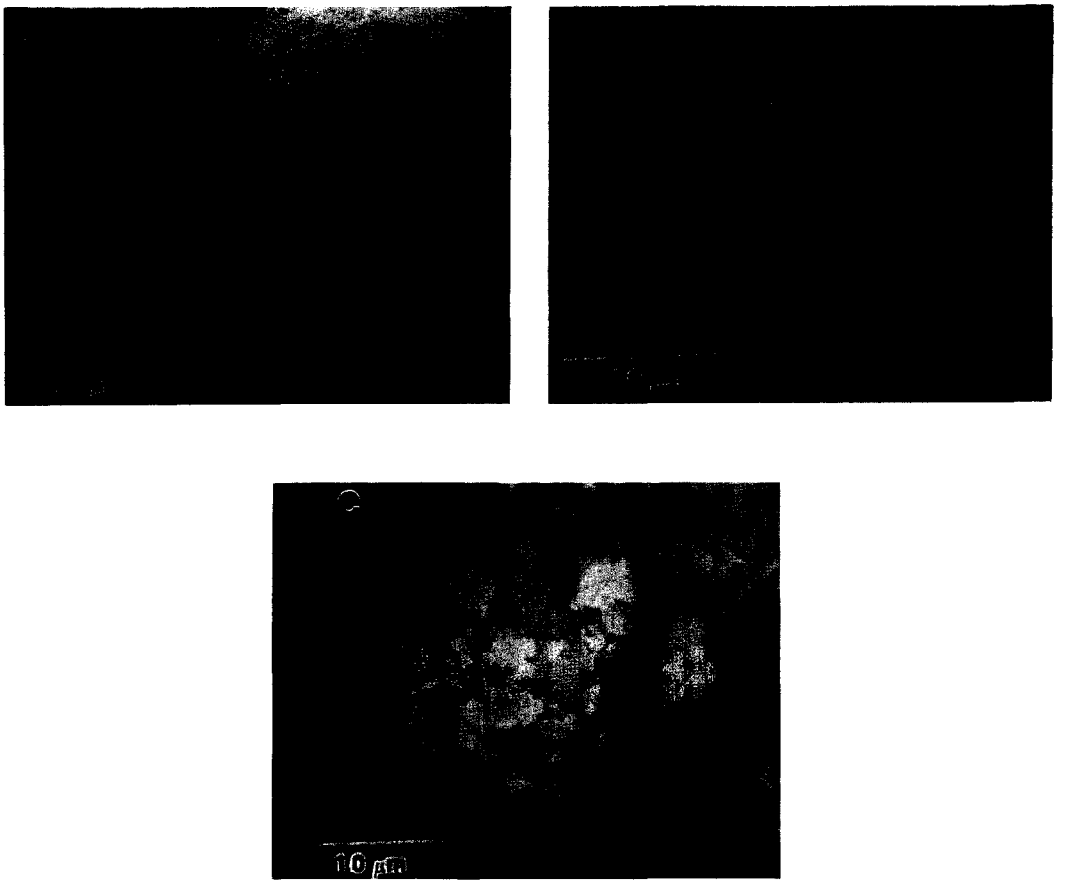

FIGURE 8

Scanning electron micrographs of $3CaO.Al_2O_3$ hydration products in the presence of CdO after 1 hour. (a) Hexagonal hydrate rosette. Hydrate is very thin, but generally poorly formed. $3CaO.Al_2O_3.6H_2O$ is present as individual grains. (b) Hexagonal hydrate as individual plates intergranular to $3CaO.Al_2O_3.6H_2O$. Plates are thin and curved, and locally of hexagonal form. (c) Back scatter image which shows little topography of the sample. Brighter spots are the cadmium rich phases interpreted to be CdO and $Cd(OH)_2$.

work with cadmium nitrate, it appears that the anionic component of the cadmium compound is a consideration for heavy metal immobilization in cementitious systems.

- The presence of CdO appeared to promote the formation of the cubic hydrated phase.

- The cadmium was retained in the hydrated cement matrix initially as CdO and later as $Cd(OH)_2$. The cadmium phases were concentrated as surface deposits mainly on the hydrated $3CaO.Al_2O_3.6H_2O$ phase.

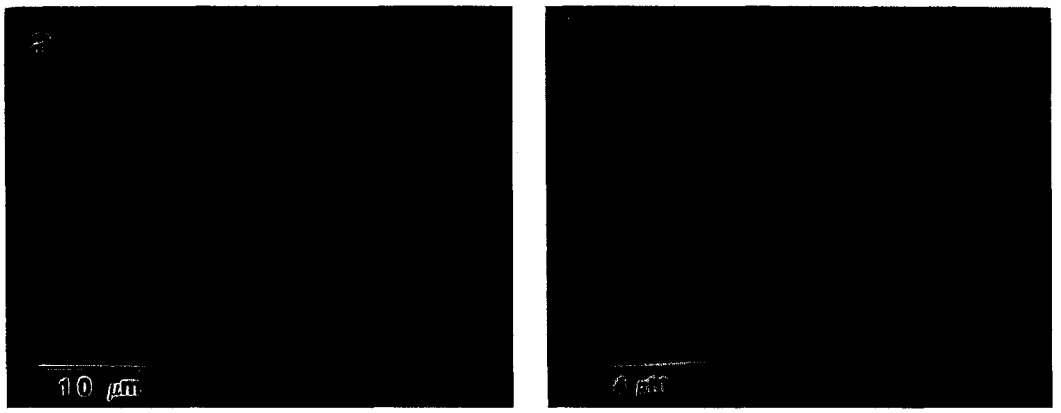

FIGURE 9
Scanning electron micrographs of $3CaO.Al_2O_3$ hydration products after 1 day. (a) Large clumps of $3CaO.Al_2O_3.6H_2O$ grains. The $3CaO.Al_2O_3.6H_2O$ phase is also present as individual grains. (b) Hexagonal hydrates as well formed grains and intergranular to $3CaO.Al_2O_3.6H_2O$. Note how thick some of the plates are.

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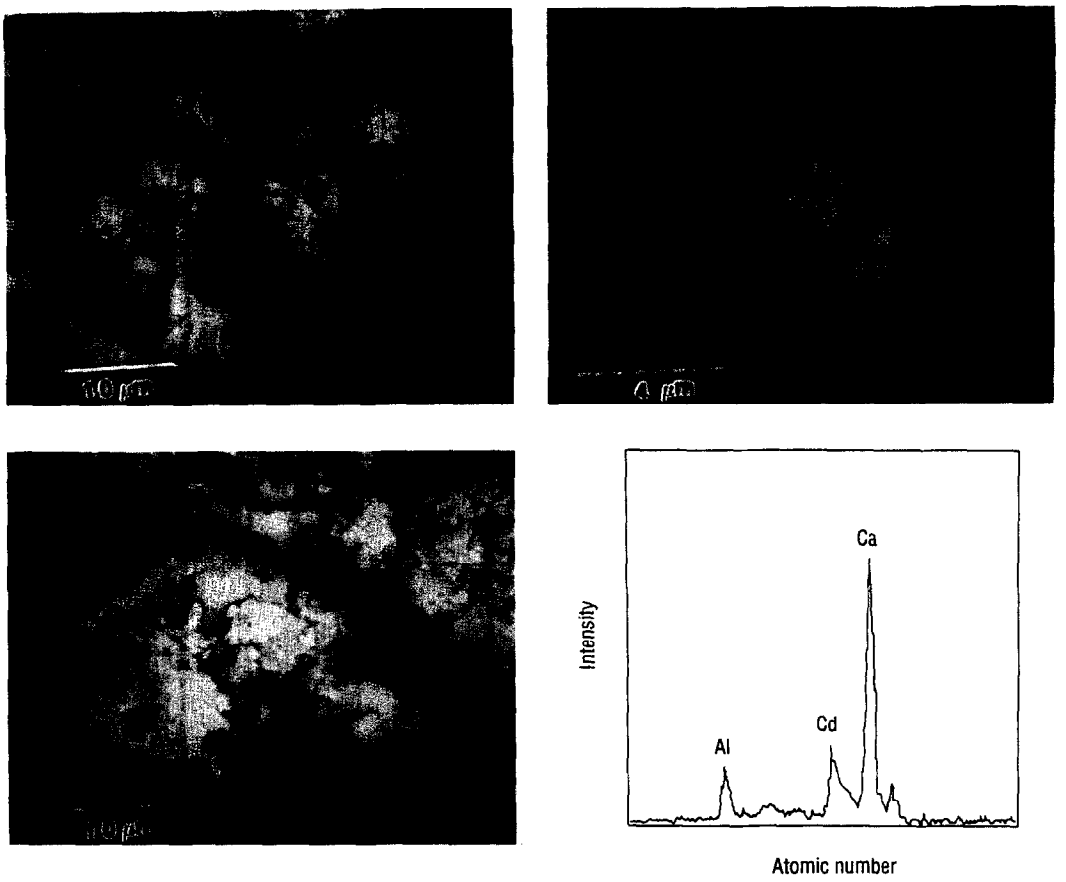

FIGURE 10

Scanning electron micrographs of $3CaO.Al_2O_3$ hydration products in the presence of CdO after 1 day. (a) Overview of the hydration products. $3CaO.Al_2O_3.6H_2O$ occurs as clumps, clusters and individual grains. The hexagonal hydrates are well formed plates intergranular to the $3CaO.Al_2O_3.6H_2O$. (b) Increased magnifications of (a) showing possible deposition of $Cd(OH)_2$ on a $3CaO.Al_2O_3.6H_2O$ surface. (c) Back scatter image of (a) without apparent topography. Bright spots represent the presence of cadmium. The cadmium phase appears to be encrustations on the hydrated phase. (d) EDAX analysis of (c). Area is rich in cadmium, but calcium and aluminum are also present, suggesting analysis of surrounding hydrates has been included.

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