Chemical Engineering Journal 155 (2009) 881–885

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Facile preparation of pure CaAl-layered double hydroxides and their application as a hardening accelerator in concrete

Sailong Xu, Zhanrui Chen, Bowen Zhang, Jianhui Yu, Fazhi Zhang*, David G. Evans

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 17 March 2009
Received in revised form 22 July 2009
Accepted 10 August 2009

Keywords:
Layered double hydroxides
Separate nucleation and aging steps
Concrete
Hardening accelerator
Compressive and flexural strength

ABSTRACT

CaAl-layered double hydroxide (CaAl-LDH), one of anionic functional layered materials, has recently been proposed as potential concrete hardening accelerators. Previous laboratory synthesis shows the necessity of employing a protective nitrogen atmosphere to avoid the formation of large amounts of $CaCO_3$ byproduct. Here, we present a preparation of pure CaAl-LDHs which are readily free of contamination by $CaCO_3$. The CaAl-LDHs were prepared via a scalable method of separate nucleation and aging steps (SNAS) by facile introduction of a mixed ethanol/water media. The application of the as-prepared CaAl-LDHs was investigated as a hardening accelerator in concrete. Standard tests of the compressive and flexural strengths of the cement mortars showed that specimens containing CaAl-LDHs as a hardening accelerator exhibited a greatly enhanced performance in respect of early compressive strength and early flexural strength; and the values increased by 61% and 71%, respectively compared to the pristine concrete specimen. The enhanced performances were addressed in terms of the results *in situ* X-ray diffraction, scanning electron microscopy, and mercury intrusion porosimetry.

1. Introduction

Layered double hydroxides (abbreviated as LDHs, and also known as hydrotalcite-like materials) are a large class of anionic layered functional materials. In recent years, LDHs have been widely used in many industries as high-performance catalytic materials, adsorbents, separation materials, additives in plastics, and as biological and pharmaceutical materials [1–6]. CaAl-LDHs have a general formula very similar to the AFm phase occurring in hydrated cement, being composed of positively charged layers $[Ca_2Al(OH)_6]^+$, and negatively charged interlayers $[X^- \cdot nH_2O]^-$ where X^- is a mineral anion. As the AFm phase is believed to act as a crystal seed accelerating cement hydration, CaAl-LDHs have been previously proposed by several research groups as potential concrete hardening accelerators [7–12].

Concrete is the building material used in the largest amount and at present the worldwide annual consumption of concrete is more than 11 billion m^3 [13,14]. Concrete additives, widely used to improve concrete properties, are needed in increasingly larger quantities and with higher performance. One class of concrete additives are hardening accelerators, which speed up concrete hardening and improve the compressive and flexural strength of concrete. In modern concrete construction, hardening accelerators are one of the most widely used concrete additives [15,16]. Traditional inorganic potassium- or sodium-based hardening accelerators have many disadvantages-for instance, their durability is not high and they suffer from leaching of the salt [17–19]. Chloride salts cause rusting of the steel bars used in reinforced concrete and sulfate salts may promote craze cracking of the concrete [19]. Organic additives such as triethanolamine and triisopropanolamine, readily suffer from escape from concrete environment involved [20–22]. The development of new types of CaAl-LDHs as a hardening accelerator for concrete has therefore attracted considerable attention in recent years [7–12]. However, the effects of adding the LDHs on the morphology, structure and mechanical properties of concrete have not been investigated.

Literature reports of the laboratory CaAl-LDHs synthesis state that it is necessary to employ a protective nitrogen atmosphere in order to avoid the formation of large amounts of $CaCO_3$ byproduct [7–12]. This is inconvenient and expensive if required in an industrial process, and therefore it is necessary to develop a facile and scalable approach to prepare highly pure CaAl-LDHs. In this paper we describe a facile route to prepare CaAl-LDHs containing different interlayer anions by a scalable method involving separate nucleation and aging steps (SNAS), the key features of which are a very rapid mixing and nucleation process in a modified colloid mill followed by a separate aging process [5,23,24]. The pure CaAl-LDH, free of contamination by $CaCO_3$, was readily prepared by facile introduction of a mixed ethanol/water media. The performance of the CaAl-LDHs as a cement hardening accelerator was evaluated by

---

* Corresponding author. Tel.: +86 10 64425105; fax: +86 10 64425385.
E-mail address: zhangfz@mail.buct.edu.cn (F. Zhang).

1385-8947/$ – see front matter. Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.08.003

testing the early compressive strengths and early flexural strengths of the cement, and a possible origin of the enhanced performances observed is proposed based on the results of *in situ* X-ray diffraction (*in situ* XRD) and scanning electronic microscopy (SEM).

2. Experimental

2.1. Synthesis of CaAl-LDHs

$CaCl_2 \cdot 2H_2O$ and $AlCl_3 \cdot 6H_2O$ (with Ca^{2+}/Al^{3+} ratios of 2.00 and Ca^{2+} concentration of 0.66 M) were dissolved in ethanol/water mixtures to give solutions A. NaOH (with a concentration of 2.30 M) was dissolved in organic/water mixtures to form a base solution B. All reactions were carried out by using reagent grade chemicals without further purification. Cement was purchased from the China Building Materials Academy. A separate nucleation and aging steps (SNAS) method [23,24] was used to prepare CaAl-LDHs. Solution A (100 mL) and solution B (100 mL) were simultaneously added to a colloid mill with rotor speed of 5000 rpm and mixed for 1 min. The resulting slurry was then removed from the colloid mill and aged at 70 °C for 24 h. Finally the resulting precipitate was washed by centrifugation and dried in vacuum for 24 h at room temperature.

2.2. Characterization of CaAl-LDHs

The products were characterized using Powder X-ray diffraction and *in situ* XRD (Rigaku XRD-6000 diffractometer, Cu Kα radiation: 40 kV, 30 mA). The samples were step-scanned in steps of 0.04° (2θ) in the range (3–70°) using a count time of 10 s/step. For *in situ* XRD experiments, specimens, being prepared by mixing of 20 g cement and 5.7 mL deionized water with or without the CaAl-LDHs additives, were investigated (6 min, 1, 3, 7 and 28), respectively. TG-MS measurements were carried out under an N_2 atmosphere on a thermogravimetric analysis-differential thermal analysis (TG-DTA) instrument equipped with a mass spectrometer (MS), with the temperature-programmed rate (10 °C/min) and the temperature range (20–900 °C). Gaseous emission was analyzed at intervals of 1 s. Analysis of the composition of metallic elements was performed by using ICP emission spectroscopy on a Shimadzu ICPS-7500 instrument. All samples were dissolved in dilute nitric acid. The morphology of cement mortars with and without CaAl-LDHs was investigated by SEM (Hitachi S-4700, 20 kV). The porosity of the hardened mortar samples was measured by mercury intrusion porosimetry.

2.3. Test of compressive and flexural strengths

The compressive strengths and flexural strengths of cement mortars with and without CaAl-LDHs were tested by the China Building Materials Academy (Beijing) in accordance with China National Standards (No. GB/T 7897-2008). The cement mortars is as follows: cement (CEM 42.5)/sand/water (1:1:0.35) for with LDHs (1 and 2 wt%) and 1:3:0.5 for cement mortars with 5 wt% LDHs, respectively. The mortar was mixed for 3 min and then cast in 40 mm × 40 mm × 160 mm cuboid molds. The specimens were demolded after moist-curing at 20 ± 2 °C for 24 h, followed by the standard measurement of compressive strength. The control specimens of the same type were subsequently placed in water at 20 ± 1 °C to continue hydration for 3, 7 and 28 d after mixing, respectively, followed by the standard measurement of compressive and flexural strength. The average values of compressive and flexural strength for each duration of hydration were performed with three specimens to obtain good reproducibility. The temperature and the relative humidity were recorded for the mortar samples with and without LDH additives within a certain period of measuring compressive strength of hardened cement (Supporting Information, Table 1).

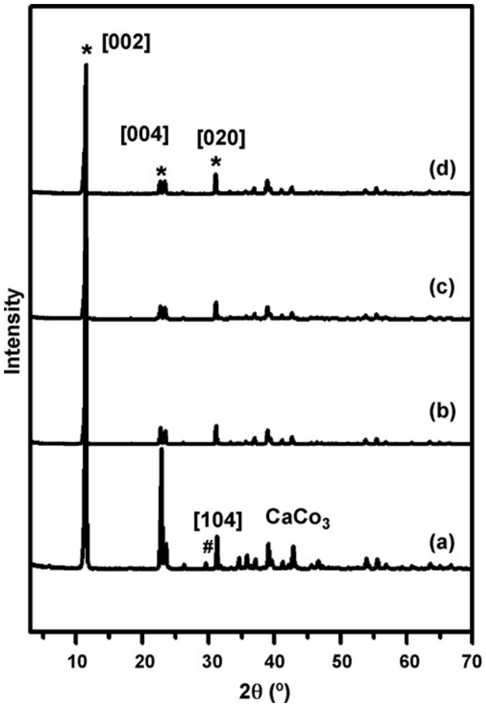

Fig. 1. XRD patterns of CaAl-LDHs prepared by the SNAS method with different volume ratios of ethanol/(water + ethanol), R: (a) $R = 0$; (b) $R = 1/4$; (c) $R = 1/2$; (d) $R = 3/4$. Symbols of * and # show the primary reflection peaks of CaAl-LDH and $CaCO_3$, respectively.

3. Results and discussion

3.1. XRD patterns of CaAl-Cl^--LDHs samples

The XRD patterns (shown in Fig. 1) of the LDHs samples prepared by using the SNAS method in pure water or different ethanol/water mixture media exhibit the characteristic [0 0 2], [0 0 4], and [0 2 0] reflections of CaAl-LDHs with interlayer Cl^- anions (Joint Committee on Powder Diffraction Standards (JCPDS) file No. 78-1219). For the LDHs prepared in pure water, a peak corresponding to the [1 0 4] reflection of $CaCO_3$ is clearly observed at about 29.4° (Fig. 1a), whereas no [1 0 4] peak was observed for samples obtained from the ethanol/water media. It is worth noting that a nitrogen atmosphere and deionized decarbonated water were not employed during the whole preparation process. Vieille et al. [9–11] have previously reported the synthesis of CaAl-LDHs at 65 °C under vigorous magnetic stirring using deionized decarbonated water as well as a nitrogen atmosphere in an attempt to prevent the incorporation of atmospheric CO_2. However, formation of $CaCO_3$ was still observed, as evidenced by the diffraction peak at $2\theta = 29.4°$ in the XRD pattern of their material.

3.2. TG-MS measurements and ICP analysis of pure CaAl-Cl^--LDHs samples

TG-MS measurements (Fig. 2A and B) show that the CaAl-Cl^--LDHs prepared in a ethanol/(ethanol + water) mixture (1:4/v:v, denoted $R = 1/4$) exhibits two stages of weight loss on heating between 20 and 900 °C: based on the MS spectrum of H_2O ($m/z = 18$), the first one from 20 to 160 °C can be attributed to the removal of surface adsorbed and interlayer water molecules (Fig. 2B), corresponding to the endothermic peak at 115 °C in the

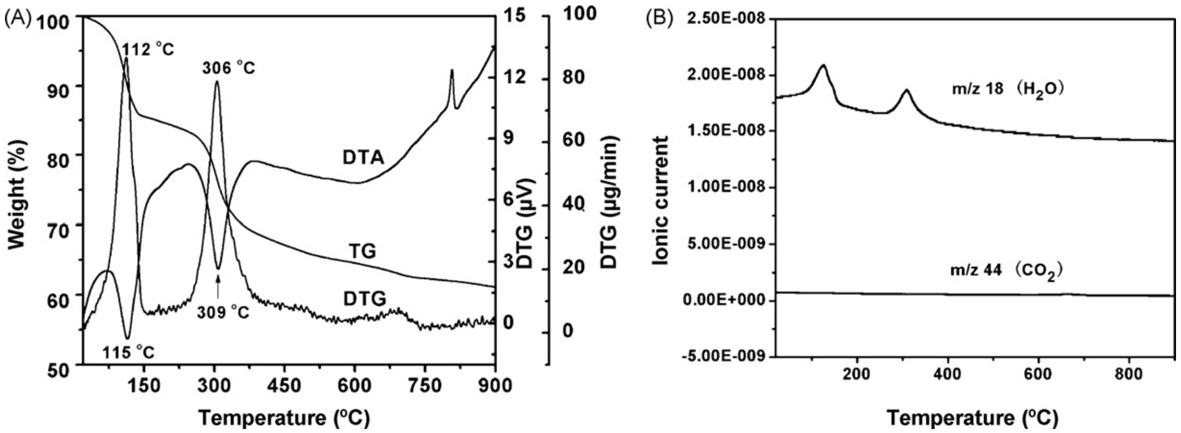

Fig. 2. TG-MS profiles for CaAl-Cl$^-$-LDHs prepared in an ethanol/water mixture with $R = 1/4$. (A) TG-DTA-DTG curves and (B) MS spectra of emission gas.

Table 1
ICP analysis of the ratio of calcium to aluminum in the LDHs.

R	0	1/4	1/2	3/4
Ca/Al	2.50	2.23	2.24	2.23

DTA curve (Fig. 3A); the second step (160–900 °C) is the result of dehydroxylation of the metal hydroxide layers (MS: m/z 18 (H_2O)). This step corresponds to the endothermic peak at 309 °C in the DTA curve. As shown in Fig. 2B, the MS trace expected for CO_2 ($m/z = 44$) does not rise above baseline to any significant extent, which confirms that there is no incorporation of carbonate in the interlayer galleries of the LDH or contamination of the material by calcium carbonate. ICP analysis, given in Table 1, shows that the Ca/Al ratios in the LDHs prepared in ethanol/water media with $R = 0$, 1/4, 1/2 and 3/4 are 2.50, 2.23, 2.24 and 2.23; these values are slightly high than in the reactant mixture (2.00). In combination with the above results of XRD and TG-MS measurements showing no formation of $CaCO_3$ byproduct, the possibility of the values obtained could be that only most Al^{3+} cations were utilized to form the CaAl-LDH sheets in the presence of Ca^{2+} cation. Similar situations were reported, showing the different molar Al^{3+} into the sheets of the LDHs obtained under the same molar stoichiometry of different bivalent metal cations [25,26].

3.3. Compressive and flexural strength

The performance of CaAl-Cl$^-$-LDHs, prepared in an ethanol/water mixture with $R = 1/4$, as a hardening accelerator in concrete was investigated. The values of the early compressive and flexural strengths are key factors in determining the suitability of a hardening accelerator for actual practical application. We can see from Fig. 3A and B and Table 2 that cement mortar with the addition of 1, 2 and 5 wt% CaAl-Cl$^-$-LDHs exhibits increased values of early compressive strength and early flexural strength. Compared to the pristine cement, the specimen with 5 wt% LDHs additive exhibits values of early compressive strength and early flexural strength which are increased by 61% and 71%, respectively.

3.4. Mechanism of action of CaAl-LDHs as a hardening accelerator

Previous literature reports have shown that the mechanism of action of concrete hardening accelerators depends on the fact that the hydration of cement occurs in the liquid phase. Addition of a crystal seed material in the cement hydration process lowers the energy barrier to formation of the hydration products precipitated from the liquid, thus accelerating their rate of precipitation [27–29]. We investigated the cement with and without the CaAl-LDHs additives by means of *in situ* XRD and SEM. Fig. 4 shows XRD patterns of the cement itself, and cement mortars with and without the

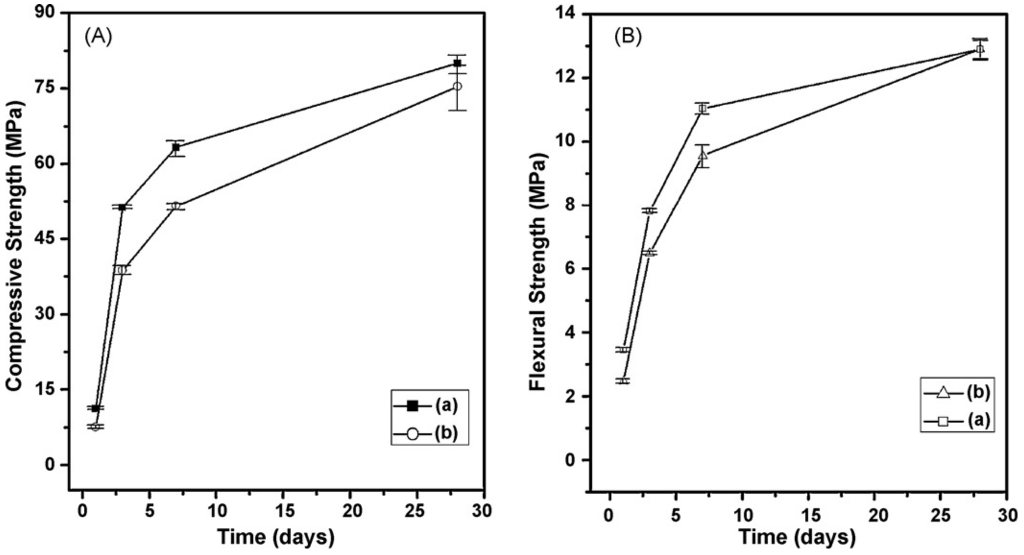

Fig. 3. Evolution of the compressive (A) and flexural (B) strengths of cement mortar after mixing containing (a) and without (b) 2 wt% LDHs additives.

Table 2
Values of compressive strength and flexural strength (in parenthesis) of cement mortars with different contents of LDHs additive relative to the corresponding values for cement mortar without LDHs (taken as 100 in each case).

Sample	Compressive strength (flexural strength) (%)			
	1 d	3 d	7 d	28 d
Cement mortar with LDHs additive (1 wt%)	143 (124)	109 (112)	107 (97)	103 (88)
Cement mortar with LDHs additive (2 wt%)	149 (140)	133 (121)	123 (115)	106 (100)
Cement mortar with LDHs additive (5 wt%)	171 (161)	128 (100)	104 (108)	92 (83)

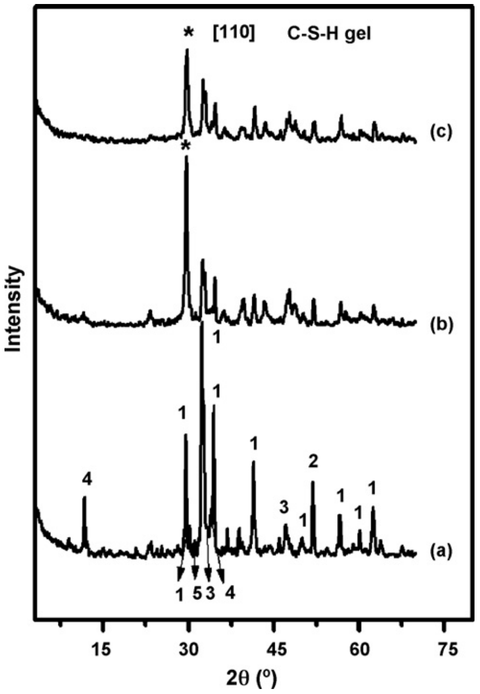

Fig. 4. XRD patterns of cement (a), cement mortar with (b) and without LDHs additives (c) (1: C3S/C2S; 2: C3S; 3: C3A; 4: C4AF; 5: C2S). Symbol of * shows the characteristic [1 1 0] reflection peak of C–S–H gel.

CaAl-LDHs additives. One can clearly see that the presence of the CaAl-LDHs additives (Fig. 4b) indeed accelerates the formation of the cement hydration product, which is the main phase contributing to the strength of cement mortar [14]. Thus, the early strength of the cement mortar increases in the presence of the CaAl-LDHs additive. Furthermore, in the *in situ* XRD patterns of cements containing CaAl-LDHs after different hydration times shown in Fig. 5, the intensity of the characteristic [1 1 0] reflection of C–S–H gel was observed to increase with increasing cement hydration time from 6 min to 28 d, indicating that increasing quantities of C–S–H gel are formed. No LDHs peak was observed due to that the content of LDHs in the cement sample is indeed less than the limitation of XRD analysis. Since the amount of C–S–H gel determines the strength of the cement hydration products, we believe that the presence of the CaAl-LDHs additives is responsible for the early strength of the cement mortars. This can be easily illustrated in terms of comparison between CaAl-LDHs additive and the currently commercial hardening accelerators in concrete, such as calcium nitrate and calcium chloride. Calcium chloride is well-known to work by diffusion of the chloride anion into the cement klinker particle [30]. This gives rise to a high release of hydroxide anions into the pore solutions which in turn increases the solubility of the silicates and hence accelerates C–S–H formation. Compared with the currently commercial calcium chloride, CaAl-LDH used in our case has the same chloride anion. One can hypothesize that the calcium salts and the CaAl-LDHs actually work along the same mechanism, i.e., the sulfate present in any cement releases the chloride anion from the CaAl-LDH by anion exchange, thus creating the same effect on the enhanced performances mentioned above.

It is generally known that the compressive strength of hardened cement derives from not only the quality of the C–S–H crystals and

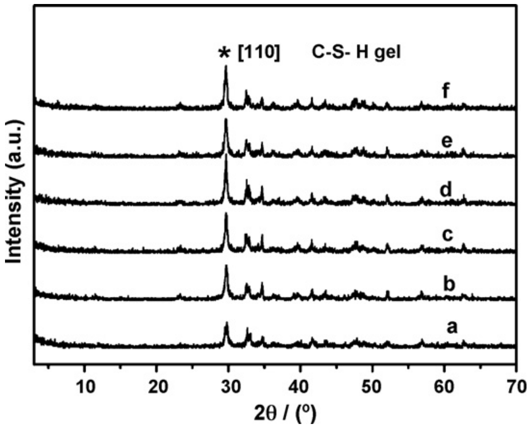

Fig. 5. *In situ* XRD patterns of cement mortar (a) without and (b–f) with LDHs additives after different aging times: (b) 6 min; (c) 1 d; (d) 3 d; (e) 7 d; (f) 28 d. Symbol of * shows the characteristic [1 1 0] reflection peak of C–S–H gel.

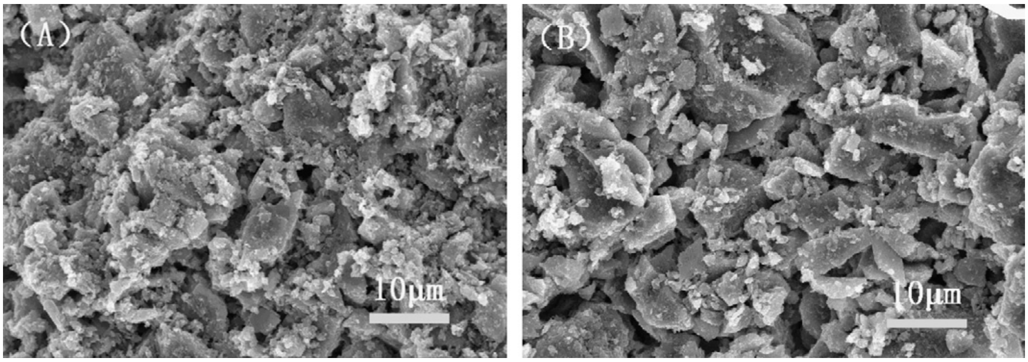

Fig. 6. . SEM images of cement mortars with (A) and without (B) LDHs additives.

also the volume of capillary pores. The SEM micrographs in Fig. 6 show the effects of the CaAl-LDHs additives on the morphology of the cement mortar. It can be seen that the cement mortar containing the LDHs is more dense and less porous than that without the LDHs. According to literature [31], the porosity in cement paste can be classified into two main groups: capillary pores and gel pores. The capillary pores, which are the remnants of water-filled spaces between hydrated cement grains are relatively large and can be observed by SEM. The effects of capillary pores on the compressive and flexural strengths and permeability of concrete are more significant than those of gel pores. The micrographs in Fig. 6 suggest that there are fewer capillary pores in the cement mortar containing the LDH additives, which is responsible for its increased compressive and flexural strengths compared to the cement mortar without LDHs.

To support the above SEM observations, the porosity of the hardened mortar samples was quantitatively measured using a method of mercury intrusion porosimetry (MIP) for the mortar samples with and without CaAl-LDHs (Fig. S1, Supporting Information). The results obtained show that the mean values of the total porosity are 33% and 85% for the mortar samples with and without CaAl-LDH, respectively. The increase is consistent with the observations by SEM on cement mortar with and without CaAl-LDHs.

4. Conclusions

We have shown a facile and scalable preparation of pristine CaAl-LDHs without any $CaCO_3$ byproduct successfully prepared in ethanol/water mixture mixtures. The resulting CaAl-LDHs were shown to be an effective hardening accelerator in concrete. It was found that the optimal dosage of LDHs to all give biggish compressive and flexural strength is about 2 wt% from 1 d to 28 d. The early compressive strength and early flexural strength of cement mortars with this dosage of LDHs were greater than the corresponding values for the mortar alone. Further investigations of *in situ* XRD, SEM and MIP of cement mortars containing the LDHs additive show that addition of the LDHs can accelerate the precipitation rate of the main cement hydration products, leading to reduced concentration of hydration products in the liquid and thus speeding up hydration; this results in the observed acceleration of the cement hardening process. Our results demonstrate that LDHs prepared by this scalable method have the potential to become a viable early strength material for concrete.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China, the 111 Project (B07004), the Program for New Century Excellent Talents in Universities, and the Beijing Nova Program (2007B021).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.08.003.

References

[1] G.R. Williams, D. O'Hare, Towards understanding, control and application of layered double hydroxide chemistry, J. Mater. Chem. 16 (30) (2006) 3065–3074.

[2] P.S. Braterman, Z.P. Xu, F. Yarberry, Layered double hydroxides (LDHs), in: S.M. Auerbach, K.A. Carrado, P.K. Dutta (Eds.), Handbook of Layered Materials, Marcel Dekker, Inc., New York, Basel, 2004, pp. 373–474.

[3] V. Rives, Layered Double Hydroxides: Present and Future, Nova Science Publishers, New York, 2001.

[4] F. Li, X. Duan, Applications of layered double hydroxides, Struct. Bond. 119 (2006) 193–223.

[5] D.G. Evans, X. Duan, Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine, Chem. Commun. 6 (5) (2006) 485–496.

[6] F. Leroux, C. Taviot-Guého, Fine tuning between organic and inorganic host structure: new trends in layered double hydroxide hybrid assemblies, J. Mater. Chem. 15 (2005) 3628–3642.

[7] G. Renaudin, J.P. Rapin, B. Humbert, M. François, Thermal behaviour of the nitrated AFm phase $Ca_4Al_2(OH)_{12}(NO_3)_2{\cdot}4H_2O$ and structure determination of the intermediate hydrate $Ca_4A_{l2}(OH)_{12}(NO_3)_2{\cdot}2H_2O$, Cement Concrete Res. 30 (2000) 307–314.

[8] G. Renaudin, M. Francois, O. Evrard, Order and disorder in the lamellar hydrated tetracalcium monocarboaluminate compound, Cement Concrete Res. 29 (1999) 63–69.

[9] L. Vieille, E.M. Moujahid, C. Taviot-Guého, J. Cellier, J.-P. Besse, F. Leroux, In situ polymerization of interleaved monomers: a comparative study between hydrotalcite and hydrocalumite host structures, J. Phys. Chem. Solids 65 (2004) 385–393.

[10] L. Vieille, C. Taviot-Guého, J.-P. Besse, F. Leroux, Hydrocalumite and its polymer derivatives. 2. Polymer incorporation versus in situ polymerization of styrene-4-sulfonate, Chem. Mater. 15 (2003) 4369–4376.

[11] L. Vieille, I. Rousselot, F. Leroux, J.-P. Besse, C. Taviot-Guého, Hydrocalumite and its polymer derivatives. 1. Reversible thermal behavior of Friedel's salt: a direct observation by means of high-temperature in situ powder X-ray diffraction, Chem. Mater. 15 (2003) 4361–4368.

[12] J. Plank, Z. Dai, N. Zouaoui, Novel hybrid materials obtained by intercalation of organic comb polymers into Ca-Al-LDH, J. Phys. Chem. Solids. 69 (2008) 1048–1051.

[13] A. Allen, J. Thomas, A. Jennings, Composition and density of nanoscale calcium–silicate–hydrate in cement, Nat. Mater. 6 (2007) 311–316.

[14] J.D. Birchall, A.J. Howard, K. Kendall, Flexural strength and porosity of cements, Nature 289 (1981) 388–390.

[15] T. Voigt, T. Malonn, S.P. Shah, Green and early age compressive strength of extruded cement mortar monitored with compression tests and ultrasonic techniques, Cement Concrete Res. 36 (2006) 858–867.

[16] A.C. Aydin, R. Gül, Influence of volcanic originated natural materials as additives on the setting time and some mechanical properties of concrete, Constr. Build. Mater. 21 (2007) 1277–1281.

[17] A. Leemann, L. Holzer, Alkali-aggregate reaction-identifying reactive silicates in complex aggregates by ESEM observation of dissolution features, Cement Concrete Comp. 27 (2005) 796–801.

[18] W.K.W. Lee, J.S.J. Van Deventer, The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements, Cement Concrete Res. 32 (2002) 577–584.

[19] A. Leemann, L. Holzer, The influence of potassium-sodium ratio in cement on concrete expansion due to alkali-aggregate reaction, Cement Concrete Res. 38 (2008) 1162–1168.

[20] S. Aggoun, M. Cheikh-Zouaoui, N. Chikh, R. Duval, Effect of some admixtures on the setting time and strength evolution of cement pastes at early ages, Constr. Build. Mater. 22 (2008) 106–110.

[21] P.J. Sandberg, F. Doncaster, On the mechanism of strength enhancement of cement paste and mortar with triisopropanolamine, Cement Concrete Res. 34 (2004) 973–976.

[22] C.Y. Leea, H.K. Leeb, K.M. Lee, Strength and microstructural characteristics of chemically activated fly ash–cement systems, Cement Concrete Res. 33 (2003) 425–431.

[23] Y. Zhao, F. Li, R. Zhang, D.G. Evans, X. Duan, Preparation of layered double-hydroxide nanomaterials with a uniform crystallite size using a new method involving separate nucleation and aging steps, Chem. Mater. 14 (2002) 4286–4291.

[24] Y.J. Feng, D.Q. Li, Y. Wang, D.G. Evans, X. Duan, Synthesis and characterization of a UV absorbent-intercalated Zn–Al layered double hydroxide, Polym. Degrad. Stabil. 91 (2006) 789–794.

[25] H.Y. Chen, F.Z. Zhang, T. Chen, S.L. Xu, D.G. Evans, X. Duan, Comparison of the evolution and growth processes of films of M/Al-layered double hydroxides with M = Ni or Zn, Chem. Eng. Sci. 64 (2009) 2617–2622.

[26] R.K. Allada, J.D. Pless, T.M. Nenoff, A. Navrotsky, Thermochemistry of hydrotalcite-like phases intercalated with $CO_3{}^{2-}$, NO^{3-}, Cl^-, I^-, and $ReO_4{}^-$, Chem. Mater. 17 (2005) 2455–2459.

[27] C.S. Liu, W. Gai, S.H. Pan, Z.S. Liu, The exothermal behavior in the hydration process of calcium phosphate cement, Biomaterials 24 (2003) 2995–3003.

[28] C.S. Liu, W. Shen, Effect of crystal seeding on the hydration of calcium phosphate cement, J. Mater. Sci. Mater. Med. 8 (1997) 803–807.

[29] H.F. Shao, C.S. Liu, Y. Huang, X.H. Cao, H.C. Yang, Shape control of hydroxyapaptite crystal seed and its effects on the in situ reinforcement of calcium phosphate cement, J. Inorg. Mater. 16 (2001) 933–939.

[30] Y. Elakneswaran, T. Nawa, K. Kurumisawa, Electrokinetic potential of hydrated cement in relation to adsorption of chlorides, Cement Concrete Res. 39 (2009) 340–344.

[31] W.Y. Kuo, J.S. Huang, C.H. Lin, Effects of organo-modified montmorillonite on strengths and permeability of cement mortars, Cement Concrete Res. 36 (2006) 886–895.