Organo-Mineral Phases Formed During Cement Hydration

J. Plank[*], *Z. Dai, H. Keller*
Technische Universität München, Garching, Germany

1. Introduction

Tricalcium aluminate (C_3A) is an important constituent and by far the most reactive phase in ordinary Portland cement [1]. Typically, 5-16 wt.% of C_3A occur in a cement clinker. The reactivity and hydration behavior of the aluminate phase determines the stiffening and setting behavior of the cement paste to a great extent. Therefore, it has a significant influence on the workability of cement containing products such as concrete and dry-mix mortars.

The hydration products of C_3A depend on the reaction temperature and the concentration of Ca^{2+} and Al^{3+} in solution. At 25 °C, tricalcium aluminate quickly hydrates to form the metastable, layered phases C_2AH_8 and C_4AH_{13} which crystallize as hexagonal plates. Also, some solid solutions of these metastable phases with variable contents of calcium (ranging from 2.0 to 2.4) and water (ranging from 8.0 to 10.2) and amorphous, gel like $Al_2O_3 \cdot 3H_2O$ are present. The metastable phases quickly convert to the stable cubic phase C_3AH_6 (katoite) which crystallizes as rhombododecahedra. $Ca(OH)_2$ (portlandite) and γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite) are formed as well [2]. C_2AH_8 and C_4AH_{13} belong to the class of layered double hydroxides (LDHs) of which many examples are known [3]. Their composition is generally expressed by the formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$ $\cdot X^{m-}_{x/m} \cdot nH_2O$ with M^{II} = Ca^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}; M^{III} = Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Mn^{3+}; X = interlayer anion, e.g. OH^-, Cl^-, NO_3^-, ClO_4^-, CO_3^{2-}, SO_4^{2-}. By replacing the hydroxide ions, numerous anions can be intercalated in between the cationic main layers of LDH compounds [4]. Examples are inorganic anions such as sulfate, carbonate or nitrate and small organic molecules like oxalate, citrate or benzoate [5]. Linear polyelectrolytes such as polyacrylate, polyvinylsulfonate, polystyrene sulfonate and others are also known to intercalate between the cationic layers [6-9].

The interlayer or gallery height between the cationic main layers depends on the size and steric orientation of the intercalated anion. **Table 1** provides data for interlayer distances of Ca-Al-A-LDH (A = anion) compounds with different anions. The water content in between the layers can vary and may result in slightly different interlayer distances [3, 5].

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[*] TU München, Institute for Inorganic Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany; email: johann.plank@bauchemie-tum.de

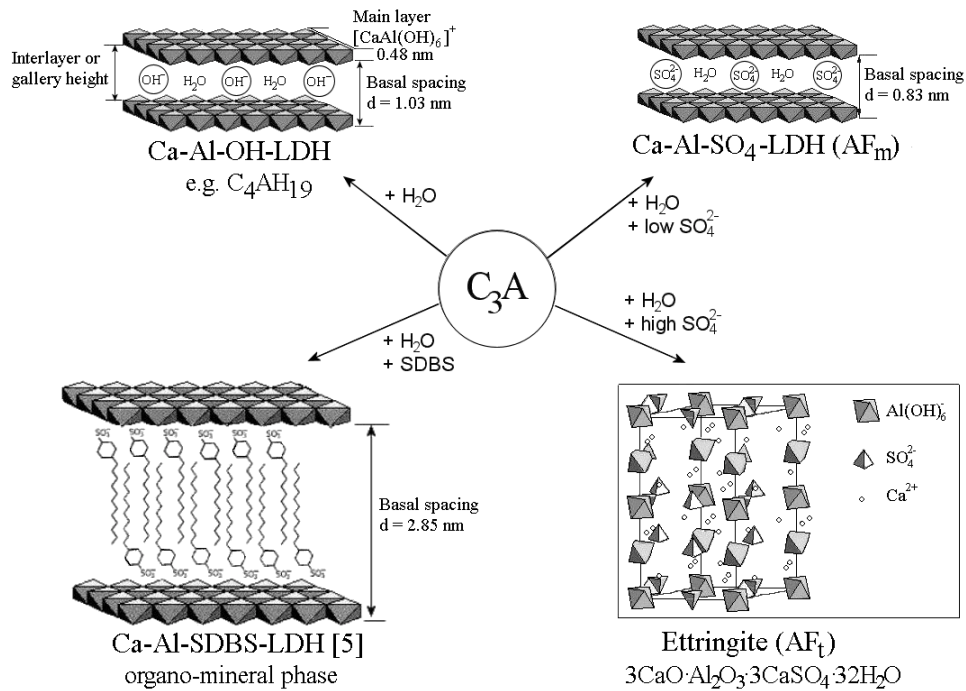Fig. 1: Hydration products of C₃A in the presence of different anions.

Fig. 1: Hydration products of C_3A in the presence of different anions.

Table 1: Basal spacing between $[Ca_2Al(OH)_6]^+$ main layers for different anions intercalated

| Intercalated anion	Basal spacing (nm)	Ref.
CO_3^{2-}	0.76	[7]
SO_4^{2-}	0.89	[10]
Citrate	1.21	[5]
Phthalate	1.47	[5]
Polyvinylsulfonate	1.32	[7]
Polystyrenesulfonate	1.96	[7]

The potential reaction patterns of C_3A hydrating in presence and absence of sulphate are shown in **Fig. 1**. Also shown is the structure of a calcium aluminate with intercalated sodium dodecylbenzenesulfonate (SDBS) surfactant.

Organic admixtures are commonly used to beneficiate the properties of concrete and mortar. Among them are water-reducers (plasticizers), superplasicizers, retarders, accelerators, shrinkage-reducers and water-retention agents. The effectiveness of charged admixtures derives from adsorption on the oppositely charged surface of hydrating cement particles, thus creating electrostatic or steric repulsion between them [11]. It has long been speculated that admixtures may not only adsorb, but can

also be absorbed into cement hydration products, resulting in new organo-mineral phases. For example, some authors have pointed out that the addition point of time of the admixture to concrete can significantly impact its performance [12]. This effect seems to be particularly strong for portland cement with a high amount of C_3A. FERNON et al. were the first to confirm the existence of an organo-mineral phase formed by intercalation of low molecular weight, β-naphthalenesulfonate formaldehyde (BNS) during C_3A hydration [13]. Very recently, the intercalation of high-molecular weight, comb-type polycarboxylate superplasticizer based on methacrylic acid/ω-methoxy(polyethylenglycol) methacrylate copolymer was shown [14]. This result was quite surprising because comb-type polycarboxylates were thought to be too bulky to allow intercalation. Consequently, a more thorough study of the intercalation potential of polycarboxylates with different chemical structures and the mechanisms influencing the formation of such organo-mineral phases was conducted.

2. Intercalation of Methacrylic Acid/ω-Methoxy poly (ethylene glycol) methacrylate (MAA/MPEG-MA) Type Polycarboxylates into C_3A Hydration Phases
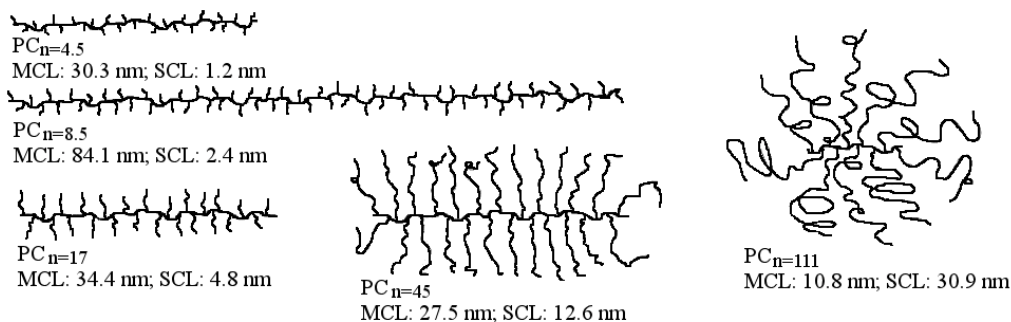
Polycarboxylates composed of methacrylic acid and MPEG methacrylate ester in a molar ratio of 6:1, thus showing a low side chain density, and side chain lengths of n_{EO}= 4.5; 8.5; 17; 45 and 111 were used. Their chemical structure is shown in **Fig. 2a.** Synthesis of the copolymers was carried out via radical copolymerization in water. Details of the synthesis and characterization (GPC, IR and light scattering detectors) are described elsewhere [15]. From the known molar composition, M_n and bond lengths and angles, the lengths of main and side chains of the copolymers can be calculated [16]. Based upon these calculations, schematic representations of the synthesized polycarboxylate macromolecules were developed, illustrating their molecular conformation and also their bulky nature (**Fig. 3a**).
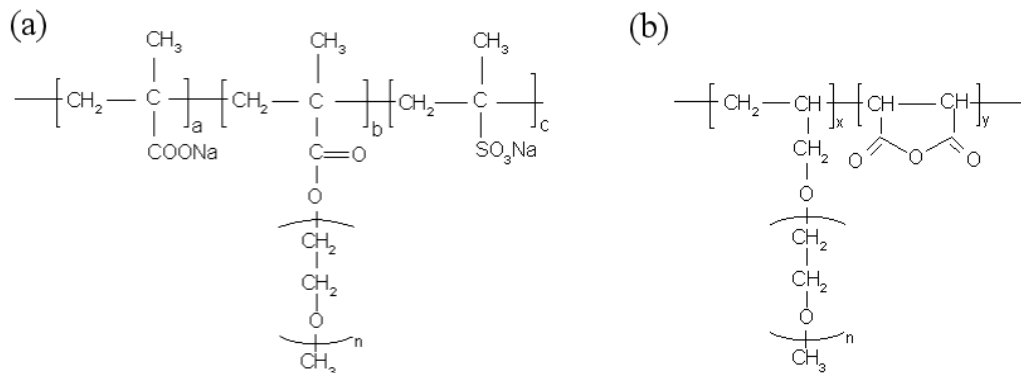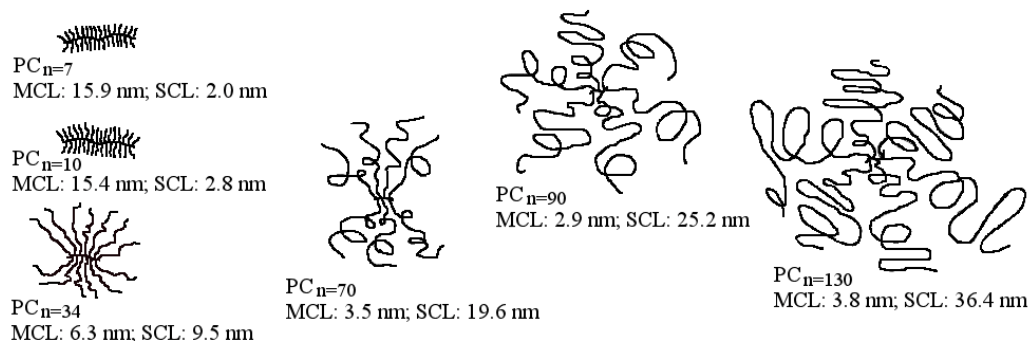

Fig. 2: Chemical structure of the synthesized MAA/MPEG-MA (a:b = 6:1) (a) and AMPEG/MAL (x:y = 1:1), (b) copolymers.

To prepare the organo-mineral phases, rehydration of C_3A in diluted aqueous solutions of MAA/MPEG-MA copolymer was used. C_3A was prepared via a sol-gel process as a precursor before calcination. Details of the synthesis are described elsewhere [14]. After 2 days reaction time, a white, micro-crystalline precipitate was obtained, filtered, washed 3 times with deionised water and dried for 12 hours at 55°C under vacuum (10^{-3} Torr). Under the SEM, sandrose type crystals of approx. 1 µm size, consisting of intergrown platelets, are observed (**Fig. 4**). The morphology of the crystals is very similar to that of calcium aluminate monosulfate (AF_m) which also possesses a lamellar structure. Note that the synthesis of these PC intercalates was carried out in the absence of sulfate. For comparison, Ca-Al-OH-LDH was prepared by the reaction of monocalcium aluminate in deionised water [17].

(a) MAA/MPEG-MA copolymers

PC$_{n=4.5}$
MCL: 30.3 nm; SCL: 1.2 nm

PC$_{n=8.5}$
MCL: 84.1 nm; SCL: 2.4 nm

PC$_{n=17}$
MCL: 34.4 nm; SCL: 4.8 nm

PC$_{n=45}$
MCL: 27.5 nm; SCL: 12.6 nm

PC$_{n=111}$
MCL: 10.8 nm; SCL: 30.9 nm

(b) AMPEG-MAL copolymers

PC$_{n=7}$
MCL: 15.9 nm; SCL: 2.0 nm

PC$_{n=10}$
MCL: 15.4 nm; SCL: 2.8 nm

PC$_{n=34}$
MCL: 6.3 nm; SCL: 9.5 nm

PC$_{n=70}$
MCL: 3.5 nm; SCL: 19.6 nm

PC$_{n=90}$
MCL: 2.9 nm; SCL: 25.2 nm

PC$_{n=130}$
MCL: 3.8 nm; SCL: 36.4 nm

Fig. 3: Schematic representation of molecular size and conformation of synthesized MAA/MPEG-MA (a) and AMPEG/MAL (b) polycarboxylates.

X-ray diffraction patterns for Ca-Al-OH-LDH as well as for the series of intercalated PC-LDHs are shown in **Fig. 5.** The diffraction pattern for the inorganic Ca-Al-OH-LDH (**Fig. 5a**) shows a typical layered structure with a basal d-value of 1.03 nm (PDF: 00-042-0487). For the organo-LDHs (**Fig. 5b-f**), intercalation of the PC macromolecules is confirmed by a shift of the d-values to higher numbers, indicating a greater distance between the

cationic $[Ca_2Al(OH)_6]^+$ main layers caused by the presence of the bulky polymer. It also can be seen that the basal spacings increase with increasing side chain length of the PC. Compared to the Ca-Al-OH-LDH, the crystallinity of the organo-LDHs appears to be lower, as shown by the broadening and the decrease in intensity of the X-ray diffraction signals. The patterns clearly indicate that this type of PC intercalates rather well when side chain length (n_{EO}) is 45 or less. Therefore, Ca-Al-PC$_{n=111}$-LDH (**Fig. 5f**) shows much less intercalated copolymer. Obviously, if the side chain becomes too long, intercalation is hindered by steric reasons.
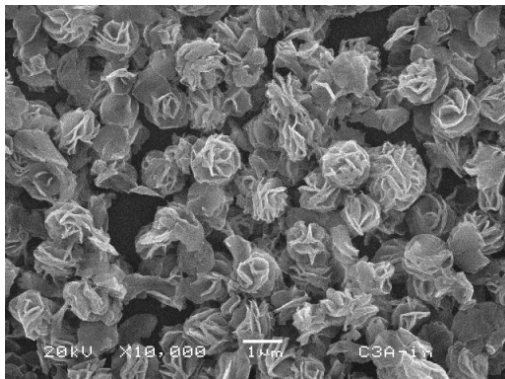
Fig. 4: SEM micrograph of organo-mineral phase formed from rehydration of C_3A in the presence of MAA/MPEG-MA polycarboxylate with n_{EO}= 4,5 (magnification: 10,000 x).
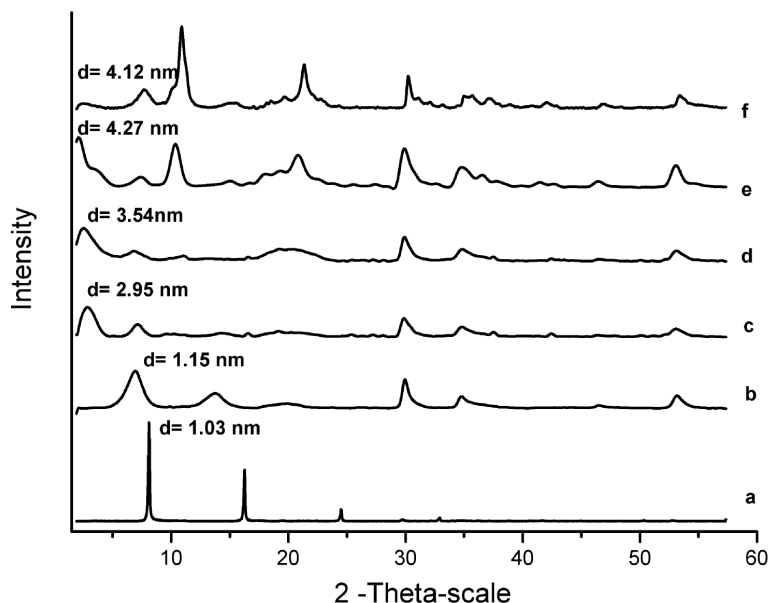

Fig. 5: X-ray diffraction patterns of Ca-Al-OH-LDH (a), Ca-Al-PC$_{n=4.5}$-LDH (b), Ca-Al-PC$_{n=8.5}$-LDH (c), Ca-Al-PC$_{n=17}$-LDH (d), Ca-Al-PC$_{n=45}$-LDH (e) and Ca-Al-PC$_{n=111}$-LDH (f) intercalates; PC=MAA/MPEG-MA copolymer; for better comparison, the relative intensity of (a) was reduced by a factor 20.

Intercalation was also confirmed by elemental analysis (**Table 2**). The organic portion in the new organo-mineral phases was calculated based on the composition formula for each PC-LDH developed using the following assumptions: a) the molar ratio of Ca to Al in the PC-LDH composites is 2:1. In case of a significant deviation from this ratio, the excess Al was attributed to $Al(OH)_3$ by-product – this phase has been detected by XRD ($2\theta=18.5°$). b) all of the carbon content is attributed to the PCs. The absence of an XRD-reflex belonging to intercalated carbonate confirms this assumption. c) Hydroxide anions are present in order to achieve complete charge compensation with the positively charged Ca-Al-layer. The amount of the organic part in the PC-LDHs ranges between 21.4 and 53.0 wt-%, resp. This is significantly higher than for surface adsorption of copolymer on cement hydrate phases which at the most was found to be 13 wt % [18], thus confirming the intercalation. Finally, TEM pictures were taken from the PC-LDHs. All samples show a layered structure, as demonstrated for the sample $PC_{n=111}$-LDH in **Fig. 6**.

Table 2: Chemical compositions of Ca-Al-OH-LDH and Ca-Al-PC-LDHs (PC = MAA/MPEG-MA copolymers).

Intercalate	Ca wt. %	Al wt.%	C wt.%	H wt.%	Organic part wt.%	calculated composition
Ca-Al-OH-LDH	19.9	16.5	-	4.43	-	$Ca_2Al(OH)_{7.00}\cdot3.48H_2O, 1.46Al(OH)_3$
Ca-Al-4.5PC-LDH	20.9	6.9	17.09	4.95	29.30	$Ca_2Al_{0.98}(OH)_{6.10}\cdot[-PC_{n=4.5}-]_{0.14}\cdot3.36H_2O$
Ca-Al-8.5PC-LDH	14.8	4.9	24.75	5.87	44.20	$Ca_2Al_{0.97}(OH)_{5.41}\cdot[-PC_{n=8.5}-]_{0.25}\cdot5.48H_2O$
Ca-Al-17PC-LDH	12.0	3.9	28.39	6.87	50.40	$Ca_2Al_{0.96}(OH)_{5.38}\cdot[-PC_{n=17}-]_{0.25}\cdot7.14H_2O$
Ca-Al-45PC-LDH	13.3	5.4	29.80	6.44	53.00	$Ca_2Al(OH)_{6.28}\cdot[-PC_{n=45}-]_{0.12}\cdot2.45H_2O, 0.21Al(OH)_3$
Ca-Al-111PC-LDH	19.9	7.4	11.70	4.88	21.42	$Ca_2Al(OH)_{6.91}\cdot[-PC_{n=111}-]_{0.015}\cdot5.00H_2O, 0.10Al(OH)_3$
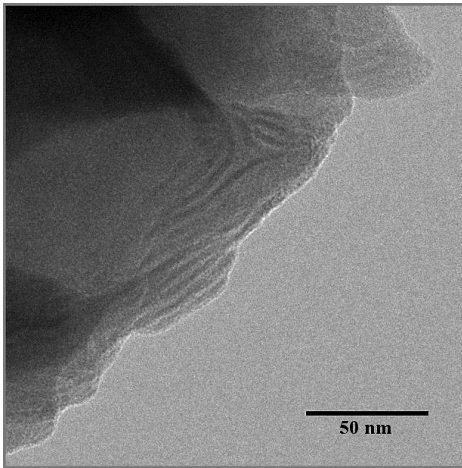
Fig. 6: TEM picture of Ca-Al-$PC_{n=111}$-LDH (PC = MAA/MPEG-MA copolymer).
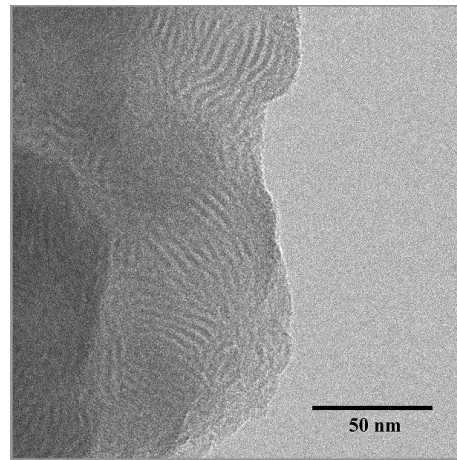
Fig. 8: TEM picture of Ca-Al-$PC_{n=7}$-LDH (PC = AMPEG/MAL copolymer).

3. Organo-Mineral Phases from α-Allyl-ω-methoxy poly ethylene glycol ether/ Maleic Anhydride (AMPEG/ MAL) Type Polycarboxylates

Allylether-based polycarboxylates represent another group of superplasticizers which have found wide-spread use [19]. In comparison to MAA/MPEG-MA type PCE, they differ in their superior temperature and hydrolysis stability, because of an ether instead of ester linkeage.

For this study, a series of copolymers based on maleic anhydride and AMPEG with ethylene oxide units (n_{EO}) in the side chain of 7; 10; 34; 70; 90 and 130 was prepared by bulk radical copolymerisation using benzoyl peroxide as initiator. Details of the synthesis and characteristic properties are described in [20]. The chemical structure of the copolymers is shown in **Fig. 2b.** In contrast to MAA/MPEG-MA copolymers, allyl ether/maleic anhydride copolymers possess a well-defined primary structure of strictly alternating monomer units (ABAB) because neither allyl ether nor maleic anhydride monomer undergoes homopolymerization [21]. Main and side chain lengths of these copolymers were calculated according to the method described in chapter 2. A schematic representation of their molecular size and conformation is shown in **Fig. 3b.** Obviously, these allyl ether copolymers show a much higher side chain density than the methacrylate copolymers. Because of this characteristic, their intercalation into C_3A hydration phases should be more difficult.

Intercalation experiments were conducted with these allyl ether copolymers using the method described before for methacrylate type copolymers. Rehydration of C_3A in the presence of these copolymers again produced a white, microcrystalline precipitate which was analysed by XRD, elemental analysis and TEM.

The powder XRD patterns of the products are shown in **Fig. 7.** As can be seen from the first basic reflection corresponding to the highest d-value, intercalation of the AMPEG/MAL copolymers possessing side chain lengths (n_{EO}) of 7 and 10, resp., intercalate very well. Organo-mineral phases with relative high crystallinity are obtained, as indicated by the sharpness of the reflection and its high intensity. AMPEG/MAL copolymers with side chain lengths between 34 and 90 intercalate much less. They produce less intense, broader signals. The copolymer with n_{EO}=130 shows almost no intercalation.

Elemental analysis also confirms that intercalation has taken place. **Table 3** shows the organic parts of the PC intercalates are between 48.27 and 76.68 wt.%. It is interesting to note that the organic part in Ca-Al-PC$_{n=34}$-LDH is lower than for Ca-Al-PC$_{n=7}$-LDH and Ca-Al-PC$_{n=10}$-LDH, in spite of their much shorter side chains. This data confirms that AMPEG/MAL copolymers with short side chains intercalate to a very high extent. This is decreasing with longer side chain.

Table 3: Chemical compositions of Ca-Al-OH-LDH and Ca-Al-PC-LDHs (PC = AMPEG/MAL copolymers).

Intercalate	Ca wt.%	Al wt.%	C wt.%	H wt.%	Organic part wt.%	calculated composition
Ca-Al-OH-LDH	19.9	16.5	-	4.43	-	$Ca_2Al(OH)_7 \cdot 3.48H_2O$, $1.46Al(OH)_3$
Ca-Al-PC$_{n=7}$-LDH	14.1	4.5	28.28	6.38	52.77	$Ca_2Al(OH)_{5.72} \cdot [PC_{n=7}]_{0.64} \cdot 3.9H_2O$, $0.115Ca(OH)_2$
Ca-Al-PC$_{n=10}$-LDH	13.1	4.3	30.56	6.12	56.75	$Ca_2Al(OH)_{5.86} \cdot [PC_{n=10}]_{0.57} \cdot 3.4H_2O$, $0.056Ca(OH)_2$
Ca-Al-PC$_{n=34}$-LDH	14.5	5.2	26.04	6.04	48.27	$Ca_2Al(OH)_{6.68} \cdot [PC_{n=34}]_{0.16} \cdot 3.5H_2O$, $0.063Al(OH)_3$
Ca-Al-PC$_{n=70}$-LDH	9.0	3.2	36.01	7.12	65.83	$Ca_2Al(OH)_{6.64} \cdot [PC_{n=70}]_{0.18} \cdot 4.5H_2O$, $0.054Al(OH)_3$
Ca-Al-PC$_{n=90}$-LDH	6.3	2.2	41.71	8.03	76.68	$Ca_2Al(OH)_{6.53} \cdot [PC_{n=90}]_{0.235} \cdot 4.2H_2O$, $0.035Al(OH)_3$
Ca-Al-PC$_{n=130}$-LDH	8.4	3.5	36.91	7.65	68.15	$Ca_2Al(OH)_{6.78} \cdot [PC_{n=130}]_{0.11} \cdot 3.5H_2O$, $0.23Al(OH)_3$
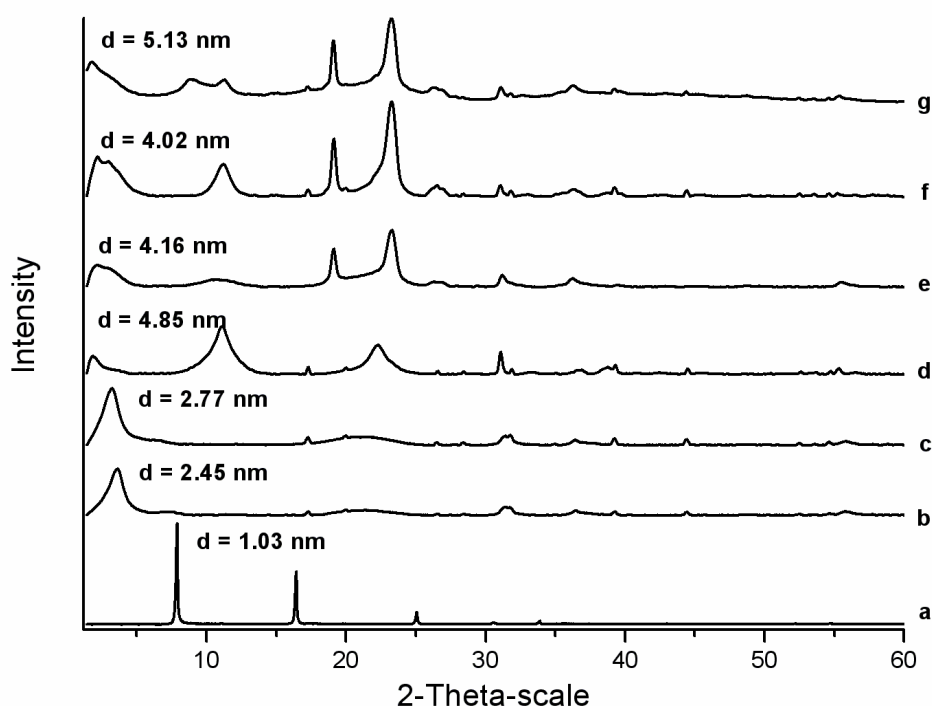
Fig. 7: X-ray diffraction patterns for Ca-Al-OH-LDH (a), Ca-Al-PC$_{n=7}$-LDH (b), Ca-Al-PC$_{n=10}$-LDH (c), Ca-Al-PC$_{n=34}$-LDH (d), Ca-Al-PC$_{n=70}$-LDH (e), Ca-Al-PC$_{n=90}$-LDH (f) and Ca-Al-PC$_{n=130}$-LDH (g) ; PC=AMPEG/MAL copolymer; for better comparison, the relative intensity of (a) was reduced by a factor of 20.

As shown in the XRD patterns for MAA/MPEG-MA and AMPEG/MAL copolymers, resp. (**Fig. 5** and **Fig. 7**), the tendency to form organo-mineral phases depends on the side chain density and side chain length of a copolymer: MAA/MPEG-MAL copolymers possessing low side chain density intercalate well with side chain lengths up to 45 EO units whereas AMPEG/MAL copolymers with high side chain density only intercalate well

when side chain length is 10 or less EO units. Obviously, the assembly process for the organo-mineral phase is more complicated in the presence of a copolymer with tightly packed side chains. Still, the AMPEG/MAL copolymers with 130 EO units in the side chain intercalate to some extent and shown a d-value of 5.13 nm which to our knowledge is the highest d-value reported so far for Ca-Al-LDH compounds. To investigate the layer structure, TEM micrographs of all AMPEG/MAL composite materials were taken. The picture of Ca-Al-PC-LDH incorporating the short side chain AMPEG/MAL copolymer with n_{EO}=7 (**Fig. 8**) reveals rather disordered blocks within the LDH morphology, indicating that the organo-mineral phase forms very quickly.

4. Intercalates formed in the presence of sulfate

In Portland cements, sulfates such as e.g. gypsum, $CaSO_4$-α-hemihydrate, anhydrite or soluble alkali sulfates (Na_2SO_4, K_2SO_4) are used to avoid instant gelation caused by the formation of Ca-Al-OH-LDH phases, e.g. C_2AH_8 or C_4AH_{13}. As shown in **Fig. 1**, low sulfate content results in the formation of monosulfate (AF_m) possessing a layered structure whereas high sulfate content leads to ettringite (AF_t) with column structure [1,2]. In a concrete or mortar, sulfate will compete with the anionic superplasticizer for intercalation. To investigate on the intercalation potential for PC superplasticizers under realistic conditions, MAA/MPEG-MA copolymer with a side chain length of 45 EO units was added to C_3A hydrating in water containing low, medium or high amount of sulfate (molar ratio K_2SO_4: C_3A = 0.1, 0.35, 0.7, 1 and 2, resp.).The same process for preparing and drying the samples as before was used.

XRD patterns of all samples prepared are presented in **Fig. 9.** X -ray diffraction shows that in case of high sulfate content, either a mixture of monosulfate and ettringite (**Fig. 9a**) or only monosulfate (**Fig. 9b**) are formed. No significant intercalation of PC is found. This is also confirmed by the very low carbon content (2.72 wt.% and 3.38 wt.%) of the samples. At medium sulfate content (**Fig. 9c**), partial intercalation of PC is observed, indicated by a weak reflection in the XRD pattern with a d-value at 4.29 nm and a carbon content of 9.35 wt.%. When less sulfate is present (**Fig. 9d**), however, very strong intercalation of the PC is observed. This organo-mineral phase contains 16.76 wt.% of carbon and shows an extremely high d-value of 5.18 nm with strong intensity. Such high d-value was not observed for the intercalate formed in the absence of sulfate (**Fig. 9e**). One possible explanation for the unusually high d-value is that a Ca-Al-PC-SO$_4$-LDH phase is formed composed of regularly alternating PC and sulfate filled interlayers as shown in **Fig. 10**. Very few cases of this type of LDH with different interlayer anions have been described previously [22].

Fig. 9: X-ray diffraction patterns of C₃A hydration products formed in the presence of PC and different SO₄²⁻ concentrations; PC = MA/MPEG-MA (n_EO=45) copolymer.
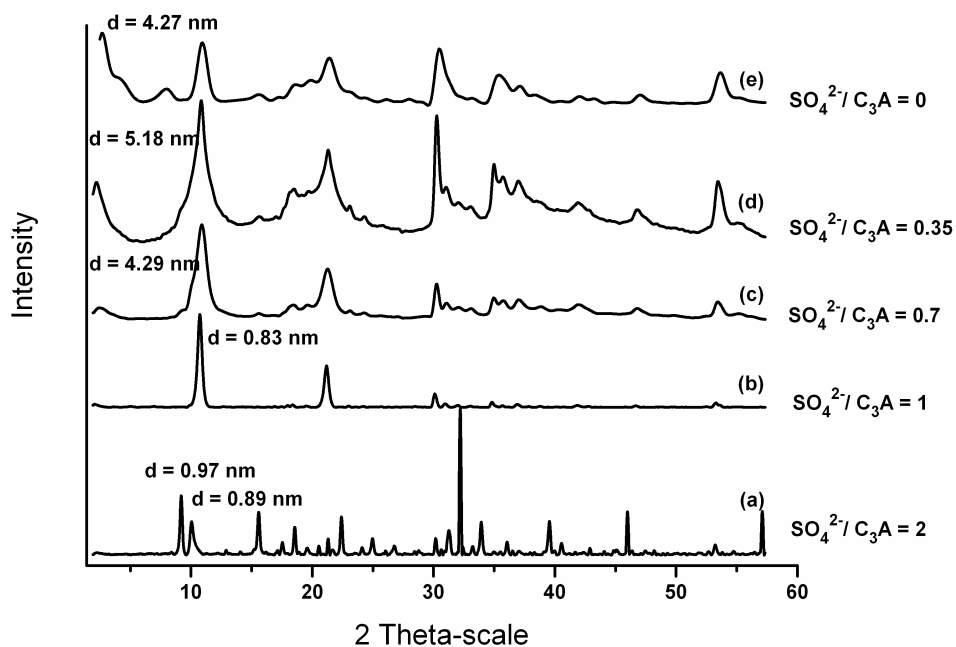
Fig. 9: X-ray diffraction patterns of C_3A hydration products formed in the presence of PC and different SO_4^{2-} concentrations; PC = MA/MPEG-MA (n_{EO}=45) copolymer.
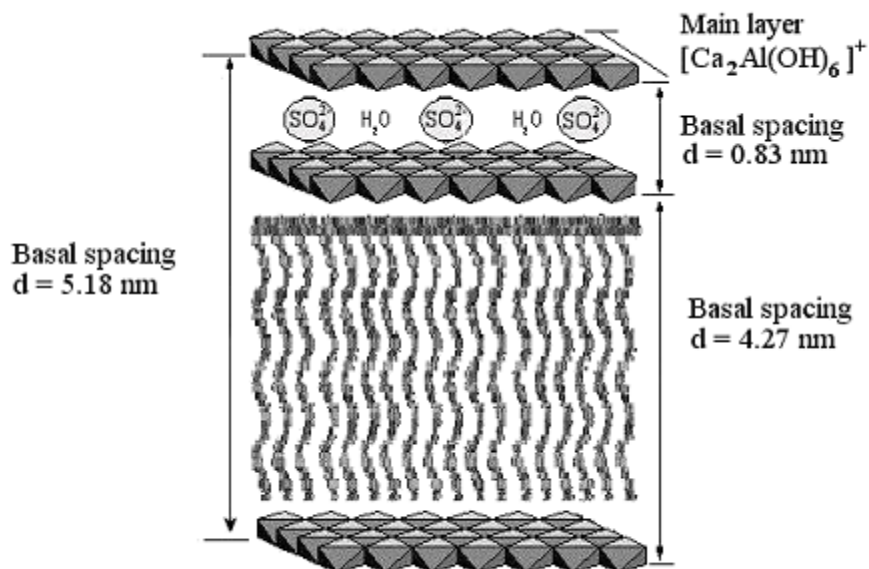

Fig. 10: Proposed model for the organo-mineral phase with alternating interlayer anions, obtained from C_3A hydration in the presence of $PC_{n=45}$ and low SO_4^{2-} content.

5. Conclusions

Polycarboxylate superplasticizers intercalate surprisingly well into C_3A hydration phases and form Ca-Al-PC-LDH compounds. The tendency to intercalate increases with shorter side chains and lower side chain density. Sulfate anions present in any Portland cement compete with the admixture anions for intercalation. Their tendency to intercalate is higher than for PC molecules. Therefore, PCs intercalate well only if low sulfate content is present. In this case, novel composite materials with mixed layers are formed. The results confirm that even bulky admixture molecules such as polycarboxylates have a potential for chemisorption. Therefore, almost any anionic admixture must be considered to not only adsorb on the surface of cement hydration products, but to incorporate into the crystal structures of the hydrates. Unfortunately, intercalation does not contribute to the effectiveness of an admixture. Consequently, new admixture technology should be looked at which minimizes the probability of intercalation.

6. Literature

[1] F.W. Locher, "Cement - Principles of production and use", Verlag Bau+Technik GmbH, Düsseldorf, 2006
[2] J. d'Ans, H. Eick, ZKG International 6 (1953) 197
[3] H.F.W. Taylor, "Cement Chemistry", Academic Press, London, 1990
[4] 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
[5] M. Meyn, K. Beneke and G. Lagaly, "Anion-Exchange Reaction of Layered Double Hydroxides", Inorg. Chem. 29 (1990) 5201-5207
[6] S. Miyata, T. Kumura, "Synthesis of new Hydrotalcite-like Compounds and Their Physico-Chemical Properties", Chem. Lett. 2 (1973) 843-848
[7] C.O. Oriakhi, I.V. Farr, M.M. Lerner, "Incorporation of poly(acrylic acid), poly(vinylsulfonate) and poly(styrenesulfonate) within layered double hydroxides", J. Mater. Chem. 6 (1996) 103-107
[8] E.M. Moujahid, J.-P. Besse, F. Leroux, "Synthesis and characterization of a polystyrene sulfonate layered double hydroxide nanocomposite. In-situ polymerization vs. polymer incorporation", J. Mater. Chem. 12 (2002) 3324-3330
[9] F. Leroux, P. Aranda, J.-P. Besse, E. Ruiz-Hitzky, "Intercalation of Poly(Ethylene Oxide) Derivatives into Layered Double Hydroxides", Eur. J. Inorg. Chem. (2003) 1242-1251
[10] A. N. Christensen, T. R. Jensen, J. C. Hanson, "Formation of ettringite, $CaAl_2(SO_4)_3(OH)_{12} \cdot 26 \ H_2O$, AF_t, and monosulfate, $Ca_4Al_2O_6(SO_4) \cdot 14H_2O$, AF_m, in hydrothermal hydration of Portland cement and of calcium aluminium oxide-calcium sulfate dihydrate

mixtures studied by in situ synchrotron X-ray powder diffraction", J. Solid. State. Chem. 177 (2004) 1944-1951

[11] T. Sugiyama, A. Ohta, T. Uomoto, "The dispersing mechcanism and applications of polycarboxylate-based superplasticizers", in: G. Grieve, G. Owens (Eds.), 11th International Congress on the Chemistry of Cement (ICCC), 2003, pp. 560-568

[12] R.J. Flatt, Y.F. Houst, "A simplified view on chemical effects perturbing the action of superplasticizers", Cem. Concr. Res. 31 (2001) 1169–1176

[13] V. Fernon, A. Vichot, N. Le Goanvic, P. Colombet, F. Corazza, U. Costa, "Interaction between Portland cement hydrates and polynaphthalene sulfonates", Fifth CANMET/ACI Conference on Superplasticizers in Concrete, ACI, SP-173 (1997) 225-248

[14] J. Plank, Z. Dai, P. Andres, "Preparation and characterisation of new Ca-Al-polycarboxylate layered double hydroxides", Mat. Lett. (2006) – in press, available online

[15] J. Plank, G. Bassioni, Z. Dai, H. Keller, B. Sachsenhauser, N. Zouaoui, "Neues zur Wechselwirkung zwischen Zementen und Polycarboxylate-Fließmitteln", 16. ibausil, Bauhaus-Universität Weimar, 2006, Tagungsband 1 , 579-598

[16] A. Ohta, T. Sugiyama, T. Uomoto, "Study of dispersing effects of polycarboxylate-based dispersants on fine particles", Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI, SP-195 (2000) 211-227

[17] P. Faucon, T. Charpentier, D. Bertrandie, A. Nonat, J. Virlet, J. C. Petit, "Characterization of Calcium Aluminate Hydrates and Related Hydrates of Cement Pastes by ^{27}Al MQ-MAS NMR", Inorg. Chem. 37 (1998) 3726-3733

[18] J. Plank, Ch. Hirsch, "Superplasticizer Adsorption on Synthetic Ettringite", Seventh CANMET/ACI Conference on Superplasticizers in Concrete (Editor V. M. Malhotra), ACI, Berlin (2003), SP-217-19; 283-298

[19] E. Sakai, K. Yamada, A. Ohta, "Molecular structure and dispersion-adsorption mechanism of comb-type superplasticizers used in Japan", J. Adv. Concr. Techn. 1 (1) (2003) 16-25

[20] J. Plank, B. Sachsenhauser, "Impact of molecular structure on zeta potential and adsorbed conformation of α-allyl-ω-methoxypoly-ethylene glycol – maleic anhydride superplasticizers", J. Adv. Concr. Techn. 4 (2) (2006) 233-239

[21] G. Odian, "Principles of Polymerization", 3rd ed., Wiley-Interscience, 23 (1991) 489

[22] M. Inoue, H. Kominami, Y. Kondo, T. Inui, "Organic Derivatives of Layered Inorganics Having the second Stage Structure", Chem. Mater. 9 (1997) 1614-1619