

The impact of water chemical potential on the hydration states of Monosulfoaluminate

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ABSTRACT

AFm phases are tetracalcium aluminate compounds belonging to the lamellar double hydroxide (LDH) family, with the general formulae $[\text{Ca}_2\text{Al}(\text{OH})_6]^{+} [\text{X} \cdot n\text{H}_2\text{O}]^{-}$. Structurally they are composed of a positively charged main layer with the composition $[\text{Ca}_2\text{Al}(\text{OH})_6]^{+}$ and a negatively charged interlayer with the general composition $[\text{X} \cdot n\text{H}_2\text{O}]^{-}$, where X is a monovalent anion or half a divalent anion. AFm phases form during the hydration of Portland cements. The chemistry of the AFm phase, i.e. its anion content, is very sensitive to cement composition and temperature. In the recent literature several paradigms to predict coexisting phase assemblages incl. AFm phases have been published. However it is also known that the interlayer water content of AFm phases varies to some extent as function of water activity (i.e. relative humidity and temperature). In this study we present observations on monosulfoaluminate $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{+} [\text{SO}_4 \cdot n\text{H}_2\text{O}]^{-}$ (or Ms_{6+n}), a typical AFm phase occurring in hydrated OPC paste, synthesized at 5°C, 23°C, 50°C and 85°C with a w/s = 20. Preliminary results suggest that the interlayer water content follows a function of the water chemical potential. A decrease of the water chemical potential i.e. during drying processes at isothermal conditions or at increasing temperatures at saturated conditions lead to a lower interlayer water content. For example at 5°C under water saturated conditions Ms_{16} ($[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{+} [\text{SO}_4 \cdot 10\text{H}_2\text{O}]^{-}$) was precipitated, while at temperatures > 20°C Ms_{14} ($[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{+} [\text{SO}_4 \cdot 8\text{H}_2\text{O}]^{-}$) was observed. By drying at room temperature Ms_{14} dehydrated quickly to Ms_{12} at RH < 95%. Additionally some kinetic aspects of the occurring changes of the hydration states are discussed.

1. INTRODUCTION

AFm ($\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{mono}$) phases are hydrated tetracalcium aluminate compounds belonging to the lamellar double hydroxide family. They occur during the hydration process of Portland cements. AFm phases are composed of positively charged main layer $[\text{Ca}_2\text{Al}(\text{OH})_6]^{+}$ and negatively charged interlayer $[\text{X} \cdot n\text{H}_2\text{O}]^{-}$ where X is either one monovalent anion or half a divalent anion. The general formulae $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$ for monovalent anions (OH^{-} , NO_3^{-}) or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX} \cdot n\text{H}_2\text{O}$ for divalent anions (SO_4^{2-} , CO_3^{2-}) are generally used in cement chemistry. Several solid solutions are known which may contain different species of X anions. The layer thickness c' depends on the nature of the X anion and the amount of interlayer water n (Taylor, 1997). The crystal structure of several AFm phases have been determined and in some cases refined (Taylor, 1973; Allmann, 1968, 1977; Francois, Renaudin and Evrard, 1998; Ahmed and Taylor, 1967; Buttler, Glasser and Taylor, 1959; Rinaldi, Sacerdoti and Passaglia, 1990).

The replacement of Ca^{2+} by the smaller Al^{3+} or Fe^{3+} ions (one Ca^{2+} ion in three by Al^{3+} or Fe^{3+}) distorts

the structure of the principal brucite like layer which

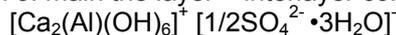
causes a displacement of alternate Ca^{2+} ions from its central plane. This allows Ca^{2+} , in addition to its six OH^{-} ions, to coordinate to another oxygen atom of an interlayer H_2O molecule. The principal layer, together with the H_2O molecules thus bonded to the Ca^{2+} ions, has the composition $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6 \cdot 2\text{H}_2\text{O}]^{+}$ (Taylor, 1973).

1.1 Monosulfoaluminate

$\text{C}_4\text{A}\hat{\text{S}}\text{H}_x$ or $\text{C}_3\text{A}\cdot\text{C}\hat{\text{S}}\cdot\text{H}_x$ or $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot n\text{H}_2\text{O}$ or Ms_{6+n} is known as monosulfoaluminate or simply monosulfate. A structural model for monosulfoaluminate was published by Allmann, 1968, 1977.

Monosulfoaluminate crystallises in a hexagonal structure with the space group R3. As described above the Al^{3+} ions are octahedrally coordinated by six OH^{-} ions, while the Ca^{2+} ions is sevenfold. The principal layer of monosulfoaluminate, together with the 2 H_2O molecules bonded to the Ca^{2+} ions has the composition $[\text{Ca}_2(\text{Al})(\text{OH})_6 \cdot 2\text{H}_2\text{O}]^{+}$ and forms octahedral cavities. One half of these cavities contain SO_4^{2-} anions and the remainder contain two H_2O molecules (Taylor, 1977). Finally

we can write the monosulfoaluminate formula as a notation of main the layer – interlayer components:



Consider that 2 of the 3 water molecules present in the interlayer are actually bonded to the 2 Ca^{2+} ions from the main layer. The remaining water can be reversely removed from the compound depending on the temperature and relative humidity of the environment. Take into account that this formula corresponds to the $12\text{H}_2\text{O}$ monosulfoaluminate. Nevertheless it is known that this phase can exist at two higher water states: the 14 and 16 H_2O monosulfate. In the course of the paper we differentiate the hydration states with the acronyms Ms_{12} , Ms_{14} and Ms_{16} .

Table 1. Interlayer content of Monosulfoaluminate exposed to different conditions (Dosh, Keller and Strassen, 1968)

Comp.	T (°C)	RH (%)	Interlayer content		Layer thickness (Å)
			Anion	Water mol	
C4AŠH16	< 10	100	SO_4^{2-}	10	10.3
C4AŠH14	> 10	100	SO_4^{2-}	8	9.5
C4AŠH12	> 10	20-95	SO_4^{2-}	6	8.93
C4AŠH10	> 10	< 20	SO_4^{2-}	4	8.15
C4AŠH8	30 - 50	~0	SO_4^{2-}	2	7.95

There are several studies related to the stability of synthetic Monosulfoaluminate but only scattered results on its hydration states as function of temperature and relative humidity. It is generally agreed that the stability of monosulfoaluminate increases with increasing temperature (Damidot and Glasser, 1992). If stoichiometric amounts of reactants are mixed together (C_3A and gypsum 1:1) at high w/s ratios and brought to equilibrium for several weeks monosulfoaluminate formed from 5°C to 90°C as shown by Matschei, 2007. Monosulfoaluminate seems persistent but small amounts of ettringite start to precipitate at low temperatures (< 50°C). The characterisation of all syntheses was done on dry powder samples conditioned at 37% rH, and gave the $12\text{H}_2\text{O}$ monosulfoaluminate Ms_{12} in all powders.

Kuzel, 1996 showed that in cements containing small amounts of carbonate (<0.1-0.4% CO_2) initially ettringite forms, which converts via reaction with the remaining aluminate phases to Ms_{16} and/or Ms_{14} . Ms_{14} seemed to be the stable phase at longer equilibration times.

The only study that dealt with a more detailed investigation of the hydration states of Monosulfoaluminate is published by Dosh, Keller and Strassen, 1968..

Table 1 shows a summary of their data on the hydration states of Monosulfoaluminate conditioned at different humidities and

temperature. Unfortunately the dataset is not complete and indicates only trends. Hence the present investigation aims to complete missing data to enable a better prediction of the hydration state of monosulfoaluminate by thermodynamic calculations.

The chemical potential of water under atmospheric conditions is defined as follows:

$$\mu(\text{H}_2\text{O}) = \mu_{\text{H}_2\text{O}(l,T)} + RT \ln(a(\text{H}_2\text{O})) \quad (1)$$

with $\mu_{\text{H}_2\text{O}(l,T)}$ as chemical potential of liquid water as function of temperature and $a(\text{H}_2\text{O})$ as activity of water which can be linked to relative humidity RH at a given water vapor pressure p and known saturation vapor pressure of water p_w^0 according to Raoult's law by

$$a(\text{H}_2\text{O}) = p/p_w^0 = \text{RH}/100 \quad (2)$$

Thus with help of the water chemical potential equations and the known thermodynamic properties of the hydrates it should in principle be possible to predict the hydration states of monosulfoaluminate as function of temperature and RH. A similar approach was used by Albert, Guy and Damidot, 2006, in order to predict changing invariant points in the system $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ as function of water chemical potential.

As described below our results are based on XRD characterizations of synthetic monosulfoaluminate, synthesized at high temperatures and later on exposed to different environmental conditions.

2. EXPERIMENTAL

2.1. Materials

All chemicals used were analytical grade reagents. The precursor used in the synthesis of monosulfoaluminate was C_3A (Tricalcium Aluminate), which was prepared from a 3:1 molar ratio of CaCO_3 and Al_2O_3 based on the procedure given by Matschei, 2007 and Wesselsky, 2009. Anhydrite CaSO_4 was prepared by dehydration of gypsum in a muffle furnace at 550°C overnight. Double distilled CO_2 free water was used in the synthesis of the hydrates.

2.2. Monosulfoaluminate Synthesis and Conditioning.

Monosulfoaluminate $\text{C}_4\text{AŠH}_x$ was prepared by suspending a 1:1 molar mixture of C_3A and CaSO_4 with a w/s of 20 at 5°C, 23°C, 50°C and 85° during 12, 10, 7 and 6 days, respectively. When preparing the sample at 85°C a Teflon bottle was used, in the other cases HDPE bottles were used. The samples were continuously stirred during the synthesis procedure.

To study the dehydration of Monosulfoaluminate at 23°C, Ms₁₄, initially synthesized at 85°C, was vacuum filtered under N₂ atmosphere with a Whatman 589 ashless filter paper and placed in desiccators at different relative humidities and 23°C (Table 2). The samples were analyzed by XRD at the specified time.

To study the rehydration of Monosulfoaluminate in saturated conditions, Ms₁₂ produced by drying Ms₁₄ at 33% RH and 23°C for 3 weeks was mixed with water at a w/s of ~50 and kept in HDPE bottles at 23°C, 50°C and 65°C for 15, 9 and 2 days, respectively. Additionally a Ms₁₄ suspension, initially conditioned at 65°C, was also stored at 5°C and 23°C for 14 and 7 days, respectively to check the impact of temperature on the hydration state at saturated conditions.

Table 2. Saturated salt solutions, corresponding equilibrium measured RH and drying time before XRD.

Salt	RH (%)	Drying time (days)
Na(OH)	8.4	18
CH ₃ CO ₂ K	23	18
MgCl ₂	33	18
K ₂ SO ₄	97.8	51
H ₂ O	100	51

2.3. X-ray diffraction analysis

X-ray analyses were carried out with a Bruker D8 Advance diffractometer (CuK α radiation, 45 mA, 35 kV) equipped with a Super Speed detector, in the range 7-40 2 θ , with a step size and time per step of 0.02° and 0.5 s, respectively. To characterize the hydration state of Monosulfoaluminate under saturated conditions, wet samples were analyzed: the solutions were placed in plastic tubes and centrifuged at 2500 rpm for 2 minutes, later on the supernatant solution was removed and the wet sample at the bottom was placed (under N₂ atmosphere) in a special airtight XRD sample holder to avoid drying and carbonation. In the case of samples dried at different RH powder samples were used.

3. RESULTS

As shown in Fig. 1 the monosulfoaluminate syntheses performed at 23°C, 50°C and 85°C produced Ms₁₄. Note that at higher temperatures the synthesis time can be significantly reduced. At 5°C Ms₁₆ was the observed, co-existing with minor ettringite impurities.

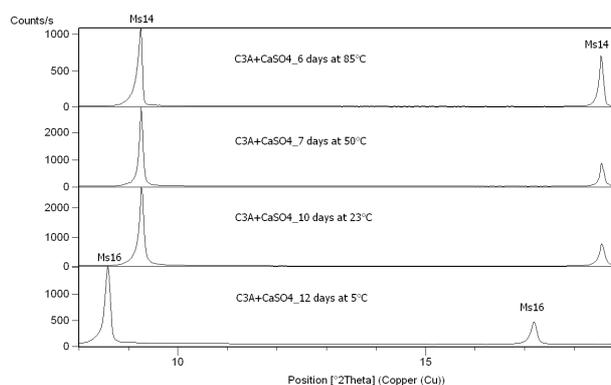


Figure 1. XRD patterns of monosulfoaluminate synthesized at 5°C, 23°C, 50°C and 85°C.

Figure 2a shows the XRD patterns of initially Ms₁₄, previously synthesized at 85°C, exposed to different RH at 23°C. As can be seen Ms₁₄ is persistent at saturated conditions (100%). However only a minor decrease of RH to ~97 - 98% leads to a dehydration of Ms₁₄, and Ms₁₂ is observed. We postulate that Ms₁₄ will be completely dehydrated to Ms₁₂ with time; nevertheless this test will be performed again in a few months to verify this hypothesis. Ms₁₂ is the persistent phase until 25%RH. At 8%RH Ms₁₀ is formed. The experimental findings are summarised as preliminary phase diagram in Fig 2b, showing the hydration states of monosulfoaluminate as function of RH at 23°C.

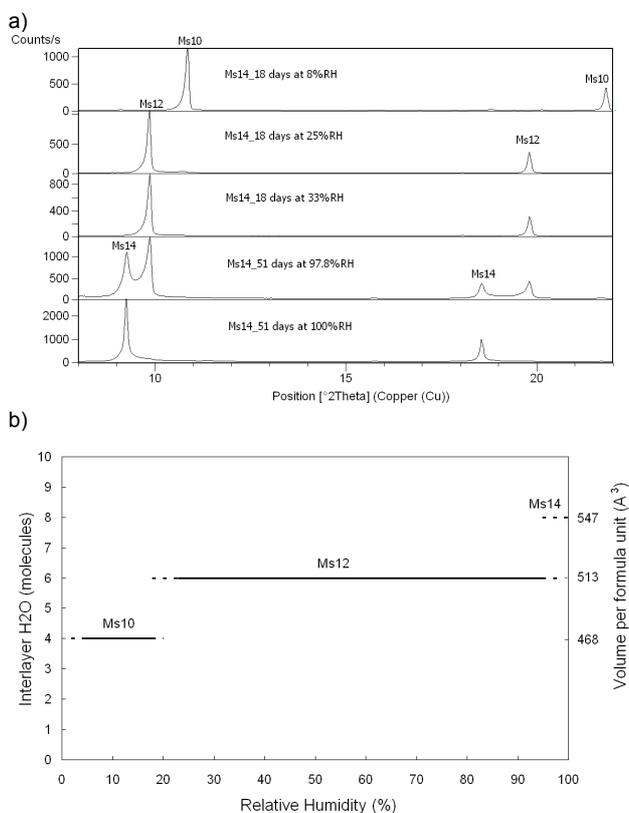


Figure 2. a) XRD patterns of Ms₁₄ dried at 23°C and different RH. b) Phase diagram showing the interlayer water content and the specific solid volume of monosulfoaluminate as a function of RH at 23°C.

In a third experimental series we investigated the rehydration behaviour of initially Ms_{12} as function of temperature under saturated conditions (Fig. 3). It is interesting to note that when a previously dry sample (Ms_{12}) is dissolved in water, during the time of investigation it did not rehydrate to Ms_{14} at temperatures between 5 and 40°C (exact range of temperatures will be determined). At higher temperatures however rehydration is very fast, i.e. at 65°C the sample is completely rehydrated in 2 days. Once Ms_{14} is obtained, it is persistent at temperatures over ~10°C (the exact temperature to be determined). On the other hand when Ms_{14} is placed at 5°C at saturated conditions, it further rehydrates to Ms_{16} , although in some experiments the rehydration took longer than 14 days (aging period is still running). The related XRD patterns of these samples are shown in Figure 3.

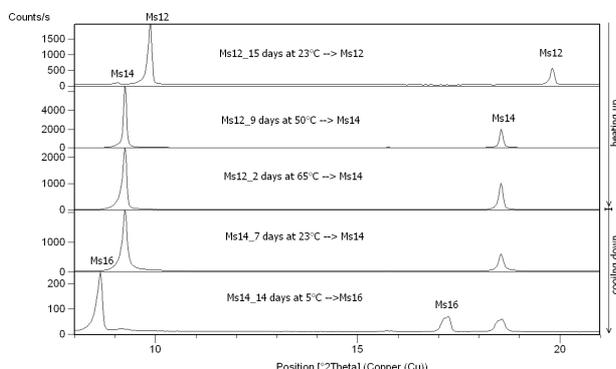


Figure 3. XRD patterns of Ms_{12} rehydrated to Ms_{14} in solution at high temperatures and subsequent rehydration of Ms_{14} to Ms_{16} at 5°C.

Based on the experiments at saturated conditions we derived a second preliminary phase diagram (Fig. 4) relevant to the hydration states of monosulfoaluminate as function of temperature in conditions close to water saturation (100% RH). Note that between ~10 and ~40°C we incorporated Ms_{12} and Ms_{14} , as both phases seem persistent depending on the chosen experimental pathway.

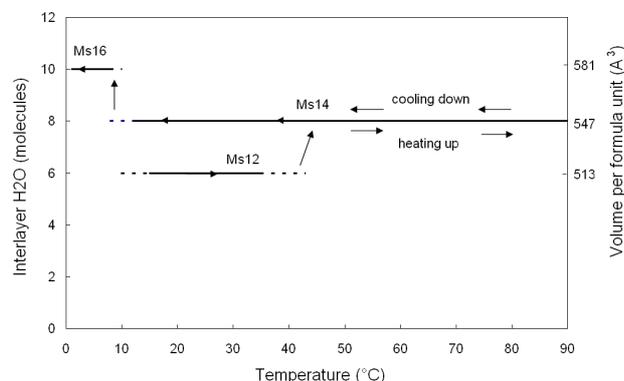


Figure 4. Phase diagram showing the interlayer water content and the specific solid volume of monosulfoaluminate as a function of temperature at saturated conditions. Note: The diagram also contains the experimental pathways followed in this study.

Additionally the phase diagrams Figure 2b and Figure 4 contain also information on the changes

of the specific solid volume / formula unit. The volume difference between Ms_{12} and Ms_{16} is ~ 13% and may thus impact the space filling properties of hydrated cement paste as function of RH, temperature and amount of monosulfoaluminate.

4. DISCUSSION

The investigations have shown that the observed hydration states of monosulfoaluminate follow a function of relative humidity and temperature, which can be thermodynamically described as change of the water chemical potential (eq. 1). In order to enable a thermodynamic prediction of the hydration states it is necessary to refine the thermodynamic properties of monosulfoaluminate with respect to its individual hydration states (Ms_{12} – Ms_{16}). In order to do so, it is necessary to estimate the thermodynamic properties of the released / taken up water molecules as function of temperature.

It was shown that a decrease of the water activity at isothermal conditions, i.e. at lowering of the relative humidity is connected to a destabilisation of the higher hydration states of monosulfoaluminate. The experiments have shown that Ms_{12} is persistent in the RH range between ~25 to ~97% RH at 23°C, whereas Ms_{14} forms at >97% RH. Therefore it is likely that the released two water molecules of the conversion $Ms_{14} \rightarrow Ms_{12}$ can be thermodynamically treated closely to pure water as they can be removed easily at a potentially relatively low driving force. On the other hand the conversion of $Ms_{12} \rightarrow Ms_{10}$ only occurs at low RH, i.e. we assume that these 2 water molecules are much stronger bound into the structure. Thus thermodynamically its properties may differ significantly from those of pure water. Further calorimetric investigations are useful in order to derive enthalpies of de- and rehydration at the different hydration states which will enable a prediction of the hydration states of monosulfoaluminate as function of temperature and RH.

5. ACKNOWLEDGMENT

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