



## Pressure induced reactions amongst calcium aluminate hydrate phases

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### ABSTRACT

The compressibilities of two AFm phases (strätlingite and calcium hemicarboaluminate hydrate) and hydrogarnet were obtained up to 5 GPa by using synchrotron high-pressure X-ray powder diffraction with a diamond anvil cell. The AFm phases show abrupt volume contraction regardless of the molecular size of the pressure-transmitting media. This volume discontinuity could be associated to a structural transition or to the movement of the weakly bound interlayer water molecules in the AFm structure. The experimental results seem to indicate that the pressure-induced dehydration is the dominant mechanism especially with hygroscopic pressure medium. The Birch–Murnaghan equation of state was used to compute the bulk modulus of the minerals. Due to the discontinuity in the pressure–volume diagram, a two stage bulk modulus of each AFm phase was calculated. The abnormal volume compressibility for the AFm phases caused a significant change to their bulk modulus. The reliability of this experiment is verified by comparing the bulk modulus of hydrogarnet with previous studies.

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### 1. Introduction

During the hydration of Portland cement, AFm ( $\text{Al}_2\text{O}_3$ – $\text{Fe}_2\text{O}_3$ –mono) phases are formed when ions are brought together in appropriate concentrations in aqueous systems at room temperature or formed hydrothermally, i.e. in the presence of water under pressure above 100 °C. They are among the hydration products of Portland cements. AFm phases have layer structures derived from that of portlandite,  $\text{Ca}(\text{OH})_2$ , whereby one third of  $\text{Ca}^{2+}$  ions are replaced by a trivalent ion, nominally  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  ion. The principal layer has the chemical formula  $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]^+$ . Between the principal layer it includes charge-balancing X anions and water molecules [1]. This interlayer region has the composition  $[\text{X}_n\text{H}_2\text{O}]^-$ . The X anion could be hydroxide, sulfate, chloride, or carbonate. The layer thickness  $c'$  depends on the nature of the X anion and the amount of interlayer water, which can be varied by stepwise dehydration at different temperature and humidity conditions [1–3].

One AFm phase, dicalcium aluminate monosilicate–8-hydrate  $\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$ , trigonal, R3, R3 or R3m (also called gehlenite hydrate) occurs in nature as strätlingite [4–7]. Its interlayer content is  $[\text{AlSi}(\text{OH})_8 \cdot \text{H}_2\text{O}]^-$ ; the Al is tetrahedrally coordinated [8]. This phase appears in the hydration of slag-containing Portland cements or

blended cements and contributes to compressive strength development in commercial high alumina cement [9].

Another AFm phase is tetracalcium aluminate hemcarbonate–12-hydrate (also called hemicarboaluminate),  $\text{Ca}_4\text{Al}_2(\text{CO}_3)_{0.5}(\text{OH})_{13} \cdot 5.5\text{H}_2\text{O}$ , trigonal, R3c or R3c system [6,10]. This phase occurs in ordinary Portland cement with very low carbonate contents. There are two types of carbon-containing AFm phases:  $\text{CO}_3^{2-}$  anion monocarboaluminate ( $\text{C}_4\text{ACH}_{11}$ , triclinic, PI system [11]) and hemicarboaluminate ( $\text{C}_4\text{AC}_{0.5}\text{H}_{12}$ ). At ambient conditions, monocarboaluminate and hemicarboaluminate have  $[1/2(\text{CO}_3^{2-}) \cdot 5/2\text{H}_2\text{O}]^-$  and  $[1/4(\text{CO}_3^{2-}) \cdot 1/2(\text{OH}^-) \cdot 11/4\text{H}_2\text{O}]^-$  as interlayer contents, respectively. The interlayer contents and layer thickness of hemicarboaluminate at varying hydration stages were studied by Fischer and Kuzel [10] and are shown in Table 1.

Changes in the water content associated with concomitant relaxation of the AFm framework have been observed in numerous variable-temperature studies, which explains why AFm phases undergo several dehydration stages at higher temperatures (see Table 1). The effects of pressure on the structure and the detailed crystal properties of dehydrated AFm phases are less well explored. Recently, Clark et al. calculated the bulk modulus of ettringite—one of AFt phases—using X-ray and infrared study [12]. But for AFm phases that are often less stable compared to the AFt phase, high-pressure structural data are not yet available.

During synthesis of AFm phases, the low stability of hydroxyl AFm results in the appearance of other phases in the course of synthesis,

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