

Hydrothermal formation of hydrated calcium silicates: an *in situ* synchrotron study

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Hydrated calcium silicate minerals, e.g. tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and xonotlite ($\text{Ca}_6\text{Si}_6\text{O}(\text{OH})_2$), are rare phases formed in hyper-alkaline, hydrothermal environments. They usually occur where fluids saturated with respect to calcium hydroxide react with basic igneous rocks e.g. Okayama, Japan. These phases are also known to form in cements and in the hyper-alkaline environments surrounding cementitious nuclear waste sites making them both mineralogically and environmentally important. There has been a lot of work in this field aimed at understanding the structural relations and the formation mechanism and kinetics. Few conclusive results have been published due to the slow reaction kinetics and the large number of stable phases, more than 30 in the calcium silicate hydrate (CSH) system. This study was initiated to investigate, *in situ*, the formation of tobermorite and the higher temperature phase, xonotlite, the main aims being to investigate the influence of temperature and aluminium content on phase stability, kinetics and reaction mechanism.

Experimental methods

We used station 16.4 of the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, and line 13 BM of the Advanced Photon Source (APS) at the Argonne National Laboratory for this work. White beam energy dispersive powder diffraction (EDPD) was used to follow the hydrothermal formation of tobermorite and xonotlite *in situ*. The synthesis equipment is shown in Fig. 1 (Evans *et al.* 1994) and consists of a stainless steel pressure vessel surrounded by a heater unit which has 2 holes to allow the incident and diffracted X-ray beam to pass through. This system relies on the ability of the high energy X-rays produced by a synchrotron to pass through the steel walls of a reaction cell. The maximum usable energy of the synchrotron radiation

utilised determines the maximum wall thickness of the cell since the higher the X-ray energy the more penetrating the beam. Ultimately, the energy of the X-ray beam determines the cell wall thickness that can be used, and because the wall thickness controls the safe working temperature, the maximum temperature permitted in the cell is a function of X-ray energy. At the SRS, cells of wall thickness up to 0.4 mm can be used; above this the diffraction data become unresolvable, limiting experiments to below 240°C. Beam line 13 BM at the APS has a X-ray beam with higher energy enabling the use of cells with wall thicknesses up to 3mm. This allowed experiments to be performed at over 300°C.

The synthesis experiments were performed by mixing an anhydrous amorphous gel of tobermorite composition, and a saturated calcium hydroxide

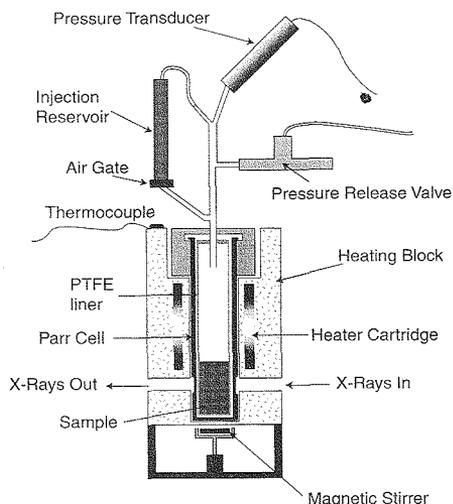


FIG. 1. Schematic diagram showing on-line hydrothermal synthesis equipment.

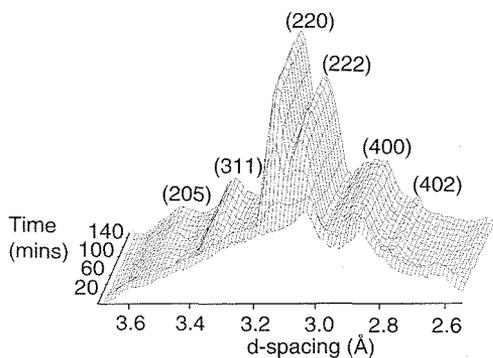


FIG. 2. Time resolved EDPD trace showing the formation of tobermorite at 270°C.

solution. This mixture was sealed inside the PTFE-lined hydrothermal cell and placed in the heater unit. As the cell was heated, hydrothermal conditions along the saturated vapour pressure curve develop within the cell and a crystalline phase was produced. This reaction was monitored by EDPD with diffraction patterns being taken every 1 or 2 minutes. Therefore the reaction was followed from the amorphous starting material to the final crystalline product.

Temperature was varied from 230°C to 290°C and aluminium content was varied from 0% to 15% aluminium replacing silicon.

Results

All the experiments were completed within 2 hours. After this the diffraction peaks stopped growing. The first peaks to form were at 3.1 Å (220) and 1.8 Å (427) and are characteristic of a CSH gel. Other peaks form subsequently due to the formation of tobermorite and/or xonotlite (Fig. 2). The basal peaks were the last to develop.

A summary of the phases that formed at various temperatures and aluminium contents is shown in Fig. 3. This gives a zone where tobermorite is the principle phase and a zone where xonotlite formed with a mixed zone in between. From the diffraction data no other phases apart from tobermorite and/or xonotlite were produced. Data reduction is in progress to quantify the reaction rates.

Conclusions

Xonotlite is formed preferentially if temperature is

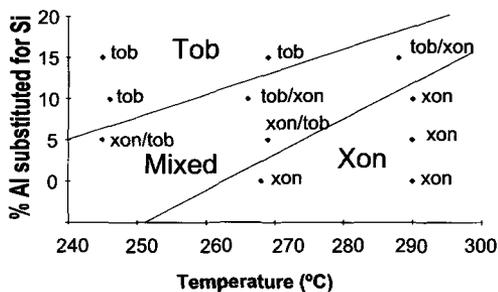


FIG. 3. Summary of all hydrothermal synthesis runs showing the zones where tobermorite and xonotlite formed as a function of temperature and Al content.

increased, and tobermorite is formed if aluminium content is increased. The mixed zone is probably the result of a kinetic hindrance factor with the real stability boundary being somewhere in this region. The order in which the diffraction peaks form indicates that the calcium silicate structure first grows in the *ab* plane (parallel to the sheets), before becoming ordered in the *c* direction, as suggested by Jaubertie *et al.* (1996)

It is important to note that the kinetics of this system are slow and vary according to many factors e.g. temperature, pH, fluid/solid ratio and composition (Mitsuda and Taylor, 1975). These experiments never produced a fully crystalline product indicating that only the first stage of crystallisation was monitored thus the experiments only apply to short term hydrothermal reactions. Mineralogical samples of tobermorite show a high degree of crystallinity. This could be due to either: formation at lower temperature over a long time period; a second reaction process that is too slow to be monitored; or by a reaction route completely different to that observed in our work.

References

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