Force of crystallisation-development during CaO hydration: theory vs. experiment and the role of fluid transport

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When chemical reactions that involve an increase in solid volume proceed in a confined space, this may under certain conditions lead to the development of a so-called force of crystallisation (FoC). In other words, reaction can result in stress being exerted on the confining boundaries of the system. In principle, any thermodynamic driving force that is able to produce a supersaturation with respect to a solid product can generate a FoC, as long as precipitation can occur under confined conditions, i.e. within load-bearing grain contacts. Well-known examples of such reactions include salt damage, where supersaturation is caused by evaporation and surface curvature effects, and a wide range of mineral reactions where the solid products comprise a larger volume than the solid reactants. Frost heave, where crystallisation is driven by fluid under-cooling, i.e. temperature change, is a similar process.

In a geological context, FoC-development is widely considered to play an important role in pseudomorphic replacement, vein formation, and reaction-driven fracturing. Chemical reactions capable of producing a FoC such as the hydration of CaO (lime), which is thermodynamically capable of producing stresses in the GPa range, also offer obvious engineering potential. Despite this, relatively few studies have been conducted where the magnitude of the FoC is determined directly. Indeed, the maximum stress obtainable by CaO hydration has not been validated or determined experimentally.

Here we report uni-axial compaction/expansion experiments performed in an oedometer-type apparatus on pre-compacted CaO powder, at 65 °C and at atmospheric pore fluid pressure. Using this set-up, the FoC generated during CaO hydration could be measured directly. Our results show FoC-induced stresses reaching up to 153 MPa, with the hydration reaction stopping or slowing down significantly before completion. Failure to achieve the GPa stresses predicted by thermodynamic theory is attributed to competition between FoC development and its inhibiting effect on reaction progress. Our microstructural observations indicate that hydration-induced stresses caused the shut-down of pathways for water into the sample, thereby hampering ongoing reaction and limiting the magnitude of stress build-up to the values observed.