



Changes in portlandite morphology with solvent composition: Atomistic simulations and experiment

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ABSTRACT

Experimental work has been done to determine changes in the particle shape of portlandite grown in the presence of different ions. To quantify the experimentally observed changes in morphology a new analysis tool was developed, allowing the calculation of the relative surface energies of the crystal facets. The observed morphology in the presence of chlorides and nitrates was faceted particles of a similar shape, the addition of sulfates leads to hexagonal platelet morphology and the addition of silicates leads to the formation of large irregular aggregates. In addition to the experimental work, the surfaces of portlandite were studied with atomistic simulation techniques. The empirical force field used has first been validated. The equilibrium morphology of portlandite in vacuum and in water was then calculated. The results indicate that the presence of water stabilizes the [20.3] surface and changes the morphology. This is consistent with the experimental observation of [20.3] surfaces.

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1. Introduction

The purpose of this work is to understand changes in portlandite (CH) morphology with the changing chemical environment of the growing crystal as encountered in cementitious systems. If these changes in morphology can be understood, they may be controlled and modified. As portlandite is a major component of hydrated cementitious systems and concrete, a change in morphology might modify the durability and may allow the fine tuning of the physical properties of concrete structures. However while the crystal structure of portlandite is well known [1–3], not much experimental work has been done to study the growth mechanisms. Work from Gallucci and Scrivener [4] shows a change in portlandite morphology from large clusters to small dispersed and sometimes hexagonal platelets on addition of gypsum (C\$) and tricalcium aluminate (C₃A). This indicates that the interaction of portlandite surfaces and surface steps with gypsum and C₃A dissolution products might give some insight into the working mechanisms of the observed change in morphology. Harutyunyan et al., used soft X-ray techniques to observe the growth of CH near cement particles in a CH and C\$ saturated solution [5]. The observed portlandite particles had a hexagonal platelet morphology with an aspect ratio of 2.5 to 2.7. The

surface energy of the particles was estimated to be approximately 0.114 J/m². Berger and McGregor, used optical microscopy to observe the influence of different additives on the morphology of CH formed upon hydration of tricalcium silicate (C₃S) [4]. They observed that the addition of nitrates and chlorides led to the formation of rod-like instead of platelet-like morphologies whereas the addition of sulfates reinforced the platelet morphology. The addition of hydroxides led to more but smaller particles.

So far the studies were carried out in complex systems with a large number of different ions present in the solvent surrounding the growing portlandite crystals. In these systems it is difficult to assess how the observed changes in morphology were brought about and which species in solution were responsible for it. Consequently experimental work on pure model systems has been carried out. Portlandite particles were produced by coprecipitation of a calcium and a hydroxide salt. Chloride, nitrate, sulfate and silicate salts were then added to different batches to observe their influence on the morphology of portlandite.

To understand the changes in portlandite morphology and to characterize portlandite surfaces, atomistic simulation techniques, namely classical energy minimization and classical molecular dynamics, have been employed. These techniques use empirical force fields to describe the forces between the atoms and the choice and validation of the employed force field is described. Using these results the equilibrium or Wulff shape of portlandite in vacuum and in water was calculated.

Apart from several articles using portlandite for the atomistic potential development and validation [6–8] there is, to our knowledge, only one group who have used atomistic simulation to study

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