

Phosphonate mediated surface reaction and reorganization: implications for the mechanism controlling cement hydration inhibition

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Vertical scanning interferometry and XPS show the reaction of CaCO_3 with the hydration retarder nitrilo-*tris*-(methylene)phosphonic acid follows a pathway of dissolution of the calcium followed by precipitation of a calcium phosphonate; subsequent surface reorganization/restructuring of the calcium phosphonate exposes the underlying CaCO_3 for further hydration.

Oil wells of ever increasing depths require support by Portland cement. Only a high degree of control over the setting kinetics allows the cement to be pumped down successfully.¹ In addition to the commonly accepted mechanisms for hydration inhibition (calcium complexation, nucleation poisoning, surface adsorption and protective coating²) we recently proposed a new mechanism for phosphonate inhibitor agents. This mechanism involves a dissolution step associated with calcium removal from the substrate, followed by a precipitation reaction due to the formation of a calcium phosphonate complex.³ Our present work uses vertical scanning interferometry (VSI),^{4,5} to quantify this new mechanism by monitoring surface reactivity, topographical changes, and the evolution of mineral surface composition. Most importantly, evidence for surface reorganization provides the key to a full understanding of the mechanism by which a hydration inhibition agent delays the onset of the setting of cement materials.

Our previous investigations of the role of phosphonic acids in the inhibition of cement hydration used NMR spectroscopy and X-ray diffraction to show that nitrilo-*tris*-(methylene)phosphonic acid (H_6ntmp) complexes calcium from cements, calcium silicates and calcium aluminates.³ This process forms a transiently soluble phosphonate complex that subsequently deposits on the mineral surface as an insoluble calcium phosphonate, $[\text{Ca}(\text{H}_4\text{ntmp})(\text{H}_2\text{O})]_x$. The new phase exhibits a layered structure that inhibits further hydration.³ Our initial goal of the present study was to probe and clarify the inhibition hydration mechanism by using a fast, non-destructive, non-UHV method that could be adapted to a range of substrates. Vertical scanning interferometry (VSI) offers these attributes and allows monitoring of topographical changes in real-time with sub-nanometer vertical resolution and sub-micrometer scale lateral resolution.⁴⁻⁷ As an important complementary tool X-ray photoelectron spectroscopy (XPS) was used to determine surface speciation.

While cement is a complex mineral mixture,^{1,2} our previous work³ has shown that significant insight may be gained by the study of individual calcium containing components. In this regard our investigation was performed on single crystals of calcite

(CaCO_3) as a “model” system to analyze the inhibition hydration mechanism because of the relative ease of sample preparation suitable for VSI. Calcite crystals have a fine cleavage along the (10 $\bar{1}$ 4) plane revealing surfaces of only 2–4 Å reliefs and, along with their air stability, allow for a reference surface prior to any chemical reaction. High purity sample substrates of calcite (CaCO_3) (1 × 0.5 × 0.2 mm) were cleaved from a synthetic single crystal. Samples were air cleaned to remove any particulates prior to an inert polymer mask being applied to maintain a pristine region, allowing for absolute height change determination by VSI.⁴ The masked surfaces were reacted with 40 μL of 1% H_6ntmp solution for 10 min, 30 min, 1 h and 3 h. The polymer masks were removed prior to VSI and XPS analysis.†

Fig. 1 shows the evolution of surface morphology with reaction time. Fig. 2a shows the absolute mean change in height relative to the unreacted (masked) surface region. We can distinguish a reaction sequence: an initial etching of the surface followed by subsequent precipitation. This result is consistent with our previous

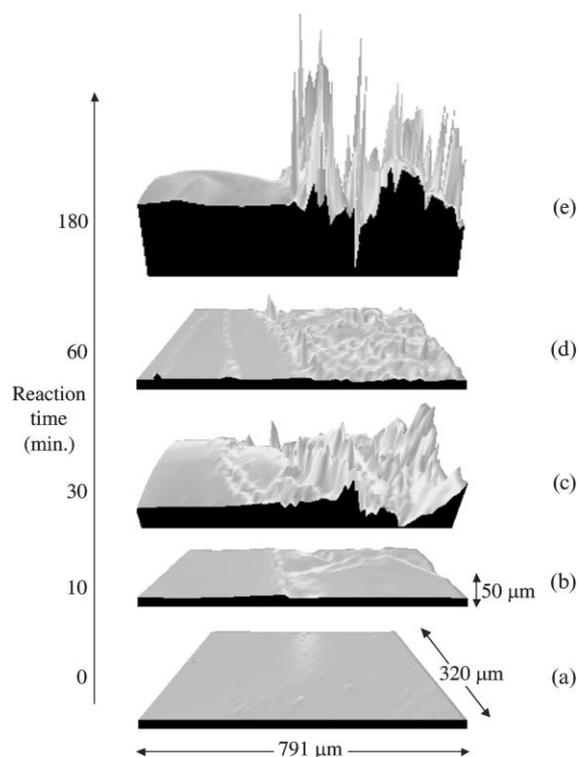


Fig. 1 VSI height maps of a calcite (10 $\bar{1}$ 4) cleavage surface (10× Mirau objective). Initial surface (a) and reaction sequence of this surface exposed to 1% H_6ntmp at 10 min (b), 30 min (c), 1 h (d), and 3 h (e).

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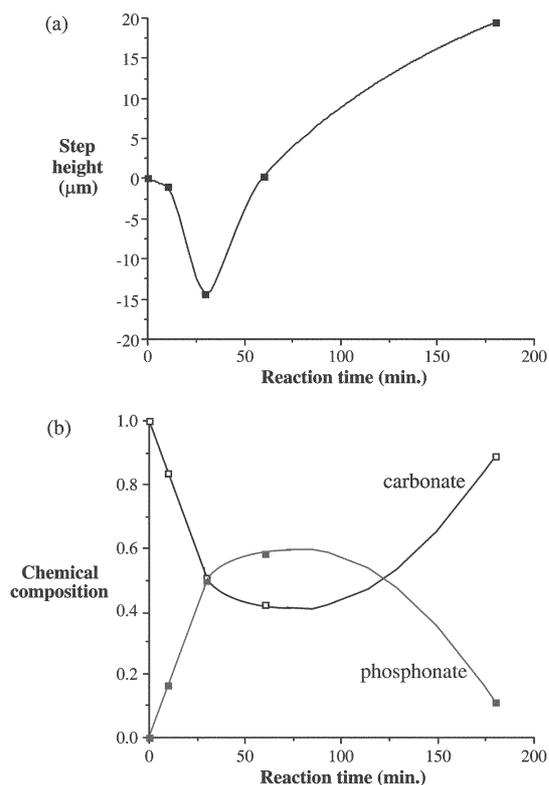


Fig. 2 Variation of (a) step heights as determined by VSI, and (b) chemical composition as determined by XPS, for CaCO_3 surfaces reacted with H_6ntmp as a function of reaction time (min).

observation³ that calcium is removed from a calcium-bearing mineral by the H_6ntmp to form an insoluble phosphonate.

The morphology of the surface during the etching phase (Fig. 1b and Fig. 3a) shows the development of etch pits. The round shape of the pits can be interpreted as anisotropic inhibition of step movement. Previous studies⁸ have discussed the effects of various dissolved components on etch pit morphology in calcite.

Phosphonate deposition occurs as an organized crystallographically oriented network of layered crystals that are each about $40 \times 40 \mu\text{m}$ in size (Fig. 3b). VSI measurements determine the height of these newly formed plates to be $2.2 \mu\text{m}$ consistent with the layered structure we have reported for $[\text{Ca}(\text{H}_4\text{ntmp})(\text{H}_2\text{O})_\infty]$ type materials.³ As expected, formation of calcium phosphonate and

the relative *surface* composition, *i.e.*, the calcite : phosphonate ratio are confirmed by XPS (Fig. 2b).

The XPS data do show one feature that is surprising. After 3 h the relative detectable fraction of phosphonate decreases and calcite increases. This is contrary to traditional theories² that would predict that once the phosphonate over-layer is formed no further reaction would be expected: the final calcite/phosphonate ratio being determined by the amount of H_6ntmp in comparison with the surface area to which it is exposed. Our result is in direct contrast to this and prompted further study of the surface.

The detection of calcite by XPS may be most simply explained by (a) the dissolution of the calcium phosphonate from the surface; (b) the growth of calcite from solution as an over-layer on the calcium phosphonate. If the calcium phosphonate was re-dissolving or otherwise “falling off” the surface, uniformly or selectively, then the surface height (as compared to the unreacted region) would decrease or remain unchanged. As may be seen (Fig. 1d and e) the surface height increases significantly between the first and third hour of reaction. If a calcite layer is overgrowing the calcium phosphonate then XPS depth profile data would show this; however, this is not observed. Thus an alternative mechanism must be considered. Such an alternative is indicated by a study of the VSI and optical micrographs (Fig. 1 and 3).

The roughness of the reaction surface increases significantly between 1 and 3 hours (Fig. 1). It is worth noting that the troughs (Fig. 1e) are of a depth comparable to the etched surface (Fig. 1c), and the highest areas ($20 \mu\text{m}$) are significantly higher than at 1 hour (Fig. 1d). Observation of optical micrographs (Fig. 3) also show that the entire morphology of the surface has changed between 1 and 3 hours. Instead of plate-like crystals there are asymmetric pyramidal crystals ($50\text{--}100 \mu\text{m}$ in diameter) within areas of relatively flat surface. Based upon these results and the XPS data, we propose that a restructuring of the calcium phosphonate surface occurs exposing unreacted calcite. A schematic representation of this process is shown in Fig. 4.

We propose that the calcium phosphonate undergoes a surface restructuring over a period of time; exposing unreacted mineral substrate is a key to understanding the failure of an inhibition agent in mineral hydration. Thus, our results indicate that the reaction proceeds in three steps. First, a rapid surface etching occurs bringing about an overall reduction in surface height and substantial increase in surface area and roughness. The duration of this phase is dependent on the concentration of inhibitor (*i.e.*, phosphonate). Second, etching is followed by a slow growth phase,

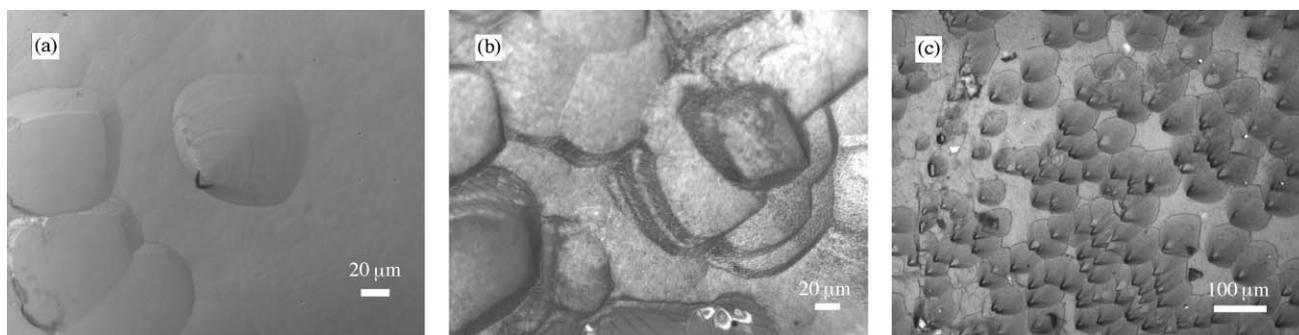


Fig. 3 Reflected light images of CaCO_3 surfaces reacted with H_6ntmp after (a) 30 min, (b) 1 h, and (c) 3 h.

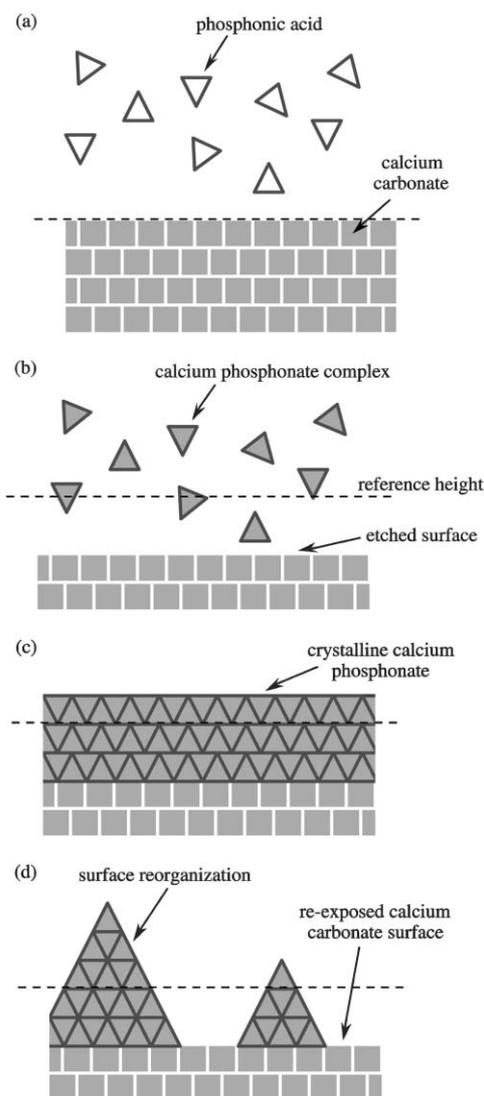


Fig. 4 Schematic representation of the reaction between H_6ntmp with the calcite surface.

in which the surface shows net growth and increase in height. This stage is associated with the formation of a calcium phosphonate complex. The development of this overgrowth layer can justify the inhibitory role of phosphonic acid as was established previously.³ Third, crystallization, orientation and/or rearrangement of the calcium phosphonate complex occur exposing some of the pristine mineral surface lying underneath for further reaction (*i.e.*, hydration in the case of cementitious minerals). This mechanism can be well correlated with the evolution of inhibition hydration processes observed with the hydration of cement.

The inhibition process of cement is known to pass through four stages.² Hydration of cement is not linear through time; it proceeds very slowly at first, allowing the thin water/cement mixture to be properly placed before setting. Prior studies have concentrated on the use of agents to initiate inhibition,^{9–12} however, a rationale for the “length of action” of an inhibition agent (*i.e.*, the time between

the induction and setting) has received far less attention. It has been generally assumed that the inhibition failure occurs *via* osmotic breakage of any coating.¹³ The study described herein shows an alternative mechanism for the length of time that a specific inhibitor will show efficacy: the rate of surface reorganization/restructuring. Thus, an understanding of the factors that control the rate of this surface restructuring will allow for the design of new hydration inhibition agents, and our future studies are aimed towards this end. Finally, we have demonstrated VSI as a powerful technique for the study of the important area of surface inhibition and growth reactions on mineral surfaces.¹⁴

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Notes and references

† The morphological surface changes and quantitative dissolution/precipitation rates were obtained using a white light VSI system (MicroXAM MP-8, ADE Phase Shift) with a vertical resolution of ± 1 nm. The lateral (x, y) resolution depends on the Mirau objective used. Each sample was measured using a $10\times$ and a $50\times$ objective with a lateral resolution of 1.2 microns and 500 nm, respectively. The $50\times$ objective provides a field of view of $165\ \mu\text{m} \times 124\ \mu\text{m}$. A series of 3D height maps were collected for each reaction time. XPS measurements were performed on a PHI 5700 ESCA (Al- K_{2p}). In order to compensate for charging an electron beam was directed to the sample having a current of $10\ \mu\text{A}$. Optical images were collected using a polarizing optical microscope.

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