Morphological Control of Ca$_3$Al$_2$(OH)$_{12}$

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The effect of a range of inorganic and organic crystal growth modifiers on the morphology of Ca$_3$Al$_2$(OH)$_{12}$ has been studied. It has been found that some additives show a strong preference for a single crystal face forming polyhedral crystals whilst others are less selective, producing crystals with a less well defined morphology. In this way sulphite and dithionite preferentially interact with the \{111\} face producing octahedral crystals and nitrilotriacetic acid stabilises the \{110\} face forming rhombic dodecahedral crystals. Phosphate, however, leads to the formation of small needle-like crystals and the organic acids, \(\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{PO}_3\text{H}_2)\), \(\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)_2\), \(\text{HN}(\text{CH}_2\text{PO}_3\text{H}_2)_2\), and \(\text{H}_3\text{CN}(\text{CH}_2\text{PO}_3\text{H}_2)_2\), produce near spherical crystals.

The ability to be able to control the morphology of a material is of great importance in a variety of fields. This control is brought about by varying the crystallising conditions, typically by the addition of a crystal growth modifier to the solution. For molecular crystals, morphological modification has been brought about by the use of stereospecific inhibition of the growth of particular crystal faces. [1,2]
In inorganic systems such a strategy is not generally applicable and a more empirical approach exploiting the bonding and packing in the crystal structure must be used. In this way it has proved possible to introduce crystal faces into the morphology of materials such as CaCO₃, [3] KNO₃ [4] and K₂SO₄ [5] that are not normally observed. In extreme cases the morphology can be so completely altered that it is comprised of a single different crystal face. For example, the growth of KCl in the presence of sodium hexametaphosphate leads to the formation of octahedral crystals ({111} face) rather than the usual cubic morphology ({100} face). [6]

In many cases the crystal growth modifier leads to the observation of more complex morphologies that do not simply consist of a combination of crystal faces. One material that has been shown to be particularly flexible in the morphologies adopted is CaCO₃. Variation of the additive used in the synthesis has lead to morphologies as diverse as spheres, [7-9] helices, [10] and hollow porous shells. [11]

Ca₃Al₂(OH)₁₂ is the silicon free member of the garnet family of minerals, having a cubic structure in which Al is in an octahedral environment and Ca is eight co-ordinate in a square anti-prismatic arrangement. [12,13] It is an important constituent of cement [14] and a by-product of the Bayer Process. [15]

The morphology of Ca₃Al₂(OH)₁₂ grown from basic solution is generally poorly defined though some of the smaller crystals display a 24-sided deltoidal icositetrahedral morphology. [16] In another paper we have shown the morphology of Ca₃Al₂(OH)₁₂ to be strongly dependant on the presence of crystal growth modifiers in the reaction solution. [17] It was found that in the presence of sulphate, octahedral crystals were formed by stabilisation of the {111} face, oxalate preferentially interacts with the {110} face leading
to rhombic dodecahedral crystals and EDTA with the \{210\} face forming crystals with a
tetrakis hexahedral morphology.

**Experimental Details**

The synthesis of Ca$_3$Al$_2$(OH)$_{12}$ was based on the method described previously by
Whittington *et al.* [16] In a typical experiment 6.44g (0.0826mol) gibbsite was dissolved
in 10mL of 13.3M NaOH solution at 95°C. 3.47g (0.0468mol) Ca(OH)$_2$, slurried in 40mL
de-ionised water, was then added to the original solution and maintained at 95°C for 24
hours. Experiments were also performed in the presence of the following crystal growth
modifiers: sodium chloride, sodium sulphite (Na$_2$SO$_3$), sodium thiosulphate (Na$_2$S$_2$O$_3$),
sodium dithionite (Na$_2$S$_2$O$_4$), sodium phosphate (Na$_3$PO$_4$), sodium formate (NaCHO$_2$),
sodium acetate (NaCH$_3$CO$_2$), sodium succinate (Na$_2$C$_4$H$_4$O$_4$), and the organic polyacids
shown in Figure 1. In each case the additives were used as purchased except for
NDMPA, NMPDA, NDP and MNDP which were synthesised according to the literature
preparations. [18] In these experiments the crystal growth modifiers were added to the
slurried Ca(OH)$_2$ at a concentration of 0.035 mol/L in the final solution. Powder XRD
patterns of the products were recorded on a Philips PW3020 diffractometer using Cu K\(\alpha\)
radiation and showed them to be Ca$_3$Al$_2$(OH)$_{12}$ with a small amount of residual Ca(OH)$_2$.
No discernable changes in the diffraction patterns were observed in any of the reactions
with the crystal growth modifiers. The morphology of the samples was investigated by
SEM on a Philips XL30 instrument.

**Results and Discussion**

The morphology of Ca$_3$Al$_2$(OH)$_{12}$ grown in the absence of any crystal growth modifiers,
shown in Figure 2, was found to be poorly defined in that no distinct crystal faces could
be identified and that the shape was not consistent throughout the sample. Our observed morphology is in agreement with that reported by Whittington et al. [16]. Repetition of this experiment in the presence of crystal growth modifiers such as sulphate, oxalate and EDTA showed that they have a strong influence on the experimental morphology, leading to well defined shapes comprised of a single crystal face. Full details of these experiments will be published elsewhere [17]. As an extension of this study, the effects of several other related additive anions on the morphology have been investigated in the present work, and are also found to alter the morphology of Ca$_3$Al$_2$(OH)$_{12}$.

The sulphur-oxygen anions sulphite and dithionite have a similar effect to sulphate on the morphology of Ca$_3$Al$_2$(OH)$_{12}$ in that they lead to the formation of octahedral crystals dominated by the {111} face. SEM images of these crystals are shown in Figure 3(a)-(b), from which it can be seen that particularly in the case of sulphite the transformation to octahedral crystals is not uniform throughout the sample. In contrast to this, thiosulphate was not observed to have any significant effect on the morphology of Ca$_3$Al$_2$(OH)$_{12}$ under these conditions.

In the previous study, the carboxylate anions oxalate and EDTA were found to have significant effects on the morphology of Ca$_3$Al$_2$(OH)$_{12}$. Several other carboxylate anions including formate, acetate and succinate had no observable effect on the morphology. The polycarboxylic acid, nitrilotriacetic acid (N(CH$_2$CO$_2$H)$_3$), did however alter the morphology of Ca$_3$Al$_2$(OH)$_{12}$. In this case, the dominant crystal morphology was the rhombic dodecahedron formed by the {110} face and observed previously in the presence of oxalate. An SEM image of these crystals is shown in Figure 3(c). The expected
morphologies of crystals comprising the {111} or {110} faces are shown in Figure 3(d)-(e).

In all of these cases, the crystal growth modifier has targeted a single crystal face, leading to the formation of well defined polyhedral crystals. Other additive anions have, however, have led to the growth of crystals with a less well defined morphology but still significantly different to that of the Ca$_3$Al$_2$(OH)$_{12}$ blank. For example, growth of Ca$_3$Al$_2$(OH)$_{12}$ in the presence of phosphate leads to the formation of small needle-like crystals which typically agglomerate into balls as shown in Figure 4.

The organic phosphonic acids, HN(CH$_2$PO$_3$H$_2$)$_2$ and H$_3$CN(CH$_2$PO$_3$H$_2$)$_2$, and the mixed carboxylic/phosphonic acids, N(CH$_2$CO$_2$H)$_2$(CH$_2$PO$_3$H$_2$) and N(CH$_2$CO$_2$H)(CH$_2$PO$_3$H$_2$)$_2$, each produced a near spherical morphology for Ca$_3$Al$_2$(OH)$_{12}$ indicating they have a similar stabilising or inhibiting effect on each crystal face. Typical SEM images of these crystals are shown in Figure 5.

Conclusions

We have shown that by variation of the crystal growth modifier, the morphology of Ca$_3$Al$_2$(OH)$_{12}$ can be carefully controlled. The experimental morphologies range from regular polyhedral crystals such as octahedra and rhombic dodecahedra grown in the presence of dithionite and nitrilotriacetic acid, respectively, to small needles when phosphate is the additive anion, and spheres with the organic acids HN(CH$_2$PO$_3$H$_2$)$_2$, H$_3$CN(CH$_2$PO$_3$H$_2$)$_2$, N(CH$_2$CO$_2$H)$_2$(CH$_2$PO$_3$H$_2$) and N(CH$_2$CO$_2$H)(CH$_2$PO$_3$H$_2$)$_2$. The results suggest that the control of TCA6 formation and morphologies through the use of simple additives is possible.
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References


Figure Captions

Figure 1 Organic polyacids used as crystal growth modifiers during the preparation of Ca₃Al₂(OH)₁₂.

Figure 2 SEM images of the morphology of Ca₃Al₂(OH)₁₂ grown in the absence of any crystal growth modifiers.

Figure 3 SEM images of the morphology of Ca₃Al₂(OH)₁₂ grown in the presence of (a) sulphite, (b) dithionite and (c) nitrilotriacetic acid. The expected morphologies of crystals comprising (d) {111} and (e) {110} faces.

Figure 4 SEM images of the morphology of Ca₃Al₂(OH)₁₂ grown in the presence of phosphate.

Figure 5 SEM images of the morphology of Ca₃Al₂(OH)₁₂ grown in the presence of (a) N(CH₂CO₂H)₂(CH₂PO₃H₂), (b) N(CH₂CO₂H)(CH₂PO₃H₂)₂, (c) HN(CH₂PO₃H₂)₂ and (d) H₃CN(CH₂PO₃H₂)₂.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5