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Letter to the Editor

Hydration kinetics of calcium sulphate hemihydrate—a comment

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Hand [1] has cited a work of mine [2] on the hydration of calcium sulphate hemihydrate as by Taplin, D., whereas my name is Taplin, John Hubert. The index of reaction [3] was left to be determined for crystal growth because theory predicts 1/3 for diffusion control, 2/3 for a single crop of nuclei and 3/4 for continued nucleation. Hand considered my 1965 equation but not my 1973 versions [4], which allow for the possibility that the rate of precipitation of gypsum depends on the supersaturation squared, and that the rate of dissolution of hemihydrate depends on undersaturation squared. Beretka and van der Trouw [5] fitted various equations to one plaster and found that my 1965 equation was the best fit for that plaster. He did not test my 1973 equations.

The equation of Ridge can be seen as an approximation to my 1965 equation

$$\mathrm{d}F/\mathrm{d}t = ghF^{x}(1-F)^{y}/[gF^{x}+h(1-F)^{y}] \tag{1}$$

For my control plaster, x=0.8, y=1.3, g=0.14 (min^{-1}), h=0.94 (min^{-1}), the denominator of Eq. (1) then decreases monotonically with F, that if it is ignored, we should increase x and decrease y slightly. Hence, $\mathrm{d}F/\mathrm{d}t=kF^{x}(1-F)^{y}$, with x=1, y=2/3 or y=1, is a plausible approximation. Similar approximations hold for the relevant equation for rate dependence on concentration difference squared, with x and y both slightly increased from those found fitting Eq. (1). Fitting equations in the integrated form is insensitive to changes in x and y. The product equation of Beretka and van der Trouw [5] is Eq. (1) with g=h and x=y=1.

As shown previously [4], the Avrami equation, when applied to the hydration of hemihydrate, has a term $1-bF$ replacing $1-F$, where b decreases from unity with increasing water–plaster ratio. This is because the gypsum does not occupy all the space, and the extent of crystal-to-crystal contact depends on the water content.

If, as is widely believed, the setting of plaster is, at first, largely controlled by the rate of gypsum growth and, later, largely by the dissolution of hemihydrate, then we need kinetic and particle/crystal size data that are good enough to determine the two rate constants and the (at least) two geometric parameters for the two phases. Single parameter equations tell us nothing about the relative rates of the two processes. Information about the relative rate constants for dissolution and crystal growth is in the position of the rate maximum. It is also a most useful statistic for distinguishing between models.

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