Predicting salt damage in practice: A theoretical insight into laboratory tests – supplementary material: Basic equation of crystallization pressure

Supplementary material

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Let us consider a large salt crystal C at a pressure P_C and in contact with a solution at pressure P_0. In this case, "large" means that its interfacial curvature does not significantly affect its solubility. According to Fig. 1, the pressure P_c is applied by the pore walls to the loaded faces of the crystal while the free faces are under pressure P_0. The crystal dissociates into a number of species that we will note X_i with a stoichiometric coefficient v_i determined for one mole of the crystal. For such a large crystal, the free energy change of dissolution is given by:

$$\Delta G = \Delta G° + RT \ln Q \qquad (1)$$

in which Q is the ion activity product given by:

$$Q = \prod a_{X_i}^{v_i} \qquad (2)$$

and where a_{X_i} is the activity of compound X_i and v_i is the corresponding stoichiometric coefficient, which for the crystal is -1. For the compounds released by the crystal all stoichiometric coefficients are positive.

In Eq. (1), $\Delta G°$ is related to the chemical potentials of the pure substances, μ_i^{0,P_i} at the corresponding pressure:

$$\Delta G^0 = \sum v_i \mu_i^{0,P_i} \qquad (3)$$

Through the Gibbs-Duhem equation, it is possible to express the chemical potential of the crystal face at P_C, μ_i^{0,P_C}, as a function of its value at P_0, μ_i^{0,P_0} [15,95]:

$$\mu_C^{0,P_C} = \mu_C^{0,P_0} + v_C(P_C - P_0) \qquad (4)$$

which holds if we assume that the crystal is incompressible. Inserting Eq.(4) into Eq.(3), we get:

$$\Delta G^0 = \Delta G^{0,P_0} - v_C(P_C - P_0) \qquad (5)$$

With

$$\Delta G^{0,P_0} = \sum v_i \mu_i^{0,P_0} \qquad (6)$$

With Eq.(1), we get:

$$\Delta G = \Delta G^{0,P_0} + RT \ln Q - v_C(P_C - P_0) \qquad (7)$$

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At equilibrium $\Delta G = 0$. Therefore, if the pressure P_C is the same as in the solution, then we recover the well established relation:

$$\Delta G^{0,P_0} = -RTlnK \tag{8}$$

where K is the value of Q at equilibrium when all phases are at the same pressure P_0.

Substitution of Eq.(10) into Eq.(7) gives:

$$\Delta G = RTln\frac{Q}{K} - v_C(P_C - P_0) \tag{9}$$

Therefore, for the equilibrium between a large crystal at pressure P_C and a solution at pressure P_0, we obtain the well established equation of (maximum) crystallization pressure [15,30]:

$$(P_C - P_0) = \frac{RT}{v_C}ln\frac{Q}{K} \tag{10}$$

This represents the upper bound on the pressure exerted on a pore wall, and can be reached at equilibrium only when a large crystal is trapped in a pore with small entries. It is also the peak transient pressure that can be exerted when a crystal growing in a large pore first makes contact with the wall. As the crystal grows, it reduces the local supersaturation and the pressure decreases.