# EFFECT OF THE PORE SIZE DISTRIBUTION ON CRYSTALLIZATION PRESSURE

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**Abstract:** A novel graphical method is introduced for evaluation of the state of equilibrium of a solution crystallizing within a porous medium. This tool makes it easy to anticipate the effects of changes in pore size distribution, initial concentration of salt, or type of salt, on the crystallization pressure at equilibrium.

**Key words:** salt crystallization, stress, supersaturation, pore size distribution

## 1. INTRODUCTION

Salt crystallization is widely recognized as a cause of weathering of porous building materials, including stone, mortar and concrete[1,2,3]. A century of research has revealed the key mechanisms involved in such phenomena[4,5,6], and the thermodynamic aspects of the problem are well understood[7,8]. However, predicting damage to porous media by salt crystallization requires consideration of crystal growth kinetics and fracture mechanics, and no detailed theory is yet available, although progress is being made[9]. In this paper we consider the influence of a pore size distribution on crystallization pressure, using a novel graphical approach that will be described in detail in a future publication[10].

## 2. SUPERSATURATION AND PRESSURE

The solubility product for a crystal whose chemical formula is of the form $A_aB_bC_c$ is

$$K = \{a_A\}^a \{a_B\}^b \{a_C\}^c \tag{1}$$

where $\{a_i\}$ is the activity of ion type $i$. The equilibrium value of the solubility product, $K_0$, is the value of $K$ when a macroscopic crystal is in equilibrium with a solution. If $K > K_0$, the solution is said to be supersaturated, and the crystal will grow until the supersaturation is consumed (i.e., until $K$ is reduced to $K_0$). The supersaturation is written as $\beta = K/K_0$.

Chemical equilibrium is reached when $\beta = 1$, leading to a macroscopic crystal with a radius of curvature equal to zero. As the curvature, $\kappa_{CL}$, of the crystal/liquid interface increases (i.e., as the radius decreases), equilibrium requires a higher salt concentration in the solution, according to the Ostwald-Freundlich equation[11]:

$$\gamma_{CL}\,\kappa_{CL} = \frac{RT}{v_C}\ln(\beta) \tag{2}$$

where $\gamma_{CL}$ is the crystal/solution interfacial energy, $R$ is the gas constant, $T$ is the absolute temperature, and $v_c$ is the molar volume of the crystal. Consequently, the smaller the pore, the higher $\beta$ must be to allow a crystal to penetrate [8].

As crystals grow they consume ions from the solution and consequently its supersaturation decreases. At a given supersaturation, equilibrium requires that all the crystals present have the same radius of curvature. If two crystals (one large and one small) are in the same solution, the smaller crystal will be more soluble, so it will dissolve as the larger one grows. Of course, crystal growth and dissolution depend on solute transport by diffusion. This can be the critical mechanism leading to a transient state of equilibrium.

The pore size distribution can be represented as a cumulative curve of the pore volumes, beginning with the larger pores. If $V_p(r)\,dr$ is the volume of pores with radii between $r$ and $r+dr$, then the cumulative volume fraction of pores larger than $r$ is

$$V_p^c\left(r_p\right) = \frac{\int_{r_p}^{\infty} V_p\left(r_p\right)dr_p}{V_p^T} \tag{3}$$

The volume is normalized by the total porous volume, $V_p^T$. During crystallization, the pore volume will be filled beginning with the larger pores. The normalized pore size distribution is therefore equivalent to a degree of salt saturation in the pores.

Crystals growing in pores are separated from the pore walls by a film of solution[8], owing to disjoining forces that oppose contact of the dissimilar crystals. The portion of the crystal in contact with the pore liquid, but not against the pore wall, has a curvature dictated by eq. (2). Elsewhere, the curvature of the crystal is dictated by the shape of the pore wall, even though it is in contact with the same solution. To preserve equilibrium, a mechanical pressure must be applied on the crystal by the pore wall. In the simple case of a cylindrical pore (and neglecting the thickness of the solution film), the pressure on the pore wall is expressed by[3,12]

$$P_w = \gamma_{CL}\left(\frac{2}{r_p} - \frac{1}{r_p}\right) = \frac{\gamma_{CL}}{r_p} \tag{4}$$

where $2/r_p$ is the curvature of the hemispheric ends and $1/r_p$ is the curvature of the pore wall. For a crystal of arbitrary shape, the pressure varies from point to point on the pore wall, according to the difference in curvature at that point and at the pore entry where the free crystal is in contact with the pore liquid[8].

Now consider the case of a crystal that has filled a large pore and continues to grow into smaller pores (as a result of an increase in $\beta$ brought about by evaporation or a change in temperature). The smaller pore radius controls the curvature of the advancing (hemispherical) end. The pressure on the pore wall increases in the larger pores and becomes proportional to the difference between the local curvature and that of the hemispherical end in the pore being invaded. The average pressure exerted on the pore walls by salt crystallization in the pores can be evaluated[13,14] as a pore volume-weighted average of the local pressure over all pore radii containing crystals. If $\beta$ is in equilibrium with radius $r_p$, then the average pressure in the body is

$$\bar{P}\left(r_p\right) = \frac{\int_{r_p}^{r^{\max}} V_p\left(r\right) P_W\left(r\right) dr}{V_p^T} \tag{5}$$

The smaller $r_p$ is, the higher the average pressure exerted on the pore walls. It is clear that when the average pressure increases, the risk of damage to the porous medium also increases.

## 2. EQUILIBRIUM DIAGRAM

Equilibrium of a crystal in a porous medium can be represented on a unique graph, illustrated in . The four axes correspond to the relative volume (porosity or salt saturation), molality of the solution, supersaturation, and the pore radius. The average pressure versus pore radius is also included on this graph (dashed curve) introducing an additional axis called the pressure axis.

The two curves on the left side of Figure 1 are only dependent on the chemistry of the crystal, whereas the two curves on the right are specific to the porous medium. The top-right curve (Quandrant I) represents the solution's molality in the pores and its evolution when the salts precipitate. The bottom-right curve (Quadrant IV) describes the pore size distribution of the porous medium. Any change in the pore size distribution will affect this curve and, consequently, the average pressure curve. The unique state of equilibrium is indicated by the rectangular dashed frame.

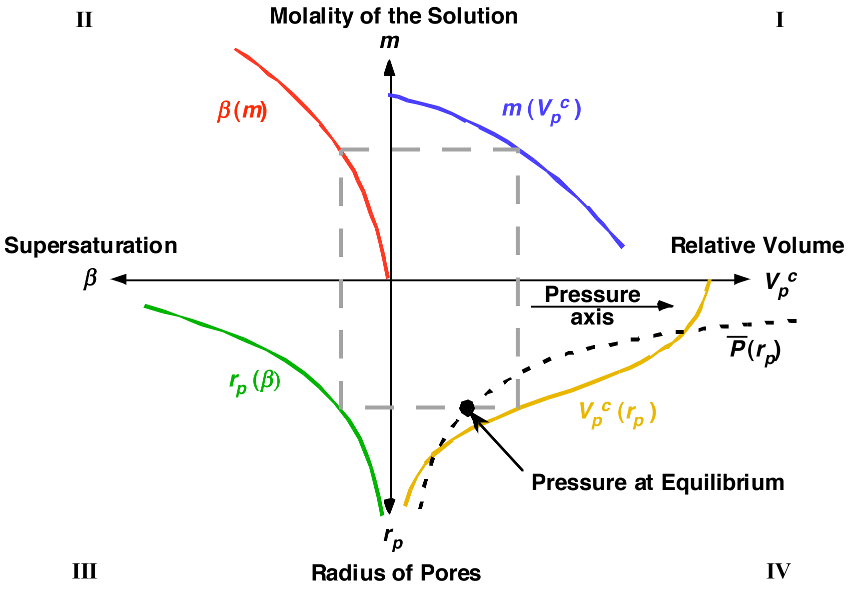

Figure 1. Four quadrant diagram showing the parameters controlling equilibrium. Quadrant I contains molality ($m$) as a function of fraction of pore volume crystallized ( $V_p^c$ ), Quadrant II shows supersaturation ($\beta$) as a function of molality, Quadrant III shows the pore size ($r_p$) in equilibrium at supersaturation $\beta$, and Quadrant IV shows the cumulative pore size distribution. Also shown in Quadrant IV is the crystallization pressure from eq. (5) versus $r_p$. The vertices of the rectangle identify the values of each of the quantities at the state of equilibrium.

Beginning in Quadrant I and turning counter clockwise, the functions are successively $m(V_p^c)$, $\beta(m)$, $r_p(\beta)$, and $V_p^c(r_p)$. Each of these four functions is monotonic, meaning that the signs of their derivatives are constant. Suppose that we pick a particular value of the relative volume, say $\bar{V}_p^c$. The molality of the solution at the point where the salt fills that volume fraction is $m(\bar{V}_p^c)$, the supersaturation of the solution at that point is $\beta(m(\bar{V}_p^c))$, the size of the crystal that would be in equilibrium with that supersaturation is $r_p(\beta(m(\bar{V}_p^c)))$, and the cumulative pore volume up to that pore size is $V_p^c(r_p(\beta(m(\bar{V}_p^c))))$. If the system is in equilibrium, then the latter quantity must be equal to $\bar{V}_p^c$. It can be shown that the root $\bar{V}_p^c$ exists and is unique[10].

Convergence to the solution can be graphically illustrated: starting at any point on one of the curves and circulating clockwise, as in Figure 2, the loop inevitably converges on the equilibrium rectangle.

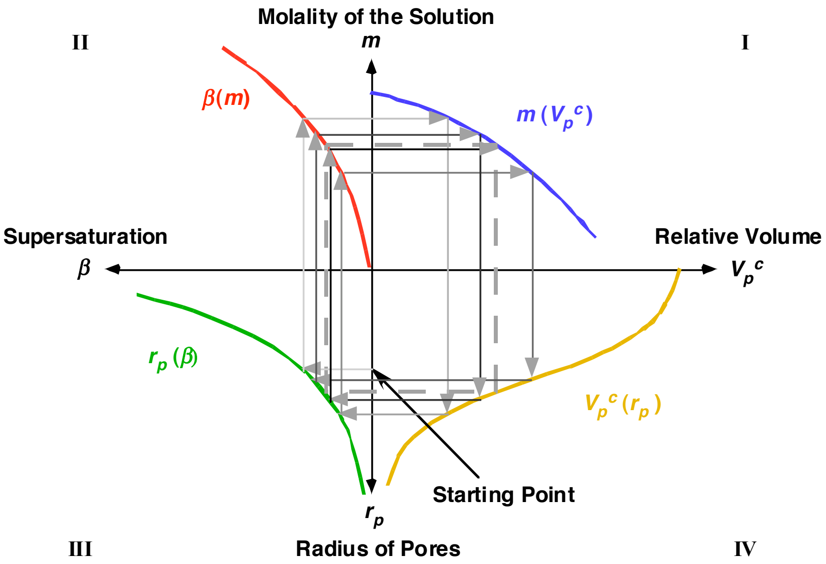

Figure 2. Demonstration of convergence on equilibrium from an arbitrary starting point.

This diagram makes is easy to anticipate the consequences of changes in the parameters. For example, increasing the initial molality of the solution in the pores (i.e., shifting the curve $m(V_p^c)$ upward) raises the equilibrium crystallization pressure by a predictable amount. Similarly, the effects of changes in the type of solute, which affects $\beta(m)$, or in the shape of the pore size distribution can be quantified.

## 3. CONCLUSIONS

A novel graphical approach facilitates the prediction of crystallization pressure, taking account of the effects of supersaturation and the shape of the pore size distribution. Application of this tool to the stress caused by sodium sulfate in limestone will be presented in a forthcoming paper[15].

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