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UNAMBIGUOUS DEMONSTRATION OF DESTRUCTIVE CRYSTAL GROWTH PRESSURE

S. Chatterji and N. Thaulow
Carl Bernhardsvej 13B; St.4
G.M.Idorn Consult A/S, Bredevej 2, DK-2830 Virum

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ABSTRACT

At 48°C sodium thiosulphate pentahydrate, $Na_2S_2O_3 . 5H_2O$ melts in its own water of crystallization forming a concentrated solution. On cooling, this melt forms a highly supersaturated solution and subsequently $Na_2S_2O_3 . 5H_2O$ crystallizes out directly without any intermediate anhydrous phase. Pyrex glass test tubes or beakers, containing more than a critical volume of this melt, crack when stored in a refrigerator at 5°C. Prolonged storage of the cracked containers in the refrigerator causes an increase in the apparent diameter of the crystalline mass. This cracking and subsequent expansion unambiguously demonstrate the existence of destructive crystal growth pressure. Necessary conditions for a damage to occur to a porous matrix due to crystal growth pressure have been delineated. © *1997 Elsevier Science Ltd*

Introduction

Crystal growth pressure is often invoked to explain certain types of breakdown of building materials e.g. concrete, brick, natural stone etc. (1,2,3). However, the existence of the destructive crystal growth pressure has also been questioned by many researchers pointing out that its existence has not been unambiguously demonstrated. Many of its apparent demonstration could also be explained by other mechanisms. For example the breakdown of porous solids due to the formation of $Na_2SO_4 \cdot 10H_2O$ from Na_2SO_4 and H_2O may be explained either by crystal growth pressure or by a solid state reaction between anhydrous Na_2SO_4 and water forming $Na_2SO_4 . 10H_2O$ and accompanying solid volume increase (4,5). The object of this paper is to unambiguously demonstrate the existence and efficacy of destructive crystal growth pressure and to draw attention to some of its corollaries.

It is known that sodium thiosulphate pentahydrate ($Na_2S_2O_3 . 5H_2O$) melts at 48°C forming a concentrated solution (6). Storage of this melt at a lower temperature results in the formation of a highly supersaturated solution and crystallization of $Na_2S_2O_3 . 5H_2O$ without formation of any intermediate anhydrous phase. This melt has been used in this investigation.

Theory

A solute in a supersaturated solution has higher potential energy than in a corresponding saturated solution. Under certain conditions this excess potential energy can be utilized to perform work against an external restraining pressure. In the process of performing this work the solute crystallizes out of its supersaturated solution. If the above crystallization occurs within a porous medium i.e. the medium exerts the restraining pressure, then the medium may be damaged provided sufficient volume of solid crystallize out and a high degree of supersaturation is maintained.

The chemical potential of a solute in a solution is given by Equation 1; where μ_i is the chemical potential of the solute in a solution of activity of a_i, μ_o is its chemical potential in the standard state, R is the gas constant and T is the absolute temperature of the solution.

$$\mu_i = \mu_o + RTlna_i \tag{1}$$

The difference in the chemical potential, $\Delta\mu$, between a supersaturated solution and the saturated solution is Eq.2:

$$\Delta\mu = RT\ln\frac{a_i}{a_o} \tag{2}$$

where a_o is the activity in the saturated solution at normal pressure.

Consider a small crystal of the solute, clamped between a fixed and a spring loaded plates such that a constant pressure, P, is applied to the crystal, is placed in contact with a large volume of the supersaturated solution of activity a_S. If a mole of solute is isothermally and reversibly transferred from the supersaturated solution to the crystal then work done during growth of the crystal is PV_M where V_M is the molar volume of the solute. Equating loss of potential energy to the external work done during the crystal growth gives Eq.3:

$$P = \frac{RT}{V_M}\ln\frac{a_s}{a_o} \tag{3}$$

Since V_M is a constant, Eq.3 gives the pressure, P, which is necessary to stop crystal growth and external work. This P is known as the crystal growth pressure. Equation of this type has earlier been derived, among others, by Correns (7).

Consider the case of a small crystal, in a container of bursting strength σ, is placed in contact with a large volume of the supersaturated solution. In this case the growing crystal will exert a bursting pressure, B, to the container and at the same time itself will be under increasing compressive stress. This increasing compressive stress in its turn will increase the solubility of the crystal above that at the normal pressure. If P is higher than σ then both B and the solubility of the crystal will increase until σ is exceeded. At this point the container will fail.

At the failure B is given by Eq.4.

$$B = \sigma = \frac{RT}{V_M}\ln\frac{a_S}{a_\sigma} \tag{4}$$

Thereafter a further crystal growth will occur until a_S is lowered to a_0. If on the other hand the volume of supersaturated solution is such that at the break point the supersaturation is lowered to a_s then a further crystal growth will occur until a_s is lowered to a_0.

It is important to note that a failure or damage to occur Eq.4 has to be satisfied, i.e. any supersaturation will not do; it has to be above a critical degree. Furthermore for semirigid bodies e.g. cement paste or concrete etc., sufficient degree of crystal growth has to occur to take care of the pre-failure creep of the matrix i.e. either the volume of the supersaturated solution should be sufficient or the supersaturation has to be maintained by some other means.

Materials and Experimental Methods

Photographic quality sodium thiosulphate pentahydrate ($Na_2S_2O_3 . 5H_2O$) (Hypo) was used in this investigation. Pyrex glass beakers and test tubes of different diameter to length ratios were used as sample holders. Different amounts of pentahydrate were weighed in a number of sample holders of each type; the open ends of the sample holders were covered with aluminium foil to avoid evaporation. The sample holders were then heated in a water bath maintained at 60°C until clear melts formed.

The sample holders were then transferred to a refrigerator at 5°C. Initially the sample holders were examined every 24 hours for any crystallization and cracking of the containers; subsequently they were examined every 7th day. Experiments were repeated a few times.

Results and Discussion

As experiments with beakers and test tubes gave very similar results only those with one size test tubes are reported. Table 1 shows the experimental conditions and results.

TABLE 1

Experiments with $Na_2S_2O_3 . 5H_2O$ melts

Exp. No.	Test tube dia, mm	Wt. of penta hydrate, g.	State of the test tube at 24 hr.	Remark.
1	15	2	Intact	Crystallized
2	15	5	Intact	Crystallized
3	14.5	10	Broken*	Crystallized
4	14.5	20	Broken*	Crystallized
5	15	40	Broken*	Crystallized

*Broken only when fully crystallized. However, on occasions melt only partially crystallized. If the supercooled melt is seeded with a small crystal of $Na_2S_2O_3 . 5H_2O$ further crystallization occurs with a slight rise in temperature with no immediate fracture of the test tubes. Further storage in the refrigerator always results in a fracture.

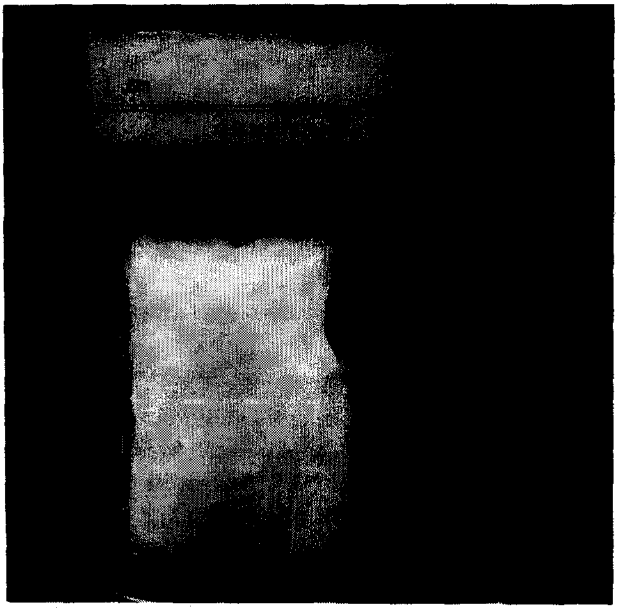

FIG. 1.
Photo shows a broken test tube partly filled with white mass of sodium thiosulphate pentahydrate. Notice that the diameter of the white mass is larger at the bottom than at the top.

From Table 1 it can be seen that test tubes remain intact if they contain 2 or 5 g of pentahydrate. However, they crack if their content is 10 g or above and the melt is fully crystallized. At the initial stages only cracks could be seen in the walls of the test tubes. Storage of the cracked tubes in the refrigerator causes further crystal growth; diameters of the polycrystalline masses grow beyond that of the test tubes and broken parts of the test tubes are pushed apart. Fig. 1 shows a test tube at this stage. Notice how the lower part of the test tube has been pushed apart from the rest and increase in the diameter of the white mass of pentahydrate at the bottom of the tube compared to that in the top part of the test tube. This delayed expansion is in accordance with the theoretical expectation. This two stage expansion unambiguously demonstrates the existence and efficacy of destructive crystal growth pressure. Fig. 2 shows metastable supersaturated melt in contact with crystalline pentahydrate; in this particular case the metastability continued beyond 28 days when the experiment was discontinued.

Table 1 also shows that a test tube must contain a critical volume, corresponding to a weight between 5 and 10 g of pentahydrate, before it cracks. Existence of similar critical volume has earlier been reported (2,8). This critical volume increases with the increase in temperature (8).

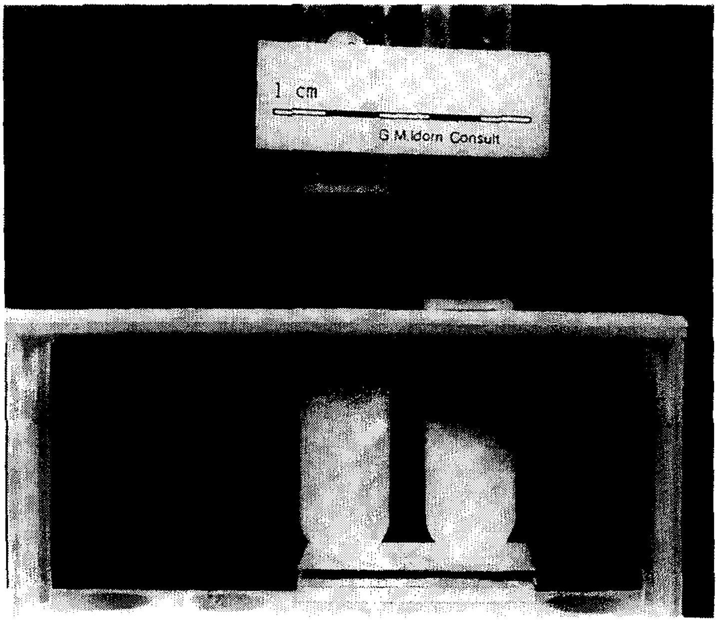

FIG. 2.
Two test tubes filled partly with supercooled melt and partly with white mass of sodium thiosulphate pentahydrate.

Conclusions

From the above the following conclusions could be drawn:

a) A porous material may be damaged during crystallization of a solid if crystallization pressure is sufficiently high.
b) The necessary supersaturation need to be above a critical value. The existence of a supersaturated solution in the porous matrix is a necessary but not a sufficient condition for damage.
c) A supersaturated solution may remain in a metastable state for a long time even when in contact with its crystalline product. In this state no damage occurs.
d) For a semirigid body e.g. cement paste or concrete etc., sufficient degree of crystal growth has to occur to take care of the pre-failure creep of the matrix i.e. either the volume of the supersaturated solution need to be sufficiently large or the supersaturation has to be maintained by some other means.
e) The potential volume of the crystallized solid need to be higher than a critical value. This critical volume increases with increasing temperature.

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