EFFLORESCENCE AND BREAKDOWN OF BUILDING
MATERIALS

S. Chatterji, M.Sc., D.Phil. and
A.D. Jensen, M.Sc.
Teknologisk Institut
DK - 2630 Taastrup

ABSTRACT

Efflorescence, i.e. crystallization of salts,
occurs on most building materials under ap-
propriate environmental conditons. It may or
may not be accompanied by a breakdown. On the
basis of model laboratory experiments, it has
been suggested that the breakdown is due to a
development of a crystal growth pressure.
When the crystal growth pressure is higher
than the tensile strength of the relevant ma-
terial a breakdown occurs. The equation which
relates the crystal growth pressure to the
environment also defines the condition of
breakdown.

Key-words: Efflorescence, crystal growth,
breakdown, materials.

1. INTRODUCTION

The term "efflorescence" in broad sense refers to any number of
white crystalline salt growing on and just inside the exposed
surfaces of building materials. During efflorescence salt bearing
solutions rise into the drier portions of the material, and with
evaporation of the water salt crystallization commences. For mas-
sive structures, sources of solution could be internal; however,
more commonly the source is the ground water. The pore characte-
ristics, which favours the necessary flow of solution is very
often met in bricks, natural stones, etc. and fortunately met
less often in concrete structures. An efflorescence may or may
not be accompanied by a breakdown of the relevant building mate-
rial. The main object of this paper is to propose a mechanism
which will define the condition of breakdown.

1.1 Salt assemblage in efflorescents and some relevant characteristics

Chemical analysis by a large number of workers, including the
present ones, showed that efflorescents consist mainly of sulpha-
tes and carbonates of sodium. Though gypsum may also be present.
X-ray diffraction analyses showed that efflorescents contain both
anhydrous and hydrated salts, eg. it can be a mixture of Na_2SO_4
and $Na_2SO_4.10H_2O$. Many of these hydrated salts may be reversibly
decomposed to corresponding anhydrous salts when cycled through

critical points, eg. $Na_2SO_4.10H_2O$ could be reversibly decomposed
to Na_2SO_4 when cycled through 32.4°C. They may also be reversibly
transformed when cycled through their equilibrium relative humi-
dity points at any other temperature lower than the critical tem-
perature. Arnold (1) has shown that hydration and dehydration of
efflorescencing salts, e.i. $Na_2SO_4.10H_2O$, $Na_2CO_3.10H_2O$ etc. can
occur daily over long periods of the year. If one considers on-
ly the solid components of a relevant hydration-dehydration reac-
tion then the formation of a hydrated salt is accompanied by a
volume increase. In the case $Na_2SO_4-Na_2SO_4.10H_2O$ system the solid
volume increase is 314% as is shown by the following equation:

$$Na_2SO_4 + 10H_2O \; \rightleftarrows \; Na_2SO_4.10H_2O \tag{1}$$
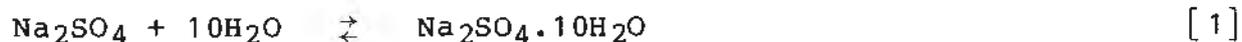
53 ml + 180 ml   220.7 ml

although the Na_2SO_4-water system as a whole undergoes a volume
shrinkage of 5%. Similar calculations could be made for Na_2CO_3-
water and $CaSO_4.1/2H_2O$-water systems. The breakdown associated
with efflorescence has generally been attributed to this solid
volume increase associated with the formation of hydrated cry-
stals (2). Implicit in this attribution is an assumption of a
solid state or insitu conversion eg. Na_2SO_4 to $Na_2SO4.10H_2O$. How-
ever, the crystal structures of anhydrous and hydrated compounds
are so different as to exclude a solid state or insitu conver-
sion. To gain a better understanding of the mechanism of break-
down associated with efflorescence the following laboratory ex-
periments were carried out.

2.   EXPERIMENTAL

2.1   Experiments with a model porous system

In these experiments Pyrex glass test tubes of various diameters
were used as idealised capillary pores. In each series glass
tubes of a fixed diameter were used. In each series a number of
glass tubes were filled with different amounts of $Na_2SO_4.10H_2O$
crystals and the tubes were stoppered with rubber bungs so as to
avoid water loss. The test tubes were then heated to 50°C to de-
compose decahydrate completely. The test tubes were then stored
either at 5° or 20°C until the reformation of decahydrate was
complete. The test tubes were then examined for any crack.

2.2   Experiments with bricks

In this series, three bricks without any visible cracks were
chosen. From the middle part of each of the bricks two 40 mm
cubes were cut out. The cubes were divided into two groups such
that each group contained a cube from each brick. The cubes were
then soaked for 24 hours in a saturated solution of Na_2SO_4 main-
tained at 40°C. The cubes were then dried at 60°C for 24 hours.
The soaking-drying cycles were repeated five times. After last
drying, the cubes were cooled to room temperature and cleaned of

their surface coating of Na_2SO_4 with a wet cloth. One group of three cubes was then placed in a closed container at 20^oC and the other group in a closed container at 30^oC. Each of the containers contained sufficient amount of saturated Na_2SO_4 solutions to immerse bottom 1 mm of the cubes. After 24 hours storage, when cubes were fully soaked, they were dried at 60^oC for 24 hours, cooled to their storage temperature, and then returned to their respective containers. The drying-soaking cycle was repated 15 times. After every 5th cycle, the cubes were examined for any sign of damage.

3.   RESULTS AND DISCUSSION

3.1   The model porous system

The results of a typical set of experiments are shown in Table 1.

TABLE 1

$Na_2SO_4.10H_2O$ crystallization experiments.
Test tube size ⌀15x155 mm

Storage Temp. in ^oC	$Na_2SO_4.10H_2O$ in g	Observation
5	10	Broken
5	8	Broken
5	6	Unbroken
5	4	Unbroken
20	18	Broken
20	16	Broken
20	14	Unbroken
20	12	Unbroken

From Table 1 it can be seen that for each temperature of storage a minimum critical amount of $Na_2SO_4.10H_2O$ is necessary to cause a breakdown of the test tubes. Furthermore, this critical amount decreases with decreasing temperature. Similar results were obtained using test tubes of different diameters. If one assumes that test tubes of each diameter need a definete force to cause their breakdown, then it will appear that at a higher temperature of storage a larger amount of $Na_2SO_4.10H_2O$ is needed to generate that force. This will suggest that for each size of pores there is a temperature aoove which the critical amount, necessary to cause a breakdown will exceed the holding capacity of the pores.

3.2 The brick cubes

None of the brick cubes used for the experiement at 30°C showed any sign of distress even at the end of 15 cycles. The brick cubes which were used for the experiment at 20°C on the other hand started to crumble after 5 cycles and went on crumbling in subsequent cycles. It should be noted that anhydrous Na_2SO_4, formed during drying at 60°C, will reform $Na_2SO_4.10H_2O$ when come in contact with Na_2SO_4 solution both at 20 and 30°C.

The experiments with Pyrex test tubes indicate and those with brick cubes show that reformation of $Na_2SO_4.10H_2O$ from anhydrous Na_2SO_4 may not cause any damage when occurs at a sufficiently high temperature but will cause damage when occurs at a lower temperature. This observation is difficult to reconcile with the assumption of solid state conversion of Na_2SO_4 to $Na_2SO_4.10H_2O$.

4. A MECHANISM

In order to explain the varying behaviour of Na_2SO_4 - $Na_2SO_4.10H_2O$ system at different temperatures we propose that in the above system newly formed $Na_2SO4.10H_2O$ crystals are in contact with a supersaturated solution formed by the dissolution of Na_2SO_4 crystals. Growing $Na_2SO_4.10H_2O$ crystals, when constrained by a matrix, eg. brick, concrete, etc., develop a bursting pressure on the matrix; when this pressure overcomes the tensile strength of the matrix a breakdown occurs.

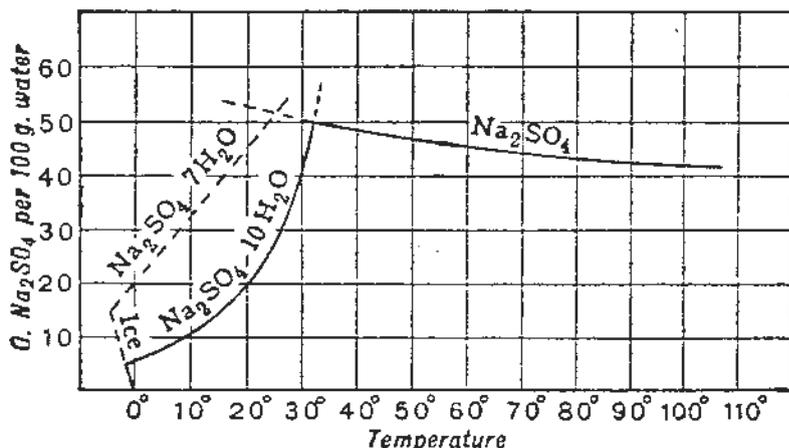In this context it will be profitable to examine Na_2SO_4-water phase diagram (Fig. 1) (3).

Fig. 1. Solubility curves of sodium sulphate.

Na_2SO_4 is the stable phase above 32.4°C; however, it persists as a metastable phase at least down to about 15°C. More importantly Na_2SO_4 readily forms supersaturated solutions (3). Below 32.4°C $Na_2SO_4.10H_2O$ is the stable phase. At any temperature below 32.4°C Na_2SO_4 produces more concentrated solution than $Na_2SO_4.10H_2O$ and this concentration difference increases with decreasing temperature. It is important to note that the phase diagram of Na_2CO_3-water system is very similar to Fig. 1 (4).

Now consider the case of Na_2SO_4 crystals in contact with water at $20^{\circ}C$. Anhydrous Na_2SO_4 crystals will tend to form a solution containing Ca 50 g $Na_2SO_4/100$ g water; whereas newly crystallized $Na_2SO_4.10H_2O$ has a solubility of 20 g $Na_2SO_4/100$ g water, i.e. $Na_2SO_4.10H_2O$ crystals will be surrounded by a supersaturated solution. In these circumstances, $Na_2SO_4.10H_2O$ crystals will grow in size; this growth will stop only when they are under a triaxial compressive stress, P. The magnitude of P could be approximately calculated from the following relationship (5)

$$P = \frac{RT}{V} \ln \frac{C_1}{C_0} \qquad [2]$$

where

R   is the gas constant

V   is the molar volume of the hydrated phase

T   is the reaction temperature in $^{\circ}K$ up to the critical temperature

C_1 is the actual concentration in the liquid phase

C_0 is the concentration of a saturated solution of the hydrated crystals.

From Fig. 1 it can be seen that the ratio C_1/C_0 increases with decreasing temperature so that P will increase with decreasing temperature of reaction. If P overcomes the tensile strength of the matrix a breakdown will occur. The equation [2] explains not only the results of the experiments, but also defines the conditions of a breakdown.

The equation [2] also indicates why damages associated with efflorescence are less frequent in the case of concrete structures than in the case of structures built with clay bricks or natural stones. To achieve sufficiently high pressure, P, to overcome the tensile strength of concrete one has to deal with saturated solutions of Na_2SO_4 or Na_2CO_3 i.e. the concrete structure has to be in contact with a ground water high in Na_2SO_4 or Na_2CO_3. Under usual conditions one would not build a concrete structure on such ground without using a migration barrier. However, the conditions may be fulfilled in acid zones like the Middle Eastern countries and there one has to take precautions against efflorescence if a structure cycles through the relevant critical temperature.

5. REFERENCES

/1/   Arnold, A., 2nd Inter. Symp. Deterioration of Building
Stones. Athens. 1976, p. 27.

/2/   Schaffer, R.J., The weathering of Natural Building
Stones. Special Report No. 18. D.S.I.R. England. 1932.

/3/   Partington, J.R., General and Inorganic Chemistry.
Macmillan & Co. Ltd. London 1961, p. 315.

/4/   Partington, J.R., General and Inorganic Chemistry.
Macmillan & Co. Ltd. London 1961, p. 308.

/5/   Chatterji, S. and Jeffery, J.W., Trans. Faraday Soc.
<u>60</u>, 1947-50, 1964.