

# STRENGTH AND MICROSTRUCTURE OF CAST GYPSUM

VLADIMÍR ŠATAVA

*Laboratory of Inorganic Materials  
of the Institute of Inorganic Chemistry ASCR,  
and the Institute of Chemical Technology,  
Technická 5, 166 28 Prague*

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*On the basis of experimentally established data on the size and shape of gypsum crystals which constitute the solid phase in hardened suspensions of  $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ , and on that of the size of pores in the materials it was shown that the strength of hardened gypsum was proportional to the area of mutual contacts between the gypsum crystals. Mechanical failure occurs at these contacts which represent the points with weakest bonds. Analyses of the microstructure of fracture surfaces resulted in the same conclusions.*

## INTRODUCTION

Gypsum binders, based on formable suspensions of calcium sulphate hemihydrate, solidify spontaneously producing materials whose strength after drying depends primarily on porosity, which, as demonstrated by Schiller [1], is given by the ratio of water to hemihydrate  $w$  in the mix:

$$p = \frac{w - 0.15}{w + 0.36} \quad (1)$$

The dependence of strength  $\sigma$  on porosity is then described by the equation

$$\sigma = q \log \frac{p_{cr}}{p} \quad (2)$$

where  $q$  and  $p_{cr}$  are empirical constants. This relationship was also established by Schiller who attempted to find the physical significance of the two constants [2]. He based his considerations on the assumption that the binder is composed of two continuous interlinked phases where the solid phase comprises gypsum microcrystals mutually intergrown into a continuous skeleton, and the other phase consists of a continuous network of pores. Schiller ascribes the loss of integrity of such a microstructure under mechanical load to stress concentration in the solid phase in the vicinity of pores.

Mori and Yamana [3], however, suggested that the loss in strength is not due to stress concentration, but rather to impaired bond between gypsum crystals,

associated with a decrease in the area of contacts between the gypsum microcrystals. They reached this conclusion on the basis of fractographic measurements.

The same concept of strength is used in the theory of strength of porous materials [4]. According to this theory, the relation between strength and porosity has the following form:

$$\sigma = k (f - f_{cr}) \quad (3)$$

where  $k$  is constant including the factors of shape and orientation of microcrystals characterizing the porous material, and function  $f$  has the form:

$$f = (1 - p)^{4/3} p^{-1/3} \quad (4)$$

Over a wide range of porosities, this function exhibits the same course as that of  $\log p$ .

Evidence for the correctness of the primary theory (and at the same time of Mori's concept) would be provided by experimental verification showing that the strength of a cast gypsum is proportional to the area of contacts between gypsum microcrystals in a unit volume of the material. Direct determination of the contact areas is difficult, but it may be assumed that the difference between the surface area which the gypsum crystals would have if not intergrown, and the surface area actually exhibited by the crystals in the hardened material, that is the surface area of the pores, can be regarded as a measure of the contact area of the crystals. The former characteristic can be determined by measuring the surface area of undamaged crystals on fracture surfaces of cast gypsum, and the latter can be

calculated from pore size distribution measurements. The present study was aimed at verifying this assumption.

EXPERIMENTAL PART

Alpha hemihydrate with a corpuscular character of non-porous particles, prepared by the autoclave process from natural microcrystalline high-purity gypsum, was used as the initial raw material. Test specimens  $1 \times 1 \times 5$  cm in size were then produced from suspensions with several mixing ratios  $w$  by casting into metal moulds. Following removal of air bubbles from the suspension in the moulds by vibration, the mixes were allowed to harden at a constant temperature of  $20\text{ }^\circ\text{C}$  and at 100 % relative humidity. After four hours, the specimens were removed from the moulds and dried at  $40\text{ }^\circ\text{C}$  in air to constant weight.

The porosity of the material was calculated from apparent weight and checked by water absorption.

The tensile bending strength was determined on a Schopper tester using at least five specimens. The test results are plotted in figure 1 as strength vs. logarithm of porosity, and evidently conform to Schiller's equation [2].

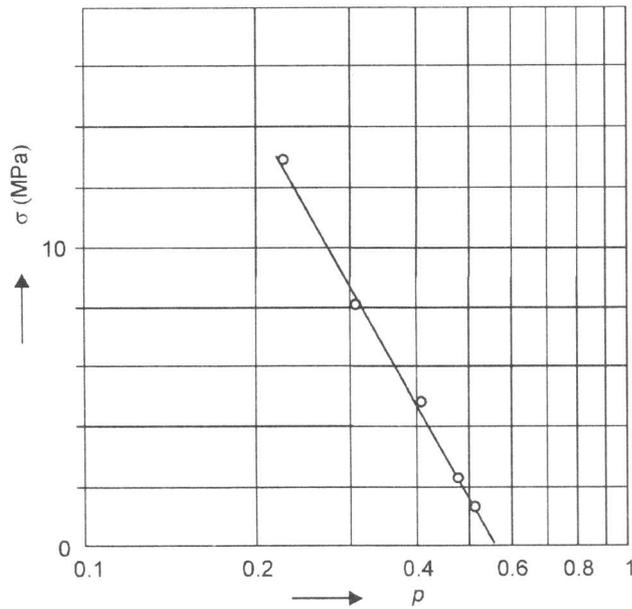
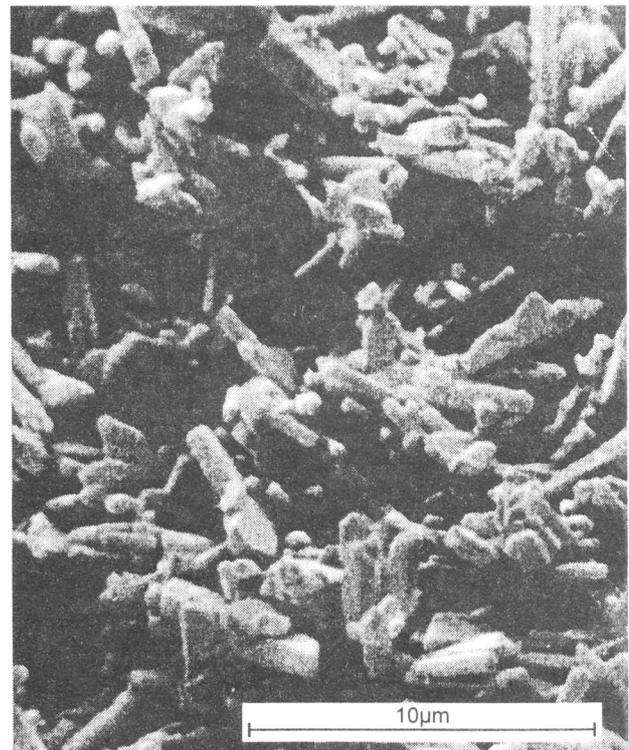


Figure 1. Tensile bending strength vs. porosity.

The shape and size distribution of the gypsum crystals was determined on the fracture surfaces of specimens used in the strength tests. The shape and size of the crystals was measured on scanning electron micrographs of the surfaces; two typical micrographs are shown in figure 2. Many of the crystals originally forming the skeleton were completely undamaged and thus



a)



b)

Figure 2. Scanning electron micrographs of fracture surfaces. a)  $w = 0.8$  ( $p = 0.56$ ); b)  $w = 0.4$  ( $p = 0.32$ )

allowed their dimensions to be measured. The size of the crystals increases with porosity; however, their prismatic shape undergoes very little change, their width being approximately equal to their thickness. The mean values of length  $L$  and thickness  $d$  of the crystals in terms of porosity of the material are plotted in figure 3.

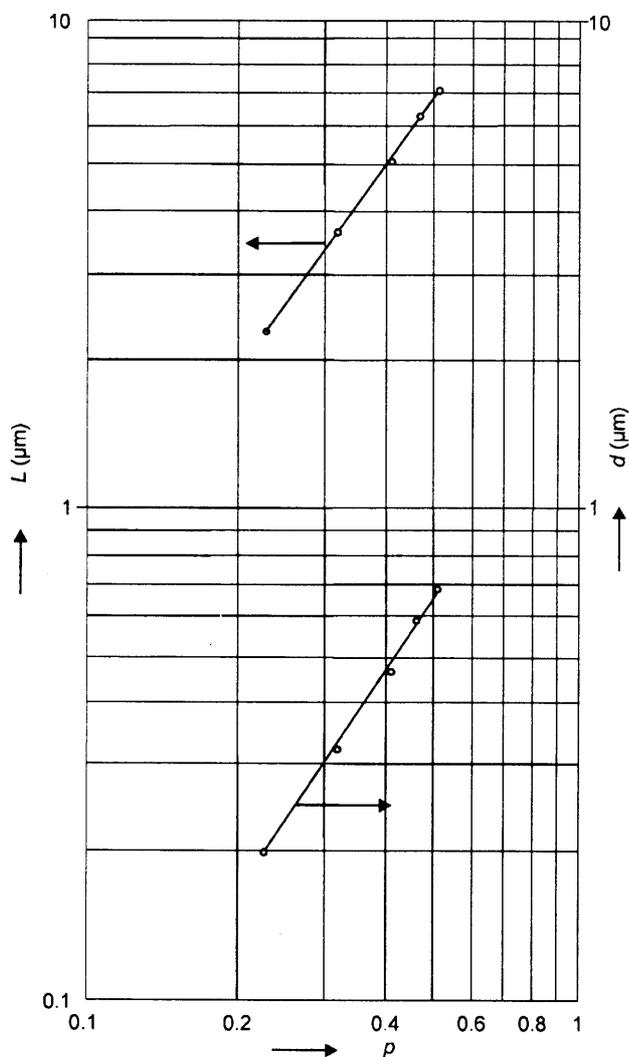


Figure 3. Mean length  $L$  and width  $d$  of gypsum crystals vs. porosity.

The surface area of the prismatic crystals in a unit volume of the material will be equal to

$$S_0 = N (4Ld + 2d^2) \cong 4NLd \quad (5)$$

where  $N$  is the number of crystals in unit volume of the material, and the quadratic term can be neglected, because  $L/d \cong 10$ .

Since

$$N = \frac{1 - p}{Ld^2} \quad (6)$$

then

$$N = \frac{4(1 - p)}{d^2} \quad (7)$$

The pore size distribution was again determined on the fractured tensile bending strength specimens using the mercury test [4,6] on the Carlo Erba porosimeter. One can imagine the pore space as a continuous network of cavities of irregular shapes interconnected by roughly circular openings. However, the mercury porosimetry is only capable of determining the size of the openings rather than the actual pore sizes. The pore size distribution plotted in figure 4 shows that the majority of the pores falls within a narrow size interval, which justifies the assumption that the mean pore size will be adequate for calculating the surface area of the pore space. The dependence of mean pore size on porosity is shown in figure 5.

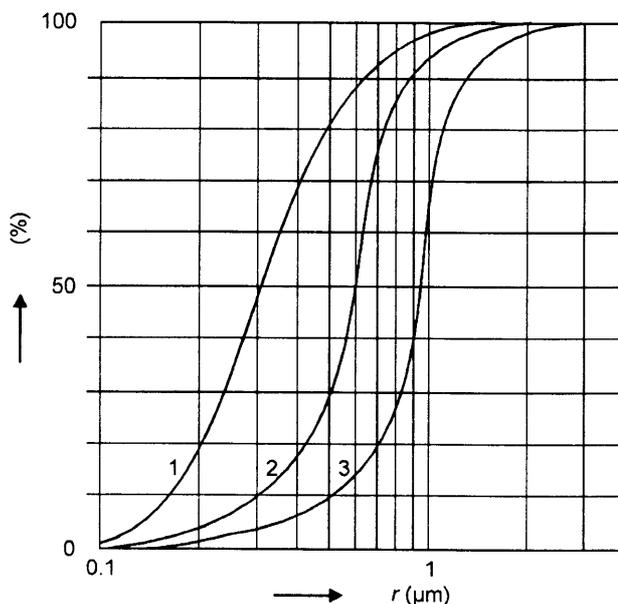


Figure 4. Pore size distribution curves. 1 -  $p = 0.23$ ; 2 -  $p = 0.41$ ; 3 -  $p = 0.51$

The surface of pore walls in a unit volume of the material, on the assumption of their cylindrical shape, will then be

$$S_1 = 2\pi r_m l N^* \quad (8)$$

where  $l$  is the pore length and  $N^*$  the number of pores in unit volume.

However, for porosity it also holds that

$$p = N^* \pi r_m^2 l \quad (9)$$

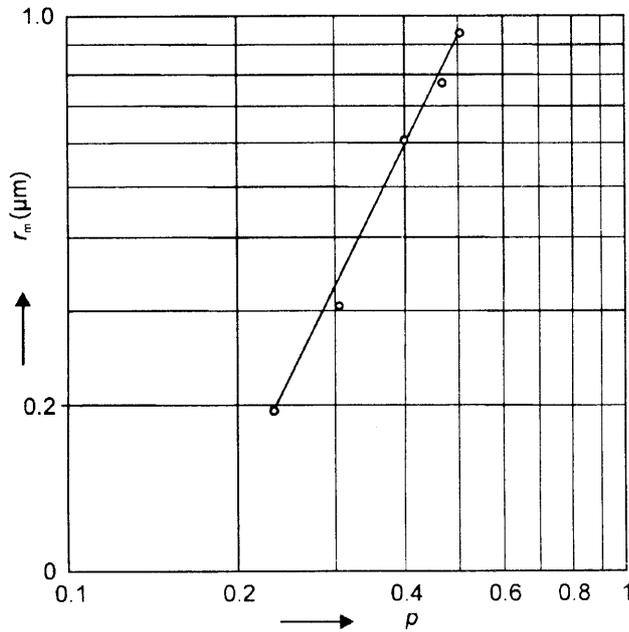


Figure 5. Mean pore size vs. porosity.

and by substitution into (8) one obtains the equation

$$S_1 = \frac{2p}{r_m} \quad (10)$$

The results of measurements and the calculated values of contact areas between the crystals in a unit volume of the material are summarized in table 1.

The diagram in figure 6 shows that the dependence of strength on the contact area  $S_0 - S_1$  is linear.

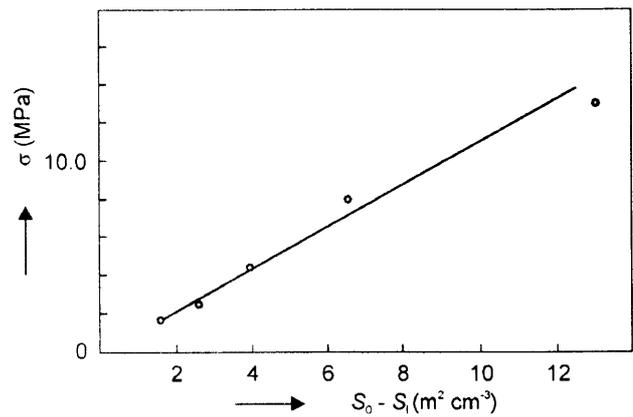


Figure 6. Strength vs. size of contact area between crystals in unit volume of the materials.

Table 1. The computed values of surface areas.

$w$	$p$	$r_m$ ( $\mu\text{m}$ )	$S_1$ ( $\text{m}^2 \text{cm}^{-3}$ )	$d$ ( $\mu\text{m}$ )	$S_0$ ( $\text{m}^2 \text{cm}^{-3}$ )	$S_0 - S_1$ ( $\text{m}^2 \text{cm}^{-3}$ )	$\sigma$ (MPa)
0.3	0.23	0.20	2.30	0.20	16.1	13.0	13.2
0.4	0.32	0.30	2.13	0.32	8.5	6.4	8.0
0.5	0.41	0.60	1.37	0.45	5.24	3.9	3.4
0.6	0.47	0.75	1.25	0.60	3.85	2.6	2.3
0.7	0.52	0.95	1.09	0.70	2.74	1.6	1.5
0.8	0.56	1.05	1.06	0.80	2.34	1.3	0.0

### DISCUSSION

A study of the fracture surfaces of cast gypsum showed the fracture to occur preferentially between the individual gypsum crystals which form a strong skeleton of the porous structure, and not across the crystals proper. Many of the crystals remain undamaged (cf. figure 2). This fact, already established by Mori and Yamana, can be taken as a proof of a not entirely homogeneous character of the solid phase in the porous material. The contact areas between the crystals represent

inhomogeneities and at the same time points of the weakest bonds, which then give way under mechanical loading. Although the accuracy of measuring the dimensions of undamaged crystals is relatively poor and a number of simplifications have been introduced in the calculations of surface areas  $S_0$  and  $S_1$ , on the basis of the diagram in figure 6 it may be assumed that the strength is directly proportional to the area of contacts in a unit volume. This fact provides a satisfactory explanation of the conclusions reached by fractographic measurements.

It would seem logical to assume that the strength of the skeletons is due to oriented overgrowths of gypsum crystals along the planes having Miller's indices (100), (101) or (201) [7], or even to penetration concretions [8]. However, the microstructure of fracture surfaces shows that the crystals in low-porosity materials are for the most part mutually attached by planes (010), and that they have an entirely random orientation. There is therefore only a very small proportion of true overgrowths. The bonds between the crystals are probably mediated by van der Waals forces in a way similar to dried clay specimens [9], where the strength also depends on the number of contacts in a unit volume and on the area over which adhesion between the crystals occurs [4].

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#### PEVNOST A MIKROSTRUKTURA SÁDROVÝCH ODLITKŮ

VLADIMÍR ŠATAVA

*Laboratoř anorganických materiálů,  
společné pracoviště Ústavu anorganické chemie AV ČR  
a Vysoké školy chemicko-technologické,  
Technická 5, 166 28 Praha 6*

Na základě stanovení velikosti a tvaru krystalků sádrovce, které tvoří pevnou fázi ve ztvrdlé suspenzi hemihydrátové sádry a stanovení velikosti pórů v tomto materiálu, bylo ukázáno, že pevnost je úměrná ploše vzájemných kontaktů mezi krystalky sádrovce. K porušení celistvosti materiálu dochází v těchto kontaktech, které jsou místy s nejslabší vazbou. Ke stejnému závěru vedly i analýzy mikrostruktury lomových ploch.