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STRENGTH DEVELOPMENT IN MAGNESIUM OXYSULFATE CEMENT

ANALYZED

by J. J. Beaudoin and V. S. Ramachandran

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STRENGTH DEVELOPMENT IN MAGNESIUM OXYSULFATE CEMENT

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ABSTRACT: Modulus of elasticity and microhardness measurements were made on magnesium oxysulfate systems (paste and compacted) having a wide range of porosity. Three sets of compacts were made; each set was made with particles having a different size range (5 to 150 μm ; 150 to 300 μm ; 300 to 600 μm). The log mechanical property versus porosity curves for paste samples were linear. The curves for compacted samples had a change in slope at 7.5 per cent porosity. At porosities less than 7.5 per cent, the data for paste and compacted samples were on the same curve. At higher porosities microhardness values for compacted samples were greater than those for paste samples; modulus of elasticity values were less. Compacted samples made with finest particles had higher values for mechanical properties at a given porosity. The mechanical behaviour of these systems was explained on the basis of the relative contribution of porosity, pore size distribution, inter-particle bonds and strength of the solid phase.

Des mesures du module d'élasticité et de la microdureté ont été prises sur de l'oxysulfate de magnésium (en pâte et comprimé) ayant une porosité très variée. Trois ensembles de comprimés ont été fabriqués; chacun a été fait de trois séries de particules de grosseur différente (5 à 100 μm ; 150 à 300 μm ; 300 à 600 μm). Les courbes de propriété mécanique logarithmique et de porosité des échantillons en pâte étaient linéaires. Les courbes des échantillons comprimés avaient un changement d'inclinaison à 7.5 pour cent de porosité. A des porosités moindres que 7.5 pour cent les données des échantillons en pâte et comprimés se situaient sur la même courbe. Les valeurs de microdureté des échantillons comprimés à des porosités plus élevées étaient plus grandes que celles des échantillons en pâte; les valeurs du module d'élasticité étaient moindres. Les échantillons comprimés faits avec les particules les plus fines avaient des propriétés mécaniques de valeurs plus grandes à une porosité donnée. Le comportement mécanique de ces systèmes a été expliqué en se fondant sur la contribution relative de la porosité, la distribution de la grosseur du pore, les liants entre les particules et la résistance de la phase solide.

Introduction

The potential of magnesium oxysulfate as a binder in building materials has been recognized since the discovery of magnesia-based cements by Sorel in 1867 (1). Unlike oxychloride cement, use of oxysulfate cement does not present a potential source for corrosion of reinforcing steel. The oxysulfate cement has good fire resistance, low thermal conductivity and is recently being considered for nuclear applications. Wood wool boards can be made using oxysulfate cement as a binder and waste products such as wood shavings or sawdust as fillers.

Depending on the temperature and conditions of formation, four types of oxysulfate complexes are known to form in the $\text{MgO-MgSO}_4\text{-H}_2\text{O}$ system. They are $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$ (or $2\text{H}_2\text{O}$), $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 5\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2\cdot 2\text{MgSO}_4\cdot 3\text{H}_2\text{O}$ (2,3). At temperatures below 35°C , $3\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 8\text{H}_2\text{O}$ appears to be the most stable phase (3). However, Hall, Read and Brandt (4) have also identified the presence of $5\text{Mg}(\text{OH})_2\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$. Widespread use of magnesium oxysulfate cement has been limited because of loss of strength on prolonged exposure to water. The oxysulfate cement system is generally considered to be weaker than the oxychloride cement system. Studies have shown that many cementitious systems that normally produce weak bodies can be made to have higher strengths by modifying certain conditions of preparation (5,6). Pressed tiles made from oxychloride cement are known to have better durability. One objective of this study was to determine if applying pressure to the oxysulfate cement system would produce a stronger body than would be obtained by normal paste hydration.

In portland cement systems, it has been shown that compacted paste and that formed under in situ hydration yield similar strengths for comparable porosities, suggesting that the compaction technique is a useful method to study this system (7, 8). It is a further objective of this study to test whether this technique is also applicable to the oxysulfate cement system.

It is also hoped that an investigation of pressed oxysulfate systems will provide a better understanding of the mechanism of bonding in pressed systems.

Experimental

Materials

The following materials were used:

1. Magnesium Oxide. The MgO powder was supplied by Basic Chemicals, Cleveland, Ohio. It had the following characteristics: N_2 surface area, $20\text{ m}^2/\text{g}$; active CaO , 1.5 per cent; ignition loss 4 per cent; fraction passing through 200 mesh, 98 per cent. The material satisfied the requirements of ASTM C-275-61.
2. Magnesium Sulphate Solutions. Aqueous solution of specific gravity 1.18 was prepared by mixing $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, supplied by Anachemia, in a dry form with distilled water. Saturated solutions (specific gravity 1.303) were also used for the preparation of samples.

Preparation of Specimens

Series I

Cement paste samples were prepared at $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}/\text{MgO}$ solution-solid ratios of 0.59, 0.72, 0.84, 0.96, 1.07 and 1.43 by weight using aqueous solution having specific gravity 1.18. Mixes having solution-solid ratios 0.59 and 0.72 were cast in cubic moulds and cured at 50 per cent relative humidity for two weeks. They were then cored and sliced into discs 3.2 cm in diameter, 1.33 mm thick; the discs were conditioned at 11 per cent relative humidity for periods of up to three months. All other mixes were cast in 3.2 cm diameter cylindrical tubes which were rotated as hydration proceeded to prevent segregation. Discs 1.3 mm thick were cut from the cylinders and subjected to the same curing procedure as the discs obtained from cores.

Series II

Cement paste samples were prepared using a saturated solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (specific gravity 1.303); solution-solid ratios and curing conditions were the same as for the mixes in Series I.

Series III

The cement paste samples from Series I were ground into powder consisting of a mixture containing equal weight fractions of material for each solution-solid ratio prepared. One set of samples were prepared with particles 300 to 600 μm ; these particles were further ground to 150 to 300 μm and a second set of samples was prepared. The finest particle size range 5 to 150 μm , obtained by grinding 150 to 300 μm particles, constituted the third set. Compacts 3.2 cm in diameter, 1.3 mm thick, were made under compaction pressures of 133 MPa to 1665 MPa to obtain a wide range of porosity.

Measurements

A helium pycnometer was used to measure the solid volume of the cement specimens of known geometry. Porosity was determined from the apparent volume and the solid volume. This avoids the problem of dissolution that arises when water is used as the displacement medium. Samples were conditioned at 11 per cent relative humidity for each measurement. Application of this technique to other inorganic cement systems is described elsewhere (9).

The modulus of elasticity was measured on discs with a diameter of 3.2 cm and a thickness of 1.3 mm. This procedure involves measuring the deflection of a specimen when it is loaded at its centre and supported at three points located on the circumference of a circle 2.5 cm in diameter. Each value given in this paper is the average of measurements on three specimens. Microhardness was measured with a Leitz microhardness testing machine with a Vickers indenter. Each microhardness value recorded herein is the average for three discs; five microhardness measurements were made on each disc. Differential thermograms were obtained using the 990 DuPont thermal analysis system. Twenty mg of the material were used for each run. The rate of heating was $20^\circ\text{C}/\text{min}$. ($T = 150 \text{ sec}/\text{in.}$) and the sensitivity was $\Delta T = 5 \text{ mcal}/\text{sec}/\text{in.}$

The microstructure of some of the samples was examined using a Cambridge Stereoscan Mark 2A. The examination was done on fractured surfaces.

Fig. 1
Compaction pressure vs porosity for
magnesium oxysulfate cement compacts

FIG. 2
Microhardness vs porosity for
magnesium oxysulfate cement

X-ray examinations were carried out with a Debye Scherrer camera. Microdensitometer traces were made from the X-ray films. Surface area was obtained by means of a Numinco-Orr surface area-pore volume analyser with N_2 as the adsorbate. Powdered samples were vacuum dried for 3 hr at $50^\circ C$ prior to measurements.

Results

The logarithm of compaction pressure is plotted against porosity on Figure 1. Two linear regions can be seen, one up to approximately 7.5 per cent porosity and the other from 7.5 to approximately 35 per cent porosity. The slope of the line up to 7.5 per cent porosity is much steeper than that for the line at higher porosity. Other systems such as gypsum, halite and cement paste, showed a linear relationship over the range of porosity studied. (7, 10).

The logarithm of microhardness and modulus of elasticity are plotted against porosity in Figures 2 and 3; these plots are linear for Series I and II paste samples and obey the general relationship $H, E = (H_0, E_0) \exp [(-b_H, b_E)p]$ where H and E are microhardness and modulus of elasticity, respectively, and p is porosity.

For microhardness data, however, the results for Series III compacts are linear only when the porosity is less than 7.5 per cent. This behaviour is similar to that for compaction pressure versus porosity (Figure 1). The log microhardness versus porosity relationship for Series III compacts follows more closely the relationship for Series I and II pastes up to 7.5 per cent porosity than for higher porosities. The data for Series III compacts fabricated from particles 5 to 150 μm lie slightly above the data for Series III compacts made with coarser size particles. For porosity greater than 7.5 per cent

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FIG. 3

Modulus of elasticity vs porosity
for magnesium oxysulfate cement

the relationships become non linear. Microhardness values for all compacts were greater than microhardness values for paste samples at all porosities greater than 7.5 per cent.

At the point where there is a change in slope, microhardness values of 160, 126 and 102 MPa were obtained for compacts made with particles 5 to 150 μm , 150 to 300 μm and 300 to 600 μm , respectively. Microhardness values are greater for compacts made with finer particles for porosity up to 30 per cent.

The log modulus of elasticity versus porosity relationships (Figure 3) for all Series III compacts lie below the relationship for paste samples. The relationship for compacts, particles 5 to 150 μm , is linear up to approximately 23 per cent porosity. The modulus data for all compacts approach the values for Series I paste samples at low porosities. The relationships for the compacts made with particles 150 to 300 μm and 300 to 600 μm have a change in slope between 6 and 7 per cent porosity and generally the modulus values are lower as particle size increases. There is a separate modulus of elasticity-porosity relationship for Series I and Series II paste samples (Figure 3); however, there is a single microhardness-porosity relationship for all Series I and Series II samples (Figure 2).

Mercury pore size distributions for paste hydrated and compacted samples are given in Figures 4(a) and 4(b). It can be seen that the compacted samples have a larger number of fine pores than do paste samples at the same porosity (15 per cent).

Mercury porosimetry results show that in compacts (porosity = 15 per cent) made with the finest particles the finer pores contribute to a larger share of the total porosity than those made with particles $>150 \mu\text{m}$.

Figure 5(a) is a micrograph of oxysulfate paste having solution/solid ratio of 0.72. The compacted or consolidated structure at this solution/solid ratio generally leads to better strength than that prepared at a ratio of 1.43 in

FIG. 4

Pore size distributions for
paste hydrated and compacted
magnesium oxysulfate samples

FIG. 5(a)
Magnesium oxysulfate paste
solution/solid = 0.72

FIG. 5(b)
Magnesium oxysulfate paste
solution/solid = 1.43

which porosity is higher and an increased amount of platy material is observed (Figure 5(b)).

Figure 5(c) illustrates the surface features of an oxysulfate sample compacted at 133 MPa. The appearance is generally amorphous and denser with some evidence of platy material and the sample is much stronger than in 5(b), although the porosities are about 15 per cent in both samples.

Figure 6 is a plot of the relationship between modulus of elasticity and microhardness for samples studied. The relationships are linear; the line for the paste samples having a steeper slope. Soroka and Sereda have observed similar results for portland cement paste and compacts (11).

FIG. 5(c)
Magnesium oxysulfate compact;
compaction pressure = 133 MPa

In Figure 7, typical thermograms for Series I and II magnesium oxysulfate samples are presented. There are two low temperature endothermal peaks at 105°C and 155°C. There is also a large endothermal peak at approximately 450°C. The two low temperature peaks have been attributed to the dehydration of $3 \text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ (3). The large peak at 475°C is due to the decomposition of $\text{Mg}(\text{OH})_2$. There is less $\text{Mg}(\text{OH})_2$ present in Series II samples. Also, the ratio of the low temperature peak heights to the peak height at

450°C is greater for Series II samples than for Series I samples. The areas of the two low temperature peaks are greater for Series II samples indicating more magnesium oxysulfate complexes have formed.

X-ray diffraction measurements were made on all Series I samples and Series II samples having solution/solid = 0.72 and 1.07. The results indicate the presence of $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$, large amounts of $\text{Mg}(\text{OH})_2$ and some anhydrous MgO in Series I samples. In addition to the above presence of $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ was detected in Series II samples. However, the presence of $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ in both Series I and II was more readily apparent from DTA traces; it is suggested that for identification of oxysulfate complexes DTA is a more sensitive tool than XRD. DTA results clearly show that the amount of $\text{Mg}(\text{OH})_2$ is less in Series II samples compared with Series I samples; also, the amount of oxysulfate complex formed is greater than that formed for Series I samples. In Series II samples, more MgO has preferentially reacted to form the oxysulfate complex leaving less $\text{Mg}(\text{OH})_2$.

Surface area and microhardness measurements for paste samples are given in Table I. It is apparent that there is no direct relationship between surface area and strength development for the various oxysulfate preparations, e.g., samples at solution/solid = 0.84 have higher surface area but lower microhardness than samples with solution/solid = 0.59.

FIG. 6
Microhardness vs modulus of elasticity for magnesium oxysulfate cement

FIG. 7
Differential thermogram for magnesium oxysulfate cement

TABLE I
Surface area and microhardness data for
magnesium oxysulfate paste samples

Soln/Solid	Surface Area (m ² /g)	Microhardness (MPa)
0.59	11.5	303
0.72	15.6	175
0.84	24.8	101
0.96	23.8	62
1.07	20.4	59
1.43	14.6	22

Discussion

The change in slope of the log compaction pressure versus porosity curve (Figure 1) may possibly be explained as follows: The particles themselves are porous, although it was observed that pore sizes larger than 1 μm were absent in the finest particle size range. Particles in the 300 to 600 μm size range had the following pore size distribution: 58 to 10 μm (4 per cent), 10 to 1 μm (2.5 per cent), 1 to .1 μm (3.1 per cent) and .1 to .01 μm (9.4 per cent); particles 150 to 300 μm : 35 to 10 μm (1 per cent), 10 to 1 μm (3 per cent), 1 to .1 μm (3.4 per cent) and .1 to .01 μm (9.8 per cent); particles 5 to 150 μm : 1 to .1 μm (3.4 per cent) and .1 to .01 μm (4.4 per cent). In the high porosity region, compaction probably occurs mostly by sliding of particles past one another with some deformation and fracture. In the region below 7.5 per cent porosity, most of the compaction may involve a decrease of small pores which can be accomplished only by deformation and fracture. It is noteworthy that the region below 7.5 per cent covers a porosity range of only 3.5 per cent.

Figure 4(b) shows that by increasing the compacting pressure from 102 MPa to 680 MPa there is a decrease in the over-all porosity due to elimination of some larger pores and a 60 per cent decrease in the percentage of fine pores. Compaction at low porosities occurs mostly by fracture of particles that have already been fractured; these crushed particles are probably stronger and are confined by the interference with their neighbours. Also at low porosities, it is possible that bond strength may increase partly as the result of chemical bond formation and possibly also due to strain hardening. Smaller particles form stronger bodies, not only because of the foregoing reasons but because of increased bond area.

Generally, strength of cementitious systems, for a particular porosity, increases as the average pore radius decreases (12). This is consistent with the results of this study for compacted and paste hydrated samples.

The explanation as to why the modulus of elasticity values for compacts are lower than the values obtained for paste samples, while the converse is true for microhardness, is not clear. However, the results may be tentatively explained if it is assumed that for compacted samples the interparticle bonds are weaker than they are for paste hydrated samples. The interparticle bonds may play a dominant role in determining the modulus of elasticity. One would expect lower values of modulus of elasticity for compacted samples than for paste samples if the bonds are not all remade on compaction of the powder. On

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the other hand, if microhardness is dependent to a large extent on the strength of the solid component, it would be possible for paste samples to have lower values of microhardness than compacted samples. Pastes are weaker than compacts at porosities greater than 7.5 per cent; in paste hydrated samples precipitation and crystallization leads to formation of larger crystals with less bond area (see Figure 5(b)). For pastes at low porosities, there is more intimate surface-to-surface contact between particles of the hydrated product because there is less space for migration or formation of discrete crystals (Figure 5(a)).

In some cementitious systems, the increase in compressive strength has been explained in terms of the development of high surface area (13). Recent evidence has indicated that there is no correlation between surface area and strength development in such systems (14, 15).

Surface area measurements provided little insight into the observed mechanical behaviour of magnesium oxysulfate cement system as there was no correlation between surface area and strength development.

Oxysulfate cement has been generally considered to be weaker than oxychloride cement, but this comparison has not been done on the basis of equal porosity. A comparison of the present results with observations on oxychloride cement (8) indicates that for the same porosity, oxychloride samples are stronger than oxysulfate samples.

Conclusions

The oxysulfate system behaves differently than the portland cement system when these systems are formed by compaction, i.e., the oxysulfate paste, unlike the portland cement system, is weaker than the compacted system at higher porosities. It is apparent that the use of compacts as structural models for the oxysulfate system is limited to low porosities, i.e., less than 7.5 per cent. It is also apparent that compaction processes at higher porosities alter the morphology, pore size distribution and the extent of bonding between particles resulting in differences in strength of paste and compacted systems. From the practical point of view, however, it appears that pressing the oxysulfate system can produce specimens having good strength.

There appears to be no direct relationship between surface area and strength development for the various oxysulfate preparations studied. The mechanical behaviour of magnesium oxysulfate cement can be explained on the basis of the relative contribution of porosity, pore size distribution, interparticle bonds and strength of the solid phase.

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