

THE SULPHOALUMINATES OF CALCIUM

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ABSTRACT

Two calcium sulphoaluminates have been prepared and their compositions and optical characteristics determined. One of these, having the composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$, is relatively stable in aqueous solutions but is decomposed by solutions of magnesium salts and of carbonates. The other, having the composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$, is relatively unstable except in high concentration of hydroxyl ion. It is readily converted to the high sulphate form in aqueous solutions but is decomposed by magnesium salts and carbonates. In sulphate solutions the high sulphate form may be produced, but in the presence of a slight excess of magnesium salts or carbonates neither of the sulphoaluminates can continue to exist. In these cases the less soluble magnesium hydroxide and calcium carbonate, respectively, are formed.

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I. INTRODUCTION

Among the products formed by the action of sulphate waters on Portland cement there has been observed, under some conditions, a calcium sulphoaluminate. This has been ascribed by some investigators to be responsible for certain expansion effects observed at times in concrete which is exposed to sea water and to alkali soil waters. The exact nature of this compound and its conditions of formation and stability have not been adequately treated, however.

The present investigation is concerned with the formation, properties, and conditions of equilibrium of such compounds as may be obtained by the interaction of CaO , Al_2O_3 , and SO_3 in aqueous solutions with especial reference to the conditions under which these compounds may be formed in concrete. In addition to the above, attempts were made to obtain a compound of lime, alumina, silica, and sulphate.

II. REVIEW OF THE LITERATURE

Candlot¹ appears to have been the first to establish the formation of a definite compound by the interaction of an aqueous solution of calcium aluminate with calcium sulphate. He mixed saturated solutions of a calcium aluminate and calcium sulphate and observed the formation of small crystalline spherulites 2 to 3 mm. in diameter. The addition of a saturated solution of calcium hydroxide caused a more abundant precipitation of the crystals, as they seem to be less soluble in calcium hydroxide solutions. From analysis of a sample of these crystals Candlot ascribed to them the composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 59\text{H}_2\text{O}$. He described the crystals as being only slightly soluble in water and insoluble in alcohol and in lime-water containing more than 0.2 g. CaO per liter.

Because of the widespread interest in the action of sulphate waters on concrete the identification of a calcium sulphoaluminate immediately attracted the attention of cement chemists. Michaelis² prepared the compound by the reaction of a solution of aluminum sulphate with limewater. The crystals resembled bacilli in size and shape and so were called by him "cement bacilli." Michaelis described the crystals as broad, needle-shaped prisms belonging to the tetragonal system, some with and some without truncated ends.

From analysis of a sample dried to constant weight over sulphuric acid he derived the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$. Although this formula is not identical to that given by Candlot to the sulphoaluminate, yet from the descriptions given it seems probable that the two preparations were indeed the same compound. The formula of Michaelis for the anhydrous material, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$, has been confirmed by Deval,³ Poirson,⁴ Klein and Phillips,⁵ Kühl and Albert,⁶ Lafuma,⁷ and McIntire and Shaw.⁸ There is, however, a difference of opinion on the number of combined molecules of water, due probably to different methods of procedure in the preparation and drying of the samples.

Some authors have believed that they obtained still other calcium sulphoaluminates. Klinkenberg⁹ claimed to have obtained three definite compounds by adding to a sintered mixture of "dicalcium aluminate" 1, 2, and 3 equivalents of gypsum and allowing the

¹ Bull. soc. encour. ind. nat., p. 682; 1890.

² Tonind. Ztg., 16, p. 105; 1892.

³ Bull. soc. encour. ind. nat. (5th ser.), Pt. I, 5, 49; 1900.

⁴ Zentr. hydraul. Zement, 1, p. 151; 1910 C. A., 5, p. 1328; 1911.

⁵ B. S. Tech. Paper, No. 43; 1914.

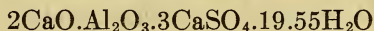
⁶ Zement, 12, p. 279; 1923.

⁷ Ciment, 30, p. 175; 1925.

⁸ Soil Science, 19, p. 125; 1925.

⁹ Dinglers polytech. J., 249, p. 89, 1894; J. Soc. Chem. Ind., 14, p. 365; 1895.

reactions to proceed for six months. He has assigned to them the formulas:



However, there is no evidence given that the products were definite chemical compounds and not mixtures.

On determining the quantity of water fixed by mixtures of "dicalcium aluminate" and calcium sulphate in variable proportions, Schott¹⁰ thought he demonstrated the existence of the compound



Rebuffat¹¹ criticized the work and conclusions of Schott and claimed to have produced two calcium sulphoaluminates. To one of these he gave the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$. This, he said, is formed when a solution of calcium sulphate is mixed with an aqueous solution of any calcium aluminate, or when either tricalcium aluminate or "dicalcium aluminate" in the solid form is shaken with a solution of calcium sulphate. The second calcium sulphoaluminate, to which he gave the formula $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 10\text{H}_2\text{O}$, was said to be formed when the solid monocalcium aluminate was shaken with calcium sulphate solution.

In a later paper, from a study of his own work and that of Candlot, Deval, and others Rebuffat¹² concludes that the formula for the first calcium sulphoaluminate should be $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$. This, he says, is formed from any calcium aluminate and calcium sulphate in the presence of calcium hydroxide.

Klein and Phillips,¹³ however, found that monocalcium aluminate, 5-3 calcium aluminate, and tricalcium aluminate all react with calcium sulphate to give the same calcium sulphoaluminate. They give the formula for the compound as $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, the value of x varying with the method of drying. The crystals are described as long, slender needles showing very low interference colors and a biaxial, positive interference figure, with a large optic axial angle. Elongation was negative and extinction parallel. Refractive indices were less than 1.48. Twinning was not noted, but occasional irregular intergrowths were observed. The ends of the needles were said to be flat and perpendicular to the long axis of the needles.

¹⁰ Tonind. Ztg., 18, p. 819; 1894.

¹¹ Rend. accad. sci. (Napoli), 35, No. 11, p. 280; 1896.

¹² Gazz. chim. ital., 32, No. 2, p. 158; 1902.

¹³ See footnote 5.

Shelton¹⁴ has reported that all the calcium aluminates react with magnesium sulphate when present in dilute solution (less than 0.1 M) or with sodium sulphate in all concentrations to form the same calcium sulphoaluminate. In higher concentrations of magnesium sulphate than 0.1 M the only crystalline product was gypsum. The calcium sulphoaluminate is said by Shelton to occur usually as fine needles but sometimes as coarse prisms, frequently with short needles growing parallel to each other from opposite ends of a prism. Optical properties were determined on the coarse prisms, after separating them from the solution, washing with water and drying in a desiccator until just dry, usually less than an hour. The optical character was reported to be positive and optic angle large, but the interference figure was indistinct. Elongation was negative and refractive indices were $\gamma = 1.463 \pm 0.003$, $\alpha = 1.461 \pm 0.003$.

Deval¹⁵ attempted to show, by a rather indirect method, that the amount of calcium sulphate fixed by a cement may greatly exceed that required to convert all of the alumina to calcium sulphoaluminate. Lafuma¹⁶ has reported similar results and has suggested the formation of a calcium sulphosilicoaluminate.

III. EXPERIMENTAL PROCEDURE

In the course of experimentation it was observed that there were two sulphoaluminates of calcium characterized by different chemical composition, optical properties, and crystal form. To avoid confusion, the two are treated separately below. In addition to these, the formation of a more complex compound, reported by Lafuma¹⁶ as a calcium sulphosilicoaluminate, has been investigated.

1. THE HIGH SULPHATE CALCIUM SULPHOALUMINATE

Several methods were employed in the preparation of this calcium sulphoaluminate. By far the most important of these was by the interaction of calcium sulphate and calcium aluminate. This method was essentially the same as had been recommended by Candlot¹⁷ and later by Klein and Phillips.¹⁸ A calcium aluminate solution was prepared by adding 20 g of the 5-3 calcium aluminate to 1 liter of water and shaking for one hour. The solution was filtered off and 200 ml of saturated calcium sulphate solution added. Under these conditions the crystals formed very slowly, but the addition of 200 ml of a saturated solution of calcium hydroxide greatly increased the rate of crystallization. After one week the crystalline phase consisted of very fine needles.

¹⁴ *Ind. Eng. Chem.*, **17**, p. 1267; 1925.

¹⁵ *Bull. soc. encour. ind. nat.*, **101**, Pt. II, pp. 96 and 784; 1901; *J. Soc. Chem. Ind.*, **21**, p. 971; 1902.

¹⁶ See footnote 7, p. 716.

¹⁷ See footnote 1, p. 716.

¹⁸ See footnote 5, p. 716.

The chemical analyses of a number of these preparations showed them to be somewhat variable in composition. In some cases the ratio of CaO, Al₂O₃, and SO₃ was found to be represented by the composition 3CaO.Al₂O₃.2.5CaSO₄.aq, and in other cases the CaSO₄ content was somewhat higher. In no one of these preparations was there sufficient CaSO₄ present to give the composition 3CaO.-Al₂O₃.3CaSO₄.aq.

Preparations were then made by using a larger quantity of calcium hydroxide and calcium sulphate. Five hundred and 750 ml, respectively, of the calcium aluminate solution were added to 1,500 ml of a solution saturated with calcium hydroxide and calcium sulphate. The preparations were allowed a week to approach equilibrium. The precipitates were then filtered off, washed with alcohol and ether to remove the excess water and dried to constant weight in air. The analysis of these crystals is given in Table 1.

TABLE 1.—Analysis of high sulphate calcium sulphoaluminate

	1, 500 ml Ca(OH) ₂ +CaSO ₄ solution			
	No. 1, 500 ml calcium aluminate solution		No. 2, 750 ml calcium aluminate solution	
	Per cent composition	Molecular composition	Per cent composition	Molecular composition
Al ₂ O ₃	8.24	1.00	8.21	1.00
CaO.....	27.20	6.01	27.15	6.02
SO ₃	19.30	2.99	19.20	2.98
H ₂ O by difference.....	45.26	31.10	45.44	31.30

On calculating these analyses to molecular composition the compound is found to have a composition which may be represented by the formula:



The composition of the crystalline phases obtained by the above methods of preparation is thus seen to vary and appears to be determined by the concentration of calcium sulphate present in the mother liquor. In the presence of low concentrations of calcium sulphate the crystalline phase is found to have a composition which approaches the formula 3CaO.Al₂O₃.2.5CaSO₄.aq, but in the presence of higher concentrations of calcium sulphate as given in Table 1 the composition becomes



Two possible explanations may be advanced for this variation in composition: (1) That the actual composition of the crystalline phase is 3CaO.Al₂O₃.2.5CaSO₄.aq, and that the crystals adsorb calcium

sulphate from the solution; (2) that the composition of the crystalline phase is $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot\text{aq}$, but that in the presence of low concentrations of calcium sulphate this compound forms an equilibrium mixture with $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{aq}$.

If the adsorption theory were correct, the amount of calcium sulphate adsorbed would vary with the calcium sulphate concentration of the solution and would reach a maximum value only when the solution was saturated with calcium sulphate. The results reported in Table 1 indicate a uniformity of composition in the two preparations, even though the calcium sulphate concentration of the mother liquor in preparation No. 1 was considerably greater than in preparation No. 2. These results support the belief that the lower values for the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio obtained in some of the preparations is due to an equilibrium between the compounds $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot\text{aq}$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{aq}$. On increasing the concentration of calcium sulphate in the mother liquor the amount of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{aq}$ in solution decreases and eventually disappears.

The size of the crystals appears to vary through a wide range, dependent on the concentration of the reacting solutions. In the presence of high concentrations of calcium sulphate and calcium hydroxide, as in the samples prepared for the chemical analysis, the crystals are submicroscopic. In other samples prepared by the interaction of solutions of the calcium aluminates with less concentrated solutions of calcium sulphate and calcium hydroxide the needle like crystals were present as shown in Figure 1. These were about 0.002 to 0.003 mm wide and 0.15 to 0.25 mm long. In some solutions which had been allowed to stand in the laboratory several months a few of the crystals attained a length of 1 cm or more.

In order to obtain crystals of larger cross section for optical examination, two modifications of the above procedure were employed. In one of these the crystals were allowed to grow by slow diffusion in a gel.¹⁹ The calcium aluminate solution was incorporated into a 5 per cent agar gel and the gel then placed in a solution saturated with calcium sulphate and calcium hydroxide. After about two months the crystals of calcium sulphoaluminate had grown to much greater dimensions than were ordinarily obtained by the other methods. Some of these were about 0.06 mm long and 0.03 to 0.04 mm on cross section.

By another procedure 90 per cent $3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ and 10 per cent calcium sulphate were mixed and a few grains placed on a glass slide with a drop of water. A cover glass was sealed on to prevent evaporation. Large crystals appeared in about a week, one of which is shown in Figure 2. The photomicrograph with higher magnification shows beautifully the hexagonal cross section of the crystal.

¹⁹ Performed by L. T. Brownmiller.



FIGURE 1.—*Calcium sulphoaluminate needles. High sulphate form. Analyzer out. $\times 200$*

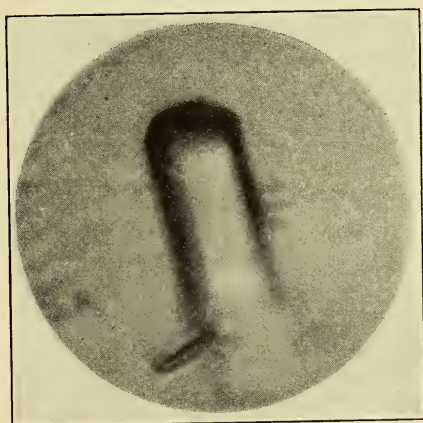


FIGURE 2.—*Crystal of calcium sulphoaluminate (high sulphate form) showing hexagonal prismatic habit. No nicols. $\times 1,290$*

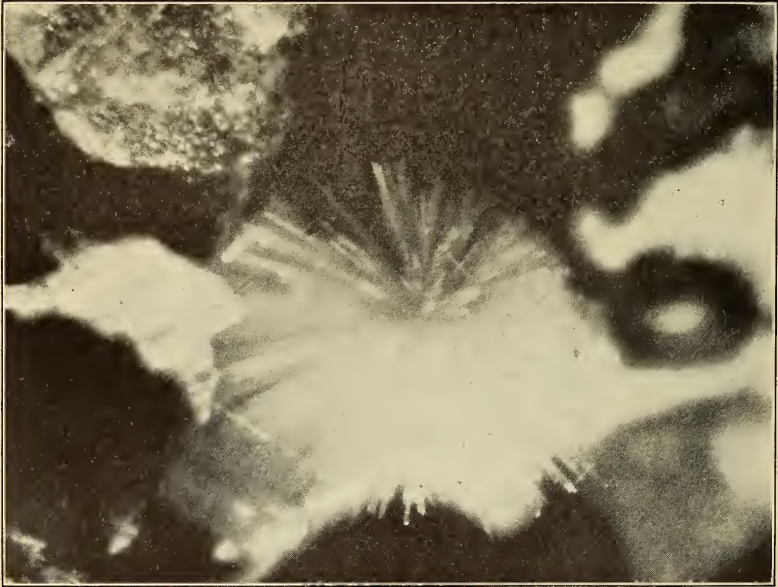


FIGURE 3.—*Calcium sulphoaluminate spherulite from an old briquette. High sulphate form. Reflected light.*
× 75

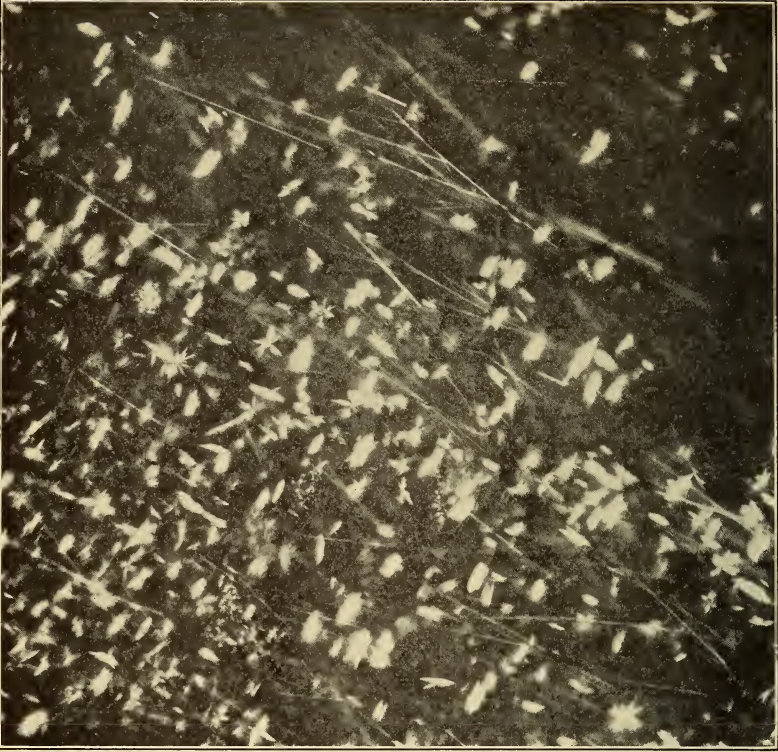


FIGURE 4.—*A mixture of calcium sulphoaluminates. Crossed nicols.*
× 150

The needles are the high sulphate form. The star shaped aggregates are the low sulphate form.

These larger crystals were used for the optical determinations. The crystals show parallel extinction and negative elongation and appear isotropic when seen on end. The refractive indices for sodium light obtained by the immersion method were $\omega_D = 1.464 \pm 0.002$ $\epsilon_D = 1.458 \pm 0.002$, birefracton 0.006. The interference figure is uniaxial negative.

A spherulite of the high sulphate form of calcium sulphoaluminate from an old mortar briquette is shown in Figure 3. The crystals sometimes occur in this spherulitic structure.

Upon dehydration of the sulphoaluminate crystals at 110°C . the water content dropped to an equivalent of $7\text{H}_2\text{O}$ and remained constant. This loss of water was accompanied by a longitudinal cracking or splitting of the crystals and a change in optical properties. The mean refractive index rose to about 1.50, and the character of elongation changed from negative to positive. On placing the dehydrated crystals in an atmosphere saturated with water vapor the character of elongation again changed and the mean refractive index dropped. The final value is close to 1.45, somewhat higher than the index of the original crystals.

The specific gravity of the compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ determined in absolute alcohol was found to be 1.48 at 20°C .

Three other methods were used for the preparation of the calcium sulphoaluminate crystals. The interaction of aluminum sulphate with saturated limewater (3 g added to 1 liter) gave first a flocculent precipitate characteristic of aluminum hydroxide. This gradually changed in appearance and assumed the more crystalline character of the calcium sulphoaluminate. After three months a microscopic examination showed it to consist almost entirely of the latter.

Another sample was prepared by the action of a solution containing calcium hydroxide and calcium sulphate on precipitated aluminum hydroxide. In this case the action was very slow, but after a month the residue was shown microscopically to contain a large amount of calcium sulphoaluminate.

Still another method consisted in the addition of sodium sulphate solutions (20 ml of 0.5, 1.0, 2.5, and 5.0 per cent) to 1 g each of the four anhydrous calcium aluminates (3:5, 1:1, 5:3, 3:1). The aluminates each reacted with these solutions to produce a large increase in the volume of the solid phase. In the 2.5 and 5.0 per cent solutions this increase in volume was sufficient in three hours to produce a gel. In each case the material when examined under the microscope was found to contain large quantities of calcium sulphoaluminate, with the exception of the tricalcium aluminate in the 0.5 and 1.0 per cent solutions. Evidence obtained by determining the loss of SO_3 from a solution containing 5 g of tricalcium aluminate in 200 ml of 1 per cent sodium sulphate solution (a decrease from 0.5714 g per 100 ml in the

solution after six days of reaction) suggests that the formation of calcium sulphoaluminate from the tricalcium aluminate probably has occurred as in the other solutions but that the crystals are too small for positive identification.

A naturally occurring calcium sulphoaluminate; Ettringite, has been described by Dana²⁰ and Larsen.²¹

This is given the formula $6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 33\text{H}_2\text{O}$, but the actual analyses could equally well be represented by a somewhat lower SO_3 content. The system is given as hexagonal, the optical character as uniaxial negative, and the average refractive index as 1.49 with a birefracton ± 0.01 . An examination in this laboratory of a sample of this mineral, obtained through the courtesy of the United States National Museum, gave $\omega_D = 1.489 \pm 0.003$ and $\epsilon_D = 1.475 \pm 0.003$ for white light. In other respects the sample was similar to that described by Dana and Larsen. Since the analyses of the Ettringite and of the artificial sulphoaluminate correspond so closely, and since the indices of the artificial material after heating and rehydration approach those obtained for the Ettringite, it seems probable that the two are essentially the same material.

Moses²² describes a sample of Ettringite from Tombstone, Ariz., which he believes is slightly different from the one described by Lehman²³ and Dana. He gives the formula $10\text{CaO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SO}_3\cdot 54\text{H}_2\text{O}$ for this material and $10\text{CaO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SO}_3\cdot 22\text{H}_2\text{O}$ for the dried material. He describes the crystals but gives no optical measurements.

2. THE LOW SULPHATE CALCIUM SULPHOALUMINATE

In the preparation of the high sulphate form of calcium sulphoaluminate it had been observed that when the calcium hydroxide content of the aluminate solution was high the addition of calcium sulphate solution caused the almost immediate formation of a very fine-grained precipitate. On allowing this to stand in the mother liquor for a week or so the appearance of the precipitate changed completely. It then resembled the matted masses of long needles described above. This change in macroscopic character was so striking that further investigation of the fine-grained material was undertaken.

A sample of this material was prepared as follows: Two hundred milliliters of saturated limewater were added to 500 ml of a calcium aluminate solution prepared from the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. The precipitate which formed was filtered off and 200 ml of saturated calcium sulphate solution added to the clear filtrate. After two hours the precipitate which formed was separated by filtration. This residue did

²⁰ System of Mineralogy, New York, 6th ed., p. 976; 1911.

²¹ U. S. Geol. Survey, Bull., p. 679; 1921.

²² Am. J. Sci., 45, p. 489; 1893.

²³ Jahrb. Min., p. 273; 1847; C. F. Dana, loc. cit. No. 15,



FIGURE 5.—*Low sulphate calcium sulphoaluminate. Crossed nicols.*
× 200



FIGURE 6.—*Low sulphate calcium sulfoaluminate showing the platy form. Analyzer out. $\times 200$*

Note the star-shaped aggregates on several of the plates

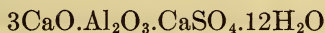
not form a mat on the filter paper but was loose, light, and granular in character.

A chemical analysis was made of a portion of this material which had been washed with alcohol and ether and dried to constant weight in air. The results are given in Table 2.²⁴

TABLE 2.—Analysis of low sulphate calcium sulphoaluminate

	Per cent composition	Molecular composition
Al ₂ O ₃	16.06	1.00
CaO.....	35.30	4.01
SO ₃	12.90	1.02
H ₂ O.....	35.80	12.20

This gives a molecular composition which may be represented by the formula



It is thus seen that there is an essential difference in composition between the two forms, the ratio of tricalcium aluminate to calcium sulphate in the first preparation being 1 to 3 and in this preparation being 1 to 1. Hence, the former is referred to as the high sulphate form; the latter as the low sulphate form.

Microscopic examination of this sulphoaluminate showed it to be very different from the long needles of the compound first described. The difference is brought out very clearly in Figure 4, which shows a photomicrograph with crossed nicols of a mixture of the two sulphoaluminates. Figure 5 shows the most common appearance of the low sulphate compound with crossed nicols, and Figure 6 is a photomicrograph with ordinary light of a sample showing the platy habit. The star-shaped or spherulitic birefracting masses seen in Figure 5 are groups of these plates joined together at an edge and standing more or less perpendicularly to the plane of the paper. They are often joined to a basal plate and then present the appearance seen in Figure 6. As may be seen in Figure 4, the crystals appear much smaller than the needles of the high sulphate calcium sulphoaluminate. In the usual preparations of the low sulphate calcium sulphoaluminate the length of the needles (edges of the plates) is seldom over 0.015 mm. and the thickness is about 0.002 mm. Occasionally a sample will consist of plates much larger than this, the largest measured having a diagonal length of nearly 0.14 mm.

The crystals of the low sulphate calcium sulphoaluminate belong to the hexagonal system and are uniaxial negative in character. Refractive indices are $\omega_D = 1.504 \pm 0.002$, $\epsilon_D = 1.488 \pm 0.002$. The

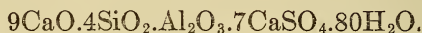
²⁴ Analysis performed by the chemistry division of the Bureau of Standards.

radiating needles (or edges of plates) seen in the star-shaped aggregates show parallel extinction and positive elongation. This sulphoaluminate is therefore easily distinguished by its optical and crystallographic properties from that first described. Its refractive indices are higher, its crystal habit platy instead of acicular, and the character of elongation is positive instead of negative. The specific gravity of this compound determined in absolute alcohol was found to be 1.95 at 20° C.

On dehydrating the low sulphate calcium sulphoaluminate to constant weight at 110° C. the water content was reduced to an equivalent of 6H₂O. The crystals were so altered in size and form that satisfactory optical and crystallographic measurements were not obtainable. The refractive indices were somewhat variable and may indicate a decomposition as well as dehydration. The values obtained were $\alpha = 1.510-1.527$, $\gamma = 1.529-1.535$.

3. CALCIUM SULPHOSILICOALUMINATE

Lafuma²⁵ has given the results of some experiments which he believes indicate the formation of a calcium sulphosilicoaluminate. He prepared a special cement of the composition 17CaO + Al₂O₃ + 5SiO₂, burned at 1,500° C., and mixed this with definite quantities of sulphuric acid, aluminum sulphate, water, and after a week, lime. This was left for five months and then the excess of calcium sulphate and lime extracted. The ratio of alumina to calcium sulphate in the residue was calculated to be 1 to 6.9, indicating to Lafuma an amount of calcium sulphate greatly in excess of that which could be combined with the alumina in the formation of a calcium sulphoaluminate, and suggesting to him the existence of a calcium sulphosilicoaluminate to which he assigned the formula



A repetition of this experiment was performed in this laboratory because it is very important to establish definitely the products of hydrolysis and interaction with salts in the setting of cement or the disintegration of the set cement.

The final residue obtained was found to contain alumina and calcium sulphate in the ratio of about 1 to 3.5, which does not approach the ratio of 1 to 6.9 reported by Lafuma.

A microscopic examination of this residue showed that it contained several phases and was not a homogeneous material. Not all of the materials present were susceptible of microscopic identification, but there were found a large number of very small needles of the high

²⁵ See footnote 7, p. 716.

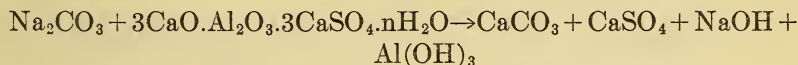
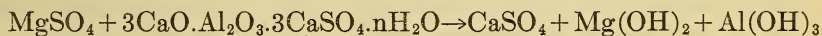
sulphate form of calcium sulphoaluminate. The presence of this calcium sulphoaluminate, and the ratio of alumina to calcium sulphate in these residues, seem to make very improbable the existence of the calcium sulphosilicoaluminate in these preparations.

IV. CONDITIONS OF STABILITY IN SALT SOLUTIONS

A study of the stability of the calcium sulphoaluminates in solutions of the various salts which are present in sea water and "alkali" soil waters is of especial importance as a means for determining the rôle played by these calcium sulphoaluminates when formed in concrete exposed to such waters. In studying these relations 0.5 g of each of the calcium sulphoaluminates was placed separately in 100 ml portions of the salt solutions to be studied and allowed to stand for a period of time varying from 10 to 60 days. The residues were then filtered off and examined under the microscope. The filtrates in some instances were analyzed for lime, alumina, and SO_3 .

The results obtained with the high sulphate form of calcium sulphoaluminate are given in Table 3. The compound is found to be only slightly hydrolyzed in distilled water and is probably more stable in solutions of calcium sulphate and calcium hydroxide than in pure water. With sodium chloride and sodium sulphate there is a greater hydrolysis than in water.

With solutions of sodium carbonate and of magnesium sulphate the results were different. In these solutions the crystals of calcium sulphoaluminate were completely decomposed. In the magnesium sulphate solution, the residue consisted of crystals of gypsum and an amorphous material. The residue from the sodium carbonate solutions contained calcium carbonate as the only crystalline phase. The probable reactions may be represented in an incompleated form, as follows:



These are left unbalanced as an indication that they are not complete nor stoichiometric. Various other products will doubtless be present, as aluminates of calcium, magnesium, or sodium.

TABLE 3.—High sulphate calcium sulphoaluminate placed in aqueous solutions for three weeks; residues then filtered off and examined under the microscope and solutions analyzed in some cases for CaO, Al₂O₃, and SO₃

Solution used	In 100 ml of solution			Microscopic report	Remarks
	CaO	Al ₂ O ₃	SO ₃		
H ₂ O.....	<i>g</i>	<i>g</i>	<i>g</i>	Contained the high sulphate needle-like crystals of calcium sulphoaluminate, unchanged.	Hydrolysis slight; condition of greatest stability.
0.17 per cent Ca(OH) ₂ (saturated).	0.0045	0.0012	0.0050		
3 per cent CaCl ₂		None.	.0010		
0.18 per cent CaSO ₄ (saturated).		None.	(¹)		
3 per cent NaOH.....		None.			
3 per cent NaCl.....	.0258	.0085	.0169	} do.....	Hydrolysis pronounced.
30 per cent NaCl.....	.0268	.0097	.0205		
3 per cent Na ₂ SO ₄ ·10H ₂ O.....	.0220	.0081			
0.6 per cent MgSO ₄				} No calcium sulphoaluminate present; gypsum crystals and amorphous material present.	} Calcium sulphoaluminate does not exist in excess of these reagents.
1.2 per cent MgSO ₄					
3 per cent Na ₂ CO ₃				Calcium carbonate only crystalline phase present.	

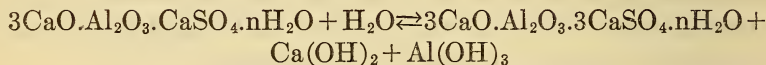
¹ Small amount.

Blanks indicate "not determined."

The results obtained on placing the low sulphate form of calcium sulphoaluminate in the various solutions are given in Table 4. In water and in solutions of calcium sulphate, sodium sulphate, calcium chloride, and sodium chloride there is a tendency for this compound to change to the high sulphate form of calcium sulphoaluminate. This conversion proceeds less rapidly in a saturated solution of calcium hydroxide than in water and does not take place at all in a 3 per cent solution of sodium hydroxide. It would seem, therefore, that a high hydroxyl-ion concentration is one of the factors determining the stability of the low sulphate form of calcium sulphoaluminate. These results are to be expected on the basis of a consideration of the hydrolytic reactions involved. Thus, we may write the probable reactions, in aqueous solution, in the incompleated form



and



An application of the mass law to these hypothetical reactions would indicate that the direction of the reaction would be thrown to the right by the addition of sulphates or calcium salts and to the left by the addition of hydroxyl-ion or aluminum salts.

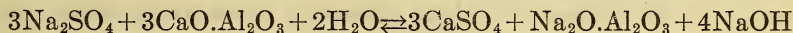
TABLE 4.—Low sulphate calcium sulphoaluminate placed in aqueous solutions for varying periods; residue filtered off and examined under the microscope

Solution used	Time of contact	Microscopic and chemical report	Remarks
H ₂ O.....	Days 10	Consisted largely of the high sulphate calcium sulphoaluminate with some of original material; solution contained CaO, Al ₂ O ₃ , and trace of SO ₃ .	Changes rapidly to high sulphate form.
0.18 per cent CaSO ₄ (Sat.)	10	Consisted entirely of long needles of high sulphate form.	
10 per cent Na ₂ SO ₄ . 10H ₂ O.	10	Consisted largely of high sulphate form, some amorphous material; solution contained CaO, SO ₃ , and trace of Al ₂ O ₃ .	
3 per cent CaCl ₂	10	Contained both high and low sulphate forms; no calcium chloraluminate present; solution free of SO ₃ and Al ₂ O ₃ .	
10 per cent NaCl.....	10	Mostly the high sulphate form present; solution contained CaO, Al ₂ O ₃ , and SO ₃ .	Changes slowly to high sulphate form.
0.17 per cent Ca(OH) ₂ (Sat.)	10	Almost entirely the low sulphate form with some needles of high sulphate sulphoaluminate.	
	40	About equal amounts of the two forms present.	
3 per cent NaOH.....	30	Only low sulphate form present.....	Condition of stability for low sulphate form.
	60		
0.6 per cent MgSO ₄	30	Some gypsum, amorphous material.....	Decomposed by these solutions.
1.2 per cent MgSO ₄	30	Gypsum and amorphous material.....	
3 per cent Na ₂ CO ₃	30	Calcium carbonate only crystal phase present.	

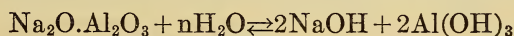
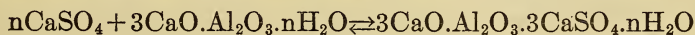
This compound, like the high sulphate calcium sulphoaluminate, is decomposed by solutions of magnesium sulphate and sodium carbonate when these salts are present in excess.

It appears from these experiments that only the high sulphate form of calcium sulphoaluminate can be stable under the usual conditions in which a calcium sulphoaluminate may be formed in concrete. Even if a little of a low sulphate form were produced it would be converted more or less rapidly to the high sulphate form.

Chlorides and sulphates of sodium, calcium, and magnesium are the principal constituents present in sea water and "alkali" soil waters. It has been found that sodium sulphate and calcium sulphate solutions of any concentration react with all of the calcium aluminates to form calcium sulphoaluminate. In the case of calcium sulphate solution, no other reactions appear to take place. With sodium sulphate, however, there seems to be a preliminary reaction of the calcium aluminate and sodium sulphate to form calcium sulphate and sodium aluminate

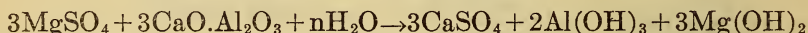


The calcium sulphate thus formed reacts with the calcium aluminate which remains to form calcium sulphoaluminate, and the sodium aluminate hydrolyzes to sodium hydroxide and aluminum hydroxide



Since the calcium sulphoaluminate is stable in the presence of calcium sulphate, sodium sulphate, and sodium hydroxide solutions it will not be subsequently destroyed by the presence of these substances.

Still other reactions appear with magnesium sulphate solutions. Here, again, there is doubtless a preliminary reaction between magnesium sulphate and the calcium aluminate



The products formed are calcium sulphate, aluminum hydroxide, and magnesium hydroxide, the latter being an amorphous, colloidal substance, highly insoluble in neutral or alkaline solutions. Due to the insolubility of the magnesium hydroxide, this preliminary reaction proceeds until practically all of the available magnesium sulphate has been used. It is only after the available magnesium sulphate has been almost completely precipitated in this first reaction that the calcium sulphoaluminate can be formed by the reaction of calcium sulphate with any remaining calcium aluminate.

This viewpoint was confirmed by the following experiments:

(a) Eight one-hundredths of a gram of tricalcium aluminate was added to 5 ml of 0.6 per cent (0.05 M) magnesium sulphate solution. A large quantity of calcium sulphoaluminate was formed, but no gypsum crystallized out. In this case the lime present was in excess of the amount required to precipitate all of the magnesia.

(b) Eight one-hundredths of a gram of tricalcium aluminate was added to 5 ml of 4.8 per cent (0.4 M) magnesium sulphate solution. No calcium sulphoaluminate was formed, but a large number of gypsum crystals were present. In this case the magnesium sulphate was present in excess.

(c) Five-tenths of a gram of tricalcium aluminate was added to 5 ml of 4.8 per cent magnesium sulphate solution. In this case both gypsum and calcium sulphoaluminate crystallized out. This amount of tricalcium aluminate gives an excess of lime, and in this case so much gypsum was formed that, even after the formation of the calcium sulphoaluminate, some crystals of gypsum remained in the solid phase.

With the other calcium aluminates it was necessary to vary the amount of the compound added to the magnesium sulphate solution because of the differences in lime content of these compounds. However, in each case it could be shown that the formation of calcium sulphoaluminate was dependent on the ratio of the lime content of the calcium aluminate to magnesium sulphate and not entirely on the original concentration of magnesium sulphate, as had been suggested by Shelton.²⁶

²⁶ See footnote 13, p. 717.

V. RELATIVE STABILITY WITH CALCIUM CHLORALUMINATE

Friedel²⁷ demonstrated the existence of a calcium chloraluminat, a double salt containing tricalcium aluminat and calcium chloride. Since chlorides and sulphates generally occur together in sea water and "alkali" ground waters, it seemed desirable to examine the relative stability of this calcium chloraluminat and calcium sulphoaluminat. To do this three experiments were performed.

(a) Two hundred milliliters of a 2.0 per cent solution of calcium chloride and 200 ml of a saturated calcium sulphate solution were added to 500 ml of a calcium aluminat solution. This mixture contained initially approximately the same concentrations of sulphate and chloride ions. After a week the precipitate which had formed was found by microscopic examination to consist entirely of the high sulphate calcium sulphoaluminat. No calcium chloraluminat could be found. Qualitative examinations of the precipitate indicated the presence of a large amount of lime, alumina, and sulphate but only a trace of chloride.

(b) Some calcium chloraluminat was prepared by adding 200 ml of 2.0 per cent calcium chloride solution to 500 ml of calcium aluminat solution. After standing for a day a precipitate had formed which was identified by optical examination as calcium chloraluminat. About 0.5 g of this precipitate was allowed to remain in 200 ml of saturated calcium sulphate solution for three weeks. The precipitate was then found to be composed entirely of the high sulphate calcium sulphoaluminat.

(c) About 0.5 g of calcium chloraluminat was placed in 600 ml of a solution containing 0.6 per cent calcium chloride, 0.6 per cent calcium sulphate, and 0.6 per cent calcium hydroxide. After three weeks it was found that the calcium chloraluminat had been converted completely to the high sulphate calcium sulphoaluminat.

Thus, it seems that the product formed by the reaction of the calcium aluminates with solutions containing both chlorides and sulphates will be the high sulphate calcium sulphoaluminat. The calcium chloraluminat will not be formed until all or practically all of the available sulphate has been combined as the calcium sulphoaluminat.

VI. SUMMARY

From a review of the literature it appears that the formation of one calcium sulphoaluminat had been definitely established. The results of different workers show slight variations in the sulphate content and wide variations in the amount of water of crystallization of the compound, but, due to the similarity in optical properties,

²⁷ Bull. soc. franc. mineral., 26, p. 121; 1903.

there is little doubt that the compounds described by these different workers are the same. The composition of the compound as reported had varied from $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2.5\text{CaSO}_4\cdot\text{aq}$ to $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot\text{aq}$.

Samples have been prepared in this laboratory by several methods, but that which has given most satisfactory results consists in the interaction of solutions of calcium sulphate and calcium aluminate, preferably with added calcium hydroxide. An analysis of the pure material indicates a composition which may be expressed by the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$. In the presence of dilute solutions of calcium sulphate, precipitates have been obtained which contain less than 3 mols of calcium sulphate to 1 mol of tricalcium aluminate. The ratio in some cases was of such a value that the composition of the precipitate could be expressed by the formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2.5\text{CaSO}_4\cdot\text{aq}$. This ratio appears to vary with the concentration of the calcium sulphate in solution and indicates an equilibrium mixture of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot\text{aq}$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{aq}$. As the concentration of calcium sulphate increases the amount of the hydrated calcium aluminate decreases and eventually disappears. This would explain the difference in composition assigned to this compound by different writers.

Microscopic examinations of some of the larger crystals have shown them to be long needle-like hexagonal crystals of refractive indices $\omega_D 1.464 \pm 0.002$, $\epsilon_D 1.458 \pm 0.002$, uniaxial negative in character and showing negative elongation. The specific gravity of this compound was found to be 1.48 at 20°C .

The existence of a new calcium sulphoaluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$, has been demonstrated. This compound has a lower sulphate content than the other form and may be distinguished by its higher indices of refraction $\omega_D = 1.504 \pm 0.002$, $\epsilon_D = 1.488 \pm 0.002$, and by a platy crystal habit, distinctly different from that of the high sulphate compound. In general, it may be said that this compound is unstable. Under conditions commonly encountered in concrete it is converted to the more stable form with the higher calcium sulphate content. This transformation is retarded by increasing hydroxyl-ion concentration, being slow in saturated calcium hydroxide solutions and apparently entirely prevented by a 3 per cent solution of sodium hydroxide. The specific gravity of this compound is 1.95 at 20°C .

The high sulphate calcium sulphoaluminate has been found to be slightly dissociated in water. This dissociation is somewhat repressed by solutions of calcium hydroxide and calcium sulphate and slightly increased by solutions of sodium chloride and sodium sulphate, but in all of these solvents the amount of lime, alumina, or sulphate going into solution is far less than the amount which will go into solution from a calcium aluminate or from calcium sulphate.

When carbonates are present, the lime liberated by hydrolysis of the calcium sulphoaluminates appears to be converted to the more insoluble compound, calcium carbonate. One product of the reaction being thus removed from solution, the hydrolysis proceeds until all of the calcium sulphoaluminate is decomposed, provided there is a sufficient amount of carbonate solution present. If a magnesium salt is present, the hydroxyl ions of the $\text{Ca}(\text{OH})_2$ are removed by precipitation of magnesium hydroxide. Thus, it is apparent that in the presence of only a slight excess of soluble carbonates or magnesium salts the calcium sulphoaluminates will be entirely destroyed.

It has been shown that, when both sulphate and chloride solutions are present, the high sulphate calcium sulphoaluminate will be formed to the exclusion of calcium chloroaluminate if there is sufficient calcium sulphate present to convert all of the calcium aluminate to calcium sulphoaluminate.

A tabulation of the formulas which have been reported for the calcium sulphoaluminates is given in Table 5, and a comparison of optical and crystallographic data is given in Table 6.

TABLE 5.—Formulas reported for the calcium sulphoaluminates

Authority	Date	Formula	Remarks
Lehman	1847	$6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 33\text{H}_2\text{O}$	The mineral Ettringite.
Candlot	1890	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 59\text{H}_2\text{O}$	Crystalline spherulites.
Michaelis	1892	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$	Broad, needle-shaped prisms.
Moses	1893	$10\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 54\text{H}_2\text{O}$	The mineral Ettringite.
Klinkenberg	1894	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12.49\text{H}_2\text{O}$	
Do	1894	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot 18.25\text{H}_2\text{O}$	
Do	1894	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 19.55\text{H}_2\text{O}$	
Schott	1894	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot 18\text{H}_2\text{O}$	
Rebuffat	1896	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$	This compound refuted in 1902.
Do	1896	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 10\text{H}_2\text{O}$	
Deval	1900	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	
Rebuffat	1902	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$	
Poirson	1910	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	
Klein and Phillips	1914	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	Long, slender needles.
Kühl and Lafuma	1923	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	
McIntire and Shaw	1925	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	
Lerch, Ashton, and Bogue	1929	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$	Fine needle-like crystals.
Do	1929	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$	Star-shaped spherulites.

TABLE 6.—Comparison of crystal data on the calcium sulphoaluminates

	Klein and Phillips	Shelton	Lerch, Ashton, and Bogue	
			High sulphate form	Low sulphate form
Formula	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 4q$	Not given	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$
Habit	Long, slender needles often in spherulitic form.	Long needles and coarse prisms.	Long needles often in spherulitic form.	Hexagonal plates often in star-shaped groups of 4 to 8 plates.
Optical character	Biaxial positive; large optic axial angle.	Biaxial positive	Uniaxial negative	Uniaxial negative.
Extinction	Parallel	Parallel	Parallel	Parallel.
Elongation	Negative	Negative	Negative	Positive.
Refractive indices	Less than 1.48	$\alpha = 1.461 \pm 0.003$	$\omega_D = 1.464 \pm 0.002$	$\omega_D = 1.504 \pm 0.002$
		$\gamma = 1.463 \pm .003$	$\epsilon_D = 1.458 \pm .002$	$\epsilon_D = 1.488 \pm .002$
Birefracton	Low	0.002	0.006	0.016.

WASHINGTON, October 12, 1928.

