Rheology of Fresh Portland Cement Pastes

Influence of Calcium Sulfates

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> A study of the influence of the various forms of calcium sulfate on the flow properties of fresh portland cement pastes was made with a coaxial cylinder viscometer. Both calcium sulfate hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$ and soluble anhydrite $CaSO_4$ produced high apparent viscosities and yield values in pastes of clinker or quartz. These properties are attributed to the network of gypsum crystals formed from the supersaturated solutions produced by these sulfates. Without the addition of calcium sulfate, the tricalcium aluminates hydrate quickly and the pastes stiffen abnormally.

Shear thickening properties are produced in quartz powder suspensions by both the hemihydrate and the soluble anhydrite. However, a similar trend is not definitely shown by pastes made from clinker and these calcium sulfates. A cement was heated at 120 C to dehydrate the gypsum and a paste of this cement exhibited a shear thickening flow behavior.

• IN A PREVIOUS investigation (1) of the rheology of fresh portland cement pastes, it was demonstrated that pastes usually exhibit first a shear thickening (antithixotropic) and then a shear thinning (thixotropic) flow behavior. The available information (2 through 6) indicated that the calcium sulfates influence the shear thickening properties and under certain conditions cause an abnormal stiffening. This investigation of the influence of the various calcium sulfates on the flow properties of fresh pastes was performed to gain a fundamental understanding of these properties.

In the present investigation the effects of gypsum, calcium sulfate hemihydrate, and the anhydrous forms of calcium sulfate on the flow properties of suspensions of quartz powders and of portland cement were studied with a coaxial cylinder viscometer. Although the fundamental natures of the flow properties of concentrated suspensions and gels are not yet completely understood, it is possible by the techniques and theories of rheology and physical chemistry to obtain a great deal of information about the factors that influence the flow properties of these complicated systems. Eventually by performing careful experimental and theoretical studies, a fundamental understanding of the mechanism of the flow of concentrated suspensions and gels will result.

The nomenclature for the flow properties will follow the recommendations of the Committee on Communication Problems in Rheology (7). The recommended nomenclature is based on the measurements; i.e., the shearing stress S, the rate of shear D, and time of shear t. When the ratio S/D, at a particular rate of shear, increases with time of shear, the system is called shear thickening. The ratio S/D is defined here as the apparent viscosity at a certain rate of shear. This type of behavior is exhibited (Fig. 1) by some cement pastes 20 min after the cements are placed in contact with water. A shear thinning system is exhibited by a decrease in the S/D values with time of shear at a particular rate of shear. A shear thinning behavior may be seen in Figure 1 for a cement paste 185 min after the cement was placed in contact with water. When the S/D values remain constant with time of shear the system is termed time-independent. Time-dependent effects in S/D values indicate that changes in the structure of the system are proceeding.

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It is well to review some of the chemical reactions that occur when cement is mixed with water. C_3S , the principal component of cement, hydrates continuously after it is brought in contact with water. The hydration of C_3S leads to a shear thinning flow behavior and a gradual increase in the apparent viscosities of the pastes (1). Because C_2S hydrates slowly, this component does not contribute markedly to the flow properties of the fresh pastes. Unless the hydration of C_3A and C_4AF (8) is retarded, the pastes stiffen very rapidly producing a condition called quick set. According to present information (1), the products of the reaction of C_3A lead to shear thinning flow properties and a marked increase in the apparent viscosities of the pastes. The influence of the sulfoaluminates on the flow properties has not been thoroughly investigated. However, it has been reported by Budnikov (9) that the sulfoaluminates cause high early strength in concrete.



Figure 1. S/D values as a function of shearing time for cement 15366 at 20- and 185-min hydration times (D = 658 sec⁻¹).

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Under normal conditions the C₃A dissolves (Fig. 2) to form solutions of calcium and hydroxyl ions and aluminic acid and its ions. In the absence of calcium sulfate, C_4AH_{19} is formed (10). When sufficient hydrated calcium aluminate is produced, a rapid change in flow properties results. This is accompanied by the evolution of a large amount of heat. In the presence of calcium sulfate the high sulfate sulfoaluminate, ettringite, $C_3A \cdot 3CaSO_4 \cdot 31H_2O$, is formed. A coating of the sulfoaluminates on the C₃A particles is considered the cause of the decrease in the rate of C₃A hydration (2).

When gypsum $CaSO_4 \cdot 2H_2O$ is ground with clinkers (Fig. 2), some of it is dehydrated to the hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$ and soluble anhydrite $CaSO_4$ (11). Hemihydrate is formed when the soluble anhydrite is exposed to the atmosphere. Because the hemihydrate and the soluble anhydrite are much more soluble than gypsum, the solutions in contact with these substances are supersaturated with respect to gypsum. Crystallization of gypsum will therefore proceed under the proper conditions.

Evidence for the dehydration of gypsum was found in an analysis (12) of the compositions of the aqueous phases in contact with cements. Solutions supersaturated with respect to gypsum exist for at least 30 min after the cements are mixed with water. The concentration of calcium sulfate in solution may be reduced by the formation of sulfoaluminates or by the crystallization of gypsum.

Bucchi (13) reported that a large fraction of the sulfate reacts to form sulfoaluminate in the first few minutes after mixing. It was demonstrated by him that the sulfate is removed at rates proportional to the aluminate content.

Solutions supersaturated with respect to gypsum are unstable and, in the presence of nucleating agents, a rapid crystallization of gypsum occurs. Under the proper conditions a network of gypsum crystals may result. Both gypsum and clinker may act as nucleating agents according to Manabe (6). However, exposure of the cement to the atmosphere may cause a deactivation of the clinker nuclei which could delay the crystallization process for some time after the cement had been mixed with water.

The network of gypsum crystals that is deposited from supersaturated calcium sulfate solutions causes a change in flow properties which is sometimes called plaster set. In the present study, plaster set will also refer to the network of gypsum crystals that produces the set. There was some experimental evidence that seemed to relate the plaster set to the shear thickening properties of fresh pastes:

1. The shear thickening properties are evident 15 min after the cement is mixed



Figure 2. Chemical processes in hydration of C3A and calcium sulfates.

with water. After an hour or two this behavior is no longer found. Plaster set under normal conditions would be expected almost immediately after the cement is mixed with water and the network of gypsum crystals should not dissolve completely before an hour or two have elapsed (2).

Such hydration products as the hydrated calcium silicates and aluminates produce an increase in the apparent viscosities, S/D, of the cement pastes and in the shear thinning behavior. Therefore, as the cement continues to hydrate, there will be an increase both in the apparent viscosity and in the shear thinning. Consequently, the shear thickening behavior would become less evident as the gypsum in the plaster set dissolves, and the hydration of the clinker proceeds.

2. Gypsum suspensions have been reported to exhibit a shear thickening behavior (14).

3. Suspensions of attapulgite crystals have been reported by Gabrysh, Ree, Eyring, McKee, and Cutler (15) to exhibit shear thickening properties similar to those found in cement pastes. Attapulgite exists as a network of needlelike crystals similar to that found with secondary gypsum crystals. The increase in apparent viscosity with time of shear has been attributed by these authors to the higher viscosity of the system when the networks of crystals are broken up by shearing action. It is reasonable to assume that a suspension of individual needle-shaped crystals would exhibit a higher apparent viscosity than aggregates of these crystals.

On the other hand, Dellyes (5), who first reported the shear thickening properties of freshly mixed pastes, showed that carbonates and carbonated pastes exhibit shear thickening flow behaviors. Recently it was reported (16) that calcium carbonates may cause some suspensions of silicates to show a shear thickening behavior.

One type of abnormal stiffening of portland cement pastes, mortars, and concretes is defined by committees of the American Society for Testing Materials as false set (4). This behavior is attributed to a plaster set. When this stiffening occurs, not much heat is evolved. The present paper deals with plaster set at hydration times longer than those employed in the ASTM false set test. The extension of the rheological investigation to shorter hydration times and the correlation with ASTM false set test results are left for future work.

Type	Percent of Component								
of Component	Type I Cement 15366	High Alkali 15698	Clinker 15367	LTS No. 18	Medium C ₃ A 15622A	High C₃S 15497B	Low C ₃ A 15669	Zero C ₃ A 19648	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	
C_3S	44.8	45.3	45.4	44.5	49.2	60.1	33.0	66.0	
C_2S	26.9	28.6	28.5	28.0	28.5	11.9	54.2	14.7	
C_3S/C_2S	1.67	1.58	1.59	1.59	1.73	5.05	0.61	4.50	
C ₄ AF	6.7	7.6	6.8	6.8	12.8	7.9	5.8	10.15 ^a	
C ₃ A	13.6	9.8	14.3	13.2	4.4	10.3	2.3	0.0	
CaSO ₄	3.3	3.0	-	3.1	2.7	3.1	3.1	4.3	
MgO	2.5	3.4	2.63	2.6	1.44	1.72	1.72	0.60	
Free CaO	0.93	0.08	0.98	0.3	0.49	3.14	0.15	0.58	
Total alkali									
$(Na_2O + K_2O)$	0.33	1.57	0.33	0.25	0.22	0.70	0.27	0.12	
Surface area (sq cm/g)									
(Wagner)	2,260	2,250	2,250	1,750	2,200	2,500	2,280	2,640	

TABLE 1

POTENTIAL COMPOUND COMPOSITIONS

Contains 3.16 percent C2F.

RHEOLOGICAL EQUIPMENT

For this investigation a Haake Rotovisco coaxial cylinder viscometer (Brinkmann Instruments, Inc., Great Neck, N.Y.) was employed. The radius of the MVI bob is 2.003 cm and that of the cup is 2.102 cm. The constants of the instrument were listed in a previous paper (1). The bob was rotated at speeds up to 580 rpm. Torques were measured by the displacement of springs, with three different ranges up to a shearing stress of 3,000 dynes per sq cm. By placing carbon powder on the top of a suspension in the cup and rotating the bob, it was possible to observe that the entire sample was flowing. The entire sample did not flow when wider annular spaces were used.

MATERIALS

The following portland cements were examined: Type I cement 15366, high alkali 15698, Long Time Study No. 18, medium C_3A 15622A, high C_3S 15497B, low C_3A 15669, and a zero C_3A 19648. A clinker 15367 from the batch used to make cement 15366 was ground in a ball mill to a Wagner surface area (17) of 2, 200 sq cm per g. The potential compositions of these materials are given in Table 1. The SO₃ content of the clinker is 0.41 percent. Cements 15366, 15622A, 15497B, 15669 and 19648, as well as clinker 15367 were especially prepared in commercial plants for this laboratory. The conditions of preparation were those normally used in the plants. Extensive examinations of the chemistry and properties of these cements have been made in this laboratory.

The quartz powders (Silver Bond B Grade, Tamm Industries, Chicago, Ill.) exhibited a particle size distribution similar to that of the cement 15366 with a Wagner surface area of 2,260 sq cm per g (18). All the powder passed through a 325 mesh screen.

Baker reagent grade calcium sulfate hydrate, $CaSO_4 \cdot 2H_2O$, was the source of all the calcium sulfates investigated. The X-ray diffraction pattern of the dihydrate was typical for this substance. However, low intensity peaks of the hemihydrate diffraction pattern were found. The ignition loss of 19.7 percent (th. 21.0 percent) corresponds to 8.1 percent hemihydrate.

The procedures for the preparation of the hemihydrate and anhydrous sulfates followed those of Ljunggren (19). The calcium sulfate hemihydrate, $CaSO_4$, $\frac{1}{2}H_2O$, was prepared by heating the dihydrate for one day at 120 C. The heated sample was then allowed to cool exposed to the air. Under these conditions any soluble anhydrite formed at 120 C would be rehydrated to $CaSO_4$, $\frac{1}{2}H_2O$. The hemihydrate was identified by X-ray diffraction and weight loss on ignition at 1,050 C. The soluble anhydrous calcium sulfate, α -CaSO₄, was made by dehydrating the dihydrate for one day at 200 C. This sample was allowed to cool in a dessicator. The weight loss of the sample was negligible at 1,050 C. The insoluble anhydrite, β -CaSO₄, was prepared by igniting the

TABLE 2

EFFECT OF REPEATED SHEAR STRESS ON RHEOLOGICAL BEHAVIOR OF FRESH CEMENT PASTE

Hydration Time (min)	Shearing Time (sec)	S/D (dynes-sec/sq cm) ²	$\frac{\Delta(S/D)}{S/D}$	
(1)	(2)	(3)	(4)	
20	0	0.77	-	
	15	0.79	+0.026	
	30	0.81	+0.050	
	60	0.81	+0.050	
185	0	2.34	-	
	15	1.87	-0.22	
	30	1.75	-0.29	
	60	1.68	-0.33	

 $^{a}D = 658 \text{ sec}^{-1}$.

dihydrate at 500 C for one day. No appreciable ignition loss was exhibited by this sample at 1,050 C.

PROCEDURES

In general, the procedures described in a previous study (1) were employed. However, to reduce the amount of the solids required, the method for mixing the solids and water was revised. In only a few experiments was the mixing performed in a Waring Blendor under vacuum. In the present study it was found more convenient to mix samples in a glass bottle of 120-ml capacity on a Spex Shaker (Scotch Plains, N.J.). Only about 100 g of solids are necessary in this procedure. The results obtained with samples mixed on the Spex Shaker were almost the same as those obtained with the samples mixed in the Waring Blendor.

In some experiments, to prevent the mixtures from reaching temperatures excessively above 25 C, ice was added to the mix water and included in the total weight of water. In most cases the samples were mixed for 5 min to a final temperature of approximately 25 C. The samples after mixing were placed in a 25 C constant temperature bath for 15 min. They were then inserted into the viscometer cups and the rpm-torque measurements were made.

The volume concentrations of the quartz in the suspensions were maintained constant at 43 volume percent. This volume concentration is produced by a 0.5 water to quartz ratio by weight. This weight concentration (w/c ratio of 0.5) provides 39 volume percent concentration in the case of the cement experiments. Deviations from this volume percent of solids are pointed out later.

The procedures for making the viscometer measurements were described previously (1) and are essentially the same as those recommended by Green (20). An upcurve was made which relates the rpm and torque values for increasing rpm values, and immediately afterwards a downcurve was made for decreasing rpm values. The two curves are called a flow curve. In each experiment two flow curves were made with the second curve following immediately after the first. Each flow curve corresponds to one cycle and requires about 3 min to make.

The ratio of shearing stress S to rate of shear D at a rate of shear 658 sec^{-1} is defined as the apparent viscosity and is given in dynes-seconds per square centimeter. The S/D values are taken at a rate of shear of 658 sec^{-1} . The second rheological parameter evaluated, is the yield stress f (20, 21). Theoretically the yield stress is the minimum shearing stress necessary to initiate the flow of a plastic material. The

	1st Cy	cle	2nd Cy	Orean A11	
Hemihydrate (% total CaSO4)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value` f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	$\frac{\Delta(S/D)}{S/D}$
(1)	(2)	(3)	(4)	(5)	(6)
0	0	0.20	0	0.19	-0.051
20	5	0.22	10	0.22	0
40	10	0.24	10	0.24	0
50	10	0, 27	15	0.27	0
60	40	0.34	50	0.37	+0.085
80	80	0.49	100	0.53	+0.078
100	160	0.69	180	0.76	+0.097

TABLE 3

GYPSUM MIXTURES, INFLUENCE OF HEMIHYDRATE ON FLOW PROPERTIES OF QUARTZ-WATER SYSTEM

yield stress in this investigation is determined by the extrapolation of the straight portion of the downcurve to the torque axis. The intercept in torque units is converted to the yield stress by the appropriate constants (1).

In the tables the yield stresses f in dynes per square centimeter and apparent viscosities, S/D, in dynes-seconds per square centimeter are listed for the first and second cycles. In the final column the over-all behavior is characterized by a term $\Delta(S/D)/(S/D)$. The $\Delta(S/D)$ values are the changes in apparent viscosities between the first and second cycles. When $\Delta(S/D)$ is divided by the average of the S/D values in the first and second cycles, the $\Delta(S/D)$ values are reduced to a proper order of magnitude when there is a large variation in S/D values in a set of experiments. Positive, negative, and zero values of $\Delta(S/D)/(S/D)$ correspond to shear thickening, shear thinning, and time-independent systems, respectively. The values of $\Delta(S/D)/(S/D)$ correspond to some extent to the degree of shear thickening or thinning behavior. Values of $\Delta(S/D)/(S/D)$ ranging between 0 and ±0.02 are within experimental error, but are listed because in some cases trends in the values may be noted.



Figure 3. Influence of hemihydrate-gypsum mixtures on S-D values of quartz-water system.

RESULTS

Changes in Flow Properties with Hydration Time

The apparent viscosities of cement 15366 paste with a w/c = 0.5 were determined as a function of shearing time at two hydration periods. The determinations were made on separate samples 20 and 185 min after the cements were placed in contact with water. Table 2 gives the apparent viscosities at 0, 15, 30, and 60 sec of shearing time. In Figure 1 it may be seen that at 20 min of hydration time the S/D values increase from 0.77 to 0.81 dynes-sec per sq cm with time of shear to a constant value at 30 sec. After 60 sec of shearing time the S/D values begin to decrease. A decrease in S/D values with time of shear from 2.34 to 1.68 dynes-sec per sq cm may be noted at 185 min of hydration time. The sample at 20-min hydration time illustrates a shear thickening material, whereas the sample at 185 min of hydration time demonstrates a shear thinning material.

Relationships Between the Flow Behaviors and Calcium Sulfates

Three sets of experiments were conducted to show the influences of the various forms of calcium sulfate on the flow behaviors of fresh cement pastes and quartz suspensions:

1. The effects of the calcium sulfates on the flow properties of quartz powder suspensions were examined. Quartz suspensions were used previously by Lerch and Bogue (22) to demonstrate the stiffening caused by the hemihydrate.

		1st Cy	vcle	2nd C	ycle	
Type Su of S Calcium Sulfate	Sulfate Solid Wt. (%)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Over-All Behavior $\Delta(S/D)$ $\overline{S/D}$
	(1)	(2)	(3)	(4)	(5)	(6)
Gypsium	$1\frac{1}{2}$	0	0.19	0	0.19	0
	2	0	0.19	0	0.19	0
	3	0	0.20	0	0.19	-0.051
	5	0	0.20	0	0.20	0
	7	10	0.22	0	0.22	0
Hemihydra	te $1\frac{1}{2}$	40	0.37	40	0.39	+0.053
	2	50	0.42	60	0.46	+0.091
	3	160	0.69	180	0.76	+0.097
	5	500	1.60	520	1.72	+0.072
	7	1,000	2.83	1,010	2.97	+0.048
Anhydrite:	$1\frac{1}{2}$	40	0.38	45	0.40	+0.026
soluble	2	60	0.44	60	0.47	+0.066
	3	200	0.82	210	0.95	+0.147
	5	570	1.88	580	1.98	+0.052
	7	1,080	3.24	1,050	3.25	+0.003
Insoluble	$1\frac{1}{2}$	5	0.21	10	0.21	0
	2	5	0.22	5	0.22	0
	3	10	0.22	10	0.23	+0.044
	5	10	0.25	10	0.25	0
	7	15	0.28	15	0.28	0

EFFECT OF CALCIUM SULFATE ON RHEOLOGICAL BEHAVIOR OF QUARTZ-WATER SYSTEM

TABLE 4

2. An investigation was made of the effects of the various forms of calcium sulfate on the flow properties of ground clinker pastes.

3. The effects of heating a cement to 120 C on the flow behavior of the paste were studied.

In the first set of experiments mixtures of hemihydrate and gypsum were added to 43 volume percent quartz powder suspensions. In each case the total CaSO₄ content was 3 percent by weight of the quartz. The percentages of hemihydrate ranged from 0 to 100 percent. The weights of the quartz in the mixture were 100 g minus the weight of the calcium sulfates. Inasmuch as the densities of quartz, gypsum, hemihydrate, soluble anhydrite, and insoluble anhydrite are 2.65, 2.32, 2.35, 2.45, and 2.96, respectively, the volume percents of solids are slightly different from 43 volume percent. This small variation in volume percent of solids would not be expected to cause a marked change in the yield values and apparent viscosities. The results of these experiments are given in Table 3 and Figure 3. Table 3 (col. 1) gives the percent of hemihydrate as CaSO₄. The yield values f and apparent viscosities S/D at 658 sec⁻¹ are given in columns 2 and 3, and 4 and 5 for the first and second flow cycles, respectively. The over-all behavior is demonstrated by the $\Delta(S/D)/(S/D)$ values in column 6.

Figure 3 shows the S/D values in the first and second cycles as a function of the hemihydrate content. At about a 50 percent hemihydrate content, the S/D values begin to increase sharply. Also, the first and second cycle curves cross at this point. The lower values of S/D in the second cycle up to a 50 percent concentration of hemihydrate demonstrate that the systems are shear thinning in this range. The shear thickening properties of the suspensions above a 50 percent hemihydrate are demonstrated by the higher S/D values in the second cycle. In Table 3, column 2, a rise may be seen in yield stresses from 0 to 160 dynes per sq cm with a hemihydrate increase from 0 to 100 percent. The sharpest increase in yield values begins at a 50 percent hemihydrate content. The over-all character of the flow behavior is demonstrated by the changes in $\Delta(S/D)/(S/D)$ values (column 6) from -0.051 to +0.097 with the increase in hemi-hydrate content from 0 to 100 percent. The negative values correspond to a shear thinning system, the zero values to a time-independent system and the positive values to a shear thickening system. Thus with an increase in the hemihydrate content any of these three kinds of flow behaviors may be observed.

The effects of gypsum, hemihydrate, soluble anhydrite, and insoluble anhydrite on the flow properties of the 43 volume percent quartz-water system are shown by the

	1st C	ycle	2nd C	$\frac{\text{Over-All}}{\text{Behavior}}$ $\frac{\Delta(S/D)}{S/D}$	
Hemihydrate (% total CaSO₄)	Yield Value f (dynes/sq cm)	Apparent Yield Value Viscosity f S/D lynes/sq cm) (dynes-sec/ sq cm)			Apparent Viscosity S/D (dynes-sec/ sq cm)
(1)	(2)	(3)	(4)	(5)	(6)
0	200	0.51	200	0.52	+0.019
20	190	0.49	190	0.50	+0.020
40	110	0.34	110	0.35	+0.029
50	120	0.36	120	0.36	0
60	110	0.34	110	0.34	0
70	170	0,47	170	0.48	+0.021
80	195	0.53	190	0, 54	+0.019
100	270	0.70	270	0,69	-0.014

TABLE 5

INFLUENCE OF HEMIHYDRATE-GYPSUM MIXTURES ON FLOW PROPERTIES OF A CLINKER-WATER SYSTEM data in Table 4. The amounts of sulfate solids added are listed in column 1 in weight percent of the quartz. In each experiment the total weight of the solids was held constant at 100 g. Both hemihydrate and soluble anhydrite produced shear thickening flow behaviors (col. 6). The $\Delta(S/D)/(S/D)$ values for the suspensions with these two forms of calcium sulfate do not show marked differences. The $\Delta(S/D)/(S/D)$ values increase to a maximum at 3 percent and then decrease with an increasing sulfate content. However, the yield values in the first cycle of the suspensions with hemihydrate and soluble anhydrite additions up to 7 percent. An increase in apparent viscosities from 0.37 and 0.38 to 2.83 and 3.24 dynes-sec per sq cm is found with hemihydrate and soluble anhydrite, respectively.

In general, gypsum and insoluble anhydrite produced time-independent flow behaviors in quartz suspensions. The yield values for these suspensions were less than 15 dynes per sq cm. Both gypsum and insoluble anhydrite produced relatively small effects on the yield values and apparent viscosities, but the effect of insoluble anhydrite was slightly greater.



Figure 4. Influence of hemihydrate-gypsum mixtures on S/D values of clinker-water system.

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In the second group of experiments the effects of hemihydrate-gypsum mixtures on the flow behavior of ground clinker (15367) pastes with a w/c ratio equal to 0.5 were investigated. The CaSO₄ contents of the additions were maintained constant at 3 percent by weight of the clinker. The hemihydrate contents of the mixtures ranged from 0 to 100 percent by weight of CaSO₄. The results are summarized in Table 5 and Figure 4. In general, the $\Delta(S/D)/(S/D)$ values (col. 6) indicate that the systems are slightly shear thickening. It is necessary to point out, however, that most of the values are in the range 0 ± 0.02, which is within experimental error. In Figure 4, the S/D ratios for the first cycle show a decrease in values from 0.51 to 0.34 dynes-sec per sq cm in the range of hemihydrate contents 0 to 40 percent. In the range 60 to 100 percent hemihydrate, the values increase sharply from 0.34 to 0.70 dynes-sec per sq cm. In Table 5 (col. 2), the yield values in the first cycle decrease from 200 to 110 dynes per sq cm with an increase in hemihydrate content from 0 to 40 percent. In the range 60 to 100 percent hemihydrate, the yield values increase sharply from 110 to 270 dynes per sq cm.

A hemihydrate content of 60 percent is optimum in these experiments for reducing the yield values and apparent viscosities to a minimum. Later, these effects are shown to be based on the rates of solution of the calcium sulfates, and the rates of reaction of C_3A .

Table 6 gives the results of a series of experiments to establish the effects of gypsum, hemihydrate, soluble anhydrite, and insoluble anhydrite on the flow properties of clinker pastes. The 1.5 to 7 percent calcium sulfate additions are given in column 1 in percent by weight of the solids. In each experiment the w/c is 0.5 with the calcium

		1st C	ycle	2nd C	ycle	
Type of Calcium Sulfate	Sulfate Solid Wt. (%)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Over-All Behavior $\Delta(S/D)$ $\overline{S/D}$
	(1)	(2)	(3)	(4)	(5)	(6)
Gypsium	$2^{1/2}$	175	0.47	180	0.47	0
	3	200	0.51	200	0.52	+0.019
	5	130	0.38	130	0.38	0
	7	120	0.42	120	0.43	+0.024
Hemihydra	ate $1\frac{1}{2}$	140	0.39	140	0.40	+0.025
	2	170	0.45	165	0.46	+0.022
	3	270	0.70	270	0.69	-0.014
	5	290	0.73	300	0.74	+0.014
	7	410	1.00	400	1.00	0
Anhydrite:	$1\frac{1}{2}$	120	0.35	120	0.36	+0.028
soluble	2	150	0.43	150	0.44	+0.023
	3	24 5	0,61	250	0.62	+0.016
	5	330	0.80	340	0.81	+0.012
	7	410	1.03	400	1.01	-0.020
Insoluble	$1\frac{1}{2}$	710	1.60	580	1.28	-0.222
	2	1,010	2.02	960	1.91	-0.056
	3	910	1.88	900	1.85	-0.016
	5	1,060	2.15	1,020	2.09	-0.028
	7	1,010	2.07	960	2.00	-0.034

INFLUENCE OF CALCIUM SULFATE ON RHEOLOGICAL PROPERTIES OF A CLINKER-WATER SYSTEM

TABLE 6

sulfates included in the weight of solids. Pastes with hemihydrate and soluble anhydrite showed a tendency to be slightly shear thickening. Most of the $\Delta(S/D)/(S/D)$ values (col. 6) were small enough to be in the range of experimental error. Also, no clear correlation between these values and the sulfate contents was apparent; if anything, there is a slight decrease in the $\Delta(S/D)/(S/D)$ values with sulfate content. On the other hand, yield stresses and S/D values increase markedly with sulfate content. The pastes with hemihydrate exhibited, in the first cycles, a rise in yield value from 140 to 410 dynes per sq cm in the sulfate content range 1.5 to 7 percent. In the same range of sulfate contents the S/D values rose from 0.39 to 1.00 dynes-sec per sq cm. For the same additions of soluble anhydrite the yield values rose from 120 to 410 dynes per sq cm and the S/D values increased from 0.35 to 1,03 dynes-sec per sq cm.

The addition of gypsum produced some indication of a slight shear thickening behavior at 3 and 7 percent. Small changes in yield stress and S/D values were observed, and in general there was a decrease in the values with sulfate content. On the other hand, the suspensions with insoluble anhydrite additions exhibited a marked shear thinning behavior. The $\Delta(S/D)/(S/D)$ value (col. 6) was largest for the 1.5 percent addition. The yield values in the first cycle ranged between 710 and 1,060 dynes per sq cm, which are more than double those of the pastes with the other forms of sulfate. The apparent viscosities were between 1.60 and 2.07 dynes-sec per sq cm. The high yield stresses and S/D values in this set of experiments may be attributed to the rapid hydration of C₃A in the presence of a sulfate that dissolves slowly. These relationships are discussed later.

A control paste without any sulfate added was too stiff to measure, but a shear thinning behavior was observed.

In the third set of experiments a cement was heated at 120 C to dehydrate the gypsum. The flow properties of pastes of this cement were compared to those of pastes of the unheated cement. The Long Time Study No. 18 cement was used for this set of experiments. The procedure of heating the cement for 18 hr at 120 C has been reported to encourage abnormal stiffening. Two flow curves were made at 20, 50, 125, and 185 min after the cements were added to the water. The results are summarized in Table 7 and Figure 5.

	1st C	ycle	2nd C		
Hydration Time (min)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	$\frac{\Delta(S/D)}{S/D}$
		Unhea	ated		
(1)	(2)	(3)	(4)	(5)	(6)
20	60	0.23	60	0.24	+0.043
50	60	0.23	60	0.23	0
125	110	0.37	110	0.37	0
185	170	0.55	170	0.53	-0.037
		Hea	ted	-	
20	160	0.46	165	0.47	+0.022
50	160	0.45	165	0.47	+0.044
125	300	0.78	300	0.78	0
185	375	0.92	340	0.88	-0.044

TABLE 7

EFFECTS OF HEATING AN LTS 18 CEMENT AT 120 C ON RHEOLOGICAL PROPERTIES

In Figure 5 the relationships are shown between the S/D values for two cycles for the heated and unheated cements and the hydration times. The pastes with heated cements exhibit S/D values almost twice those of the pastes with unheated cement. The values are almost constant between 20 and 50 min and then begin to increase rapidly. The yield values of the pastes with unheated cement are only about one-half those of the pastes with the heated cement (cols. 2 and 4). The $\Delta(S/D)/(S/D)$ values (col. 6) showed in both sets of experiments that the systems changed with hydration time from shear thickening to shear thinning. The shear thickening behavior of the paste of the heated cement, as indicated by the $\Delta(S/D)/(S/D)$ values, was evident even at 50 min of hydration



Figure 5. Effect of heating a cement at 120 C on S/D values as a function of hydration time.

time, whereas the paste of the unheated cement exhibited a time-independent behavior at this hydration time.

Mixing Time and Temperature

The effect of mixing time on the flow properties of cement 15366 was investigated. Because mixing exerts a heating effect, it was not possible, even with ice, to hold the temperature after mixing at 25 C beyond a 5-min period of mixing. To study the influence of temperature, two sets of experiments were performed. In one set of experiments no ice was added to the mixtures. The results of these experiments are given in Table 8. The temperature after mixing may be seen in column 2 to range from 28

TABLE 8

EFFECT OF MIXING TIME AND TEMPERATURE ON RHEOLOGICAL BEHAVIOR OF FRESH CEMENT PASTES COOLED TO LESS THAN 57 C

		1st C	ycle	2nd Cy		
Mixing Final Time Temp. (min) (^o C)	Final Temp. (°C)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	$\begin{array}{c} \text{Over-All} \\ \text{Behavior} \\ \underline{\Delta(S/D)} \\ \overline{S/D} \end{array}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	28	210	0.57	210	0.56	-0.018
2	32	200	0.53	190	0.52	-0.019
3	35	250	0.62	250	0.62	0
4	37	280	0.68	280	0.68	0
5	39	310	0.72	300	0.71	-0.014
8	47	310	0.73	300	0.72	-0.014
10	49	350	0.80	345	0.80	0
15	57	680	1.47	665	1.43	-0.028

TABLE 9

EFFECT OF MIXING TIME AND TEMPERATURE ON RHEOLOGICAL BEHAVIOR OF FRESH CEMENT PASTES COOLED TO LESS THAN 48 C

		1st Cy	vcle	2nd C		
Mixing Final Time Temp. (min) (⁰ C)	Final Temp. (°C)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Over-All Behavior $\frac{\Delta(S/D)}{S/D}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	24	230	0.62	230	0.60	-0.033
2	27	280	0,66	280	0.67	+0.015
3	24	320	0.75	325	0.76	+0.013
4	22	315	0.74	320	0.76	+0.027
5	23	400	0.92	410	0.94	+0.022
8	34	535	1.18	520	1.19	+0.008
10	40	595	1.41	540	1.40	+0.007
15	48	970	2.14	720	2.10	-0.019

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to 57 C for mixing times (col. 1) of 1 to 15 min. In the second set of experiments (Table 9) ice was added and the temperatures ranged from 22 to 48 C (col. 2) for similar mixing times. The total time between the placing of the cements in contact with water and the making of measurements was 15 min. After mixing the cements with water, the samples were allowed to stand in the constant temperature bath at 25 C.





In the case of the set B experiments (Table 9) for mixing periods of 1 to 5 min, the temperatures were 25 ± 3 C (col. 2). It is therefore possible to assume that for these experiments the temperature was essentially constant, and the effects of mixing time alone can be observed. For the first cycle (cols. 3 and 4) the yield values increase from 230 to 400 dynes per sq cm and the apparent viscosities increase from 0.62 to 0.92 dynes-sec per sq cm. Except for the case of the 1-min mixing time experiment, all the others exhibited a slight shear thickening behavior. Figure 6 shows that the $\Delta(S/D)/(S/D)$ values increase with mixing time up to 4 min.

For mixing times of from 8 to 15 min with temperatures below 48 C (Table 9), the yield values and apparent viscosities in the first cycle increased from 535 to 970 dynes per sq cm and 1.18 to 2.14 dynes-sec per sq cm, respectively. For the range of mixing times 4 to 15 min (Fig. 6) the $\Delta(S/D)/(S/D)$ values decreased from +0.027 to -0.019. In other words, with mixing time the system changed from a shear thickening to a shear thinning behavior.

In the experiments conducted without the addition of ice (Table 8) the pastes exhibited

TABLE 10

EFFECT OF BLENDING IN CaSO4 ON RHEOLOGICAL PROPERTIES OF A CLINKER

	1st Cy	cle	2nd C		
Type of CaSO₄	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	$\frac{\Delta(S/D)}{S/D}$
		Not Blend	ed		
(1)	(2)	(3)	(4)	(5)	(6)
Gypsum	790	1.69	750	1.63	-0.036
Hemihydrate	600	1.47	540	1.47	0
Sol. anhyd.	410	1.17	390	1.11	-0.053
		Blended	l		
Gypsum	200	0.51	200	0.52	+0.019
Hemihydrate	270	0.70	270	0.69	-0.014
Sol. anhyd.	24 5	0.61	250	0.62	+0.016

TABLE 11

EFFECT OF SURFACE AREA ON RHEOLOGICAL PROPERTIES OF FRESH CEMENT PASTE

	1st Cy	cle	2nd Cy		
Surface Area (sq cm/g)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Over-All Behavior $\frac{\Delta(S/D)}{S/D}$
(1)	(2)	(3)	(4)	(5)	(6)
1,100	30	0.18	25	0.14	-0.250
1,700	90	0.30	90	0.31	+0.033
1,800	150	0.43	150	0.44	+0.023
2,200	360	0.83	370	0.85	+0.024

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a rise in yield values from 210 to 680 dynes per sq cm and in apparent viscosities from 0.57 to 1.47 dynes-sec per sq cm in the mixing time range 1 to 15 min. The $\Delta(S/D)/(S/D)$ values in Figure 6 demonstrate essentially a shear thinning behavior, but only above a 10-min mixing time was there an apparent increase in shear thinning behavior with mixing time. Below a 10-min mixing time no correlation between shear thinning behavior and mixing time is apparent.

During the course of the experiments it was found that there were differences in flow behavior when the procedure was varied for adding the calcium sulfates and clinker to the water. The results obtained when the solids were blended before adding them to the water were entirely different from those obtained when the calcium sulfate was added to the water before the clinker. When gypsum, hemihydrate, or soluble anhydrite were blended with clinker before addition to the water, the yield values and apparent viscosities were much lower than the values obtained when the solids were added separately (Table 10). In each case the sulfate added contained sufficient CaSO₄ to be 3 percent by weight of the total solids. The pastes with gypsum or soluble anhydrite, in which the components were not blended, exhibited shear thinning properties, whereas the corresponding blended pastes showed shear thickening properties (col. 6). The pastes containing hemihydrate exhibit either a time-independent or slightly shear thinning behavior.

Surface Area

The effect of the surface area of a cement on the flow properties was examined. Pastes of cement 15366 with Wagner surface areas of 1,100, 1,700, 1,800, and 2,200 sq cm per g were investigated. In these experiments a w/c ratio of 0.5 was used. After the cement was mixed with water for 3 min, it was allowed to stand at 25 C for 15 min. Table 11 shows the yield values and apparent viscosities (cols. 2 and 3) in the first cycle increase with surface area from 30 to 360 dynes per sq cm and from 0.18 to 0.83 dynes-sec per sq cm, respectively. The $\Delta(S/D)/(S/D)$ values (col. 6) indicate only that with an increase in surface area there is a change from shear thinning to a shear thickening behavior.

Various Cements and Components

This series of experiments examined (a) Type I cement 15366, (b) a high alkali

Sample 1		1st Cy	cle	2nd C		
	Number	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Over-All Behavior $\Delta(S/D)$ S/D
(1)	(2)	(3)	(4)	(5)	(6)	(7)
÷	15366	400	0.94	400	0.95	+0.011
High alkal	i 15698	320	0.94	320	0.86	-0.890
Clinker	15367^{a}	-	-	-	-	-
Med. C ₃ A	15622A	65	0.27	60	0.26	-0.038
High C ₃ S	15497B	435	1.01	430	1.01	0
Low C ₃ A	15669	90	0.37	90	0.35	-0.056
Zero C ₃ A	19648	90	0.37	90	0.36	-0.027
C ₃ S	-	40	0.22	35	0.20	-0.095
C_2S	H	80	0.34	80	0.31	-0.092

TABLE 12

RHEOLOGICAL PROPERTIES OF VARIOUS CEMENTS AND CALCIUM SILICATES

^aToo stiff to measure.

cement 15698, (c) a clinker 15367, (d) a medium C_3A cement 15622A, (e) a high C_3S cement 15497B, (f) a low C_3A cement 15669, (g) a cement with no C_3A (19648), (h) C_3S , (i) C_2S , and (j) mixtures of C_3A , calcium sulfates, and quartz. Table 1 gives the computed compound compositions of the cements. The solids were shaken with the water for 5 min and then allowed to stand for 15 min at 25 C before the viscometer measurements were made. The concentrations of solids correspond to a water to solid ratio of 0.5.

The results of the experiments with the cements, C_3S and C_2S are given in Table 12. The $\Delta(S/D)/(S/D)$ values (col. 7) show a slight shear thickening behavior for pastes of cement 15366. The other cement pastes exhibited shear thinning properties of a timeindependent behavior. In the case of the clinker paste, the system was too stiff to make quantitative viscometer measurements, but a shear thinning behavior was observed. The yield values in the first cycle (col. 3) for pastes of cement 15366, high alkali cement 15698 and a high C_3S (60.1 percent) cement are 400, 320, and 435 dynes per sq cm, respectively. The apparent viscosities for these cements are 0.94, 0.94 and 1.01 dynes-sec per sq cm, respectively. Pastes containing a medium C_3A cement, a low C_3A cement, a zero C_3A cement, C_3S and C_2S exhibited much lower yield values and apparent viscosities (cols. 3 and 4). The yield values and apparent viscosities for the latter pastes ranged from 40 to 90 dynes per sq cm, and from 0.22 to 0.37 dynessec per sq cm, respectively.

In the experiments with mixtures of C_3A , quartz, and gypsum or hemihydrate, the CaSO₄ contents were 3 percent and the C_3A contents varied between 0 and 5 percent of the weight of the quartz. The weight of quartz was reduced by the weight of the C_3A and calcium sulfate added in the 43 volume percent quartz pastes. The results are summarized in Table 13.

The control experiment with 2 percent C_3A showed a relatively low yield value of 100 dynes per sq cm, an apparent viscosity of 0.43 dynes-sec per sq cm in the first

TABLE 13

EFFECT OF C₃A ON RHEOLOGICAL PROPERTIES OF A QUARTZ-CALCIUM SULFATE-WATER SYSTEM

Conc. C ₃ A (%)	1st Cycle		2nd Cycle		
	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	Yield Value f (dynes/sq cm)	Apparent Viscosity S/D (dynes-sec/ sq cm)	$\frac{\text{Over-All}}{\frac{\Delta(S/D)}{S/D}}$
Gypsum					
(1)	(2)	(3)	(4)	(5)	(6)
0	Ó	0. 20	0	0.19	-0.051
1	640	1.55	660	1.59	+0.026
3	810	1.91	830	1.91	0
5	1,380	3.26	1,290	3.00	-0.083
Hemihydrate					
0	160	0.69	180	0.76	+0.097
1	1,390	3.13	1,330	3.16	+0.010
2	1,240	2.92	1,230	2.95	+0.010
3	1,320	3.01	1,300	3.04	+0.010
5	1,420	3.41	1,450	3.35	-0.018
Control					
2	100	0.43	100	0.44	+0.023

cycle (cols. 2 and 3) and a very small shear thickening behavior (col. 6). Both the yield values and apparent viscosities for the other pastes increased with an increase in C_3A content (cols. 2 and 3). The pastes with hemihydrate exhibited, in general, a very small shear thickening behavior, whereas the $\Delta(S/D)/(S/D)$ values for the pastes with gypsum demonstrated mostly a time-independent or shear thinning behavior. An increase in C_3A content would be expected to reduce the amount of plaster set. Some evidence for this behavior is found in the experiments with hemihydrate. In these experiments the yield values and apparent viscosities increase with the amount of C_3A added, and the $\Delta(S/D)/(S/D)$ values decrease from +0.097 to -0.018. No such correlation between C_3A content and $\Delta(S/D)/(S/D)$ values was found for the pastes with gypsum. Therefore, it may be concluded that C_3A decreases the shear thickening properties and increases the yield values and apparent viscosities of pastes with dehydrated gypsum.

ANALYSIS

Normally, cement pastes stiffen gradually as the C_3S hydrates. The formation of sulfoaluminate accelerates the stiffening. When the hydration of C_3A and C_4AF occurs without the inhibiting action of the calcium sulfate, an abnormal stiffening referred to as quick set is developed. The calcium sulfates inhibit the hydration of the aluminates, but when dehydrated gypsum is present an abnormal stiffening may be produced by the deposition of gypsum crystals in a plaster set. With these concepts, it is possible to explain most of the results of this investigation.

The stiffening of quartz pastes, as shown by the yield values and apparent viscosities (Table 4), is produced by hemihydrate and soluble anhydrite. Insoluble anhydrite and gypsum produce much smaller effects. Therefore, as a result of the greater solubilities of soluble anhydrite and hemihydrate, a larger deposition of gypsum crystals occurs with these two sulfates. When more than 50 percent of the CaSO₄ in a gypsum-hemihydrate mixture is hemihydrate the pastes begin to exhibit much higher yield values and apparent viscosities (Fig. 3).

Without added calcium sulfate, a clinker paste stiffens immediately. When gypsum is present in a clinker paste, the yield values and apparent viscosities (Tables 5 and 6) are relatively low. Pastes containing hemihydrate and soluble anhydrite exhibit yield values and apparent viscosities that are much larger. The addition of insoluble anhydrite to clinker pastes produces yield values and apparent viscosities that are larger than those exhibited by any of the pastes with the other calcium sulfates. When hemihydrate-gypsum mixtures are added to clinker pastes the yield values and plastic viscosities (Table 5 and Fig. 4) decrease at first with an increase in hemihydrate content. At a 60 percent hemihydrate content the values begin to increase rapidly. These results may be explained by the concepts previously presented. Gypsum alone can provide clinker pastes with sufficient sulfate to inhibit to a large extent the rapid hydration of C₃A and C₄AF. It should be recalled that the gypsum contained about 8 percent hemihydrate. As the hemihydrate content in the mixture is increased to 60 percent (Fig. 4), the hydration of C_3A and C_4AF is further inhibited. When there is more than 60 percent hemihydrate in the mixture, the increase in yield values and apparent viscosities may be attributed to plaster set. Pastes with hemihydrate and soluble anhydrite additions show larger yield values and apparent viscosities than those with gypsum, because the higher solubilities of the dehydrated forms cause plaster set. Insoluble anhydrite, on the other hand, does not dissolve rapidly enough to inhibit completely the hydration of the C_3A and C_4AF .

The experiments with LTS No. 18 cement heated to 120 C clearly show the increases in yield values and apparent viscosities (Table 7 and Fig. 5) caused by dehydrated gypsum.

It was not possible to demonstrate a clear relationship between the shear thickening properties of fresh cement pastes and plaster set. Hemihydrate did produce a change from shear thinning to shear thickening properties in quartz pastes when the hemihydrate content in the gypsum-hemihydrate mixtures exceeded 50 percent (Table 3 and Fig. 3). In addition, hemihydrate or soluble anhydrite alone produced shear thickening flow behaviors in quartz pastes (Table 4). There is no consistent trend shown between $\Delta(S/D)/(S/D)$ values and sulfate contents. The values appear first to rise and then to decrease with increasing sulfate contents. Insoluble anhydrite and gypsum produced time-independent or slightly shear thinning properties in quartz suspensions.

Hemihydrate or soluble anhydrite caused only some indication of a shear thickening behavior in clinker pastes (Tables 5 and 6). Pastes with gypsum added exhibited timeindependent or a slight shear thickening behavior. The shear thinning behavior of a clinker paste to which insoluble anhydrite was added may be attributed to hydrated calcium aluminates because the formation of these hydrates is not very well inhibited by the slowly dissolving insoluble anhydrite.

Pastes of LTS No. 18 cement heated at 120 C showed (Table 7 and Fig. 5) a shear thickening behavior for a longer period of hydration time than that exhibited by pastes of the unheated cement. This effect may be attributed to the large amount of plaster set obtained with the cements containing completely dehydrated gypsum.

The shear thinning behavior of cement pastes seems to increase with mixing time and the temperature after mixing (Tables 8 and 9). Although 1-min mixing time is necessary to produce a shear thickening behavior, a mixing period longer than 4 min reduces the shear thickening properties. These effects may be attributed perhaps to the influences of temperature and mixing time on the rates of hydration and on the breaking up of the plaster set.

It is necessary to blend the clinker and gypsum, or soluble anhydrite, before adding them to water to produce even a small amount of shear thickening behavior (Table 10). Apparently the sulfate ions are not made readily available unless the sulfates are blended with the clinker before addition to the water.

The surface area of the cement influences the flow behavior. Shear thickening properties were only found with the higher surface area cement samples (Table 11). Nevertheless, no correlation between the degree of shear thickening behavior and surface area was observed. The influence of surface area may be attributed to the changes it produces in rates of hydration and solid-solid and solid-water interactions.

Only cement 15366 with no special characteristics exhibited a shear thickening behavior (Table 12). Shear thinning behaviors were demonstrated by the other cements, C_3S and C_2S . C_3A reduced (Table 13) the shear thickening properties of a hemihydratequartz suspension. This may be attributed to the removal of sulfate from solution by the C_3A , which reduced the degree of plaster set. The hydration of C_3A to C_4AH_{19} leads to an increase in the yield values, apparent viscosities, and shear thinning properties of quartz suspensions containing C_3A . The larger yield values and apparent viscosities produced by C_3A in hemihydrate-quartz suspensions than in gypsum-quartz suspensions is probably due to the presence of plaster set and a larger amount of sulfoaluminate crystals. The shear thinning behaviors of the cement pastes increased with the C_3A and C_3S contents of the cements (Table 12).

Whereas for quartz-calcium sulfate suspensions the relation between plaster set and shear thickening behavior was clearly demonstrated, the relation for the clinkercalcium sulfate system is not nearly so clear. Nevertheless, there is strong indication in the data presented that such a relation probably does exist. However, the clinkercalcium sulfate system is so complex and there are so many factors that have bearing on the problem, that only further research could lead to a full understanding of the shear thickening behavior. One factor, for example, on which no information exists at present is the influence of the sulfoaluminate on the flow properties of fresh pastes; it is possible that sulfoaluminates play an important role in early abnormal stiffening.

In future rheology studies both suspensions of components and mixtures of the components of cement should be examined. Such studies will lead to a better understanding of the factors that influence the flow behaviors of fresh cement pastes.

Mixtures of gypsum and mineral anhydrite have been used to reduce abnormal stiffening (2). In this investigation it was demonstrated that in the range 40 to 60 percent hemihydrate content in hemihydrate-gypsum additions to clinker pastes, the lowest yield values and apparent viscosities were found (Table 5 and Fig. 4). Therefore, it is possible to conclude that when mixtures of gypsum and the mineral anhydrite are ground with clinker, hemihydrate is produced by dehydration of some of the gypsum. When the proper mixture of the two sulfates is added to clinker there is sufficient soluble hemihydrate to react immediately with the C₃A to inhibit quick set, but not sufficient to produce a plaster set. The mineral anhydrite and the remaining gypsum in mixtures could then react slowly with the C_3A .

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