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See version note; deposited in CURVE May 2014

Original citation & hyperlink:

Claisse, P.A. , Lorimer, P. and Al, M. (1999). The effect of changes in cement on the properties of cement grouts with superplasticising admixtures. In J. G. Cabrera and R. Rivera-Villarreal (Eds), *International RILEM Conference on the Role of Admixtures in High Performance Concrete* (pp. 19-33). Cachan Cedex: RILEM publications SARL.
http://www.rilem.net/gene/main.php?base=500218&id_publication=10&id_papier=1182

Additional note:

Paper presented at the International RILEM Conference on the Role of Admixtures in High Performance Concrete, held March 21-26 1999, Monterrey, Mexico.

Version note:

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THE EFFECT OF CHANGES IN CEMENT ON THE PROPERTIES OF CEMENT GROUTS WITH SUPERPLASTICISING ADMIXTURES

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ABSTRACT

Cement grouts are used for a wide range of applications in the construction industry. These grouts require a high workability and superplasticising admixtures.

It has been found that some cement pastes and mortars perform better (i.e. flow faster and are workable for longer times without bleed and segregation) in some countries than in others. These problems may be solved on an empirical basis, but in this project the mechanisms involved are investigated in order to predict the performance of the cement pastes more effectively.

To do this, a relationship between the rheological properties of the cement paste and the chemical components, especially the different kinds of sulphates, of the Portland cement is established. First a relationship between the simple industrial tests, such as the mini slump flow cone and the efflux flow cone, and the rheological properties obtained by a rheometer has to be established. Subsequently, as set of cements with different sulphates in them were tested in the rheometer.

The results show that the use of gypsum gives substantially superior performance compared to anhydrite.

1. INTRODUCTION

Cement grouts are used throughout the world for different applications including structural void filling, rock grouting, flooring and many others. In order to achieve the workability demanded by many of these uses the grouts are normally made with superplasticising admixtures. Pre-bagged products offer the advantages of ease of use and superior quality control and are now highly developed products containing various mineral additions in combination with admixtures and cement. Due to their substantial bulk these products are often manufactured locally using locally produced cements. The research reported in this paper has been undertaken to enable different cements to be classified to determine their suitability for use in flowing grouts.

There are a number of different methods of flow measurement which are in current use for cement grouts. These methods are described below. They generally require substantial quantities of grout and only provide data on one specific rheological property. In this project an industrial rheometer has been used because this uses smaller samples and gives a more complete picture of the flow properties of the grout. In order to justify the use of this machine a number of tests have been carried out to correlate its results with the standard flow measurement tests.

In order to determine the effect of different cements on the flow properties two different approaches may be used. Either artificial cements with specific attributes may be tested or commercial cements may be chemically analysed and the results of the chemical analysis may be correlated with the flow properties. In this paper the results of an investigation using the former approach are reported. Cements have been made up with different sulphates in them and the effect of the type of sulphate on the flow properties has been analysed.

2. RHEOLOGICAL MODELS

Numerous studies of the rheological properties of cement pastes have proved these properties to depend on many factors. The most frequently cited are the water / cement ratio (w/c) [1,2], specific surface area, mineral composition [1,3,4], conditions during measurements and their duration [1,5] (i.e., time dependency, mixing time and mixing intensity) and temperature [3,6]. It has been shown that the most important are the w/c ratio and specific surface area [1].

The rheology of cement pastes is very complex because of the interplay of various physical and chemical processes arising from both the solid and the fluid phases [6,7]. Interparticle forces between the solids result in a yield stress (shear strength) that must be exceeded in order to initiate flow. Below the yield stress, the cement paste behaves as a (weak) solid. Thus, the yield stress can be regarded as the material property that represents the transition between solid-like and fluid-like behaviour. Cement pastes are chemically reactive during the hydration process, in a way that influences their behaviour and introduces changes in their rheology over time [6].

The shear rates (τ) versus the shear stress ($\dot{\gamma}$) curves obtained with viscometers depend strongly on the flow history of the cement pastes and also on the apparatus used [4]. Depending on the cement composition and experimental conditions, cement pastes exhibit flow behaviour approximating any of four main types (Fig. 1) [4]:

1) Newtonian
2) Bingham plastic
3) Pseudoplastic
4) Dilatant

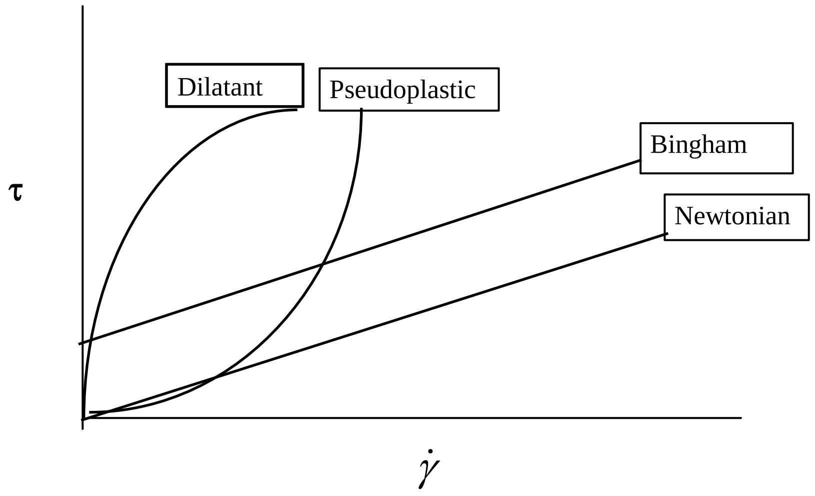

Fig. 1 Flow curves of various types of fluids

The flow curves may indicate reversible, or thixotropic (shear thinning), or anti-thixotropic (shear thickening) behaviour depending on factors such as preparation conditions and times of measurement [4,8]. Banfill [9] points out that Bingham plastics may show time-dependent behaviour in the form of a reduction in shear stress at a constant shear rate that is more severe at higher shear rates. If the thinning is permanent this behaviour is called irreversible structural breakdown, but if the structure reforms after shearing has stopped, the material is said to be thixotropic. In either case the reduction takes place as a result of the work of shearing applied during the course of the test and the flow curve of shear stress against shear rate exhibits hysteresis. The yield stress and plastic viscosity at any instant depend upon the previous shear history of the sample, and this includes the shearing during handling as well as during testing the sample. A hysteresis loop gives evidence only that the structural breakdown has occurred during the test and an infinite number of different loops are possible depending on the experimental details. Therefore hysteresis loops cannot unambiguously characterise the structural breakdown in Bingham plastics. However, when the structure has been fully broken down, the downcurve (decreasing shear rate side of the loop) conforms to the Bingham model and the yield stress and plastic viscosity may be determined from it. Alternatively, if the sample preparation and handling procedures used are reproducible the amount of structure remaining in the material at the time of testing is constant from one test to another. In this case the yield stresses and plastic viscosities determined will be reliable indicators of the flow properties on a relative quantitative scale [9].

For a Newtonian fluid, the shear stress, τ, is proportional to the shear rate, $\dot{\gamma}$, where the proportionality constant, μ, is the viscosity of the fluid (μ is dependent only on temperature and pressure) [8].

$$\tau=\mu\dot{\gamma} \qquad (1)$$

Cement pastes rarely display Newtonian flow curves, but can be transformed as such with addition of sufficient amounts of specific water-reducing chemicals [2,10-17]. There are many different rheological models that can be used to characterise cement pastes. The flow curve for cement paste has been fitted to several different mathematical forms, all of which indicate the existence of a yield stress:

Bingham	$\tau= \tau_0 + \mu_p\dot{\gamma}$	[18,19]	(2)
Herschel-Bulkley	$\tau= \tau + A\dot{\gamma}^{n}$	[18,20]	(3)
Robertson-Stiff	$\tau= A(\dot{\gamma} + C)^B$	[18,12]	(4)
Ostwald- De Waele	$\dot{\gamma} = B \sinh\{(\tau - \tau_0)/A\}$	[18,22]	(5)

Where τ is the shear stress, τ_0 the yield stress, μ_p the plastic viscosity, $\dot{\gamma}$ the shear rate, A, B and C are constants. In this project, however, the model was kept as simple as possible. Because the geometry of the media that is to be grouted is so difficult to define, a complex rheological model is not considered appropriate at the present stage. The simplest rheological model that includes a yield stress is the Bingham model. Although simple, it has been reported by many authors that this model is appropriate for some cement grouts and slurries [7,23-28].

3 EXPERIMENTAL METHODS

3.1 Mixing

The mixing procedure must be consistent and it is important that the mixing equipment be appropriate (i.e., high-speed mixers). Inadequate mixing will result in non-reproducible properties [6]. Banfill [6,23] showed that a mixing time of about five minutes is sufficient to obtain constant properties for both the yield stress and the plastic viscosity [6]. 5 kg of powder was used. The mixing was carried out in a medium size Hobart mixer for five minutes at speed 1, which is the lowest speed. High speed mixing was used using a small shear mixer, 300g samples only, for five minutes at 1100 rpm.

3.2 Flow Tests

Four tests were made to characterise the samples at 20 ± 2^{o}C

1. Flow Cone Test (small slump, FC): This test measures the spread of a cement paste in terms of centimetres, the more spread the cement paste has the more workable it is. A Brass cone, as specified in BS 6463 : Part 4 : 1987 [29], and a melamine laminated wooden flow table is used. The cone was filled with the material, and was then lifted. After allowing the cement paste to spread, the diameter was taken and recorded.

2. Efflux Flow Cone Test (EFC): This test measures the workability and flow of a cement paste in terms of seconds, the faster the cement paste the more workable it is. A stainless steel cone, as described in ASTM C 939 – 94a [30], is filled with a cement paste, then the cement paste is released and the timing started. At the first break of the cement paste's flow, and the time is recorded.

3. Flowmeter Test (FM): This test measures the velocity of a cement paste in terms of centimetres per seconds. The tundish of the small flow trough is filled with the cement paste, then the timing started when the plug is pulled. The maximum distance that the cement paste made was recorded with the time.

3.3. The Rheometer

This test measures the viscosity, the shear rate and the shear stress of a cement paste. A Rheology International Series 2 viscometer Model RI:2:M [31] was used. The viscometer was chosen with a medium spring to be able to get more accurate results at low speeds. The Bingham model was used to determine the plastic viscosity and the yield value. It should be noted that the rheology of Bingham plastics is not very sensitive to temperature, but the rate of change of rheology with time in a chemically reacting system containing cement is affected by temperature. It is preferable to standardise both the test temperature and the time after mixing at which the test is done [32]. All the tests reported here were done at 20 ± 2^{o}C. In operation the rheometer rotates a sensing element in a fluid and measures the torque necessary to overcome the viscous resistance to the movement. This is accomplished by driving the immersed element, which is called a spindle, through a spirally wound spring via the pivot point assembly. The percentage torque wind-up of the spring due to the viscosity of the fluid is the primary data reference. As the sensing element is mechanically and electronically calibrated to give a known resistance at “full scale deflection” (approx. 70 degrees deflection), and as the spindle has known rheological properties, the percentage deflection allows derivation of other necessary viscosity parameters [33]. A four-bladed vane spindle was used. The vane had four rectangular blades of radius, Rv = 9.5 mm, and height h = 38 mm and was placed in a cup of radius, 27.5 mm centrally mounted on the lower plate. Because of the restricted torsion of the spring, that moves the spindle, the spindle was smaller than recommended the ASTM [34] (Rv=19.05 mm and h=76.2 mm). The shear stress, τ, was calculated from the torque using the following conversion formula [34]:

$$\tau = 3T/(2\mu\,(R_V^3 + 3\,R_V^3 h)) \qquad (6)$$

Where T is the torque. The geometry of the spindle was chosen to achieve best results. In addition, it would be expected that the vane would be more reliable than the other geometries because the cement paste sample is sheared within itself rather than at the surface of the moving member. However, to achieve the objective of providing quantifiable energy input during the course of testing, the shear rate must be known accurately. This not possible with the vane because the position of the sheared plane and hence the dimensions of the sheared zone are not known accurately.

The computer-operated rheometer was programmed to cycle through a measurement program. The cycle started with speed 0, increased by 0.5-rpm/5 sec up to 10 rpm then decreased down to 0 by 0.5 rpm/5 sec. There were four readings at speed 10, so the test took 215 seconds.

By plotting the shear stress against the shear rate, the rheological properties of the cement paste were defined. The plastic viscosity and the yield value were obtained from the down curve of the graph. A typical output is shown in figure 2.

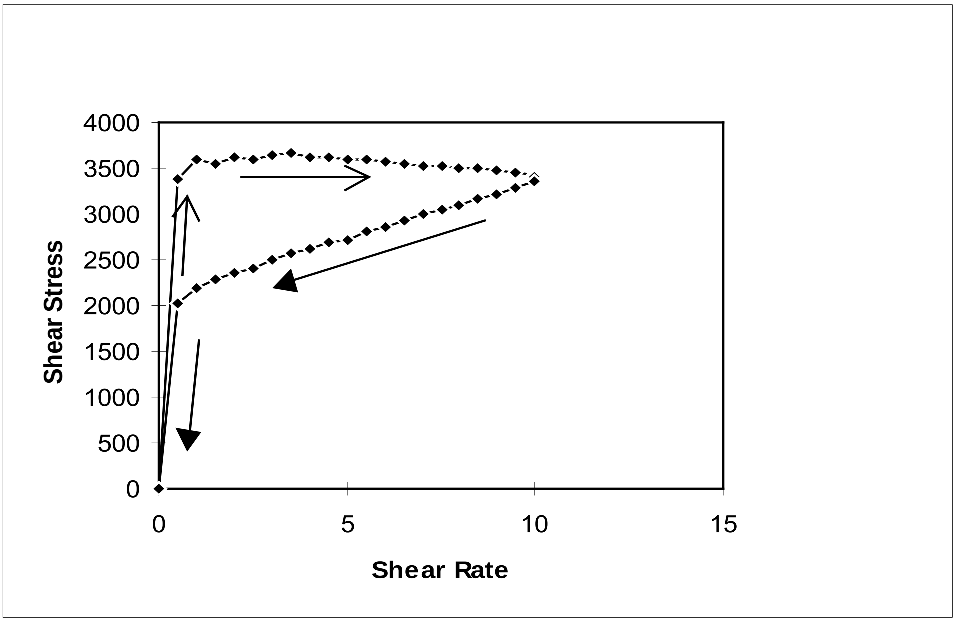

Figure 2, Typical Rheometer Output

4 EXPERIMENTAL DESIGN

4.1 Materials

Cement
Commercial cement was obtained with the following specifications:

The specific surface area was 360m^2/kg. (Measured with “R & B Automatic Permeability Apparatus” which was used according to the manufacturer’s standard).

The oxide contents are shown in Table 1 (measured with XRF):

TABLE 1. Oxide percentages in Cement

SiO_2	21.5
TiO_2	0.23
Al_2O_3	4.57
Fe_2O_3	2.34
Mn_3O_4	0.10
MgO	1.01
CaO	66.73
Na_2O	0.15
K_2O	0.67
P_2O_5	0.24
SO_3	2.30
LOI	0.60
Total	100.09

Clinker

A cement clinker without any added calcium sulphate was obtained from the same works as the cement. This clinker was ground to the same fineness as the cement in a laboratory mill.

Sulphates

Two different hydrates of calcium sulphate were obtained to blend with the cement clinker. These were pure samples obtained from laboratory chemical suppliers and were as follows:

Hydrate	Common Name	Molecular Formula
Anhydrite	Anhydrite	$CaSO_4$
Dihydrate	Gypsum	$CaSO_4.2H_2O$

Where the cement was made up from clinker the calcium sulphate was added at 5% by weight.

Admixtures

The following concrete admixtures were obtained from commercial suppliers:

Sodium Melamine Formaldehyde resin (SMF),
Sodium salt of Sulphonated Naphthalene Formaldehyde superplasticiser (SNF)
Calcium Lignosulphonate plasticiser (LS).

4.2 Mix Design

The tested samples contained a superplasticiser, cement and water. The following mix design was used:

Cement	99.70%
Superplasticiser	0.30%
w/c	0.40

4.3 Test Programme

The tests were made after 3 and 14 minutes after mixing. Each test was made, at least twice, on a sample that had been standing undisturbed from the completion of mixing until testing.

The full experimental programme is shown in Table 2:

TABLE 2 Number of Tests in the Experimental Programme

	Cement	Cement	Cement	Clinker + 5% Gypsum	Clinker + 5% Anhydrite
Plasticiser	SNF	SMF	LS	SMF	SMF
w/c	0.4	0.4	0.4	0.4	0.4
Mixing	L Speed	L Speed	L Speed	H Speed	H Speed
Flow Cone	2	2	2	0	0
Efflux Flow Cone	2	2	2	0	0
Flowmeter	2	2	2	0	0
Rheometer	2	2	2	2	2

5. RESULTS AND DISCUSSION

5.1. Relationship between different Flow Tests

The flow tests results are shown in Table 3,

TABLE 3 Flow Test Results

	Plasticisers Used					
	SMF	SMF	SNF	SNF	LS	LS
Test Time/min	3	14	3	14	3	14
Yield Value	2230	2545.7	1524.9	2355.3	2100.3	Stiff
Viscosity	89.284	121.29	32.197	68.635	58.69	Stiff
Flowmeter/s	22	21	5	18	24	24
Flowmeter/cm	52	57	70+	55	69	50
Flowmeter(cm/s)	52/22	57/21	70+/5	55/18	69/24	50/24
Velocity	2.364	2.714	14	3.056	2.875	2.083
Efflux Flow Cone/s	28	30	19	22	21	52
Flow Cone/cm	20	19.5	22	20	21	17

It was found that the superplasticisers affect the properties over a limited period of time, and that the plastic viscosity and the yield value will increase with time, these results correspond to Hakansson's results [6]. It is believed that the metal ions that are produced during the hydration process are responsible for this phenomenon [6].

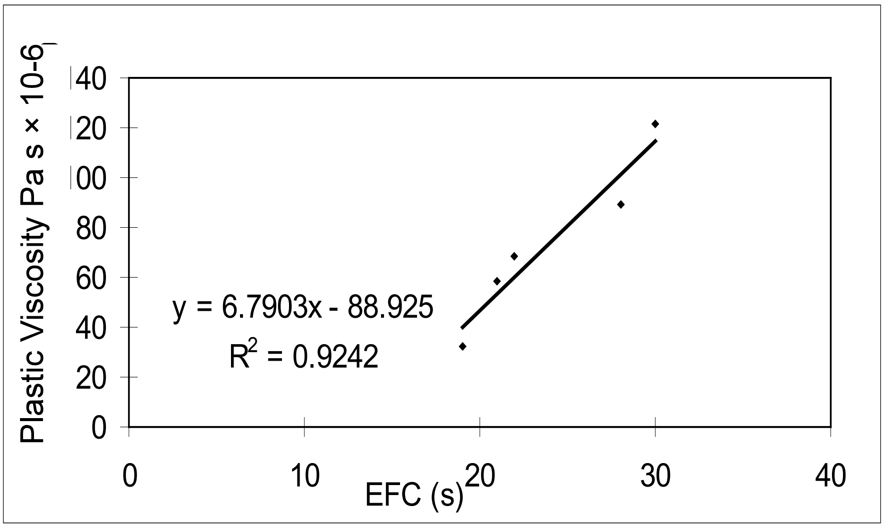

Fig.3 Plastic Viscosity vs Efflx Flow Cone

Many of relationships between the measured variables were as expected. The lower the plastic viscosity, the faster the paste goes through the EFC cone and the more spread it will have through the flow cone test (Fig.3 & Fig.4)

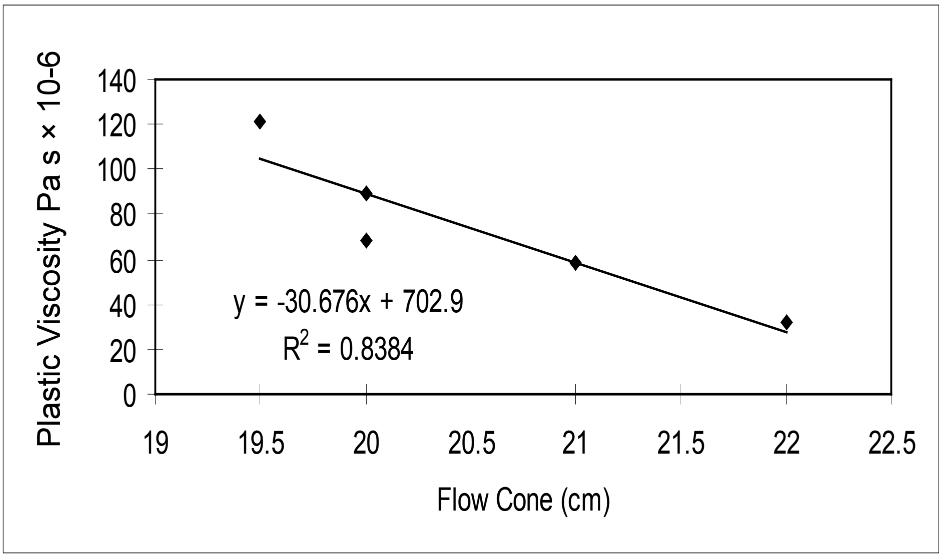

Fig. 4 Plastic Viscosity vs Flow Cone

Figure 5 shows that, as expected, the flow cone results correlate better with the yield than with the plastic viscosity.

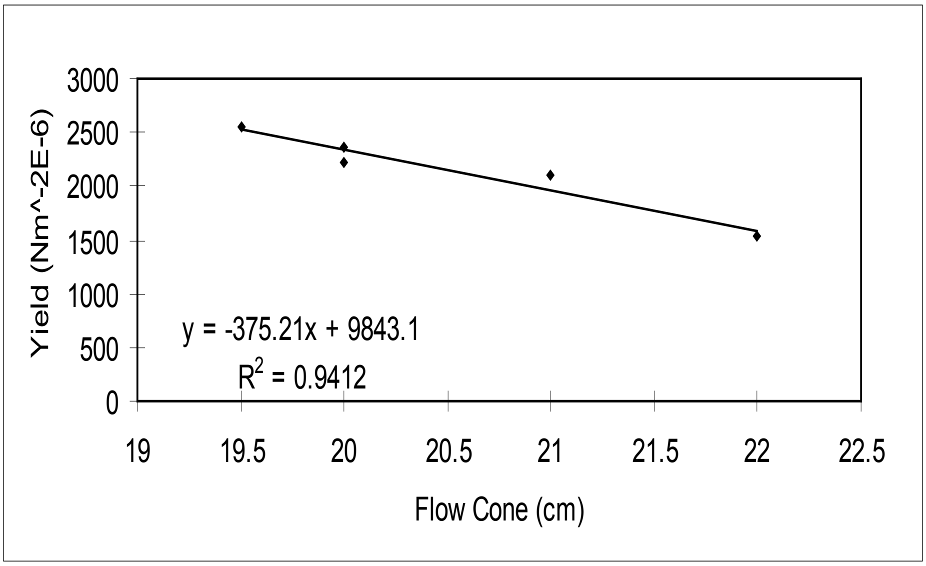

Fig.5 Yield vs Flow Cone

The flow cone test measures the “static” viscosity that is relating to the yield value.

The EFC test was affected by the standing time and by the type of superplasticiser more than the flow cone test, which makes it relate more to the thixotropy of the flow curves.

The relationships in all of the graphs correlate to a 2% confidence limit (all R^2 values are equal / higher than 0.7783).

5.2. Effect of Sulphate Type on Flow Properties

It was found that the types of sulphates in the cement affect the rheological properties of the cement pastes. The results are shown in Table 4.

TABLE 4 Effect of Sulphates

Plasticiser	Property	Gypsum	Anhydrite
SMF	Viscosity	12.7	105.5
SMF	Yield	575.2	2524.2
SNF	Viscosity	6	68
SNF	Yield	102.6	1611

It may be seen that type of sulphate in the cement has a major effect on the viscosity and yield measured with the rheometer.

The anhydrite gave viscosities and yield values that were consistently substantially greater than the gypsum. This was expected because gypsum generally gives superior workability in cements without admixtures [35]. The effect on the viscosity and the yield was, on average, a factor of 10 that is quite sufficient to cause the observed difficulties with the flow of grouts.

In order to confirm these observations and identify other factors that may contribute to the workability of the grouts a number of different commercial cements will be tested in a subsequent phase of this project. These cements will all be analysed to determine their anhydrite content and this will be correlated with their measured workability.

6. CONCLUSIONS

From the graphs above, the following relationships were concluded:

1. Plastic viscosity is inversely proportional to the EFC.

2. Plastic viscosity is directly proportional to the Flow Cone.

3. Yield is directly proportional to the Flow Cone.

4. The type of plasticiser affects the workability of cement pastes. SNF made the cement paste more workable than SMF and ligno Sulphonate, while SMF performed better than The Ligno Sulphonate.

5. The plastic viscosity and the yield value increase with time.

6. It was found that Gypsum makes the cement pastes more workable than Anhydrite.

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