Control of Fluid Properties of Particulate Grouts:
Part 1 - General Concepts

Chris Gause[1] and Donald A. Bruce[2], Member

Abstract

Historically, the challenges posed to particulate (i.e., cement-based) grouting in certain adverse environments in the geotechnical construction field have not been reliably, satisfactorily or economically solved. However, in recent years, extremely significant developments in the understanding of hydration and rheology control have been made, and which now offer extraordinary potential to the practitioner. Equally important advances have been made with grout formulations to resist washout and increase formation penetrability. This paper is the first of two companion papers, and provides general background to these new developments.

Keywords

Particulate grout mix designs; grout admixtures; hydration control; rheology control; antiwashout properties; microfine cement; lightweight grout.

1   Introduction

From the first application of grouting technology in France almost 200 years ago, the most common grout component, other than water, has been some type of Portland cement. This has reflected material availability and cost factors, as well as a high degree of comfort in, and acceptability of, the hardened

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[1]Sales Manager, Underground Division, Master Builders Technologies, Cleveland, Ohio
[2]Principal, ECO Geosystems, Inc., Venetia, Pennsylvania.

product. However, increasingly challenging demands have been placed on the construction industry in general and grouting technologies in particular (Bruce, 1995). As a consequence, the difficulties inherent in the use of particulate grouts in certain physical environments have been accentuated and until recent years had not been satisfactorily, reliably or economically resolved.

This paper introduces the recent advances which have been made in cement grout material technology, particularly in the fields of hydration and rheology control. It further outlines developments in washout resistance, enhanced penetrability via finer grinding of cement particles, and the use of foaming agents in grouts. These developments have been undertaken largely by the manufacturers and suppliers of cement based products and associated additives. In line with A.S.C.E. policy, trade names are omitted from the paper. The authors can be contacted to provide more specific information.

2   Materials For Hydration And Rheology Control

2.1 Hydration Control

2.1.1   Background

Setting and hardening involve the combination of water and cement minerals to form a rigid matrix called calcium silicate hydrate (CSH) gel. This is conventionally referred to as the process of hydration. There are four primary minerals which participate in the hydration process (Table 1).

Chemical Name	Full Chemical Formula	Shorthand Formula	Typical Proportions in Type I Portland Cement
Tricalcium Silicate	$3CaO\ SiO_2$	C_3S	50 - 60 %
Dicalcium Silicate	$2CaO\ SiO_2$	C_2S	24 %
Tricalcium Aluminate	$3CaO\ Al_2O_3$	C_3A	11 %
Calcium Aluminoferrite	$3CaO\ Al_2O_3$ Fe_2O_3	C_4AF	8 %

Table 1.   The four major components of Portland cement.

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In addition, gypsum ($CaSO_4$) is blended in during the grinding process in varying amounts. The most significant reaction involves water and C_3S to produce calcium hydroxide and a poorly crystalline hydrated calcium silicate. The C_3S makes up the largest part of normal Portland cement and is the primary producer of strength as the hydration process occurs. When water is first introduced, a sharp rise in heat generation occurs due to the wetting of the cement particles and initial hydration of C_3A in particular (Figure 1). These reactions produce a rapid release of calcium ions into solution which creates the CSH gel around the cement particles. This intense process lasts for only a few minutes after which a slower generation of heat continues. C_2S also reacts with water to form CSH gel, but this reaction is much slower and contributes primarily to later strength development. At this time the C_3A and gypsum are also reacting to form a protective crystalline crust of ettringite around the C_3A. The
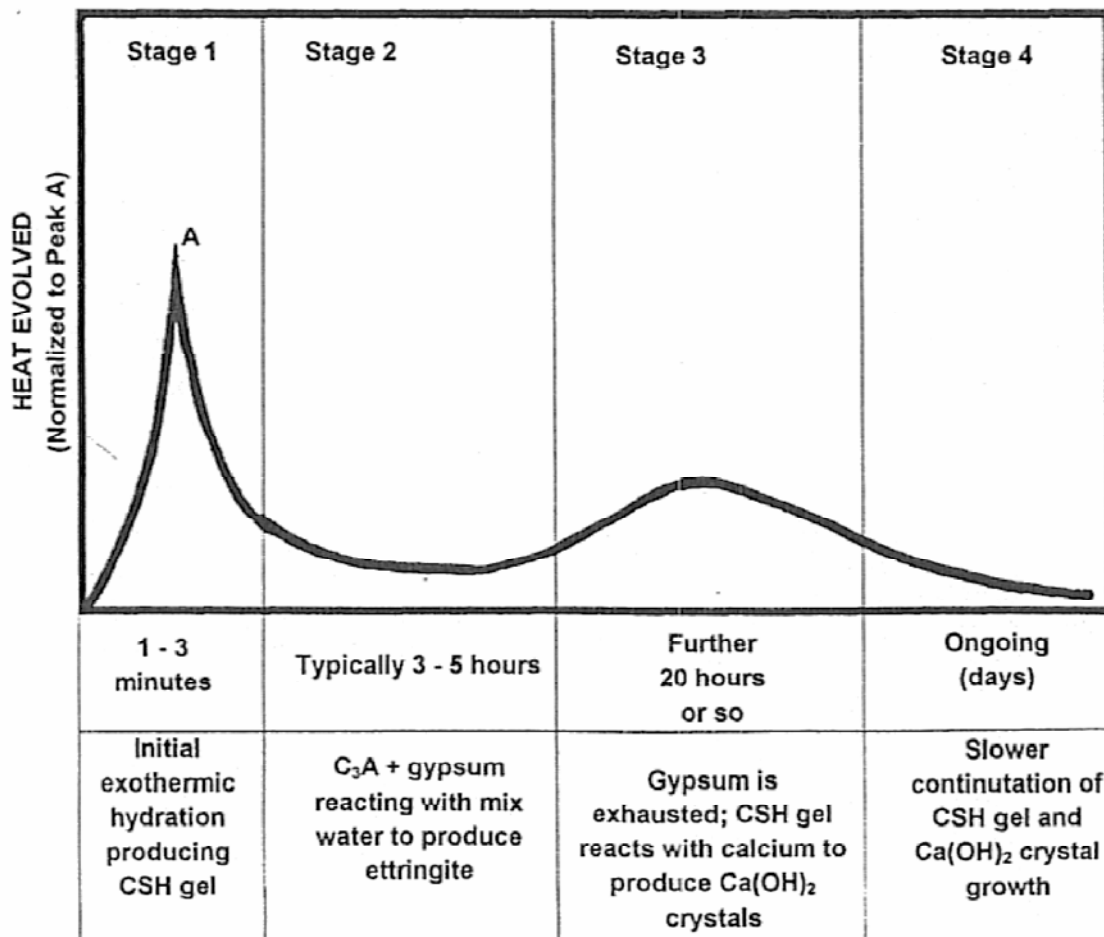
Stage 1	Stage 2	Stage 3	Stage 4
1 - 3 minutes	Typically 3 - 5 hours	Further 20 hours or so	Ongoing (days)
Initial exothermic hydration producing CSH gel	C_3A + gypsum reacting with mix water to produce ettringite	Gypsum is exhausted; CSH gel reacts with calcium to produce Ca(OH)₂ crystals	Slower continutation of CSH gel and Ca(OH)₂ crystal growth

HEAT EVOLVED (Normalized to Peak A)

Figure 1. Stages of cement hydration: neat cement-water system.

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ettringite prevents further hydration until all of the gypsum is exhausted, at which time the unreacted C_3A will resume reaction. The formation of the ettringite barrier determines working time or potlife when using Portland cement grouts. C_4AF also reacts with the water to give C_3A although not so rapidly.

If gypsum were not added to the cement, the reaction between C_3A and water would be one of a flash set, or very rapid stiffening. After several hours (3-5) the gypsum is exhausted and the CSH gel reacts with calcium to form larger amounts of the CSH gel. It is during this period that crystallization of calcium hydroxide occurs creating needle-like crystals which intimately bond the cement particles to one another (Figure 2a). At this phase of hydration setting has likely occurred, and is followed by hydration and crystal growth at a much slower rate. The principal components of the whole complex series of cement and water reactions are, in order of abundance, calcium silicate hydrate, calcium hydroxide, and a compound whose formula is $3CaO.Al_2O_3.3CaSO_4.32H_2O$ (reaction between gypsum and C_3A).

2.1.2   New Approach to Hydration Control

The recent development of a liquid, chloride-free, two component hydration control system eliminates the problems of inconveniently short workability times for concretes and grouts. The two components consist of a "stabilizer" and an "activator". The modified, hydroxylated, carbosilic acid based stabilizer arrests the cement hydration process by forming a protective barrier around the cement particles (Figure 2b). It can control hydration of all cement minerals for up to 72 hours. It is important to note that its action is different from that of conventional retarders. Conventional retarders such as those based on glucoses do not work with all cement minerals and in fact while retarding one mineral they can actually accelerate another. At high dosages some conventional retarders can even cause very rapid or flash setting.
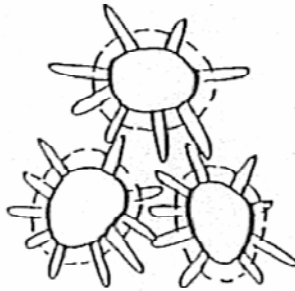
2.1.3   Fluid Properties

The stabilizing additive generally has minimal impact on the fluid properties of concrete or grout, although because of its dispersive tendency, it does slightly increase fluidity at normal doses.

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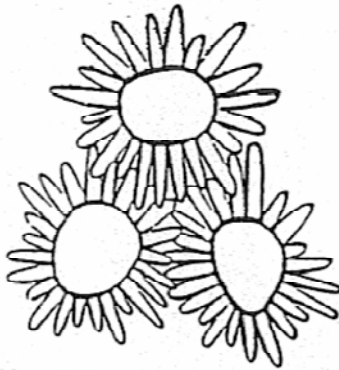
a.   Products of normal cement hydration
     flocculate.
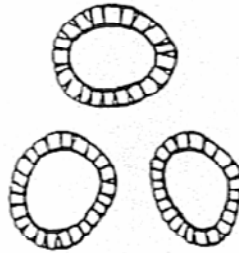
b.   Effect of stabilizer: creation of
     protective barrier to prevent
     hydration.

c.   Effect of activator: dissolution of
     protective barrier, commencement of
     crystallization.

Figure 2. Simplified illustration of crystal growth
          stages.

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2.1.4   Setting Properties

The grout containing stabilizer can be reversed (i.e., can be allowed to recommence hydration) at any given time by adding the second component of the hydration control system: an inorganic alkaline activator. The activator is added to break down or dissolve the barrier previously provided by the stabilizer (Figure 2c) and so allows for normal hydration to resume (Figure 3). The activator dosage can be adjusted to provide a predetermined set time within the range of several minutes to several hours. This system can be easily incorporated into any concrete or grout formulation. Provided some preliminary information is obtained and recorded, for example on ambient conditions, cement type and other admixtures used, tests to determine dosages for stabilization and activation can be quickly performed.
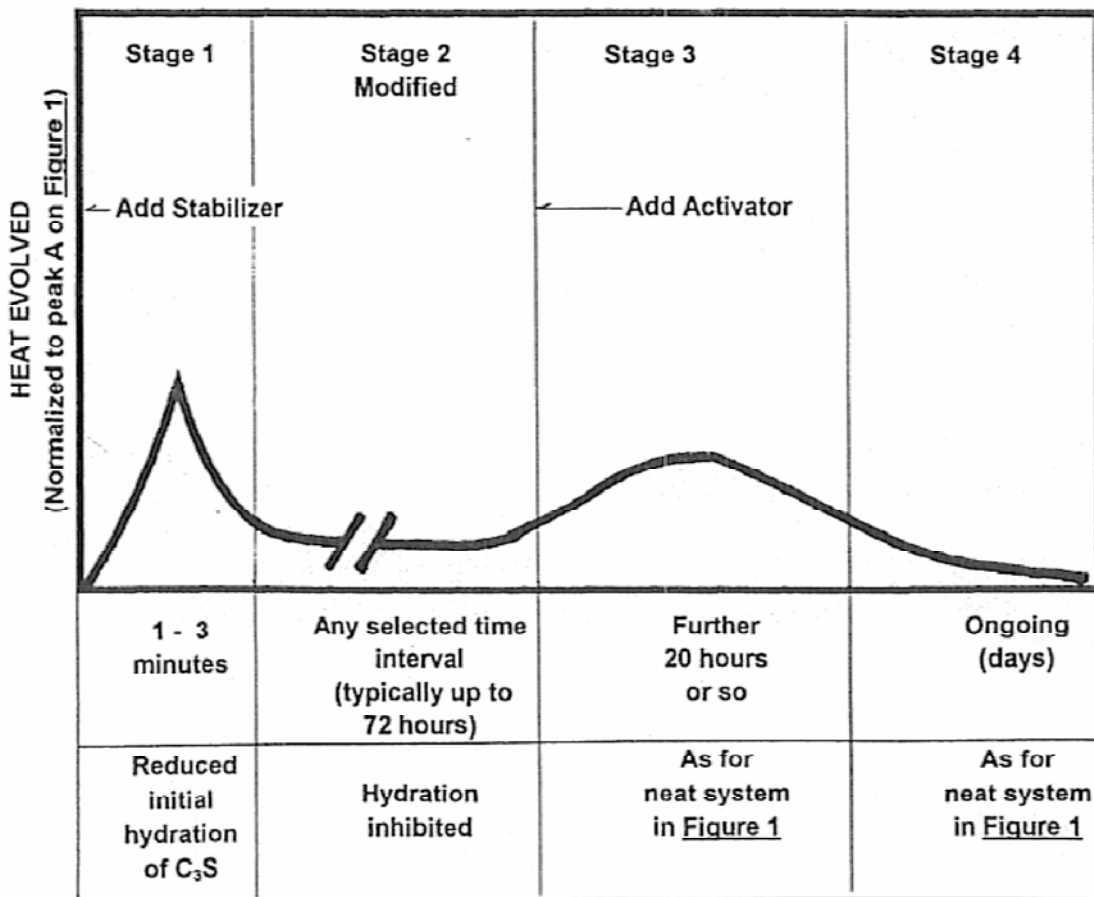

Stage 1	Stage 2 Modified	Stage 3	Stage 4
1 - 3 minutes	Any selected time interval (typically up to 72 hours)	Further 20 hours or so	Ongoing (days)
Reduced initial hydration of C_3S	Hydration inhibited	As for neat system in Figure 1	As for neat system in Figure 1

Figure 3. Stages of cement hydration: showing the impact of stabilizer/activator additives.

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2.1.5   Grout Set Properties

The use of this hydration control system influences only fluid behavior: there is no detrimental effect on long term, set properties. Indeed, it has been found that since basically "fresh" grout is being placed, the quality of this grout is therefore chemically advantageous, and so when compared to normally-aged grout, the set properties are usually superior.

2.1.6   Advantages

The hydration control system has value in many aspects of underground construction. With regard to tunneling and mining, the elapsed time from which a concrete or grout is manufactured until it reaches its point of placement can be considerable. Now stabilized concrete, shotcrete or grout mixes can be batched and transported to the point of placement, where they can be maintained in a state of gentle agitation until required for placement without fear of overheating, or having to be discarded due to age, or worse, setting up in the transport or storage equipment.

2.2   Rheology Control

2.2.1   Background

The rheologic properties of a particulate grout are conventionally reflected in three parameters: plastic viscosity, cohesion, and internal friction. Figure 4 illustrates two laws of rheological behavior: curve (1) is typical of a purely viscous fluid (Newtonian), like water: curve (2) represents the behavior of a Binghamian fluid, characterized not only by viscosity but also by cohesion. Neither of these two curves shows internal friction. If they did, and the shear strength depended also on the fluid pressure, the behavior would be as shown in Figure 5. Cement grouts are not true solutions but are particulate suspensions in water. When these suspensions are stable (i.e., during grouting the water does not separate from the cement) they will behave like a Binghamian fluid. If, however, the mixes are unstable, they will behave unpredictably, being either a Newtonian or Binghamian fluid with internal friction. As soon as internal friction occurs in the mix, injection is no longer practical.
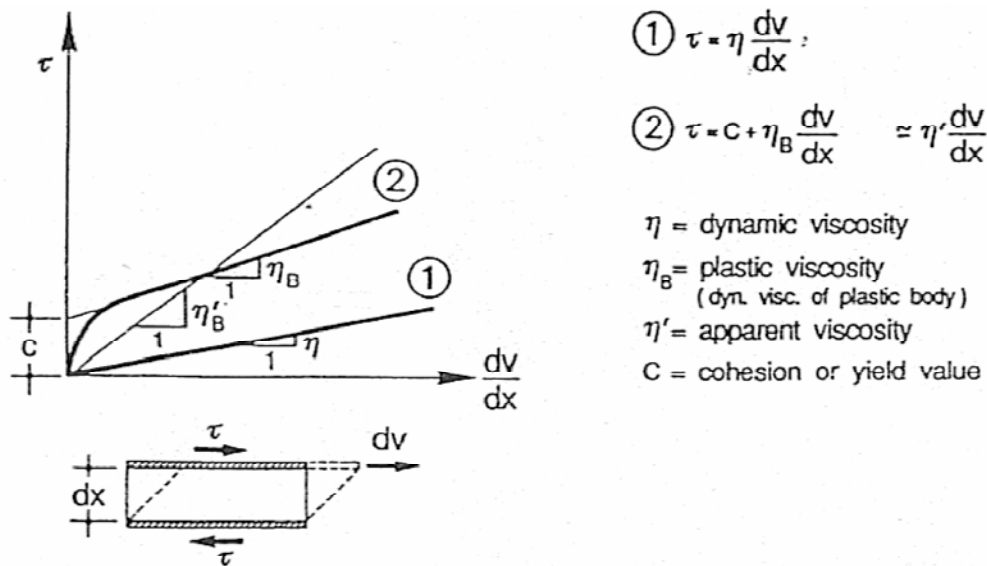
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$$\text{①} \quad \tau = \eta \frac{dv}{dx} \; :$$

$$\text{②} \quad \tau = C + \eta_B \frac{dv}{dx} \quad \simeq \eta' \frac{dv}{dx}$$

η = dynamic viscosity

η_B = plastic viscosity
(dyn. visc. of plastic body)

η' = apparent viscosity

C = cohesion or yield value

Figure 4. Rheological laws for (1) Newtonian fluid and
(2) Binghamian body.

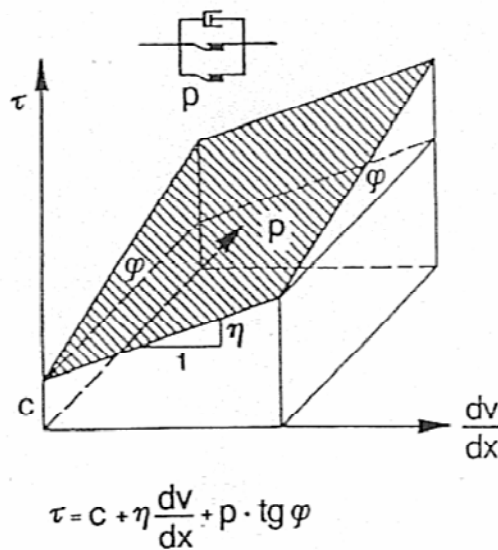$$\tau = C + \eta \frac{dv}{dx} + p \cdot tg\,\varphi$$

Figure 5. Rheological surface of a Binghamian body with
internal friction (Lombardi, 1985).

The rheology of particulate grouts is heavily
influenced by several factors, principally, and in
descending order of importance, the water/cement ratio,
the cement composition, and the cement specific surface
area.

Accelerators have long been used to shorten setting
times, but even they may result in longer setting times
than are desirable in certain situations. To further

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shorten set times, sodium silicate solution has been commonly used. Sodium silicate reacts quickly with the calcium ions liberated during initial hydration to form a calcium silicate hydrate gel (CSH). However, this is a very aggressive reaction and tends to lead to flash set, although this may indeed be the goal in certain circumstances.

Conversely, whenever very fluid grouts are required, there is still a tendency to simply add more water to the mix. However, this leads to high bleed (or instability) and inferior hardened grout properties, especially strength, durability and permeability. The role of dispersants is well known, as a means of improving rheology by reducing apparent viscosity. Cement particles have both positive and negative charges, which therefore cause a tendency to form large agglomerations. As a result, hydration can only occur around the periphery of these groups to the detriment of the fluid properties of the mix. Dispersants also alter charges on the particles, causing them to all be negative, and so they repel each other thus presenting the maximum surface area for hydration (Figure 6). Also since these particles have been efficiently dispersed and hydrated, the pore space is reduced, and so the crystals from adjacent particles can interlock more regularly and more strongly. This in turn leads to much enhanced set properties, especially strength and durability.
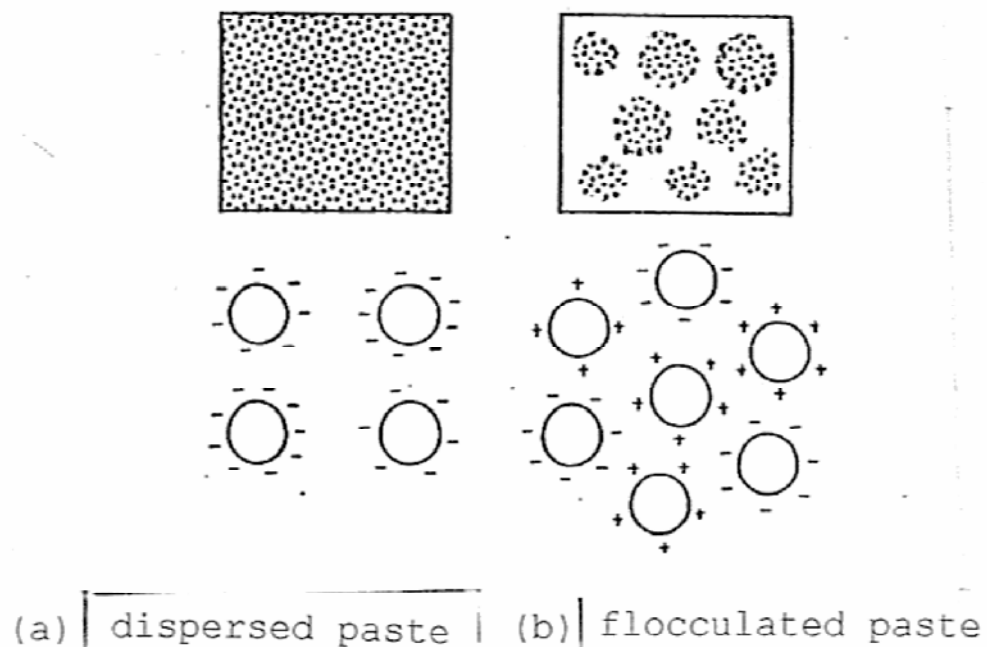

(a) | dispersed paste | (b)| flocculated paste

Figure 6. The action of dispersants on influencing grout particle polarity.

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2.2.2   New Concept of Rheology Control

New research has been conducted primarily to satisfy the demands of the tunnel precast segment backfilling market, namely the need to reliably place grout, in well defined locations, which will immediately provide load transfer and water stopping properties. This research has led to the development of a cementitious grout modified by both a napthalene-based dispersant and special consistency control admixtures. Table 2 shows the composition of a typical backfill mix.

Cement	200 - 250 kg
Flyash	200 - 250 kg
Sand 0-4 mm	1400 - 1500 kg
Water	300 - 320 kg
Dispersant	4 - 6 kg
Consistency control admixture	2 - 5 % of cementitious portion

Table 2.   Typical   backfill   mix   composition, incorporating rheology control admixtures (Per cubic meter of mix.)

The base grout components are mixed as usual at the batching station: the dispersant facilitates production of a fluid but low water content grout. This will ensure high early strength development. The dispersant also includes one of the consistency control admixtures, a long chain polymer. The grout is then pumped to the point of placement where a second alkaline consistency control admixture is metered and blended into the grout flow, immediately prior to injection. The respective admixtures are balanced to ensure that sufficient flow time (e.g., 10 to 15 minutes) remains in the final grout for complete and efficient placement prior to rapid final set.

2.2.3   Set Properties

The mixes shown in Table 2 provide grout strengths of up to 1 MPa after only 1 hour, and strengths of up to 30 MPa at 28 days. Shrinkage and bleed are minimal due to the low water cement ratio.

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2.2.4 Advantages

This type of system satisfies the challenge of achieving high early strength from an initially very fluid and pumpable grout. In addition, the system is compatible with hydration control (in projects where pumping distances are especially long), and antiwashout additives. Therefore the contractor has considerable flexibility in initially designing his grouting operations, and later in more easily accommodating unforeseen conditions or circumstances in the field.

3. Additives for Other Purposes

3.1 Antiwashout

Satisfactory concrete and grout placement in a water-filled environment has traditionally proved particularly difficult. The greatest challenge is to place grouts without their being diluted or carried off by flowing water. A secondary challenge is to allow placement while still having enough Portland cement in the matrix to accomplish the design task once the concrete or grout has reached its hardened properties.

Commonly more cement or pozzolans (i.e., flyash and silica fume) are added to increase the cohesiveness of the mix and compensate for dilution by maintaining enough cementitious fines in the grout, to achieve the designed hardened properties.

Water soluble polymers such as cellulose derivatives are common modern antiwashout admixtures. Their primary function is to increase the viscosity of the mix water. This occurs through long-chain polymer bonds with some of the mix water, polymer entanglement, and further gel formation due to absorption of additional water molecules. As a result, the antiwashout admixture limits loss of cementitous fines, minimizes or eliminates bleed, increases stability, and enhances pressure filtration characteristics.

Research continues into not only the performance characteristics of treated mixes, but also the most appropriate methods of evaluating these characteristics in fluid grouts. For example, with respect to thixotropic setting characteristics, a relatively simple method is to take penetration readings on a static shallow sample using a modified Vicat needle (ASTM C-

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472). <u>Figure 7</u> shows data for two grouts of water-cement ratio = 0.53, one of which contains a certain antiwashout agent concentration of 1%. The treated grout clearly gains significant rigidity while at rest, i.e., from the time injection would have ceased in the field.
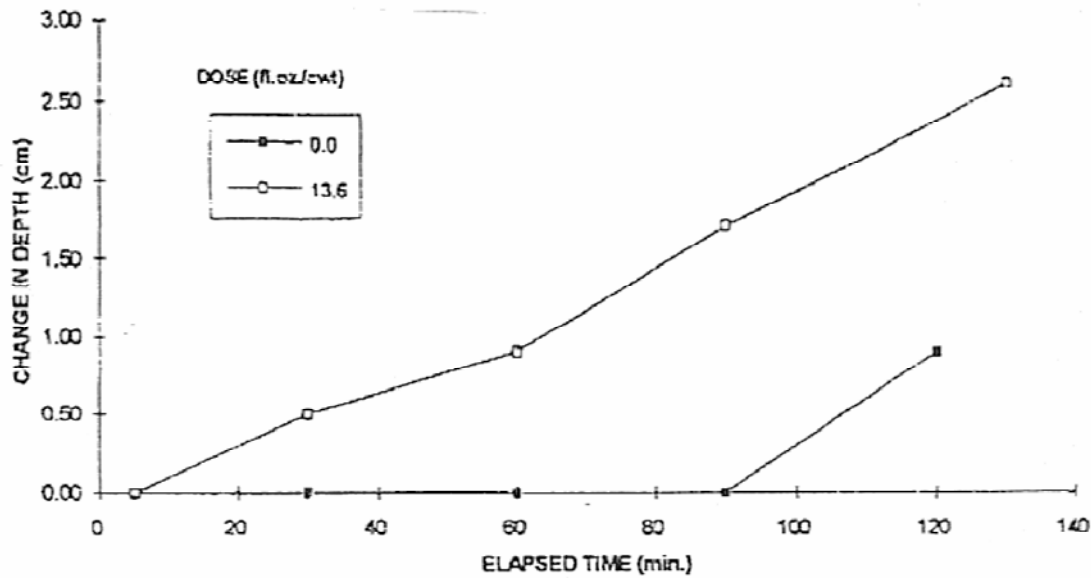

<u>Figure 7</u>. Thixotropic setting (measured by Vicat needle) of grout treated with a modified cellulose antiwashout agent.

Conventional tests to quantify washout resistance are applicable only to concretes, and so a unique test has recently been developed. A specially designed clear plastic chamber (<u>Figure 8</u>) allows grouts to be placed in static or dynamic water conditions. The "integrity" of the grout is measured by its efficiency in displacing out of the chamber a known volume of water: the lower the volume of grout needed, the less washout or dilution has occurred. Tests can also be run with the outer chamber filled with aggregate, allowing void fill efficiency and the formation of bleed water pockets to be observed. Parameters for acceptability are established on a job specific basis.

Details on typical fluid performance parameters are summarized in <u>Table 3</u>. These data confirm the action of a certain modified cellulose additive in increasing apparent viscosity, decreasing bleed, and enhancing pressure-filtration stability.
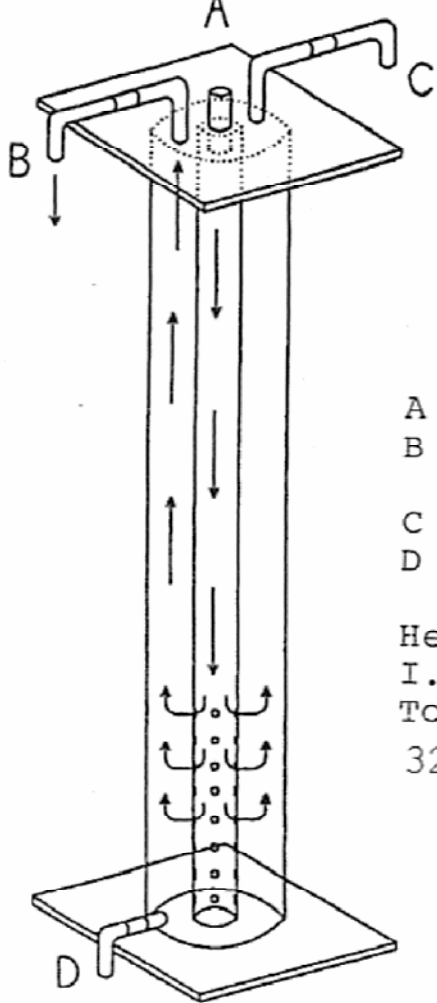
A - 1" pump connect for grout
B - 1" sample outlet for displaced
    water
C - 1" water inlet
D - 3/4" drain and crossflow outlet

Height = 52"
I.D. = 9-7/16"
Total Volume = 2.07 cu.ft.
32 holes each 3/8" in diameter

Figure 8. New test device for measuring grout washout
characteristics, developed for Logan Martin
Dam project, AL.

Mix	1	2	3
Water-cement ratio	0.53	0.53	0.53
Additive percentage	zero	0.45 %	1 %
Flow (ASTM C-939)	10.7 sec	20.2 sec	25.9 sec
Bleed (Static)	5 %	zero	zero
Pressure filtration (at 30 psi): Time to commence % of total (after 35 mins)	Immediate 66 %	27 sec 21%	30 sec 13%

Table 3. Test data on grouts with antiwashout additive.

3.2 Microfine Cements

The ability of a particulate grout to penetrate into pores or fissures depends, inter al., on two material-related factors: the rheologic properties of the mix, and the grain size distribution of the cement particles. Contemporary controls over rheology are discussed in Section 2.2, while this section focuses on the implications of particle size.

Conventional cements normally have a specific Blaine surface of 250 to 500 m^2/kg, and grain sizes which range fairly consistently from about 60 to 1 microns. Finely ground cements (grain sizes typically 20 to 0.1 microns, with *at least* 75% finer than 10 microns) have been commercially available for many years in the U.S. and the considerable volume of published data on case histories and laboratory research has contributed to their rapidly growing popularity. Indeed, on grounds of technical performance, cost, environmental impact and ease of placement, microfine cements are supplanting sodium silicate gels as the material of choice in appropriate ground conditions (i.e., soil permeabilities as low as 10^{-7} m/s.) However, it is often overlooked that it is misleading to evaluate the potential penetrability of a microfine grout by merely studying the size of the individual dry grains: penetrability may be compromised by the tendency of single grains to agglomerate thereby producing larger "flocs."

This problem can be addressed in two distinctly different ways. Firstly, (and assuming always the use of an efficient high speed mixer) dispersive additives can be used. The effect of this is illustrated in Figure 9. Alternatively, microfine grouts can be produced by the remilling of normal cement grouts during their hydration process (DePaoli et al., 1992). Although this process which can produce satisfactory cost-effective results, has been widely used in Europe, it has yet to be exploited commercially in the U.S., despite vigorous promotion in certain quarters.

Regarding the more conventional "dry" microfine cements, Table 4 summarizes the properties of a typical range of Portland cements. Other microfine cements are available which comprise solely ground blast furnace slag although these need a caustic addition to provide acceptable setting properties. Others comprise blends of Portland cement and slag and so do not require an
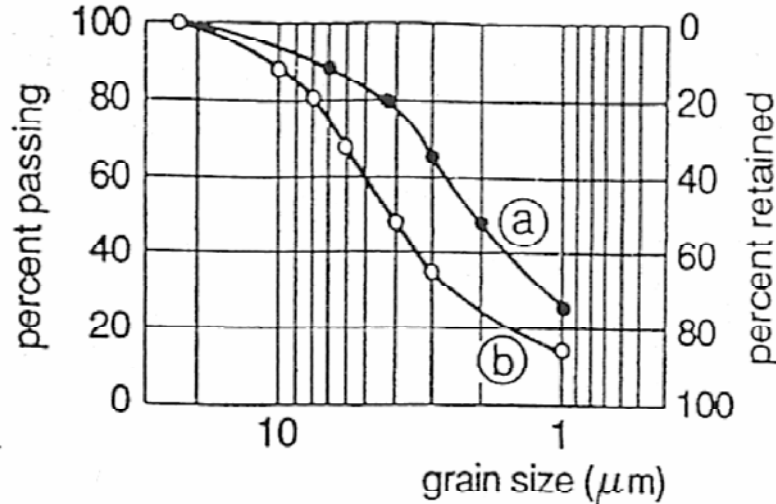
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Figure 9. Grain size distribution curves for the same microfine cement in aqueous suspension a) with, and b) without, dispersant.

additional chemical activator. For a typical mix of w/c = 1.0, plus 1.5 % dispersant, the initial setting time is 60 to 120 minutes, final setting time 120 to 150 minutes, bleed is minimal and the flow cone reading is 32 to 34 seconds. Furthermore, the hydration and rheology control additives described above can be used equally well with these microcements. Twenty-eight day strengths of over 50 MPa may be anticipated.

Surface area (m²/kg)	625 - 675	800 - 850	875 - 950
Particle size	Percent finer than		
40 micron	100	100	100
30 micron	99	100	100
20 micron	98	99	100
15 micron	93	97	99
10 micron	76	88	96
5 micron	41	53	75
2 micron	15	20	31
1 micron	Variable	Variable	13

Table 4. Properties of one group of Portland cement microfine cements.

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3.3 Cellular Concrete

Cellular Concrete or Low Density-Control Low Strength Materials (LD-CLSM) have been used in geotechnical applications for over 50 years, and are still gaining popularity. A foaming agent is used to produce pre-formed foam as the primary ingredient in the manufacturing of LD-CLSM. These liquid foaming agents are typically sold as a concentrate which is diluted with water prior to being blended with compressed air via a foam generator. This blending of diluted foaming agent and compressed air will expand the volume of the mixture up to 30 times by forming stable micro bubbles. The preformed foam is then carefully metered into the grout through a mixing nozzle. It is very important that the foaming agents are capable of producing bubbles which are durable enough to withstand the physical forces which arise from the mixing, pumping, and cement hydration of the LD-CLSM.

LD-CLSMs are of great benefit in many areas of geotechnical, mining and underground construction. Their uses include replacement of weak and compressible soils; lightweight backfill material with defined density and permeability; shock mitigating annulus fill of tunnel linings; and the provision of grouts with insulating properties. In addition, the use of foam will reduce the amount of total grout or concrete materials required to fill a given volume. This is of particular benefit in applications where jobsite access is very limited and material handling and transportation costs are atypically high. Foams also increase pumpability, and so allow the contractor greater flexibility in selecting equipment location.

Foam can be used to provide as much as a 70 percent volume increase over the neat grout or concrete mix. As a consequence of the resultant effective decrease in cement content per unit volume of cellular concrete, strengths are reduced, but sufficient data exist to enable the designer to reliably select the appropriate mix design.

According to ACI (1994), the most significant property of LD-CLSMs is the in-service density. Table 5 divides this into convenient ranges relating density with typical minimum compressive strength values.

Class	In-Service Density (Mg/m^3)	Minimum Compressive Strength (MPa)
I	0.29 - 0.39	0.07
II	0.39 - 0.48	0.28
III	0.48 - 0.58	0.56
IV	0.58 - 0.67	0.84
V	0.67 - 0.80	1.12
VI	0.80 - 1.28	2.23
VII	1.28 - 1.92	3.49

Table 5.   Typical strength properties of LD-CLSM based on density (ACI, 1994).

4.   Final Remarks

This paper provides a simple introduction to the highly significant and complex developments which are taking place in particulate grout technology. To a certain extent, the benefits are being already exploited in various fields, especially in tunneling, mining and general civil construction. To a lesser extent, they are now beginning to be exploited in the geotechnical field, where there would appear to be a growing, if not greater, need. The authors believe that a growing awareness within the grouting profession of contemporary potential for controlling hydration, rheology, washout and penetrability aspects will lead to a significant increase in the quality of grouting projects worldwide, especially on "difficult" conditions.

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