Report No. FHWA-RD-77-51

CHEMICAL GROUTS FOR SOILS

Vol.II Engineering Evaluation of Available Materials

DEPARTMENT OF TRANSPORTATION ★ UNITED STATES OF AMERICA ★

June 1977
Final Report

Prepared for
FEDERAL HIGHWAY ADMINISTRATION
Offices of Research & Development
Washington, D. C. 20590

FOREWORD

This two-volume report contains the results of a detailed study of international scope by Soletanche and Rodio, Inc. to determine the feasibility of developing cheaper chemical grouts from non-petroleum materials. The report was first written in French and then in English. The reader may note a few unusual expressions illustrating one difficulty in translation. The report contains a wealth of information about all types of chemical grouts applicable to soils and recommends laboratory test procedures for evaluating chemical grout.

Sufficient copies of the report are being distributed to provide two copies to each regional office, one copy to each division office, and two copies to each State highway agency. Direct distribution is being made to the division offices.

NOTICE

Charles F. Scheffey
Director, Office of Research
Federal Highway Administration

Technical Report Documentation Page

1. Report No. FHWA-RD-77-51	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle CHEMICAL GROUTS FOR SOILS VOL. II ENGINEERING EVALUATION OF AVAILABLE MATERIALS	5. Report Date June 1977 6. Performing Organization Code
7. Author(s) G. R. Tallard and C. Caron	8. Performing Organization Report No.
9. Performing Organization Name and Address Soletanche and Rodio, Inc. 6849 Old Dominion Drive, Suite 458 McLean, Virginia 22101	10. Work Unit No. (TRAIS) FCP No. 35B1-072 11. Contract or Grant No. DOT-FH-11-8826 13. Type of Report and Period Covered Final Report
12. Sponsoring Agency Name and Address Offices of Research and Development Federal Highway Administration U.S. Department of Transportation Washington, D.C. 20590	14. Sponsoring Agency Code

15. Supplementary Notes

FHWA Contract Manager: J. R. Sallberg (HRS-11)
Technical review by Dr. B. R. Appleman (HRS-23)

16. Abstract

The essence of this research is the search for more economical grouts not directly dependent on petroleum. The study has required an extensive investigation of 75 years of knowledge on chemical grouts in order to clear out the present diaspora of products. From this, a general classification of chemical grouts has been proposed, based on the nature of the major component. The grout materials were evaluated on the basis of several factors: injectability, permeability, setting time, strength of pure grout, strength of grouted soil, durability, toxicity. Grout families of substantial interest have been tested following these standards; further, a selected number of grouts have been tested for possible improvement. These tests indicate that lignochrome gels and furan resin derivatives are particularly promising.

A companion report, Volume I (FHWA-RD-77-50), is entitled "Available Materials."

17. Key Words Grout, injection, permeability, setting time, shear strength, unconfined compression, durability, toxicity	18. Distribution Statement No restrictions. This document is available through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 398	22. Price

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

01011

PREFACE

This is Volume II of a two-volume series entitled "Chemical Grouts for Soils". Volume I, entitled "Available Materials" (DOT-FHWA-RD-77-50), contains a Grout Classification System based on the nature of the primary grout component, and discusses and rates where possible each of the available materials classified on the basis of quality-price ratio. Volume I also contains a bibliography of available literature on grouting materials and procedures as well as patents.

Volume II of this report entitled "Engineering Evaluation of Available Materials" (DOT-FHWA-RD-77-51), defines seven criteria to be used in grout evaluation: viscosity, setting time, permeability, intrinsic strength, strength of treated ground, durability and toxicity, and recommends standard testing procedures for each.

Eight types of grout, which appear promising because of their non-dependence on petroleum, are studied in detail to determine the possibility of their further improvement for use in chemical grouting. Of this group, the two most promising materials, furfural and lignosulfite derivatives, were selected for further testing to determine the possibility of eliminating the major obstacles to their acceptance as chemical grouts (removing the danger of toxicity of the lignochromes, and replacing the acid catalyst with a basic system to polymerize the furfurals).

This report, as a whole, is intended for use as a reference and guide for grout users, the first volume as an improved classification system for chemical grouts, which can be expanded to meet future developments in the field. The second volume discusses engineering characteristics of available material, proposing test procedures to be standardized and ultimately suggesting guidelines for further research.

ACKNOWLEDGMENTS

The list would be too long to cite all individuals or organizations whose contribution has enriched the substance of this report, and the authors take this opportunity to thank them jointly.

Special acknowledgment must be made of the judicious and friendly guidance and criticism of J. R. Sallberg, Contract Manager for the Federal Highway Administration.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

GLOSSARY OF TERMS

Activator. Catalyst, hardener, reagent. The chemical solution which causes a mixture to gel or set when mixed with the base solution.

Alluvium. Clay, silt, sand, gravel, or other rock materials transported by flowing water and deposited in comparatively recent geologic time as sorted or semisorted sediments, in riverbeds, estuaries and flood plains, on lake shores and in fans at the base of mounting slopes.

Agglomerating Power. See Cohesion.

Arrhenius Rate Law. The speed of a chemical reaction is affected by changes in temperature.

$$k = Ae^{-E_A/RT}$$

A, E_A are constants characteristic of reacting substances
R is thermodynamic gas constant
T is temperature in °Kelvin

Bar. Measure of compressive strength. 1 kg/cm^2 = 0.981 bar
1 bar = 14.56 psi = 100,000 Pascals (10^5 Pa).

Baume Degrees. Indication of the density of a liquid (°B), measured with a Baume hydrometer. (36.6 °B = 1.340 density).

$$°B = \frac{144.38\ (\text{density} - 1)}{\text{density}}$$

Bentonite. A montmorillonite-type clay formed by the alteration of volcanic ash which swells in the presence of water.

Bingham Fluid. A true solution which, in addition to viscosity, tends to exhibit a certain rigidity so that, up to a certain gradient, it will behave as a solid.

Catalyst. See Activator.

Coefficient of Permeability. The rate of discharge of water under laminar flow conditions through a unit cross-sectional area of a porous medium under a unit hydraulic gradient and standard temperature conditions.

Cohesion. Agglomerating power. The capacity of sticking or adhering together. The cohesion of soil or rock is that part of its shear strength which does not depend on interparticle friction.

Consolidate, Consolidation, Grouting or Solidify. Terms applied to the binding together of soil particles into a mass of soil, such as occurs in permeation grouting.

Cut-and-Cover Tunneling. A process of installing a structure below ground by excavating an area of sufficient width, constructing the permanent structure at the bottom of the excavation, and then restoring the ground surface over the structure.

Darcy's Equation. The formula developed by Darcy to determine permeability:

$$k = \frac{Q}{t} \times \frac{1}{S} \times \frac{e}{P}$$

k is the permeability coefficient
t is time
Q is quantity of water
P is pressure
e is thickness of sample
S is section of sample

Darcy's Law. Formula developed by Darcy to determine speed of percolation in permeability testing:

$$V = ki$$

V is speed of percolation, cm/sec
k is permeability coefficient (Darcy), cm/sec
i is gradient applied to sample, cm/cm
(function of pressure and sample thickness)

Deformability. A measure of the elasticity or stress deformation characteristics of the grout in the interstitial spaces as the earth mass moves.

Density. Mass per unit volume of a substance in g/cm^3.

Diaphragm Wall. The construction of a vertical, continuous concrete wall, cast in situ or made of precast concrete panels, in a narrow trench filled with bentonite slurry to form a structural retaining wall.

Groundwater Table (Free Water Elevation). Elevations at which the pressure in the water is zero with respect to the atmospheric pressure.

Grout. A suspended cement or clay slurry or a chemical solution that can be poured or forced into the openings between soil or rock particles to solidify or to change the physical characteristics of the material.

Groutability. The ability of soil to allow grout to be forced into the interstitial spaces between the particles. As applied to grout material, its ability to be forced into the interstitial spaces between soil particles.

Hydrostatic Head. The pressure in the pore water under static conditions; the product of the unit weight of the liquid and the difference in elevation between the given point and the free water elevation.

Injectability. See Groutability.

Injection. Grouting. The process of forcing a grout into the soil to be treated, using pressure.

Joosten Process. The earliest of the chemical grouting processes, originating in 1925. In this process, a sodium silicate solution is pumped into the soil as a grout pipe is advanced downward. The pipe is then flushed with water, and calcium chloride is pumped in as the pipe is retracted. A precipitate forms upon contact between the two solutions.

Karst. An irregular limestone region with sinks, underground streams, and caverns.

Newtonian Fluid. A true solution which tends to exhibit constant viscosity at all rates of shear.

Permeability. See Coefficient of Permeability.

Permeation Grouting. Replacing the water or air in the voids of the soil mass with a grout fluid at a low injection pressure to prevent creation of a fracture, permitting the grout to set at a given time to bind the soil particles into a soil mass.

Porosity. The ratio of the volume of the voids or pores to the total volume of the soil.

Reagent. See Activator.

Resin. A synthetic addition or condensation polymerization substance or natural substance of high molecular weight, which under heat, pressure, or chemical treatment becomes a solid.

Setting Time. The time needed for a chemical grout to solidify.

Slurry. Suspension of cement or clays in water, or a mixture of both.

Slurry Trench. A relatively narrow trench which is usually dug with a clamshell while the excavated portion is kept filled with a bentonite slurry to stabilize the walls of the trench.

Specific Gravity. Ratio of the mass of a body to the mass of an equal volume of water at a specified temperature.

Star Wheel. The vane used with a Vane Test, to determine shear strength; when viewed from above, the vane is star shaped.

Syneresis. When freshly prepared sodium silicate gel is placed in a closed glass container, a significant amount of water can be observed being extruded by the gel. This is the phenomenon of syneresis, which is peculiar to silica gels.

Toxic. Poisonous or harmful.

True Solution. One in which the components are 100% soluble in the base solvent.

Tube a Manchette. A plastic tube or pipe of approximately 1-1/2" inside diameter, perforated with ringe of 4 small holes at intervals of about 12 inches. Each ring of perforations is enclosed by a short rubber sleeve fitting tightly around the pipe so as to act as a one-way valve when used with an inner pipe containing packing elements which isolate a hole for injection of grout.

Tyndall Effect. Visual scattering of light along the path of a light beam as it passed through a system containing discontinuities, such as surfaces of colloidal particles in a colloidal dispersion.

Unconfined Compressive Strength. The load per unit area at which an unconfined prismatic or cylindrical specimen of material will fail in a simple compression test.

Vane Shear Test. Device for measuring shear strength. A 4-bladed vane is attached to the bottom of a vertical rod. The assembly is lowered into the material to be tested and rotated. The torque required to turn the vane is measured and shear strength is computed using the torque measurement and the dimensions of the vane.

Viscosity. The ratio of the tangential frictional force per unit area to the velocity gradient perpendicular to the direction of flow of a liquid.

LIST OF TABLES

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

PART ONE: TESTING REQUIREMENTS

Chapter 1: Introduction

The essential characteristic required of a grout is that it be injectable, that it be able to penetrate a given porous permeable medium. Injectability depends on some of the grout's characteristic properties, mainly viscosity, in relation to the properties of the porous permeable medium under consideration, and, given the number of factors which can affect it, this concept is highly complex. It also depends upon the technology used for injection (spacing of points of injection, allowable pressure).

To define a grout's injectability, the ideal method would be to run an injection test on a model. But such tests are not very practical because it is so difficult to accurately reproduce in a laboratory a sample which would be totally representative of the actual ground conditions even if soil samples are taken from the contemplated work site. For this reason, it is common and recommended practice to conduct trial runs "in situ" with different grouts previously selected in a laboratory.

Laboratory tests for injectability can be conducted on a radial basis (in a hopper, for example) or on a linear basis (in a column). During injection, measurements are taken of pressure and flow, or the speed at which the grout moves through the porous medium.

After saturation of the laboratory model, samples are taken of grout which has already percolated and compared with control samples taken before percolation for setting time and cohesion. One can thus see whether the grout has spread evenly or whether there has been some chromatographic-type separation of its ingredients, a phenomenon which occurs in particular with emulsions or with some macromolecular grouts.

This test thus clearly points up those properties which define a grout's injectability, and some authors, including POLIVKA (48-05) [1] have been quite happy with this type of measurement on damp grout. Unfortunately, this test is cumbersome and it is usual to adopt a simpler method, that of measuring the grout's viscosity. In fact, for many grouts (at least for those in common use), viscosity is a perfectly adequate criterion of injectability.

---

[1] All references are given in Report FHWA-RD-77-50 "Chemical Grouts for Soils* Vol. 1 Available Materials".

Chapter 2: First Criterion, Viscosity

2.1 General Remarks

C. CARON (70-07) demonstrated that viscosity was a good measure of injectability for grouts which differ widely in viscosity and physico-chemical characteristics (table 1 below).

Table 1. Viscosity of Various Grouts

Type of mixture	Average viscosity during test, cP [1]
Silica gel	4.8
Acrylamide resin-gel mixture	2.25
Phenol Precondensate	3.15
Resorcin-formaldehyde monomer	1.75
Polyester 50 - Styrene 50 (without catalyst)	8.25
Water	1.1
Water + Polyox WSR 80,100 PPM	1.1
Water + Polyox WSR 301,30 PPM	1.15

It appears that the speed at which a grout runs down through a sand column is clearly inversely proportional to the grout's average viscosity during the test, while the grout's physico-chemical makeup has practically no effect. Thus, although some manufacturers recommend it, it is not necessary to consider surface tension factors.

Therefore, in defining injectability, the primary factor is the grout's viscosity. In the case of many grouts, viscosity does not remain constant during injection, it increases. This increase in viscosity means that if pressure remains constant, the flow rate will decrease, or, to maintain a constant flow rate, pressure must be increased, sometimes to a point where the ground is ruptured (C. CARON 65-04).

The time during which a grout, whose viscosity increases with time, is injectable and the time before setting may coincide or differ substantially depending on the nature of the grout. This point is discussed under the definition of setting time.

---

[1] Viscosity in millipascal seconds (mPa.s) = viscosity in centipoises (cP).

To summarize, it appears that:

a) viscosity is the essential parameter for defining a grout since it determines the grout's ability to penetrate a given permeable porous medium;

b) since the viscosity of most grouts listed [1] does not remain constant during injection, this evolution must be measured;

c) this evolution can render the grout so viscous as to make it practically uninjectable even though the grout has not set. This principle of different intervals for injectability and setting time applies to some grouts and will be accounted for in the chapter on setting time.

The correlation between injectability and viscosity has not been verified for emulsion-type systems (Category D), or for systems reacting with the ground (Category E). In both cases, measures of viscosity are not conclusive and injection tests are necessary.

2.2 Equipment for Measuring Viscosity

There are a great many devices for measuring viscosity, varying in both principle and design. For measuring the viscosity of chemical grouts, the equipment recommended is a rotation viscosimeter with coaxial cylinders (the FANN viscosimeter, for example). The choice of equipment should take into account the fact that some tests will be made under precise temperature conditions.

Only Category C-3 grouts, handled at high temperatures, require special instrumentation. The behavior of these grouts is quite special, and they require special testing procedures. Since they are of limited interest, they have not been considered here.

2.3 Determination of Initial Viscosity

With the exception of Category C-3 grouts, measurement of a grout's viscosity at a given point in time poses no problems other than that due to the changing character of the grout, for measurements are not instantaneous.

---

[1] Available grouts are classified or categorized in Report FHWA-RD-77-50 "Chemical Grouts for Soils, Vol. 1 Available Materials".

Since a grout can begin to alter as soon as it is prepared and even while it is being prepared, an arbitrary choice must be made with regard to the time at which measurements of initial viscosity will be taken.

An acceptable procedure is to place the grout in the viscosimeter's tank as soon as it has been prepared, immediately turning on the machine. In this way, a measurement can be taken one minute after preparation has been completed.

This measurement is carried out at high speed (600 revolutions per minute with a FANN viscosimeter) and at intermediate speeds (300 rpm with a FANN viscosimeter) for purposes of detecting abnormal behavior (in the case of categories B-1 and B-2, in particular).

The value used to define initial viscosity will be that obtained at high rotative speed.

Since initial viscosity is affected by temperature, it may be necessary to measure viscosity at varying temperatures. The dissolution heat of the various ingredients of the grout should also be taken into account.

2.4 Changes in Viscosity Over Time

Changes in viscosity over time are related to the reaction process which causes the grout to solidify. Unlike initial viscosity, this parameter requires that a distinction be made among the various types of grouts.

Measurements of changes in viscosity in relation to time should be made systematically for all grouts in Categories A-1, B and F as well as for Categories C-1 and C-2. Such data are included here.

Measurements for grouts in the other categories, C-3, C-4, D-1, D-2, E-1, E-2, have not been included because in these cases changes in viscosity depend on the surrounding ground.

2.41 Categories A, B, C-1, C-2, F

Most chemical grouts encountered in practice are included in Categories A (Aqueous Solutions), B (Colloids), C-1 (Synthetic Resins), C-2 (Vulcanizable Oils) and F (Combined Systems).

Table 2. Chemical Grout Classification

Category A		Aqueous Solutions
	A-1	Silicate Derivatives
	A-2	Other Mineral Gels
	A-3	Lignosulfite Derivatives
	A-4	Other Plant Derivatives
	A-5	Polyacrylamides
	A-6	Phenoplasts
	A-7	Aminoplasts
	A-8	Combination Grouts Using Elements Drawn From Categories A-1 to A-7
Category B		Colloidal Solutions
	B-1	Organic Solutions
	B-2	Mineral Solutions
Category C		Non-Aqueous Solutions
	C-1	Synthetic Resins
	C-2	Vulcanizable Oils
	C-3	Bitumen and Other Heated Materials
	C-4	Systems Containing Solvents
Category D		Emulsions
	D-1	Bituminous Emulsions
	D-2	Other Emulsions
Category E		Products Reacting With the Ground
	E-1	Reaction with Ground or Groundwater Salts
	E-2	Reaction with Groundwater
Category F		Systems Combining Grout Families

CARON (65-04) has demonstrated that for these viscosity evolutive-type grouts, injection speed (expressed in terms of apparent permeability) is at all times inversely proportional to the viscosity. Figures 1a and 1b show sands of two different gradations and four types of silica gel injected at constant pressure.

Consequently, one can accurately describe grouts in these categories in terms of measurements of viscosity up to the setting point. In theory, there should be two measurements: one under isothermal conditions and the other under adiabatic conditions.

For measurement in isothermal conditions, the grout is maintained up to the setting point at the equivalent of ground temperature (15°C), and viscosity is measured at regular intervals. The setting time will have been determined before-hand in the same conditions, then at least five readings must be taken, the first being a measurement of initial viscosity and the last a measurement taken five minutes before setting.

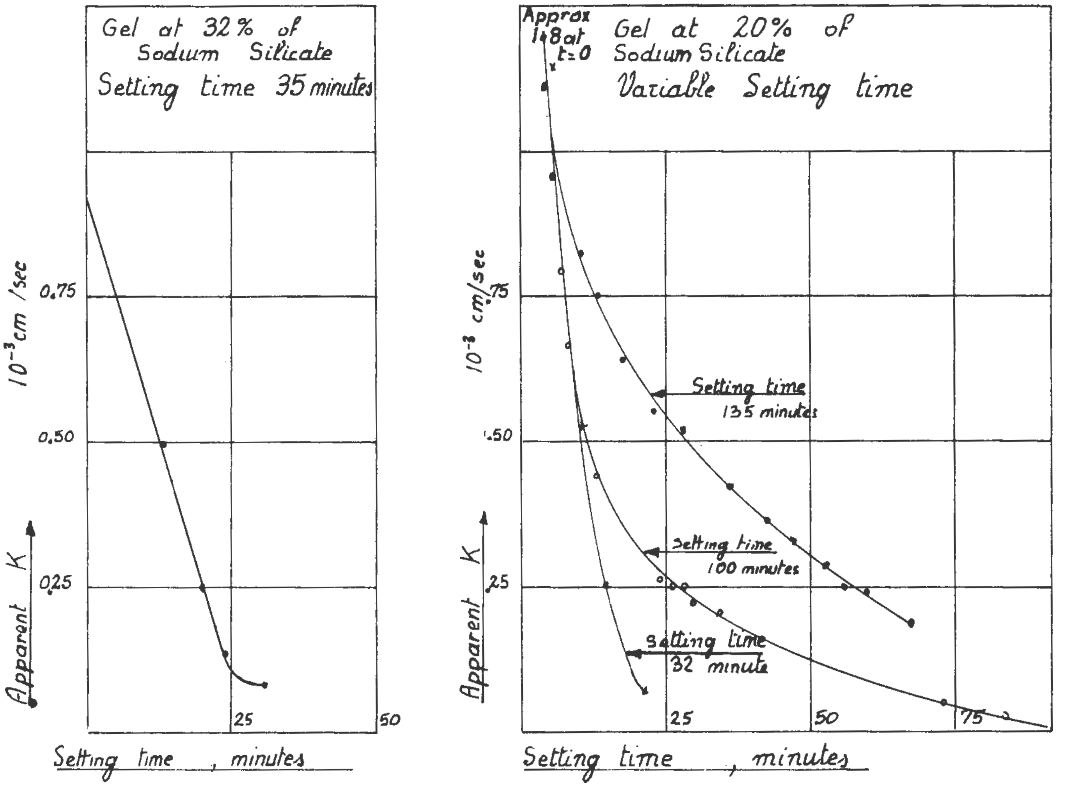
Changes in viscosity in adiabatic conditions are measured by letting the grout heat up without loss of heat to the outside. The setting time will have been determined before-hand in the same conditions, then at least five readings must be taken, the first being a measurement of initial viscosity and the last a measurement taken five minutes before setting.

The isothermal measurement requires strong refrigeration to carry off the heat resulting from the reaction. The adiabatic measurement requires an adiabatic calorimeter. In practice, a median curve obtained by placing the grout in a 500 m^3 container is deemed sufficient.

From the curves plotting viscosity in terms of time, one can determine the time needed for the grout to attain a viscosity of 100 cP. This limit corresponds to the point where, under constant pressure, the grout would penetrate too slowly or, conversely, maintenance of a constant rate of flow would require pressures so high as to risk rupturing the ground.

2.42 Categories C-3, C-4, D-1, D-2, E-1, E-2

For these grout categories, changes in viscosity are affected by the ground (in breaking an emulsion, or by reaction with the groundwater). One must run a test by injecting the grout into a column of fine sand at a constant flow rate (for Category E, the sand is first



a sand no. 1

b Clayey sand with K = 4.7 10^{-3} cm/sec

Fig. 1. Effect on Setting Time of Viscosity (Silica Gel)

saturated with water). Pressure is measured in terms of time and the test is continued until the column is injected or the pressure necessary has reached the point where there is risk of rupture.

The same injection test is necessary for the preceding categories, if, upon contact with the ground or with water (highly saline), there is some risk of flocculation or precipitation in the grout itself. Such reactions would hamper injection and could not be determined simply through a measurement of viscosity.

2.5 Conclusion

Injectability is based on two criteria: viscosity and setting time.

With regard to viscosity, the following should be taken into account:

a) initial viscosity;
b) changes in viscosity with time;
c) maximum viscosity allowable for reasonable injectability timespan.

In the majority of cases, these injectability parameters will be considerably affected by temperature. The grout's temperature will be determined by the ambient medium and also by the heat generated by the reactions which cause the grout to set. It is thus indispensable to define injectability criteria for each of the stages of application. As they convert from their initial state to their final state, most grouts undergo chemical reactions. The speed of the reaction will depend on the grout's composition and may vary over a wide range depending on the nature and concentration of the various ingredients.

Chapter 3: Second Criterion, Setting Time

3.1 Introduction

Setting time is the second fundamental criterion characterizing grout within the definition of injectability.

For the grout user, the point indicating that grout is beginning to set in the ground is indicated by a perceptible rise in the pressure necessary for grouting. Treatment must then be stopped since, if continued, there will be a rupture of the ground which must be avoided if at all possible.

Thus, the concept of injectability is characterized by this limitation of the time during which grout is workable. This limitation can affect the in-situ performance of a grout as well (imperfect penetration because the setting time is too short). The different factors governing the set of a chemical grout clearly show that many authors have arrived at quite different definitions and operating methods.

Thus, there are:

a) grouts which are transformed by an internal chemical reaction: Categories A-1, A-2, A-3, A-4, A-5, A-6, A-7, A-8, C-1, E-2, F;

b) grouts which are changed by a physical procedure: Categories B-1, B-2, D-1, C-3;

c) products which can change either by internal chemical reaction or by physical process. For Category C-4, setting can be achieved by elimination of the solvent, but can be done equally well by mass polymerization with retention of the solvent. In the same way for Categories D-1 and E-1, the setting reaction can be either chemical or physical.

3.2 Definition of Setting Time and Measuring Methods

The simplest definition and the one best suited to the common idea of the setting phenomenon is as follows: the time required by the grout to change from a liquid phase to a solid phase.

If this transformation is quite obvious, there will be no ambiguity in the measurement of setting time and, in that case, there will be a concordance in results whatever the testing procedures. However, if the transition from liquid to solid is gradual, which is common for most chemical grouts, the definition of the testing method will have an influence on the result.

In addition, with the majority of grouts, there is an evolutive aspect of the grout beyond the point defined as setting time. Thus, it is necessary to consider another time sequence at the end of which the grout will have reached its required performance for the purpose of its use (time required before allowing the opening an excavation, for example). Thus, it will be necessary to associate the concept of setting time with the concept of hardening time. Each of these points corresponds to a state of attained mechanical characteristics which will allow the grout, at a determined time, to resist the stresses to which it will be submitted.

For these reasons, some confusion can remain in a definition that can prove arbitrary. This explains the many present definitions and methods for the determination of setting time. Some (RHONE PROGIL, for example) even use different methods according to the class of grout:

-for sodium silicate gel, time needed for the grout to stop its flow from its container when inclined.

-for acrylamide resins, time needed for a 100 cc sample to raise the surrounding temperature by 2°.

The general literature gives the following variety of methods:

-Optical method (PRESARD and HATTIANGADI. J. Ind. Chem. Soc. 653-6, 1929. C. CARON. Ann. de l'ITBTP, No. 207-208, 1965.)

-Flow analysis in capillary tubes (FLEMMING. A. Physik Chem., 427-41, 1902.)

-Moment when the grout stops flowing from a given container (HOLMES. J. Phys. Chem. 51 022, 1918.)

-Moment when a glass stick remains inclined at 20° in the grout (HURD and LETTEROW. J. Phys. Chem., 604.807,1932.)

-Moment when the magnetized flipper of a magnetic agitator is idled (C. CARON. Ann. de l'ITBTP, No. 207-208, 1965.)

-Particular point of the viscosity evolution chart (C. CARON. Ann. de l'ITBTP, No. 195-196, 1964.)

-Moment when the grout is no longer dissolved in water or an appropriate solvent; when surface ripples no longer form when submitted to vibration, penetration or extrusion tests.

Other examples taken in the area of concrete, mortars, cement grouts, polymers or industrially used resins would confirm this subjective concept of setting time, showing that in the definition one relates more to the nature of the product than to its function.

3.3 Speed of Set and Chemical Kinetics: Influence of Temperature

During their evolution from initial to final state, most grouts are the scene of chemical reactions. Setting time, essentially an empirical concept, corresponds to a given instant in the reactive process. Therefore, determination of setting time must rely on chemical kinetics of the intervening reactions at the heart of each grout: speed of reaction and factors which influence it.

Influence of the composition of the grout on reaction speed is not considered here, nor are choice of reagents, catalysts, promoters or inhibitors of reaction and concentrations used to obtain the desired setting time compatible with other criteria for use (injectability, mechanical strength, etc.) These are covered, category by category, in Part Three of this Volume.

Under these conditions, temperature is the only factor capable of having an impact on speed of reaction, and thus the setting time (ARRHENIUS Equation). The influence of temperature on setting time is largely acknowledged, as many organizations have testing procedures using variable temperatures either in isothermal or in adiabatical conditions.

In general, grout mixes show exothermal chemical reactions. Due to their dissolution heat, the various components of the grout formula can also influence the mix temperature. The temperature of the grout at a given time will depend mainly on the ability of thermal exchange between the grout mass and the surrounding media.

In order to be precise, the setting time process would have to be defined in the above-mentioned conditions, but, given the number of factors influencing the thermodynamics of the system, it would not be realistic to analyze the question of setting time in its real context. In general, authors agree to define the setting time at limit conditions, the setting time being located within the interval.

Setting time shall therefore be determined in terms of initial grout temperature in adiabatic conditions and in isothermal conditions. The former corresponds to conditions in the mixing plant, the latter to the behavior of grout in its sand skeleton. If the grout is the scene of exothermal reactions, these times are not the same.

C. CARON (65-04, 70-07) has described a series of tests on sodium silicate gels (grouts characterized by very slight exothermicity and equally by a progressive change in viscosity from preparation to set.

In grouting at constant pressure in columns of fine sand, it has been noted that grout flow decreases with time and tends to cease a few minutes before setting in a sample glass.

In radial grouting at constant grout flow, which is closer to real conditions, a gradual increase in pressure has been noted, followed by a sudden rise and rupture of the ground at a time corresponding to gelification of the reference sample (fig. 2).

Thus, with silicate derivatives, gelification is observed readily at the same moment in sand as in reference samples of pure grout, all experiments being conducted at constant temperature.

When the same test is made with a resorcinol formaldehyde or liquid polyester, during a fairly long time the grout flow through the sand is constant while pressure is kept constant, but the test cannot be conducted to its end as the mass of grout being used for the test sets suddenly while the resin within its sand skeleton shows no signs of setting.

All of this clearly indicates the necessity of knowing setting time in both isothermal and adiabatical conditions. One case where knowledge of the setting time in isothermal conditions is not necessary is when a two-shot method is used, or when the gelifying or polymerizing reagent is not introduced into the grout until the last moment.

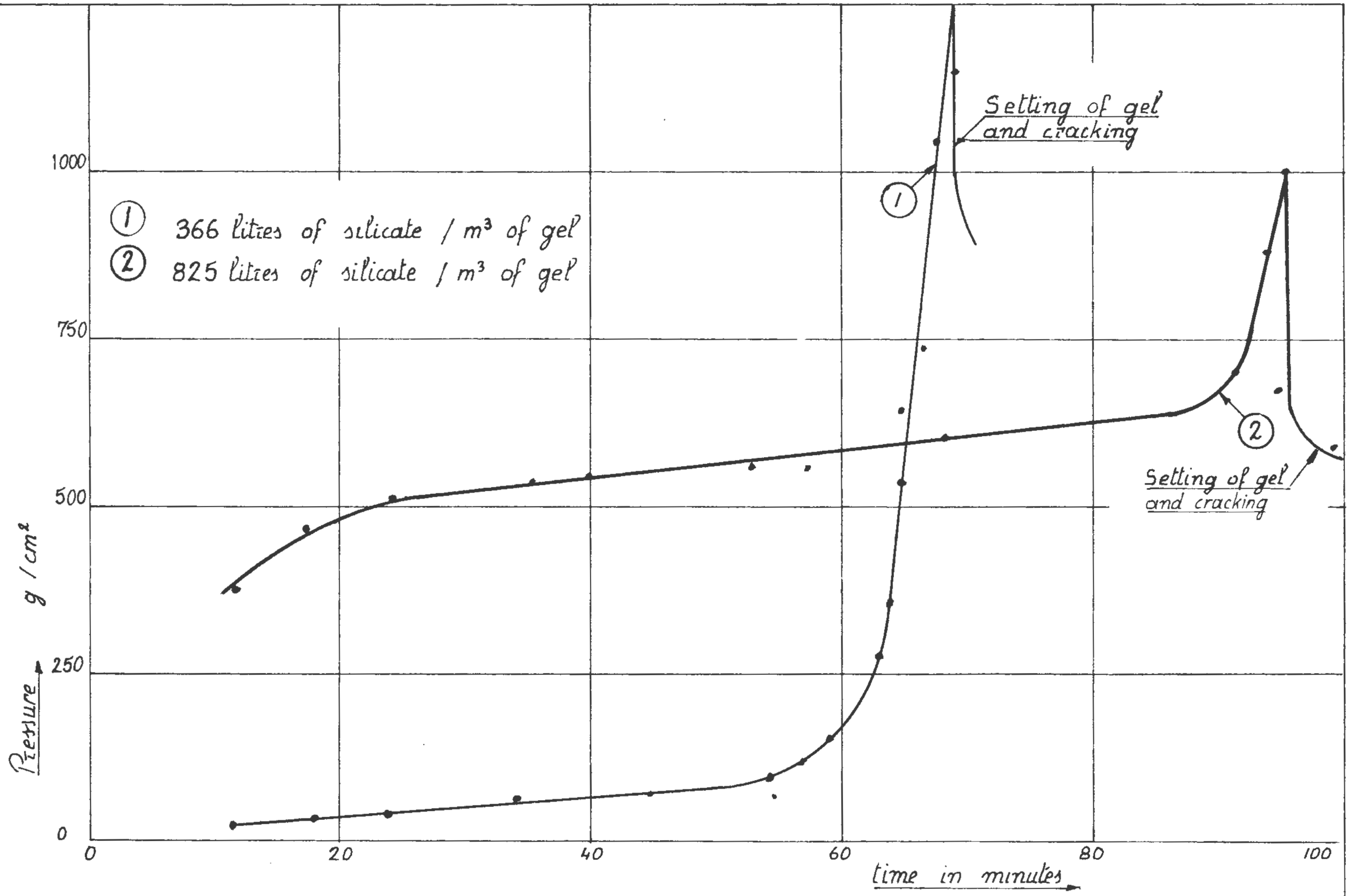


Fig. 2. Change of Grouting Pressure at Constant Flow of an Evolutive Newtonian Liquid

From the state of elementary components to the state of a finished grouted material, there are two different paths (fig. 3) which represent two production methods known as continuous and discontinuous.

Using the continuous production method, the grout becomes evolutive (subject to change with time) only when passing through the pumping unit, and the setting time concept concerns only the soil and portion of piping between the pump and the grouted zone. With the discontinuous production method, the grout becomes evolutive right in the mixing plant, and the setting time concept applies to the whole chain of grouting procedures.

Although the continuous production method seems to be the more rational, it is not widely used, because of two disadvantages:

1) more complicated equipment is required (automatic dosing pump);

2) control is more difficult since grout is not formed centrally.

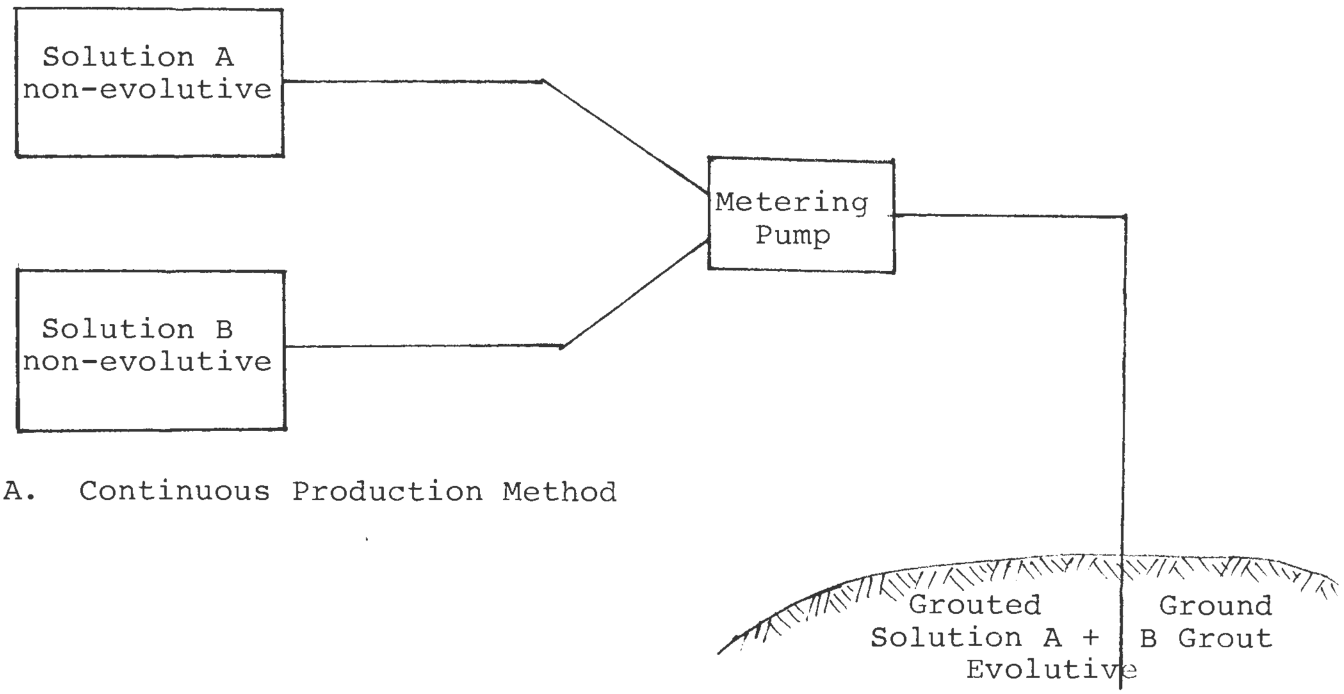
3.4 Influence of Secondary Factors

Specific factors like the evaporation of certain components of a grout, photosynthesis, anaerobical reactions, etc., will not be considered here as they refer only to certain types of grout.

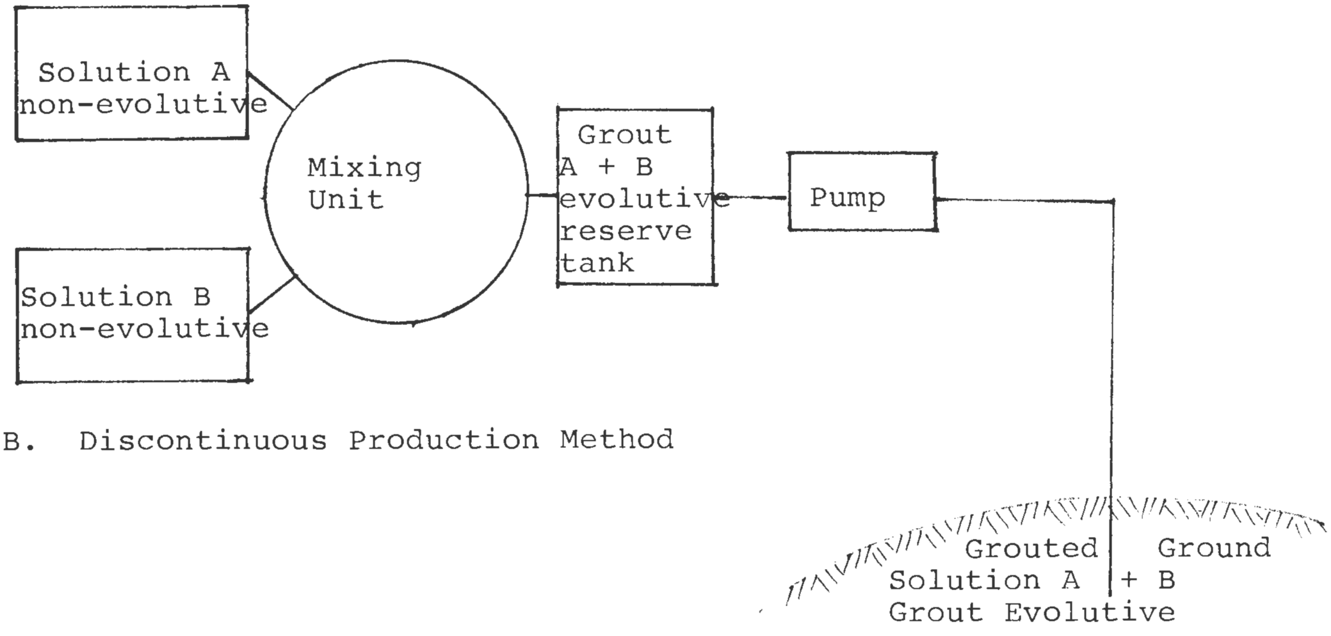
Since setting time corresponds to the kinetics of a chemical reaction, it is evidently prolonged by dilution of the reactive mixture. Also, another parameter has been advanced: dilution of grout during grouting. It has been suggested in "Guide Specifications for Chemical Grouts", ASCE Soil Mechanics and Foundation Division, Paper 5830, March 1968, that a setting time bracket be defined for different dilutions of the same grout. Based initially on the two-shot process of the Joosten type, the committee members admitted that the grout was diluted to some extent by groundwater. It should be noted that the publications of H. CAMBEFORT, C. GERBER, H. STEFAN and R. BERTHAUD (63-39, 65-02) [1] on grout flow under one-shot injection procedure show that mixture of grout and groundwater takes place only at the fringe of the boundary between the two, and to a very limited extent.

---

[1] R. BERTHAUD: Contribution to the Study of Flow in Porous Media. Doctorate Thesis in Hydrodynamics, Toulouse, 1963.



A. Continuous Production Method



B. Discontinuous Production Method

Fig. 3 . Grout Mix Preparation Methods

Consequently, we will not take dilution into account in the modification of setting time in grouted ground, with the following reservation: dilution is possible and, consequently, so is prolongation of setting time if the ground to be treated has a heavy circulation of water (fissured rock, karst, etc.), but such terrains are not usually amenable to traditional chemical grouts.

3.5 Conclusions for the Determination of Standards

3.51 Necessity for a Double Standard

Taking into account the difference of setting times for most grouts between the mixing stage and the proper injection inside the ground, it will be necessary to know and to be able to measure the setting time at these two stages of the evolution of the grout, or at least to be able to relate one to the other.

At the two stages mentioned above, the setting times are influenced by thermal conditions, and this factor has been retained for the testing program. However, variations due to unexpected dilutions will not be considered.

3.52 Influence of Grout Category

Given the great diversity of the chemical grouts under consideration (true solutions, colloidal solutions, emulsions), as general a method as possible must be used in order to determine a setting time standard with a minimum of tests.

In paragraph 3.51 the need for two types of standards was discussed briefly, one on pure grout and the other one on grouted sand. Both are not always possible with each type of grout. The transition of grout from the liquid to the solid state is, for a large number of grouts, very obvious, even dramatic at times. However, a certain number of grouts maintain after setting a pseudo-liquid consistency or evolve very slowly from the liquid state to the solid, which makes it very difficult to observe a setting stage. Certain grouts do not set in the form of a gel, as with destabilization of grout, for example. In other cases, the grout reacts only with the ground. In these cases the measurement of setting time on the pure grout loses any significance and the determination of the setting time will be based only on the treated sand.

Definition of the setting time within the injected soil seems to call for a more general approach. It will nevertheless be difficult when the grout presents a very unclear set and, consequently, a low cohesion after setting in the ground. Table 3 gives the possibilities of visual observation of the setting process.

Table 3 : Possibility of Observation of Setting

Grout Category	Pure Grout			Treated Soil		
[1]	Clearly Observable	Slightly Observable	Not Observable	Clearly Observable	Slightly Observable	Not Observable
A-1	+ →	+		+ →	+	
A-2	+ →	+			+ →	+
A-3	+ →	+			+	
A-4	+ →	+			+	
A-5	+			+		
A-6	+			+		
A-7	+			+		
A-8	+			+		
B-1		+ →	+		+ →	+
B-2		+ →	+		+ →	+
C-1	+			+		
C-2	+ →	+		+ →	+	
C-3		+		+ →	+	
C-4		+ →	+		+	
D-1		+ →	+		+	
D-2		+ →	+	+ →	+	
E-1			+	+ →	+	
E-2	+ →	→	+	+ →	+	

[1] For grout category names, refer to Table 2, page 5.

3.6 Parameters Used to Determine Setting Time

The moment at which the grout sets, in the most general sense of the term, can be expressed as a specific point in the evolution of a property characteristic of the grout.

The factor used to determine the setting point could be any of the following:

-Rheological: viscosity, rigidity, shear limit;
-Mechanical: compression strength, traction strength, shear strength;
-Thermal: critical temperature;
-Optical: nephelometry;
-Physico-chemical: pH, conductivity, electrical potential for reducing oxide;
-Physical: solubility, surface tension.

The possibilities of using these factors to define the set,on both pure grout and treated soil, are indicated in table 4.

3.61 Determination of Setting Interval in Grout Itself

For all Category A grouts (silicate derivatives), the setting interval can be determined according to changes in rheological properties.

The simplest test gives enough indication for the degree of precision needed and consists of determining the interval after which the grout can no longer be transferred from one container to another. As the container is tipped, as shown in fig. 4 below, the grout's shape remains unchanged, which indicates that it has set.

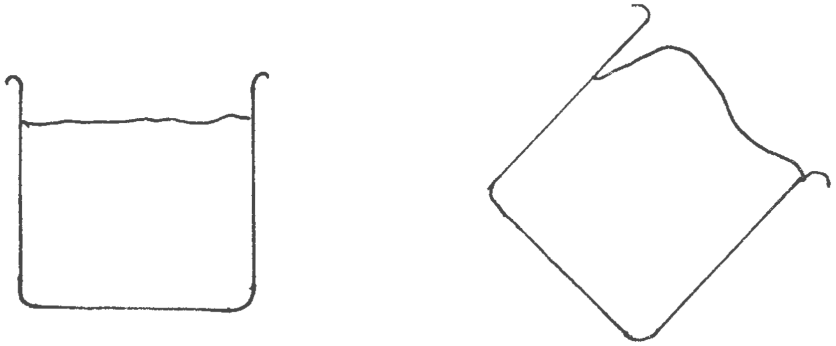


Fig.4 . Setting Time Test for Category A Grouts

Table 4. Factors Which Can Serve as Setting Criteria

Category	Rheological		Mechanical		Thermal		Optical		Solubility		Physico-Chemical		Surface Tension	
[1]	Grout	Soil	Grout	Soil	Grout	Soil	Grout	Soil	Grout	Soil	Grout	Soil	Grout	Soil
A-1	+		+	+			+		+	+			+	
A-2	+		+	+			+		+	+			+	
A-3	+		+	+					+	+	+	+	+	
A-4	+		+	+					+	+			+	
A-5	+		+	+	+	+			+	+	+	+	+	
A-6	+		+	+	+	+			+	+	+	+	+	
A-7	+		+	+	+	+			+	+	+	+	+	
A-8	+		+	+			+		+	+			+	
B-1	+			+			+						+	
B-2	+			+			+						+	
C-1	+		+	+	+	+			+	+			+	
C-2	+		+	+	+	+			+	+			+	
C-3	+		+	+	+	+							+	
C-4	+		+	+			+						+	
D-1				+			+			+			+	
D-2				+			+			+			+	
E-1				+		+				+				
E-2				+						+				
F	+			+					+	+			+	

[1] For grout category names, see Table 2, page 5.

In this category of grouts the speed of the reaction is affected by thermal condition. Thus one should conduct a series of measurements in terms of temperature, in either isothermal conditions at 15°C, or adiabatic conditions, with initial temperature constant at 5°C, 15°C, 25°C, and 35°C. The determination of the critical point below which the grout will not set or at least would take a prohibitively long time (> 24 hrs.) will be made in isothermal conditions. Determination of setting times at 5°C and 25°C in isothermal conditions using the ARRHENIUS equation can define this temperature rather accurately.

Measurements of viscosity, shear strength, resistance to failure, solubility in water, etc. are also applicable to this category as a whole. However, most of these measurements require the preliminary determination of a basic value, which is not necessarily the same for all grouts, or even for all the possible formulas for one type of grout. Moreover, there is no immediate correlation among different types of measurement. These methods have not been retained for this reason.

On-site setting of grout is controlled by placing 100 cm^3 of grout in a beaker at ambient temperature, the object being to control variations in setting time arising from variations in mixing.

Category B. The Category B grouts (colloidal solutions), in general have too low a cohesion rate for the above measurement to be applicable. It is possible to use a viscosimeter or rigidimeter to measure the limit of shear strength of the grout at rest.

As these grouts are not the scene of internal chemical reactions, it would not be helpful to work out a double study in terms of curing method.

Category C. The method used in Category A is equally applicable to grouts in Category C (non-aqueous solutions), without ambiguity for C-1 and C-2, but with some reservations for C-3 and C-4.

The grouts of Category C-3 (Bitumens) are perceptibly different from other grouts. As no chemical reaction takes place, they are nonevolutive at constant temperature. Because of this, these grouts can be kept in a liquid state at the mixing plant by maintaining the proper temperature. However, setting in the ground can be quite complex to determine as it depends on the possibilities of thermal exchange. Thus it can be established that, at the start of grouting in cold ground, setting is nearly instantaneous, becoming slower as the mass of grout injected becomes larger.

For Category C-3 grouts, one must plot a curve indicating changes in viscosity and rigidity as a function of temperature. By referring to this curve, parameters of viscosity are available and setting time can be determined by a measurement of temperature as a function of time. Equally valid would be a method analogous to the ball and ring test used to determine the softening point of bitumens.

In order to monitor the grouting process, gelification is not determined in terms of time, but of temperature (with reference to a setting standard). In situ setting can be monitored by installing temperature gauges in the ground.

For the grouts of Category C-4 (Solvent Systems), setting time is often influenced by the speed with which solvents are eliminated. Thus, this time can be measured only under working conditions, either in situ or in a representative model.

Category D. The grouts in Categories D-1 (Bituminous Emulsions) and D-2 (Other Emulsions) set through destabilization (breaking) of the emulsion. Detection of gelification in the grout alone can be made by optical measurement, but is difficult in most cases. For that reason it is preferable to carry out the measurement on a sample of treated sand.

Category E. The same type of measurement can be used on Category E-1 grouts (Reaction with the Ground). For certain Category E-2 grouts (Reaction with Groundwater) it would be equally possible to measure the setting interval by a rheological method after first adding water to the grout, but it is not certain that one can reproduce realistically the conditions of the terrain.

Category F. The same method is used for Category F grouts (Combined Systems) as for Category A.

3.62 Determination of the Setting Interval on Treated Ground

Knowledge of the instant the grout sets in the ground is of great interest to the grout user. Gelification can be determined rather precisely through variations in the mechanical properties of the sand-grout mix. One can thus use mechanical strength (compression, tension, shear) as a measurable criterion. Table 4 indicates that this method is applicable to all types of grout (with the preceding remarks for C-3 and C-4).

This measurement, which appears simple in principle, proves very complex in practice to obtain, for the cohesion that takes place in the first moments of gelification is very limited and difficult to distinguish from the natural cohesion of sand saturated with a more or less viscous or visco-plastic grout.

The method which we have developed consists of removing the test specimen of grouted sand from the mold at the end of various time intervals, and immersing each immediately in water to which is added a wetting agent. Setting has been attained when these test specimens retain dimensional stability after immersion. To make the test more clear, a small load can be applied to the immersed sample.

As determination of setting time in isothermal conditions on grout alone gives a satisfactory indication of the setting time in situ, the test on treated ground can be omitted most of the time. However, it proves to be indispensable for Categories D and E for which setting is not perceptible in grout alone.

3.7 Conclusion

Measurement of the setting interval of the different categories of grout defined in Volume I and with reference to grout user's criteria proves complex. It is possible, however, to carry out simple measurements which, for design and control will give fully adequate data. The testing procedures have been reduced to a minimum by making the tests as simple as possible.

For many grouts, setting time in the ground is not the same as that determined at the mixing plant, either because of different thermal conditions or because of reaction of the grout with the ground.

Category by category analysis permits simplification of this twofold determination:

- Categories D and E: only determination of setting time in the ground will be used as these grouts do not set outside the ground.

-other categories: since the influence of the ground affects only thermal conditions, determination of setting time will be made using only pure grout (this is simpler and more precise).

If the process of setting is athermal or only slightly exothermal (A-1, A-2, A-3, B-1, B-2, C-2), a single measurement is sufficient. For the others, two measurements are necessary, in isothermal conditions (15°C) and in adiabatic conditions. The first represents the maximum amount of time available for injection, the second represents the maximum amount of time grout can be stored on the surface.

Chapter 4: Third Criterion, Permeability

4.1 Introduction

Grouting to halt water flow is not aimed at absolute water-tightness, but at greatly reducing the permeability of the natural ground, thus cutting seepage to previously determined acceptable levels.

Absolute watertightness is in fact very hard to achieve technically and cannot be justified in practical terms. Furthermore, it would not be economical for it would demand very intensive treatment with very close boreholes, a consumption of grout far exceeding the volume of the voids, etc. In practice, relative watertightness is deemed sufficient. As long as the grouting materials are carefully chosen and certain elementary rules of grouting procedures are observed, adequate overall watertightness can be achieved. By "overall" is meant that, next to watertight or nearly watertight areas (with K at about 10^{-8} m/sec, for example) there will be spots which are less watertight.

It thus appears that the overall permeability of a piece of treated ground is only remotely comparable to permeability readings taken on a small test sample of the same grout in a laboratory. In these conditions, laboratory readings will not give precise advance indication of the effectiveness of the overall treatment.

Thus, it is very easy to design a watertight substance; however, to achieve overall watertightness in a given piece of terrain is more difficult (the same distinction applies to the waterproofing of works such as shaft linings, etc.). As a result,test requirements are divided into two parts:

a) the measurement method for determining permeability of test samples;

b) factors to be considered for determinations of overall watertightness.

4.2 Test Sample Permeability

4.21 Principle of the Test

The principle of the measurement is always the same. One measures the time (t) it takes for a certain quantity of water (Q) under a given pressure (P) to move through a sample of thickness (e) whose section would measure (S). This permits determination of a permeability coefficient (K) through the use of DARCY's equation:

$$K = \frac{Q}{t} \times \frac{1}{S} \times \frac{e}{P}$$

Different experimental systems, varying only in their details, have been outlined in the technical literature. As a general rule, laboratory measurements of permeability are conducted on grout-soil mixtures (using a standard sand for the various tests on chemical grouts). Measurements taken on pure grout do not usually give meaningful results.

Since K will be very low in laboratory samples, any secondary percolation should be avoided, especially around the sample, as any flow between the cell and the sample would distort the figures.

We thus advocate the principle employed in the permeameter developed by F. DIERNAT (fig. 5) and described in Liaison Bulletin No. 19, May-June 1966, put out by the Ponts et Chaussees, France. The inside of the permeameter is lined with a rubber membrane which can be held against the sample by air or water pressure. Since lateral pressure is always kept at slightly higher levels than percolation pressure, there is no movement at the edges of the sample and the membrane molds itself to even the slightest irregularity on the sample's surface.

4.22 Operating Procedure

Since, in these conditions the measurement cannot be made in the injection cell itself, the operation must be carried out in two stages:

a. Preparation of the test sample

A classic cell with a smooth rim is used, whose inside diameter is slightly less than that of the permeability cell (the difference in diameter being, if possible, 3 to 4 millimeters). The cell is filled with a standard sand compacted as much as possible (dry sand is placed in the cell layer by layer and is shaken down and tamped throughout this process). The grout to be tested is injected into the cell from the bottom up and continued for some minutes after the grout has passed through the sand so that voids will be filled to an optimum degree. At the end of the injection procedure, the delivery pipe is shut off to avoid

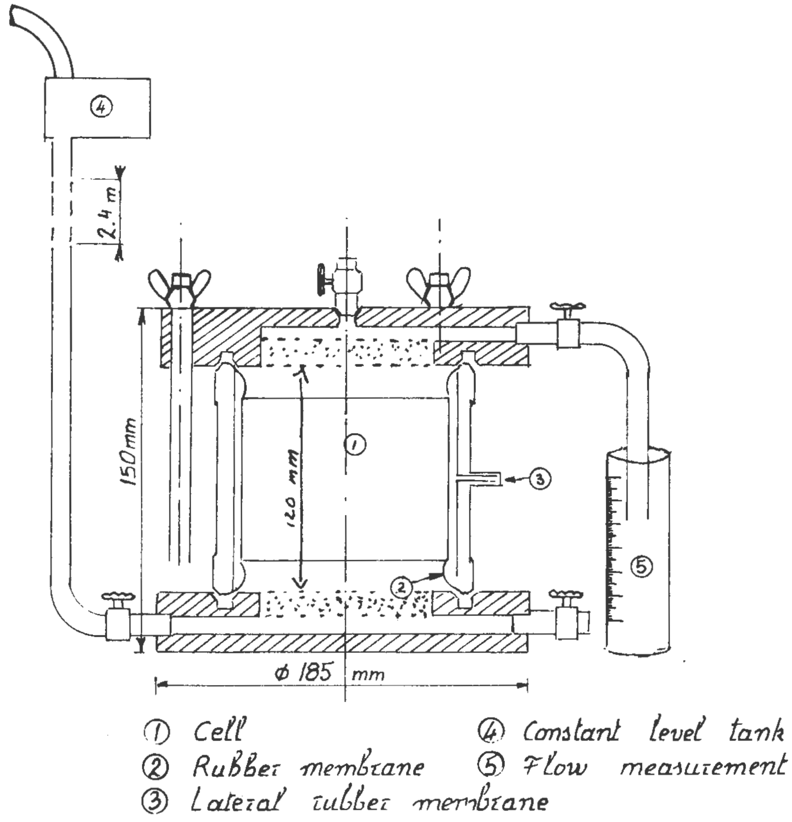


Fig. 5. Membrane Permeameter

any drainage. The grout is allowed to harden over an interval determined by the nature of the grout and its composition. In this regard, one can refer to the intervals indicated in Chapter IV, "Strength of Treated Ground".

Instead of injecting the grout into the cell, it can be mixed directly with the sand. This simplified method, noted several times in the preliminary survey, is less representative. Similarly, for on site monitoring, test samples could be taken from the grouted ground. However, this procedure is difficult to control, since if the ground is only slightly consolidated, or if it contains boulders, experience has shown that permeability test samples taken from these areas will not be representative.

b. Measurement

The test specimen is removed from the mold with a press and placed in the permeability cell with allowance made on both ends for filter-gravel. Once the cell is in place, lateral pressure is applied. This lateral pressure must always be higher than percolation pressure so that the membrane will remain flush against the sample.

While the percolation pressure must remain compatible with the capabilities of the cell, it must also be sufficient to ensure a flow rate of at least 5 cm/hr. Given the possibilities of inaccuracies inherent in the test, an excessively slow rate of flow would seriously risk distorting the permeability figures.

For very low permeabilities, distilled and deaerated water must be used.

4.3 Overall Watertightness of Ground

The permeability criterion, as defined here, means little if not considered in conjunction with other criteria. In fact, overall watertightness in treated terrain depends much more on the homogeneity of the treatment than on the grout's intrinsic permeability.

An example will illustrate this point. Imagine that one is to waterproof a vertical curtain 100 metres long, 20 metres high and 2 metres thick, the area to be grouted being composed of a homogeneous sand whose initial permeability is $3x10^{-2}$ cm/s under 20 metres head of water.

It matters little whether the grout's intrinsic permeability is 10^{-7} cm/s or only 10^{-6} cm/s. This would give a theoretical leakage rate of under 1/10 litre per second. However, if (due to a grout which was too viscous or which set too fast) there remains in this curtain an untreated opening 2 metres wide and 10 metres high (1% of the total cross-section of the curtain) the leakage rate would increase to 45 litres per second. The leakage rate resulting from an untreated area equivalent to 1% of the total cross-section of the curtain will be 500 times higher than that for the curtain as designed.

This example clearly shows the need for choosing a grout whose viscosity and setting time can be regulated according to the characteristics of the terrain to be treated, so that no areas will remain untreated.

Thus, overall watertightness depends on:

a) The viscosity of grout at the time of injection. If the grout to be injected is initially too viscous for the gradation of the ground, voids will not be completely filled and watertightness will be affected. Furthermore, there is some risk of failure. Conversely, a very fluid grout injected into rather coarse ground may miss the target area. A spectacular consequence of an unsuitable grout can be observed in places where the ground is built up in layers. If the grout used is too fluid, it will first penetrate widely into the more open layers, and then very little into the less permeable ones. But once the injection is done, the grout runs by simple gravity from the open layers down toward those which are less permeable (CARON 65-23, 66-03).

   To reduce this risk, normally a two-shot injection procedure is used: a cement-base grout is injected first to plug the most permeable layers and then a fluid grout is injected in the second phase. It can be seen that the operating procedure followed is crucial to overall watertightness.

b) The ease with which setting time can be regulated. If the setting time of the grout used is too short, the grout will be too viscous. Conversely, if the setting time is too long, the grout may filter down past the target area.

c) The intrinsic strength of the grout once in place. If the intrinsic strength of the grout in place is inadequate for the head of water in the water table, it may loosen, producing a sudden sharp increase in permeability.

d) The durability of grout once in place. It is pointless to have a good initial permeability coefficient if the grout will be vulnerable to rapid attack (dissolution upon contact with water seepage, for example), since permeability will increase rapidly.

4.4 Conclusion

This analysis demonstrates clearly that the concept of overall watertightness is far more dependent on the four criteria of viscosity, setting time, strength and durability than on that of localized permeability. In Part Three of this volume (examination of the mechanical characteristics of the principal grouts) permeability will be discussed further.

Chapter 5: Fourth Criterion, Intrinsic Strength of Grout

5.1 Definition of Intrinsic Strength and Types of Measurements Used

Strength can be characterized, a priori, by measurements as diverse as compressive strength with or without triaxial stress, tension, flexure (bending), shear strength, puncture strength, impact strength, extrusion, hardness, etc.

Where a grout is to be used for consolidation, it is usual to test it for unconfined compressive strength (WARNER 72-04). However, depending on the nature of the consolidation grout to be used, the strength of pure grout can differ so widely from the strength of ground which has been grouted, that all authors have renounced efforts to take measurements on pure grout used for consolidation. Determination of strengths of consolidation grouts will thus be examined in the following chapter.

Once a waterproofing grout has set in the voids in the ground, the grout should resist pore hydrostatic forces which would tend to displace it (level of the water table or head of water). This is a characteristic of mechanical strength, even if only slight, and it should be considered for any waterproofing applications. If the grout is to serve its purpose, it must stay where it is in the ground and not give way under pore hydrostatic pressure, unpack or wash out.

H. CAMBEFORT (64-12) has developed the following theoretical formula to express the relationship between displacement stress, the injected grout's cohesion, and the characteristics of the ground:

$$P = (1-n)\,LSC$$

where:
P is displacement stress
n is the porosity of the grouted ground
L is the length of the grouted curtain
S is the surface area of the soil [1]
C is the cohesion of the grout

The figures drawn from experiments which lead to this formula are plotted in fig. 6.

From this formula one can compute, for example, that a cohesion or shear strength of 0.5 g/cm^2 is

---

[1] $S = \frac{\text{Surface area of particle}}{\text{Volume of particle}}$

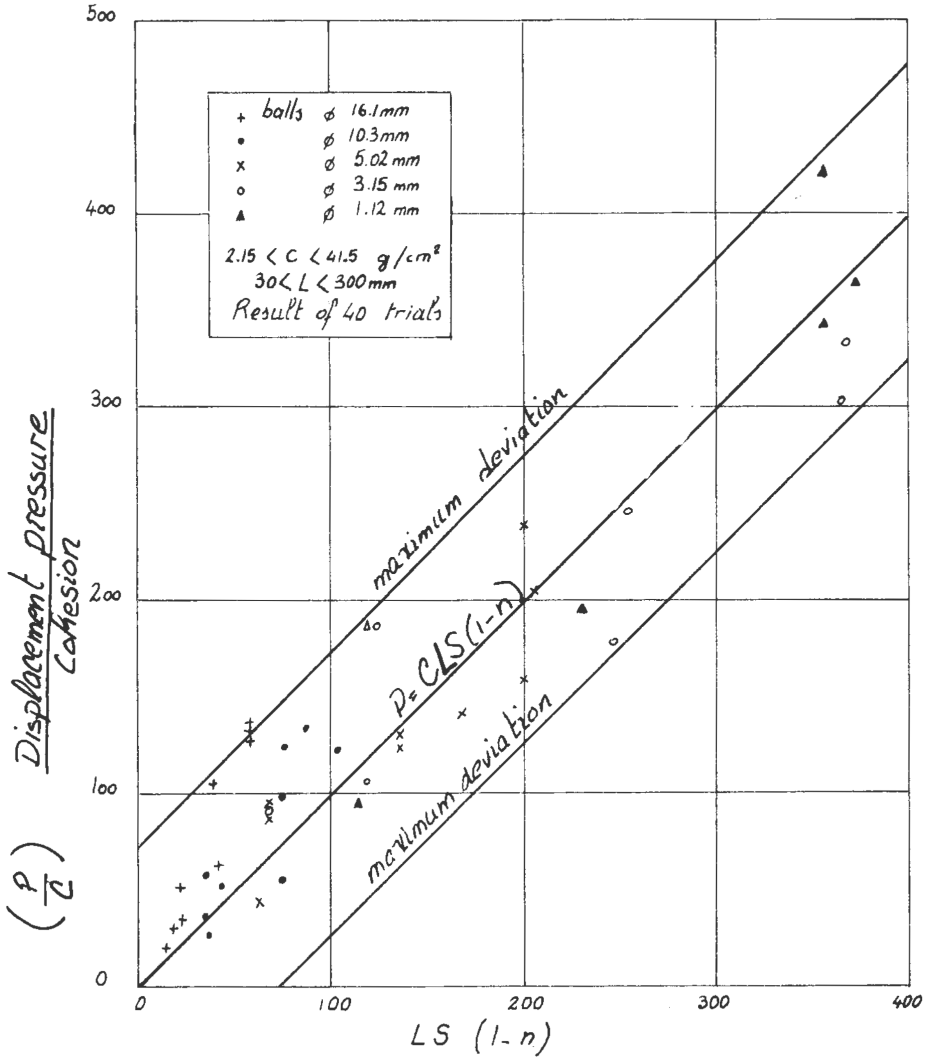


Fig. 6. Displacement Pressure (P) for a Grout with Cohesion (C) in Terms of Specific Surface (S), Porosity (n), and of the Length of Area Grouted (L)

sufficient to prevent a grout from being displaced under the pressure of 100 metres of water in a curtain two metres wide installed in ground whose specific surface area is 150 cm^{-1} and whose porosity is 0.35.

Thus, waterproofing grouts can have low strengths without incurring any disadvantages. Therefore, all measurements such as tension, impact, and unconfined compressive strength can be eliminated immediately, as most of the samples prepared would be much too soft for this type of test.

Penetration resistance, the method used by F. W. HERRICK and R. J. BRANDSTROM (66-05) with a penetrometer of the "Proctor" type standardized by the A.S.T.M. C 403-61 T, as well as a test for extrusion strength, a method proposed by Michel M. BEN ARIE in the "Journal of Polymer Science", XXVII, 1955, are methods which are easy to use, but figures obtained from them can be difficult to correlate.

For measuring the strength of pure grout, we recommend the vane shear test like that used by CARON (65-04) for silica gels. This method is the simplest and most accurate for soft mixtures. It is also the most logical since it permits accurate monitoring of changes in strength over time.

5.2 Equipment

The principle of the vane shear test can be found in EVANS and SHERRAT (J. Scientific Institute 411-25, 1948) as well as in EVANS (Geotechnique 16, 1950) and also in the Liaison Bulletin of September 1963, put out by the Ponts et Chaussees Laboratory No. 3.

Torque is usually exerted by a standard spring. The turning device can be a cylinder as long as cohesion is low, but when it increases there is some risk of extraneous slippage of the cylinder on the grout. It is better to use a notched cylinder or even a star wheel. This piece of equipment, in common use in soil mechanics laboratories, is quite suitable for testing waterproofing grouts if a few precautions are taken.

Shearmeters were designed essentially for the field of soil mechanics and for shear strengths which would be generally higher than those encountered in waterproofing grouts. Some models, such as the L.C.P.C. (FRANCE) or the PILCON Engineering (U.K.) do not give precise results for chemical waterproofing grouts.

For this reason, we have chosen the vane test of WICKEHAM-FARRANCE (U.K.). This vane test normally comes equipped with a set of four springs, which permits measurement over a rather broad range of shear strengths. In order to increase accuracy and extend the range of measurement, one can attach a set of star-wheels of varying dimensions to the set of springs. This instrument will also have the advantage of being very stable and well guided. In its motorized version, it produces a constant rotative speed of 20°/minute.

So that shear strength measurements can be taken at varying speeds, it is advisable to attach a series of gears to the motor. A non-motorized version of this apparatus exists for use at worksites.

Among the grouts listed in the different categories, some are fragile, others purely elastic or plastic or visco-elastic or even visco-plastic. From such diversity it emerges that the speed at which the measurement of strength is taken is of paramount importance. (For categories C-3 and D-1, bitumens, shear strength is of no significance since the substance is completely viscous.)

In nearly all grouts, strength changes from the moment of set (an arbitrary point in time in the grout's total evolution) up to final stabilization. In some cases strength continues to increase indefinitely over time. Conversely, in other cases final strength is attained very rapidly. The moment at which strength is to be measured must be defined.

Results of grout strength testing are not comparable from one laboratory to another if test conditions are not identical. Standardization of test procedures for determining intrinsic strength of grout will be the subject of the following paragraphs.

5.3 Preparation of Pure Grout Test Samples

Once prepared, the grout is poured into chemically inert (plastic) containers while care is taken to avoid any interaction with the grout. The inside rims of the containers should be rough so that the grout will adhere to them.

One shear test should be conducted on each container. Thus the number of containers needed will correspond to the number of measurements to be taken.

The diameter of the mold has some influence. For each type of material there is a sample diameter limit below which viscosity, by becoming paramount, will distort measures of cohesion (W. PARZONKA, "An Accurate Method for Determining Rheological Constants in Bingham Plastic Substances with a Viscosimeter of the Couette Type". La Houille Blanche, No. 8, 1964). According to the results summarized in Table 5, the containers should be at least 18 cm in diameter.

5.4 Curing Conditions

There are four principal methods used for curing test samples: in freely-circulating air, in water, in a moisture-saturated atmosphere, and in airtight containers.

The last type of cure is the best for observing progressive changes in the center of a grouted mass; this inner mass is preserved from direct contact with air or water. This type of cure, in airtight containers, is also used for measuring the shear strength of pure grout (as is the case in the following chapter for measurement of unconfined compressive strength of sand-grout compounds).

As long as the curing temperature is kept within certain limits, from 15 to 25° C, it will not have perceptible effects on curing. This type of cure precludes any shrinkage, surface crackling, or deep cracks, whatever the water-vapor content in the surrounding atmosphere.

5.5 Age of Test Samples at Shear Strength Measurement

Unlike hydraulic binders and, by extension, cement-clay grouts, chemical grouts quickly reach their final strength. In many cases, optimal characteristics are obtained after one or two days of curing. Rare are the grouts whose strength continues to increase indefinitely and even in these cases the increase in strength is slight. As a result, shear strength in chemical grouts can usually be measured quickly. Unless otherwise stipulated, one week of curing is adequate.

At actual worksites, shear strength results may be needed sooner. The times given in Table 6 for each type of grout are suitable for determining shear strength to within 10% of the long term value.

Table 5 . Effect of Sample Diameter on Shear Strength Values

Type of mixture	dia. 6 cm		dia. 12 cm		dia. 18 cm		dia. 50 cm		dia. 100 cm	
	Shear Strength in g/cm2	Yield in degrees	Shear Strength in g/cm2	Yield in degrees	Shear Strength in g/cm2	Yield in degrees	Shear Strength in g/cm2	Yield in degrees	Shear Strength in g/cm2	Yield in degrees
lignochrome gels										
(1)	38	48	34	43	32	39				
(2)	200	39.5	185	37.5	165	36.5				
(3)	111	41	92	33.5	89.5	40.5	89.5	33.5	88.5	32.5
(4)	174	32.5	165	29	162	32.5	166	30	165	31
(5)	368	31.5	368	32.5	336	31.5				
silicate-glyoxal gel	58.5	22.5	60	18	59	20	59.5	20		
silicate-aluminate gel	110	35	108	30	97.5	30.5	98	31		
clay-cement gel										
(1)	77	15	74.5	12	82	11				
(2)	237	14.5	245	15	250	16				

Table 6. Grout Aging Time for Shear Testing

Type of Grout	Strength Measured After:
A-1, silicate derivatives	24 hrs
A-2, other mineral gels	24 hrs
A-3, lignosulfite derivatives	7 days
A-4, other plant derivatives	7 days
A-5, acrylamide derivatives	24 hrs
A-6, highly concentrated phenoplasts	24 hrs
moderately concentrated phenoplasts	5 days
slightly concentrated phenoplasts	15 days
A-7, aminoplasts	
highly and moderately concentrated	24 hrs
slightly concentrated	5 days
A-8, combination grouts	2 days
B-1, organic colloids	7 days
B-2, mineral colloids	7 days
C-1, synthetic resins	too strong
C-2, vulcanizable oils	7 days
C-3, bitumens and other heated compounds	not applicable
C-4, systems incorporating solvents	not applicable
D-1, bituminous emulsions	impossible or not applicable
D-2, other emulsions	
E-1, reactions with the ground	
E-2, reactions with ground water	
F, combined systems	7 days

5.6 Preparing the Measurement

The sample container with a corrugated rim is held in such a way that it will not rotate with the sample it contains. The star-wheel attached to the shear meter is then lowered slowly into the center of the container with the substance to be tested for shear strength.

The star-wheel can be lowered until submerged in the sample or its upper face may be level with the grout surface. Such considerations must be factored into computations of shear strength:

Thus, for a face (level with sample), one would take:

$$Mt = \frac{2\Pi a^2}{3}(a + 3b)R \qquad \text{Thus, } R = \frac{3\ Mt}{2\pi a^2(a + 3b)}$$

Mt being torque
a = star-wheel radius
b = star-wheel height
R = shear strength

and, for two bases (with the star-wheel completely submerged in the substance):

$$Mt = \frac{2\Pi a^2}{3}(2a + 3b)R \qquad R = \frac{3\ Mt}{2\pi a^2(2a + 3b)}$$

5.7 Effect of Speed on Shear Strength Measurement

The rate of strain is extremely important in determining shear strength and yet its effect is poorly understood. For usual construction materials (concrete, steel), the effect of the speed with which the load is applied has often been examined and it has been demonstrated that mechanical characteristics weaken when stress is applied slowly. But this decrease is so slight that it serves no purpose to account for it in practice. In the field of soil mechanics this phenomenon is more noticeable with clays, marls, chalks, etc.

H. CAMBEFORT dealt with this matter of long-term strength as a function of the duration of applications of stress for several natural soils whose cohesion was measured by applying stress for intervals ranging from 14 seconds to 10 years. Fig. 7 shows variations in the cohesion of these soils as a function of the length of time during which stress was applied (76-03).

His conclusions are the following: laboratory tests should last several hours if comparable field results are desired. Standardization of test speeds is not enough since the amount of time the test takes will depend on the strength of the material tested. Strength after ten years will be about half (0.55 to 0.60) of what it was at the end of five hours, the average interval used for laboratory tests. The safety coefficient of 3 usually adopted with clays is thus not excessive.

Sharp increases in strength are recorded when tests are conducted very rapidly, for example when time (T) is under a half hour. This principle is particularly pertinent when penetrometers or shearmeters are used in testing.

Can these conclusions be applied to chemical grouts? The characteristics of the different chemical grouts vary widely; they can be predominantly viscous or plastic or elastic. Should they be compared to clay type materials or, conversely, to cement type materials?

In order to find the answer,the various types of materials at varying shear speeds are compared in Table 6. In order to keep variables to a minimum, the sample's diameter was the same for all tests. Similarly, the shear-

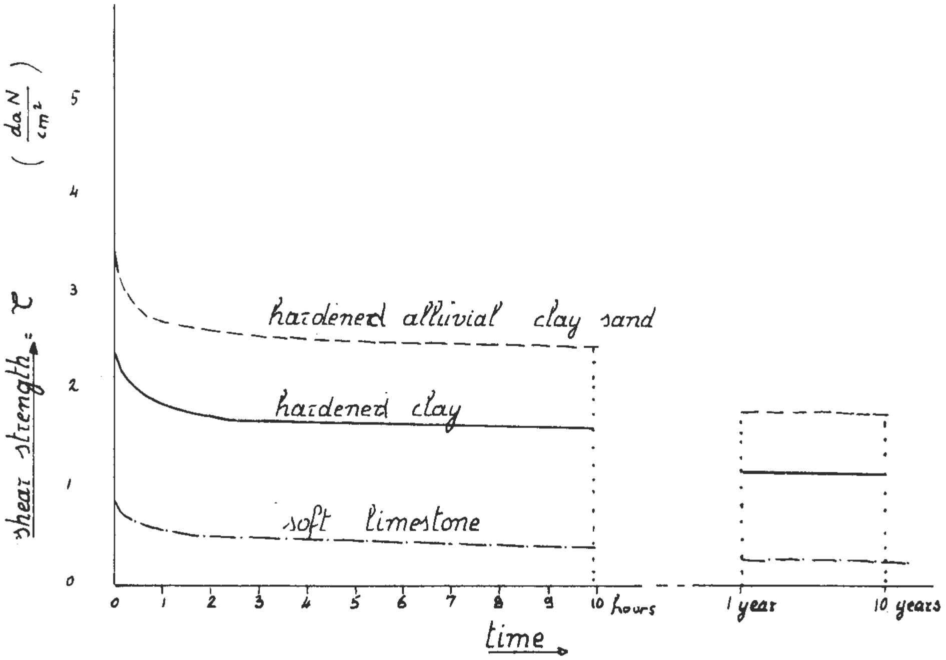


Fig. 7. Effect of Stress Duration on Cohesion of Soils

meter was always used with the same vane and, whenever possible, with the same spring. A gearing system was installed so that the speed of the shearmeter motor could be varied from 1°/min to 400°/min, the usual vane test speed being 20°/min. Table 7 shows shear strengths for only three values of $\frac{Vn}{20}$, Vn and 20 Vn (Vn being the usual speed in the vane test = 20°/min).

Table 7. Shear Strength of Various Grouts

Type of mixture	Shear strength in g/cm^2		
	$\frac{Vn}{20}$	Vn	20 Vn
Clay pastes	32.5	37.2	44.0
	43.4	51.2	55.2
	58.8	69.5	76.4
	81.5	96.2	104.5
	185.0	209.0	243.0
Cement-clay grout	86.5	82.0	84.2
Clay-plaster grout	103.0	102.2	103.0
Silica gel (with glyoxal)	35.0	87.0	112.0
Lignochrome gel	73.0	118.0	145.0
Acrylamide resin	95.6	95.8	101.0
Phenoplast resin	415.0	435.0	475.0

This table demonstrates that shear speed has a highly variable effect on shear strength depending on the nature of the material. It has been confirmed that:

a) The strength of clay-base mixtures clearly decreases as stress is applied more and more slowly.

b) Non-chemical hydraulic binder-base grouts (cement-clay or plaster-clay) are not affected by differences in shear speed for the range of speeds tested and discounting for testing errors.

c) The strengths of some visco-plastic type chemical grouts (such as silica gels) vary far more widely with different speeds than do those of clay pastes. The reverse is true with acrylamides and phenoplasts; their strengths vary only slightly.

For shear strength tests, the vane is driven by the spring in such a manner that the sample's true rate of yield is discounted from the corresponding yield of the spring. Thus it is the sample's rate of yield and not the speed of the motor which should be plotted on the graph $R = f(v)$. Another way of representing this phenomenon will account for the duration of the shear: $R = \frac{f(l)}{v}$.

These two types of formulas $R = f(v)$ and $R = \frac{f(l)}{v}$ give a precise indication of the effect of the amount of time during which stress is applied on the product's real strength. Such determinations are mandatory for each category of chemical grout for in many cases this effect is essential.

It should not be forgotten that this duration of stress application can be very long for some application cases. In others, such as excavating galleries or tunnels, the treated ground will only have to bear stress for some hours (after which the shoring supports once again carry the load); nonetheless, this interval can extend to some days or even some weeks for the initial stages of excavation work. This interval can stretch out to several decades for watertight curtains under dams and other civil engineering projects. During this period when it will undergo stress, the grout will have to maintain sufficient shear strength (disregarding risks of dissolution) to resist displacement.

Since the amount of time during which stress must be applied varies widely according to the type of application, it would not he helpful to standardize one test speed.

For routine controls (for example, checks to determine the uniformity of the grout at a worksite), the problem is different. In this case, testing at one speed is useful for purposes of comparison, even though test results may be arbitrary. For such tests conducted in series, a speed of 20°/mn should be adopted, since this is the usual speed of the WICKEHAM FARRANCE vane test used in most laboratories.

5.8 Conclusion

Because of their nature, most chemical grouts can be subjected to only one shear test to measure their strength in a pure state.

It appears that speed is the essential parameter of this test. In theory, since it is mandatory to learn the behavior of grouts under stress applied very slowly, shear tests should be conducted at varying speeds so that extrapolations may be made at very slow speeds. On a practical level, the adoption of one rather fast shear speed permits comparisons among different laboratories and also allows controls to be conducted more frequently since the test can be carried out quickly.

Chapter 6: Fifth Criterion, Strength of Treated Ground

6.1 Definition and Factors Affecting Strength

A ground mass must be able to support mechanical stress created by the ground itself or the weight of structures which tend to deform it, or destroy its cohesion. Thus the treated area (the grouted soil mass) must withstand the effect of various forces. This is a realistic definition of strength.

As is the case with pure grout, this strength can be characterized by measures as diverse as unconfined compressive strength with or without triaxial confinement, tensile strength, bending strength, shear strength, puncture strength, impact strength, extrusion strength, hardness, and others. All these tests are used in the field of soil mechanics to determine the characteristics of soils.

The preceding chapter showed that the intrinsic strength of nearly all grouts changes variously after setting; the same is true of grouted ground. Thus, the moment at which the measurement will be taken must be defined, and the type of cure to be used between the moment of preparation and the time when the measurement will be taken must be defined. Finally, as with pure grout, the size of the test samples must be standardized, as well as testing speed.

These various influences on strength were examined in the preceding chapter on pure grouts. The influence of the terrain itself must be added, using a reference sand to be defined as to particle size and compactness.

Most chemical grouts (silica gels, lignochrome gels, aqueous resins, bituminous or polyester emulsions, etc.) are essentially glues whose nature is such that the strength of the grouted ground will have nothing in common with the strength of the pure grout. Thus, the standardization of mechanical characteristics will concern mixtures of sand and gel or sand and resin. All the respondents to our survey were in agreement on this point: they all conduct measurements on mechanical characteristics of grout-ground mixtures.

It is essential that the ground chosen for the strength test be as close as possible to the natural ground in particle size, compactness and chemical makeup. In the last case, this resemblance is imperative if the grout's set is linked to the chemical nature of the ground, as with Category E-1 grout.

A grouted ground's strength (Rg) is a function of both the characteristics of the pure grout (Cp) and the characteristics of the terrain (Ct) that is, Rg = f(Cp,Ct) and, with a reference sand, Ct becomes constant. It would seem possible then that strength tests could be conducted on pure grout, factoring in a coefficient (determined from laboratory tests) to obtain the strength of the treated terrain. In fact, this simplified method is not valid, for, apart from strength, another very important characteristic of a grout is its adhesiveness. Two pure grouts with the same intrinsic strength may not have identical strengths in combination with the ground. In such conditions, the determination of grout-ground strength cannot be extrapolated from the strength of the pure grout.

6.2 Choice of Strength Test

Since a mass which has been grouted for purposes of ground consolidation will be subjected mainly to mechanical stress (compression), the usual test would be for unconfined compressive strength. This test is sufficiently representative for control and comparison purposes. However, for each particular study carried out at a worksite, triaxial tests are a necessity and must correspond exactly to the stress exerted by the terrain to be treated.

No laboratory concerned with grouts conducts tests for tensile strength. Thus, very little information is available on compressive strength/tensile strength ratios.

The two sources found were:

1) In the range of epoxy products and polyesters (Category C-1), relatively extensive research on synthetic mortars indicates a ratio Rc/Rt of 2 to 4, but these products are rarely used as chemical grouts.

2) More interesting is VAN LOON's (71-06) research on phenoplasts (Category A-6). For unconfirmed compressive and tensile strengths (by the Brazilian test), 12 formulas were tested with two types of sand. The 24 figures obtained give an average Rc/Rt ratio of 5.

As in the preceding case, the figures are given in order of importance. In a given category, the type of formula will affect the Rc/Rt ratio. The 24 figures derived from VAN LOON's study are as follows: 4.27, 4.66, 5.43, 5.77, 5.41, 4.41, 4.37, 4.61, 4.79, 5.52, 6.39, 6.66, 4.66, 4.52 4.54, 4.18, 4.17, 3.20, 7.20, 7.74, 7.77, 5.78, 6.11, 5.42.

The unconfined compression test on a grout-ground mixture is applicable to nearly all the grouts classified. There are, however, two cases where this test is not suitable: the C-3 and D-1 families, bitumens and bituminous emulsions. Here the highly plastic character of the binder used renders the compression test meaningless. However, these two categories are rarely used in grouting.

6.3 Choice of a Reference Soil

It appears obvious that before standardizing the method to be used for preparing grout-soil test samples, as well as the parameters pertinent to compression tests, one must define a reference soil which can be easily reproduced from one laboratory to another. The choice is at once delicate and, of necessity, arbitrary.

6.31 Influence of Particle Size

Chemical grouts without particles are used only for grouting ground composed of medium to very fine sands, even silty ground. Thus for particle size, the HAZEN d_{10} ranges from about 0.02 to 0.5 mm, or with corresponding specific surfaces of 100 cm^{-1} to 1,000 cm^{-1}.

While the strength of a coarse soil treated with a clay-cement grout depends little on the gradation of the soil, this is not the case with chemical grouts. CARON (65-04), in a general study of silica gels, has shown that the influence of a soil's gradation could be expressed as follows:

$$Rs = Rc(1+k\sqrt{s})$$

where:
Rs is the unconfined compressive strength of the grouted soil
Rc is the theoretical unconfined compressive strength of the pure grout
S is the sand's specific surface
k is the coefficient which depends on the grout's strength or, more precisely, on its cohesion. This coefficient varies widely depending on the nature of the gel.

An example of the influence of specific surface, and thus of the sand's gradation, on strength is shown in fig. 8. In general, this type of relationship is not unique to silica gels; the same relationship for aqueous phenoplast resins is shown in fig. 9.

In research such as VAN LOON's (71-06) experiments were conducted on sands of different gradations. Results of strength testing in terms of specific surface in many cases corresponded to those predicted by CARON's formula. In general, this formula can be used to determine the strength of any terrain with a specific surface (St) from the standardized strength of a sand with a specific surface (Sn).

As a secondary factor, the coefficient of uniformity in the sand exerts some influence; in general, widely graded sands give better strengths than closely graded sands (in figures 8 and 9, they are above the median). All other things being equal, a sand composed of angular particles will perform better than a sand with rounded particles.

Upon comparing the results of a phenoplast resin injected into a natural sand with the same resin injected into a sand obtained by mechanical crushing, but having the same gradation, their strengths were 7.0 and 10.7 bars, respectively.

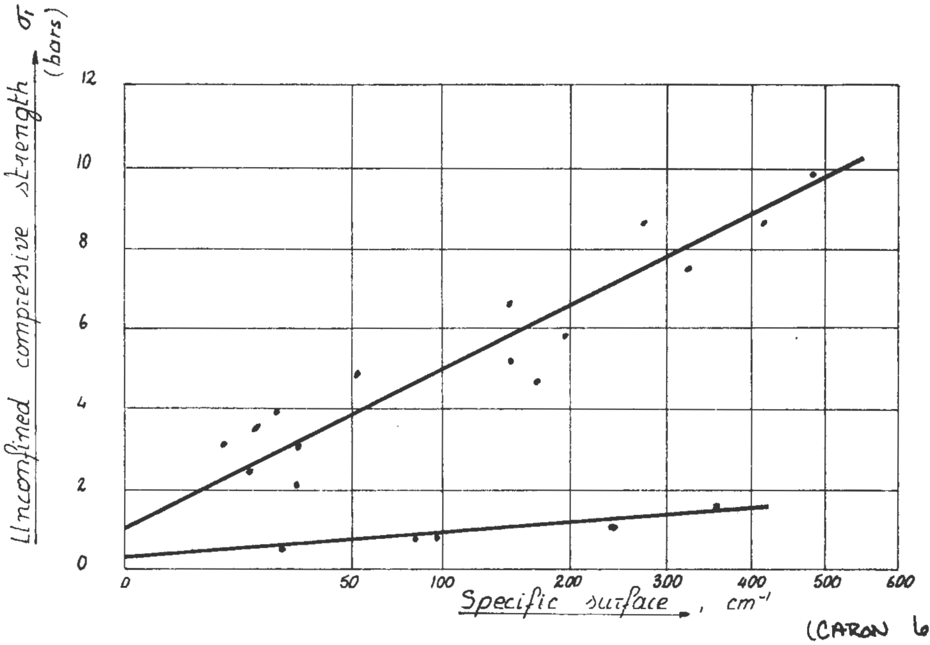
6.32 Influence of the Sand's Chemical Nature

Since naturally occurring sands are generally silicious and calcareous, it is logical to assume that the relative percentage of silica and calcium might have an effect on strength.

No research was available on this topic in the professional literature so that the following testing was necessary. Two sands of strictly identical particle size were reconstituted by sifting, one being a pure silica sand, the other very rich in calcium (63% Co_3Ca). The two were mixed together at ratios of 100/0, 75/25, 50/50, 25/75, 0/100. The different mixtures were injected with various grouts (silica gels and phenoplast resins at varying degrees of diluteness). Figs. 10 and 11 indicate that silicious sand tends to give slightly better results than calcareous sand.

6.33 Influence of Compactness

The distance between the grains also has some influence. The more compact the sand, the greater will be



(CARON 65-04)

Fig. 8. Influence of Specific Surface on Strength of Silica Gel

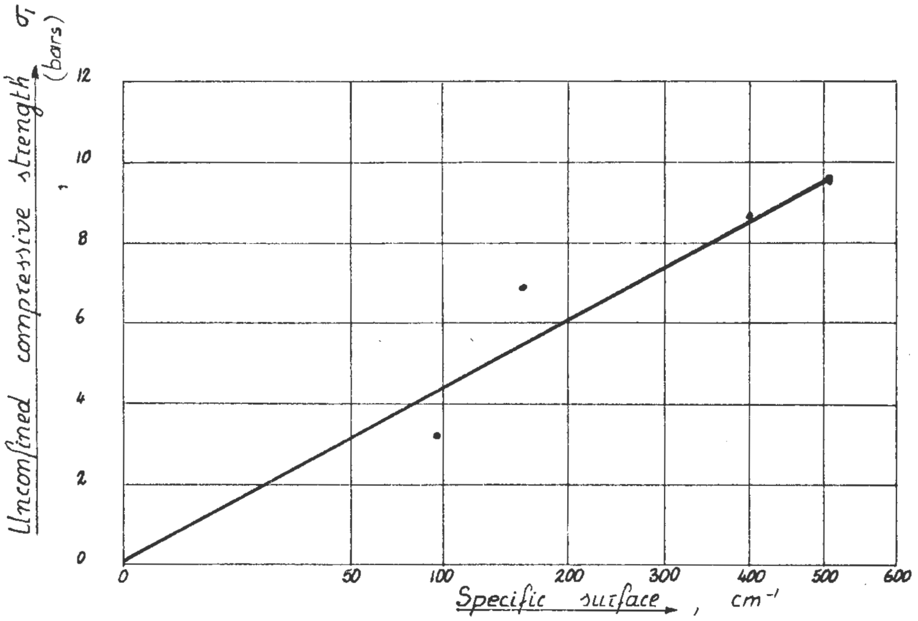


Fig. 9. Effect of Specific Surface on Strength of Phenoplast Resin

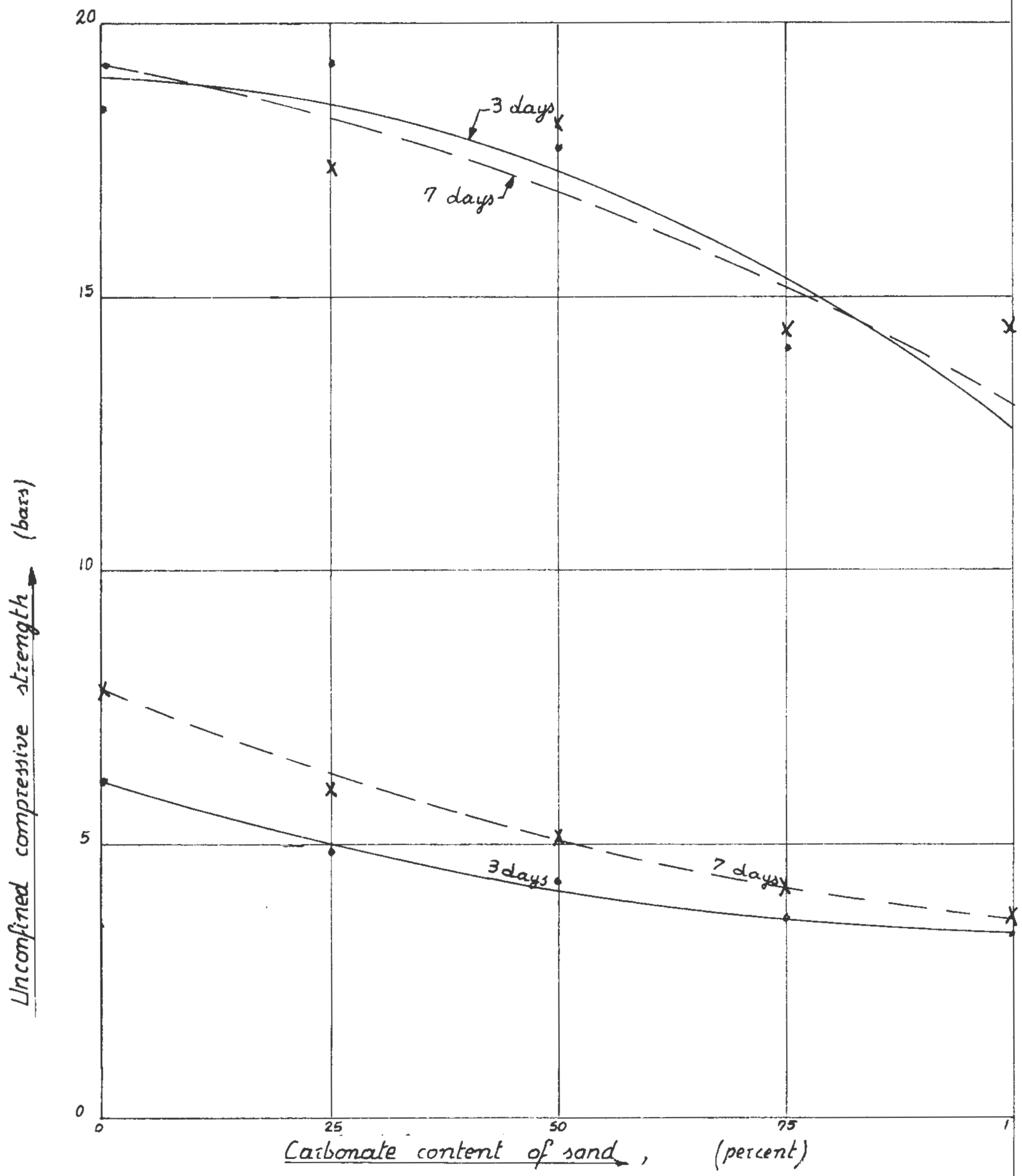


Fig. 10. Effect of Carbonate Content of Sand on Unconfined Compressive Strength of Silica Gel

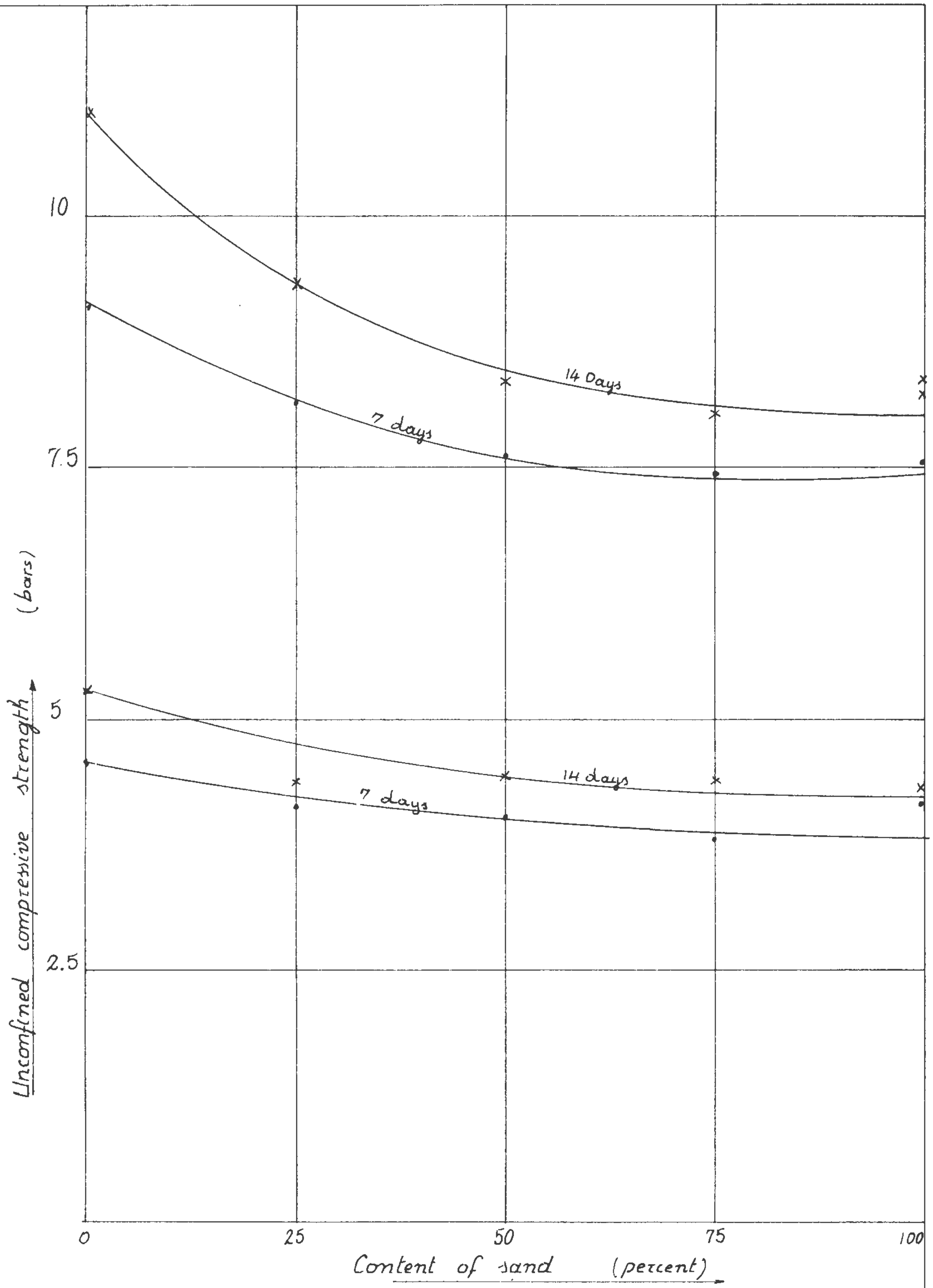


Fig. 11. Effect of Carbonate Content of Sand on Unconfined Compressive Strength of Phenoplast Resin

the strength of the sand-grout mixture. A sample which is tamped and then injected will be stronger than a test sample obtained by mixing the sand with the grout, the sand and grout being constant. For this reason most laboratories use the grouted column method for strength tests. This phenomenon also explains why strength readings taken "in situ" (with very compact sands) are generally higher than those taken in laboratories.

Finding no previous research on the influence of degree of compactness, we conducted tests on two types of silica gel (hard and semi-hard) mixed with fine sand, 0.1 to 0.3 mm, at varying densities. Figs. 12 and 13 show the significant influence of this factor.

6.34 Influence of Percentage of Voids Filled by Grout

If the proportion of the voids filled is low, strength will drop. This is shown in table 8 below for two silica gels of differing diluteness.

Table 8. Correlation Between Void Size and Strength

% Void Filled	Strength in Bars as Function of % of Voids Filled	
	50% Dilution	60% Dilution
100	3.100	2.040
85	2.450	1.370
70	1.750	0.700
44.5	0.360	0.220

6.35 Choice of Reference Sand

a) Since naturally occurring sands are rounded and not crushed, the reference sand should not be artifically ground.

b) A reference sand should correspond to the particle sizes encountered in chemical grouting. Fig. 14 shows the range of reference sand particle sizes used by the various laboratories responding to our preliminary survey. In view of the importance of his work, we have also indicated the gradation used by WARNER (72-04).

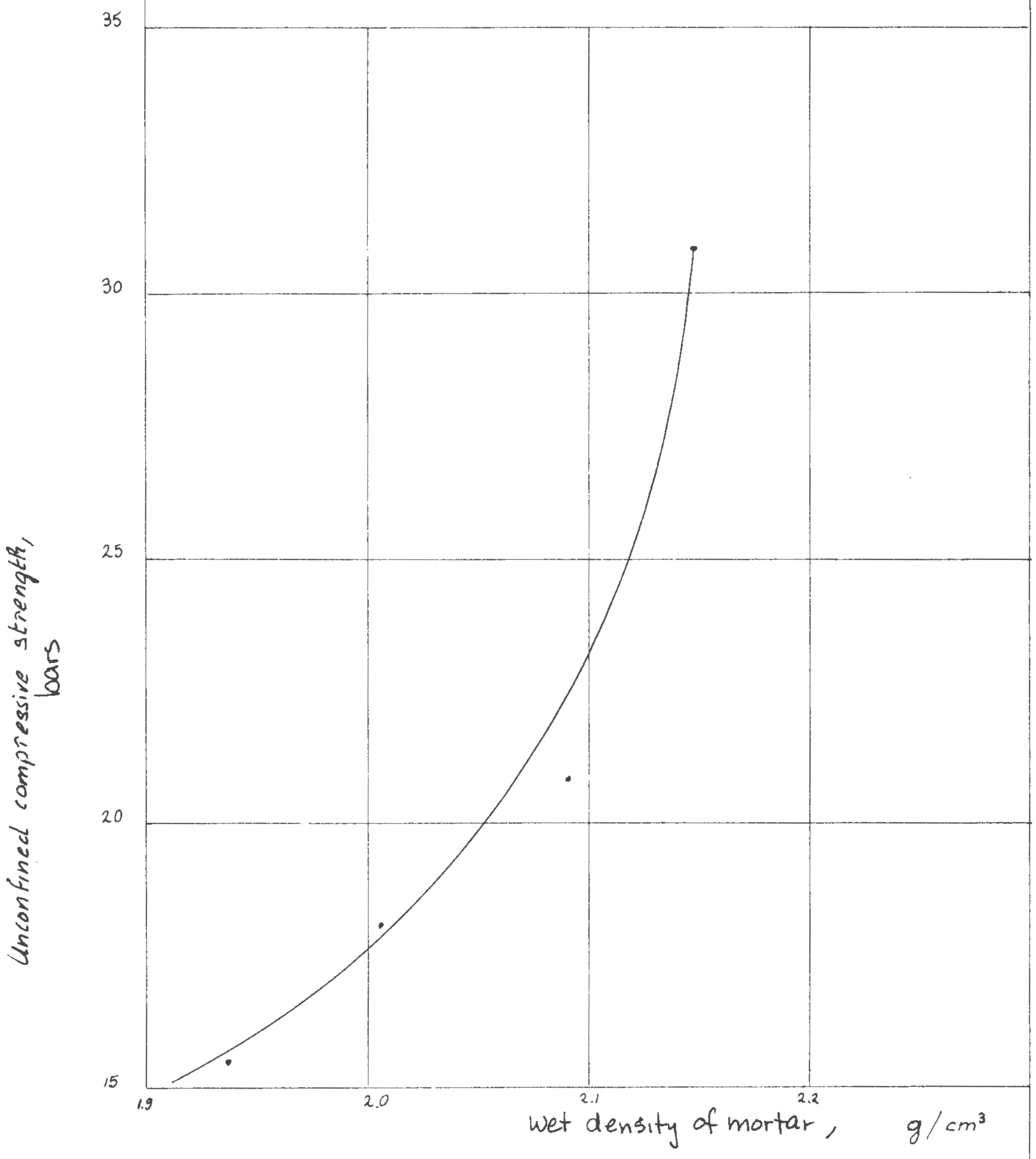


Fig. 12. Relation of Wet Density to Strength for Silica Gel Mortar (Hard Gel)

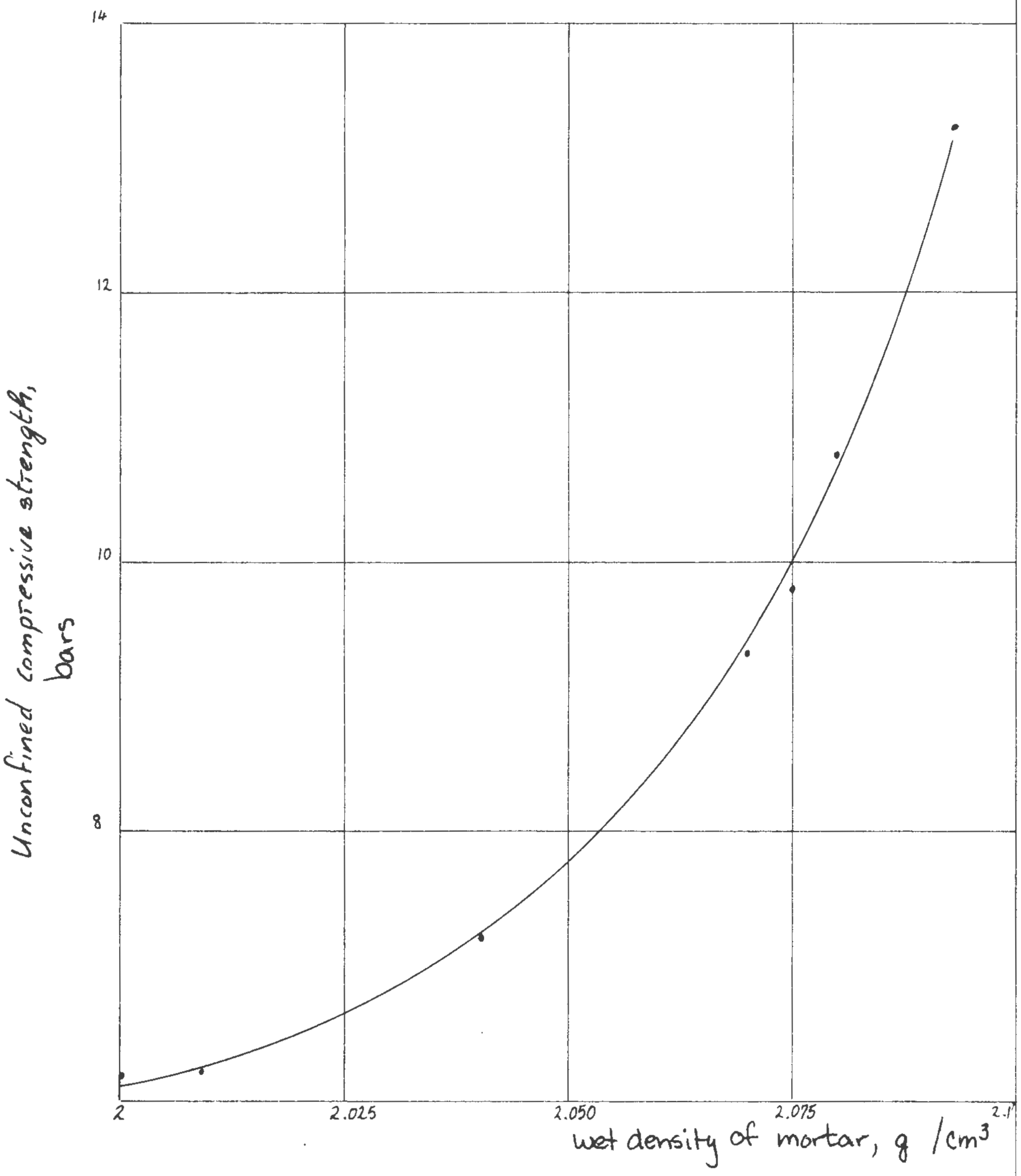
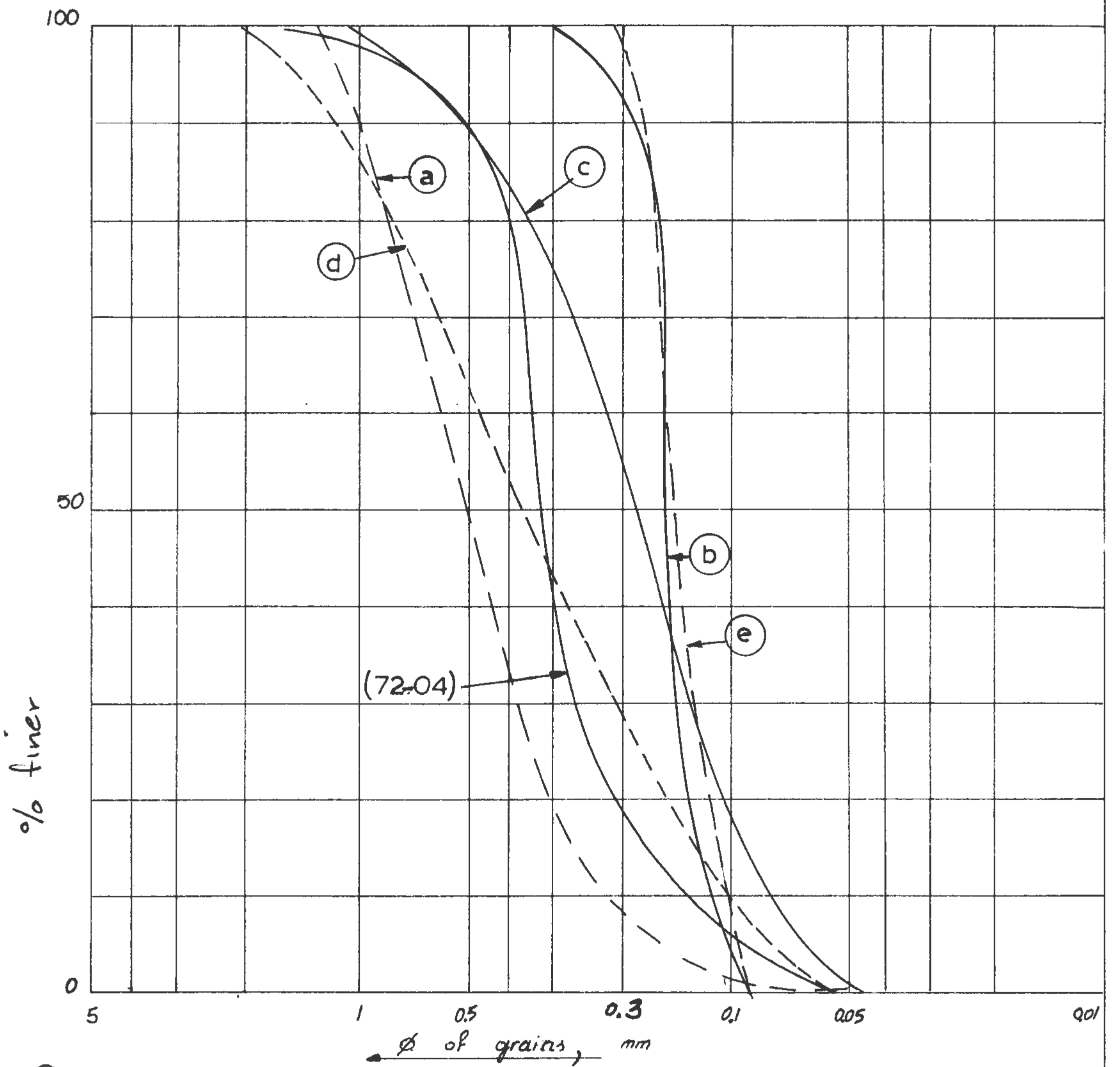


Fig. 13. Relation of Wet Density to Strength for Silica Gel Mortar (Semi-Hard Gel)



ⓑ Standard sand, gradation 0.1 to 0.3 mm

Fig. 14. Reference Sands

c) Since the more or less pronounced interaction of chemical grouts with carbonates can lead to serious difficulties in the selection of an easily reproducible calcareous sand, we have limited the choice to a purely silicious sand.

This sand, whose particle size can be easily reproduced, has been adopted as a reference sand by the PHONE-PROGIL (99-02) laboratories, and on a larger scale, has been made standard for grouting work by A.F.T.E.S. (French Association for Underground Construction Work), which includes the major French grouting firms. Its characteristics are as follows:

chemical composition: $SiO_2 > 99\%$
specific surface: 380 cm^{-1}, or 250 cm^2/g [1]
specific gravity: 2.65
permeability: 8.4×10^{-3} cm/s for an apparent density of 1.626.
gradation: 0.1 mm to 0.3 mm

Since the reference sand is not calcareous, it obviously cannot emphasize disturbances in acid grouts in the presence of carbonates.

A calcareous sand is not recommended since the carbonate content in naturally occurring sands is not constant and to reconstitute an artificial reference sand (pure silicious sand to which a certain percentage of calcium carbonate with the same size particles has been added) would complicate the preparation. As a consequence, the grout should be checked to make sure that its pH is below 4.5.

6.4 Preparation of Reference Sand-Grout Test Samples

Once the reference sand has been precisely defined, the strength of the sand-grout mixture, even at the moment of preparation, remains dependent on the very important fact of the degree of compaction of the sand in the test sample.

Since sands 10 to 20 metres deep in the ground are generally highly compact, the best sample preparation method will obtain comparable compaction and ensure good reproducibility.

---

[1] Specific surface can also be expressed as surface area of the particle divided by the weight of the particle.

6.41 Mixing Method

The method of preparation for cement mortar test samples consists of carefully making a mixture, then placing it in molds according to precise rules. This method, which has been standardized for decades, is satisfactory for cements. As applied to grouts, it consists of preparing a rather moist sand and grout mixture and placing it in molds layer upon layer while tamping or subjecting it to vibration.

The disadvantage to this fast and easy method is its lack of reproducibility when the grout contains volatile elements. Mixing of the sand with the grout, even if done rather quickly, encourages evaporation of volatile elements in the grout, resulting in a severe drop in mechanical characteristics.

A typical case would be that of hard gels using an organic reagent. Fig. 15 shows, for two gels of widely differing composition (both for the diluteness of the sodium silicate and the proportion of reagent), the evaporation rate of ethyl acetate (a volatile product) as a function of the time consumed in mixing the sand and grout in the preparation of the mortar. It can been seen that if the preparation of the test samples is conducted too conscientiously, taking 5 minutes for the mixing, the gel will lose in both cases about 60% of its reagent, which will obviously mean a marked drop in strength.

The following test was conducted to determine the relationship between mixing time and loss of strength. Having been well homogenized with a spatula for 100 seconds, the sand-gel mixture was used to make up a first series of test samples. The substance was then mixed again for 20 seconds and used for a second series of test samples, and so forth. This test was conducted on 5 gels of differing composition. Fig. 16 shows the strength figures in terms of time consumed for mixing. By extrapolation, from 0 time (assuming that the loss of reagent and resultant drop in strength are porportional to mixing time) one can determine the mortar's true strength. In some cases strength drops by more than 50%. The longer the mixing time, the less there is of organic setting reagent, the more strength decreases. It is more serious to lose 15 cm^3/litre of ester through evaporation from a gel which initially contained 30cm^3 than to lose the same amount from one which contained 60cm^3. This is shown clearly on fig. 17 where a comparison was made of strengths of ethyl acetate-silicate

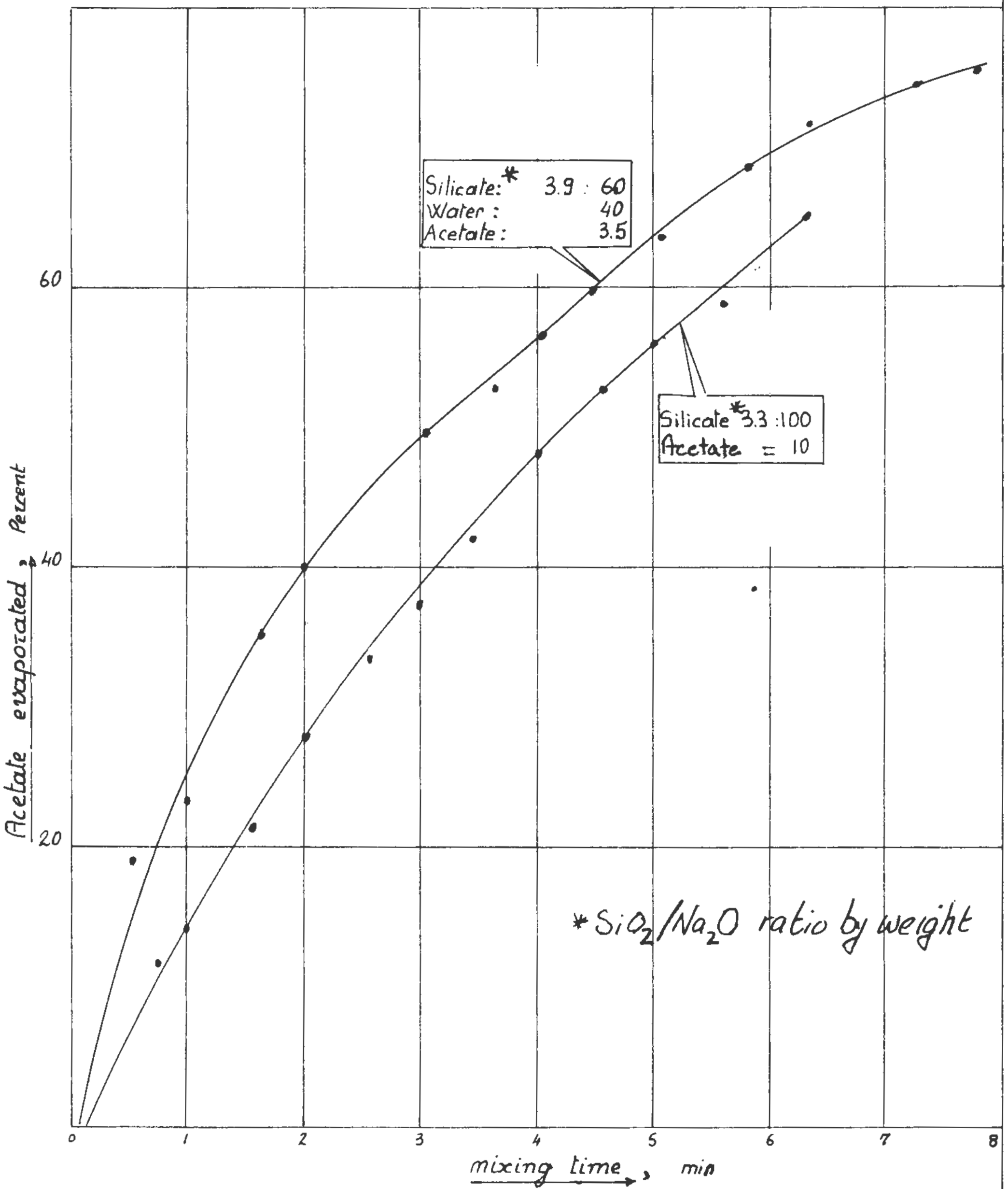
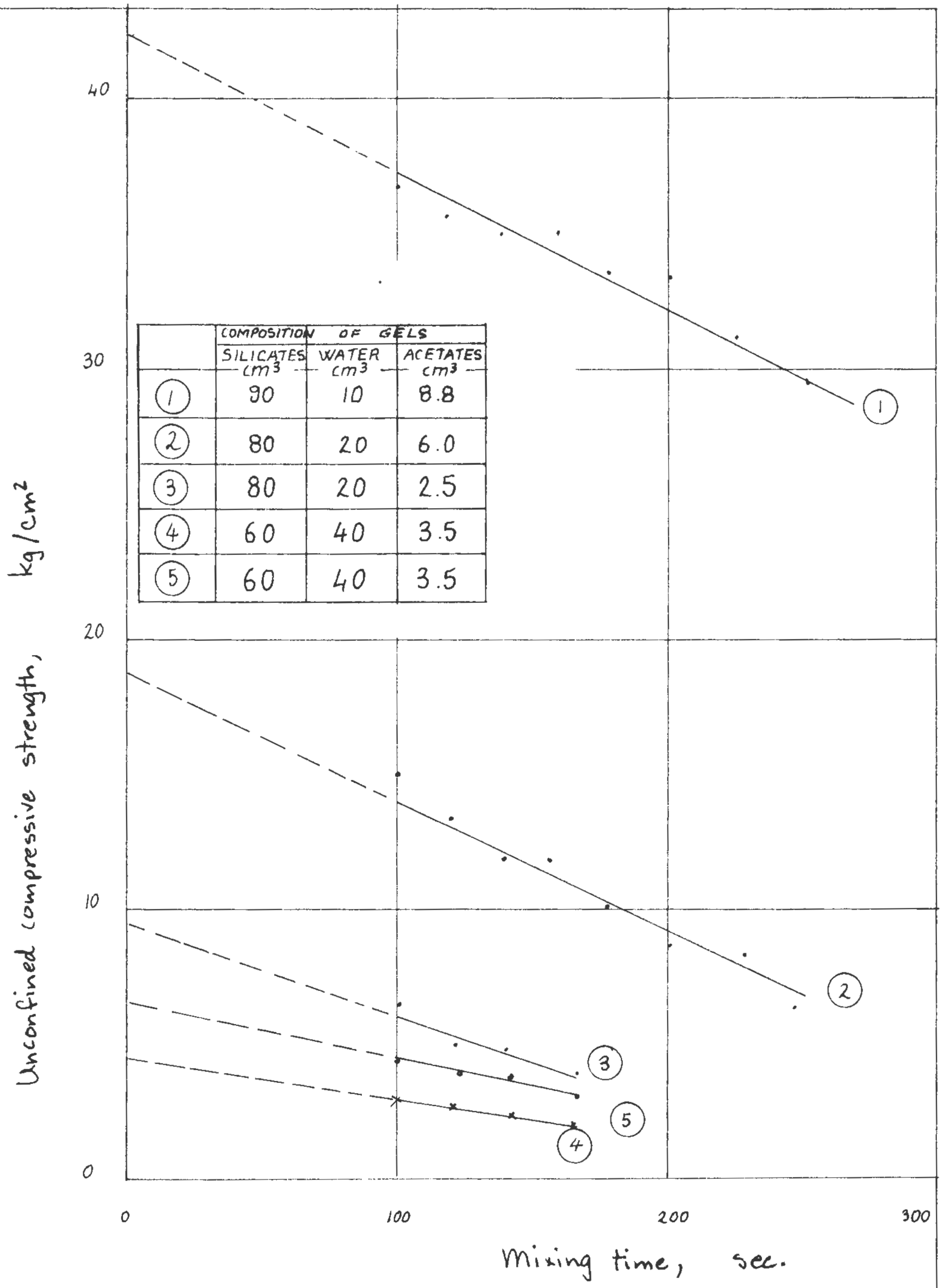


Fig. 15. Acetate Evaporated During Mortar Preparation



	COMPOSITION OF GELS		
	SILICATES cm^3	WATER cm^3	ACETATES cm^3
①	90	10	8.8
②	80	20	6.0
③	80	20	2.5
④	60	40	3.5
⑤	60	40	3.5

Fig. 16. Effect of Mixing Time of Sand-Gel Mortars on Strength

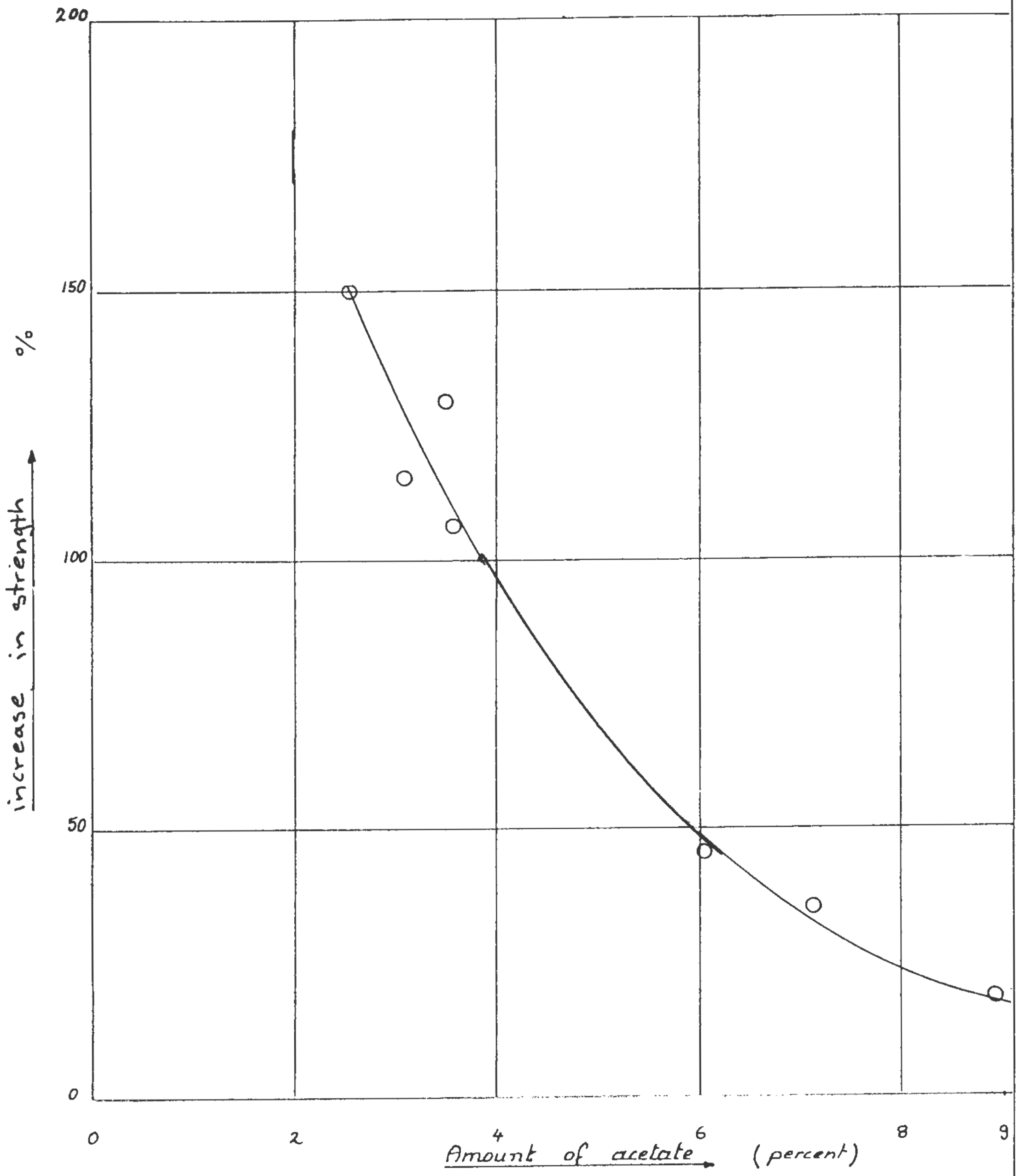


Fig. 17. Effect of Mixing Method on Strength

gel mortars prepared either by direct mixing (with mixing lasting two minutes), or by the method of direct molding as described below. Since it is not universal, the method of preparation by mixing was abandoned and is not recommended.

6.42 Molding Method

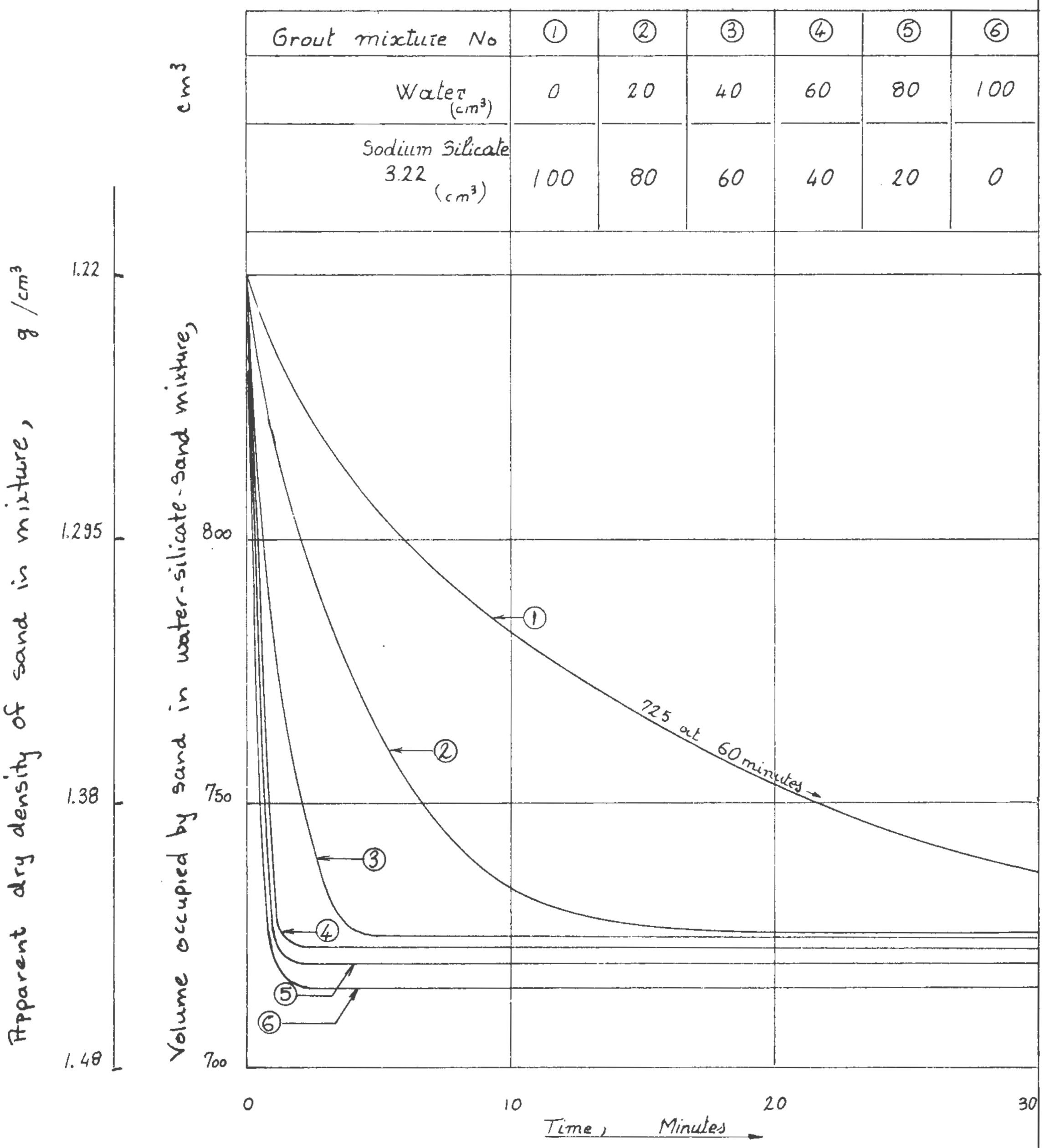
This method consists of placing the dry sand in a mold into which a given quantity of grout has already been poured. This method is advocated and used by J. WARNER (72-04). There are some general considerations to be observed regarding the placing of a fine sand in a viscous fluid. If a fine sand is poured into solutions of varying viscosity (for example, a silicate-water mixture at varying concentrations), the sand will assume a practically constant density. However, this density, which is very low, is attained only after an interval whose length depends on the solution's viscosity (fig. 18).

A test was conducted by pouring 1,000 grams of standardized sand (0.1 to 0.3 mm) in a continuous stream for one minute into a graduated container of a silicate and water mixture while simultaneously tamping. The operation is clocked from the moment the piston is withdrawn from the sample. Initial apparent volume of the sand is 850 cm^3 (independent of the viscosity of the medium), and will decrease in the minutes that follow until it stabilizes at between 715 and 725 cm^3. Apart from 80/20 and 100/0 mixtures (the latter being pure silicate) which are not used in practice, stabilization is attained in less than five minutes.

If at the end of some minutes (i.e. after stabilization), the different mixtures are vibrated, new density figures will be obtained. The more fluid the mixture, the higher these figures will be (table 9).

Table. 9 . Effect of Vibration on Density of Sand-Grout Mixture

sodium silicate water	100 0	80 20	60 40	40 60	20 80	0 100
density after filling	1.425	1.43	1.43	1.435	1.44	1.45
density after vibration	1.425	1.445	1.535	1.58	1.63	1.63



Grout mixture No	①	②	③	④	⑤	⑥
Water (cm³)	0	20	40	60	80	100
Sodium Silicate 3.22 (cm³)	100	80	60	40	20	0

Fig. 18. Effect of Viscosity of Medium on Placement of Fine Sand

In order to increase compactness, the placing of the sand in a viscous liquid should be carried out in two phases:

1) pouring of loose sand, followed by
2) tamping of the sand by mechanical means some minutes after the first phase.

These considerations formed the basis for the direct molding method of preparation as described below.

A cylindrical mold is used, 100 mm high, with an inside diameter of 40 mm, and with adjusted parallel bases. It is closed off at the bottom by a rubber stopper, in the cup of a liquid limit apparatus. The test sample can be fastened in the cup with a simple spring arrangement which requires no modification in the apparatus (fig. 19). The only precaution necessary is to make sure the sample is perfectly vertical.

The mold is filled to 1/3 with pure grout, followed immediately by slow pouring of the standardized sand until the mold is full, simultaneously jarring the container 25 times (depth of drop set at 1 cm). When the mold has been filled a light flake of grout should float on top of the sand. The purpose of the 25 taps is to ensure that the sand will be evenly distributed, and to expel air bubbles brought in during the sand pouring. They also hasten equilibrium, especially in cases where the viscosity of the medium is relatively high. Five minutes after completion of the first phase, the mold is given 5 additional taps to further compact the sand (second phase).

The figures in table10 were derived from this method of 25 taps and then 5 taps with an interval of 5 minutes between the two series. In this table the best strengths were sought in terms of operating procedure.

When preparation is complete, the tops of the test samples are closed off with rubber stoppers.

In practice, this method allows for sufficiently precise reproduction of desired strengths even with grouts containing volatile elements. Those grouts whose strengths were markedly disturbed by the method of mixing mortars resume their normal characteristics with this direct molding method. This method is universal, very simple, fast, dependable, requires practically no equipment, and can be standardized for tests in laboratories and at worksites. At most, it has only two drawbacks:

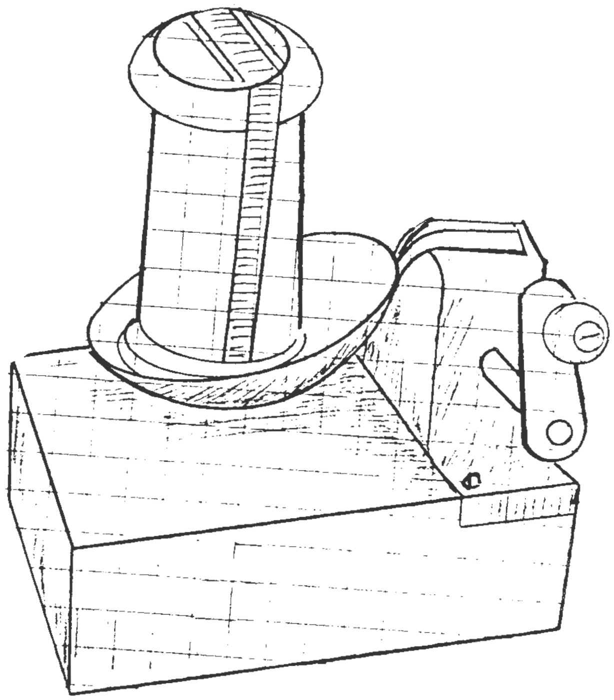


Fig. 19. Mortar Preparation System

1) It is not conducive to compaction as great as with the following method and, as a result, compressive strengths are lower.

2) The apparent density obtained depends somewhat on the grout's basic viscosity.

Table 10. Relation of Sample Compaction to Strength

initial number of taps	number of min after which 5 more	formulas used: silicate gel-ethyl acetate			
		40% water*(Rc, bars) (viscosity: 7 cP)		20% water *(Rc, bars) (viscosity: 15 cP)	
		figures	average	figures	average
5	none	2.8,2.95,2.9	2.85	15.95,17.7,14.6	16.1
10		4.0,3.5,3.75	3.75	18.5,18.2,17.85	18.2
25		4.0,4.0,4.3	4.1	20.15,18.7,23.6	20.85
5		4.6,4.45,4.5	4.5	20.25,20.85,21.1	20.7
10	none	4.6,4.7,5.0	4.8	23.1,23.1,20.75	22.3
25		4.6,5.0,4.7	4.8	21.85,21.5,21.7	21.7
5		4.0,4.3,4.15	4.15	19.55,19.0,18.45	19.0
10		4.4,4.2,4.5	4.35	20.7,22.3,21.7	21.6
25	none	4.6,4.6,4.25	4.5	23.9,21.9,25.35	23.7
5		4.05,4.05,4.3	4.15	20.3,18.7,21.5	20.05
10	none	3.9,3.9,4.2	4.0	19.6,21.35,20.7	20.6
25		4.3,4.15,4.4	4.3	20.7,24.3,20.7	21.9

*Rc = Unconfined compressive strength

6.43 Injection Method

Where the first two methods described consist of tamping or vibrating the damp sand, this third method is based on the principle of vibrating a column of dry sand (in successive layers) and impregnating it by injection under pressure (fig. 20). Rather high dry sand densities can be obtained with this method, since a 0.1 to 0.3 mm standardized sand can produce an apparent density (da) of 1.7 (that is, a wet mortar density of 2.1). This is closer to actual soil conditions.

The amount of pressure used for the injection is regulated according to the grout's viscosity since the rate of flow is held as constant as possible, varying from about 0.1 to 3 bars (1 x 10^4 to 30 x 10^4 pascals). So that the grout may diffuse well, 2 cm of sand filter of 1 to 2 mm particle size is placed at the bottom of the column and, to avoid decompression of the sand, the upper part of the column is stoppered.

Fig. 20. Preparing Samples by Injection

In the hands of different practitioners, this method can be subject to certain variations in the speed of injection, the size and nature of the column (J. WARNER 72-04, POLISKA 44-04). These variations do not significantly affect the results obtained.

We advocate a column 1 meter high and 4 cm in diameter, which, after being divided up,will allow at least 10 test samples 9 cm high and give representative strength figures for the mixture. As a precaution, the first test sample (the lower part of the column) should be eliminated, as it is sometimes disturbed. The column may be rigid (a polyvinyl chloride or steel tube) or flexible (a rolled plastic sheet), which facilitates the dismantling and the extraction of the samples to be tested. It should be noted that the flexible column leads to a slightly greater spread in the figures, since the sand is allowed a certain amount of movement (table 11).

Table 11. Effect of Test Column Rigidity on Strength

	Compressive Strength in Bars			
	Rigid Column		Flexible Column	
	test 1	test 2	test 1	test 2
Strength figures obtained from the column	33.81	31.40	32.83	24.56
	38.33	31.84	26.65	31.40
	31.10	31.60	30.48	30.65
	28.71	31.56	29.60	29.85
	30.39	32.78	27.22	27.96
	32.37	31.73	24.33	29.75
	31.67	30.63	31.02	28.34
	33.40	32.66	30.97	31.40
	29.34	30.23	32.69	33.33
	33.33	30.68	31.33	37.60
	31.83	34.16	38.02	27.07
Average	31.75	31.75	30.40	30.20
Quadratic speed	1.74	1.12	3.62	3.48

By comparison with the direct molding method, the injection method has the disadvantage of requiring more complicated equipment and the advantage of being able to use more compact sand (with a 0.1 to 0.3 standard sand one obtains an apparent density (d_a) of 1.7 as opposed to 1.5 to 1.6 with direct molding), and more representative strengths.

As shown in the ratios given in fig. 17 and 18, the result is a gain in strength. With the aqueous resin type mixtures, of very low viscosity, this gain is on the order of 35%. With more viscous mixtures of the hard silica gel type, the gain in strength is even more pronounced since the sand's apparent density is even lower with the direct molding method (table 12).

Table 12. Unconfined Compressive Strength of Various Hard Gels (Silicate Plus Organic Reagent)

Strength in bars Molding method	Strength in bars Injection method	$\frac{R3}{R2}$
30	45	1.50
28	38	1.36
21	31	1.47
12.5	18	1.44
7.3	10.5	1.45
7.2	11.7	1.65
4.9	7.4	1.50

It should be noted that the injected column method must be modified for the following special cases:

1) For Category C-3, asphalt and other heated compounds, the column must be enclosed in a heated container (heating jacket, thermostatic bath, etc.).
2) If Category E-1 (reactions with the ground) set only by chemical reaction with the ground, the ground to be grouted must be used in the test, and not a standardized sand.
3) For Category E-2, reaction with ground water, after the column has been prepared in the usual way, it must then first be saturated with ground water of the type to be found at the site to be grouted before it is injected with the grout itself.

6.5 Curing Conditions Before Testing

The same curing method should be used for sand-grout mortars as for pure grouts, namely airtight molds. This type of cure most closely approximates conditions inside the grouted mass. The curing of small samples in the open air can only lead to aberrant results. Some mortars undergo such dessication that they crumble or lose an important part of their strength. Conversely, with other grouts, drying leads to an insignificant increase in strength. An example, the result of research of J. WARNER (72-04) is given in fig. 21, showing that the resin mortar (AM-9 and G.V.S.) attains mechanical characteristics which have no bearing on its intrinsic strength.

6.6 Aging Time for Test Samples Before Measuring Strength

Changes in the unconfined compressive strength of sand-grout mortars over time obviously correspond to those of grouts with an occasional slight delay due to the delay in the set to which some grouts are subject upon contact with the ground. As a precaution, table 13 shows aging times which are sometimes longer than those given for pure grouts.

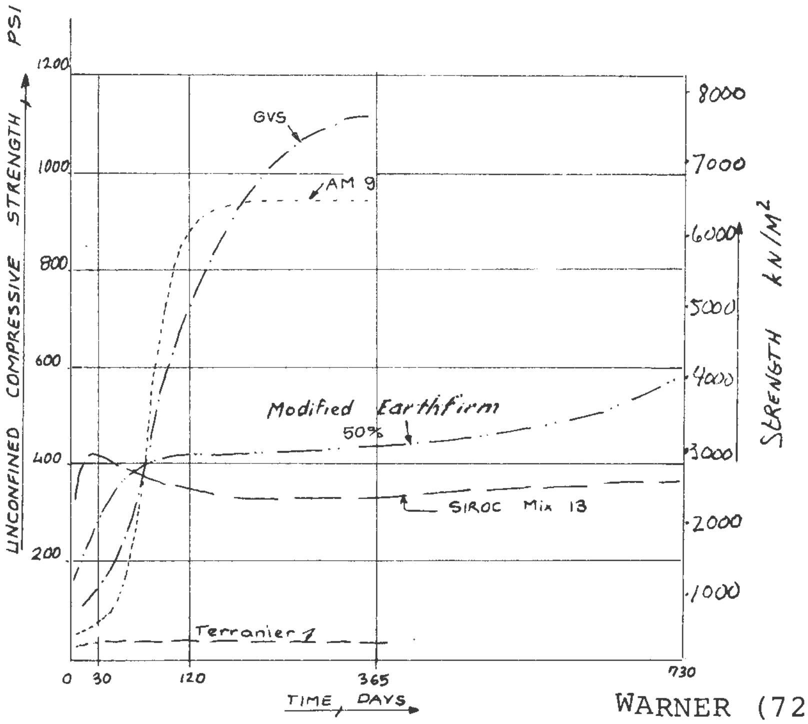
Table 13. Recommended Sample Aging Time for Strength Test

Grout Type			Aging Time
A-1	Silicate Derivatives		48 hours
A-2	Other Mineral Gels		48 hours
A-3	Lignosulfite Derivatives		7 days
A-4	Other Plant Derivatives		7 days
A-5	Polyacrylamides		24 hours
A-6	Phenoplasts:	high concentration	48 hours
		average concentration	7 days
		low concentration	28 days
A-7	Aminoplasts:	high concentration	48 hours
		average concentration	48 hours
		low concentration	7 days
A-8	Combinations of A-1 to A-8		2 days
B-1	Organic Colloid Solutions		7 days
B-2	Mineral Colloid Solutions		7 days
C-1	Synthetic Resins		24 hours
C-2	Vulcanizable Oils		7 days
C-3	Bitumen and Other Heated Materials		-
C-4	Systems Containing Solvents		- not significant
D-1	Bituminous Emulsions		-
D-2	Other Emulsions		24 hours
E-1	Reaction with Ground or Salts		24 hours
E-2	Reaction with Groundwater		24 hours
F	Combinations		7 hours

6.7 Measurement of Unconfined Compressive Strength

6.71 Preparation of Test Samples

For the compression test, the column of grouted sand is cut into test samples 80 mm high, with parallel



WARNER (72-04)

Fig. 21. Evolution of Strength of Several Grouts Under Dry Cure

bases, using a rotary cutter. Because of possible disturbance of the mortar, the samples cut from the top and bottom of the column are eliminated, yielding 10 samples, 80 mm in height, 40 mm in diameter (slenderness ratio = 2).

If standardized sand is used, it is unnecessary to grind the surfaces of the samples. The samples, left in a rough state after being cut and removed from their plastic envelope, are then subjected to unconfined compression testing. If the sample is made up of sand taken directly from the ground, it may contain some coarse elements, and it may be necessary to grind the surface of the sample bases. Grinding is generally necessary when particles exceed 1.6 mm in diameter. In such cases, columns with a larger diameter must be used and, when cut up, a slenderness ratio close to 2 will be maintained.

6.72 Crushing Speed

For unconfined compression tests on mortars, testing speed produces the same effect as on pure grout. The sand, even if highly compact, alters this phenomenon very little. The primary rheological characteristic of the binder continues to be crucial (76-01). With grouts of a markedly plastic character (gels) the effect of testing speed will be most pronounced, but even within the same grout category, this effect can vary with the composition of the mixture.

The data for unconfined compressive strength should thus include the testing speed used. So that figures comparable from one laboratory to another can be obtained, testing speed must be standardized. The A.F.T.E.S. advocates a crushing speed of 20 mm per minute for samples 80 mm long, A.S.T.M. D 1633 recommends that stress be increased to 20 psi per second, that is, 1.4 bar/second. These are fast speeds which have the advantage of being practical. However, for more precise work, it would be advisable to plot the curve $Rc = f(V)$ in order to forecast the mortar's median and long-term behavior.

6.8 Conclusion

Throughout the world, the structure of ground areas which can be grouted with chemical grouts varies infinitely (particle size, specific surface, particle porosity, different chemical nature, etc.). It is not generally feasible to take undisturbed soil samples from the site where grouting is planned. Thus, the compaction of soil reconstituted for testing is lower than that of the soil on site.

These considerations call for the standardization of a single sand for measuring strengths of grouted ground, as well as a method of preparing test samples which will be as close as possible in compactness to normal conditions.

For many grouts, unconfined compressive strength figures for mortars will depend on the speed at which the test is performed on the test samples, and test speed is always determined by practical considerations.

This indicates the necessarily arbitrary character of standardized procedures for measuring the strength of grouted areas. However, such standardization is useful, since it permits comparison of mechanical characteristics of sand-grout mixtures from one laboratory to another.

Chapter 7: Sixth Criterion, Durability

7.1 Introduction

Durability is the most complex field in this review of the technical characteristics of chemical grouts. To define the durability of grouts is difficult and to define the conditions under which it should be studied is even more so.

All prior documentation on durability has been inventoried. As James K. MITCHELL (70-01) noted in 1970, there is a serious lack of experience in the durability of grouts in general. Although some authors have studied the setting process in detail (gelling or polymerization of grouts), injectability characteristics (progressive changes in viscosity, setting time), and mechanical characteristics, very few have taken up the preservation of grouts over time.

There are standard tests for the long term behavior of concrete, metals, etc. For a field closer to grouting, the stabilization of ground surfaces, there are the recommendations made by the British Standards Institute 1377, 1961, but for grouts there has been no standardization and even durability studies are rare. However, the responses to the questionnaire sent to manufacturers, users, contractors and consulting firms indicate that tests for durability have been carried out, focussing on changes in mechanical characteristics and sometimes on changes in watertightness.

7.2 Definition of Durability and Possible Causes of Grout Degradation with Time

Grouts are used for consolidation or for waterproofing or for both purposes at once. In the first case, durability implies the preservation over time of mechanical characteristics acquired by the treated ground; in the second case, it implies the preservation over time of the permeability coefficient of the treated ground. It is generally desirable that these two conditions be fulfulled simultaneously.

This preservation of watertightness and/or strength cannot be guaranteed for all grouts in all terrains. The causes of failure in preservation are numerous and often interact with one another. The following are three causes of long-term disturbance.

7.21 Changes in the Grout Itself

99% of the chemical grouts currently in use are aqueous mixtures whose water content is physically or chemically linked. Non-aqueous grouts are used only in exceptional instances because of their distinctly higher price and generally greater viscosity. Water incorporated into the grout can disappear over a period of time for many reasons; condensation of the macromolecule, syneresis, dessication, etc.

7.22 Dissolution

It is important to recall that voids in the ground are never 100% filled by grouting. Grouted ground, whether treated for purposes of consolidation or watertightness, will never attain zero permeability since the grout is intended only to decrease permeability. Generally, water can seep through the treated ground, and in the long run, may have a harmful effect on the grout.

This phenomenon can be accelerated by an aggressive ambient medium. Some types of grouts are sensitive to acidic water, others, to basic water. A portion of the ingredients of ordinary grouts can even be soluble in normal water with a pH of between 7 and 9.

In addition, for nearly all grouts, the conversion from a liquid to a solid state involves a chemical reaction which is rarely complete and irreversible. Those parts insufficiently gelled or polymerized will be more vulnerable to degradation through seepage.

7.23 Stress Exerted on the Grouted Mass

If the dimensions or strength of a grouted mass have been miscalculated, the treatment can be ruined by excessive loads. This is most likely to occur when the grout is of the visco-plastic type (silica gels, for example), where the grouted mass can be ruined by creep under load.

Mechanical stress can also be exerted on the grout. Theoretically, if water pressure is very high, the grouted curtain could even loosen, especially if, by miscalculation, it was made too thin, or if the ground's particle size is too coarse for the type of grout used. Another possibility is the destruction of the grout by vibration.

Thus, a grouted curtain may cease to fulfill its function after some years because:

a) the grout's water content has partially disappeared and some voids which initially were plugged have opened.

b) underground water crossing the curtain has dissolved some parts of the grout.

c) gradual stress has loosened the grout or lessened its real strength.

These three causes can often interact and aggravate one another .

7.3 Curing Methods

Durability does not depend on the grout alone, but also on the terrain and the environment in general. Thus, for the preceding example of a grouted curtain, there are three very different areas of behavior over time:

1) The part outside the water table risks dessication.

2) The intermediate part, in an area of fluctuating conditions, is subject to drying-wetting cycles.

c) The part deep in the ground is subject to dissolution and loosening.

The environment of the grouted mass has a significant influence on the grout's durability. The effects of five possible methods of cure are discussed below.

7.31 Hermetic Mold Cure

This type of cure allows an examination of the evolution of a grout when the water included by polycondensation of the macromolecule has been eliminated. It also permits an examination of the effect of syneresis on the final behavior of the grout matrix, or the general evolution of the matrix itself.

This evolution can be followed by shear strength measurement on pure grout and unconfined compression testing of sand-grout mixture.

7.32 Dry Cure

Through measurements of unconfined compressive strength, the grout's capacity for losing surplus water without degradation of the matrix can be assessed.

This dry curing method corresponds to a grouted mass in dry ground which is then excavated (by tunneling above the water table, for instance). This mode of cure permits an examination of a grout subject to an outside influence; dryness in the environment. There can thus be a loss of water, incorporated or not, leading eventually to disturbances in the grout's very matrix. This mode of cure has been studied by WARNER (72-04) for five chemical grouts.

7.33 Cure in a Wet Medium

This mode of cure, representing the behavior of a grouted mass under non-circulating water, permits an assessment of the extent to which the matrix will dissolve by the loss of insufficiently gelled or polymerized parts of the grout which were not incorporated into the macromolecule (a chemical reaction which is never complete), or by dissolving some of the skeleton's components.

Several authors have used this water cure method to test chemical grouts for durability:

-WARNER (72-04), G. Y. CZERNY, A. REGELE, B. SHIVOY (69-07), RHONE PROGIL (99-09), for silica gels;

-WARNER (72-04), BURROWS, H.J. GIBBS and H.M. HUNTER (52-17), JULIAN C. SMITH (52-05), E.K. HOUGH and J.C. SMITH, for lignochromes;

-R.H.KAROL (57-01), R.C. CHELLIS (61-05), ROBERT SCHIFFMANN and CHARLES WILSON (58-01), SUMITOMO CHEMICAL CO., Japan (99-14), MARKUS T.A. (55-09), for acrylic compounds;

-SCHNITTER (70-02), V.F. DEMINE (73-07), JAMES WARNER (72-04), for phenoplast resins.

In these various studies, data on the volume of water in contrast to the volume of material, and the frequency with which the water was changed are not comparative.

7.34 Drying-Wetting Cycle Cure

Using this cure the capacity of the grout's matrix to lose and then reabsorb water, whether chemically bound or not, can be assessed through measurement of variations in weight and unconfined compressive strength.

This type of cure closely corresponds to a grouted mass subjected only to rainwater runoff, such as for an excavation grouted at the time it was opened. The following could thus occur in alternating phases:

a) changes in the grout through loss of water during the drying phase;

b) dissolution of the grout's matrix during the wetting phase.

R.W. BURROWS, H.J. GIBBS and H.M. HUNTER (52-17) have investigated this mode of cure with lignochrome gels. R.H. KAROL (57-01) cites an experiment which subjected acrylamide resins to alternating wetting-drying cycles:

> Half-scale experiments were conducted on pure resin and rather tightly packed coarse sand treated with the same acrylamide resin covered with an equal amount of natural earth. After 13 years of cure in these conditions, the two samples were dug up and examined. In the first case, the uppermost 10 to 15 cm of resin showed signs of degradation due to direct exposure to the atmosphere (drying and wetting cycles), below, the resin had preserved its initial properties. In the second case, no traces of destruction were apparent in the sand; unconfined compression tests showed that it had suffered no decrease in strength when compared to control samples only a few days old.

The insert that accompanies American Cyanamid's AM-9 chemical grout also notes results obtained with acrylamide resins subjected to cycles of wetting and drying.

7.35 Cure with Water Percolating Under Pressure

This mode of cure is by far the most important for research on durability, as it corresponds to the most common and most severe conditions. It also demonstrates one of the most frequent causes of degradation in grouts over time: the dissolution of the matrix. This curing method can help assess the potential for displacement of a grouted curtain subjected to water under pressure.

This type of cure also corresponds to the test for leaching. Although it is most important, it was rarely mentioned by the manufacturers and users who responded positively to the questionnaire. This lack of interest may be due to the fact that this test requires more complicated equipment. In previous surveys, this mode of cure has been described in connection with:

-silica gels: CLAUDE H. HURLEY and THOMAS H. THORNBURN (71-01), H. CAMBEFORT and C. CARON (57-13), C. CARON (65-04) as well as in the RHONE PROGIL insert containing descriptive material (99-09).

-lignochrome gels: A. WESTON and R.A. KENNERLEY (58-15) and CARON, GAILLEDREAU and BELOT (52-21).

This type of cure could conceivably be used by circulating water across an axial hole in a cylinder of sand-grout mortar. Sample weight losses could be measured as well as the quantity of water drained off, thus indicating the extent of destruction. However, this test more closely represents a test for erosion.

7.4 Critical Examination of Curing Methods

These five curing methods can present close to natural curing conditions or rather arbitrary conditions.

1) The grout-sand mixture is not subjected to outside influences in hermetic mold curing (method 1). The size of the test sample will make no difference since it is the grout itself which is being examined. With this mode of cure, strengths will usually increase for some time, then level off. After having attained optimum strength, silica gels can lose some of this property over time, although the loss is only marginal. This is due to syneresis and is peculiar to silica gels.

2) The sand-grout mixture is subjected to an homogeneous outside influence when cured in water percolating under pressure (method 5). In nature, a grouted curtain subjected to water pressure will suffer the same type of disturbances as a reduced scale sample, since this percolation will affect the whole curtain. Thus, as in the previous case, a model on a reduced scale can still be valid (with some reservations with regard to operating procedure, as described later).

3) The grout-sand mixture is subjected to a variable outside influence depending on the size of the sample and the duration of the test in methods 3, 4 and 5. Disturbances in the sample will be a function of many factors.

(a) volume of the sample. The greater the volume of the test sample, the lower will be the percentage of the volume disturbed for two grout-sand mixtures having the same composition and cured under identical conditions.

(b) time. The disturbance spreads progressively from the edges toward the center of the test sample. A test sample can thus behave well over a certain length of cure time and then deteriorate.

Two examples of the combined effects of time and volume for a sand-silica gel mixture are as follows:

A semi-soft silica gel mortar is poured into a series of four tanks, 60 cm long and 5 cm across. Contact with constantly renewed water is ensured at both ends of each tank. Changes in strength over time can be demonstrated by measurements of unconfined compressive strength taken along the side of the tanks. Table 14 gives the results obtained.

Table 14. Effect of Testing Time and Volume on Strength

Time in Contact w/water	Length Eroded		Unconfined Compression Strength of Mortar, Bars (Taken Along Side of Tank) [1]
	Top	Bottom	
1 day	1 cm	1 cm	13.3 14.2 13.6 12.1 11.7 11.8 9.5 7.1
4 days	2 cm	2 cm	10.4 15.6 15.6 16.6 15.4 14.0 13.2 10.8
21 days	2 cm	2 cm	10.0 18.6 19.3 19.0 18.5 17.8 15.3 9.9
3 months	3 cm	3 cm	2.7 3.4 3.8 4.0 3.7 3.8 3.9 2.7

The same test was conducted on a semi-soft gel of nearly identical composition, but having a silicate of different nature. The results are reported in table 15.

---

[1] bars x 10^5 = pascals

Table 15. Effect of Testing Time and Volume on Strength

Time in Contact w/water	Length Eroded		Unconfined Compression Strength of Mortar, Bars (Taken Along Side of Tank)							
	Top	Bottom								
1 day	2.5 cm	2.5 cm	6.8	8.0	8.0	9.0	9.1	7.5	7.0	5.7
4 days	3 cm	3 cm	5.4	5.7	7.3	7.0	7.0	7.0	5.2	4.8
15 days	5 cm	5 cm	4.2	5.1	5.3	6.1	6.1	6.2	5.8	4.7
30 days	7 cm	7 cm	2.7	3.5	3.9	4.2	3.8	3.1	2.9	2.7

These two examples prove that only the part of the gel in contact with water is disturbed initially and that this disturbed fringe spreads with time. This spreading can, however, vary widely from one test to another. The size of the sample and the duration of the measurement are of paramount importance in interpreting the test.

It is also obvious that if, in these two tests, cubes 5 cm on each side (of identical composition) had been used instead of elongated parallelepipeds, the cubes would have been completely eroded in a few days, and it would have been concluded that silica gels behave badly when exposed to water, when in fact only the peripheral area was disturbed.

(c) surrounding environmental conditions. In the preceding test, if the water is not renewed during the test, it becomes progressively saturated with sodium salt and speed of attack is slowed. Similarly, in an air drying test, it is obvious that the dryer the air, and the higher the temperature, the faster the disturbance occurs in a test sample. And if the grout is surrounded by a layer of sand, the rate of dehydration will be much slower. In fact, the part of the sand next to the grout will draw water from the grouted mass which quickly results in a state of equilibrium and which in turn creates an effective barrier to any further dehydration of the center of the mass. This result, which applies to most aqueous chemical grouts, shows that in situ, the grout will often regulate itself and a state of equilibrium will be created with the surrounding medium.

Thus, it seems apparent that there are cure methods which could easily be standardized since they could be applied to reduced scale samples, the hermetic mold cure and percolation under pressure, for example. The other modes of cure are much more arbitrary since they depend on many factors which cannot be standardized.

The following discussion of standardization thus considers only the two types of cure which are free of ambiguities, as well as being the two most important. However, each of the chapters on a class of products gives the results of prior experiments carried out with non-standardized methods.

7.5 Standardization

7.51 Hermetic Mold Cure

This cure tests the behavior of the grout in the middle of a grouted mass, where it is protected against outside influences. This mode of cure is thus very important since it reflects nearly the whole treatment, even when under water. With this type of cure, the grout is examined in itself, excluding any outside influences.

Observations are made of the rapidity of changes in strength (for example, through polycondensation of the macromolecule), the state attained at the point of stabilization, and potential disturbances.

The standardization of cures in an hermetic medium should meet the following requirements:

-test sample: cylindrical form, slim, length/diameter ratio = 2:1, volume of no consequence (if possible, test samples of less than 100 cm^3 should be avoided).

-cure: mold as airtight as possible, for example, plastic molds with rubber stoppers on both ends.

-measurement of unconfined compressive strength: consult standardization of this test as given in Chapter 6.

7.52 Cure Under Water Percolating Under Pressure

This mode of cure is by far the most important for studies of durability since it corresponds to the conditions most frequently found in nature (all watertight curtains and, frequently, masses grouted for consolidation).

Percolation under pressure can dissolve the grout's matrix and in the most severe cases, can loosen the watertight curtain.

The principle of the test involves forcing water under pressure across a permeability cell containing a sand previously injected with the grout to be tested. With this type of test, the primary measurement is the rate of change in permeability over time, which will indicate the degree of stability in the grouted mass. This can be carried a step further by chemically analyzing the water which has percolated through the sample and by measuring the sample's compressive strength and comparing these results with those obtained from an unleached control sample.

The procedure followed in these experiments is always the same to within a few details. Since the percolation under pressure test chronologically follows the permeability test, standardization of equipment has already been described in the chapter on permeability, and the following details should be added concerning the execution of the test:

a) The initial gradient should be maintained throughout.

b) The filter sand placed at the two ends of the cell should be checked periodically to avoid any clogging which might distort the measurements.

c) The percolation water should be distilled and deaerated. For some specific tests, special water should be used, such as that found on the worksite.

d) The percolation test should be continued over at least 28 days. At the end of this time, the shape of the curve $K = f(t)$ will be sufficiently precise to show the stability of the grout. Shortening testing time by use of pressure gradients much higher than those actually encountered on the worksite is not advisable since this factor may reflect a non-existant condition.

After percolation is completed, the test can be supplemented by a measurement of unconfined compressive strength. Undisturbed samples (40 mm in diameter, if possible) from the leached cell should be used for unconfined compressive strength testing and undisturbed control samples can be taken from the non-leached cell and tested at the same time.

7.6 Conclusion

As the measurement of durability is so complex, a judgement made about a given grout will depend primarily on the mode of cure adopted for the durability test. Depending on the conditions under which it was tested, the same grout might be judged particularly stable or, conversely, degradable over time.

Durability is thus a criterion which should be examined with extreme care. In order to avoid as much as possible the rather haphazard and subjective character of any interpretations concerning the durability of grouts, two easily reproduced curing methods are recommended:

-airtight mold cure:
-cure under circulating water.

As explained above, the scale can be reduced for these two modes of cure and thus can be used in a laboratory to obtain valid readings. This is not true for other types of cure where scale plays an important role.

Thanks to their reproducibility, these two tests, thus standardized, allow a valid judgment to be made with regard to a grout's behavior over time. Using the hermetic mold cure, it can be determined if the grout itself is stable, while the purpose of the leaching test is to determine whether water running through a grouted sand will disturb the grout (through dissolution, swelling or any other cause).

Chapter 8: Seventh Criterion, Toxicity

8.1 Introduction

The problem of grout toxicity is a complex one. In the field of medicinal, cosmetic and even food products, it is not unusual for products which have been used widely for years to suddenly be withdrawn from the market because recent research has indicated some degree of toxicity. If toxicological issues are poorly defined even for consumer products, it is easily understandable that grout toxicology is only in its infancy. The subject should be examined from two aspects:

1) industrial toxicology of primary products used in making grouts;

2) toxicology of the hardened grout in the ground.

The first point concerns industrial hygiene and should include the following considerations:

-risk of flammability and explosion;
-risk of extreme or near-extreme toxicity resulting from accidental inhalation;
-chronic toxicity;
-effect on skin and mucous membranes.

Precautionary measures to be taken at time of use should be thoroughly defined.

The second point concerns the grout's effect on its environment. This is much more difficult to define since it depends on the possibility of exchange between the hardened grout and the surrounding medium. This point is discussed in the chapter on durability.

Our preliminary survey indicated that manufacturers and users are aware of toxicity problems but present information is highly fragmentary.

8.2 Toxicology of Primary Products

The series of formulas represented in the bibliographical study has produced a list of about 200 products which may be included in various grouts. Most of these products are toxic or caustic in varying degrees. Thus it is virtually impossible to use only non-toxic and non-caustic products for grouting. To try to do so would leave only categories B and D available and produce poor technical performances. As a result, risks must be assessed and relevant precautionary measures taken at the worksite.

As an illustration, formaldehyde is used in large quantities in the composition of Category A-6 and A-7 grouts (phenoplasts and aminoplasts) in a 30 to 40% solution in water, which gives off formaldehyde gas. In a gaseous state this product is flammable and can be explosive when mixed with air. In addition, its vapor is toxic when inhaled and, in low doses, causes irritation of the respiratory tract. Large quantities can have a highly toxic effect and, over a long period, repeated inhalation can cause chronic irritation. Finally, whether in the form of a vapor or in solution in water, formaldehyde will have a more or less serious effect on the skin depending on its concentration.

Since the risks are known, precautionary measures must be taken: fire must be guarded against, the places where the toxic substance is used, mixing plant, tunnels, excavations, must be well ventilated. The concentration of its mixture with air must be constantly or semi-constantly monitored to ensure that it does not exceed permissible levels. Users must wear the necessary protective clothing (gloves, goggles, masks in some cases, etc.)

The same analysis can be made for all ingredients used in grouts with the resultant hygiene and safety measures to be taken in view of potential synergistic effects of the mixtures obtained. In general, it is unnecessary to conduct tests to learn the precise risks inherent in these products. Specialized literature and industrial hygiene standards are available, such as in the works which appear in the list of grout toxicology references at the end of this chapter.

The third part of this volume examines the toxicity thresholds of primary products used in grouting.

8.3 Toxicology of Grout in the Ground

Fortunately, once they are combined to form a hardened grout, most of these primary products neutralize, combine and lose their high toxicity. Thus, although resorcinol and formaldehyde are both toxic in a pure state, the high phenolic polymer formed by their combination is not toxic. Although in a combined form the level of intrinsic toxicity is decreased, the possibility of long-range effects is still present. Instead of being localized in time (the period of the construction work) and space (the mixing plant), the concern now is for much longer periods and for the whole environment, even extending to distant points since harmful products can be carried by underground water.

Investigations bearing on the toxicological character of grouts in the ground are still in their infancy and are proving most complex. Risks of pollution stem from two causes, the first normal, the second resulting from accidents, both of which are discussed below:

- intrinsic toxicity of the hardened grout;
- toxicity resulting from the fraction of the grout which did not set, either because of an error in dosage, or because the grout was diluted by ground water before it set.

8.31 Intrinsic Toxicity of Hardened Grout

Most of the recommended grouts undergo chemical reactions demanding a trigger substance, or catalyst. These products play a part in the reaction, but either do not combine or give intermediate products which do not combine. These products can be exuded from the grout's matrix, by seepage or syneresis, and thus find their way into underground water. Since chemical reactions are never perfect, other ingredients in the grout can also be released in small quantities and some reactions can be reversible (hydrolysis).

Although it is relatively simple to identify those products which can be extracted from a grout by chemical analysis of seepage through and around it (test for permeability and durability), the same does not apply to concentrations obtained from underground water circulating at the edges of the grouted areas. Thus, to assess maximum toxicity of hardened grout, we recommend the following test for high toxicity:

> The hardened grout is administered orally in varying doses (g/kg) to rats. The grout is first ground or dispersed, according to its nature. For oral administration to animals:
>
> - if physically possible, an oesophageal tube is used. The grout is first dispersed and put into suspension in a 10% gum arabic aqueous solution.

-if this is not physically possible (because the paste is of rubbery consistency, or heterogeneous powder, for example), the grout, properly divided into doses, can be mixed with honey and powdered milk so the rat will voluntarily ingest an appropriate amount of the substance.

After treatment, the observation period lasts 15 days. During this time, the animals should be weighed every 5 days. After 15 days, the animals are killed and autopsied for microscopic examination.

The animals used for tests undertaken on chosen categories of grouts whose results were used in the preceding chapters, were CD rats from the CHARLES RIVERS farm in France (Caesarian Originated, Barrier Sustained) (1).

It is obviously possible that some grouts (for example, Category B-1) will deteriorate over time through a biological process (action of a microorganism) and there is some risk that a grout which initially was non-toxic can become toxic through degradation. Such an eventuality would not be indicated by the test above. Fortunately, in the promising grout categories, this biological process does not occur.

8.32 Toxicity of Fractions Which Did Not Set

If a fraction of the grout does not set, the problem is once again toxicity of the basic ingredients. A dosage error at the time of fabrication can cause a considerable increase in the amount of grout or its components which will not set. In this case, risks of contaminating underground water are very high, the degree of danger depending on the grout's toxicity. Because of the many potential toxicological consequences which can ensue, such an error is very serious and the only way to avoid the problem is to adopt a system of preventive measures which will allow for constant control over the uniform composition of products injected.

Dilution of the grout in ground water at the time of injection can also prevent setting. In the chapter on setting time it was noted that some dilution of the grout can occur in a narrow band around the edges of the grouted mass. This phenomenon has no technical effect, but should be considered for toxicological consequences. It is possible that the diluted grout along this fringe may never set, thus ruling out even small doses of highly toxic products.

---

(1) Barrier Sustained = raised in isolation

8.4 Conclusion

Lack of legislation and the absence of serious accidents have not encouraged research on grout toxicology. Aside from one case in Japan, no accident has been reported along the perimeter of any injection carried out according to the rules of the art over the last decades.

Toxicological problems which can emerge at the time of preparation are relatively well known since industrial safety and hygiene regulations are available, but knowledge of the behavior of grouts in situ is much more fragmentary. We suggest that this situation be remedied by the high toxicity test on rats as described above.

8.5 Grout Toxicology References

1. Registry of Toxic Effects of Chemical Substances, 1975 edition, H.E. Christensen, Ed., U.S. Department of Health, Education, and Welfare, Rockville, Maryland 20852

2. Dangerous Properties of Industrial Materials, Fourth Edition, N. Irving Sax, Van Nostrand Reinhold Company

3. Industrial Hygiene and Toxicology, F. A. Patty, New York, Interscience, Second Revised Edition, 1967.

4. Documentation of the Threshold Limit Values for Substances in Workroom Air, American Conference of Governmental Industrial Hygienists.

PART TWO

PROPOSED STANDARD TESTING PROCEDURES

1. Introduction

At present there are many laboratories engaged in research into the engineering characteristics of grouts. All the information disclosed by such testing is useful and desirable , since precise information enables the grout user to choose the most appropriate material for his purpose. However, if the available information cannot be correlated between sources, the net effect of the accumulated information is lost and much of the testing is unnecessarily duplicated.

Part Two of this report is an attempt to clarify and simplify this situation by proposing one testing procedure for defining each engineering characteristic for each chemical grout within the definition of this project.

The process of choosing the most suitable test procedure was difficult and even arbitrary at times, given the many different kinds of material to be tested under these procedures. However, a general common understanding requires universal adoption of testing procedures, the results being well worth the efforts taken by individual testing facilities to change or modify their methods. Information developed at one facility can be verified and augmented at another, without difficulty. Some of the procedures are quite simple and can even be carried out at a worksite, facilitating control of ground treatment. The information thus gathered can then be correlated easily to laboratory test results.

Thus a standardization of testing procedures can lead to greater improvements in the methods and materials of ground treatment, leading to a wider acceptance of ground waterproofing and consolidation using chemical grouts when required as a demystified and normal construction procedure.

2. VISCOSITY TEST

2.1 Equipment

-FANN Viscosimeter
-glass beaker, 1 litre capacity
-accurate timing device
-chemical grout to be tested, 500 cm^3 prepared according to manufacturer's directions

2.2 General Directions

1. Maintain all grout ingredients at 20°C for test duration.

2. All test measurements are to be taken at 600 rpm.

2.3 Directions

In the beaker, prepare 500 cm^3 of grout to be tested, according to manufacturer's directions. Transfer prepared grout to the tank of the FANN viscosimeter, immediately putting it into rotation.

2.4 Measurements

a. Initial Viscosity

Take viscosity measurement at the end of one minute, beginning count at the end of grout preparation.

b. Changes in Viscosity Over Time

Retaining the grout in the viscosimeter tank, take viscosity measurements according to the following timetable until the grout sets: 3 min. 6 min., 10 min., 15 min., 20 min., 25 min., 30 min., 40 min., 50 min., 60 min., 80 min., 100 min., 120 min., 150 min., 180 min., etc.

c. Injectability Time Limit

Using the timetable as the abscissa (x-axis) and viscosity measurements as the ordinate (y-axis), plot each viscosity measurement and its corresponding time on

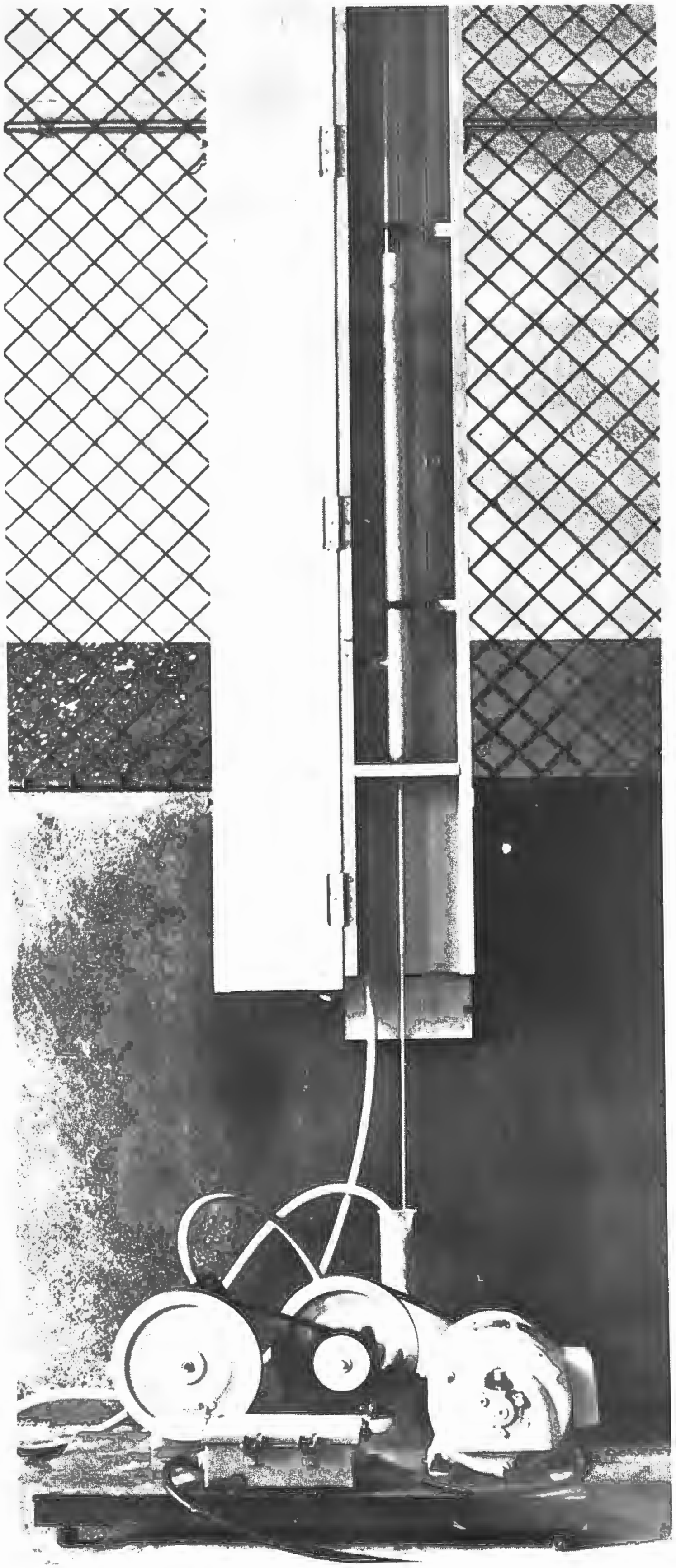
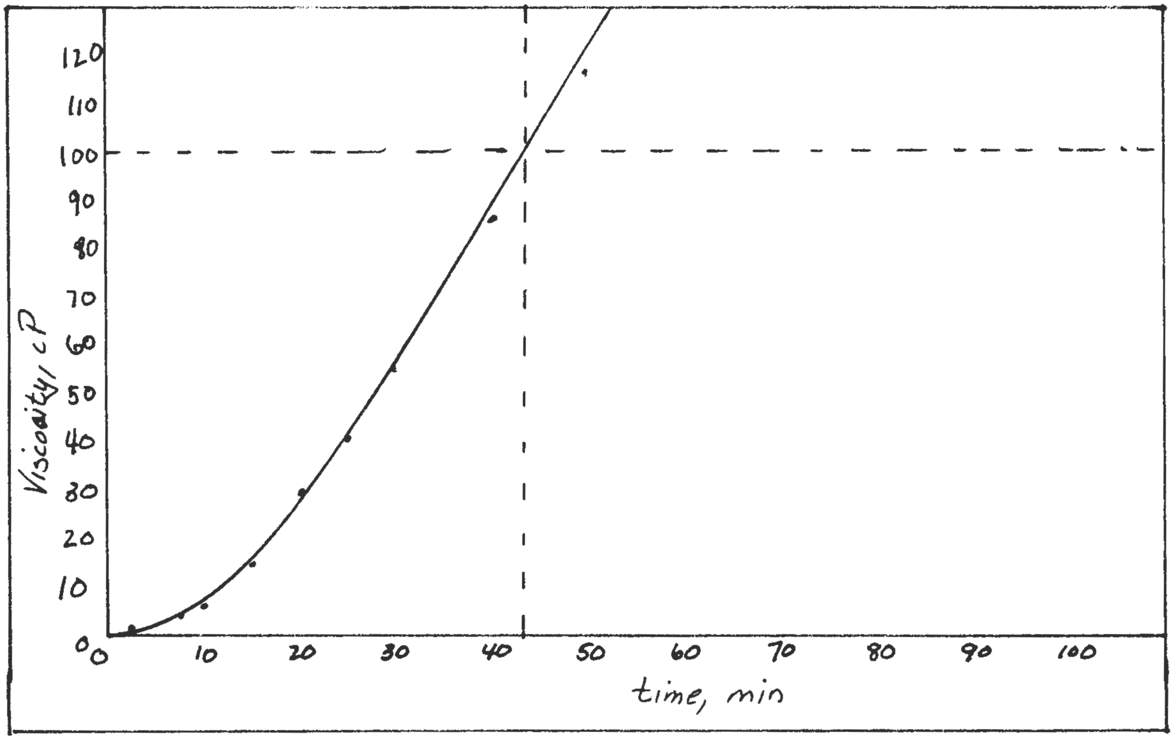


Fig. 22. Viscosimeter

a graph. Time limit of injectability will be the time corresponding to viscosity of 100 cP.



Thus, for a theoretical chemical grout plotted on the graph above, time limit of injectability is 43 minutes. This corresponds to the maximum length of time a grout may be kept in a mixing tank or holding tank before being injected.

3. SETTING TIME TEST

3.1 Equipment

- -2 glass beakers, 1 litre capacity
- -accurate timing device
- -grout to be tested, 500 cm^3 prepared according to manufacturer's directions

3.2 General Directions

Maintain all ingredients at 15°C for the duration of the test.

3.3 Procedure

In one of the beakers prepare 500 cm^3 of grout according to the manufacturer's directions.

Counting zero time as the end of grout preparation, allow the grout to rest for 3 minutes. At the end of the interval begin pouring the grout from one beaker into the other, using slow and regular movements. Continue transferring the grout from one beaker to the other. Setting time is reached when the grout no longer flows from a container inclined slowly to 45° (Fig. 23).

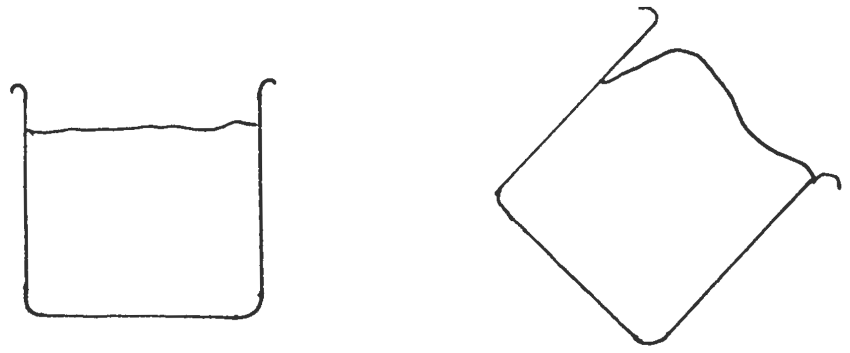


Fig. 23 . Setting Time Test

3.4 Note

While this may seem a rather imprecise definition of setting time, it is applicable to any type of chemical grout and gives sufficient information for the grout user.

4. PERMEABILITY TEST

4.1 Equipment

- standard sand, pure siliceous, 99% SiO_2, gradation 0.1 to 0.3 mm
- membrane permeameter (fig.24)
- timing device
- polyester tube, 80 mm x 1,200 mm (internal dimensions)
- 2 synthetic rubber stoppers
- injection pipe
- 2 porous cover plates
- injection pump
- latex membrane
- 2 kg sliding block for tamping sand
- grout to be tested, prepared according to manufacturer's directions
- distilled deaerated water

4.2 Directions

a. Preparing Injection Column

Using the 80 mm x 1,200 mm tube sealed at bottom with one synthetic rubber stopper equipped with an injection entry pipe and porous cover plate, fill with standard sand in 4 successive layers, tamping each layer with the 2 kg sliding block, and settling each layer by dropping the column 10 consecutive times from a height of 25 cm.

When the column is filled with sand and tamped, seal the top of the column with the other synthetic rubber stopper equipped with porous cover plate.

b. Grout Preparation

Prepare grout according to manufacturer's directions and, using the appropriate grout pump, inject immediately into sand column under 1 bar pressure (14.3 psi). Continue injection procedure until column is completely grouted and 1 litre of grout has been recovered from upper vent.

Seal grouting tube and vent and store column vertically for 15 days.

c. Sample Preparation

After 15 days, cut 100 mm from each end of the grouted column and discard. Cut the remaining length into

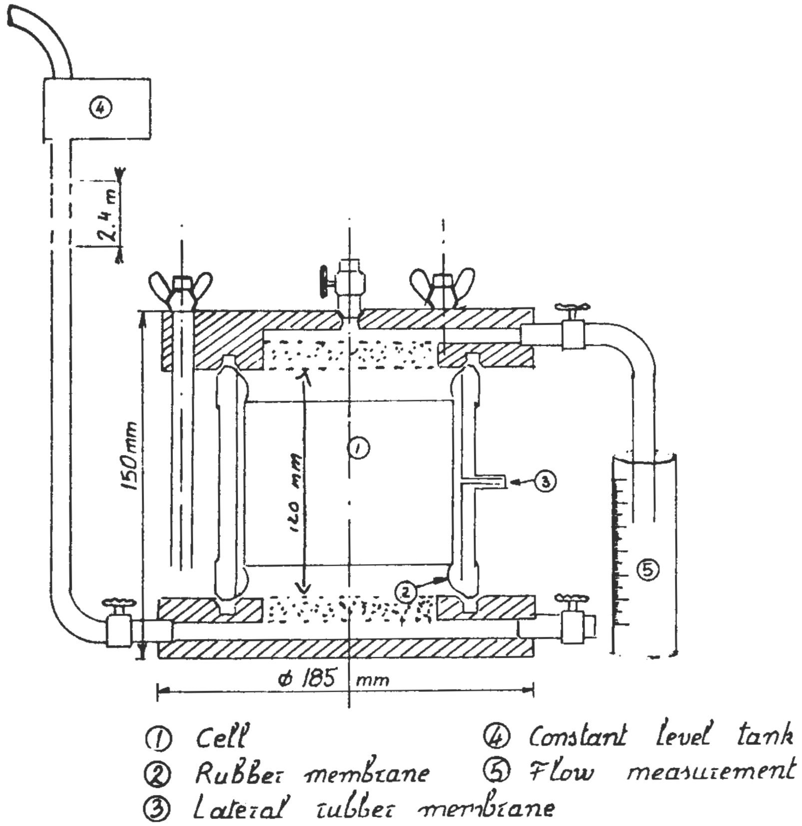


Fig.24. Membrane Permeameter

6 sections 160 mm long.

Use three test samples for the permeability test. Retain the three remaining samples for a test of unconfined compression to verify grout conformity.

d. Placing Samples in Permeameter

Place the latex membrane in the permeability cell against the exterior wall. A slight vacuum should be drawn so that the membrane remains flat against the wall of the cell.

Coat lateral surfaces of test sample with silicone grease and put into position in the cell. Release vacuum so that membrane will press against sample sides. Complete assembly of the permeameter.

e. Permeability Test

Apply a vacuum to both ends of the sample for 4 hours. Eliminate vacuum on lower end of sample, (maintain vacuum on upper part) and inject distilled deaerated water under 1 bar pressure (14.56 psi) to the lower end of sample until water appears in vacuum pipe of upper part, then release vacuum.

To measure permeability, apply latex membrane to sample under 1.5 bar confining pressure and inject distilled deaerated water to the base of the sample.

Measure quantities of percolation water every 2 hours for an 8-hour period. If, at the end of 8 hours, discharge is not constant, plus or minus 10%, allow the test to continue through the night and take another series of measurements the following day.

If constant discharge is not attained by the end of 72 hours, allow test to continue following the procedure described in the chapter on Durability.

When discharge becomes constant, calculate permeability according to DARCY's Law:

$$V=ki \qquad \frac{cm}{sec}$$

V	is speed of percolation	cm/sec
k	is permeability coefficient (Darcy)	cm/sec
i	is gradient applied to sample (function of pressure and sample thickness)	cm/cm

During testing the flow (Q) is measured in cm^3/sec by the quantity of water percolating between two readings.

Relation between Q and V is:

$$V = Q \times A \quad \frac{[cm^3]}{[sec]} \times [cm^2] = \left[\frac{cm}{sec}\right]$$

5. TEST FOR INTRINSIC STRENGTH OF GROUT

5.1 Equipment

- -12 molds, internal dimensions 18 cm diam., 10 cm height, with sanded lateral surfaces, equipped with hermetic sealing device, and made of chemically inert material
- -VANE Shear test (WICKEHAM-FARRANCE), with spring and vane chosen either by advice from grout supplier or by preliminary testing
- -30 litres of grout to be tested, prepared according to manufacturers directions

5.2 Directions

a. Sample Preparation

Fill the molds with the grout as soon as preparation is complete and seal hermetically. Store all test samples at room temperature (between 15 and 25°C) until needed for testing.

b. Shear Strength Test

Using 3 samples for each time period, measure shear strength, by the WICKEHAM-FARRANCE Vane test, at 3 days, 7 days, 14 days, and 28 days after grout preparation, using rotation speed of 20°/min. The sample container should be held in the VANE Test apparatus in such a way that it will not rotate. For each time period, take the average of the 3 results as shear strength.

c. Shear Strength Formula

c.1 Vane level with grout surface

$$Mt = \frac{2\pi a}{3}(a + 3b)R$$

Mt is torque
a = star-wheel (vane) radius
b = star-wheel (vane) height
R = shear strength

Thus, $$R = \frac{3\,Mt}{2\,\pi a^2(a + 3b)}$$

Fig. 25. Vane Shear Test

c.2 Completely submerged vane

$$Mt = \frac{2\pi a^2}{3}(2a + 3b)R$$

Thus, $$R = \frac{3\ Mt}{2\pi a^2(2a + 3b)}$$

6. TEST FOR STRENGTH OF TREATED GROUND

6.1 Equipment

- -4 rigid polyester or polyethylene columns, internal dimensions: 40 mm diam., 1200 mm height, equipped with an expansion packer at base, an injection vent and topped with a filter cloth.
- -injection pump or small johnny
- -filter sand
- -600 g expansible weight for each column, equipped with a vent
- -grout to be tested, prepared according to manufacturer's directions
- -standard sand: purely siliceus, 99% SiO_2; gradation 0.1 to 0.3 mm

6.2 Directions

a. Preparation of Injection Column

In the bottom of each column place a bed of filter sand 1 to 2 mm by 2 cm thick. Fill the column with standard sand, settling it in place by dropping the column 10 consecutive times from a height of 25 cm. Add more standard sand to restore the sand column to required height (1200 mm), and block the expansible weight against the sides of the column.

b. Injection of Column

Prepare a maximum of 3 litres of grout at a time. When this supply is exhausted, prepare 3 more litres. Continue grout preparation in this manner as needed for column injection.

As soon as grout preparation is complete, inject it into the sand column under 1 bar (14.56 psi) pressure, using the appropriate pump or a small johnny. Continue injection until there is an overflow of 500 cm^3 of grout. Use this overflow grout for testing viscosity and setting time, comparing the results with those obtained from the grout in the holding tank.

Store grouted columns vertically at room temperature (between 15 and 25°C) until needed for testing.

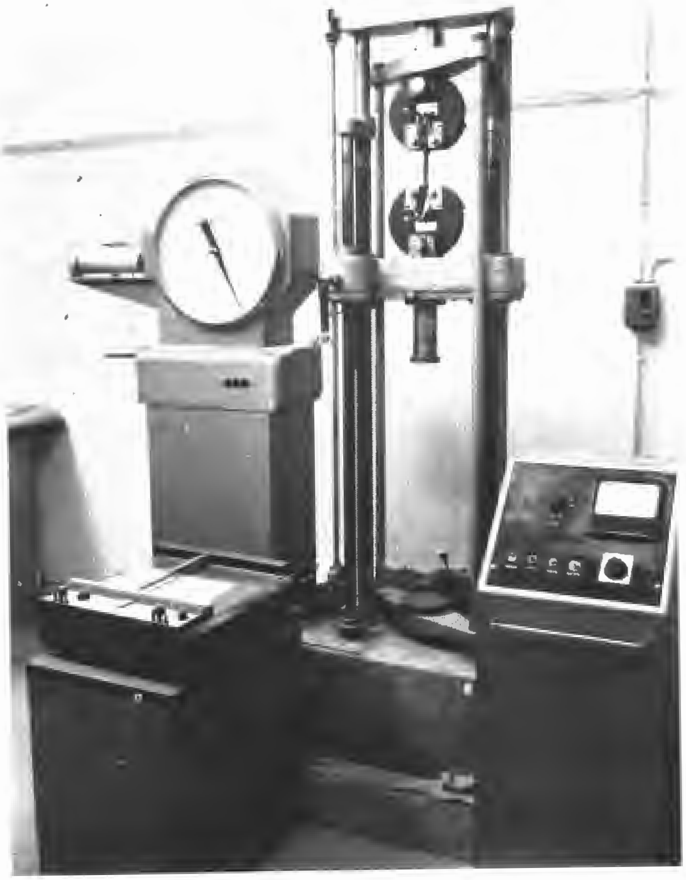


Fig. 26. Unconfined Compression Apparatus (Trayvou)

c. Unconfined Compression Test

Using 1 complete grouted column for each time period, measure unconfined compressive strength at 3, 7, 14 and 28 days after injection of column.

Eliminate the extreme ends of the column, and cut the remaining length into 10 samples, 80 mm high.

Remove the samples from their plastic envelope just before testing and immediately compress at a rate of 20 mm/min until failure. (fig. 26).

Eliminating the highest and the lowest figure, unconfined compressive strength will be the average of the remaining 8 test results.

7. DURABILITY TEST

Durability testing produces a qualitative indication which is difficult to interpret. The evolutionary tendency disclosed in these tests must be complemented by tests specific to the worksite where the grouting is to be done for interpretation to be representative. However, laboratory testing does allow the elimination of grouts which would behave very poorly.

For durability, grouts should be tested both for unconfined compression in hermetic molds to indicate the evolution of mechanical characteristics, and for permeability, to determine the possibility of dissolution of the grout matrix.

The length of testing time in each case will depend on the purpose for which the grout is intended.

7.1 Unconfined Compression Test

a. Equipment

-10 rigid polyester or polyethylene columns: internal dimensions, 40 mm diam., 1200 mm high, equipped with an expansion packer at base, an injection tube and topped with a filter cloth
-injection pump or small johnny
-filter sand
-600 g expansible weight for each column, equipped with a vent
-3 litres of grout to be tested, prepared according to manufacturer's directions
-standard sand: purely siliceous, 99% SiO_2, gradation 0.1 to 0.3 mm

b. Preparation of Injection Column

In the bottom of each column, place a bed of filter sand 1 to 2 mm by 2 cm thick. Fill the column with standard sand, settling it in place by dropping the column 10 consecutive times from a height of 24 cm. Add more standard sand to restore the sand column to required height (1200 mm) and block the expansible weight against the sides of the column.

c. Injection of Column

Prepare a maximum of 3 litres of grout at a time. When this supply is exhausted, prepare 3 more litres. Continue grout preparation in this manner as needed for column injection.

As soon as grout preparation is complete, inject it into the sand column under 1 bar pressure (14.3 psi), using the appropriate pump or a small johnny. Continue injection until there is an overflow of 500 cm^3 of grout. Use this overflow grout for testing viscosity and setting time, comparing the results with those obtained from the grout in the holding tank.

Store grouted columns vertically at room temperature (between 15 and 25°C) until needed for testing.

d. Unconfined Compression Test

Using 1 complete grouted column for each time period, measure unconfined compression strength at 3 days, 7 days, 14 days, 28 days, 90 days, 180 days, 1 year, 2 years, 5 years, 10 years.

Eliminate the extreme ends of the column, and cut the remaining length into 10 samples, 80 mm high.

Remove the samples from their plastic envelope just before testing and immediately compress at a rate of 20 mm/min until failure. (fig. 27).

Eliminating the highest and the lowest figure, unconfined compressive strength will be the average of the remaining 8 test results.

When test results stabilize, plus or minus a 10% difference, the grout is considered stable.

Any variation in test results greater than 10% indicates that testing should be continued.

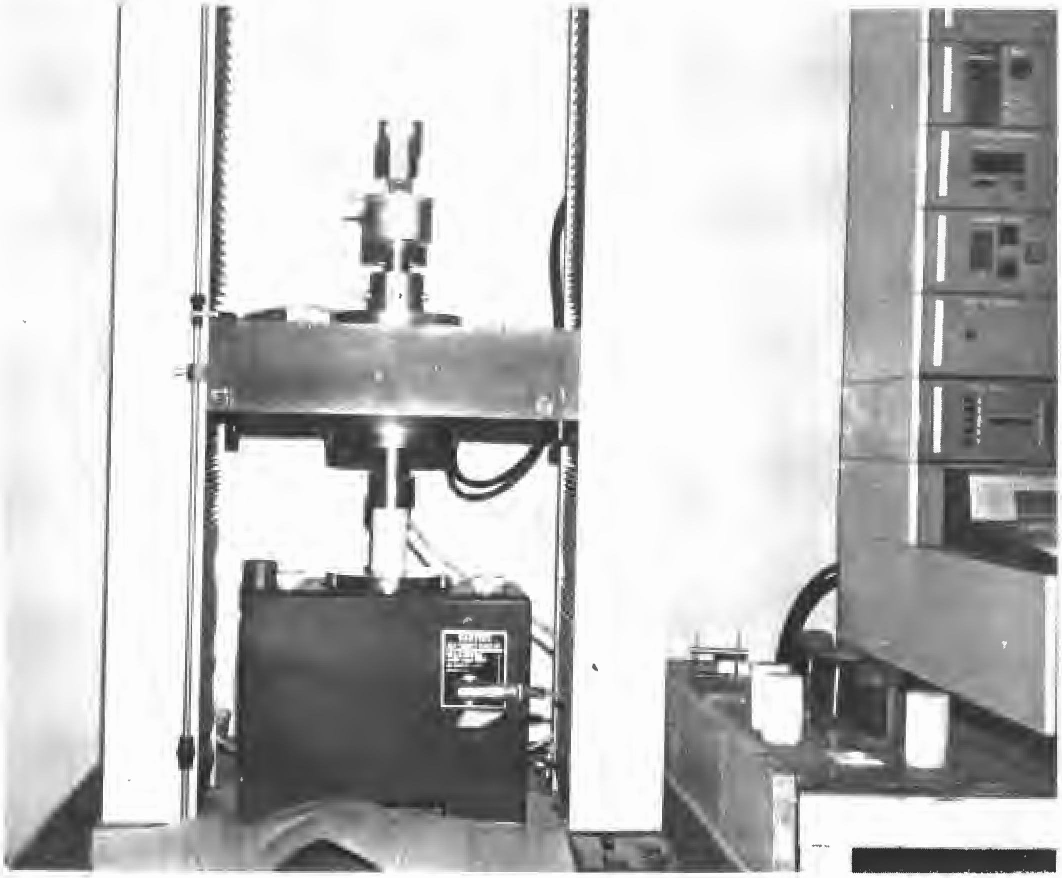


Fig. 27. Unconfined Compression Apparatus (Instron)

7.2 Permeability Test

a. Equipment

- -standard sand: purely siliceous, 99% SiO_2, gradation 0.1 to 0.3 mm
- -membrane permeameter (fig. 28)
- -timing device
- -7 tubes, 80 mm x 1200 mm (internal dimensions)
For each tube:
- -2 synthetic rubber stoppers
- -injection pipe
- -2 porous cover plates
- -injection pump
- -latex membrane
- -2 kg sliding bock, for tamping sand
- -grout to be tested, prepared according to manufacturer's directions
- -distilled deaerated water

b. Preparing Injection Columns

Using the 80 X 1200 mm tubes, sealed at bottom with one synthetic rubber stopper, equipped with an injection entry pipe and porous cover plate, fill with standard sand, in 4 successive layers, tamping each layer with the 2 kg sliding block, and settling each layer by dropping the column 10 consecutive times from a height of 25 cm.

When the column is filled with sand and tamped, seal the top of the column with the other synthetic rubber stopper, equipped with porous cover plate.

c. Injection of Columns

Prepare grout according to manufacturer's directions and, using the appropriate grout pump, inject immediately into sand column under 1 bar pressure (14.56 psi). Continue injection procedure until column is completely grouted and 1 litre of grout has been recovered from upper vent.

Seal grouting tube and vent and store column vertically until needed for testing.

d. Sample Preparation

One complete column will be tested for each period of the following timetable: 28 days, 90 days, 180 days, 1 year, 2 years, 5 years and 10 years after injection of column. For each test, cut 100 mm from each end of the grouted column and discard. Divide the remaining length into 6 samples of equal size.

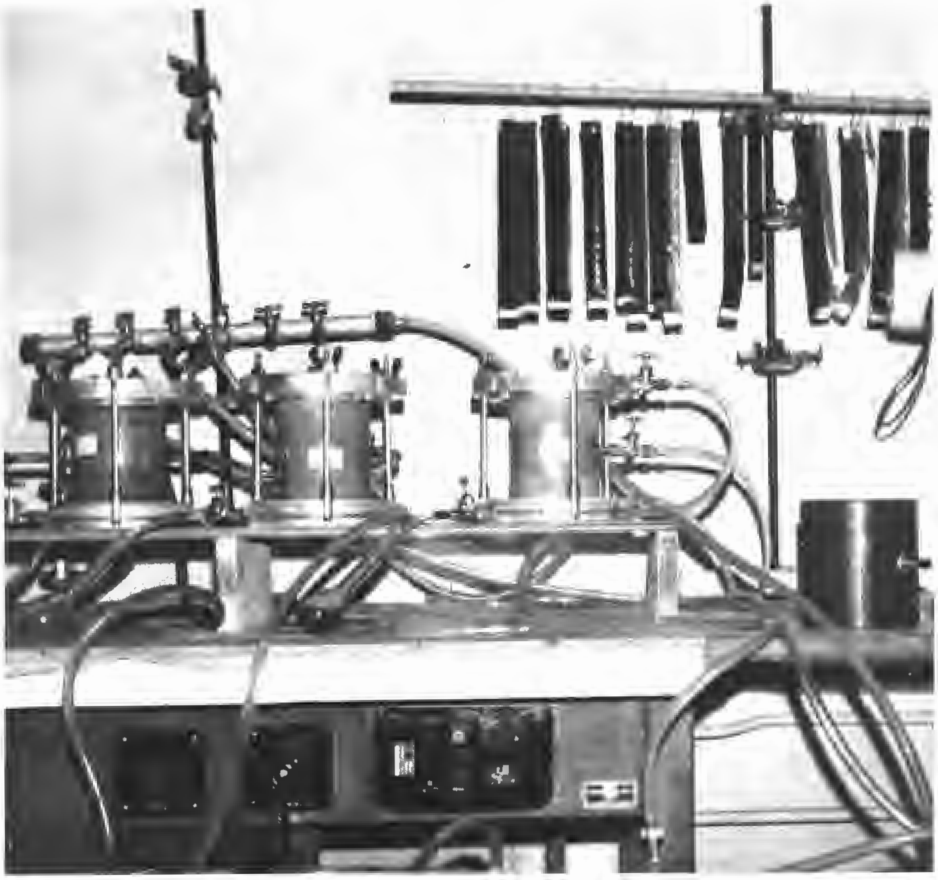


Fig. 28. Bank of Permeameters

Use 3 samples for the permeability test and 3 samples as a control group to be tested for unconfined compression, comparing the results with the samples tested for permeability.

e. Placing Samples in Permeameter

Place the latex membrane in the permeability cell against the exterior wall. A slight vacuum should be drawn so that the membrane remains flat against the wall of the cell.

Coat lateral surfaces of test sample with silicone grease and put into position in the cell. Release vacuum so that membrane will press against sample and complete assembly of the permeameter.

f. Permeability Test

Apply a vacuum to both ends of the sample for 4 hours. Eliminate vacuum on lower end of sample, maintaining vacuum on upper part, and inject distilled deaerated water under 1 bar pressure (14.56 psi) to the lower end of sample until water appears in vacuum pipe of upper part, then release vacuum.

To measure permeability, apply latex membrane to sample under 1.5 bar pressure and inject distilled deaerated water to the base of the sample. The filter sand at the extreme ends of the cell should be checked periodically to avoid possible clogging.

Measure pH, resistivity and quantities of percolation water every 2 hours for an 8 hour period. Any variation in discharge or in pH and resistivity, as compared to the values for the distilled deaerated water on entrance, is a suspicious element of behavior.

Make a visual examination of each sample to estimate the disturbed zone or zones and the size of the disturbance, then take 2 core samples of the cell, one of 39.5 mm diam., the other of 12.5 mm diam.

Divide the 39.5 mm diam. core sample into 2 test samples and submit them to an unconfined compression test, comparing the results with those obtained from samples cured hermetically.

Divide the 12.5 mm diam. core sample into 5 test samples, and submit them to unconfined compression test. Between them, the test results delineate the disturbed zone.

When pH and resistivity show variations, proceed to a qualitative chemical analysis of the percolation water. Compare the types of chemicals found to those contained in the grout before setting.

Keep the percolation water as a whole in separate containers, submitting it to quantitative chemical analysis. Comparison of the successive analyses will disclose the evolution of the phenomenon, and the accumulation of the results obtained will give the total quantity of elements dissolved.

8. TOXICITY TEST

Testing procedures for toxicity evaluation have been described for each of the grouts considered in Part Three of this volume.

However, no universal toxicity tests can be recommended for standardization because of the many and varied toxicity standards of the various governmental regulatory agencies.

The question of grout toxicity is divided into 2 distinct parts:

1) Toxicity of the individual ingredients of the grout at the preparation stage; and

2) Toxicity of the hardened grout in the ground.

Any substance proposed for temporary or permanent use in the ground must be evaluated in terms of its possible impact on the environment. However, there are many types of grout available, as well as additives and reagents, and all of these can be combined in almost limitless variations. Thus, it is doubtful that any one testing procedure could adequately define such a delicate and important factor as toxicity for each and every possible chemical grout.

It is far less difficult to discover the toxicity of the individual ingredients of a chemical grout, in order to adequately protect personnel in contact with the substances. A commercial preparation will usually have such information available, or at least a listing of precautions to be taken, while the toxicity of the basic ingredients of a non-commercial grout will be readily available from chemical literature, manufacturers or governmental agencies.

PART THREE:
PROPERTIES OF PROMISING GROUT MATERIALS

I. Introduction

Volume I of this report gives a detailed classification of available materials used for chemical grouting. Eight of the most promising materials were selected for further study under the guidelines of the physico-chemical characteristics defined in Part I of this volume.

For each grout, each characteristic is discussed in turn, including the possible external factors influencing the suitability of the grout materials for various situations. Possible effects on each criterion are enumerated and discussed in order to fully understand all aspects of any possible problems.

A great deal of research data was available for the silicate derivates, but somewhat less information could be found for the other grouts studied. Where information was unavailable, testing was conducted to determine the effect of a given situation on the specific criterion in question.

Using the information gathered, the most promising two grout materials were selected for further study in Part Four, to determine the possiblity of overcoming their disadvantages.

II. CATEGORY A-1 SILICATE DERIVATIVES

1. Viscosity

1.1 Initial Viscosity

Initial viscosity in Category A-1 grouts cannot be defined by a specific value for several reasons:

1) Since the basic ingredient (generally sodium silicate) does not have a clearly defined composition, its viscosity cannot be specified.

2) Depending on the formulations adopted for the grout, the silicate used will be more or less dilute.

3) The system's setting reagent can cause viscosity to increase suddenly.

1.11 Viscosity of Pure Silicate

In this category of silicate derivatives, the product most universally used is sodium silicate. It is marketed in the form of a concentrated syrupy liquid. Sodium silicate contains in varying proportions: orthosilicates ($Na_4Si_2O_4$), metasilicates (Na_2SiO_3), and compounds with a high silicate content ($Na_2Si_4O_5$).

Three factors affect the viscosity of these syrups:

a) The effect of the silica/alkali ratio is shown in fig. 29 below:

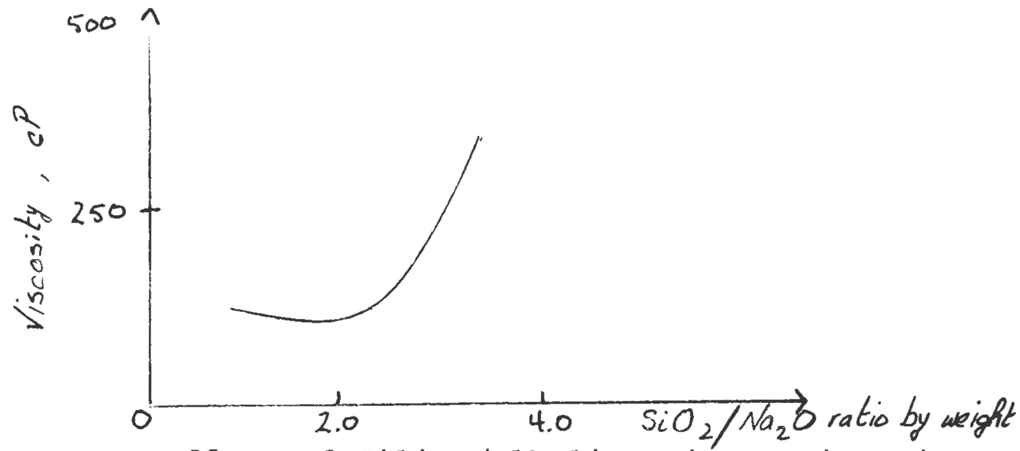


Fig. 29 . Effect of Silica/Alkali Ratio on Viscosity at 20°C (% dry extract constant)

b) The effect of concentration is shown in fig. 30 below:

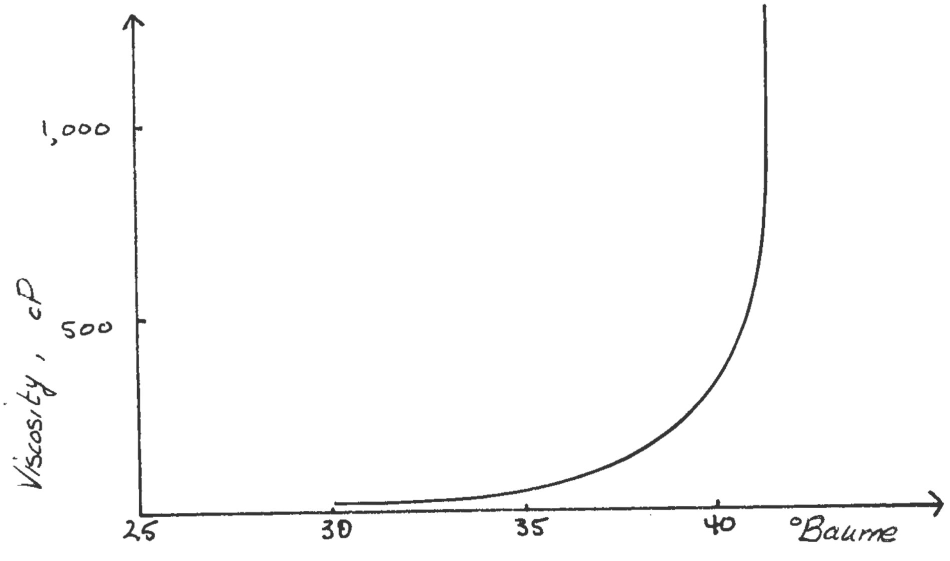


Fig. 30 . Effect of Concentration on Viscosity at 20°C (Silica/alkali ratio = 3.3)

c) The effect of temperature, of which an example is given in fig. 31 .

The sodium silicates most commonly used for grouting have a weight ratio SiO_2/Na_2O of between 3.2 and 4, with silica concentration between 23 and 26%. Viscosity thus ranges from 40 to 90 cP at ambient temperature.

1.12 Viscosity of Silicate Solution

Silica gels usually involve sodium silicate solutions which are diluted with water according to the purpose for which they are being used. For consolidation gels, the dilution is 0 to 60% in theory, but 25 to 60% in practice. For waterproofing gels, the dilution is 70 to 90%.

For a given sodium silicate, the initial viscosity of the sodium silicate-water solution will depend on the ratio of silicate to water in the mixture.

In fig. 32 the variations in viscosity at 20°C are given in terms of dilution for two of the principal sodium silicates used in grouting. With the minimum dilution of 25% used with silica gels, viscosity is always below the 20 cP threshold and within the following ranges:

-consolidation: 6 to 16 cP
-waterproofing: 3 to 5 cP

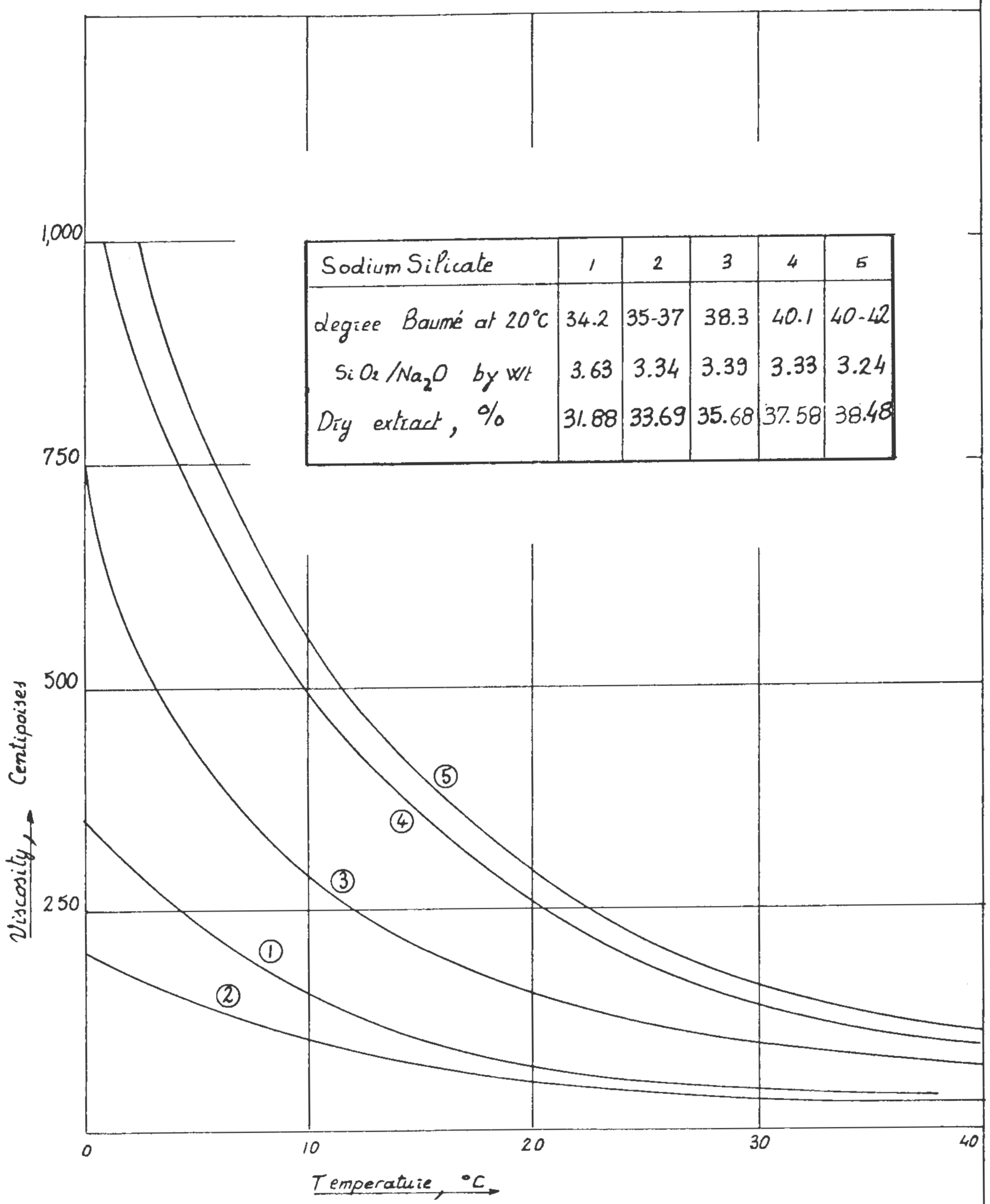
1.13 Grout Viscosity

Addition of the reagent immediately causes viscosity to increase, whatever the type of gel. This increase is imperceptible with very diluted waterproofing gels, appearing more clearly with certain concentrated gels and becoming more pronounced as reagent content increases. Fig. 33 shows examples for a commonly used silicate.

1.2 Evolution in Viscosity with Time

For this consideration, a distinction must be made between waterproofing gels, which generally use inorganic reagents, and consolidation gels, which use organic reagents.

Waterproofing gels are dilute and thus have low initial viscosity, but they react almost immediately with their setting reagents. Thus, for a gel with a short setting time, changes in viscosity will occur rapidly, while for gels with a long setting time changes in viscosity will occur more slowly (fig. 34).



Sodium Silicate	1	2	3	4	5
degree Baumé at 20°C	34.2	35-37	38.3	40.1	40-42
SiO_2/Na_2O by wt	3.63	3.34	3.39	3.33	3.24
Dry extract, %	31.88	33.69	35.68	37.58	38.48

Fig. 31. Effect of Temperature on Viscosity

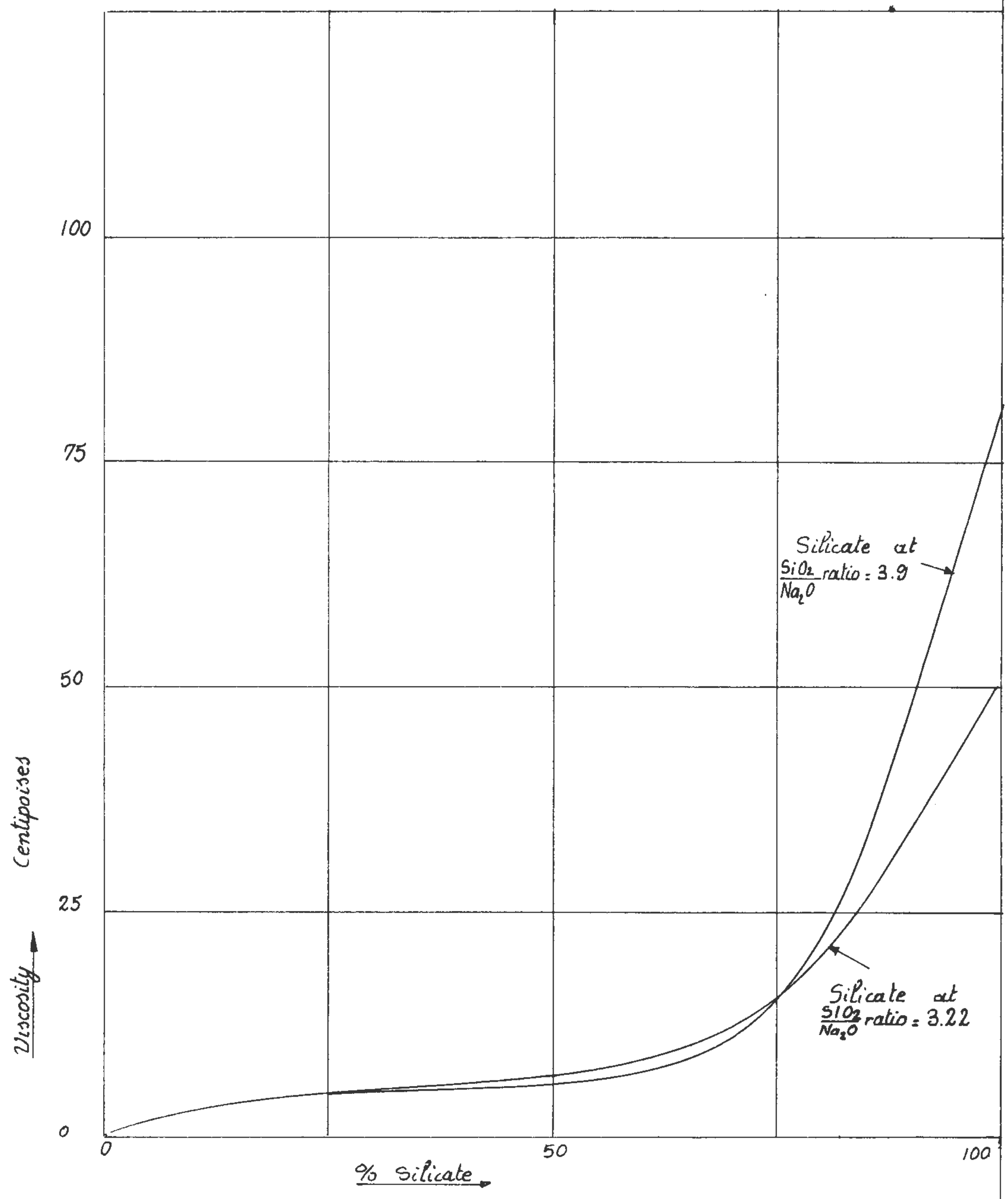


Fig. 32. Effect of Dilution on Initial Viscosity of Silica Gels

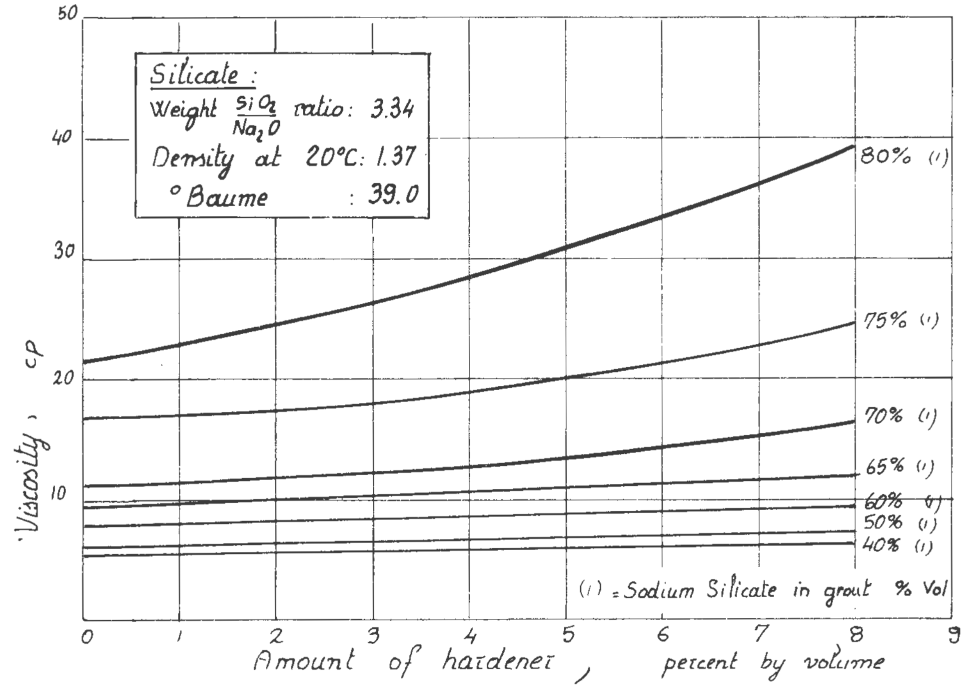


Fig. 33. Evolution of Viscosity in Silica Gels After Addition of Hardener

RHONE-PROGIL (99-09)

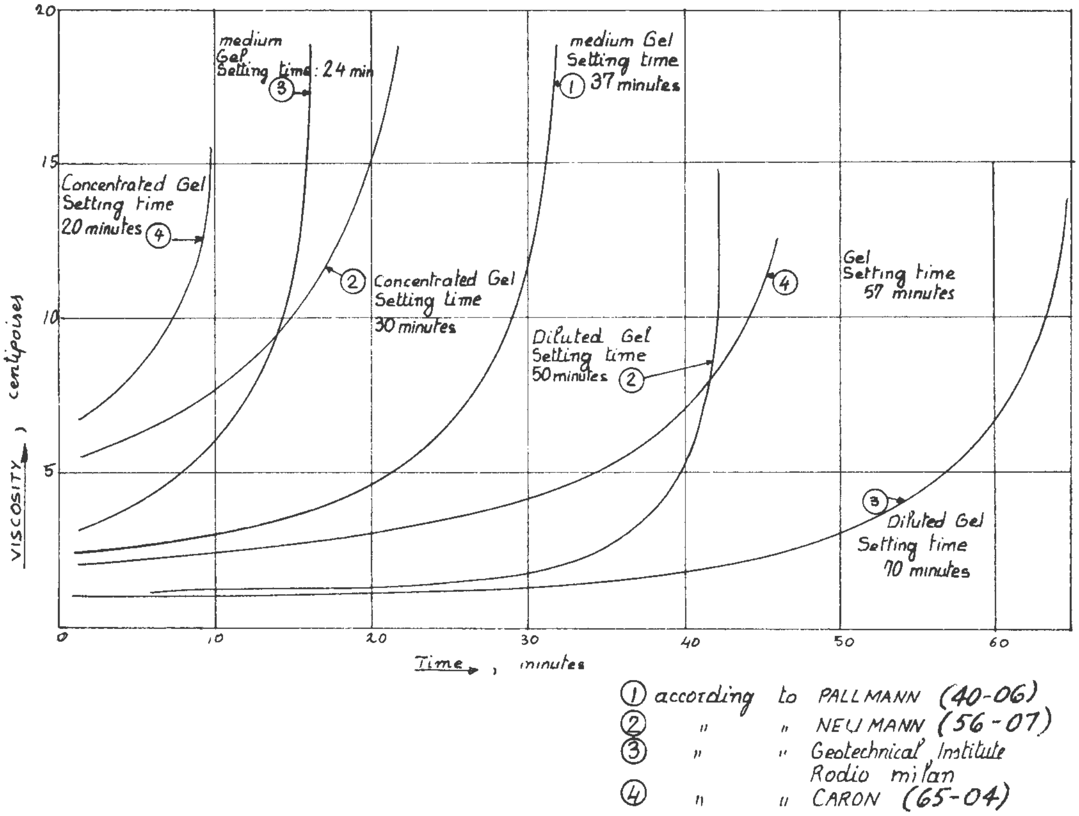


Fig. 34. Effect of Setting Time on Viscosity for Waterproofing Gels

As consolidation gels use an organic reagent which decomposes slowly, releasing one or more products likely to gel the silicate, the reaction is always very gradual. Changes in viscosity will depend on the nature of the setting reagent; that is, the rate of hydrolysis (CANIZZARO reaction, saponification) will depend on the nature and diluteness of the silicate used, which can vary widely. Fig. 35 shows changes in viscosity observed over a number of different experiments.

As is the case with the silicate solution itself, the progressive changes in the viscosity of the gel of a given composition will be affected by temperature, as shown in fig. 36 .

2. Regulation of Setting Time

As with any other grout, the setting time of a silica gel must be adjustable to take into account:

a) the conditions in the ground. A fast setting time is desirable if the rate of absorption is high, in order to prevent the grout from flowing outside the area to be treated, while a long setting time is preferred if the rate of absorption is low.

b) ambient air and ground temperature. As shown in fig. 37 , and according to VAN T'HOFF-ARRHENIUS, the setting of silica gels is a function of their temperature, the rate of set (for a 10°C rise or decrease in temperature) being about 1.3 to 1.4 for moderately dilute gels with organic reagents and 2 for highly dilute gels with inorganic reagents.

The phenomenon is more complicated with high silica content gels used for strong consolidation: the setting time curve in terms of temperature shows a retrogression at low temperatures. The longest setting time will therefore occur at between 11°C and 18°C, depending on the concentration of silicate. This is shown in fig. 38 for 3 gels of varying composition. The setting time is shortened outside this temperature range.

It thus appears to be vital to be able to regulate a gel's setting time in terms of these two factors, either by acceleration or retardation, the latter being much more common in practice.

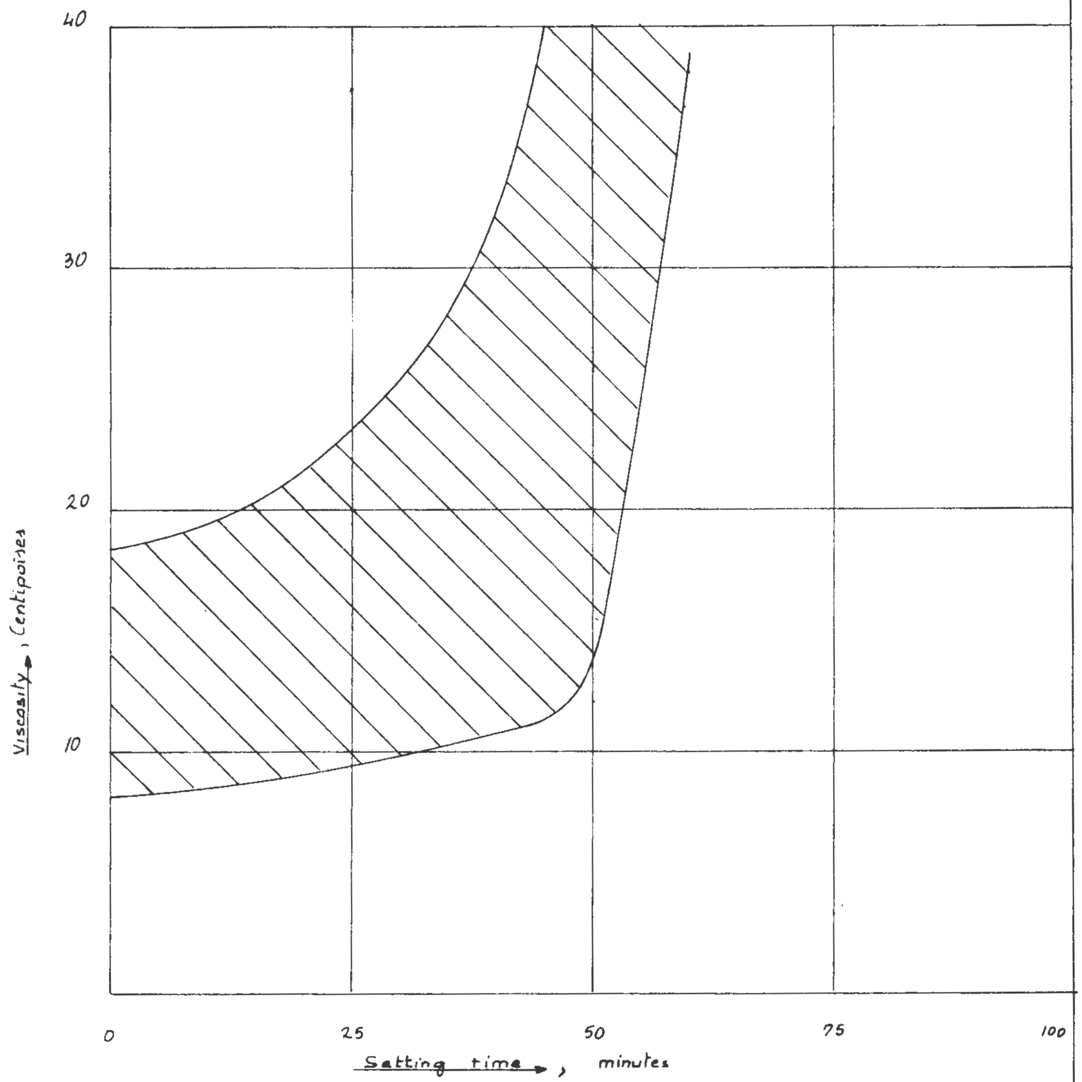


Fig. 35. Effect of Time on Viscosity for Several Semi-Hard Gels (Setting Time Approximately 60 Minutes)

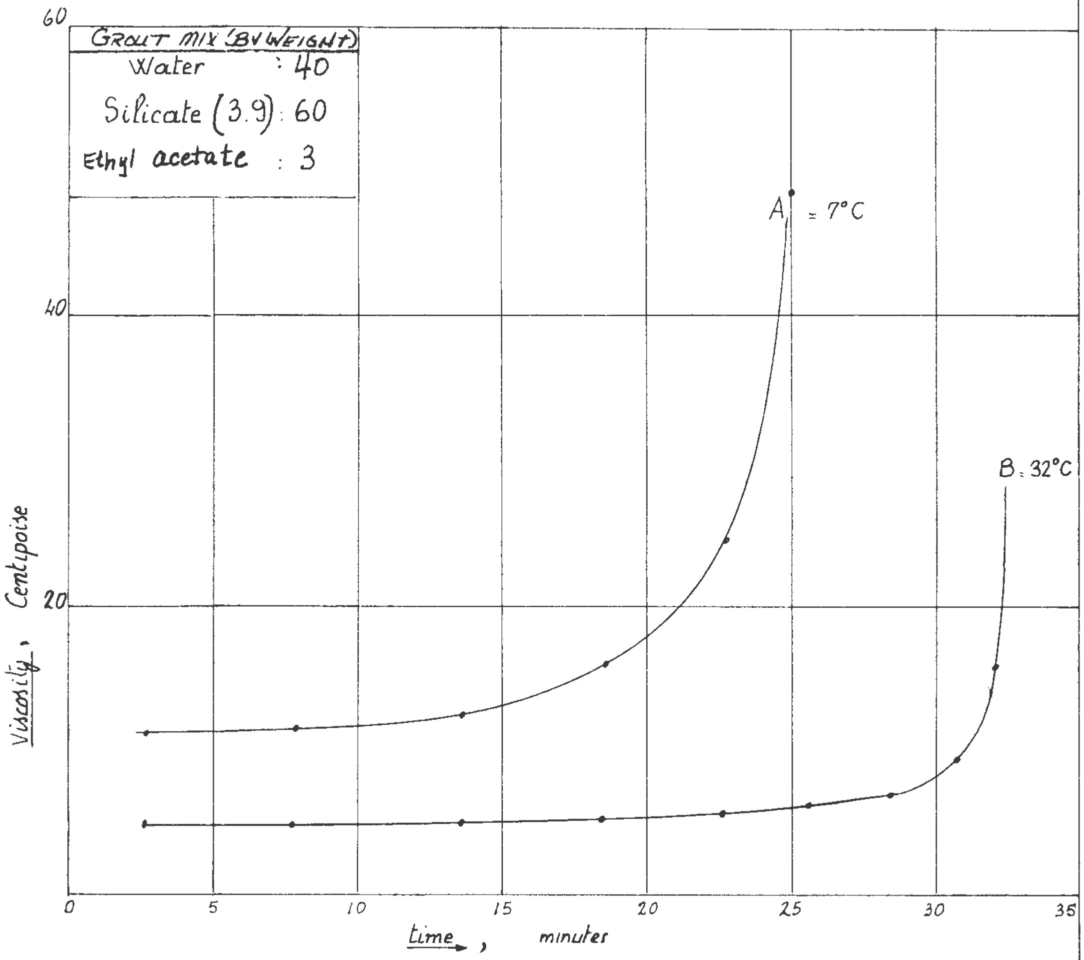


Fig. 36. Effect of Temperature on Viscosity

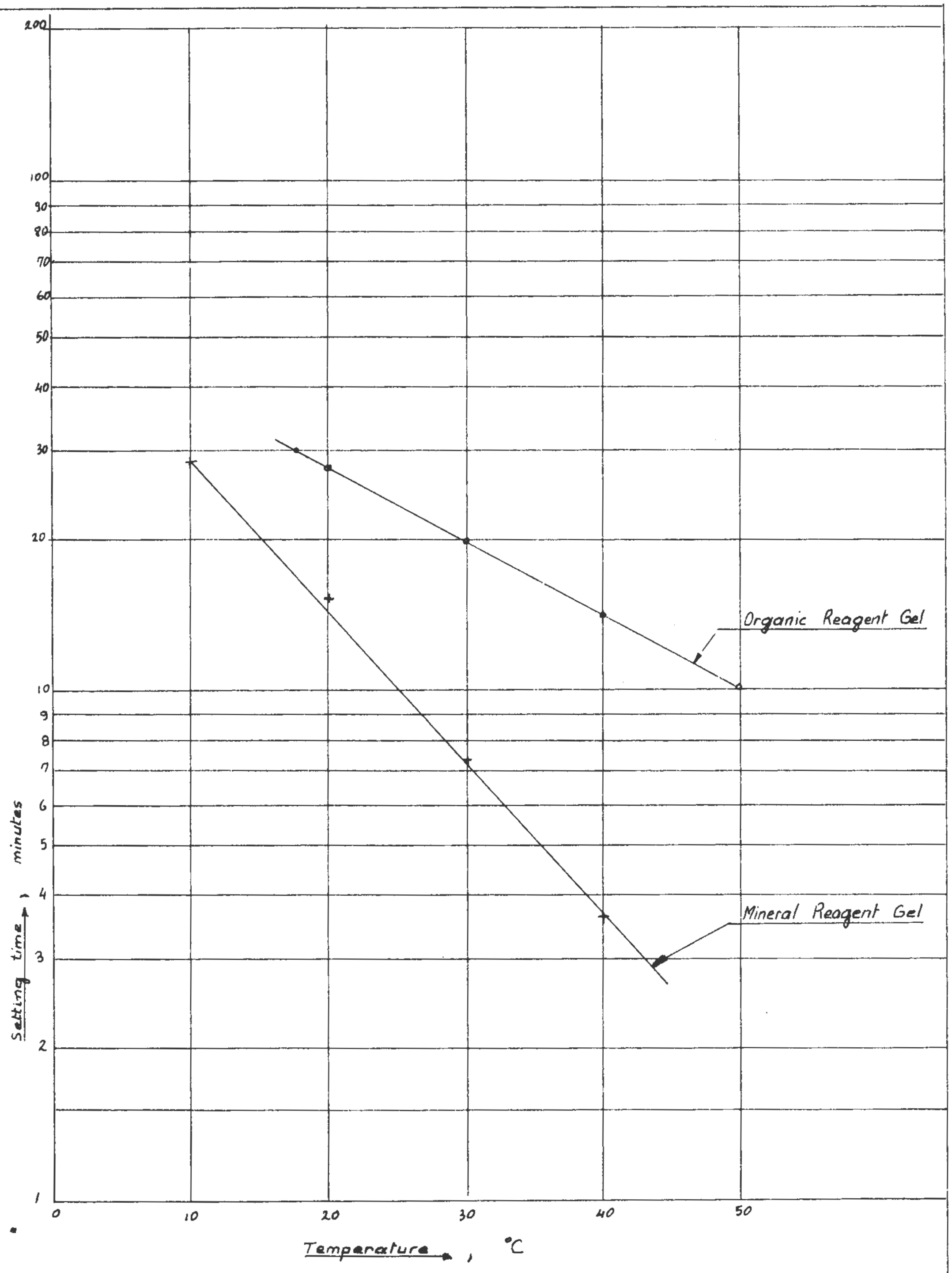
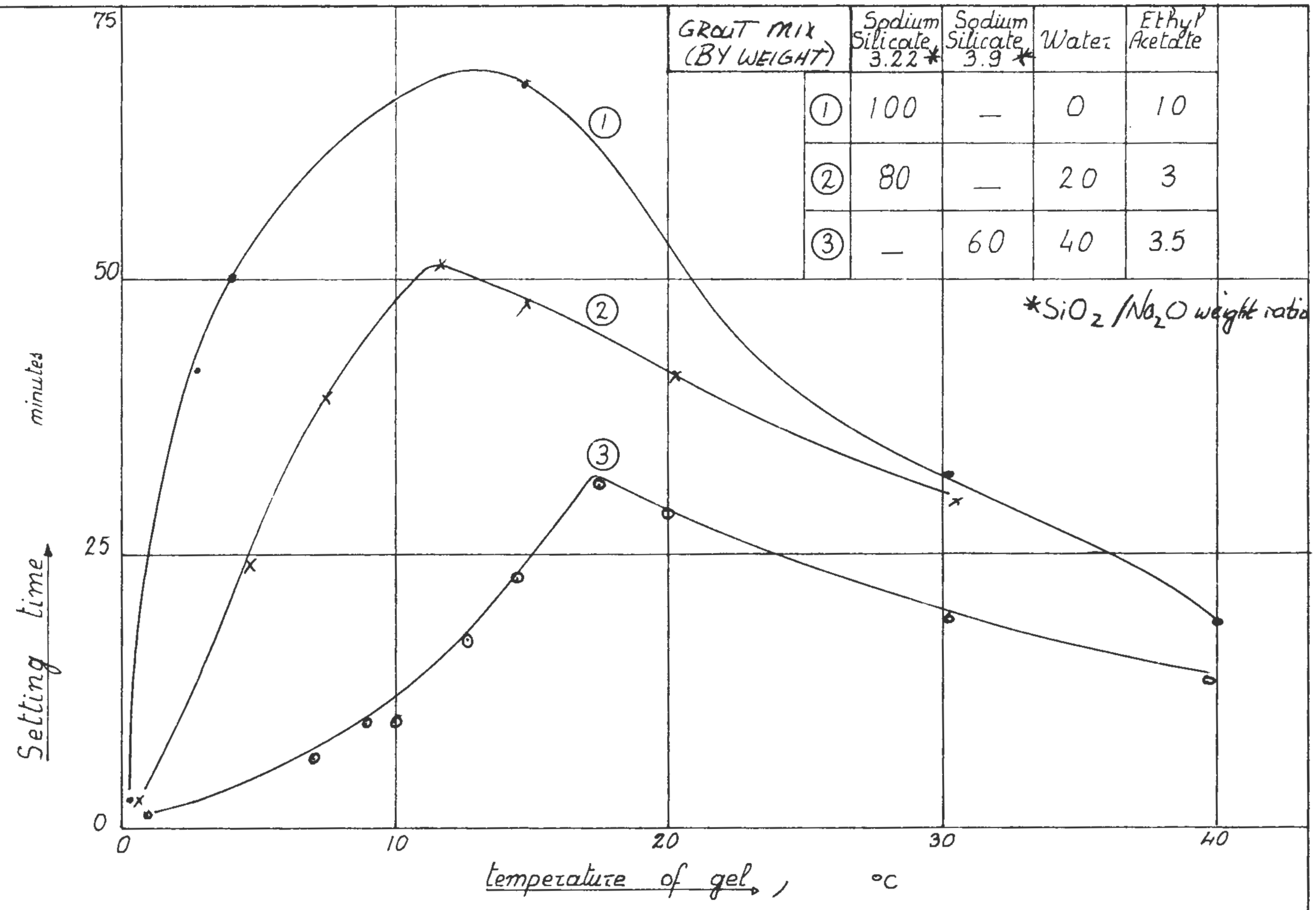


Fig. 37 . Effect of Temperature on Setting Time of Silica Gels .



GROUT MIX (BY WEIGHT)	Sodium Silicate 3.22*	Sodium Silicate 3.9*	Water	Ethyl Acetate
①	100	—	0	10
②	80	—	20	3
③	—	60	40	3.5

*SiO_2/Na_2O weight ratio

Fig. 38. Effect of Temperature on Setting Time of Silica Gels

2.1 Waterproofing Gels

The setting time of dilute gels (with inorganic reagents) is regulated primarily by varying the amount of setting reagent. In a basic medium, the only one used in grouting, setting time will vary inversely with the amount of reagent.

In the range commonly used (several minutes to around ten hours), the relationship of setting time as a function of the concentration of setting reagent can be expressed as follows:

$$t = e^{-kc}$$

where t is the setting time
c is the concentration of reagent
k is a constant which is independent from the nature of the reagent, but varies with the nature of the silicate (expressed by the ratio SiO_2/Na_2O), diluteness, as well as temperature. This is shown on fig. 39 (C. CARON 65-04).

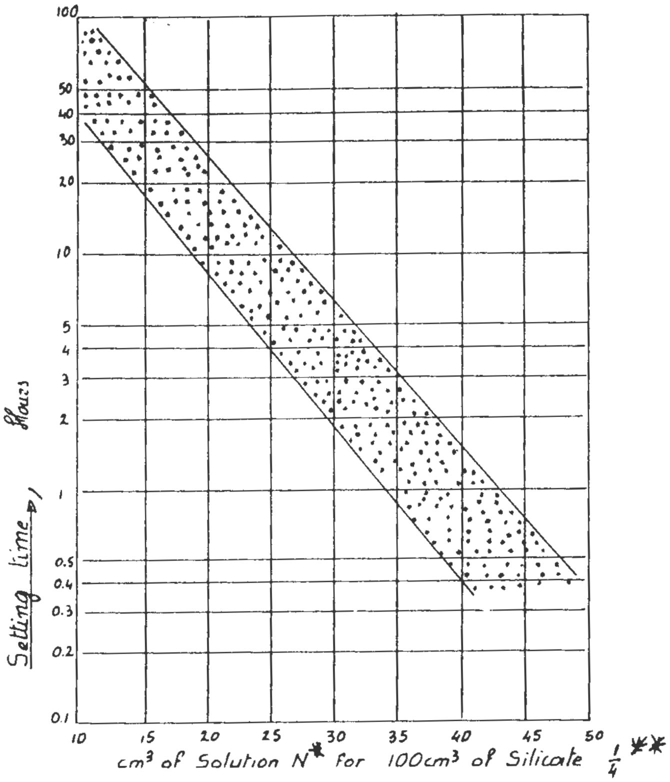
The effect of the nature of the silicate is thus expressed by factor "k". Since the sodium silicate is to be neutralized, its chemical composition will affect setting time. All else being equal, the lower the SiO_2/Na_2O ratio, the longer the setting time will be.

It should be stressed that a prolongation of the setting time achieved by reducing the proportion of setting reagent will lead to a weakening of the gel's strength.

2.2 Consolidation Gels

Consolidation gels always use organic reagents. For these gels, as in the case with gels using inorganic reagents, setting time can be regulated by varying the nature and concentration of sodium silicate as well as by varying the proportion of hardener used. Examples are given in fig. 40, drawn from RHONE-PROGIL's records for Hardener 600 B, and in fig. 41 for glyoxal and fig. 42 for formamide. However, since the variation of any of these factors will necessarily have a detrimental effect on mechanical characteristics, such variations are generally not practiced.

Setting time can also be modified by changing or combining the characteristics of different organic reagents. The chemical reactiveness of organic reagents compatible with sodium silicates is sufficiently varied to



*Solution N: normal solution, ie containing 1 molecule-gram of reagent per litre of water

** Silicate 1/4: 25 ml of silicate (3.3) in 75 ml of water

Fig. 39. Relation Between Setting Time and Reagent Content in the Basic Zone

CARON (65-04)

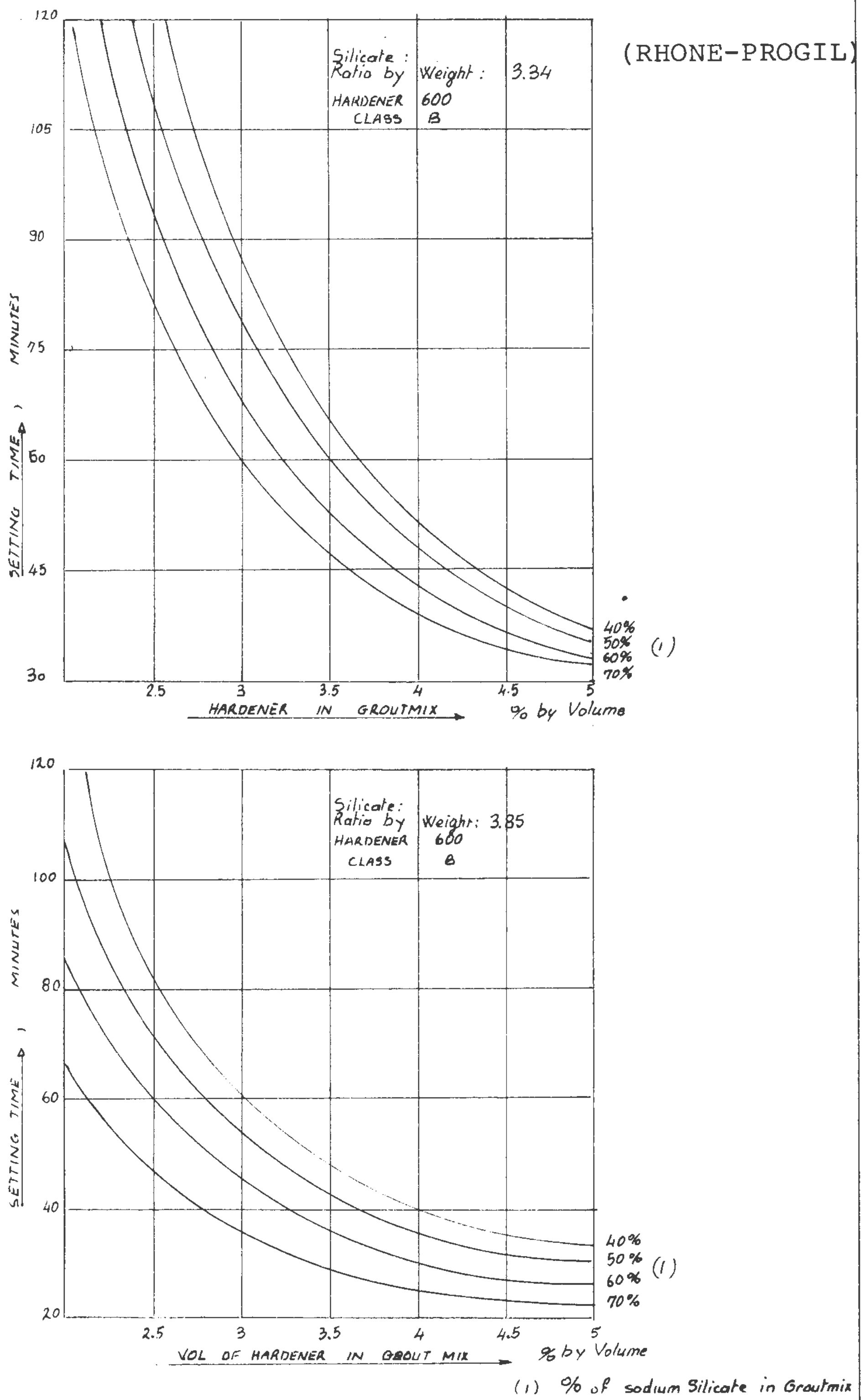


Fig. 40. Effect of Nature and Concentration of Sodium Silicate and Reagent Content on Setting Time

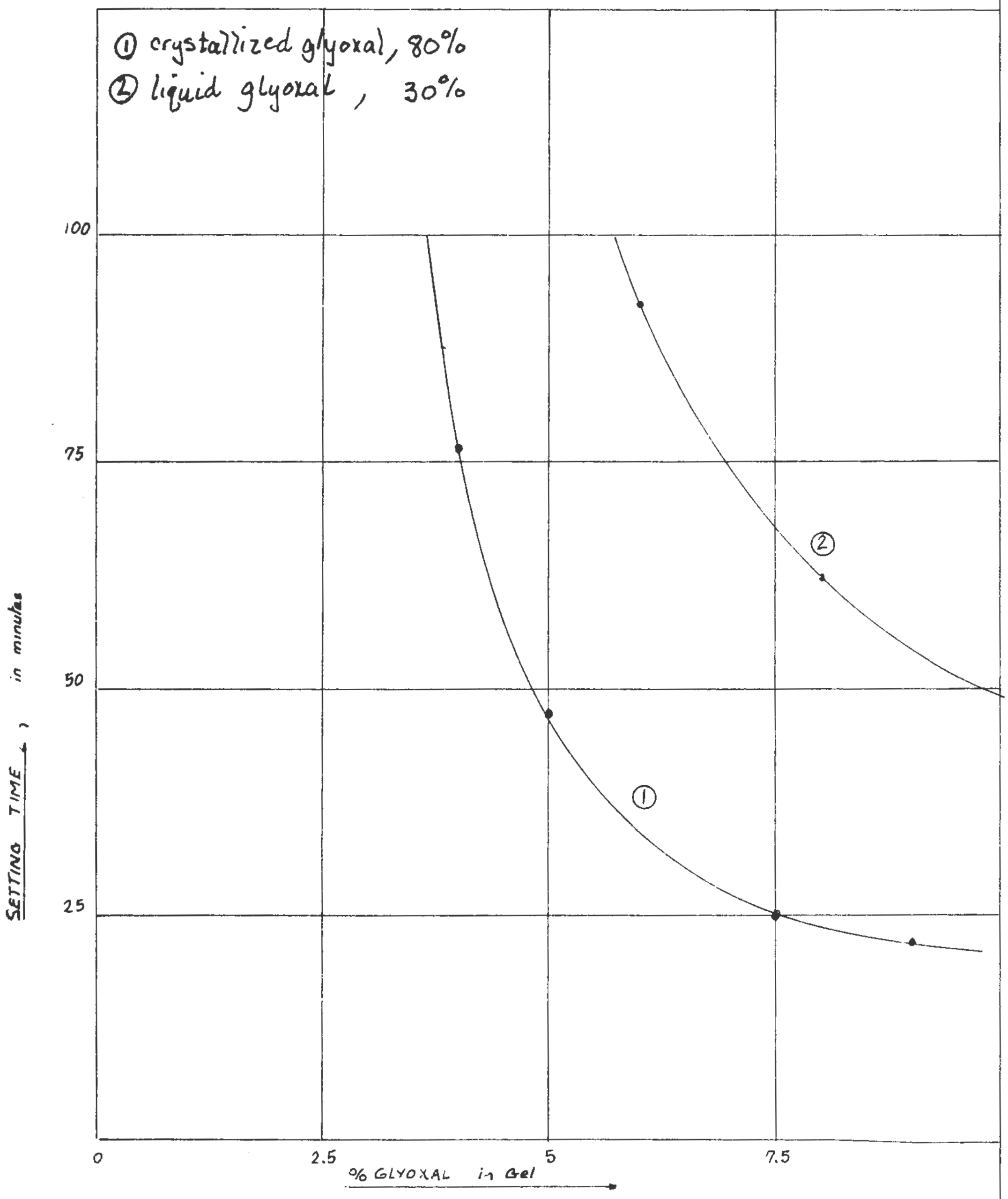


Fig. 41. Effect of Technical Glyoxal Content on Setting Time

(RHONE-PROGIL)

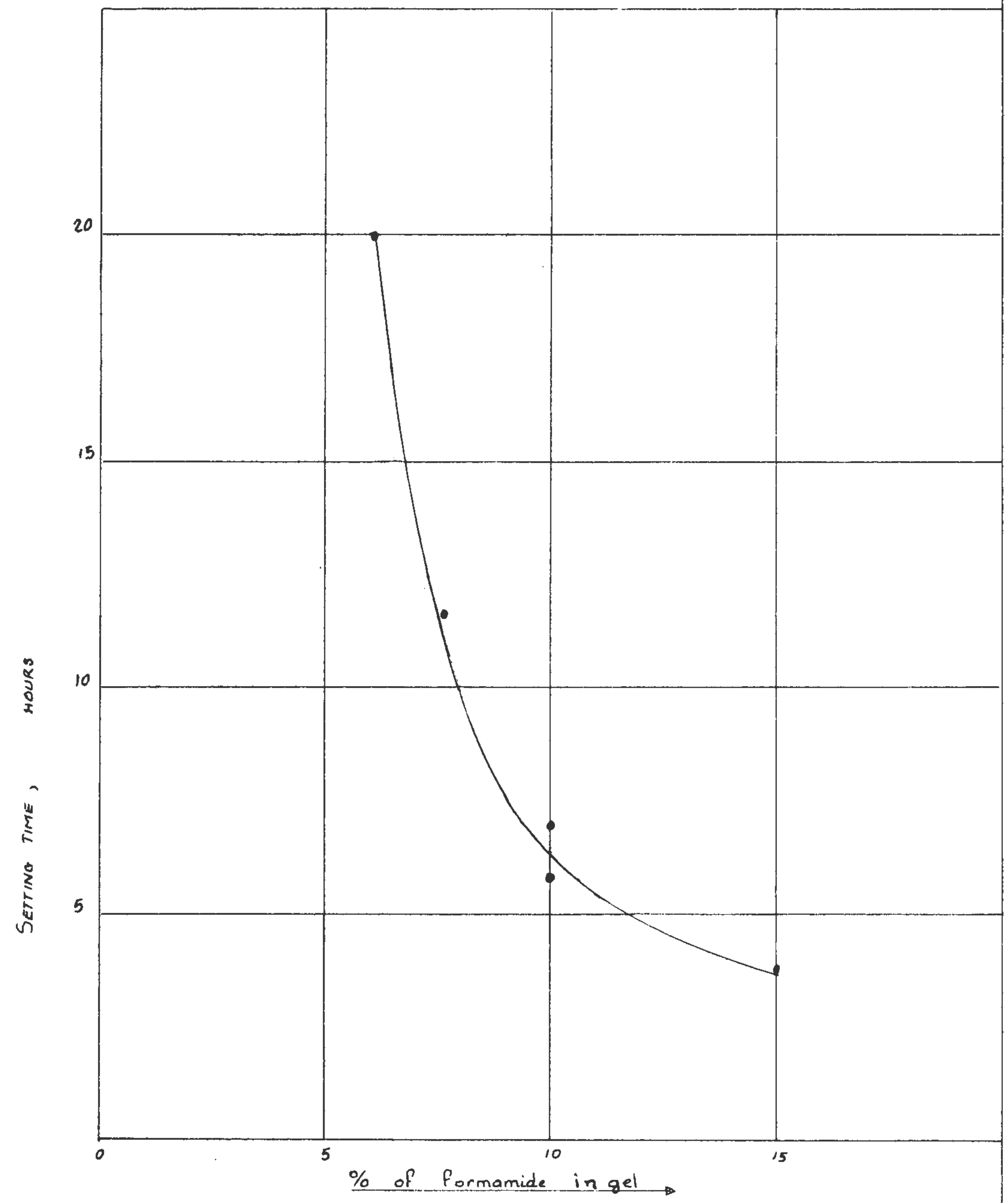


Fig. 42. Effect of Formamide Content on Setting Time

(RHONE-PROGIL)

enable setting times to range from 10 minutes up to 6 or 7 hours without altering mechanical characteristics, since the formula remains perfectly balanced.

Esters are the most commonly used reagents. For the frequently used ethyl acetate, average setting time for a well balanced formula will be 50 minutes, and will often have to be extended. This can easily be accomplished by combining ethyl acetate with less reactive esters, such as butyl acetate or isopropyl acetate. In fig. 43 are several examples or instances where such combinations allowed setting times to extend to 6 or 7 hours without difficulty. For very long setting times (over 6 to 7 hours), low-reaction esters alone can be used. Conversely, some high reaction esters can be used to obtain very short setting times if necessary. For such purposes the product most commonly used is isopropylformiate.

With dimethyl succinate (recommended by RHONE-POULENC and marketed under the name of Hardener 600 B), as with ethyl acetate, setting time will generally be too short. In fig. 43, for the well-balanced formulas with the proportion of reagent over 4%, setting time is under 50 minutes. The problem thus frequently consists of prolonging the setting time, and for this purpose, the succinate should be combined with adipates. RHONE-POULENC uses this combination for its Hardeners 600 C and 600 D. An example is given in fig. 44 which should be compared with fig. 45.

Shortening of setting time occurs with formamide (SIROC GROUT Process) which, used alone, is very slow, causing a setting time of approximately 15 hours. The process is accelerated by the addition of aluminum chloride or dilute phosphoric acid.

In all of these cases, modifications of setting time have no effect on strength.

3. Strength of Pure Grout

Research into strengths of chemical grouts in a pure state is of interest only for waterproofing. In Part One, Chapter 5, it was noted that, in consolidation, the strength of the sand-grout combination has no relation to the strength of the pure grout, as it is the agglutinizing effect of the pure grout that is important. However, in waterproofing, results depend on the ability of the grout alone to withstand erosion. This section is devoted exclusively to the strengths of waterproofing gels in a pure state, as measured by the shear test.

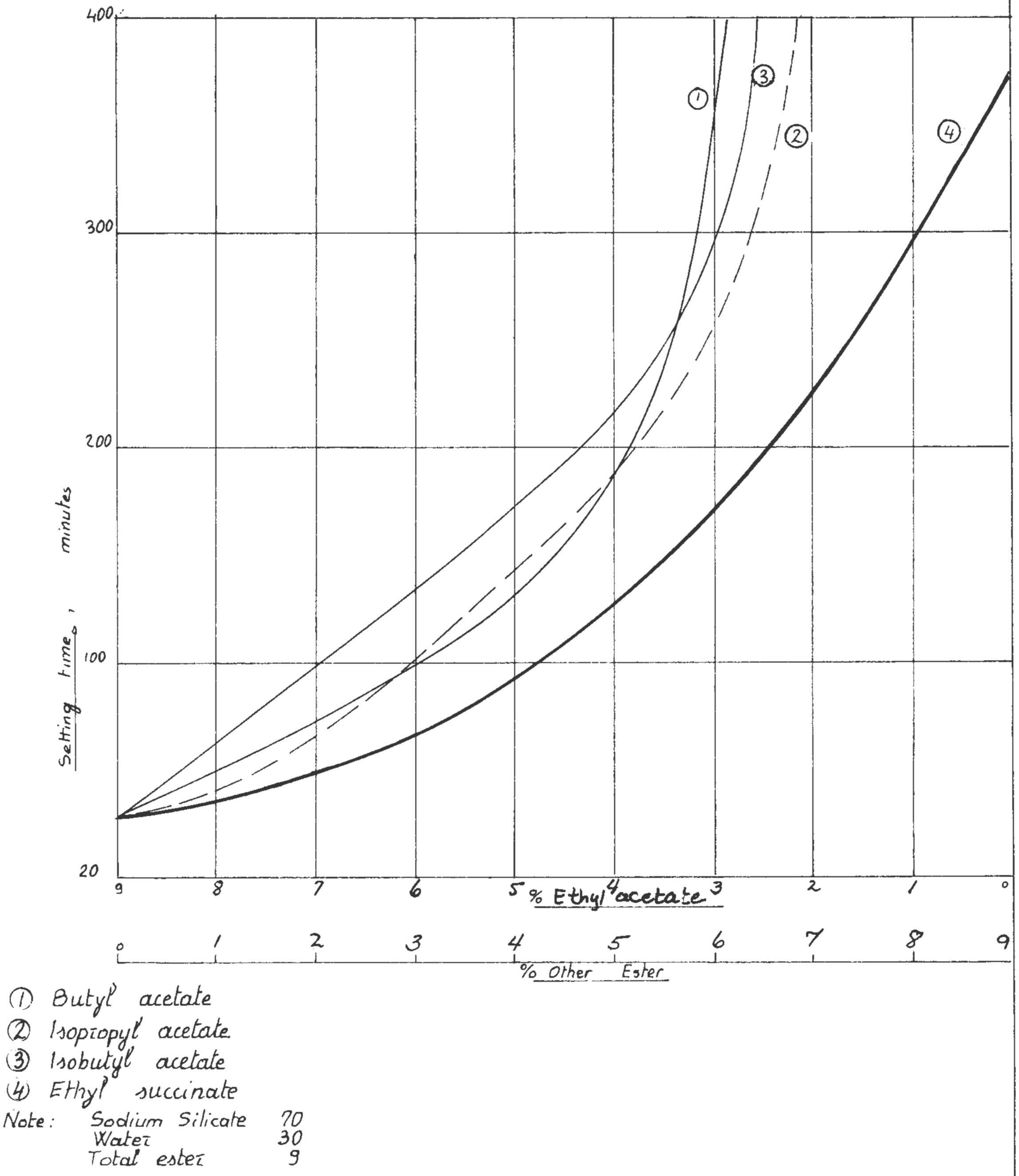


Fig. 43. Effect on Setting Time of Relative Dosage of Ethyl Acetate and Low Reaction Esters (Agitated Until Set, Test Temperature about 15°C)

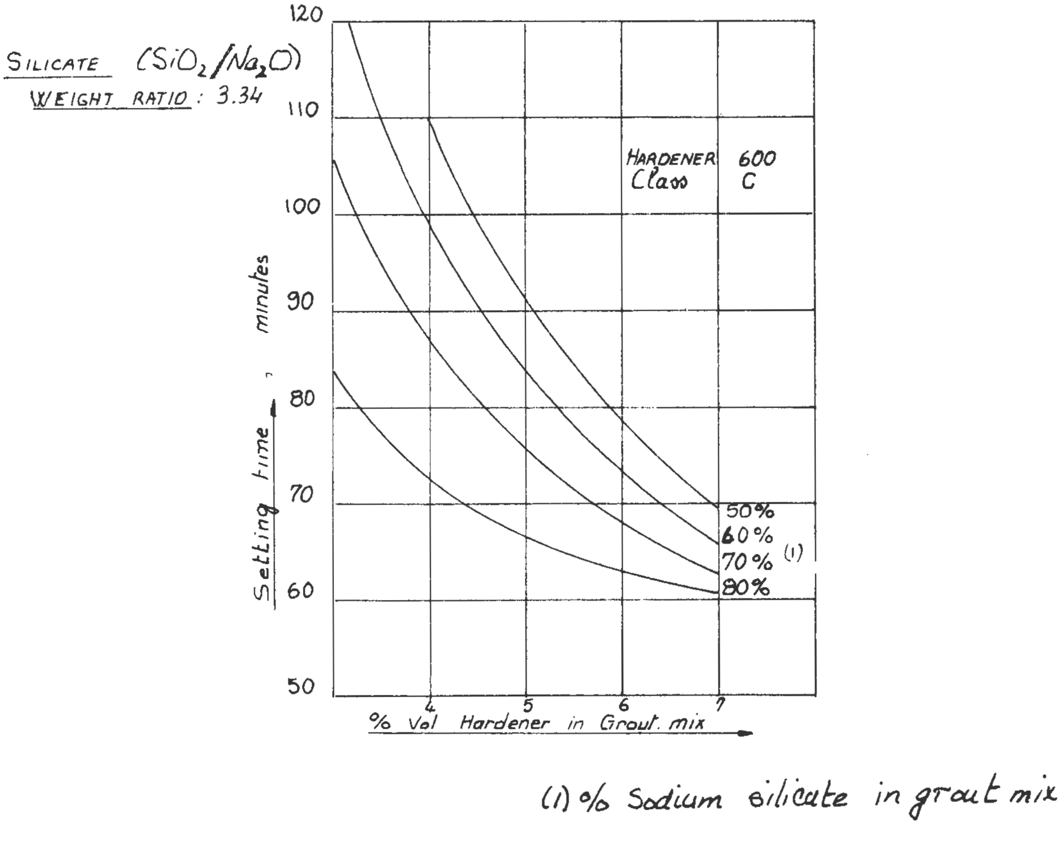
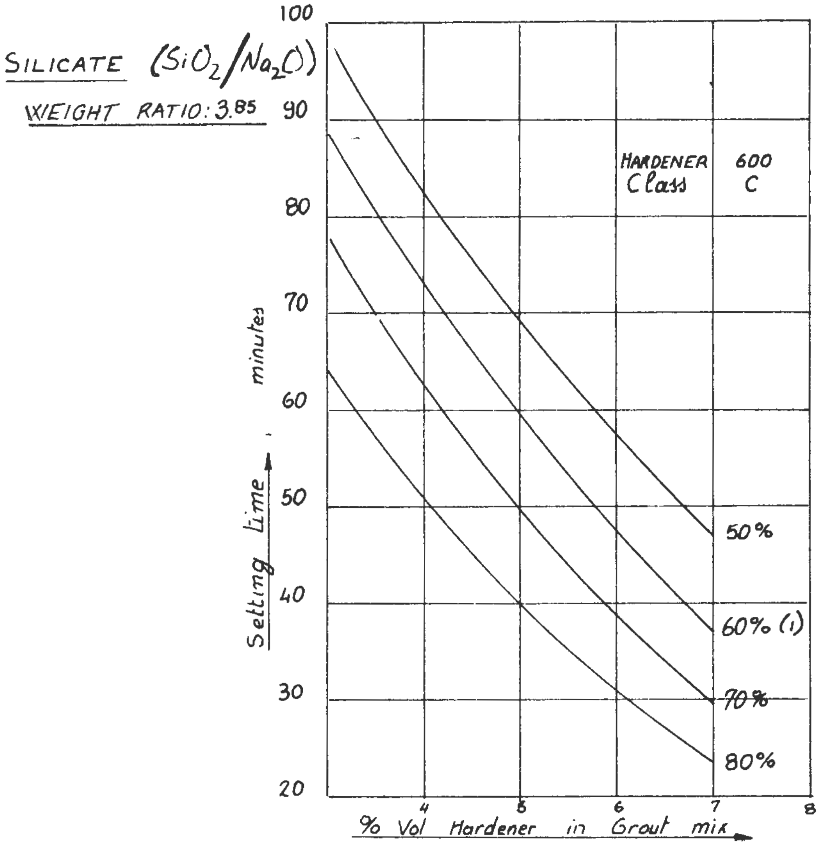


Fig. 44. Effect of Reagent Content on Setting Time



(1) % Sodium silicate in grout mix

Fig. 45. Effect of Reagent Content on Setting Time

In this category, the gels used for waterproofing have a low sodium silicate content and use many different sorts of inorganic or similar reagents. Such gels have the following characteristics:

-range of initial viscosity: 3 to 5 cP
-setting time can be regulated to extend from one minute to several hours.
-shear strength (under fast test) from 1 to 150 g/cm^2 (usually a few dozen g/cm^2).

C. CARON (65-04) has set forth the following rules for the shear strength of silica gels:

1) For a given amount of silicate, the faster the silicate's rate of destabilization, the higher the shear strength will be, which favors shorter setting times. The equation is of the type $R = \frac{a}{1 + bt}$. The converse is thus linear: strength is inversely proportional to setting time (figs. 46 and 47). Factors a and b can be computed without difficulty: a is the inverse of the abcissa at origin and b is equal to the slope divided by the abcissa at origin. With each reagent, it can be observed that strength increases proportionally with concentration, while b remains constant.

2) As strength can be expressed by equation $R = \frac{f\ (c)}{1+bt}$, the effect of silicate concentration can be studied without considering setting time, since one can compute the theoretical strength Ro at time 0 by the equation $Ro = Rt\ (1 + bt)$. In order to avoid the ever-possible variations in dosage between SiO_2 and Na_2O, for each silicate the strength test was made in terms of its SiO_2 content (called C and expressed in grams per litre of gel) and, using these assumptions, the gel's strength could be expressed, whatever the nature of the setting reagent, by the formula $R = \frac{k\ (c - 10)}{1 + bt}$ (figs. 48 to 49), t being the setting time in minutes.

3) Coefficients k and b summarized in table 16 show the effect of the setting reagent.

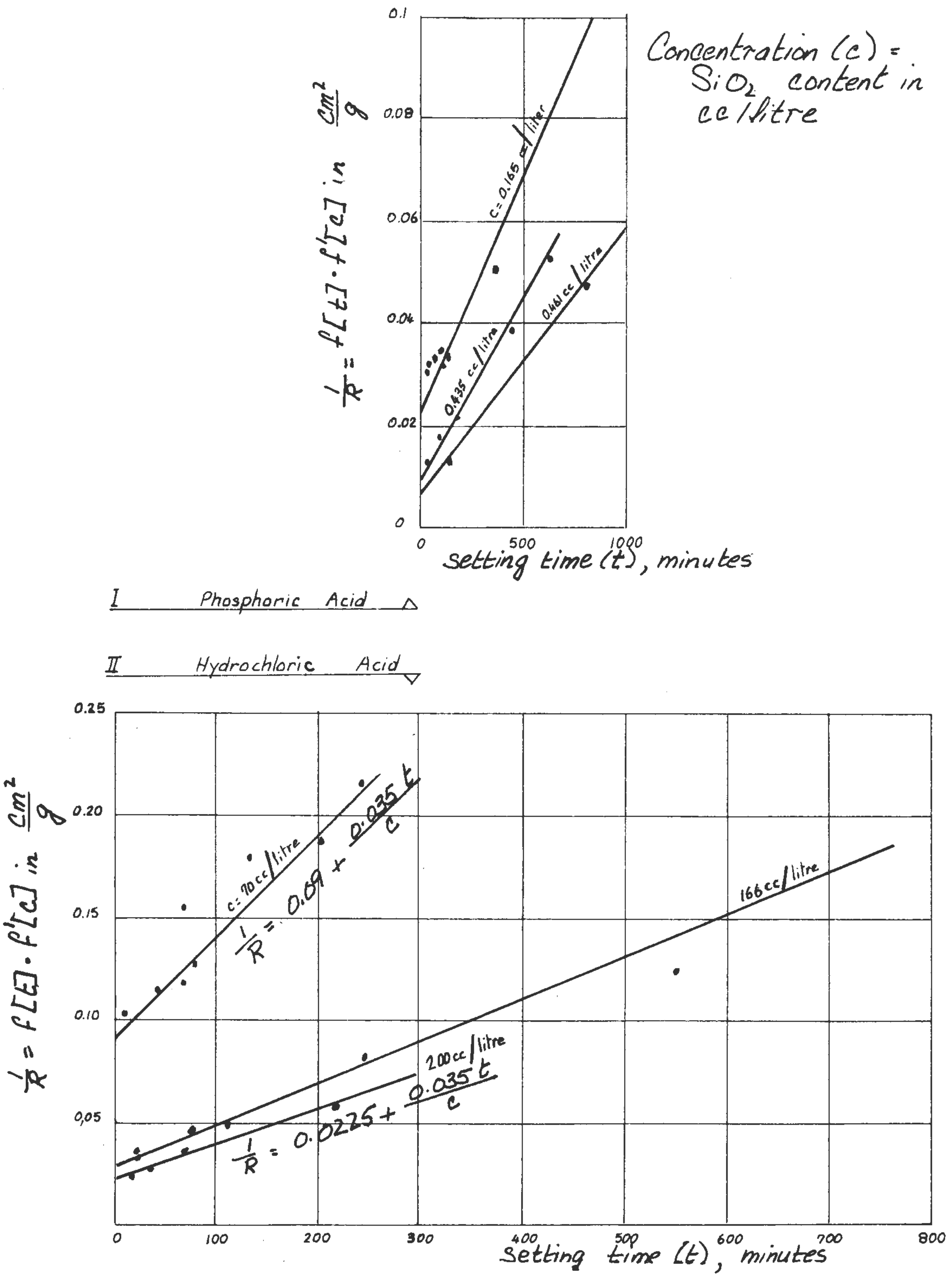
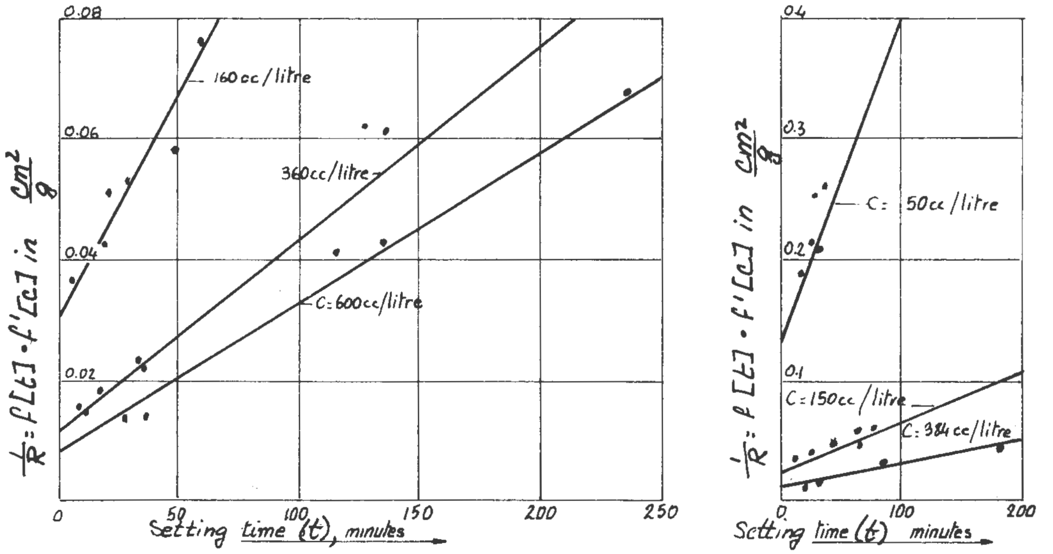


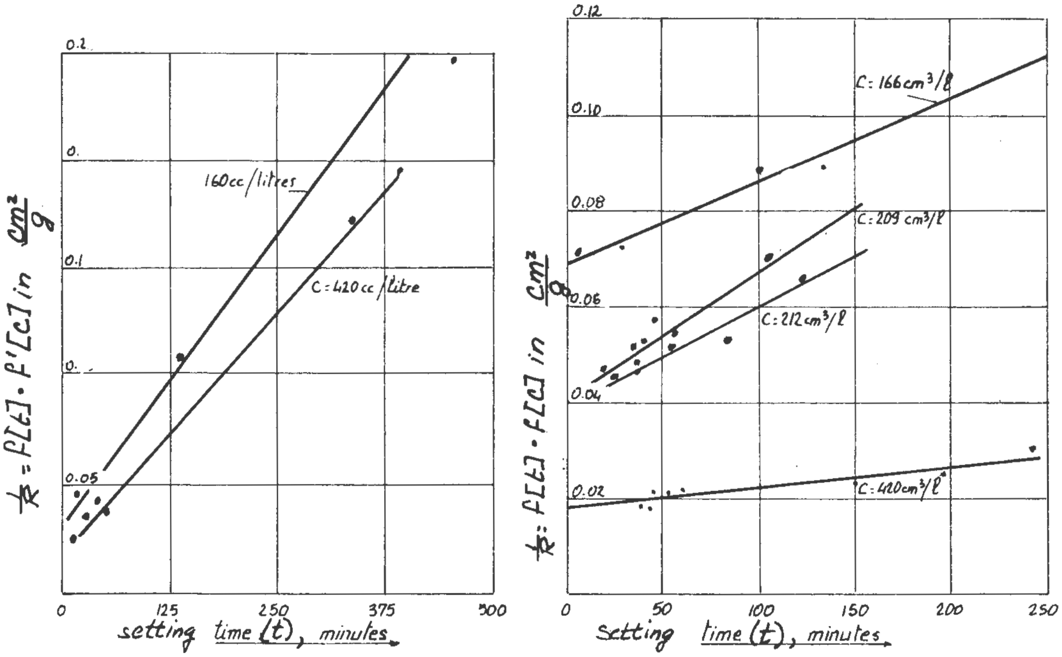
Fig. 46. Strength (R) is Inversely Proportional to Setting Time (t)



I GLYCOLIC ACID

II MONOSODIUM PHOSPHATE

Concentration (c) = SiO_2 content in cc/litre (for I, II and III)
(in cm^3/litre for IV)



III SODIUM BICARBONATE

IV SODIUM ALUMINATE

Fig. 47. Strength (R) is Inversely Proportional to Setting Time (t)

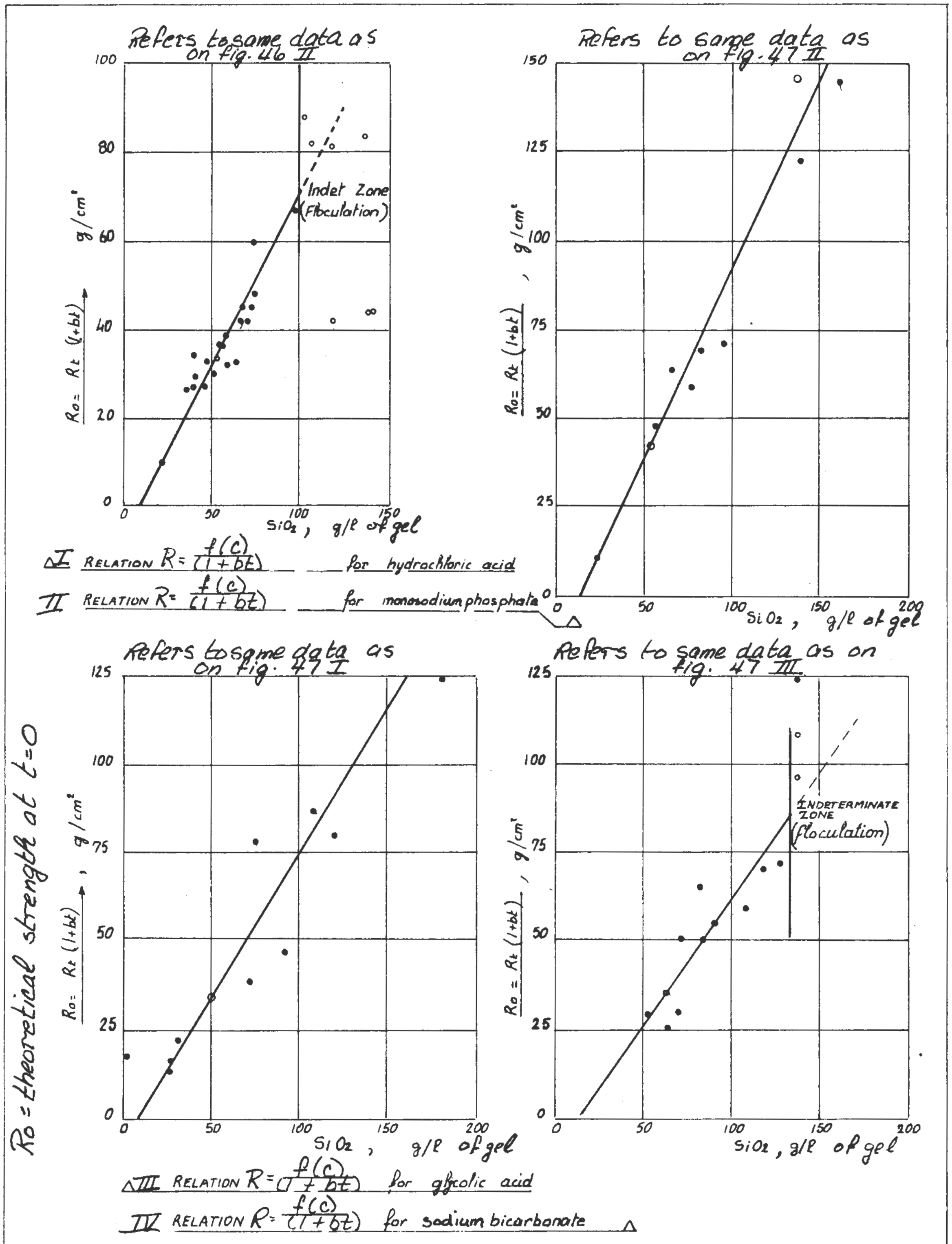


Fig. 48. Effect of Silicate Concentration on Strength of Silica Gels

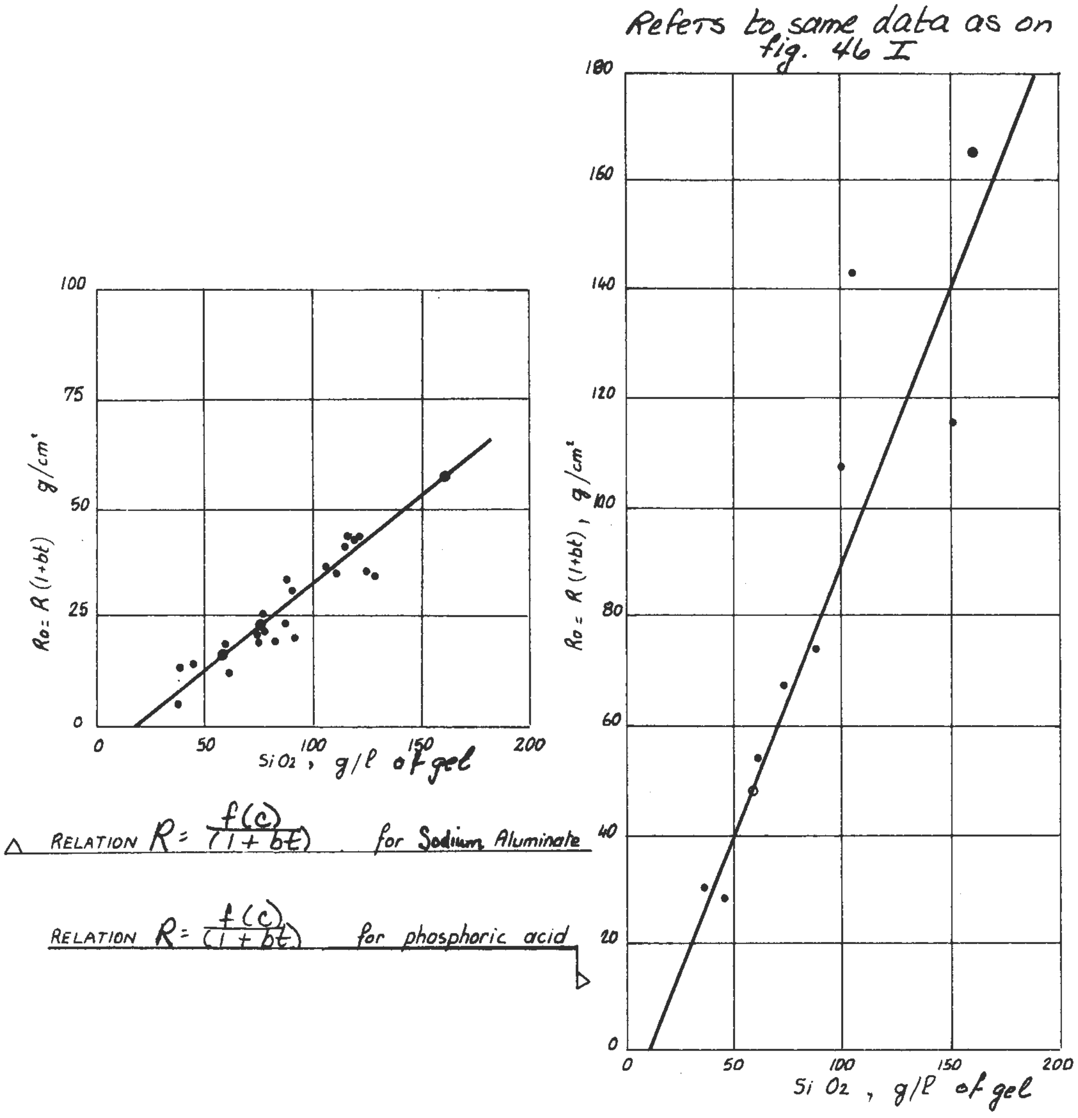


Fig. 49. Effect of Silicate Concentration on Strength of Silica Gels

Table 16 . Effect of Setting Reagent on Coefficients k and b

Nature of Reagent	k	b
Phosphoric acid	1.02	0.0073
Hydrochloric acid	0.78	0.0070
Glycolic acid	0.83	0.0283
Monosodium phosphate	1.02	0.0210
Sodium bicarbonate	0.68	0.0205
Sodium aluminate	0.37	0.0041

4) Finally, the yield strength tests (example in fig. 50) indicate the viscoplastic nature of these gels. Whatever their composition and their strength, they will fit BURGERS' rheological model, which indicates both delayed elasticity and creep. The values for immediate elasticity, delayed elasticity and creep depend on the nature of the setting reagent.

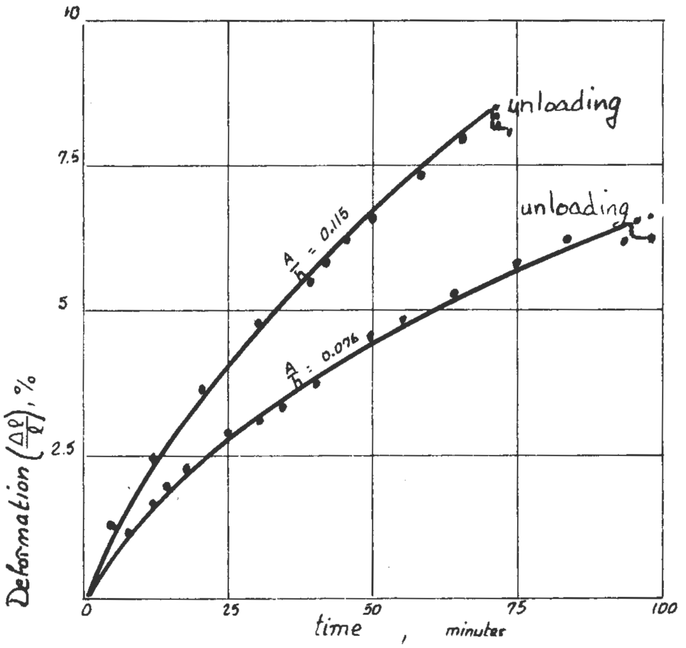
It is thus only natural that these gels should be very sensitive to shear speed. Using the variable speed method as described in Part One, Chapter 5, we examined three formulas for waterproofing gels of variable immediate strength. Fig. 51 shows the pronounced effect of shear speed. Fig. 52 shows the same relationship as $Rc = f\frac{(1)}{V}$, which demonstrates the effect of shear duration.

However, this effect (decrease in strength when the test is conducted at slower speeds) depends on the gel's composition, the nature of relative concentration of sodium silicate and the reagent used, which particularly affects the silicate's rate of destabilization.

These figures show that knowledge of shear strength alone, as measured at the usual VANE TEST speed, is not sufficient, since some gels can behave very well at high shear speeds, which become mediocre at low speeds and, once in the ground, would probably erode.

4. Strength of Treated Ground

While the strength of pure gel is of interest only for waterproofing, the study of the strength of treated ground is mainly of interest for consolidation work. However, it should be specified that the unconfined compressive



$\frac{A}{h} = \frac{\text{Cross Section}}{\text{Height}}$: Slenderness ratio

Fig. 50. Deformation and Yield of Silica Gels with Hydrochloric Acid

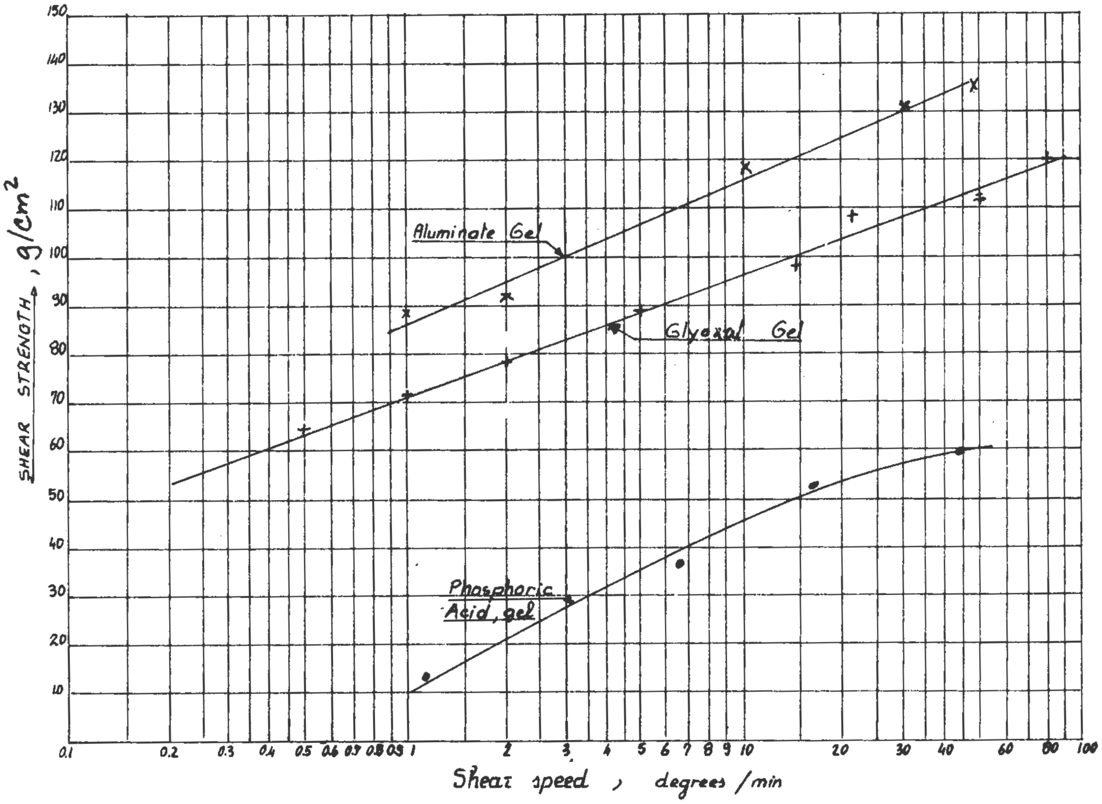


Fig. 51. Effect of Rate of Loading on Shear Strength of Silica Gels

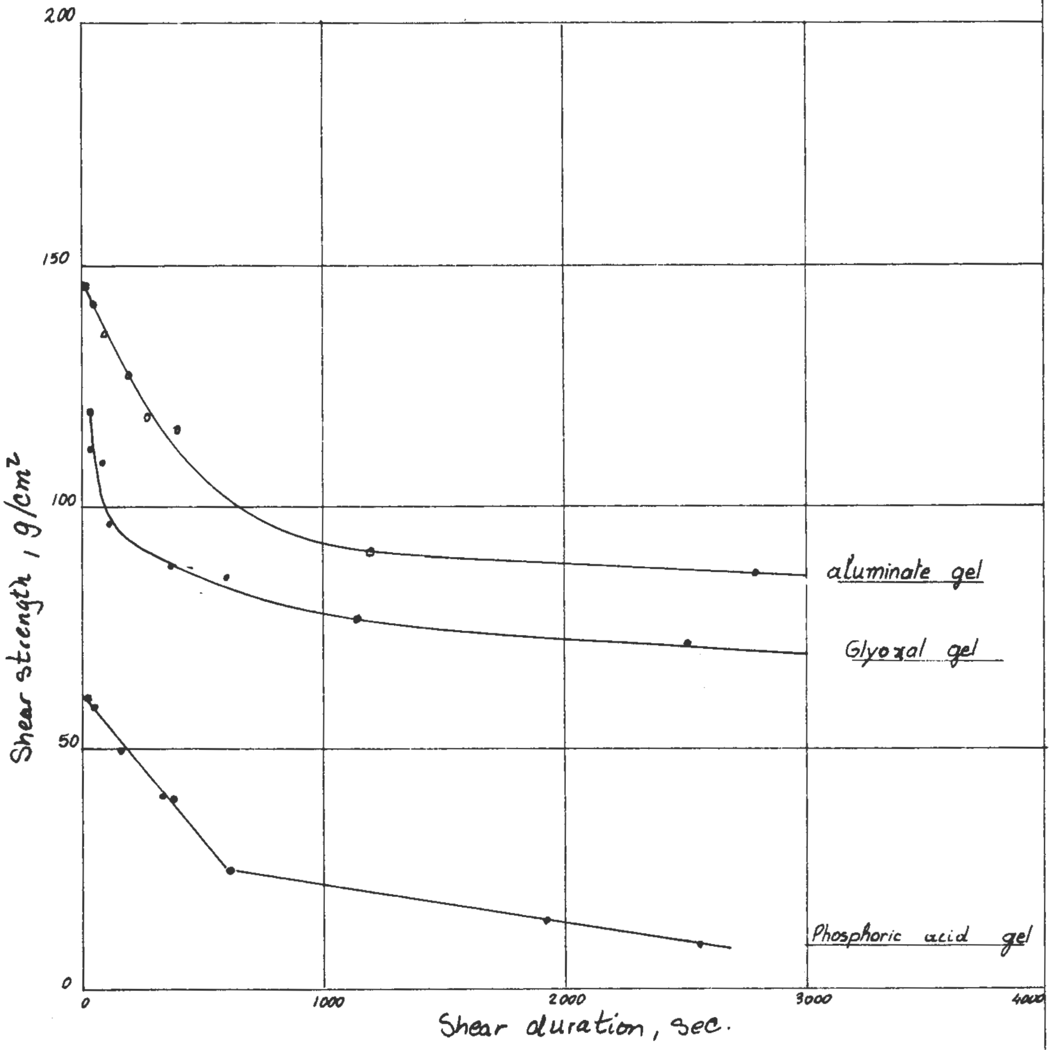


Fig. 52. Effect of Shear Duration on Shear Strength of Silica Gels

strength of ground treated with a waterproofing gel should be on the order of 2 bars. The following general relationship can be used: $R_m = R_g (1 + k\sqrt{s})$.

If the usual numerical values for a waterproofing treatment are applied:

-shear strength of pure gel (R_g) = 50 g/cm^2 or 0.1 bar for unconfined compression,
-the coefficient k for R_g = 50 g/cm^2 is 1.12.
-the standard sand has a specific surface of 380 cm^{-1}.

then, $R_m \simeq 0.1 (1 + 1.12 \sqrt{380}) = 2.3$ bars.

Many inorganic reagents enable unconfined compressive strengths on the order of 2 bars to be attained. For the higher strengths necessary for consolidation, one can turn to gels with organic reagents, omitting two-shot gels using inorganic reagents which are technically obsolete (the JOOSTEN Process for example).

4.1 Comparison of Setting Reagents for Hard Gel

The organic reagents most commonly used for setting silicates are esters such as ethyl, butyl or isopropyl acetate and the Progil 600 hardeners, ethyl and methyl succinate and adipate. Since the atomic chains of these esters are of differing lengths, there is no reason why equivalent amounts, by weight or by volume, of these substances should confer the same strengths. However, if the dosage is expressed in gramequivalent (weight divided by the molecular mass and multiplied by the valence), a satisfactory correlation among the various esters can be found.

In table 17 below are the corresponding weights of some of the possible esters for setting sodium silicate,

Table 17. Esters Used for Setting Sodium Silicate

Reagent	Weight equivalency in relation to ethyl acetate
Ethyl acetate	1
Isopropyl acetate	0.85
Butyl acetate	0.75
Triacetin	1.21
Ethoxyethyl acetate	1.04
Glycol acetate	1.27
Glycerol monoacetate	1.31
Glycol diacetate	1.15
Dimethyl succinate	1.20
Diethyl succinate	1.01

This weight equivalency method allows comparison of the real prices of the reagents, and thus substitution according to market fluctuations. It also allows strengths to be kept constant in cases where esters are combined to alter setting time, since it uses chemical equivalencies. An example is given in fig.53 .

In cases where the proposed reagents are poorly defined commercial products, there is an indirect method of comparison with a well known reagent: one measures the unconfined compressive strength of one or, preferably, several grouts of differing composition which have been prepared, in varying degrees of diluteness, with the commercial reagent. The results obtained are plotted on a graph which has already been drawn up for the known reagent in corresponding degrees of diluteness. For the same unconfined compression value, one can thus define a volumetric or weight equivalancy of known reagent to commercial hardener.

An example of the establishment of equivalencies for two reagents is given in fig. 54. In this case, the known reagent chosen was ethyl acetate and the commercial product whose reactive characteristics were to be defined was Hardener 600 B. The hardener is already known to be largely made up of a mixture of esters (diethylsuccinate and dimethylsuccinate), but probably contains other ingredients as well.

According to the graph described above, the volumetric equivalency ethyl acetate/Hardener 600 gives an average value of 1.275 at 48 hours and 1.18 at 72 hours. We have used an average correlation coefficient of 1.227 by volume or a weight ratio of 1.03. The mortar test samples for this study were obtained by the direct molding method.

Thus it can be concluded that the chemical reactiveness of a setting agent can be unequivocally defined whether a chemically well-defined product or a commercial product. The strength of the mortar can be precisely identified as soon as the following characteristics are known:

- the nature and concentration of sodium silicate in the gel;
- the proportion of reagent in the gel and its chemical equivalency value.

4.2 Establishment of Graphs Showing Strengths Measured at Standardized Speed (Fast)

The establishment of strength graphs can be accomplished using the standardized method by grouting

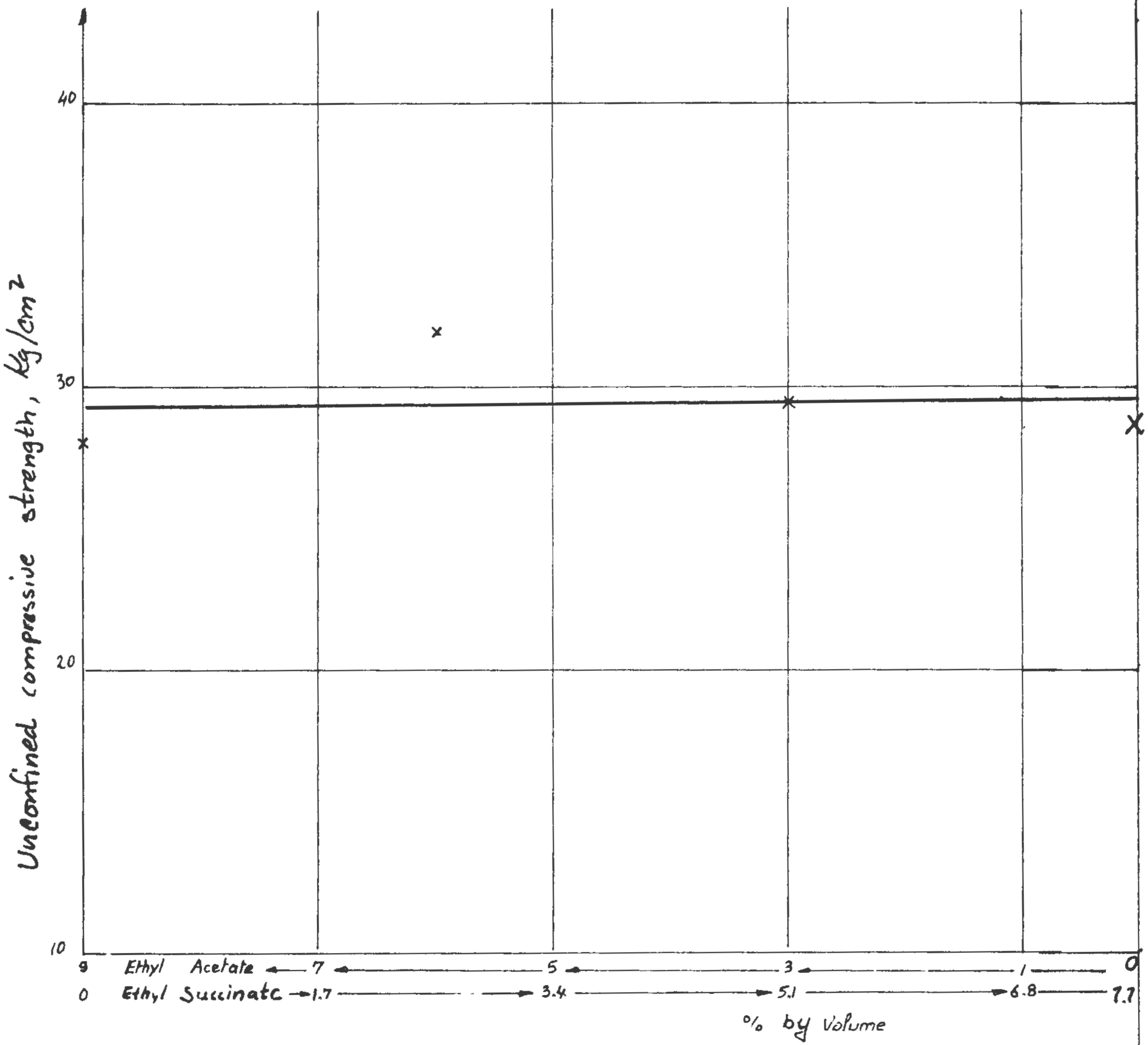


Fig. 53. Effect of Substitution of Ethyl Acetate by Ethyl Succinate on Mortar Strength

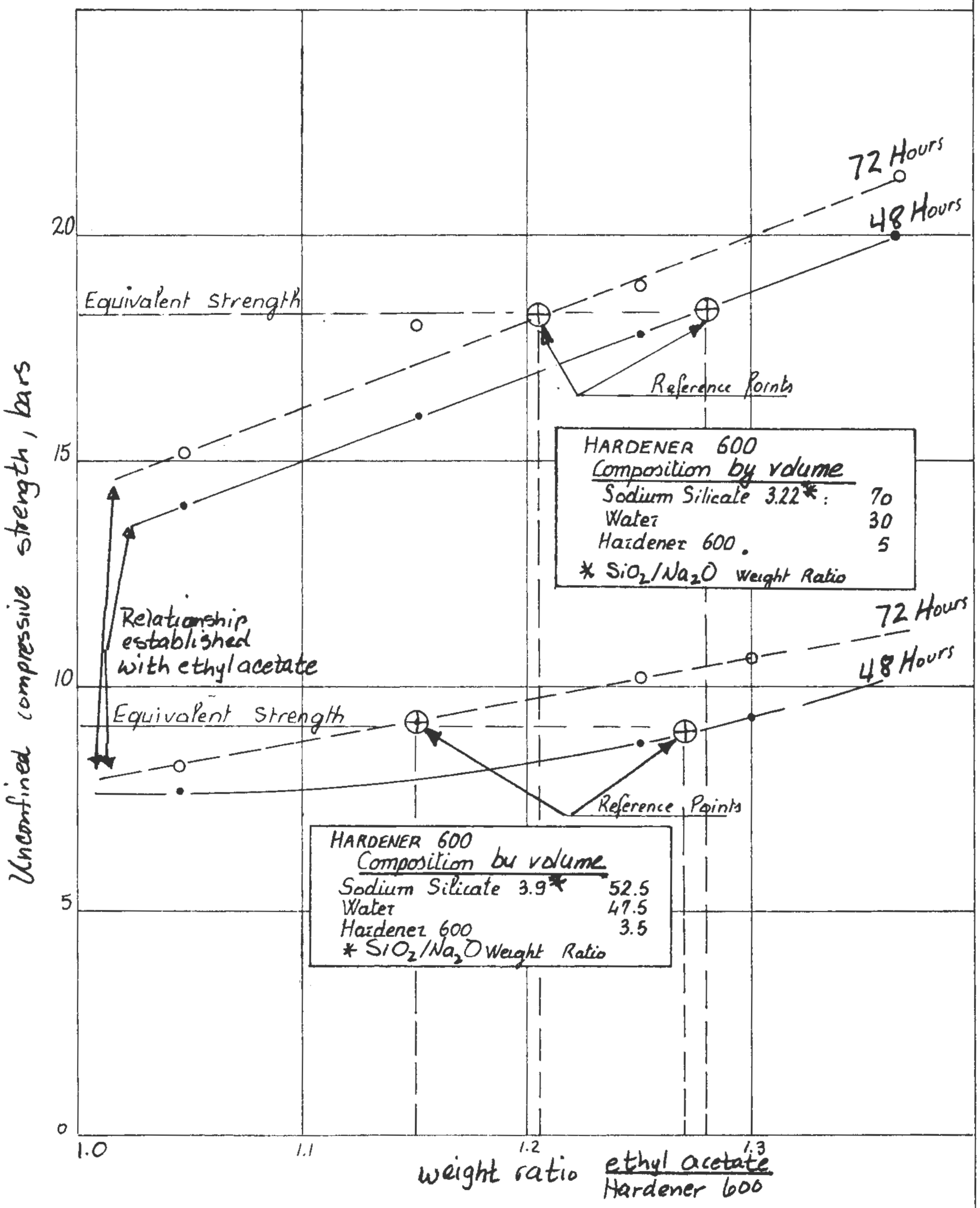


Fig. 54. Comparison of Reactiveness of Ethyl Acetate and Hardener 600 B

columns of 0.1 to 0.3 mm sand. The 10 or 11 test samples obtained from each column are then crushed and their average is taken. Tables 18 and 19 show that there is little disparity among the figures.

Table 18. Results of Strength Tests

Sodium silicate 3.9 *	50 **	50	70	70
Water	50	50	30	30
Ethyl acetate	2.5	4	2	3.1
Strength figures obtained from column (bars)	9.68	11.16	9.45	13.72
	11.62	11.61	12.45	18.10
	9.28	12.52	11.85	22.02
	8.31	11.46	12.90	20.36
	9.28	11.76	14.40	19.91
	10.18	11.76	13.95	20.51
	9.58	11.31	14.70	19.76
	10.33	11.31	13.95	20.51
	11.52	11.76	15.30	21.26
	10.93	11.76	16.05	17.34
	11.08	11.61	16.20	18.70
Average (bars)	10.2	11.6	13.7	19.3

Table 19. Results of Strength Tests

Sodium silicate 3.21 *	50 **	50	70	70
Water	50	50	30	30
Ethyl acetate	3	7	4	7
Stabilizing agent	0.15	1.05	0.15	0.15
Strength figures obtained from column (bars)	4.21	10.52	9.75	32.32
	5.40	18.00	12.91	26.55
	5.26	16.22	14.51	30.42
	5.92	16.93	14.90	29.50
	4.70	14.36	12.91	27.22
	4.89	13.27	13.27	24.33
	5.92	15.01	13.63	31.02
	6.33	15.76	12.10	30.87
	5.26	16.22	12.31	32.69
	5.77	15.46	14.07	31.33
	5.92	13.27	12.91	38.02
Average (bars)	5.5	15.0	13.0	30.4

* SiO_2/Na_2O weight ratio

** parts by volume

In figs. 55 and 56 are shown strengths determined through the standardized grouting method for the two silicates most commonly used in grouting (weight ratios 3.21 and 3.9), in differing degrees of diluteness compatible with the 20 cP viscosity in terms of the volumetric proportion of acetate. Fig. 57 shows the same behavior for formamide.

Finally, figs. 58 to 60 give the strength curves plotted by RHONE-PROGIL, again using the standardized grouting method for different types of sodium silicates with the 600 B hardener. It should be noted that RHONE-PROGIL's terminology is slightly different from that used elsewhere in this report. Generally a 70% concentration means 70% silicate and 30% water (the hardener, in varying doses, being on top), while on RHONE-PROGIL's graphs, a 70% concentration signifies 70% silicate and 22 to 28% water (the hardener, in varying dosages, being factored into the formula). There is the same discrepancy for the dosage of hardener: 7% hardener, according to our graphs, applies to 100% silicate plus water, while for RHONE-PROGIL, it corresponds to 93% silicate plus water.

4.3 Effect of Speed of Unconfined Compression Test on Strength Results

All the figures given so far in this section concern unconfined compression values obtained with a testing speed of 20 mm/min. We have seen, however, in the Part One of this volume, in the section concerning standardization of treated ground strength testing, that crushing speed has a major effect on the strengths of mortars and that, for close examinations, it is advisable to plot the curve $R_c = f(V)$ in order to predict the median and long-term behavior of the material.

Fig. 61 corresponds to table 20 (p. 152) and gives some examples for silica gels of varying composition using different reagents. It is notable that, between the standardized speed (underlined in the table) and the lowest speed used, strength ratios can vary widely. Again, these low speeds are only relative with regard to stress speeds actually encountered in nature.

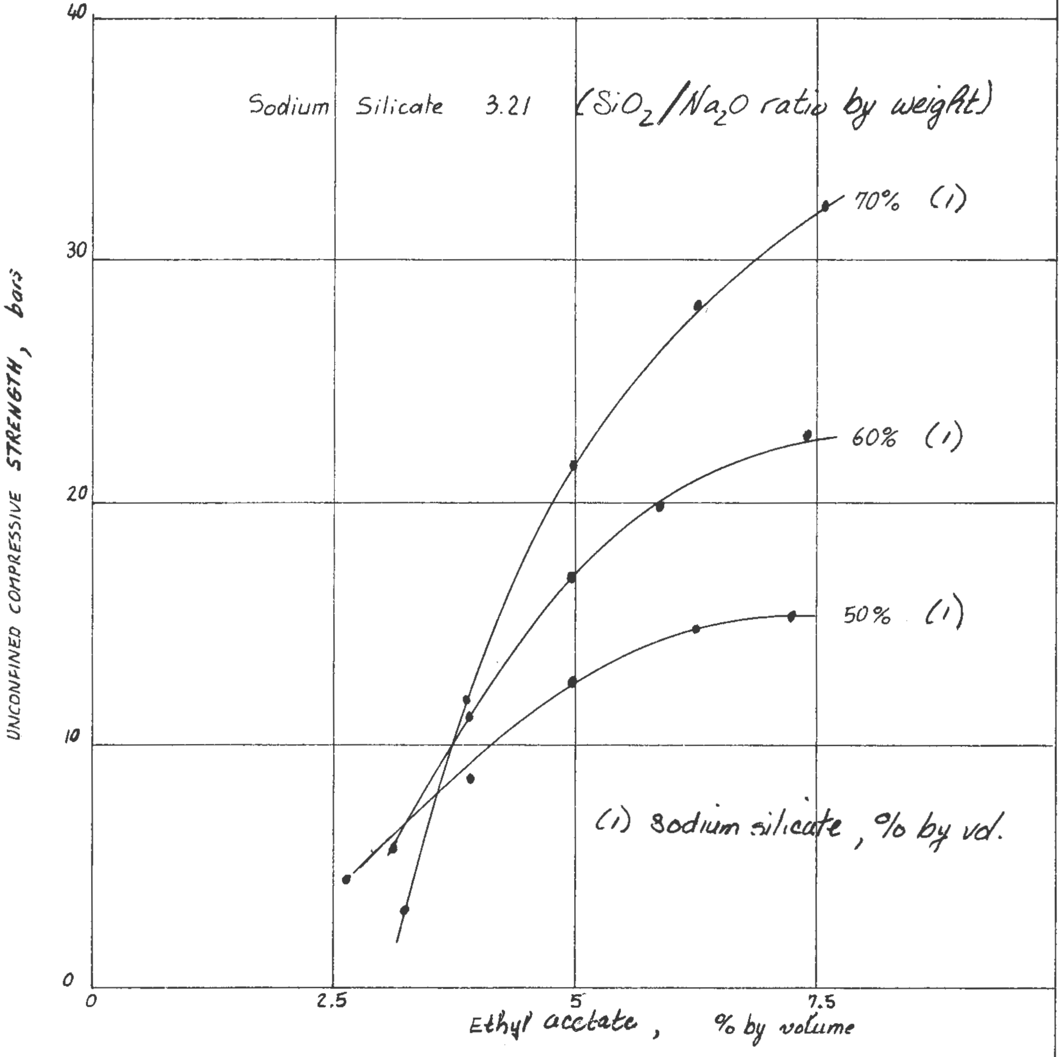


Fig. 55. Unconfined Compressive Strength (Standardized Method) of Sodium Silicate 3.21 with Ethyl Acetate

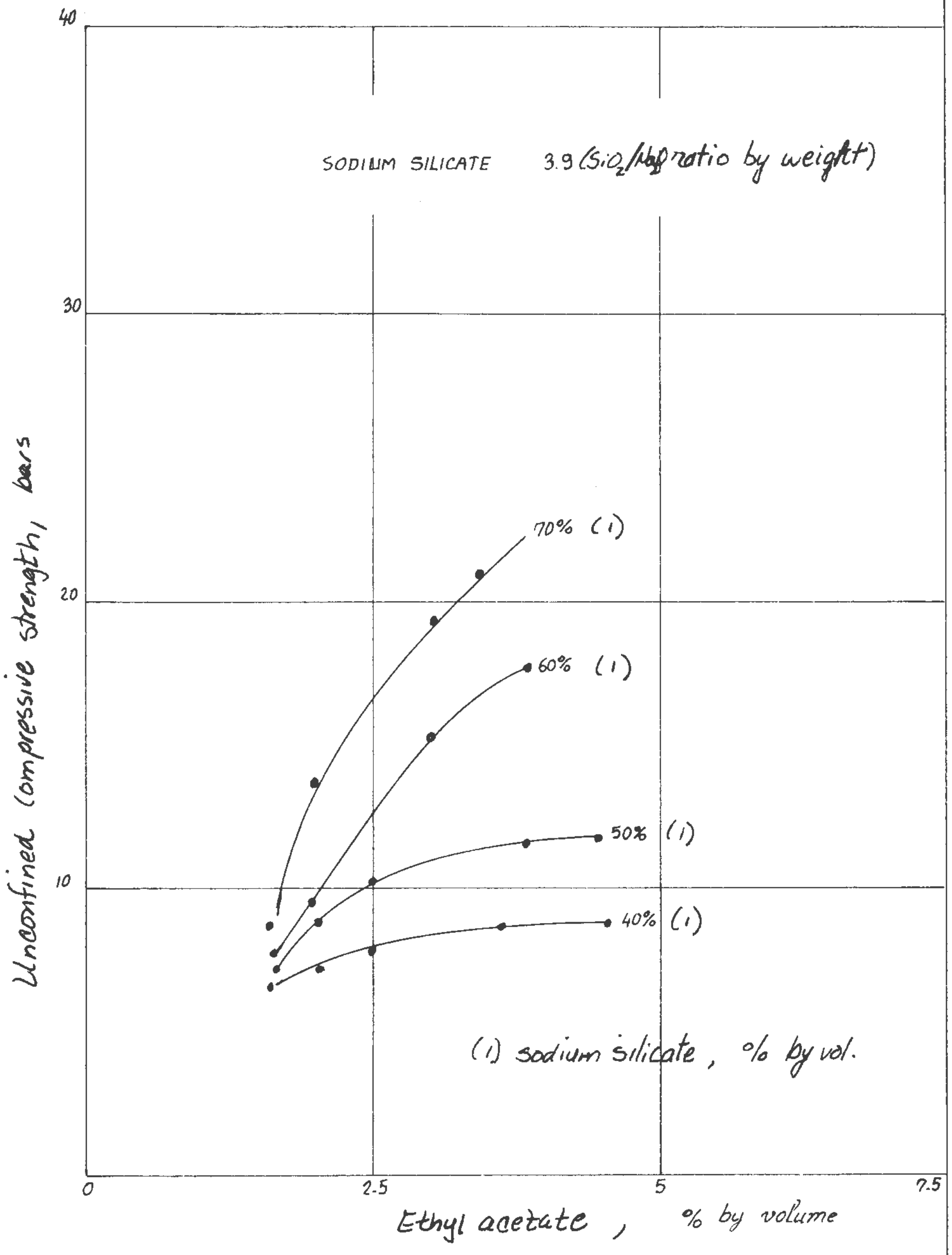


Fig. 56. Unconfined Compressive Strength (Standardized Method) of Sodium Silicate 3.9 with Ethyl Acetate

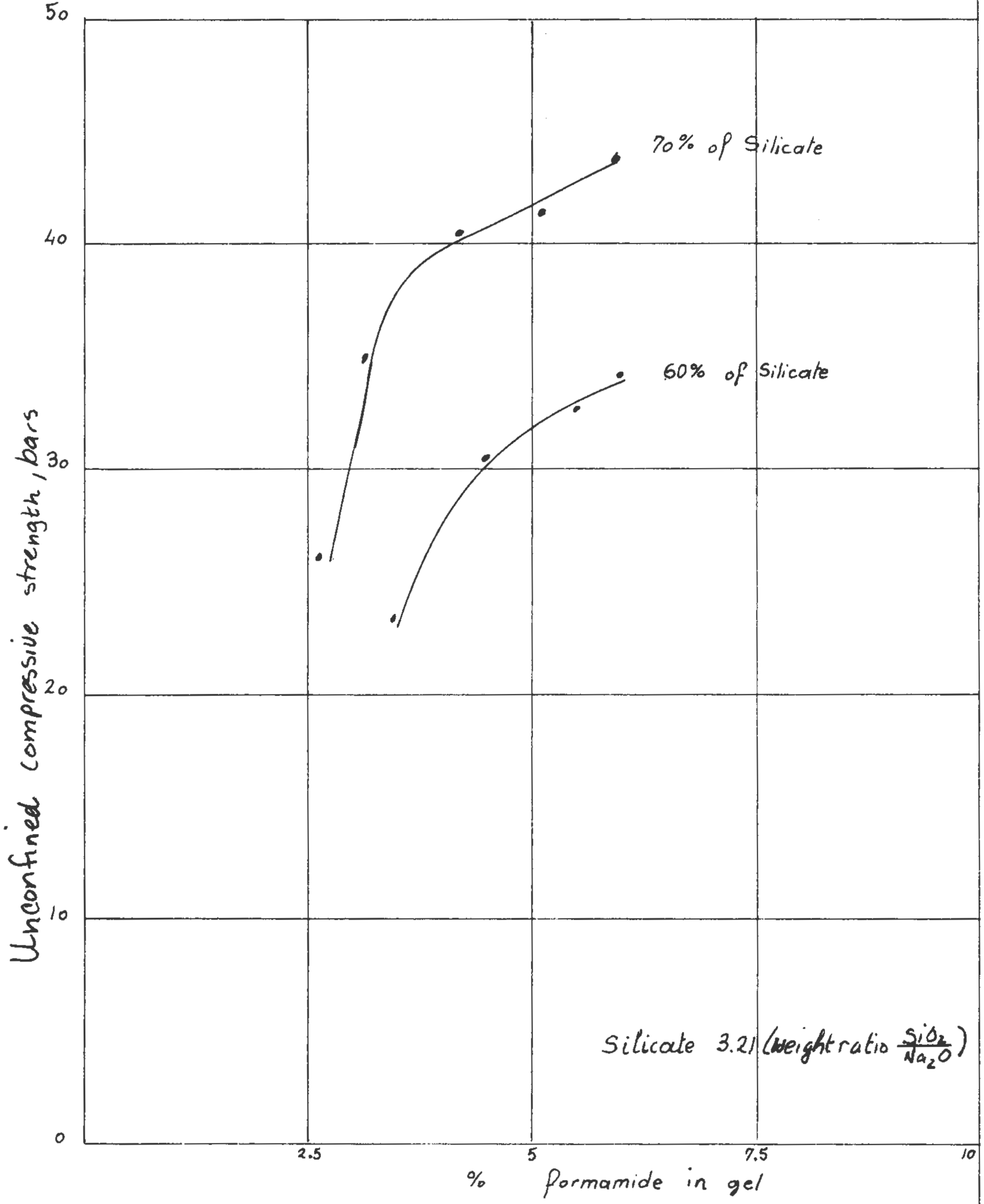


Fig. 57. Effect of Formamide Content on Strength of Semi-Hard Gels

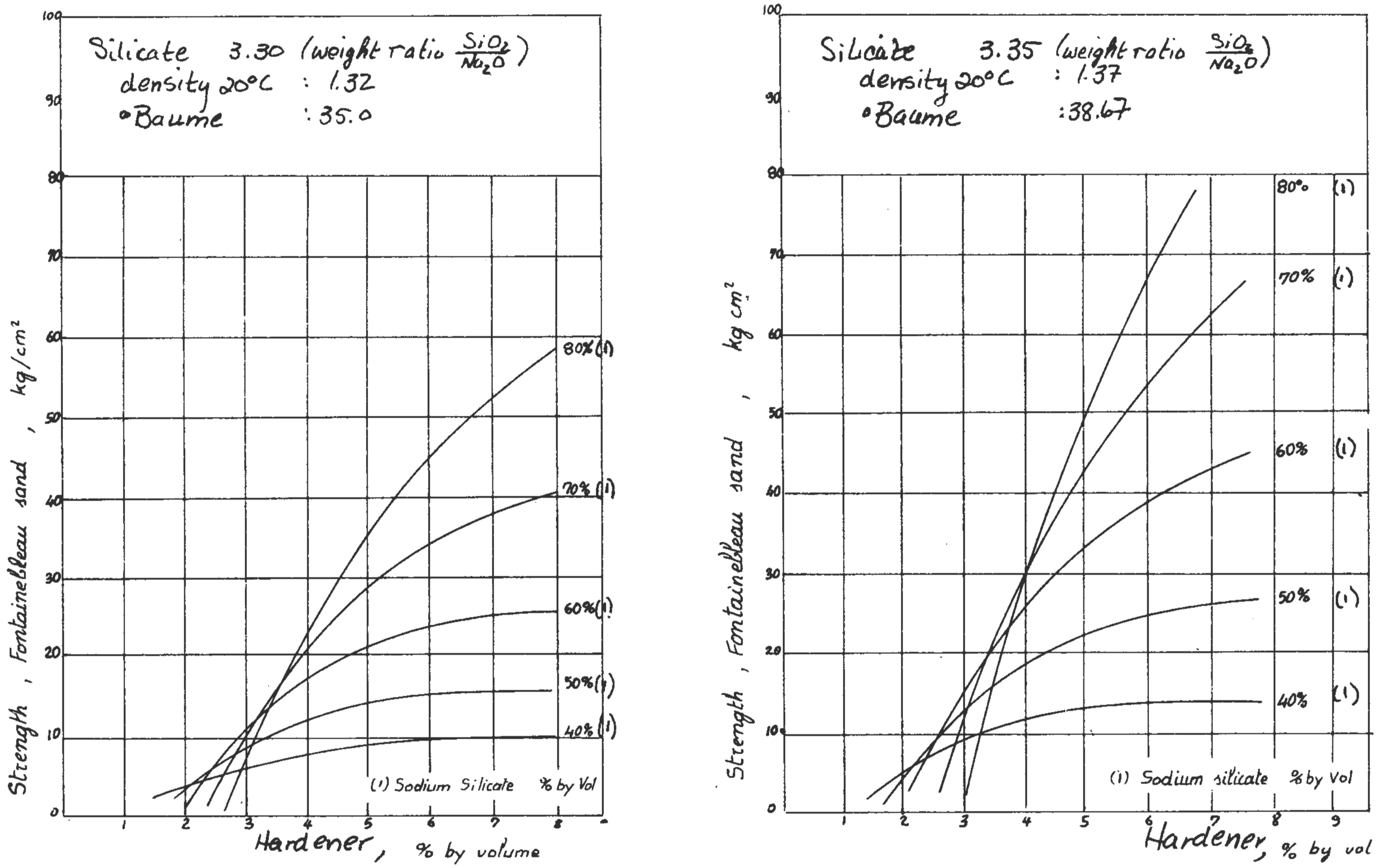


Fig. 58. Effect of Hardener 600 Content on Strength of Sodium Silicates (Standardized Method)

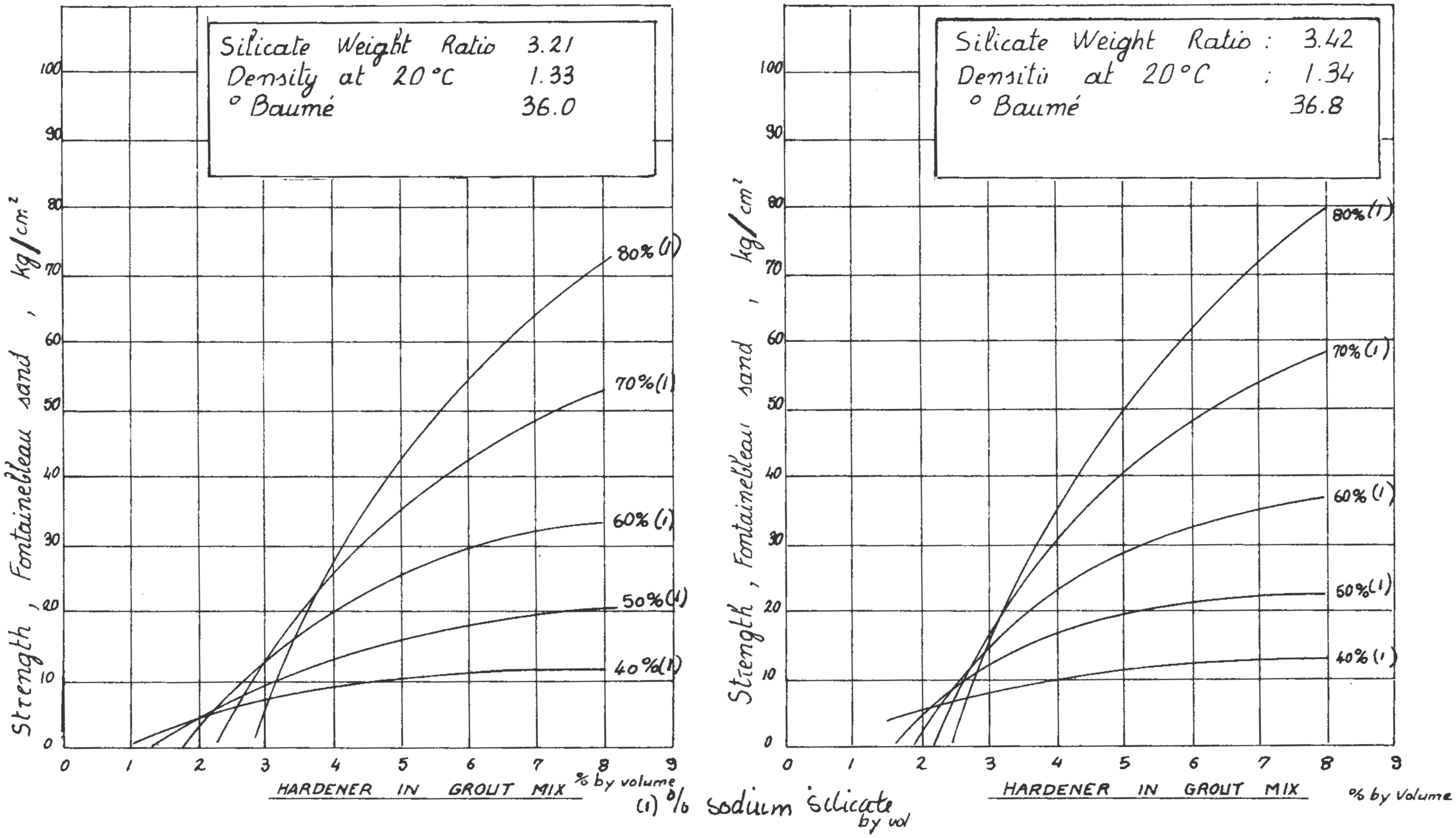


Fig. 59. Effect of Hardener 600 content on Strength of Sodium Silicates (Standardized Method)

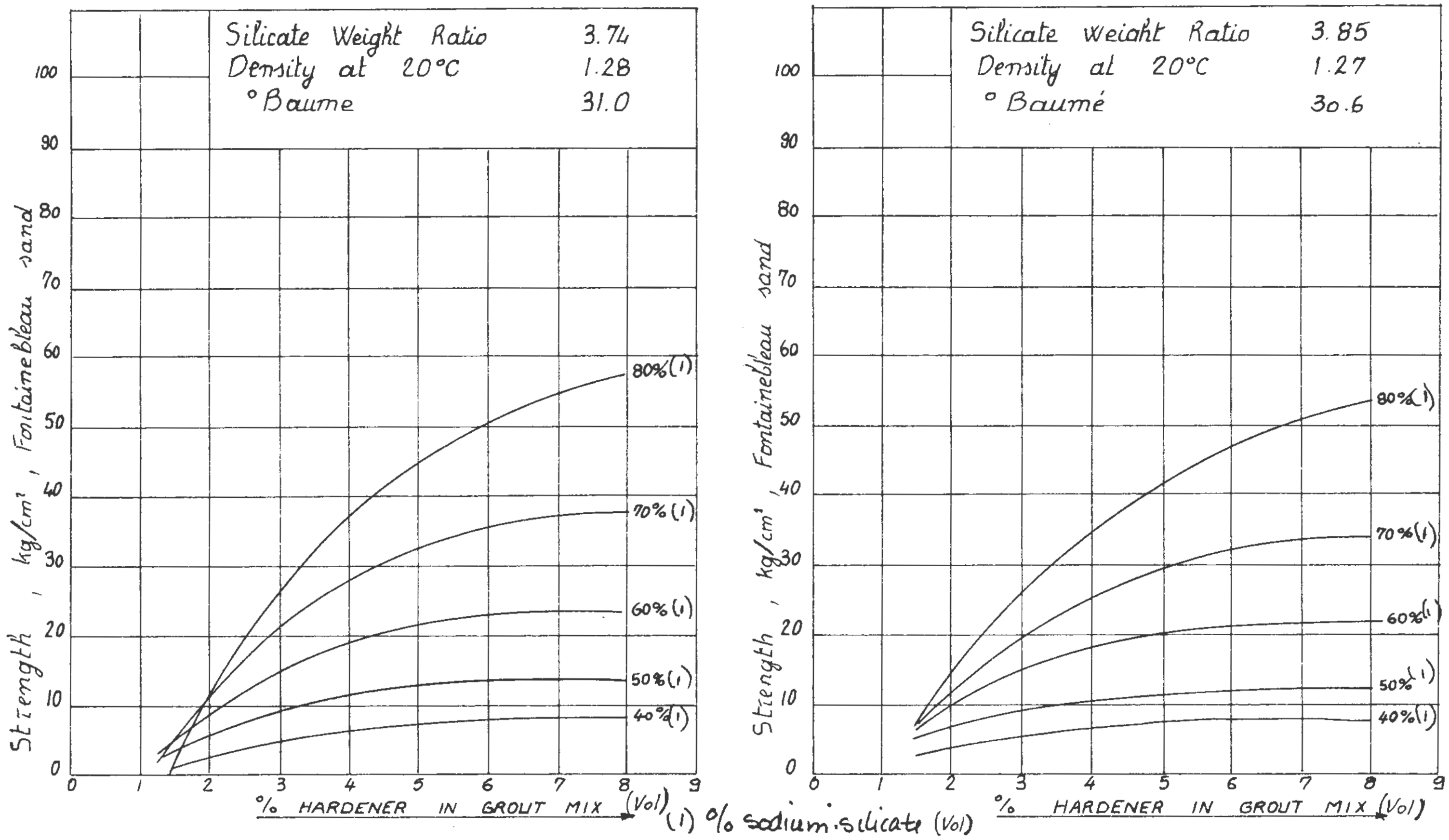


Fig. 60. Effect of Hardener 600 Content on Strength of Sodium Silicate (Standardized Method)

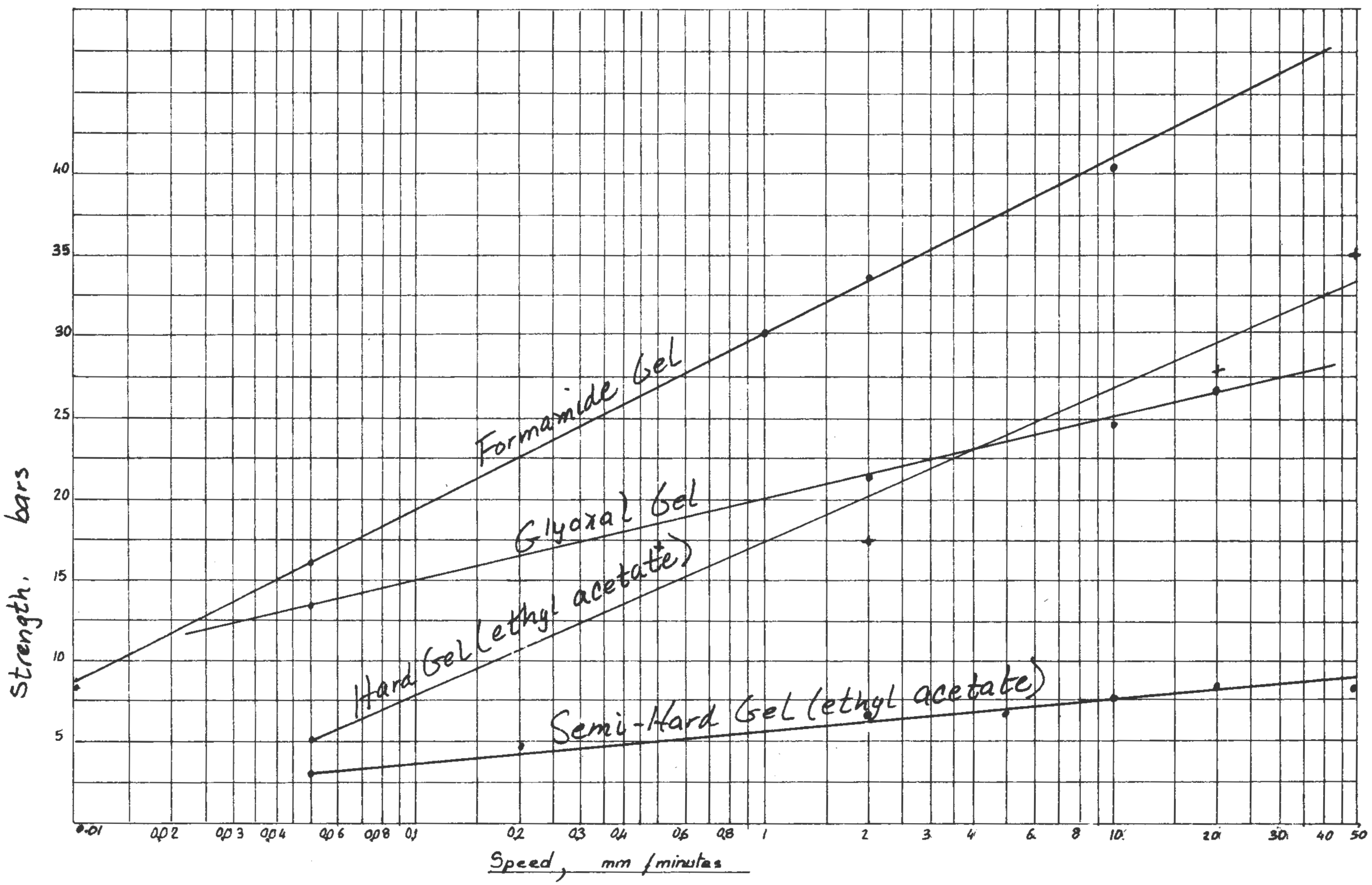


Fig. 61. Effect of Crushing Speed on Unconfined Compressive Strength of Silica Gels

Table 20. Effect of Rate of Loading on Strength of Various Silica Gels

Rate of Loading mm/min.	Unconf. Compressive Strength in Bars at 48 h			
	Ethyl Acetate gel (semi-hard)	Ethyl Acetate gel (hard)	Glyoxal gel	Formamide gel
0.01				7.95
0.05	2.95	5.0	13.2	17.5
0.2	4.55			
0.5	4.6	16.7		
1	5.8			30.1
2		17.5	21.4	33.5
5	6.85			
10	7.7		24.8	40.0
20	8.05	27.8	27.0	42.1
50	8.35	34.8		

5. Durability

After setting, the silica gel is subject to various alterations which may affect its durability in varying degrees:

a) As is the case with most other grouts, silica gel contains a soluble fraction which will be thrown off in wet curing, a phenomenon which entails a more or less considerable decrease in mechanical characteristics.

b) Similarly, in air curing, the loss of free water in the long run leads to a decrease in mechanical characteristics.

c) While these two causes of disturbances are common to most chemical grouts, there is a third, syneresis, which is unique to silica gels whatever their composition. This phenomenon results from the polycondensation of silicic acid and causes salt-charged water to be expelled.

After setting, the silicate-water-reagent mixture, whatever the nature of the silicate and the setting reagent, produces a mixture of complex composition which includes silicic acid and chemically bound water (the sodium salts are able to be absorbed by the gel), and free water containing, in true or colloidal solution, sodium salts, colloidal silica and anions of the setting reagent.

Thus, this is a two-phase system which appears homogeneous while the gel is fresh, and includes a solid or pseudo-solid phase and a liquid phase containing salts in solution, the gel's total water being distributed over the two phases. After a while, the gel loses its homogeneity, the sample contacts and gradually expels the liquid phase. This is the phenomenon of syneresis which can occur during approximately two months and will necessarily have a detrimental effect on strength and the permeability coefficient of the treated sand. It should be pointed out, however, that the finer the sand, the less intense will be the disturbances caused by syneresis (CARON 65-04).

In order to identify the possible effect of these different phenomena in specific terms, the behavior of the gel will be examined in various curing methods, as defined in Chapter VII, "Durability".

5.1 Cure in an Airtight Medium

In fig. 62 are shown schematic changes in unconfined compressive strength for two silica gels, one with ethyl acetate, the other with formamide, cured in hermetically sealed molds (direct molding method of preparation). For the gel with ethyl acetate, it was noted that the sand-gel mixture had practically attained its optimum strength at the end of 48 hours. This interval was a bit longer for the gel with formamide, a very slow reagent. In both cases, a slight decrease in strength was noted over time.

The same experiment with a coarser sand (1 to 2 mm), then with gravel (5 to 10 mm), showed greater drops in strength with time. In both cases, the drop in strength can be attributed to syneresis, but the finer the sand, the less this decrease will be.

5.2 Dry Cure

Fig. 63 shows in general how a silica gel-ethyl acetate mortar changes over time with air cure, having already attained its optimum strength in an hermetic mold (direct molding method of preparation). Strength first increases very quickly over a short period and then slowly decreases over time. WARNER (72-04) gives essentially the same curve for the behavior of a silica-formamide gel over time. Note the curve for SIROC shown in fig. 21 in Part One, Chapter 6, "Strength of Treated Ground".

This drop is due to a major loss of water around the edges, which affects the gel's adhesiveness and thus its mechanical characteristics. The curve can be highly variable depending on the composition of the grout, the volume applied and other factors, but its shape will remain the same.

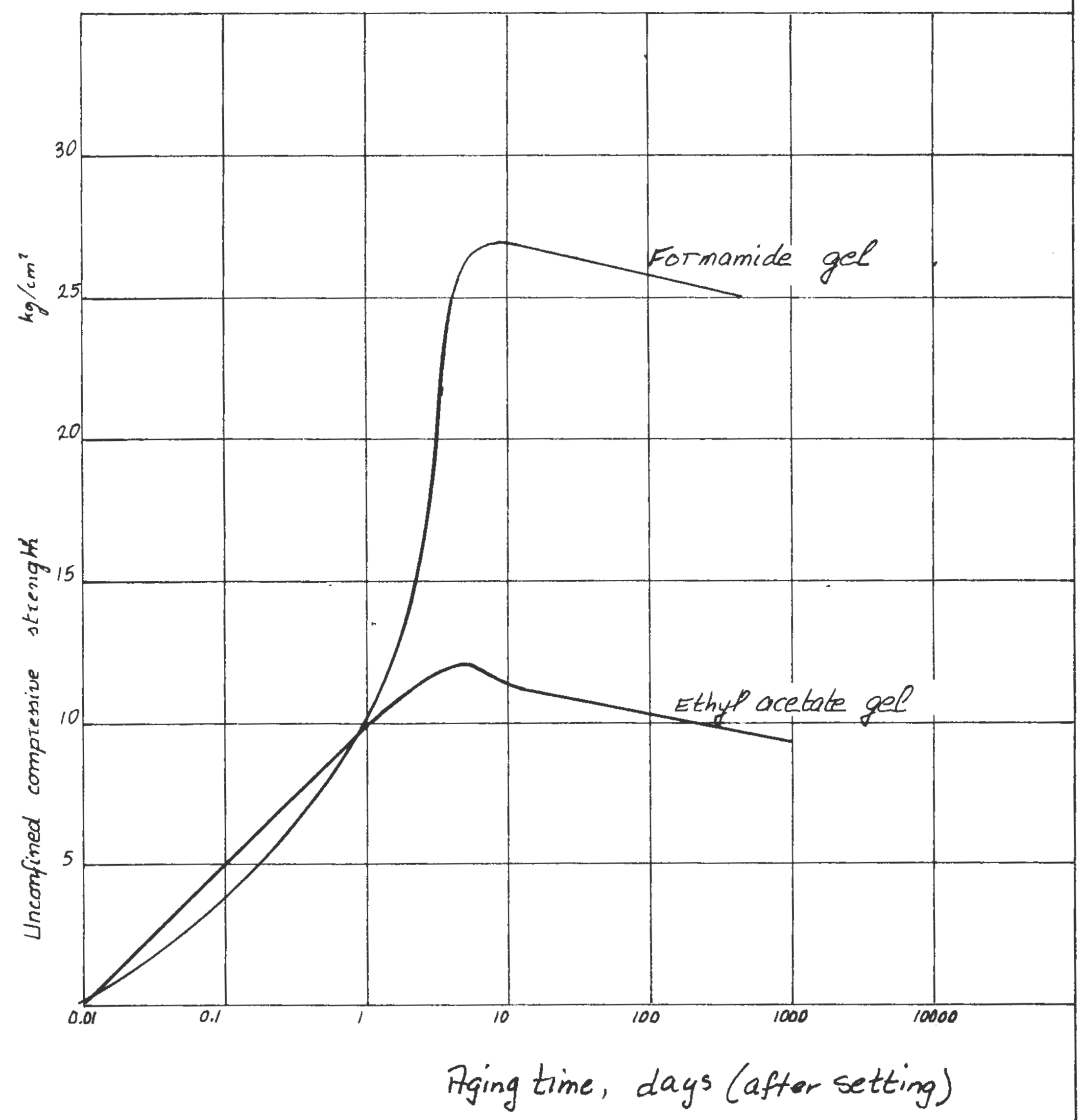


Fig. 62. General Effect of Hermetic Mold Curing on Long-Term Strength of Silica Gels

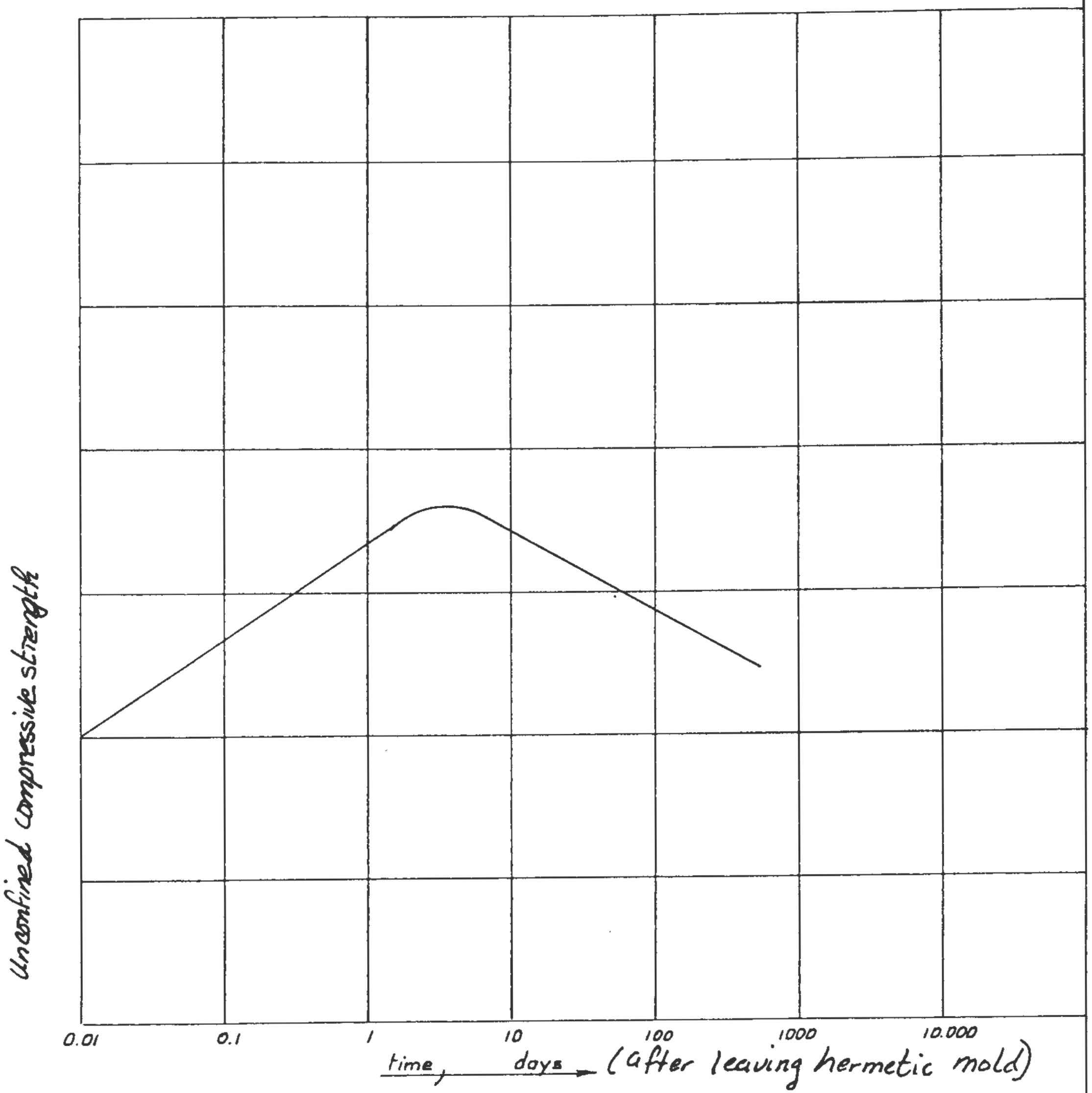


Fig. 63. Effect of Air Curing on Strength of Silica Gel Mortar

5.3 Cure in a Wet Medium

The RHONE-PROGIL (99-09) descriptive material mentions the changes in unconfined compressive strength of silica gel-sand test samples immersed in water, in terms of the sodium silicate's rate of destabilization (ratio reagent/sodium silicate in the gel). Fig. 64, drawn from the descriptive insert, shows that strength can be seriously disturbed over time if the silicate's rate of destabilization is low.

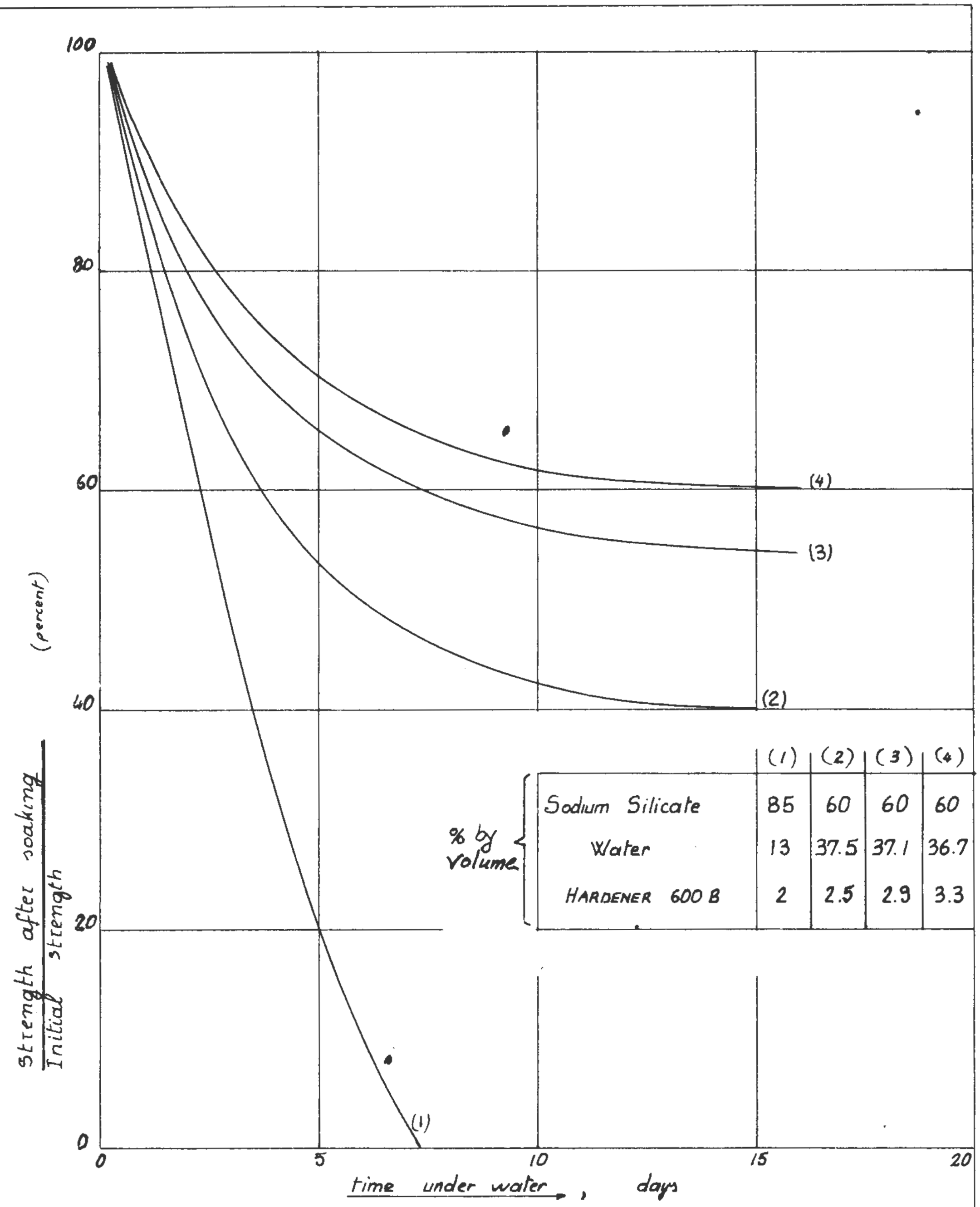
These figures were confirmed by a similar study which we carried out. In table 20, the drop in strength in a water cure varies inversely to the percentage of setting reagent. The orgin of the silicate also plays a definite part (comparison of the 3 silicates used in this study). The silicate used in this study had a SiO_2/Na_2O ratio of between 3.22 and 3.30. The composition of the gel used was:

silicate	70 cm^3
water	30 cm^3
ethyl acetate	variable (7,8 and 9 cm^3)

After curing for 48 hours, the 100 cm^3 by volume mortar samples (prepared by the direct molding method) were placed in water. The results are given in table 21 below.

Table 21 Effect of Silicate Origin and Reagent Dosage on Strength (Wet Cure)

Origin of Silicate	Reagent Dosage cm^3	Unconfined Compressive Strength in Bars		
		Control Samples (hermetic molds)	24 hours in water	40 days in water
French	7	20.1	11.3	0.8
	8	21.8		2.1
	9	23.1	13.8	3.3
Italian	7	25.9	16.3	4.0
	8	26.7	20.0	4.8
	9	29.4	25.0	8.0
Greek	7	30.0	21.9	1.5
	8	32.9	25.5	1.8
	9	35.5	28.5	3.4



% by Volume	(1)	(2)	(3)	(4)
Sodium Silicate	85	60	60	60
Water	13	37.5	37.1	36.7
HARDENER 600 B	2	2.5	2.9	3.3

Fig. 64. Effect of Wet Curing on Strength of Silica Gel Mortar

In addition, there is some swelling of the gel in water cures. If this swelling is stopped by maintaining the samples under pressure, the strength readings are improved.

The 9 preceding series (3 silicates, 3 dosages of reagent) were divided into 2 lots. The first was placed in a water-saturated sand, the other was placed in the same medium, but kept under pressure. The loss of strength in the second was lower, as shown in table 22.

Table 22. Effect of Pressure, Silicate Origin, and Reagent Dosage on Strength (Wet Cure)

Origin of Silicate	Reagent Dosage cm3	Unconfined Compressive Strength in Bars (at 20 days)		
		Control Samples (hermetic)	Cure in water-saturated sand	Cure in water-saturated sand under pressure
French	7	20.1	0.75	0.9
	8	21.8	1.5	3.7
	9	23.1	3.1	5.1
Italian	7	25.9	2.6	5.7
	8	26.7	3.7	6.8
	9	29.4	5.2	8.4
Greek	7	30.0	1.0	1.0
	8	32.9	4.0	4.5
	9	35.5	7.1	8.7

In the presence of an excess of water, the gel's soluble salts dissolve, and there is a partial inverse reaction gel → sol. These phenomena cannot occur in a pure state since salts from the syneresis water are found among the dissolved salts. When syneresis is over, the dissolved salts contain sodium almost exclusively.

The silica gel's tendency to dissolve in water is aggravated by non-neutralized sodium which passes into the cure water and attacks the polysilic acid which forms during the setting process. The higher the concentration of non-neutralized sodium, the greater the loss in strength will be.

For silica gels, this curing method is extremely unfavorable for two reasons:

1) In nature, non-neutralized sodium is gradually drained off by underground seepage.

2) In a more general sense, there is the totally arbitrary character of volumetric scale (small volume of gel mortar in a huge excess of water or saturated sand).

It should be noted that if an intermediate curing method, midway between the hermetic mold and the water cure, is adopted, the gel is no longer disturbed. This alternative is shown in table 23 below for two silica gels, diluted respectively with 20 and 40% water, after 14 months of cure in a humidity saturated atmosphere (test samples cured in a closed glass container over a tank of water).

Table 23. Effect of Dilution and Cure Method on Strength

Composition of gel	Unconfined Compressive Strength in Bars After 14 Months [1]	
	in water-saturated air	in hermetic molds
Gel diluted at 40%	5.1	4.9
Gel diluted at 20%	23.75	24.8

5.4 Cure in Water Percolating Under Pressure

Claude H. HURLEY and Thomas H. THORNBURN (71-01) cite the results of lab tests for leaching where the permeability coefficient of some gels increased several hundred times in 24 hours; in most of these cases, the permeability coefficient increases with percolation time.

In regard to erosion, H. CAMBEFORT and C. CARON (57-13) analyzed the permeability of silica gels with inorganic reagents as a function of those reagents. Fig. 65 shows that after a time permeability stopped increasing; figure 66 shows that the leach water no longer contained silica after a certain time. The water's pH gradually moved toward neutral. This stability was confirmed by measurements of resistivity which gave the same figures

---

[1] Strength in pascals = strength in bars x 10^5

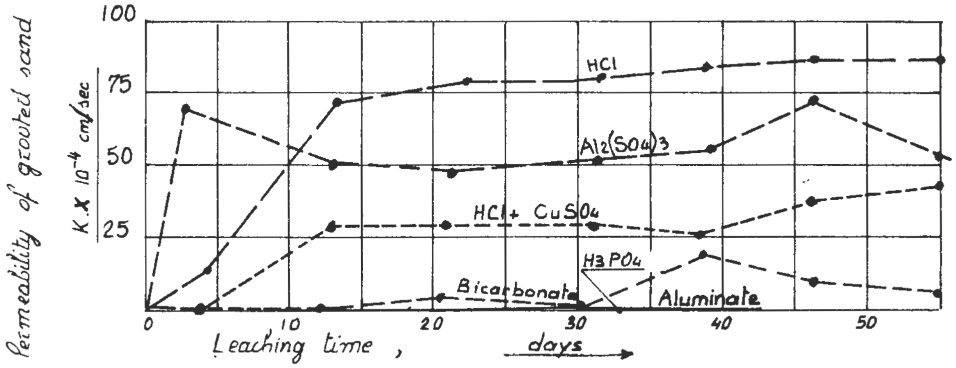


Fig. 65. Effect of Reagent Type on Leaching and Permeability of Silica Gels

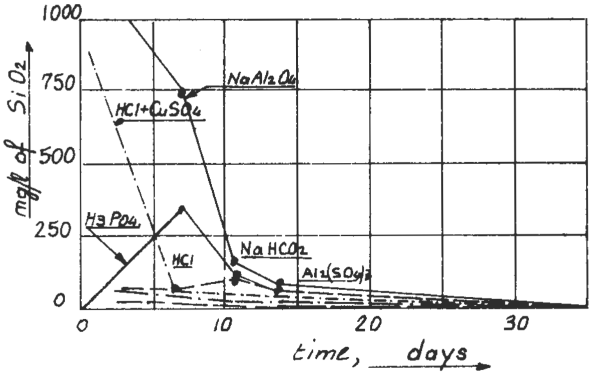


Fig. 66. Quantity of Silica in Leach Water

at the two ends of the cells. The gel was then stable, and it was found that the more permeable the gel, the faster this state would be reached. This state can be considered attained when all the products of syneresis have been leached out.

It was concluded that the effect of the nature of the reagent was quite clear in this respect. Some reagents, such as sodium aluminate or phosphoric acid, produce very stable gels with little loss of silica, while other reagents produce particularly unstable gels which eventually dissolve almost completely, such as the case of hydrochloric acid, illustrated in fig. 67.

Using the same procedure, CARON (65-04) determined the effect on the gel's resistance to leaching of the particle size of the sand or soil with which a silica gel is mixed. The conclusion was that gravel-type coarse substances favor syneresis and, thus, leaching, and quickly lead to decomposition of the test sample. Conversely, fine sands considerably diminished syneresis so the sand-grout combination would behave much better when subjected to leaching. The results of the research are shown in fig. 68. It must be pointed out, however, that these different figures did not result from a percolation method applying lateral confinement.

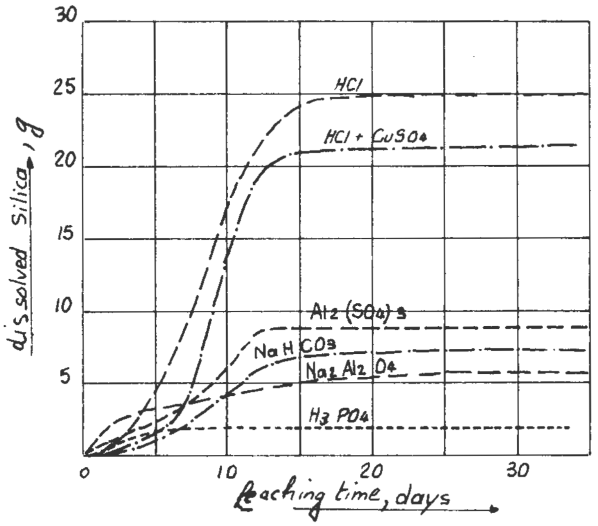
Using the standardized method, RHONE-PROGIL (99-09) obtained the following findings for seepage erosion on silica gels with RHONE-POULENC Hardener 600:

1) The water's rate of flow increases during the first days, then stabilizes and finally decreases.

2) The percolated water's pH evolves slowly toward neutral.

3) At the end of the test, when the samples were removed from the molds, it was found that the end where the water entered was completely disintegrated, while unconfined compressive strength of the opposite end was well over the theoretical value.

From these findings, it can be deduced that, under the effect of water circulation, a fraction of the silica precipitated by setting dissolved at one end, was partially carried along by the water's current and then reprecipitated at the other end, thus decreasing overall permeability. RHONE-PROGIL's brochure concluded that this test shows that, in a thick section of treated ground, the partial dissolution of the silica gel does not harm the durability of treatments for waterproofing.



Each sample originally contained 30 g silica

Fig. 67. Total Quantity of Silica Dissolved

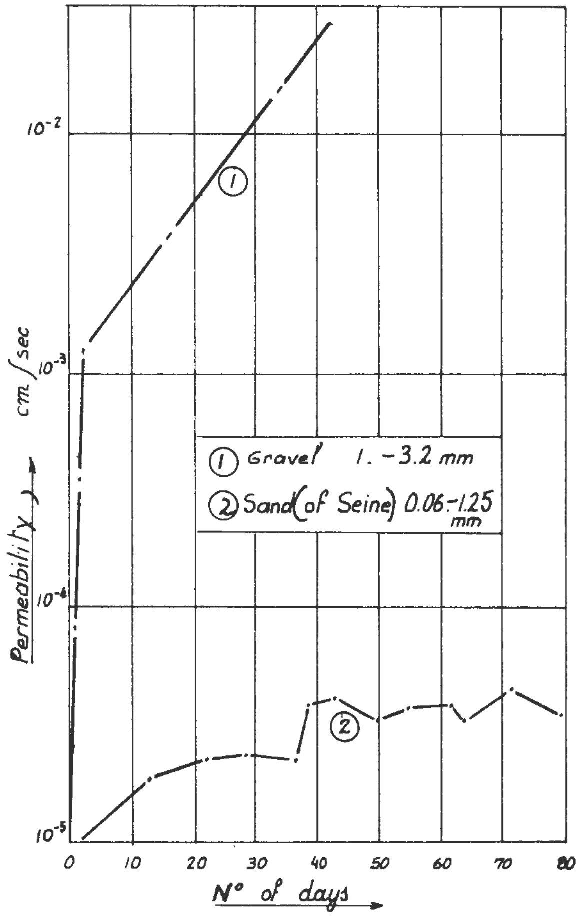


Fig. 68 . Effect of Soil Particle Size on Leaching

Having examined the behavior of waterproofing or consolidation gels by the recommended method, we can confirm RHONE-PROGIL's conclusions. Fig. 69 indicates the following:

1) The permeability coefficient of the two waterproofing gels studied is stable from the beginning and remains so with time. This result is due to the fact that sodium aluminate and monosodium phosphate are both silicate setting reagents which cause only low rates of syneresis. When these substances are incorporated into a skeleton of fine sand, syneresis does not occur.

2) The behavior of the two consolidation gels is rather different from that of the waterproofing gels. The rate of water flow increases rather sharply during the first few days, then stabilizes. This result, which confirms RHONE-PROGIL's tests, is caused by the expulsion of all ingredients which did not set, or set incompletely (sodium salts, free sodium, silica and free water) during the first days of leaching.

The destabilization rate of the silica is less effective in a consolidation grout than with a waterproofing grout, because of much higher silica content. Once erosion is over, there is an insoluble polycondensed silicic acid. The medium's permeability ceases to increase. Fig. 70 also clearly shows the effect of the destabilization rate of sodium silicate when subjected to percolation under pressure, for a consolidation gel at 30% dilution and using a variable proportion of ethyl acetate as reagent.

1) If the gel is highly destabilized, the permeability coefficient will stabilize at a value relatively close to the initial coefficient.

2) If the gel is insufficiently destabilized, the permeability coefficient will increase gradually over time, and can even ruin the test sample.

6. Toxicity

As is the case with all chemical grouts, the distinction must be made between the toxicity of the basic ingredients and the grout before it sets, and the toxicity of the hardened grout.

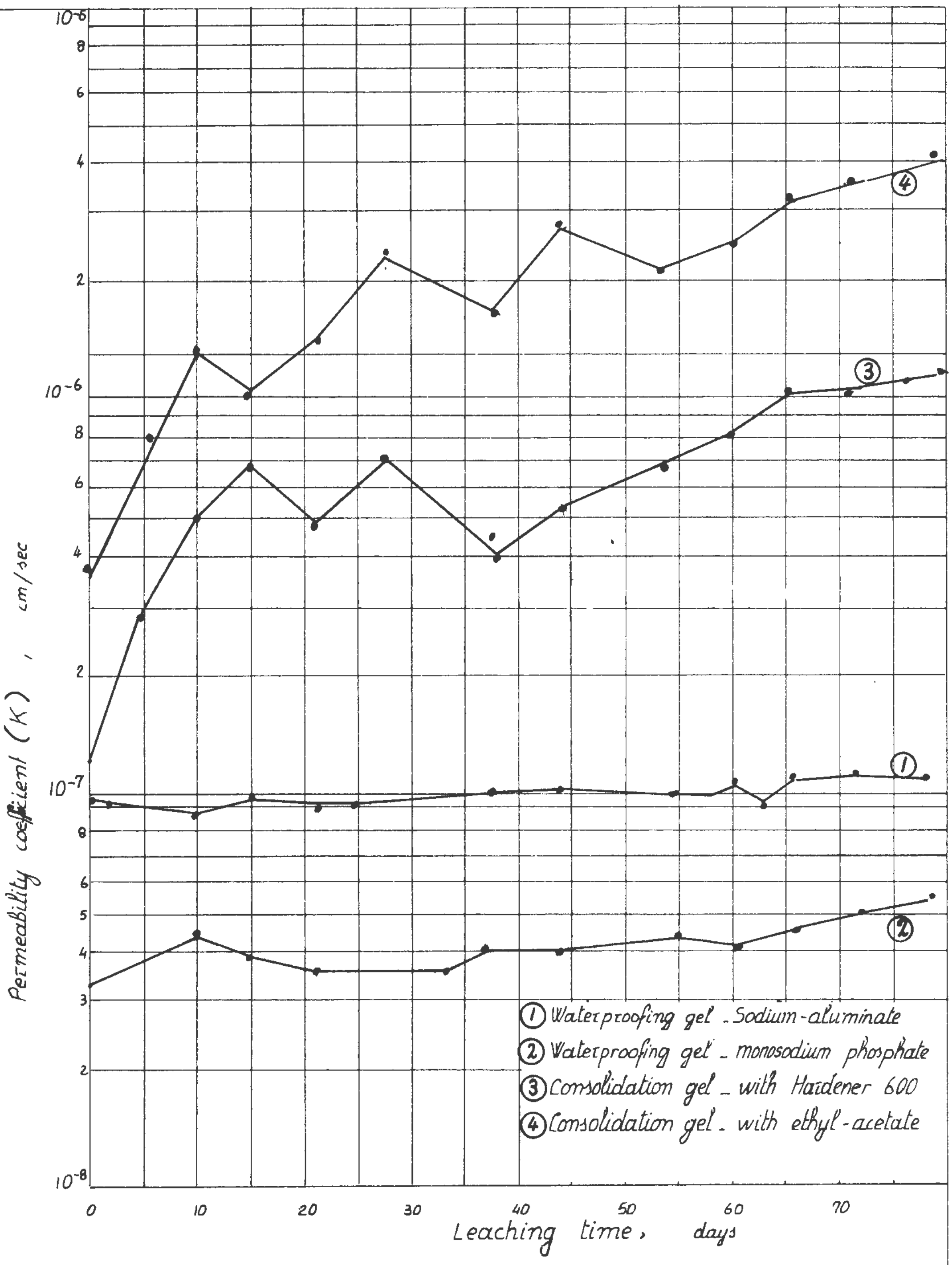


Fig. 69. Effect of Time on Permeability of Several Gels

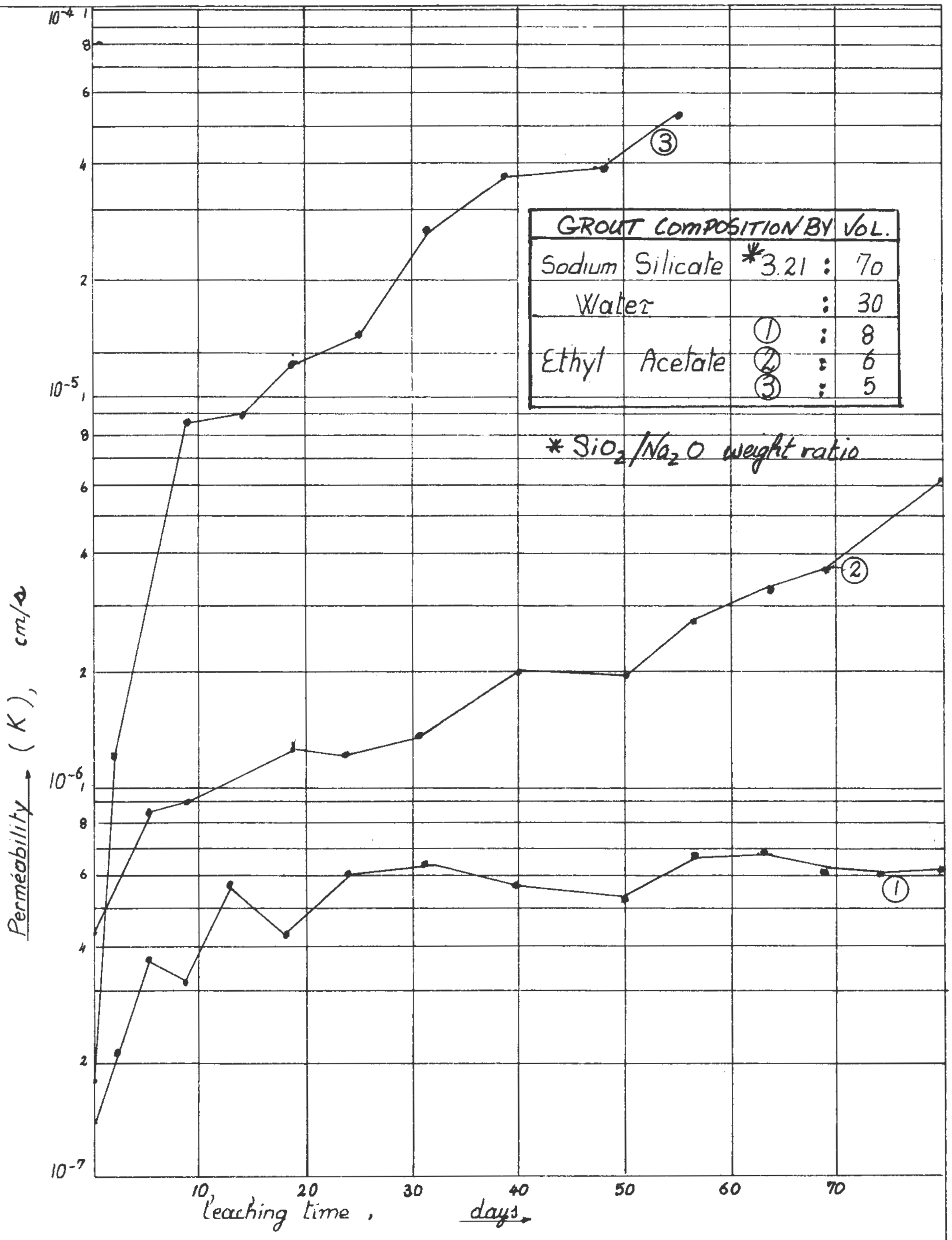


Fig. 70. Effect of Destabilization Rate on Mortar Permeability

6.1 Toxicity of Basic Ingredients

6.11 Sodium Silicates

Because of the presence of sodium in the silicate, ingestion should be avoided, and protection goggles should be worn. Contact with the skin poses no particular danger.

6.12 The Hardeners

As with the silicates, ingestion of the hardeners should be avoided. The volatile hardeners of the ester type are dangerous in the case of prolonged inhalation. Others, such as the amides, are skin irritants. In general, there should be adequate ventilation in areas where these hardeners are handled.

Table 24 indicates the toxicity of possible ingredients of silica gels as drawn from the toxicological literature. (The abbreviations are explained at the end of the table.)

Table 24 . Toxicity of Silica Gel Ingredients

Nature of ingredients	Toxicity in mg/kg			Toxicity Miscellaneous
	LD 50[1] rat	oral mouse	ipr mouse LD 50	
sodium silicate		1100	70	
fluosilicates K_2F_6Si				oral guinea pig LD 50: 500 mg/kg
CaF_6, $2H_2O$				oral guinea pig LD 50: 250 mg/kg
MgF_6Si, $6H_2O$				oral guinea pig LD 50: 200 mg/kg
silica halogenides ($SiCl_4$)				inhalation rat LC 50:8000 mg/kg
phosphoric acids (ortho)	1530			rabbit skin LD 50: 2740 mg/kg
citric				ipr rat. LD 50: 975 mg/kg
hydrofluoric				M.A.C. 2 mg/cm^3
hydrochloric				M.A.C. 7 mg/cm^3
sulfuric	2140			
sodium				M.A.C. 2 mg/cm^3
potassium	365			
ammonia	350			

[1] Abbreviations defined on page 169.

Table 24. Toxicity of Silica Gel Ingredients (Continued)

Nature of ingredients	Toxicity in mg/kg			Toxicity Miscellaneous
	LD 50 rat	oral mouse	ipr mouse LD 50	
calcium chloride	1000		280	
magnesium chloride	2800		342	
aluminum sulfate		4210	270	
ammonium chloride	1650		1300	
ammonium sulfate	58			
ammonium acetate				mouse ivn LD 50 98 mg/kg
ferric chloride	900		68	
aluminum chloride	3700	3800		
copper sulfate	300		7	
sodium chloride	3000		2602	
chlorine				inhal. rat LC 50: 293 ppm/1h
sodium bisulfate				inhal. mouse LC 50:127ppm/1h
ethyl acetate				inh. rat LC 50: 1600 ppm scu rat LD 50: 5000 mg/kg
triacetin	3000			scu rat LD 50: 3250 mg/kg
glycol diacetate			1070	oral guinea pig LD 50:4940mg/kg
ethyl formate	1850			oral guinea pig LD 50:1100 mg/kg
ethyl oxalate (diethyl ester)	400			
diethyl succinate	8530			
formamide				ims guinea pig LD50:2539 mg/kg
dimethylformamide	1500			ivn rat LD 50: 2350 mg/kg
glyoxal				oral guinea pig LD 50:760 mg/kg
formaldehyde	800			oral guinea pig LD 50:260 mg/kg scu rat LD 50: 420 mg/kg scu mouse LD 50: 300 mg/kg

Table 24. Toxicity of Silica Gel Ingredients (Continued)

Nature of ingredients	Toxicity in mg/kg			Toxicity Miscellaneous
	LD 50 rat	oral mouse	ipr mouse LD 50	
benzaldehyde	1300. .	. . . . .	. . . .	oral guinea pig LD 50:1000 mg/kg
furfural	127			
trimethylacetaldehyde	. . . .	. . . . .	. . . .	oral dog LD 50: 3500 mg/kg

oral = orally
ipr = intraperitoneal
M.A.C. = maximum allowable concentration (U.S.A.)
scu = subcutaneous
imu = intramuscular
ivn = intravenous
LD 50 = dose causing 50% mortality
LC 50 = lethal concentration (in the air), causing 50% mortality

The degree of risk and the precautionary measures to be taken in handling the grout before it sets are essentially the same as with the basic ingredients. In general, when using these grouts, safety and hygiene standards should be consulted for the basic ingredients used.

6.2 Toxicity of Hardened Grout

The toxicity of a waterproofing gel (silicate-aluminate) and a consolidation gel (silicate-Hardener 600B) have been examined by RHONE-PROGIL's toxicology laboratory. Test conditions and results were the same for both cases.

The compounds used were as follows:

1) Silicate-sodium aluminate

silicate 3.21	300 cm^3
water	300 cm^3
sodium aluminate, 10%	200 cm^3

2) Silicate-Hardener 600 B

silicate 35/37	600 cm^3
water	400 cm^3
Hardener 600 B	80 cm^3

Test Conditions

1) CD rats (C.O.B.S.) [1] from the CHARLES RIVER France Farm, weighing 150 to 185 grams, fasted 24 hours before administration, 10 rats (5 males, 5 females).

2) Product put into suspension (with a Teflon head grinder) in a 10% gum arabic aqueous solution and administered by aesophageal tube.

3) Dosage: 15 g/kg p.o. 2 administrations at 3 hour intervals of 20 ml/kg of a 37.5% suspension.

4) Duration of observation period: 15 days, animals weighed every 5 days.

5) Sacrificed with sodium pentobarbital administered intravenously and autopsied on the 15th day for macroscopic examination of the principal thoracic and abdominal viscera.

Results

Mortality	none
Symptoms	none
Weight gain	normal
Autopsy	no anomaly

Conclusion

Administered orally to rats, silica gels are not toxic at doses of 15 g/kg.

---

[1] C.O.B.S. = Caesarian Originated, Barrier Sustained

III. CATEGORY A-3 LIGNOSULFITE DERIVATIVES

1. Viscosity

1.1 Initial Viscosity

1.11 Viscosity of Lignosulfite Solution

As with silicate derivatives, one single value cannot be assigned for the initial viscosity of Category A-3 grouts. The diluteness of the lignosulfite solution will depend on the particular formula adopted for the grout. The product's origin can have a slight influence on the solution's viscosity, but this influence is negligible in practice.

In this lignosulfonate derivative category, sodium and, especially, calcium lignosulfite are the products most often used in grouting. They are marketed as concentrated viscous liquors or powders assaying out at up to 65% dry extract. The average composition by weight of a lignosulfite is: dry matter, 95%; moisture, 5%.

The dry matter breaks down as follows:

sulfonate lignin salts	76%
reducing sugars	19%
inorganic ash	4%

Calcium and sodium lignosulfite are easily dissolved in water for the range of diluteness used in grouting. Lignochrome gels intended for waterproofing are used at concentrations of 200 to 350 grams/litre of water, and, for consolidation, at concentrations of 450 to 600 grams/litre. Within this range of concentrations, 200 to 600 grams/litre, the nature and origin of the product have relatively little influence on viscosity, which ranges from 2.5 to 10 centipoises at 20°C. Fig. 71 shows changes in the viscosity of lignosulfite suspensions in relation to concentration of dry matter in the water.

It should be specified that, as lignosulfonate solutions will tend to foam, the curve may be slightly distorted if viscosity is measured on a fresh solution (increase of about 10%).

As a general rule, lignosulfite suspensions whose viscosity does not exceed 4 cP are intended for waterproofing, while suspensions with higher viscosities are used for consolidation work. This distinction, however, is not absolute. The higher the concentration, the more sensitive the lignosulfite solution will be to temperature as shown in fig. 72.

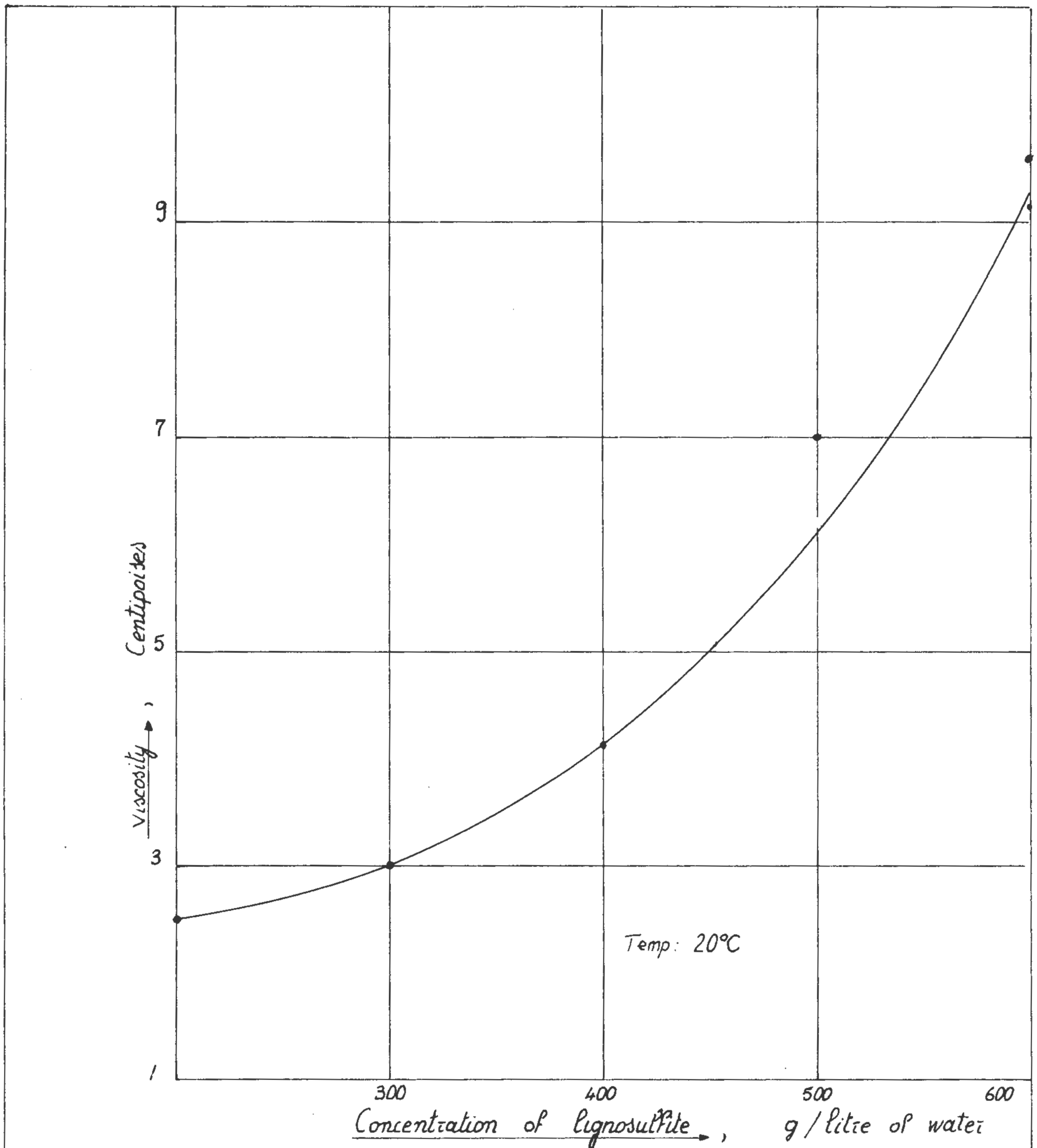


Fig. 71 . Effect of Dry Matter Content on Viscosity of Lignosulfite Suspensions

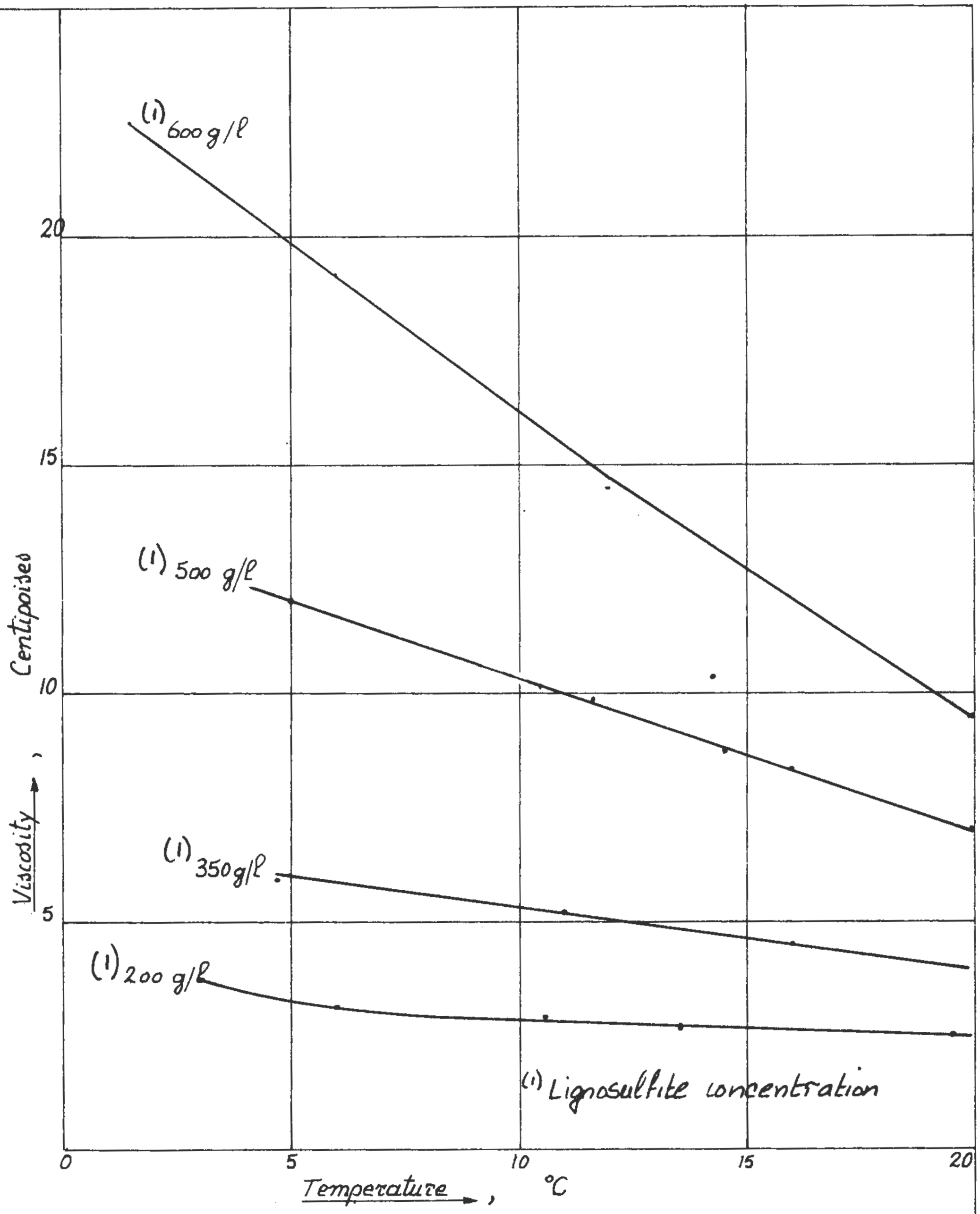


Fig. 72. Effect of Temperature on Viscosity of Lignosulfite Solutions

1.12 Viscosity of Grout

Unlike silica gels, the initial viscosity of these mixtures is not affected by the addition of setting reagents, except in the case of highly reactive mixtures with the following characteristics: Lignosulfite concentration exceeding 350 grams/litre, preparation in a definitely acid medium, high proportion of dichromate.

In these conditions, the viscosity of the mixture will change very rapidly and may even increase instantaneously. As an illustration, a 500 g/l lignosulfite solution having a viscosity of 7 cP at 20°C will attain a viscosity of 15 cP upon addition of the catalyst.

As these highly reactive mixtures are rarely used, the grout's viscosity in most cases is solely determined by that of the lignosulfite solution.

1.2 Changes in Viscosity in Relation of Time

At constant ambient temperature, changes in viscosity in a lignochrome gel will depend on the gel's setting time. If setting time is short, less than 30 minutes, the increase in viscosity will be very abrupt. Conversely, when the setting time is long, more than 1 hour, changes in viscosity will occur gradually. In these circumstances, time limit of injectability will actually be about 2/3 of the setting time.

Fig. 73 , for classic lignochrome gels, and fig. 74 for a commercial product (BLOX-ALL grout of the HALLIBURTON Company) show this change in viscosity with time.

2. Regulation of Setting Time

The general considerations set forth in connection with silica gels also apply to lignochrome gels. Setting time should thus be adjustable for ground conditions and air and ground temperature.

Like silica gels, lignochrome gels obey VAN'T HOFF-ARRHENIUS' Law. Fig. 75 shows that the setting time coefficient for a 10°C variation in temperature will be about 2. This has been confirmed by studies conducted at Cornell University (U.S.A.) which are included in fig. 75 . This value is also applicable to setting times of highly dilute silica gels using inorganic reagents.

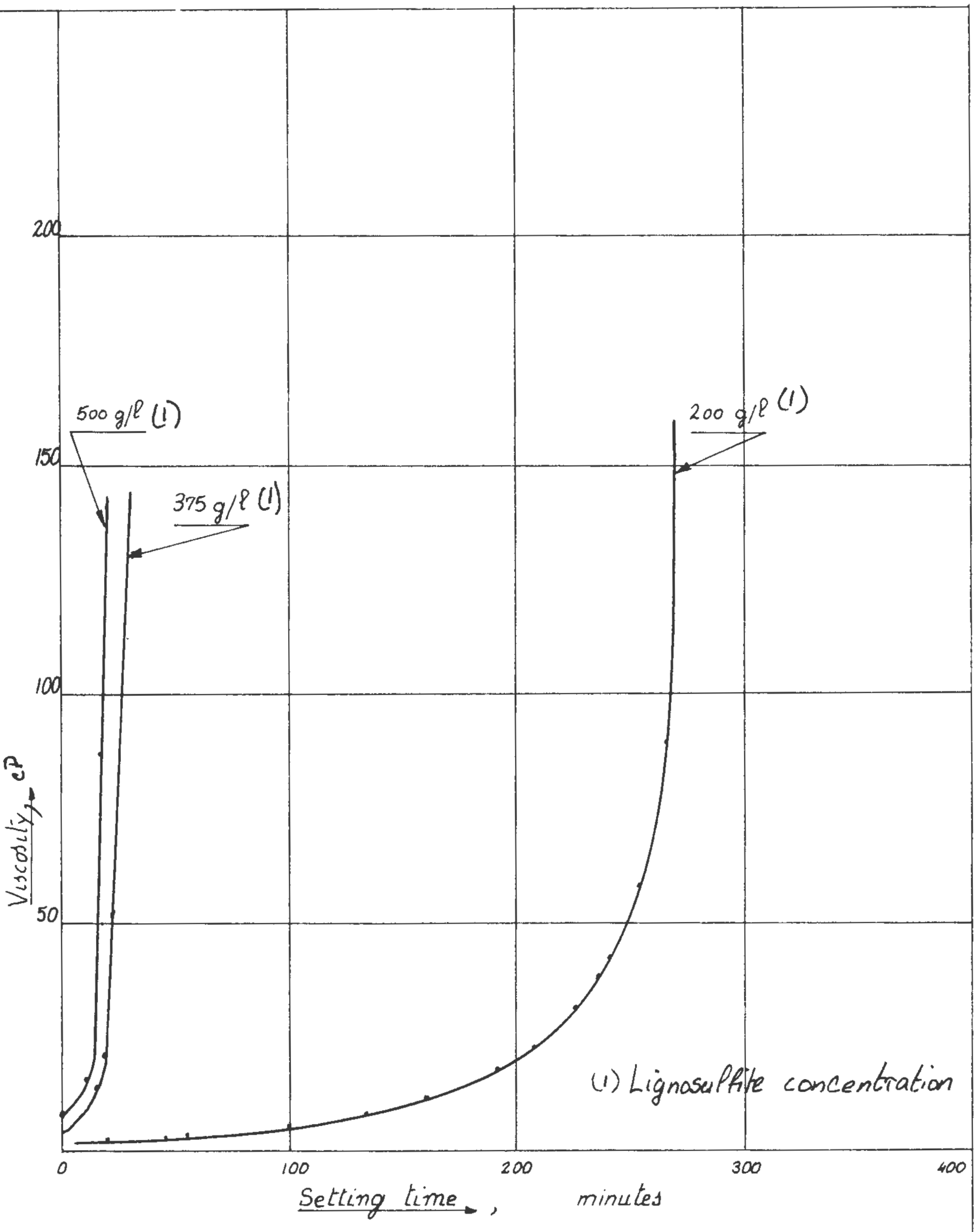


Fig. 73. Effect of Setting Time on Viscosity of Lignochrome Gels

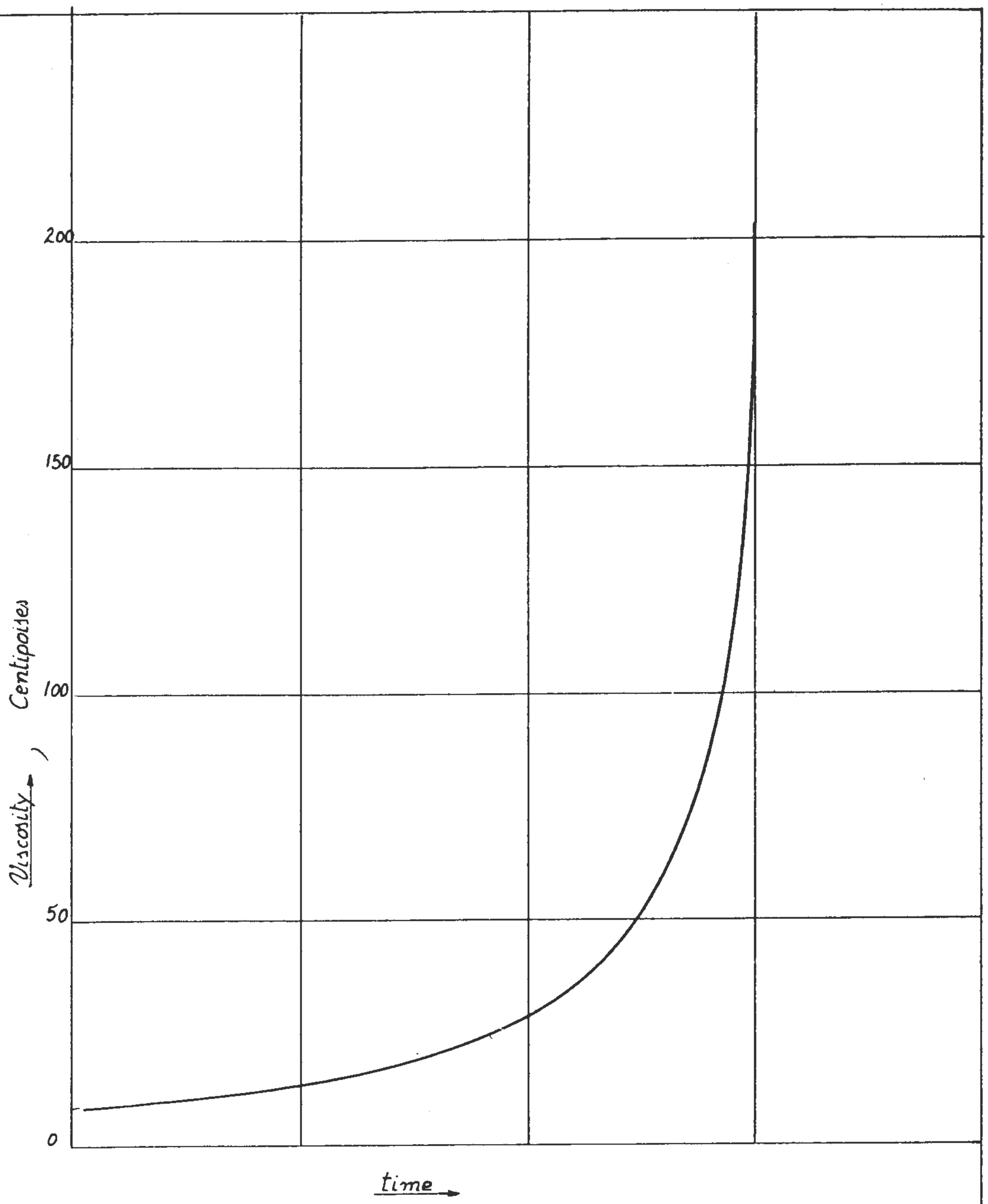


Fig. 74. Effect of Setting Time on Viscosity of Lignochrome Gel BLOX-ALL GROUT (Halliburton Co.)

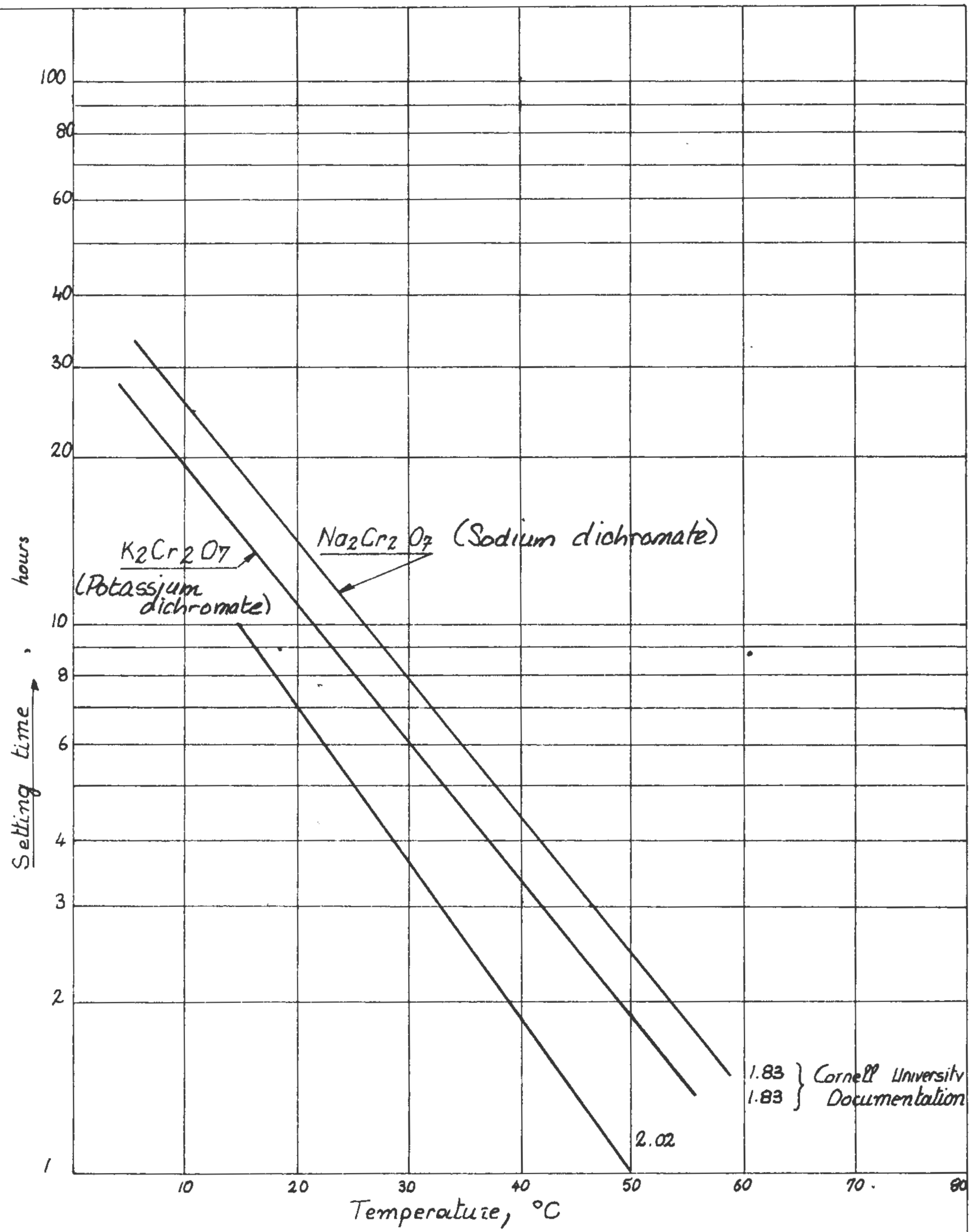


Fig. 75. Effect of Temperature on Setting Time of Lignochrome Gels

Setting time can be shortened by increasing the lignosulfite and, especially, the dichromate concentration as shown in fig. 76 to 78. However, this method is not recommended as mechanical characteristics would be altered by changes in lignosulfite and dichromate proportions.

It would seem that the nature of the lignosulfite might have some influence. Figs. 76, 77 and 78, reporting on three different lignosulfites, show that the setting times for various dilutions are not identical. More precisely, if the setting times of these three lignosulfites in the same amounts (400 g/l) are plotted on a graph, and then the setting times for three other lignosulfites as a function of the sodium dichromate content are added, it can be seen that changing the nature of the lignosulfite gives a great deal of latitude in the adjustment of setting time. Unfortunately, this method is hardly practical at worksites where only one type of lignosulfite is generally available. Furthermore, setting times remain long in all cases, even where the proportion of Cr^6 is high, as shown in table 25.

Table 25. Effect of Type of Lignosulfite and Sodium Dichromate Concentration on Setting Time

Nature and origin of lignosulfite	Setting time in hours	
	20% sodium dichromate	25% sodium dichromate
English calcium lignosulfite	4 h 30 m	3 h 20 m
French " "	3 h 35 m	2 h 30 m
Swedish " "	6 h 00 m	3 h 20 m
English sodium "	5 h 35 m	3 h 00 m
Swedish "(WAFEX) "	4 h 00 m	2 h 35 m
Swedish " "	4 h 00 m	3 h 00 m
French " "	42 h 00 m	6 h 00 m

The best method of accelerating setting time is to acidify the mixture. The lower the pH, the more reactive the Cr^6 will be. This acidification is carried out (fig. 79) directly at the worksite with orthophosphoric acid (fig. 80), ferric chloride, aluminum potassium sulfate, monsodium phosphate, or by using preacidified lignosulfonates (French R lignosulfonate, fig. 81).

Acidification thus produces gels whose setting time can be easily regulated from about ten minutes to more than 10 hours, an adequate range for ordinary purposes.

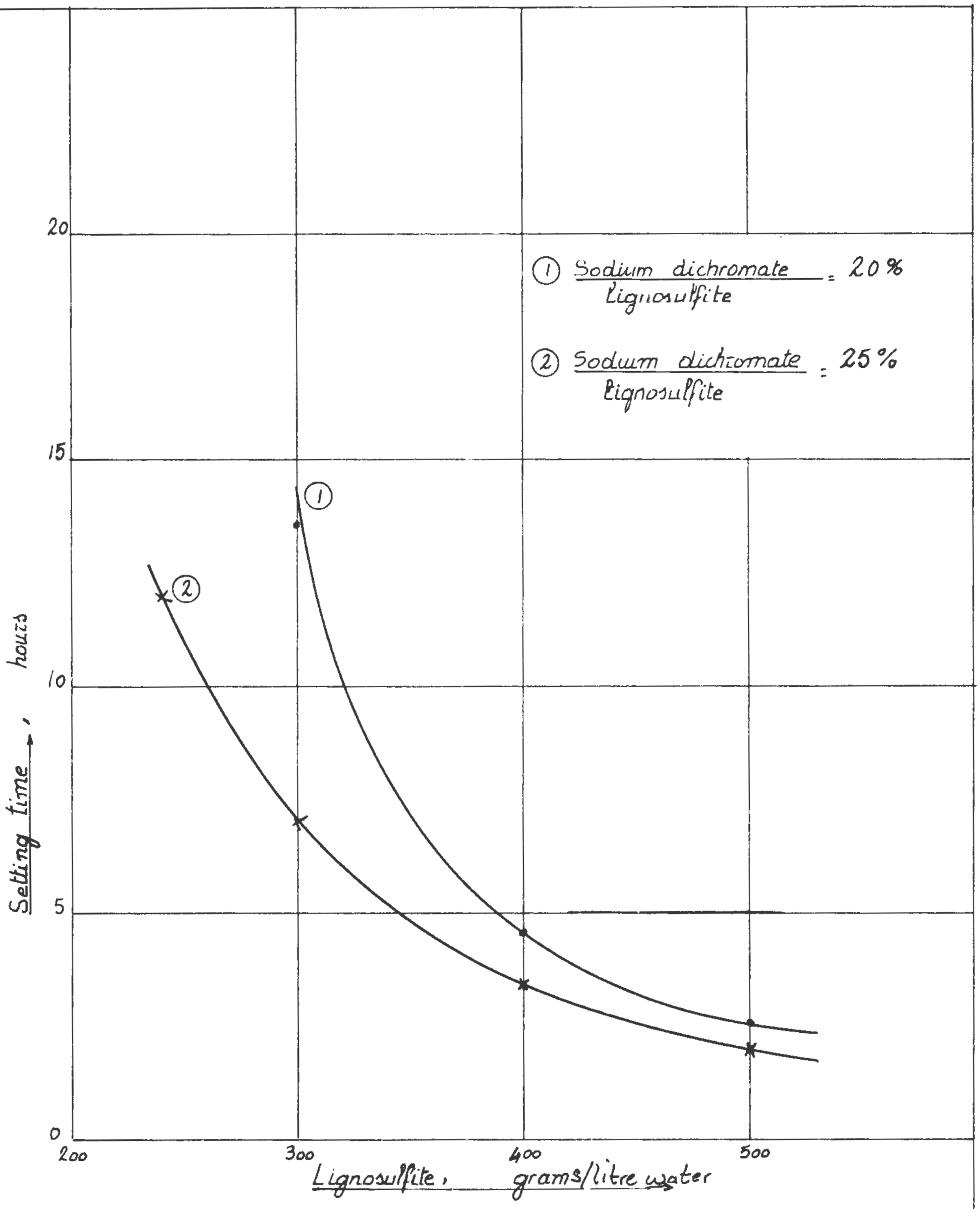


Fig. 76. Effect on Setting Time of Lignosulfite and Sodium Dichromate Content (English Calcium Lignosulfite)

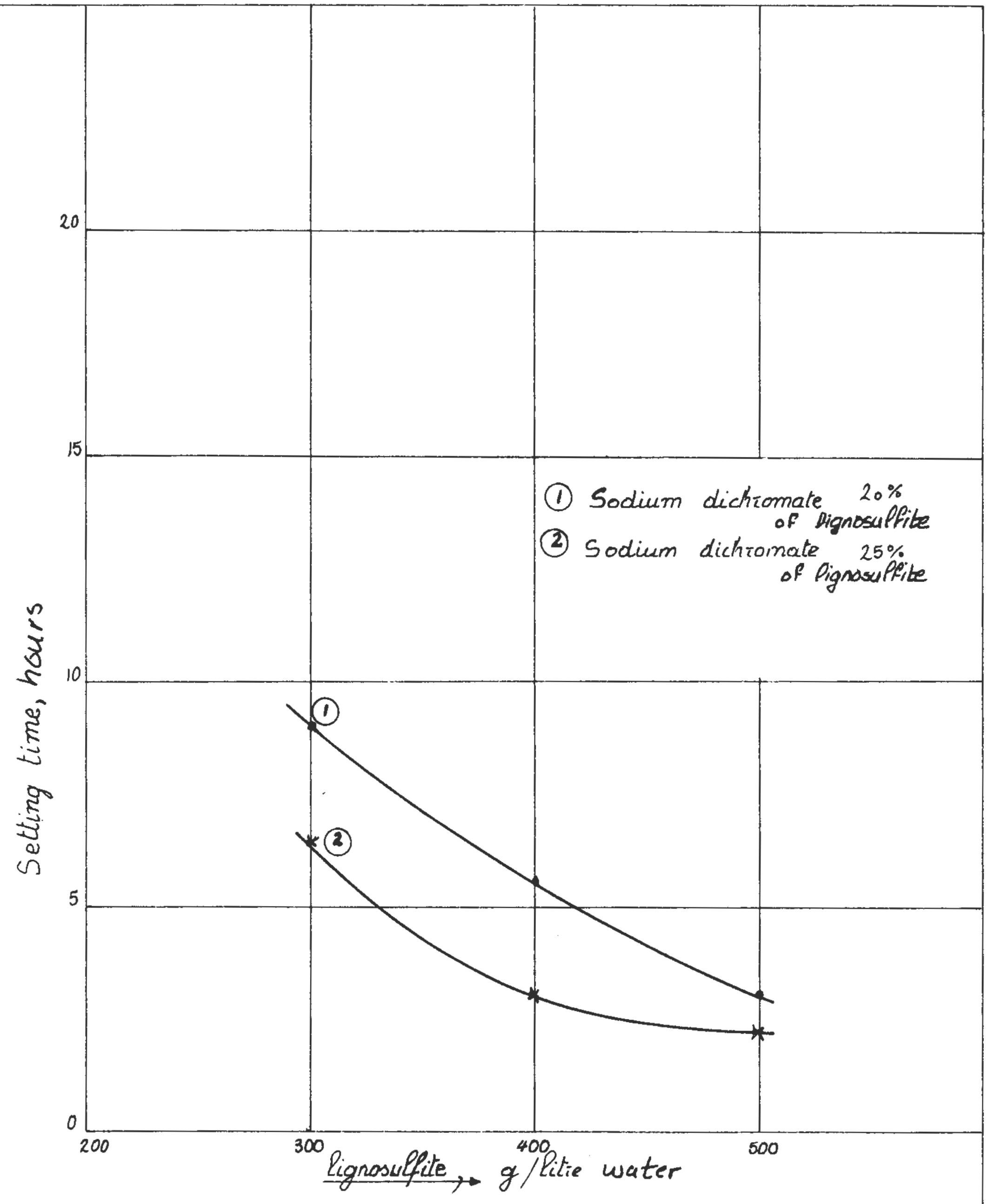


Fig. 77. Effect on Setting Time of Lignosulfite and Sodium Dichromate Content (English Sodium Lignosulfite)

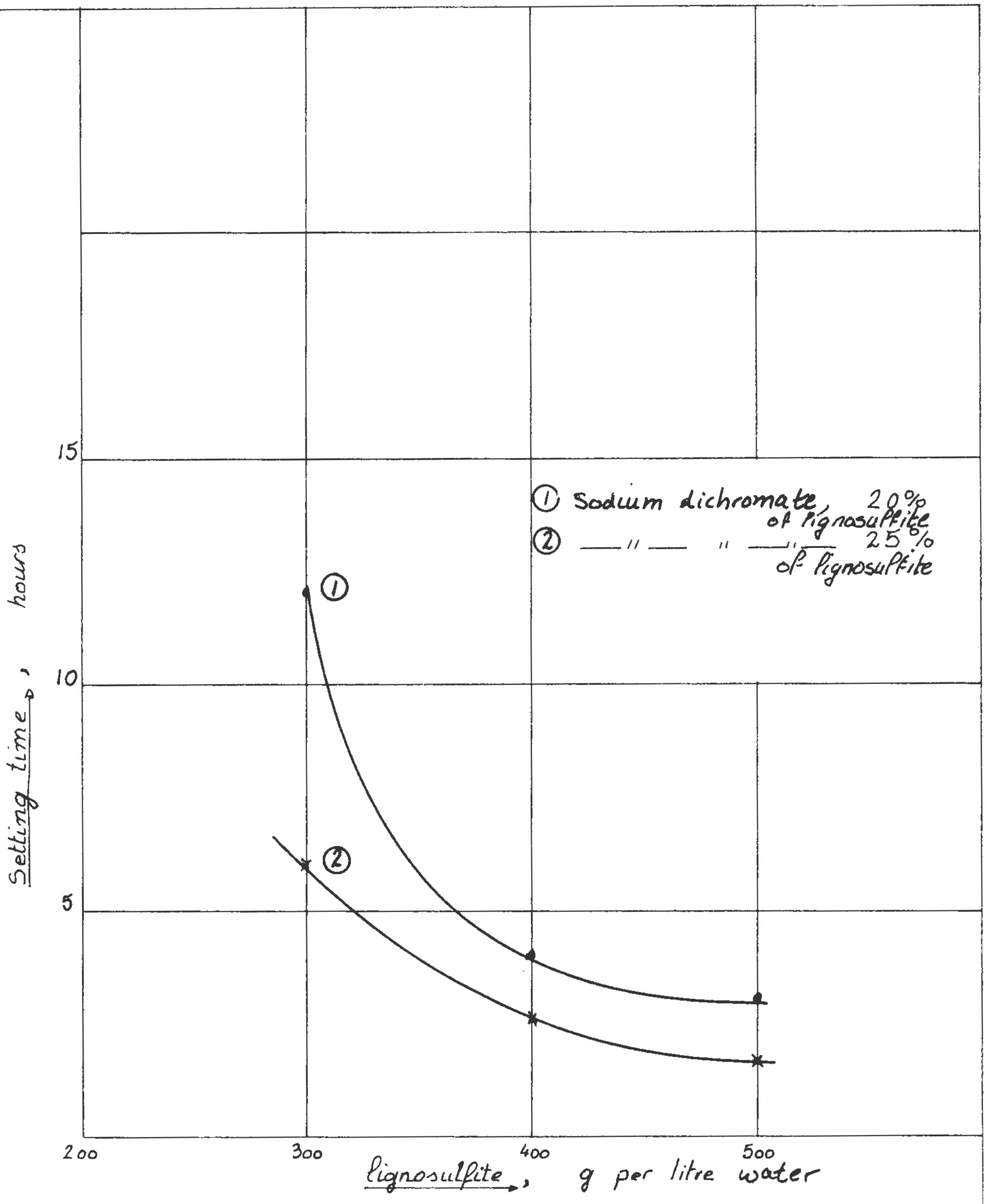


Fig. 78. Effect on Setting Time of Lignosulfite and Sodium Dichromate Content (Sodium Lignosulfite WAFEX)

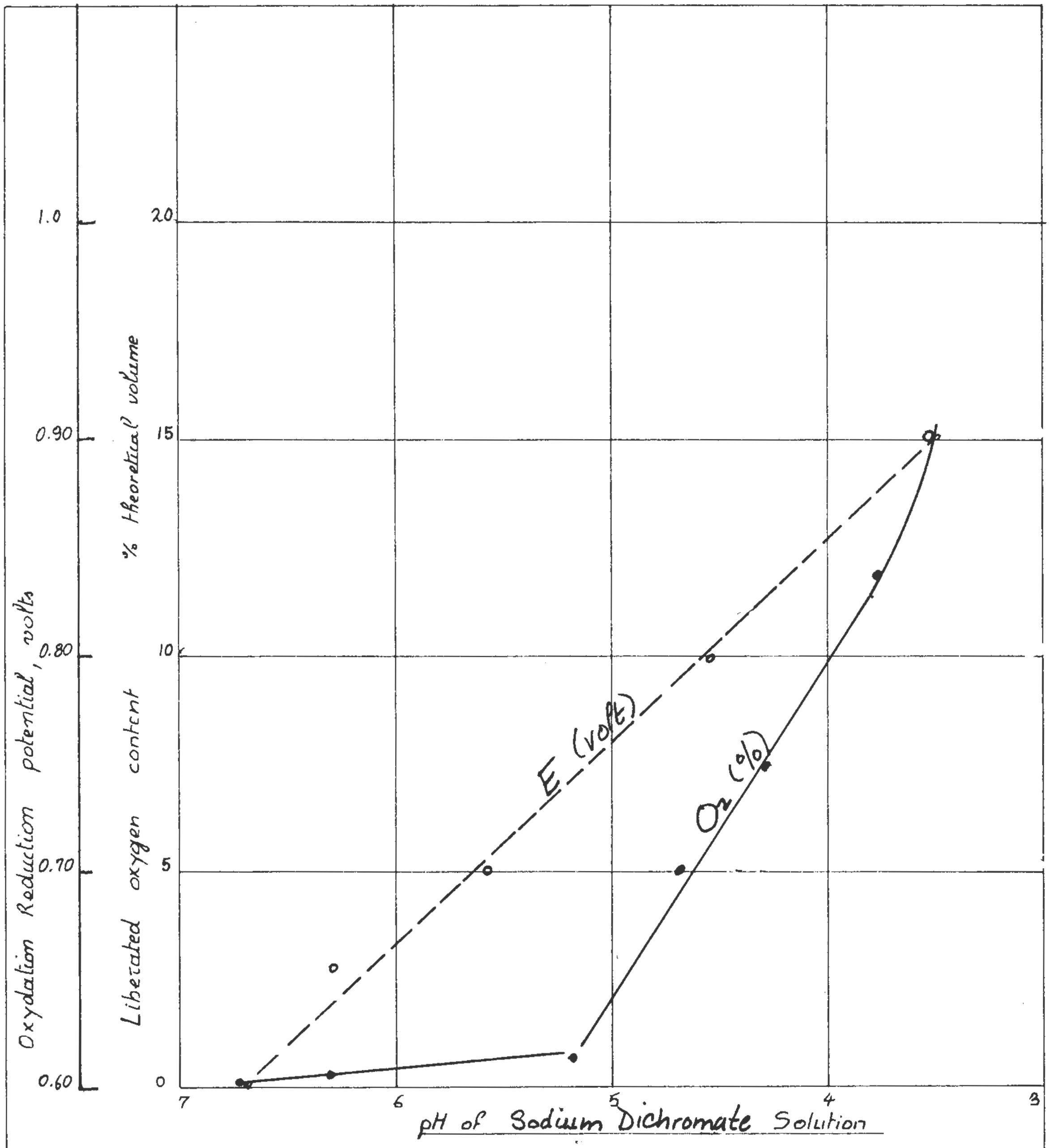


Fig. 79. Effect of pH on Oxydizing Power of Sodium Dichromate

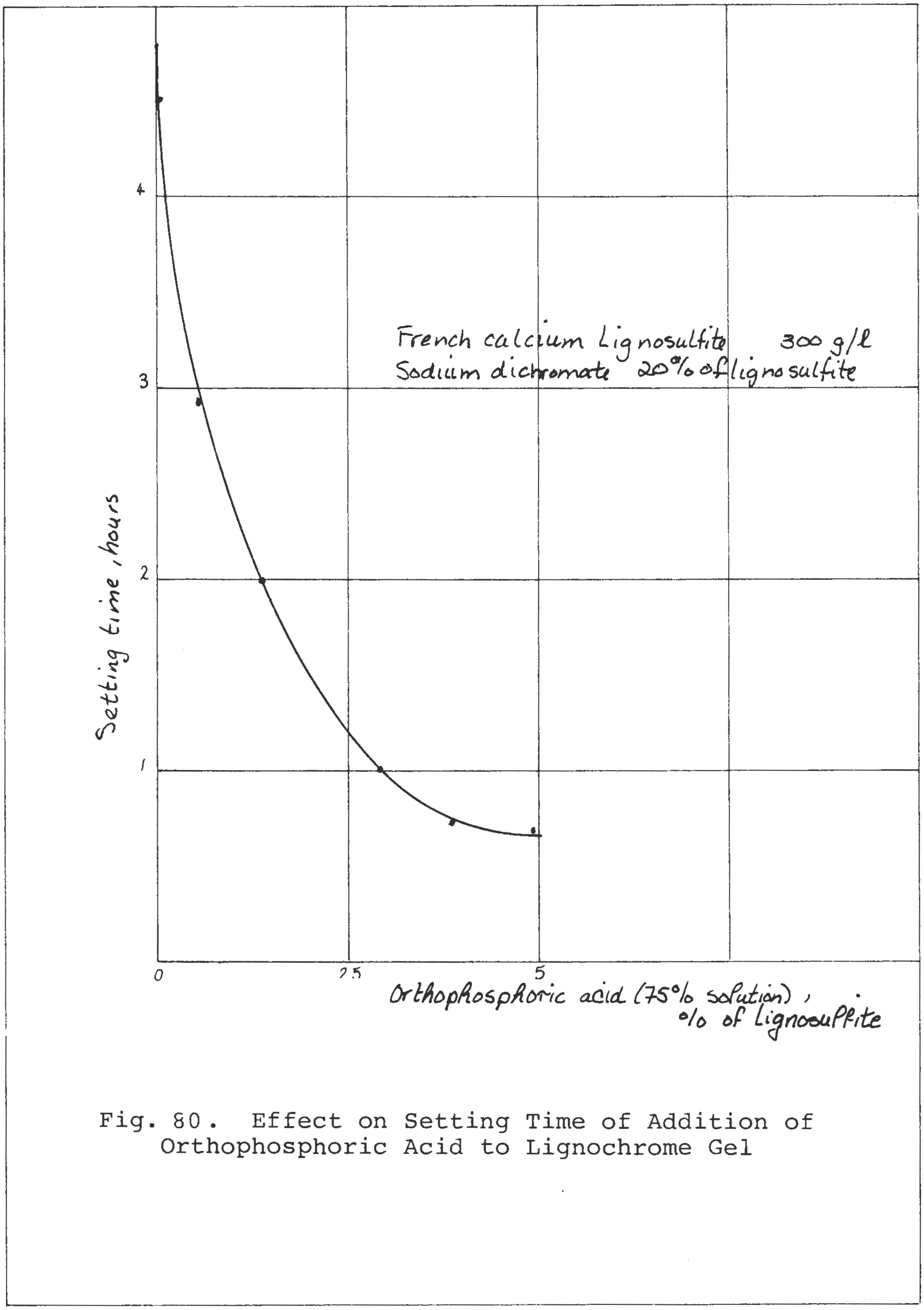


Fig. 80. Effect on Setting Time of Addition of Orthophosphoric Acid to Lignochrome Gel

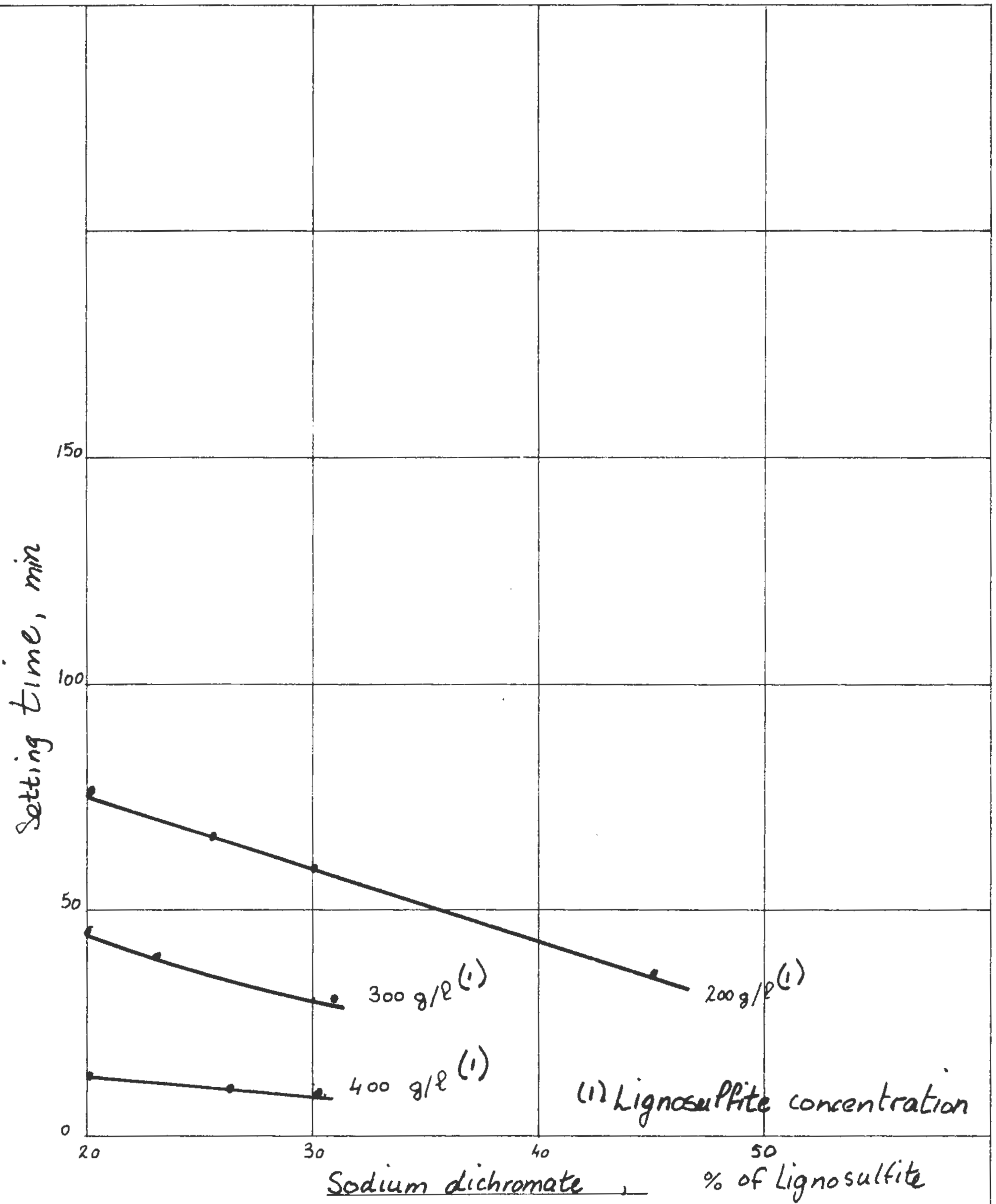


Fig. 81. Effect of Sodium Dichromate on Setting Time of French R Lignosulfonate for Various Lignosulfonate Concentrations

Lowering of the pH also has a very favorable effect on mechanical characteristics.

3. Intrinsic Strength of Pure Grout

3.1 Proportion of Basic Ingredients (lignosulfite and sodium dichromate)

Figs. 82 and 83 give the shear strengths of lignochrome gels as measured by the standard method, as recommended in Part Two, in relation to their sodium dichromate content, for three lignosulfite concentrations: 300, 400 and 500 grams/litre.

Those gels with higher lignosulfite concentrations are stronger, but it appears that the dichromate concentration also has an important effect on shear strength. Thus, the same strength can be obtained using variable proportions of lignosulfite and sodium dichromate, and the most economical mixture will take into account the relative prices of lignosulfite and sodium dichromate.

3.2 Nature and Origin of Lignosulfite

As lignosulfite is obtained from a rather broad variety of trees, its chemical composition is not clearly defined. The strength of the composition is affected by the nature as well as the origin of the lignosulfite. This effect is shown in fig. 84, for a constant lignosulfite concentration (400 grams/litre) of seven different lignosulfites.

The basic lignosulfite's reducing sugar content is certainly a major factor, since these sugars uselessly consume dichromate, but the basic lignosulfite's pH is also of paramount importance.

3.3 pH

Since, in its oxidation reaction with the lignosulfite, hexavalent chromium passes from a state of Cr^{6+} to Cr^{3+} only in an acid medium (fig. 79), it is obvious that the more acid the medium, the better will be the performance of the gel formed (lignosulfite and dichromate). An example is given in fig. 85.

This acidification can be accomplished with phosphoric acid (fig. 86) or with an acid salt such as monosodium phosphate, ferric chloride, and others, or with a preacidified lignosulfite such as French R lignosulfonate (fig. 87).

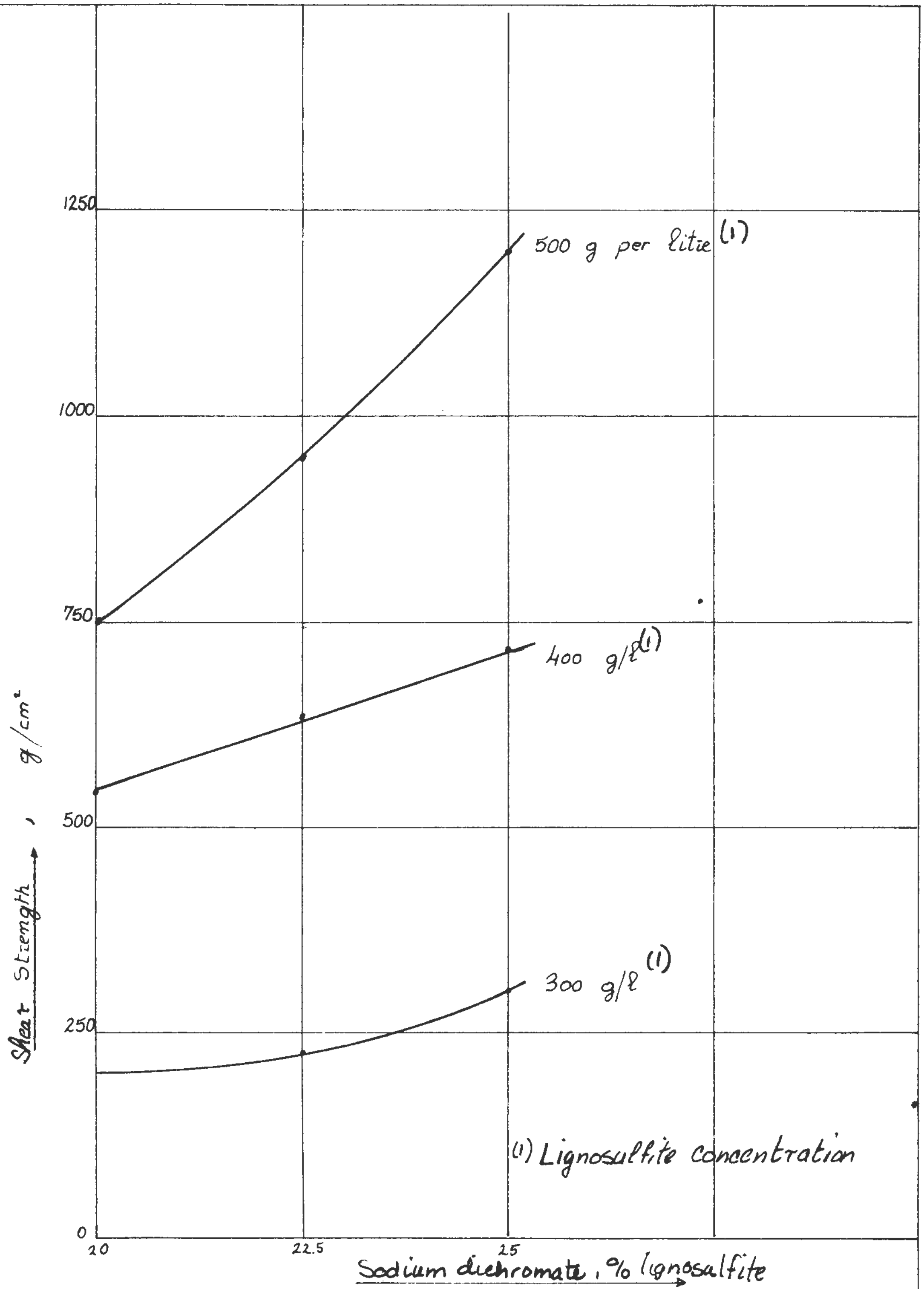


Fig. 82. Effect of Lignosulfite and Sodium Dichromate Concentration on Shear Strength of Pure Lignochrome Gels (Swedish Sodium Lignosulfite, WAFEX)

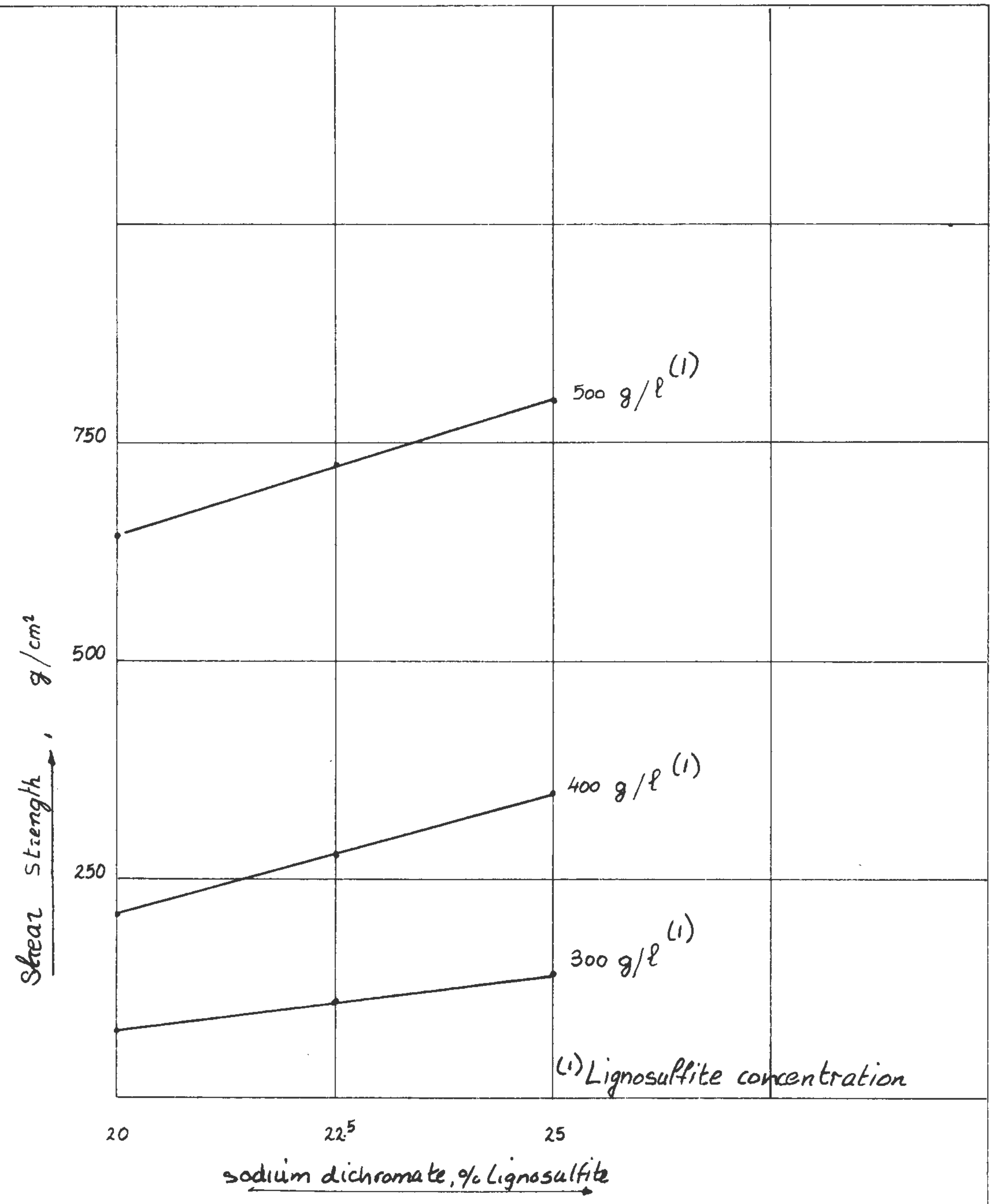


Fig. 83. Effect of Lignosulfite and Sodium Dichromate Concentration on Shear Strength of Pure Lignochrome Gels (English Calcium Lignosulfite)

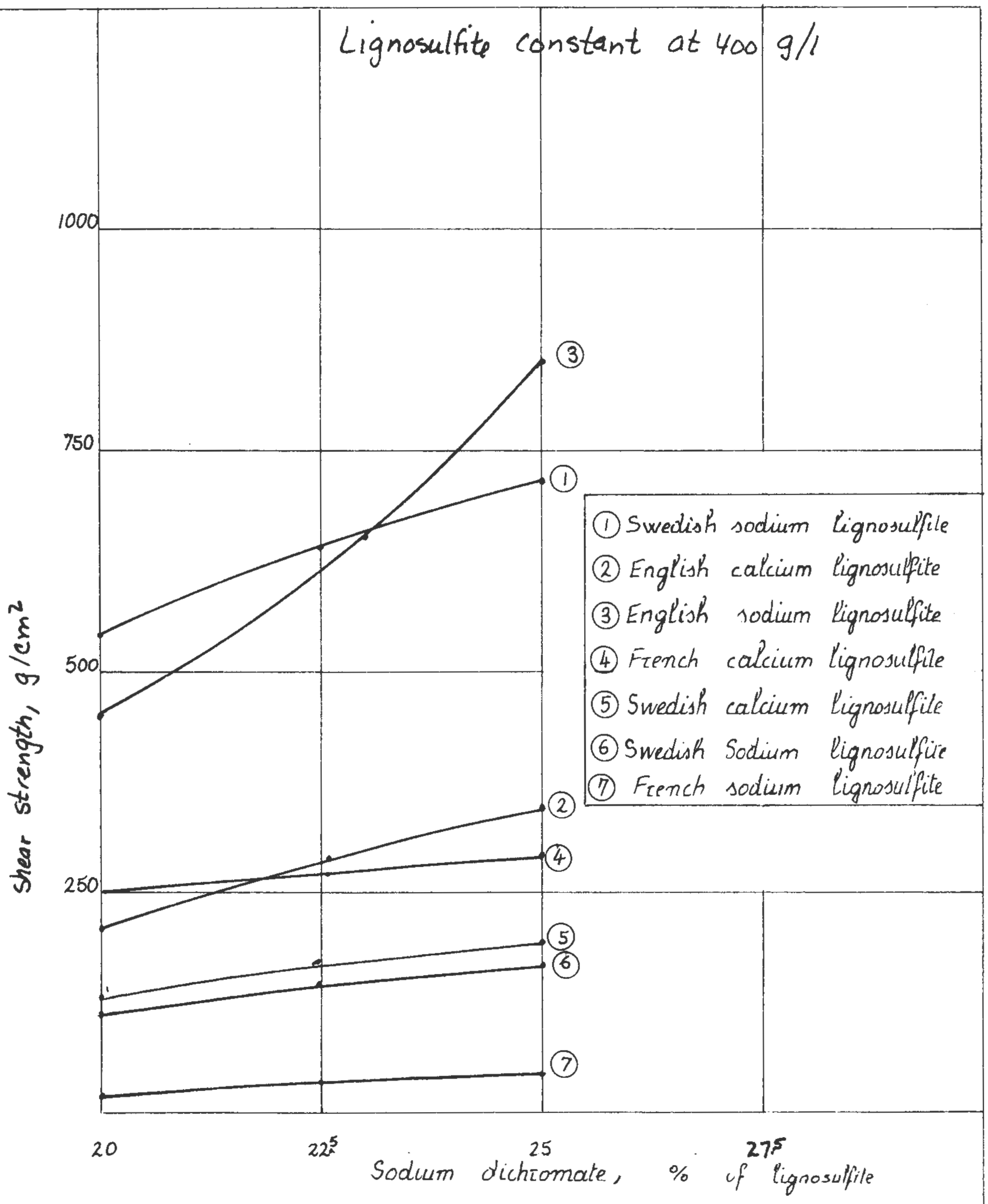


Fig. 84. Effect of Nature and Origin of Lignosulfite on Shear Strength of Pure Lignochrome Gel

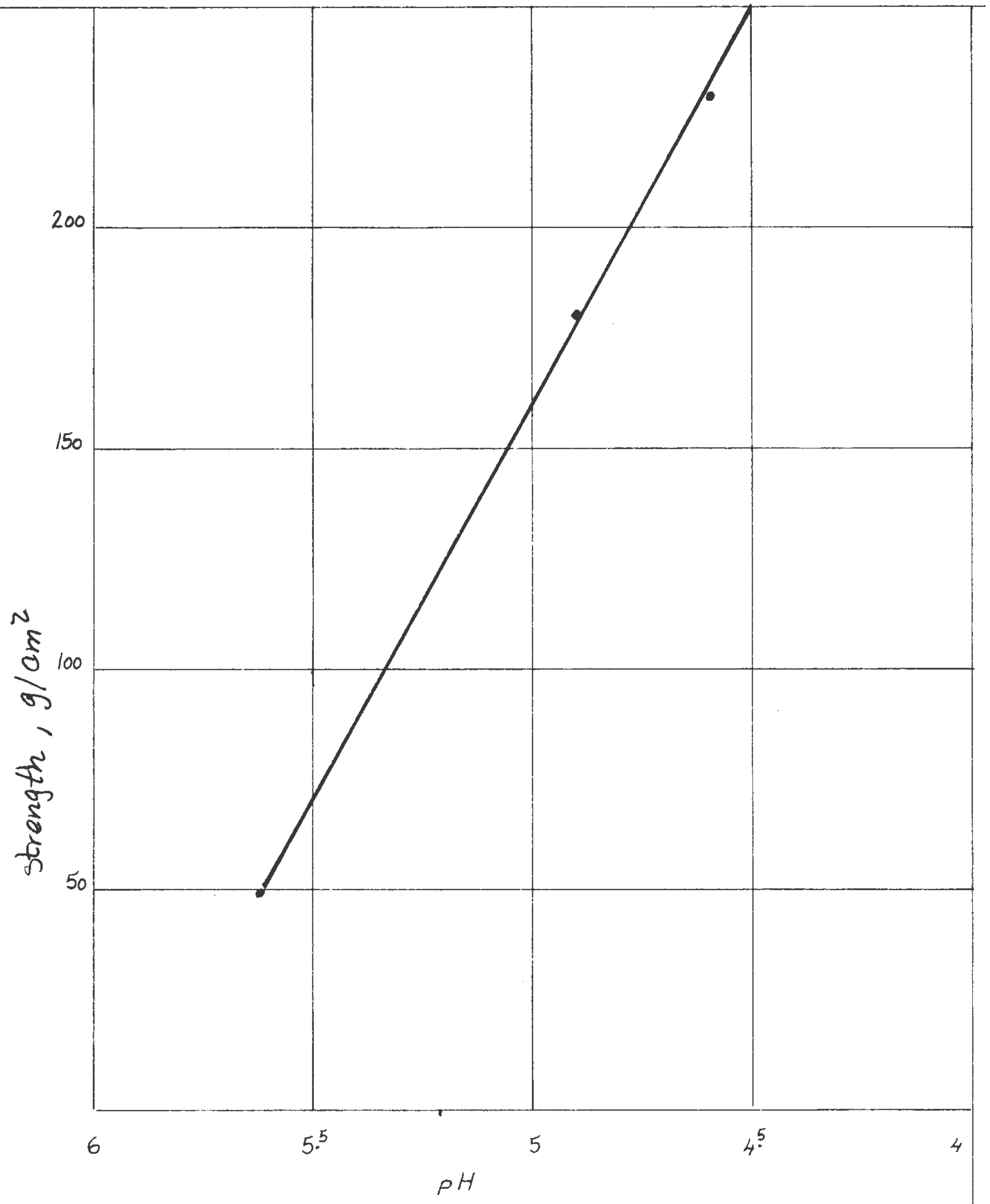


Fig. 85. Effect of pH on Shear Strength of Pure Lignochrome Gel (Calcium Lignosulfite)

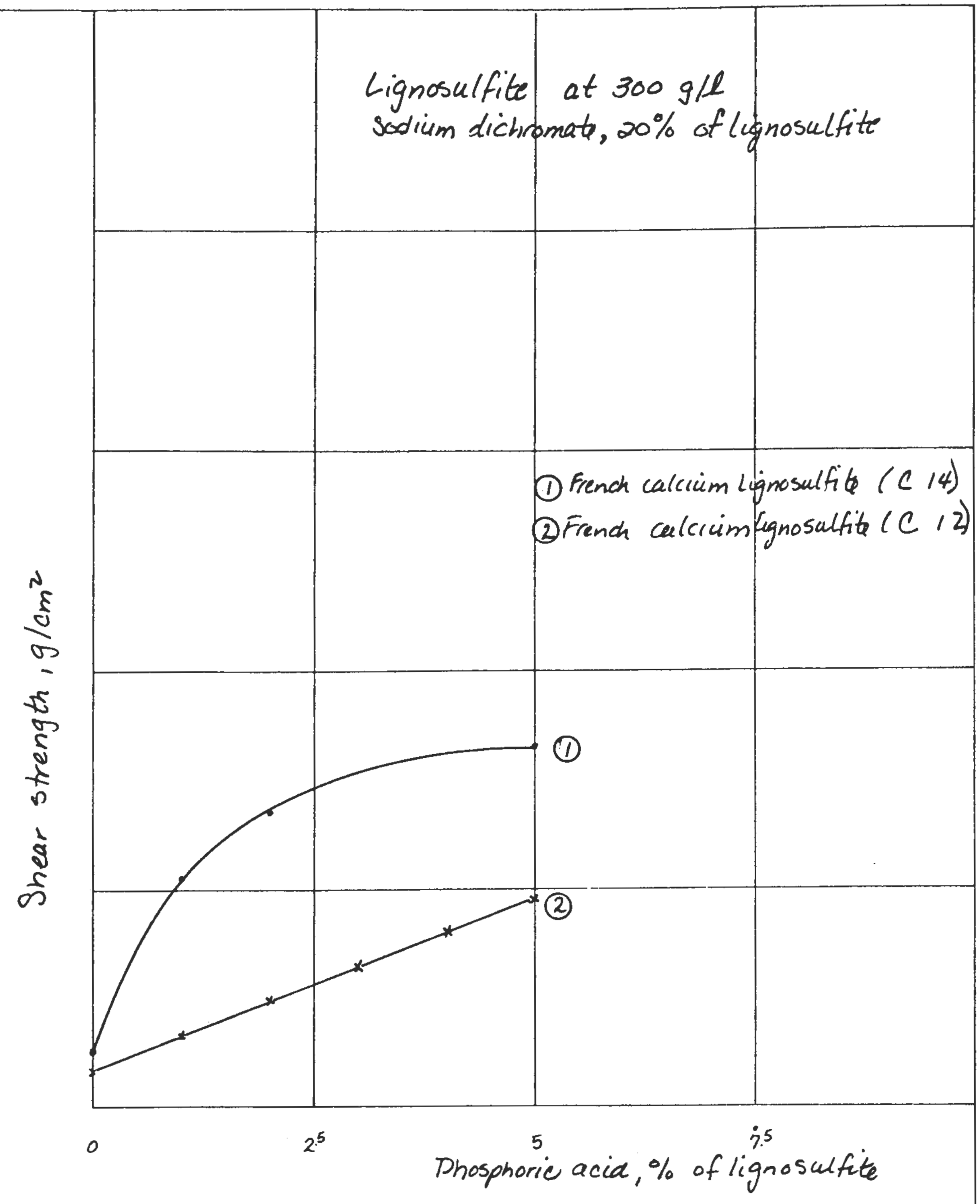


Fig. 86. Effect of Phosphoric Acid on Shear Strength of Pure Lignochrome Gels

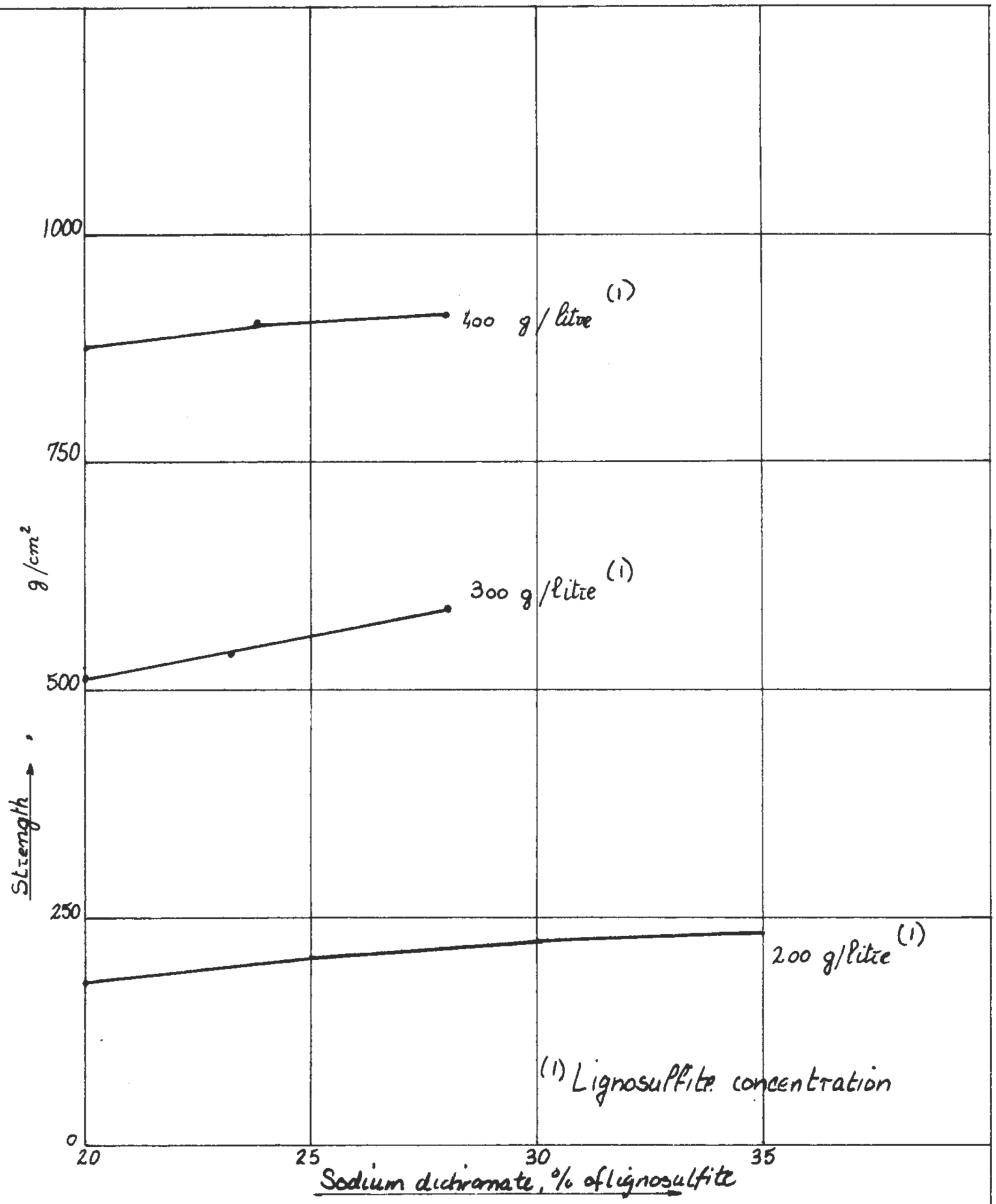


Fig. 87. Effect of Lignosulfite and Sodium Dichromate Concentration on Shear Strength of Pure Lignochrome Gel (French R Lignosulfite)

3.4 Shear Speed

The visco-plastic character of lignochrome gels is less pronounced than that of silica gels, but still sufficient to make them sensitive to shear speed.

Fig. 88 shows the effect of shear speed on a lignochrome gel with average characteristics, using the variable speed method described in the chapter on "Intrinsic Strength of Grout". The same ratio in the form $Rc = f\,\frac{(1)}{v}$ (fig. 89) demonstrates the effect of the duration of shear stress.

However, as with silica gels, the effect of shear speed will depend on the gel's composition and, notably, on the lignosulfonate's degree of gelification.

4. Strength of Treated Ground

Lignochrome gels are always made up of soluble and non-volatile products. As a result, test samples can be prepared by any method, which was not the case with silica gels.

Lignochrome gels are initially acid and, as noted above, an increase in acidity will have a favorable effect on the strength of the pure grout. In the ground, unless confronted by purely siliceous sands, acidity should be limited to a pH of about 4.5 to 5, a level corresponding to the carbonate attack threshold. It is thus inadvisable to use any lignochrome gel whose pH is under 4.5 for highly calcareous sands. This factor must be considered for grouting.

4.1 Proportion of Basic Ingredients in the Gel

The higher the lignosulfite content, the greater the strength, as shown in figs. 90 and 91 for two different lignosulfites. Given the high proportion of sodium dichromate used in lignochromes, an increase in this proportion will have relatively little effect on strength (figs. 90 and 91).

As noted previously, any lignochrome gel with a very low pH is inadvisable for use in highly calcareous sands.

4.2 Nature and Origin of the Lignosulfite

The effect of these two factors on the cohesiveness of pure gels decreases considerably with mortars, as shown in fig. 92 for 6 lignosulfites, all having lignosulfite levels of 400 g/l.

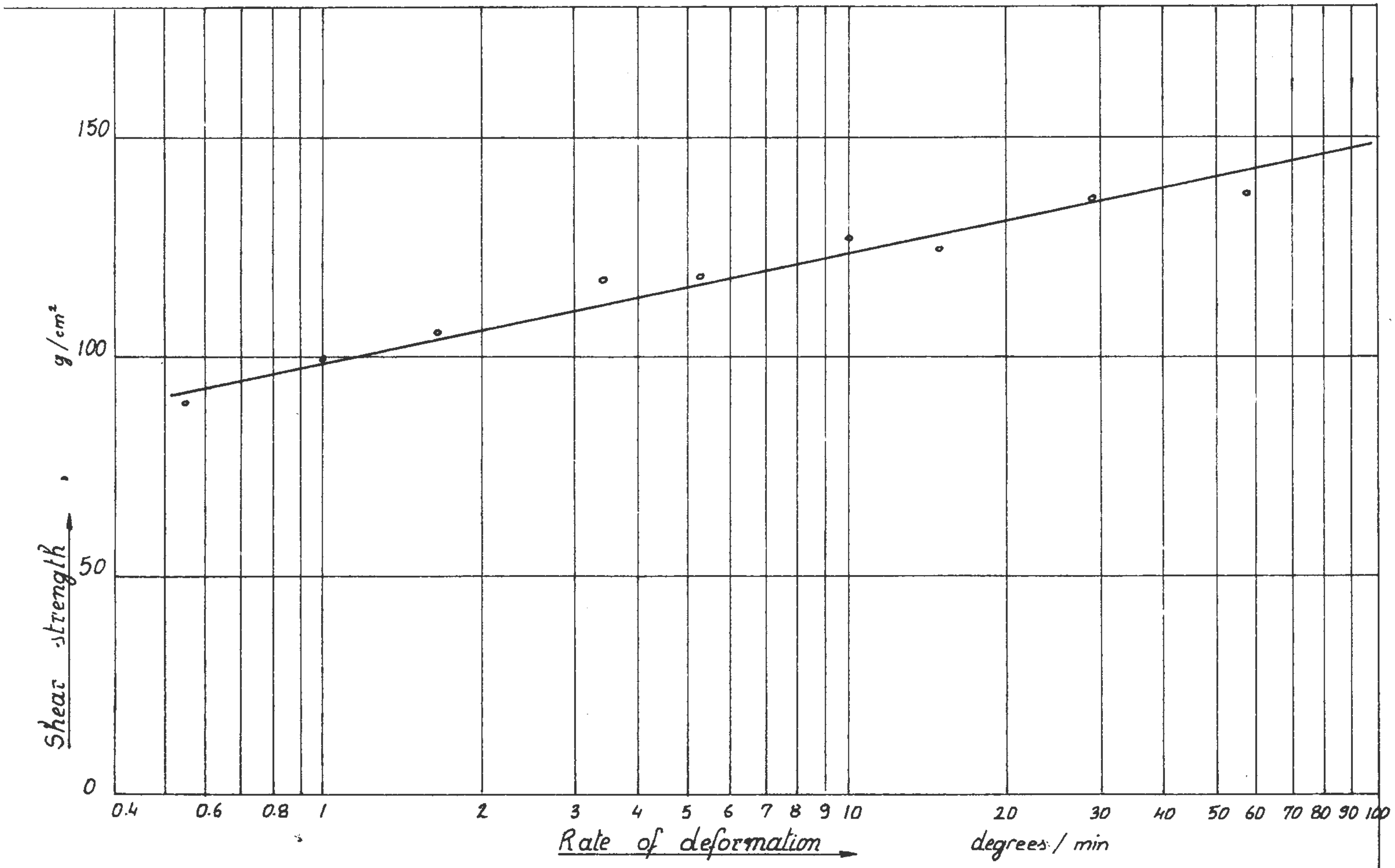


Fig. 88. Effect of Shear Speed on Strength of Lignochrome Gel

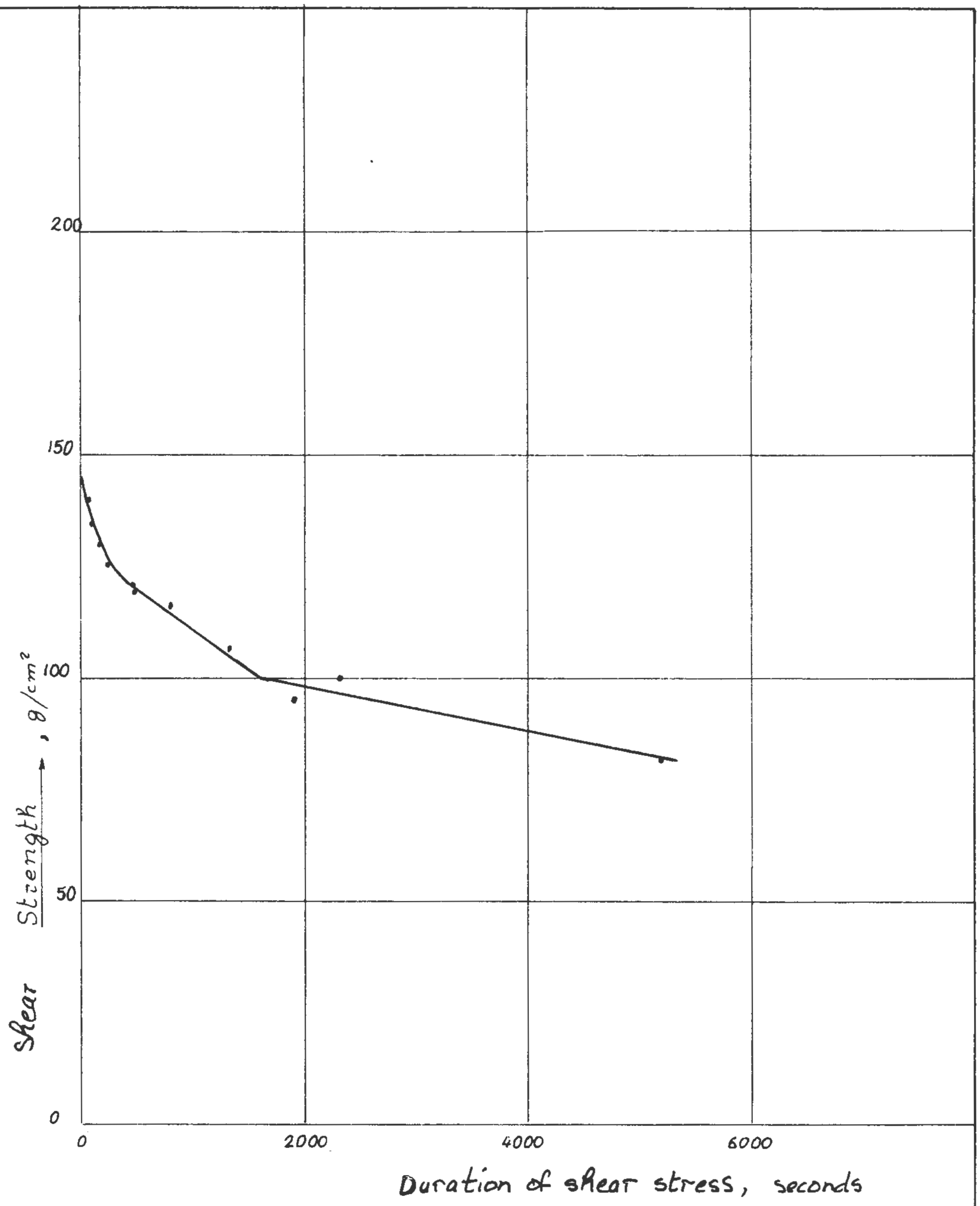


Fig. 89. Effect of Shear Duration on Strength of Lignochrome Gel

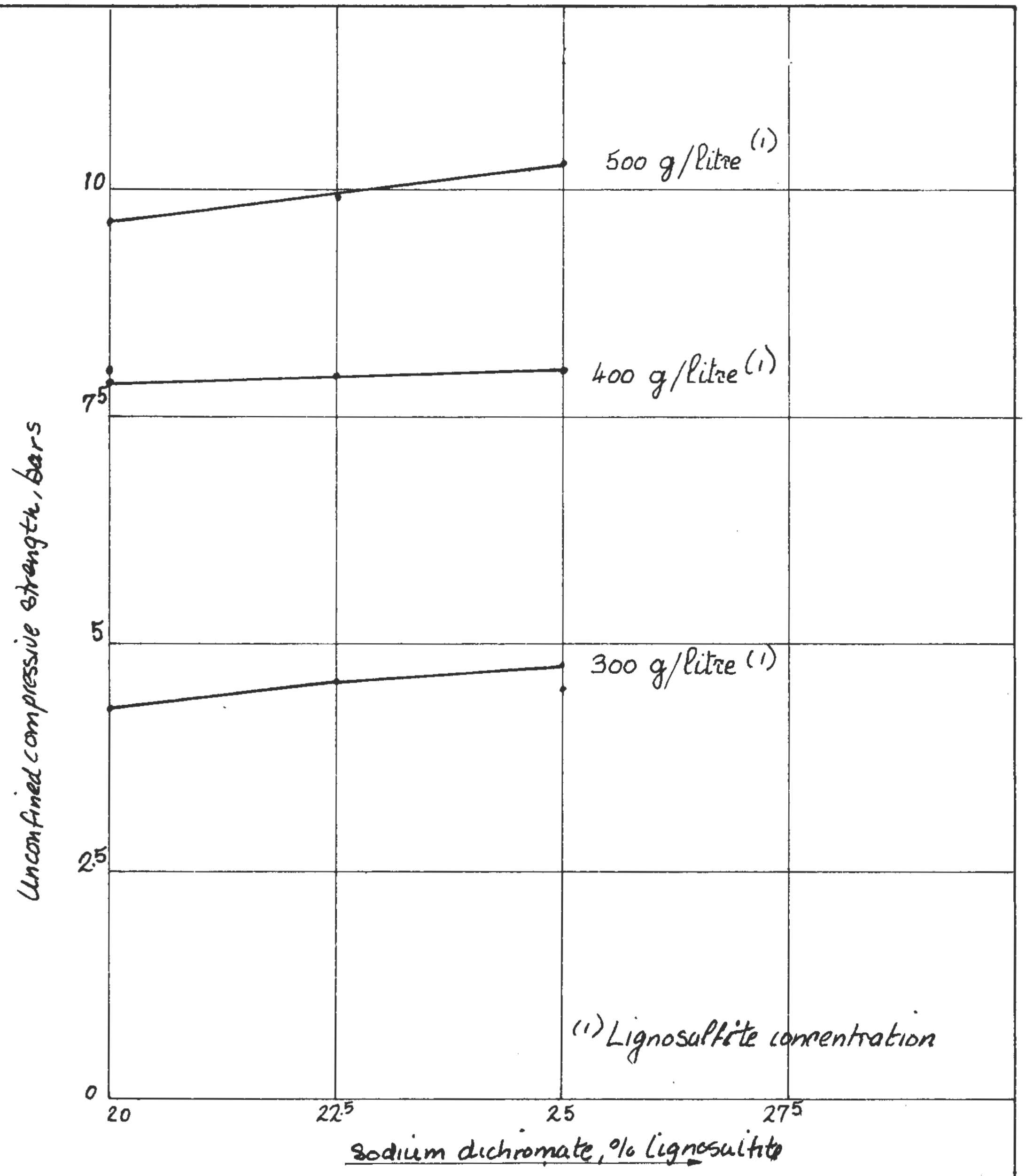


Fig. 90. Effect of Lignosulfite and Sodium Dichromate Concentration on Strength of Lignochrome Mortar (Swedish Sodium Lignosulfite, WAFEX)

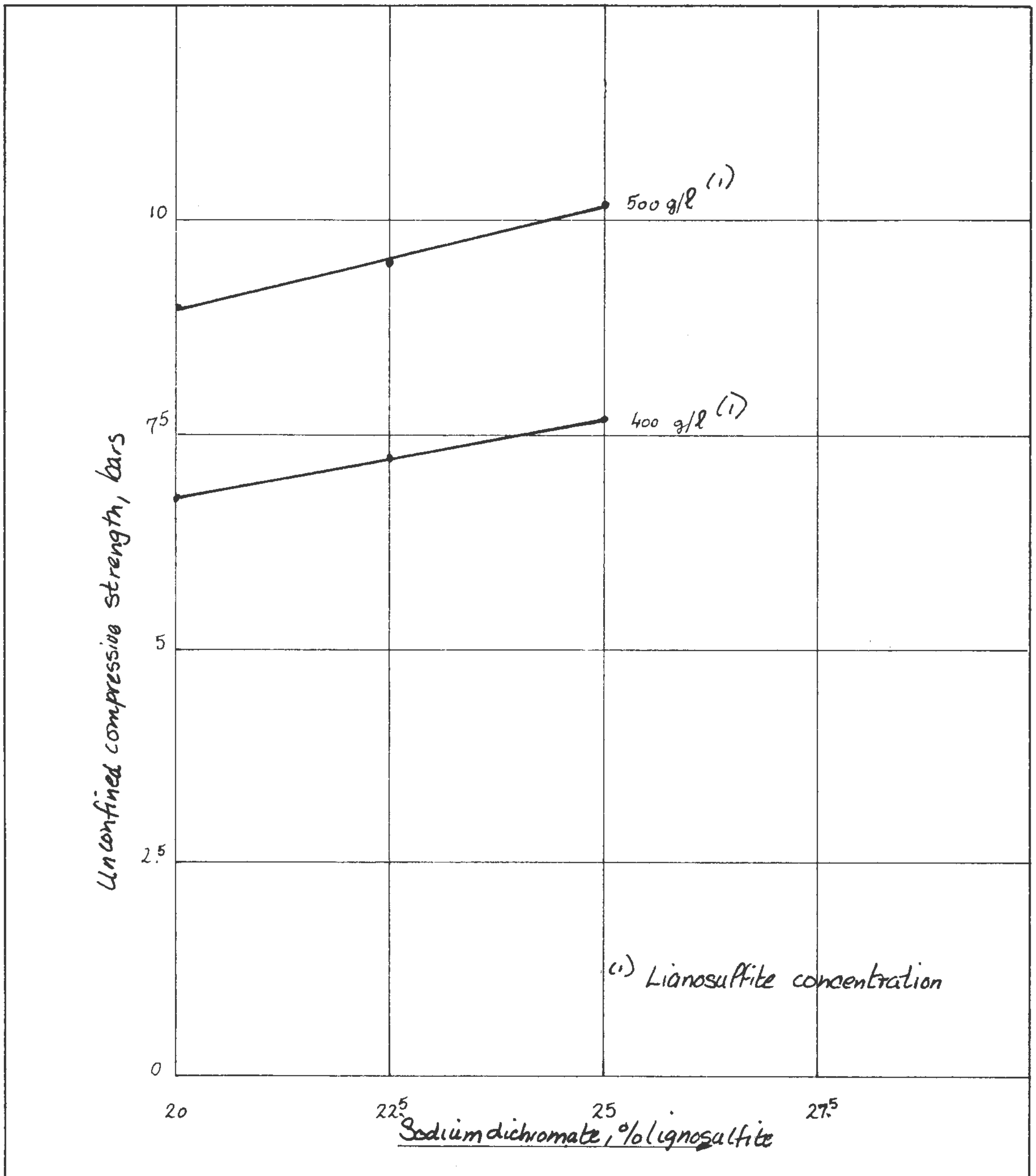


Fig. 91. Effect of Lignosulfite and Sodium Dichromate Concentration on Strength of Lignochrome Mortar (English Sodium Lignosulfite)

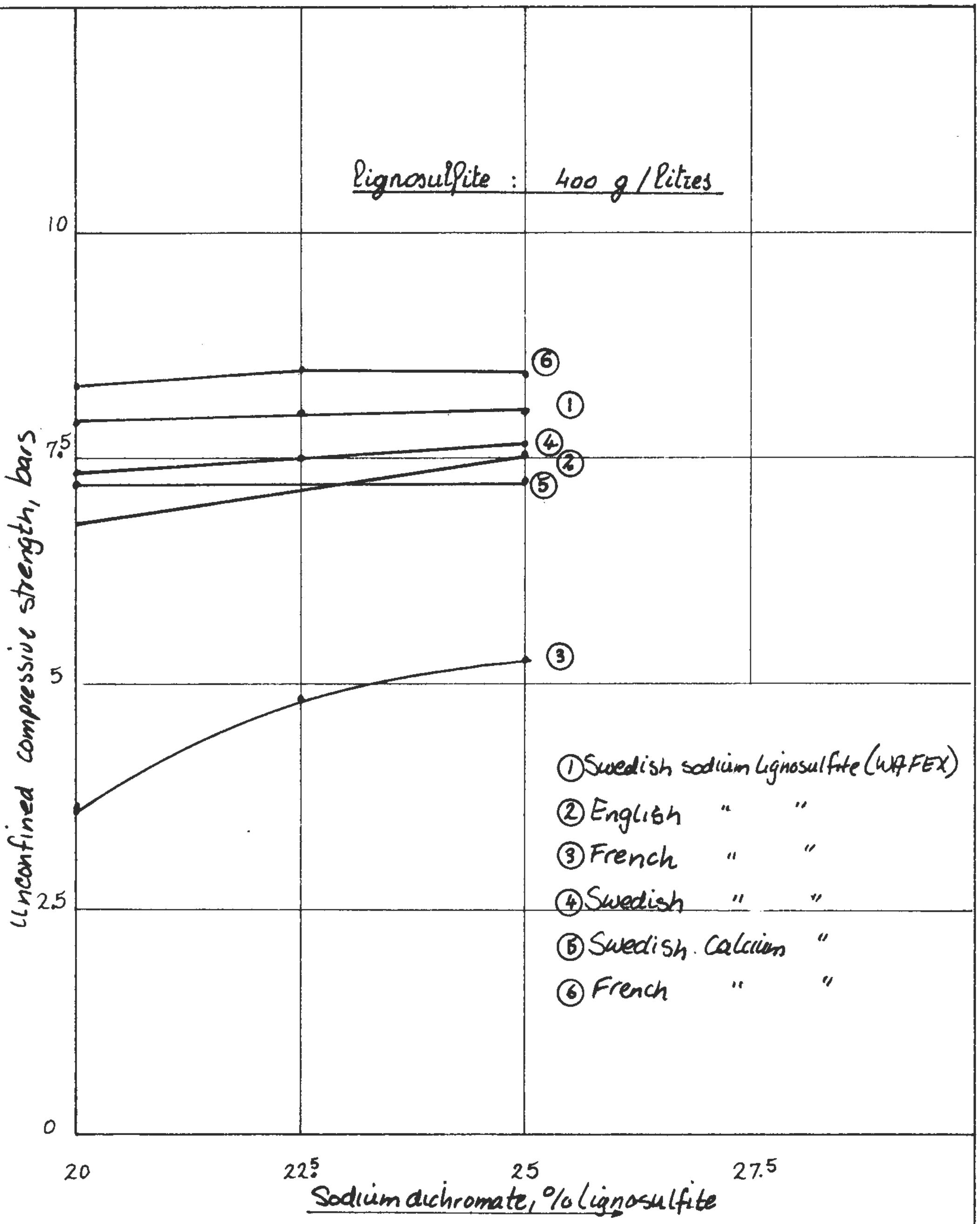


Fig. 92. Effect of Nature and Origin of Lignosulfite on Strength of Lignochrome Mortar

4.3 pH

The effect of pH on pure grout is also applicable for mortars, as long as it does not dip below 4.5. Thus, it may be helpful to make the mixture more acid, which produces greater cohesiveness and greater unconfined compressive strength. This result can be obtained through the addition of phosphoric acid. Fig. 93 shows a spectacular increase in strength for two lignochrome gels. Monosodium phosphate can also be used, producing an interesting phenomenon. In this case, the more dilute the substance is, the greater the relative increase will be.

Compounds such as ferric chloride or aluminum potassium sulfate have a very slight effect on mortar, but the effect disappears completely with sodium lignosulfites.

4.4 Unconfined Compression Speed

All the preceding results are for unconfined compressive strength recorded for a strain rate of 20 mm/min. As noted in Part One, standard testing for the strength of treated ground, crushing speed has an important effect on the strength of mortars.

We have subjected a lignochrome gel with average characteristics to different crushing speeds. Fig. 94, as well as table 26, shows that there is a ratio of two between the strength readings obtained at standard speed (underlined in the table) and those obtained at the slowest speed used in the test. The slowest speed used in the test is still fast compared with naturally occurring strain rates.

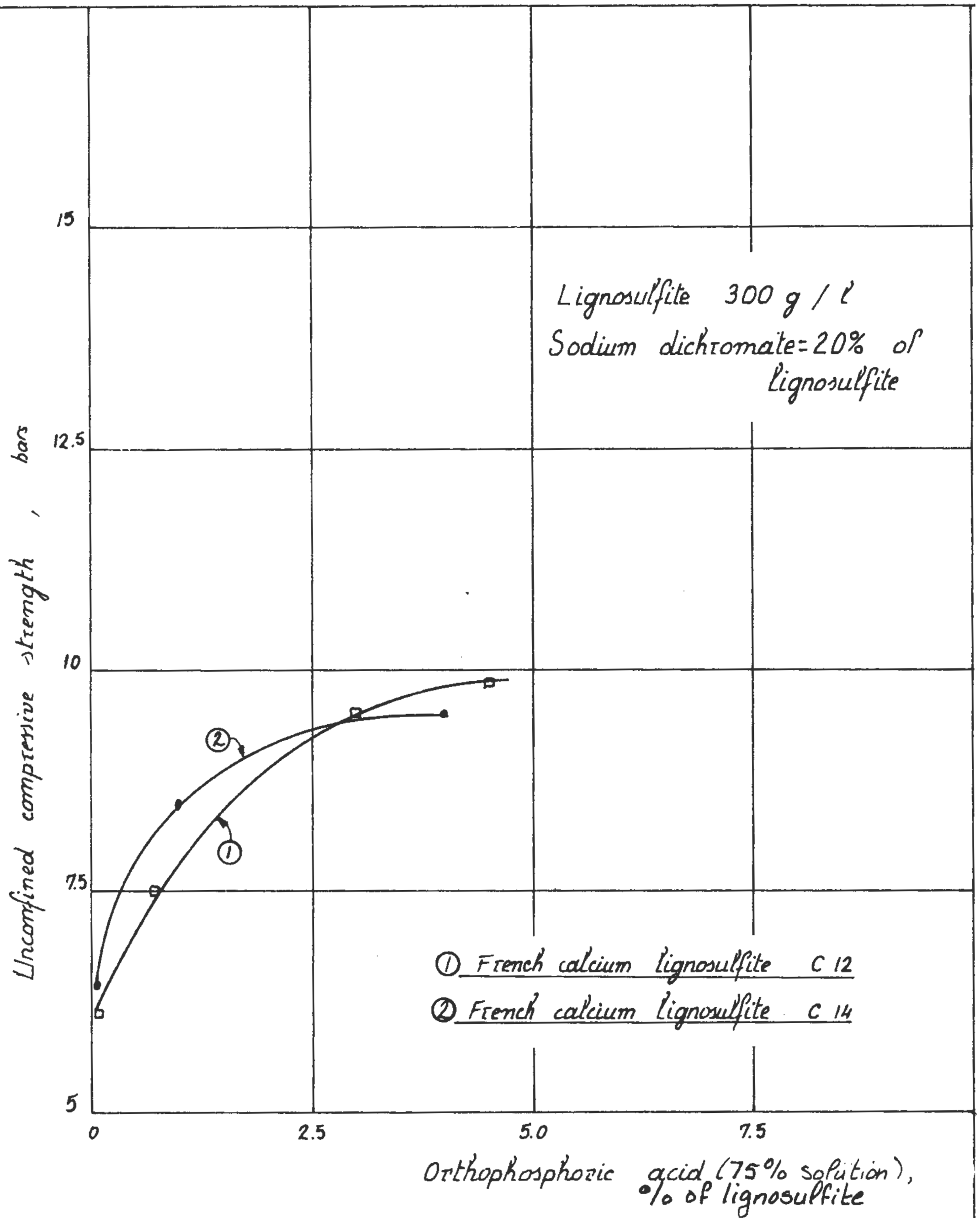


Fig. 93. Effect of Orthophosphoric Acid on Strength of Lignochrome Mortar

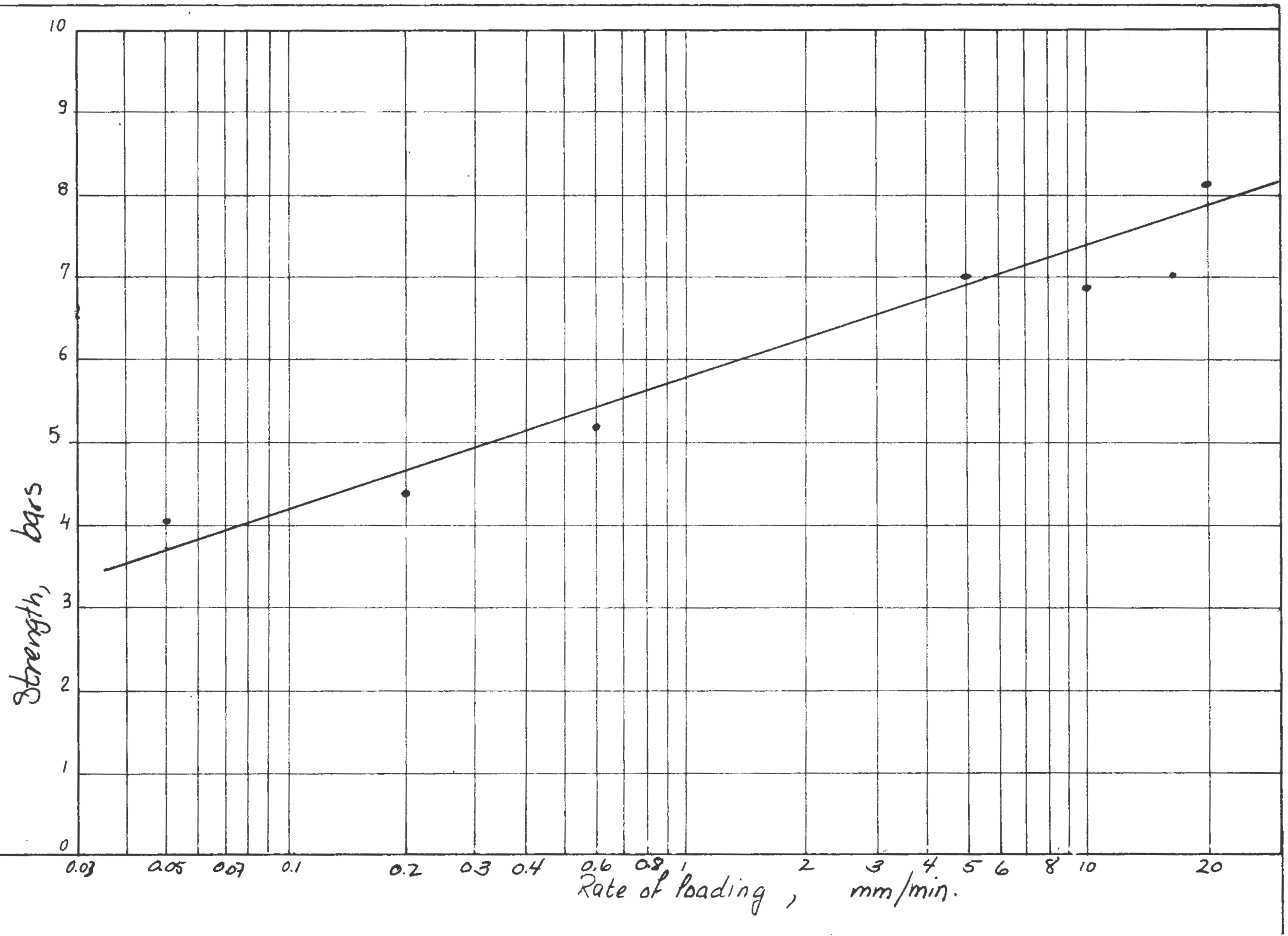


Fig. 94. Effect of Testing Speed on Unconfined Compressive Strength of Lignochrome Gel

Table 26. Effect of Testing Speed on Strength

Rate of Loading, mm/min	Unconfined Compressive Strength at 48 hrs,bars
0.05	4.1
0.2	4.4
0.5	5.2
5	7.0
10	6.7
20	8.2
50	8.4

5. Durability

Of the two phenomena to which silica gels are subjected after they set, syneresis and dissolution in an excess of water, the first does not occur with lignochrome gels. In fact, even where the support is coarse, there is good preservation over time of the material filling the voids, whatever the composition of the gel used. This phenomenon has a very definite effect on changes in the permeability coefficient. For the second phenomenon, dissolution in an excess of water, it might be feared that the behavior of lignochrome gels would be the same as that of silica gels.

As with all aqueous grouts, lignochrome gels contain a large proportion of water, with the inherent risk of dessication in a dry medium, which would affect mechanical characteristics.

5.1 Hermetic Mold Cure

For concentrated gels with short setting times, 90% of the final strength is attained the day after injection. For highly dilute gels with longer setting times, this threshold is attained after 7 days. There is no subsequent drop in strength such as that observed with silica gels, since the syneresis phenomenon does not occur.

5.2 Dry Cure

Fig. 95 shows the results of studies by the U.S. Bureau of Reclamation and Cornell University, indicating the abnormally high strength readings obtainable with lignochrome mortars under air cure (curves 1 and 2). The increase in strength is particularly pronounced over the first days.

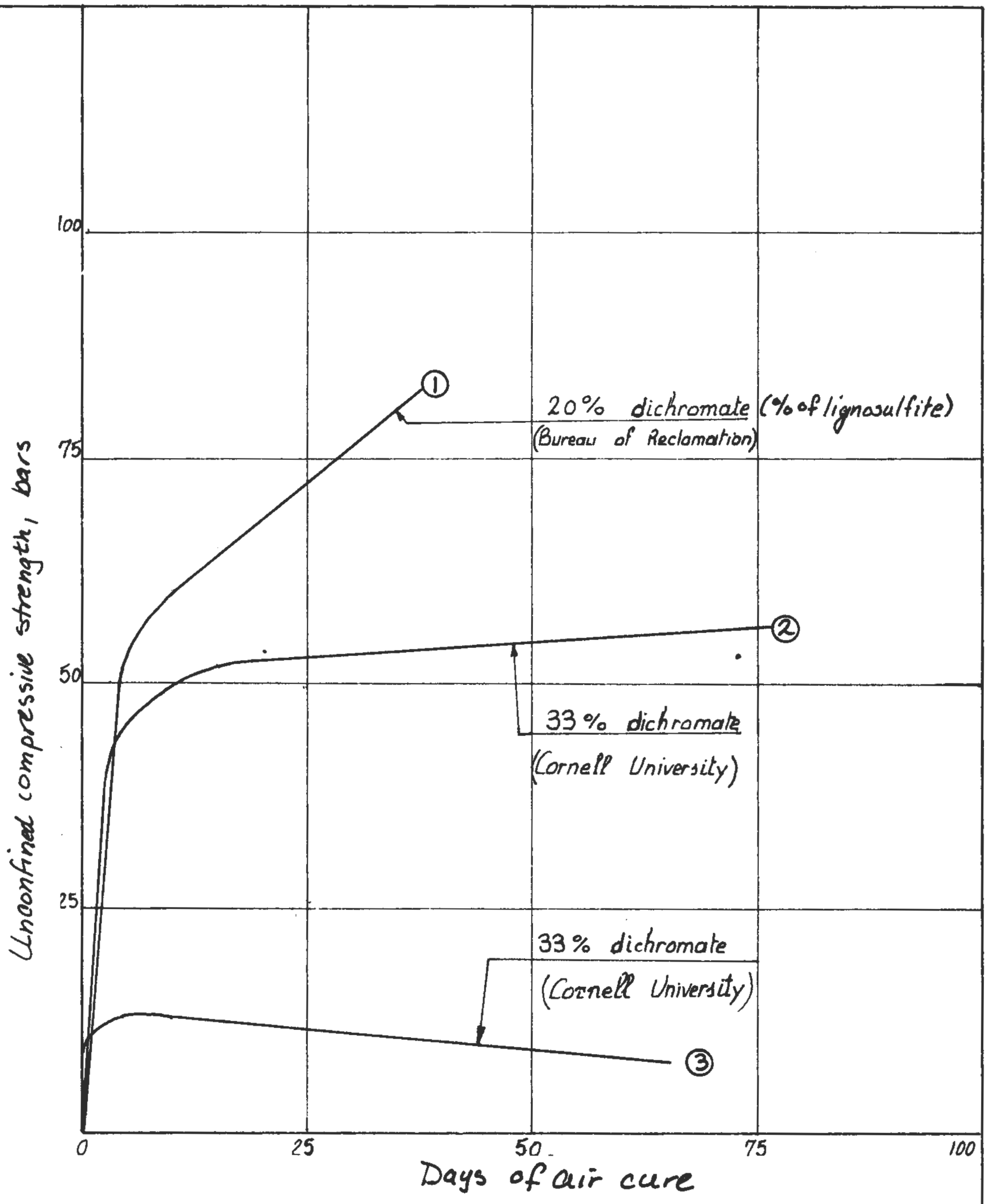


Fig. 95. Effect of Dry Curing on Strength of Lignochrome Gel

(52-17)

No apparent drop in strength was noted over time, even though the matrix of the gel in these test samples was subjected to a major disturbance. This phenomenon is shown indirectly in curve 3 of fig. 95. Identical test samples were dry cured for a rather long period, and then immersed in water 24 hours before the crushing test, resulting in greatly decreased strength. This effect is explained by the loss of a large proportion of the gel's water content and, therefore, its agglomerating power.

5.3 Wet Cure

Results reported by R. W. BURROWS, H. J. GIBBS and H. M. HUNTER (Bureau of Reclamation Construction) (52-17) show that immersion of lignochrome mortars in water does not disturb them as long as the immersion is continuous (curves 1, 2 and 4 in fig. 96). However, any drying in the air, even for a brief period, before or after immersion, will cause pronounced weakening of mechanical characteristics, as shown on curves 3 and 5 of the same figure. This last finding confirms the disturbing effect of dry cure.

JULIAN C. SMITH (52-05) asserts, without further details, that test samples of lignochrome mortar immersed for a period of months showed no decrease in watertightness. Our tests of erosion by immersion showed no notable changes either in the weight or the strength of immersed samples.

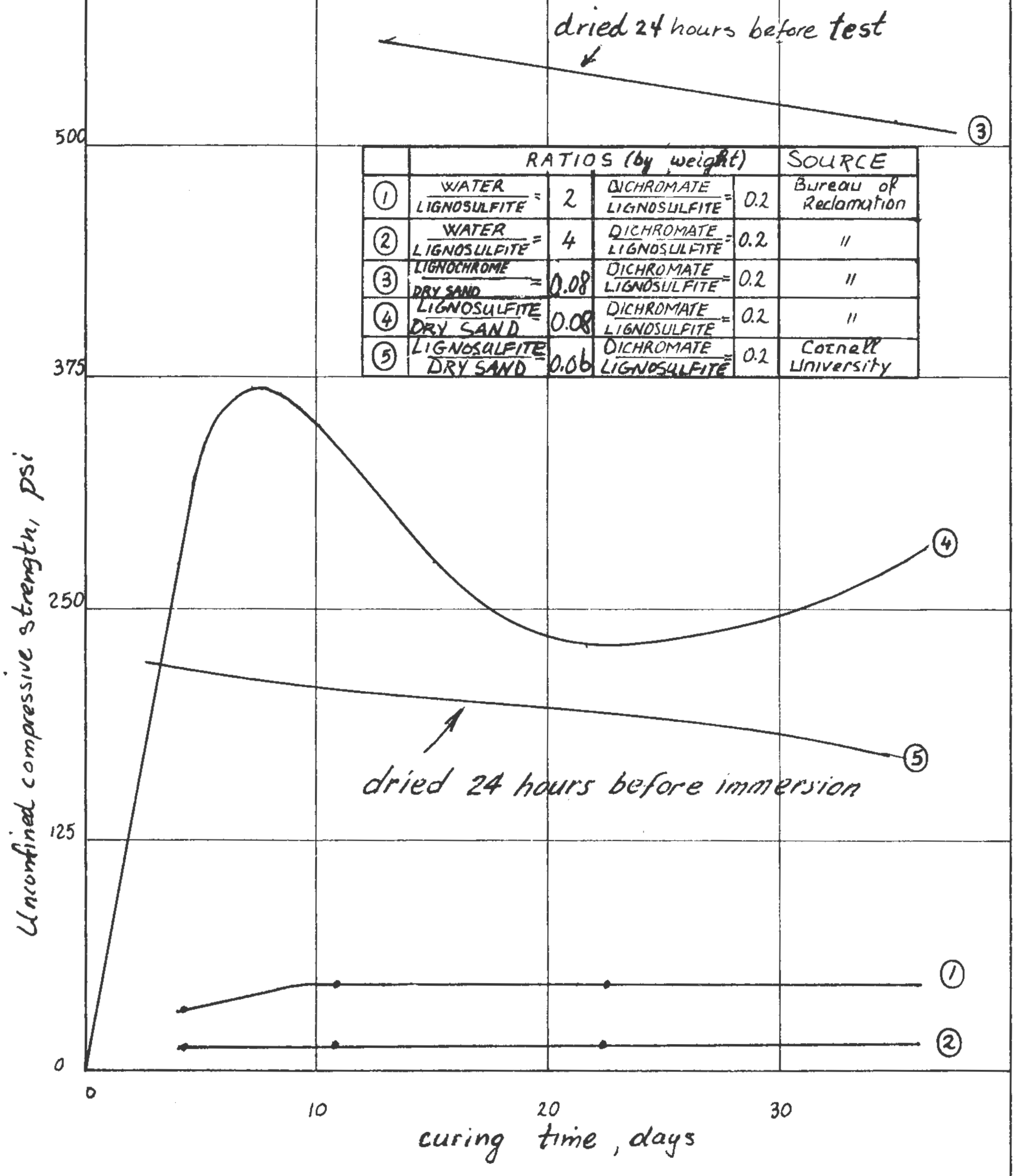
5.4 Alternate Drying and Wetting Cycles

Fig. 97 shows the changes in strength of a lignochrome gel subjected to drying and wetting cycles. Although the first drying cycle is very beneficial to the sample, this benefit is gradually lost over the ensuing cycles (52-17).

5.5 Percolation Under Pressure

The literature offers only fragmentary information about this type of cure. WESTON and KENNERLY (58-15) indicate good behavior for lignochromes, but do not give further details.

On mixtures containing a radioactive Strontium 90 nitrate dissolved in the water used to dilute the gel, CARON, GAILLEDREAU and BELOT (52-21) indicate losses of Strontium 90 of approximately 24% after 12 days.



	RATIOS (by weight)				SOURCE
①	$\frac{\text{WATER}}{\text{LIGNOSULFITE}}$ =	2	$\frac{\text{DICHROMATE}}{\text{LIGNOSULFITE}}$ =	0.2	Bureau of Reclamation
②	$\frac{\text{WATER}}{\text{LIGNOSULFITE}}$ =	4	$\frac{\text{DICHROMATE}}{\text{LIGNOSULFITE}}$ =	0.2	"
③	$\frac{\text{LIGNOCHROME}}{\text{DRY SAND}}$ =	0.08	$\frac{\text{DICHROMATE}}{\text{LIGNOSULFITE}}$ =	0.2	"
④	$\frac{\text{LIGNOSULFITE}}{\text{DRY SAND}}$ =	0.08	$\frac{\text{DICHROMATE}}{\text{LIGNOSULFITE}}$ =	0.2	"
⑤	$\frac{\text{LIGNOSULFITE}}{\text{DRY SAND}}$ =	0.06	$\frac{\text{DICHROMATE}}{\text{LIGNOSULFITE}}$ =	0.2	Cornell University

Fig. 96. Effect of Wet Cure on Strength of Lignochrome Gel

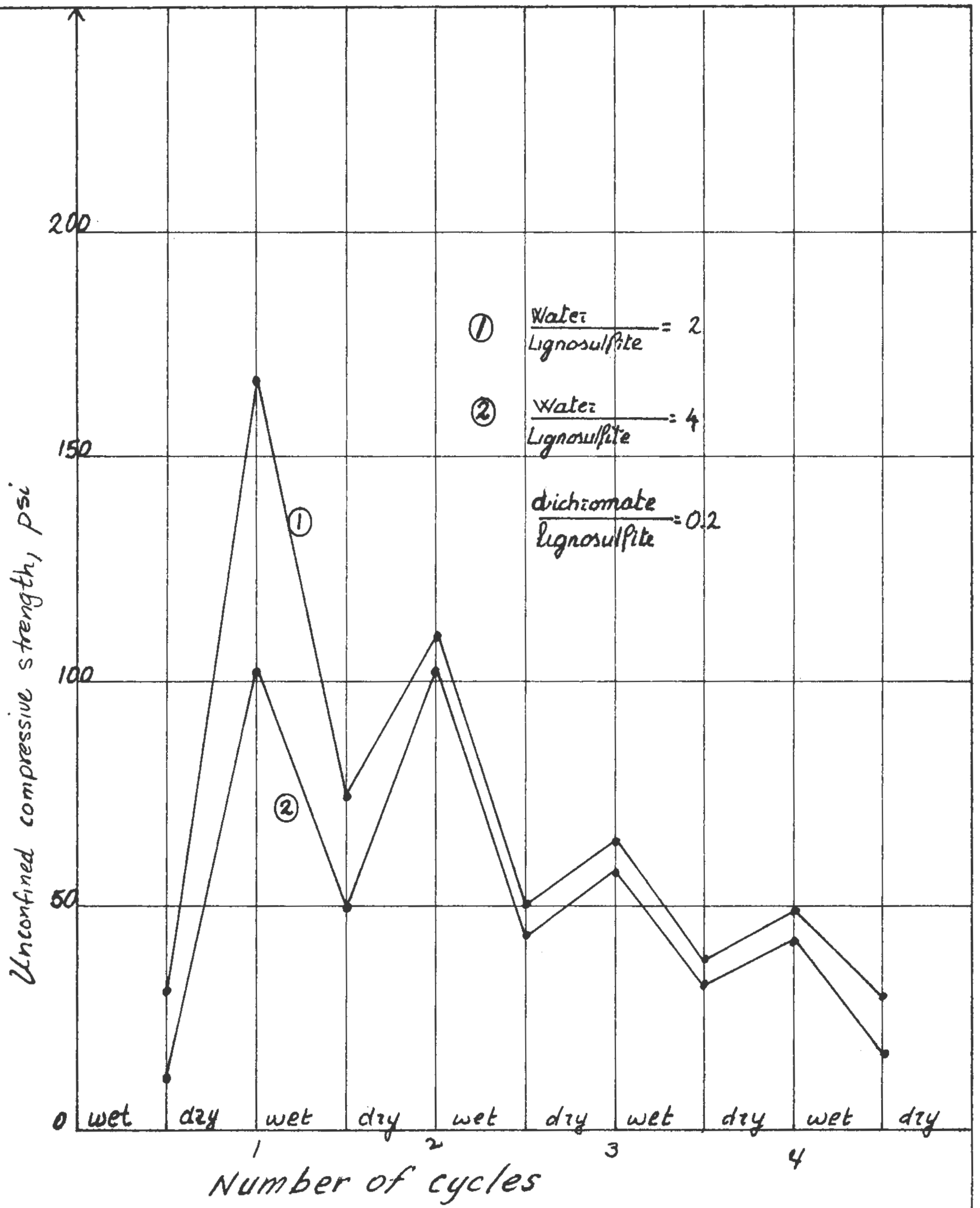


Fig. 97. Effect of Drying-Wetting Cycles on Strength of Lignochrome Gel

(52-17)

A. WESTON and R. A. KENNERLEY (58-15) have classified gels according to their stability by using as a criterion the nature of the lignosulfite's cation. Calcium lignosulfonate seems to perform slightly better than ammonium lignosulfonate. The stability of a sodium lignosulfonate-base gel is ranked very low. They further indicate that the most dilute gels are slightly less stable.

By the recommended percolation test, we have measured changes in permeability over time in a lignochrome gel with the following composition:

water	100 g
calcium lignosulfite	400 g
sodium dichromate	80 g

The results shown on fig. 98 indicate that this type of gel is stable.

6. Toxicity

6.1 Toxicity of Base Ingredients

6.11 Lignosulfites

These products are not dangerous. However, health regulations require the use of a mask to protect the respiratory tract for anyone handling these products in powder form.

6.12 Reagents

It is dangerous to ingest sodium dichromate, the basic reagent used with lignochromes. All necessary precautions should be taken. As it is in crystallized form, there is no risk of inhalation.

Table 27, summarizes the toxicity of some other reagents which can be included in lignochrome gels; most are relatively harmless.

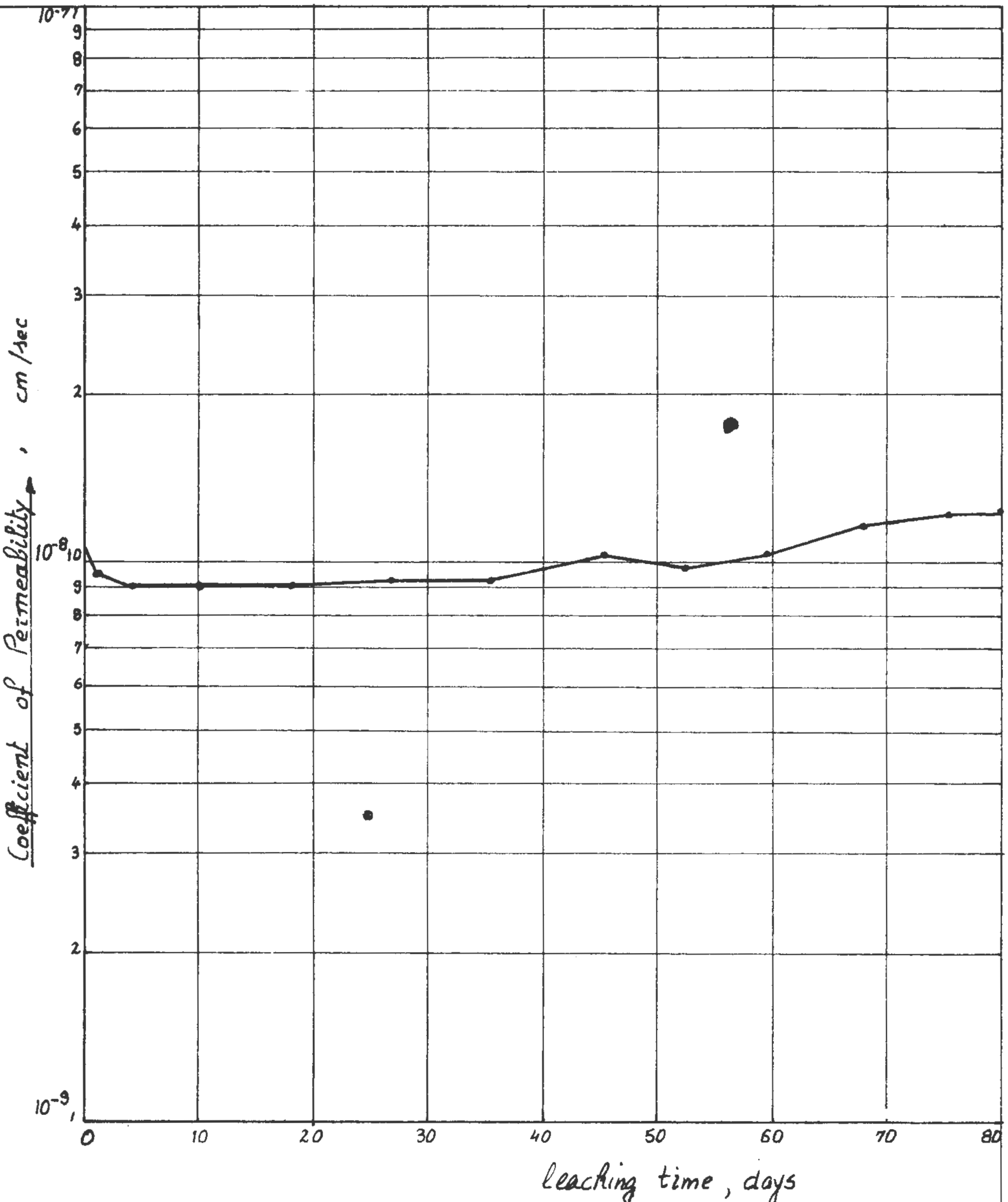


Fig. 98. Effect of Time on Permeability of Lignochrome Gel

Table 27. Toxicity of Reagents Used With Lignochrome Gels

Reagent	Dosage in mg/kg, DL 50		
	oral, rat	ipr, mouse	Miscellaneous
ferric chloride	900	68	
aluminum "	3700		oral mouse, 3800
copper sulfate	300	7	
aluminum sulfate		270	
sulfuric acid	2140		
orthophosphoric acid	1530		rabbit skin, 2740

NOTE: oral: orally
ipr: intraperitoneal
DL 50: dose causing 50% mortality rate

6.2 Toxicity of Fresh Lignochromes

It is dangerous to ingest fresh lignochrome, due to the presence of hexavalent chromium in the sodium dichromate. ATHERTON and GARRETT (59-05) mention dermatoses contracted by its handlers. It is also important to prevent leaks and contamination of ground water outside the mixing plant. The United States Public Health Service tolerates no more than 0.05 PPM of hexavalent chromium in drinking water; this is the approximate level of the chromium content in the unset grout. Thus, all necessary precautions must be taken.

6.3 Toxicity of Hardened Lignochromes

Highly toxic hexavalent chromium is reduced to non-toxic trivalent chromium in a polymerized lignochrome gel (CARON 63-03). However, carelessness with regard to stoechiometric proportions, always possible at a worksite, or slowness of the reaction, can bring about a release of hexavalent chromium. Several authors have measured the amount of time during which hexavalent chromium can be released.

Tests conducted by the U.S. Bureau of Reclamations show that, after erosion, 7-day old samples released about 4 times less hexavalent chromium than did those

24 hours old. These tests were further refined by ALLETTE WESTON and R. A. KENNERLEY (58-15). Fig. 99, which summarizes their measurements, shows that after about 15 days of aging , the gel releases practically no more hexavalent chromium, while the release of non-toxic trivalent chromium continues for a longer time.

In the preparation of this product it is absolutely necessary to have the proper facilities to ensure accurate measuring of proportions and thus minimize possibilities of hexavalent chromium in the hardened grout. When proportions are correct and the formula thoroughly homogenized, there will be no excess of chromium, and the grout will not be toxic. This has been confirmed by research in the RHONE POULENC Company toxicology laboratory on the following polymerized lignochrome gel.

Composition

lignosulfite C_{12}	400 g
water	1000 g
sodium dichromate	80 g

Physical Appearance

A black gelatinous mass.

Test Conditions

-CD rats (C.O.B.S.)[1]from the CHARLES RIVER FRANCE farm, weighing 150 to 185 g, unfed for 24 hours prior to administration of substance. 10 rats: 5 males, 5 females.

-Product put into suspension with a Teflon-headed grinder in a 10% gum arabic aqueous solution and adminitered by oesophagal tube.

-Dosage level: 15 g/kg p.o., in two administrations, with an interval of 3 hours, of 20 ml/kg of a 37.5% suspension.

-Duration of observation period: 15 days, with rats weighed every 5 days.

-Sacrificed by intravenous injection of sodium pentobarbital and autopsied on the 15th day for macroscopic examination of the principal thoracic and abdominal viscera.

---

[1] Caesarian Originated, Barrier Sustained

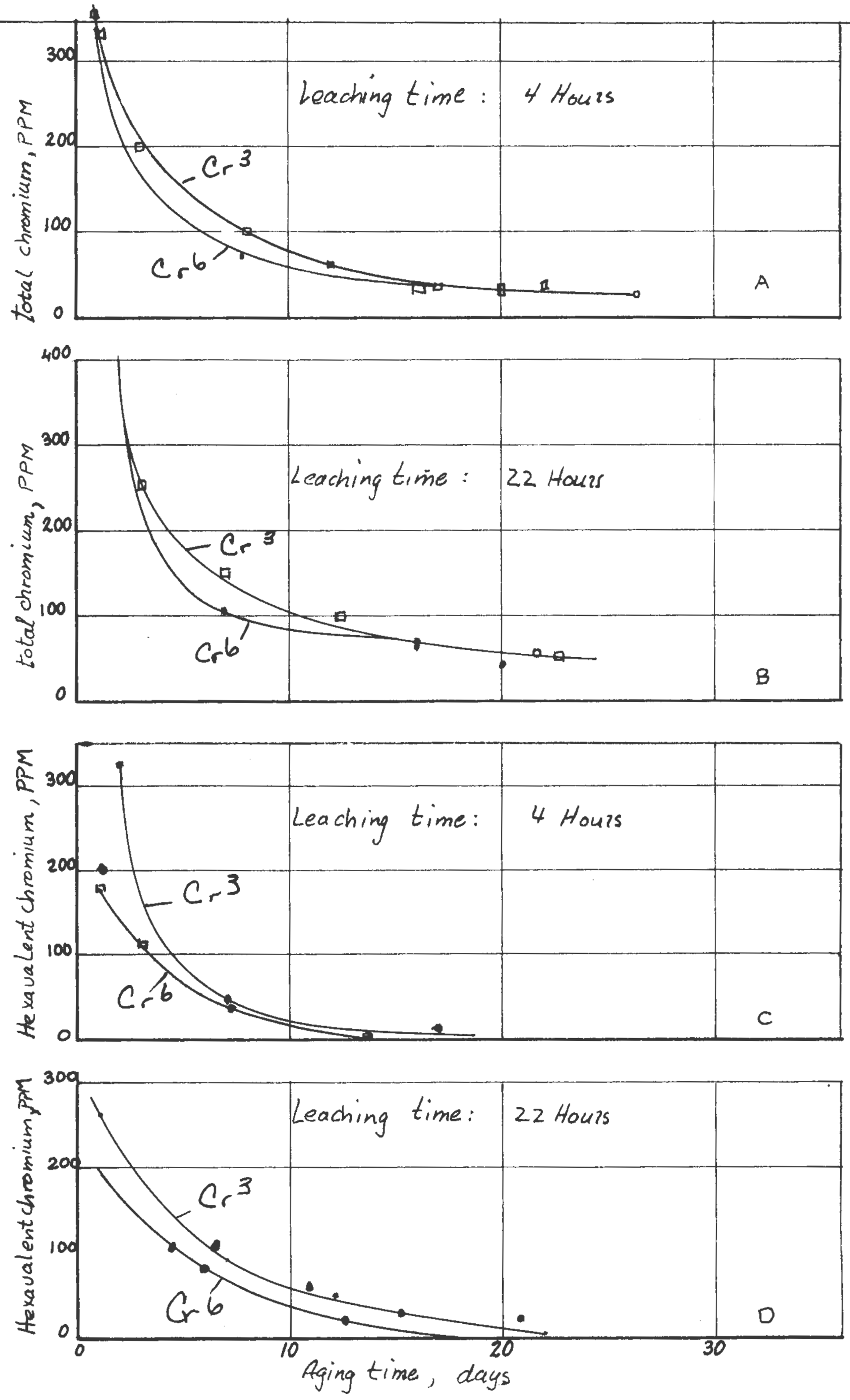


Fig. 99. Effect of Time on Leaching of Lignochrome Gel

Results

-mortality	none
-symptoms	none
-weight gain	normal
-autopsy	no anomaly

Conclusion

As administered orally to rats, lignochrome is non-toxic at a dosage level of 15 g/kg.

IV. CATEGORY A-4: OTHER PLANT DERIVATIVES

In the section of Volume I on Category A-4, it was pointed out that the resins derived from furfural were promising, because of their non-dependence on petroleum and their properties related to fields other than grouting.

But, these products have virtually never been used as grout, as defined in this report, and their properties do not correspond to those specified in this survey. For this reason, in Part Four, Chapter III, furfural derivatives are not analyzed in the same way as for the lignosulfonate base grouts, in order to improve their properties, but rather as a beginning of research attempting to define the adaptation of these products to soils grouting. Thus, the remarkable properties of this grout cannot be defined according to the criteria defined in Volume I.

At present, it is possible to obtain furfural-resorcinol grouts with a viscosity of less than 20 cPo, but with a setting time both short and difficult to control, since dilution leads to a wide range of strengths. Replacing the resorcinol with a less reactive commercial phenolic syrup (ROCAGIL 3555) produces a range of setting times compatible with grouting (11 hours to 45 minutes) for strengths of 10 to 20 bars.

The results obtained from this research are still fragmentary compared to what is known about traditional grouts and additional research will be necessary to define the characteristic properties of these grouts.

V. CATEGORY A-5 POLYACRYLAMIDES

1. Viscosity

1.1 Initial Viscosity

The initial viscosity of an acrylamide-base grout varies little according to dilution, provided that a prepolymer is not used (fig. 100). At concentrations close to 45%, the maximum which can be used, the grout's viscosity at normal temperature will not exceed 8 cP.

At normal concentrations (5 to 15% dry extract), viscosity remains practically constant and is very close to that of water: between 1.2 and 1.8 cP. The figures remain the same whatever the type of product used (AM-9, SUMISOIL, RACAGIL). The addition of polymerizing agents (ammonium persulfate and DMAPN, for example) considerably alters this viscosity, raising it to 4 or 5 cP (fig. 100).

1.2 Changes in Viscosity in Relation to Time

As indicated by most authors who have studied this grout, our tests confirm that viscosity remains practically unchanged during the entire incubation period, increasing abruptly just before setting.

For those grouts whose setting time is around 15 to 30 minutes, this change takes place in 2 minutes. Thus viscosity can be considered to remain constant over the period T = Tp - 2. Some examples are given in fig. 101.

2. Regulation of Setting Time

As with other grouts, setting time should be adjustable to take the following factors into account:

a) <u>the ground to be grouted</u>: short setting time for very coarse ground, long setting time for very fine ground. These grouts are particularly effective on very fine, relatively impermeable soils which are hard to treat with chemical grouts, and so relatively long setting times are the usual goal.

b) <u>ambient air and ground temperature</u>: the speed of the reaction in these grouts is affected by temperature. Fig. 102 shows that setting time varies in a ratio of 2 when the mixture's temperature passes from 6° to 7° C. It is therefore vital that setting time be adjustable so that grouting can be effectively carried out in most normal thermal conditions.

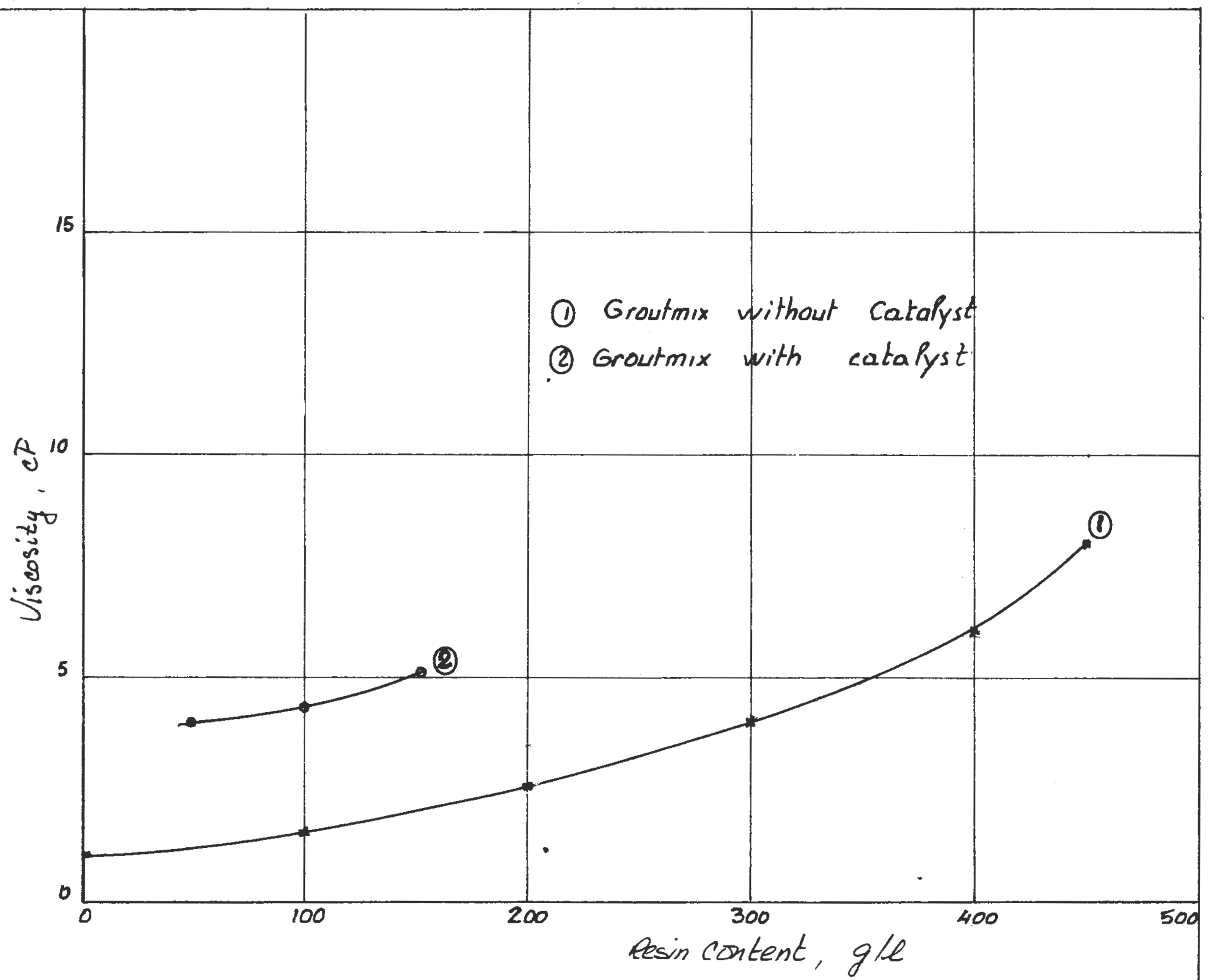


Fig. 100. Effect of Resin Content on Initial Viscosity of Polyacrylamide Grout

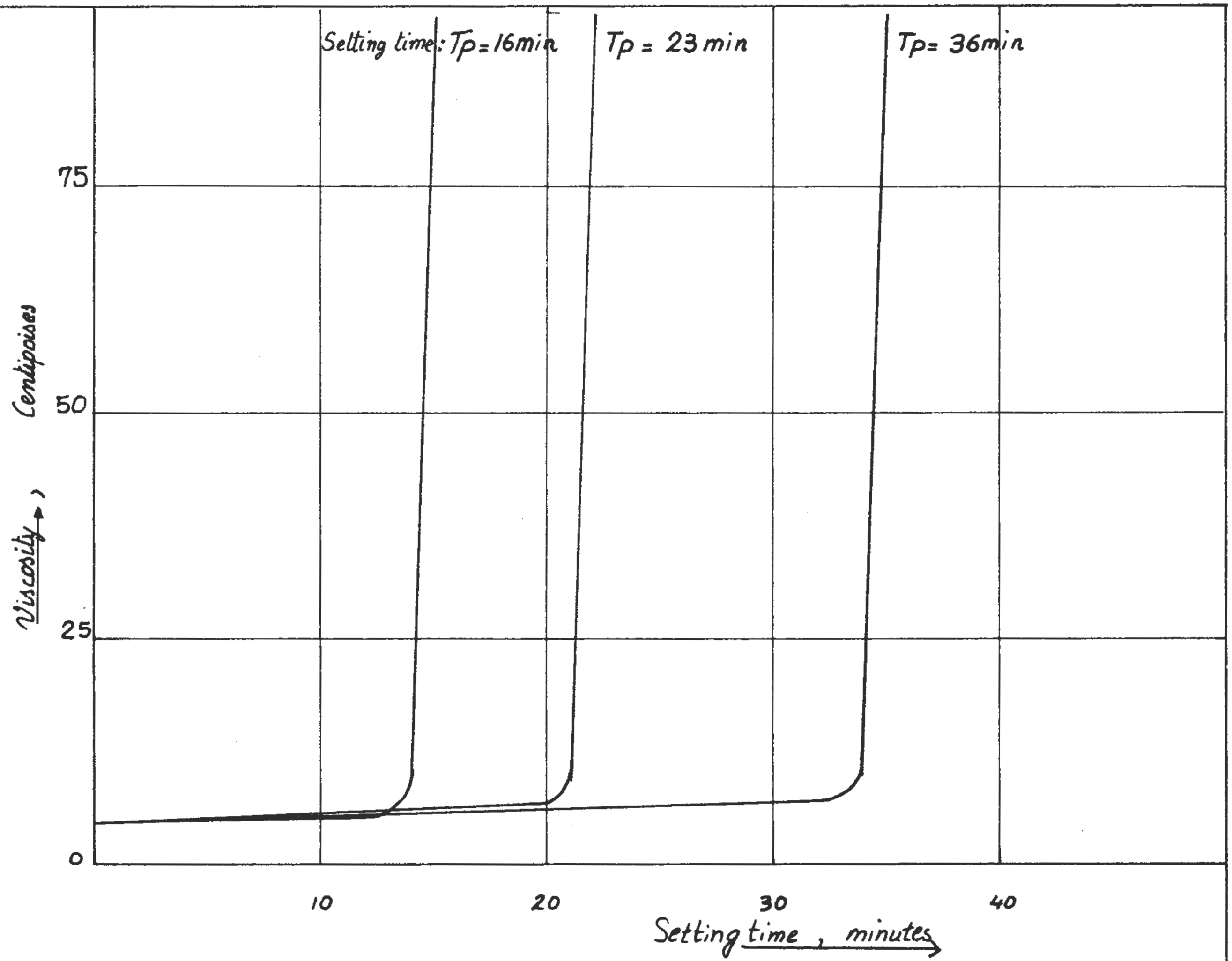


Fig.101. Effect of Time on Viscosity of Polyacrylamide Grout (10% Resin Content)

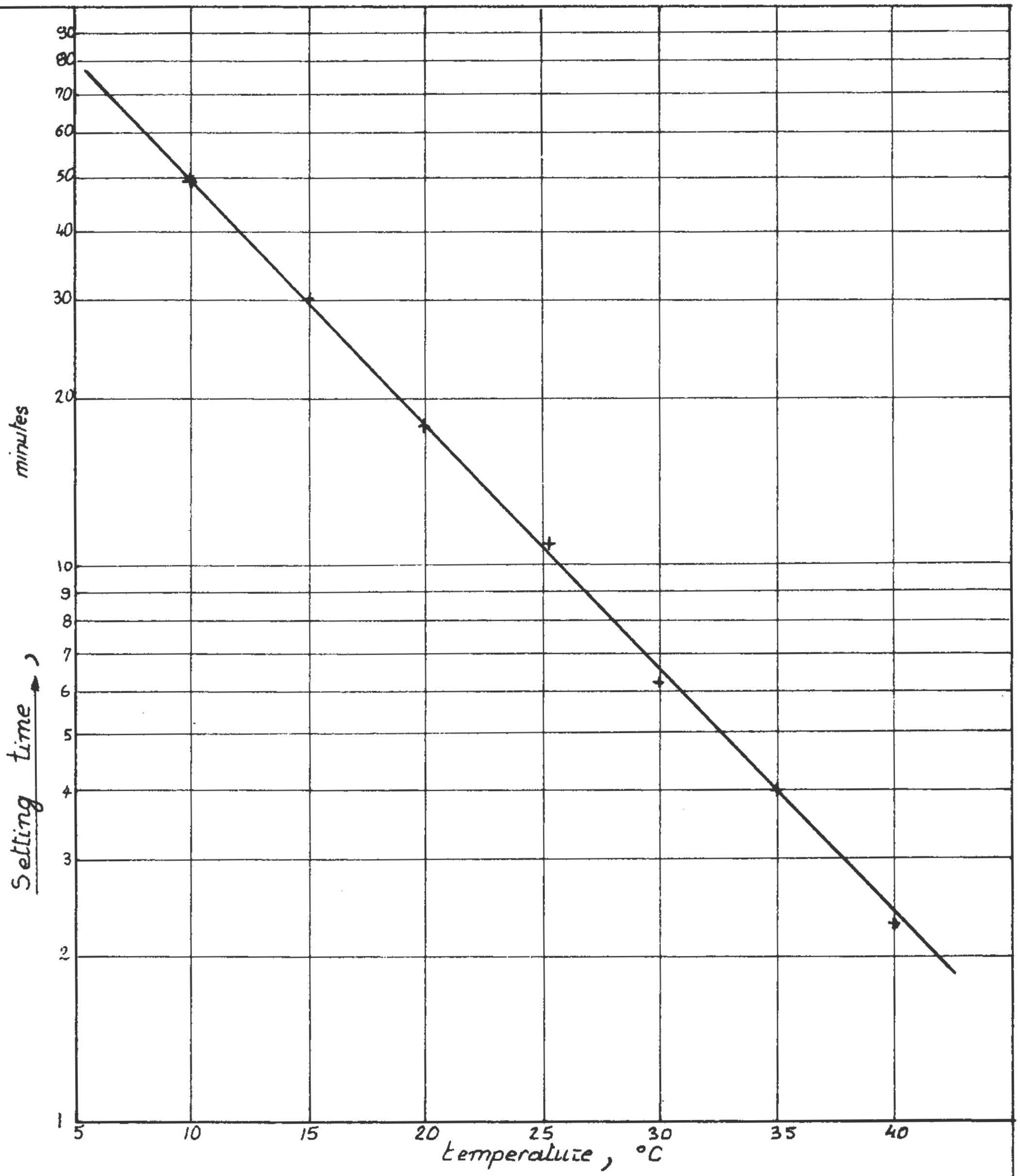


Fig.102. Effect of Temperature on Setting Time of Polyacrylamide Grout (10% Resin Content)

For a given concentration of basic resin, with setting time varying according to concentration, and all other factors constant, setting time can be adjusted by modifying the proportions of catalyst ingredients. Following formal operating procedures, the catalyst will be composed of:

-ammonium persulfate (AP)
-dimethylaminopropionitrile (DMAPN)
-potassium ferricyanide (KFe)

If diethylaminopropionitrile (DEAPN) is used in place of DMAPN, the results obtained will be identical if molecular proportions are unchanged.

If all other factors remain constant, setting time will vary:

-in inverse proportion to the dosage of AP (fig. 103)

-in inverse proportion to the dosage of DMAPN (fig. 104)

-in direct proportion to the dosage of KFe (fig. 105)

For short setting times, from one minute to one hour, only AP and DMAPN should be used, by varying either product indiscriminately. For longer setting times small quantities of KFe, a reaction inhibitor, should be added to the mixture. If even longer setting times must be obtained (for ground which is only very slightly permeable), unusual catalyst systems must sometimes be used, especially in the presence of high temperatures.

Tests have been conducted at a temperature of 45°C. By using AP with KFe, it was possible to obtain setting times varying from 1 to more than 8 hours at this temperature. Table 28 gives three examples.

Table 28. Formulas for Variable Setting Times

10% acrylamide (ml)	10% AP [1] (ml)	10% KFe [2] (ml)	Setting Time
1,000	20	1.25	8 h 15 m
1,000	20	1	6 h 15 m
1,000	20	0.75	4 h 30 m

[1] ammonium persulfate
[2] potassium ferrocyanide

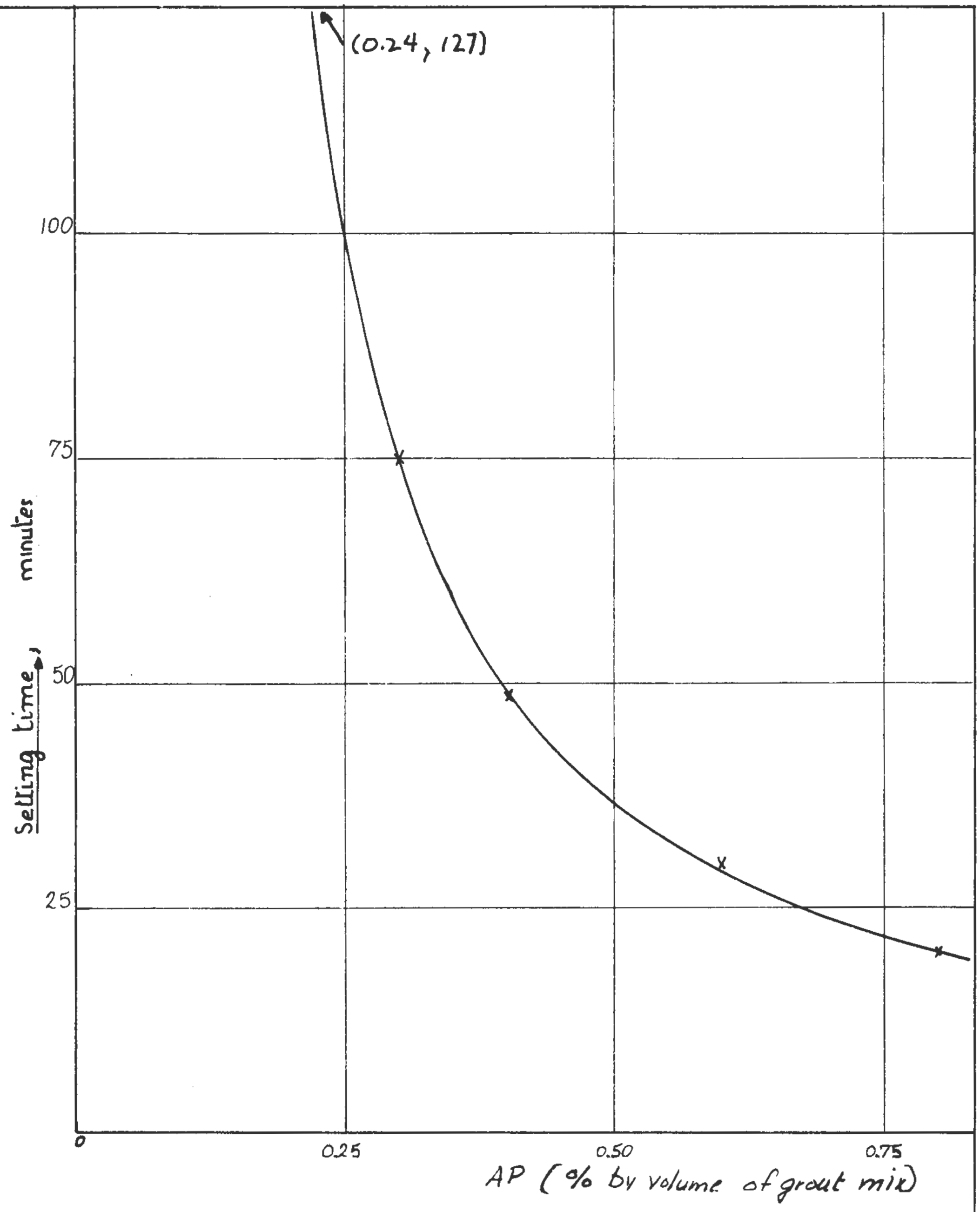


Fig. 103. Effect of Ammonium Persulfate on Setting Time

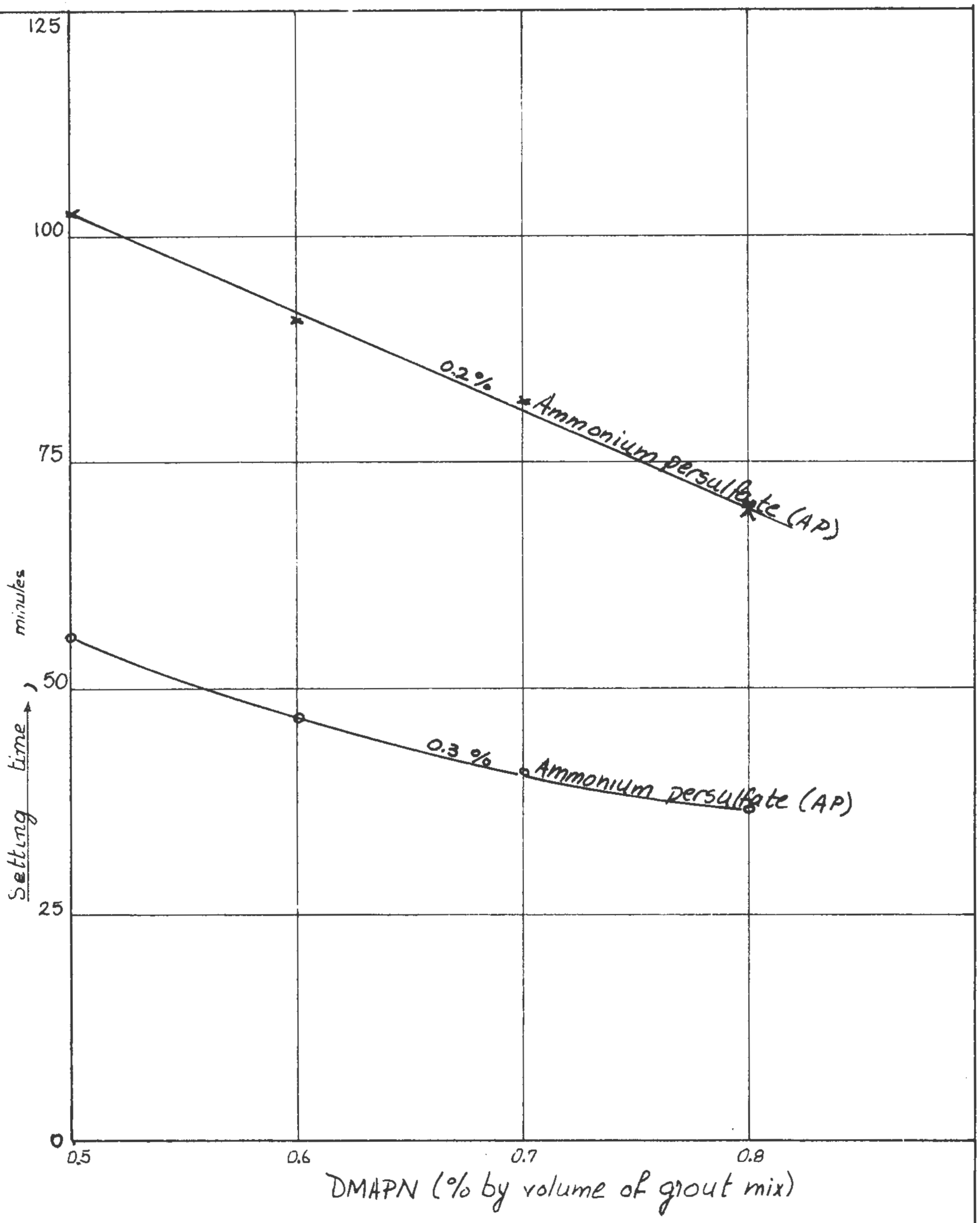


Fig.104. Effect of DMAPN Content on Setting Time

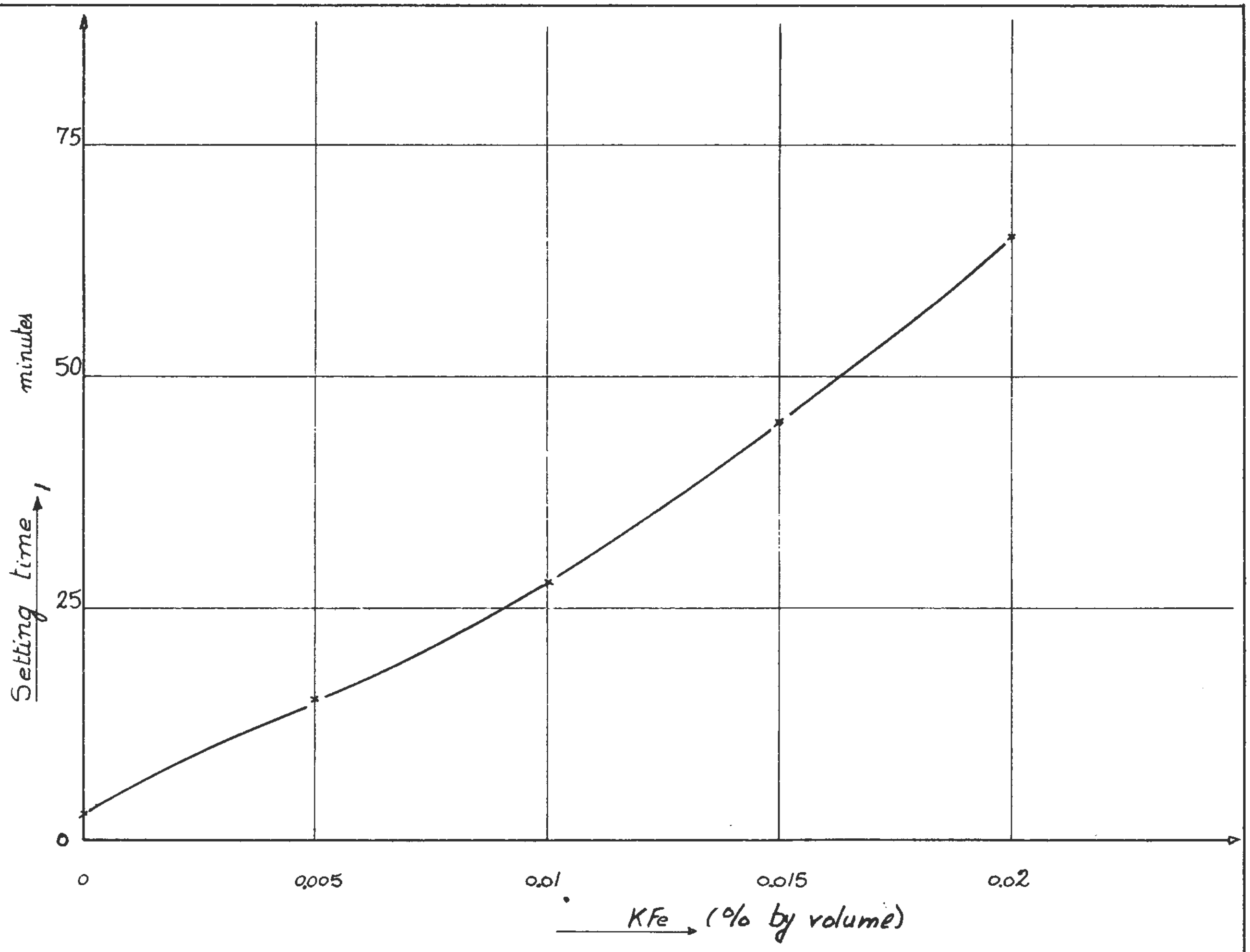


Fig. 105. Effect of Potassium Ferricyanide (KFe) on Setting Time

As can be seen, the control of setting times for acrylamides is possible, and even easy, over a wide spectrum, even at high temperatures.

3. Strength of Pure Grout

Shear strength characterizes the grout's ability to resist loosening stress, and thus maintain its waterproofing function.

A polyacrylamide's shear strength will depend primarily on its resin content (fig. 106). As a secondary factor, strength (for the same resin content) will be affected by the proportion of catalyst system used, and principally by the amount of persulfate and reticulant incorporated into the acrylamide (in general, diethylenediacrylamide). These tendencies are summarized in table 29 and fig. 107).

Table 29. Effect of Grout Ingredient Content on Strength

Ingredient	Shear Strength	Failure Strain
Resin ↗ AP ↗ Reticulation ↗	↗ ↗ ↗	↘ ↘ ↘

In most cases, the behavior of these gels will be elastic. The load-deformation curve is perfectly linear. Two examples are given for a measurement with unconfined compression in fig. 108 and another with shear stress in fig. 109. However, viscoelastic behavior can be observed in slightly reticulated resins.

Other than in the case of only slightly reticulated mixtures, shear speed has practically no effect on strength readings. In table 30 below, the maximum discrepancy at normal speed (the figure underlined) is 6.5%.

Table 30. Effect of Shear Speed for a 12% Dry Matter Acrylamide Grout

shear speed in degrees/minute	0.19	0.41	6.95	24.1	52	84	126
shear strength in g/cm^2	96	95.6	95.8	100	95.8	102	101

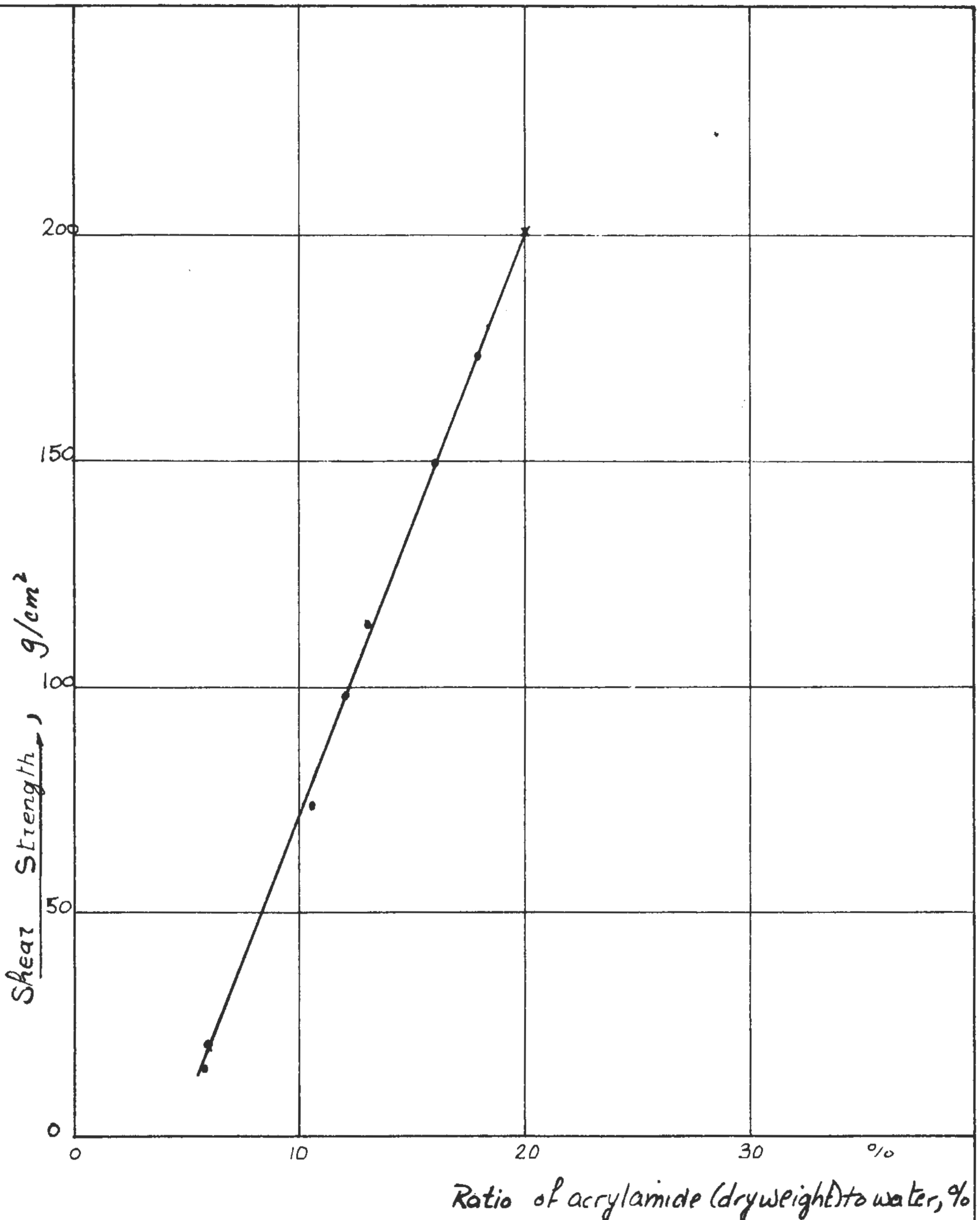


Fig. 106. Effect of Acrylamide Content on Shear Strength (AP and DMAPN Constant at 5 g/l)

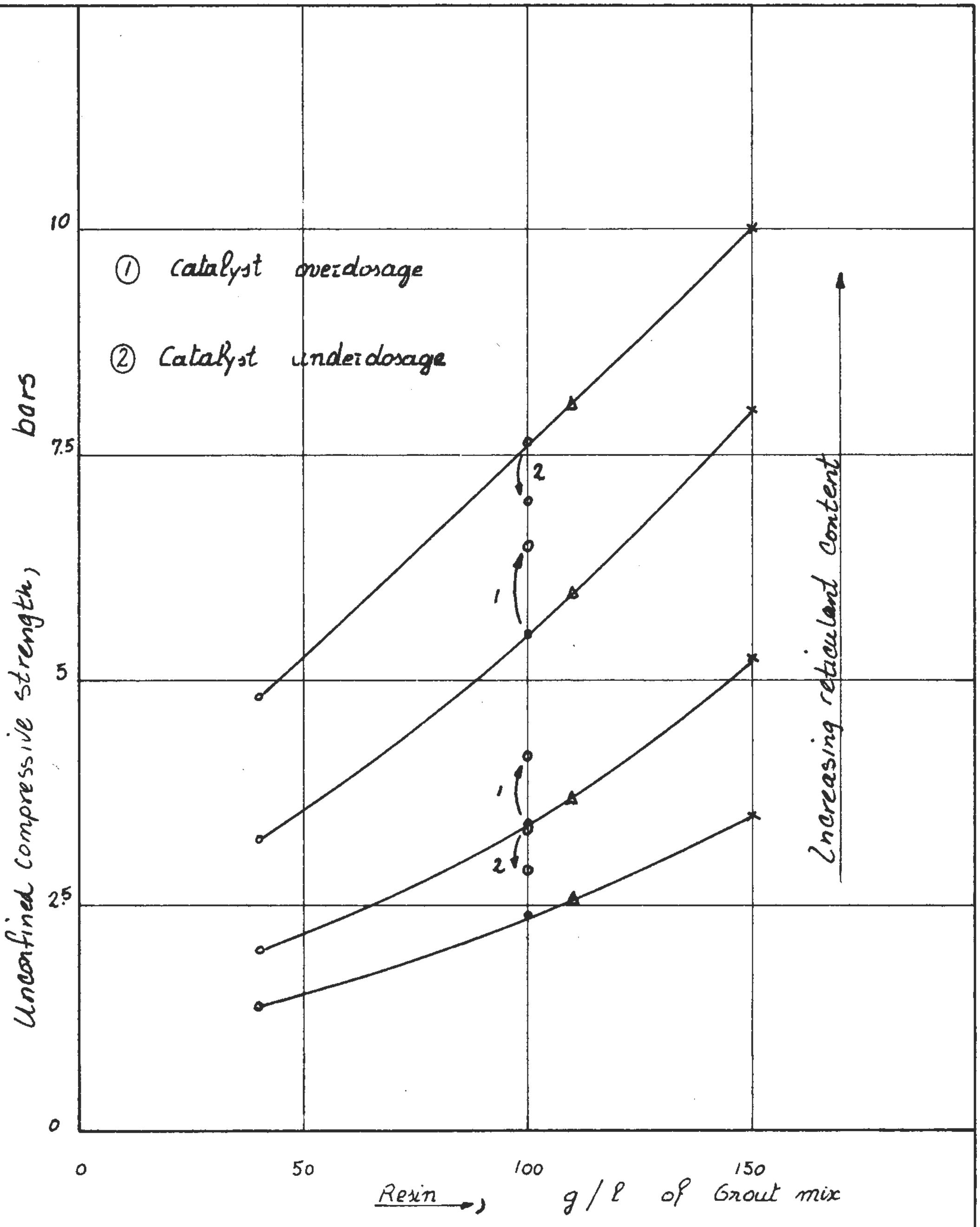


Fig. 107. Examples of Effect of Resin Content in Grout on Compressive Strength of Mortar (Influence of Catalyst and Reticulant Dosage)

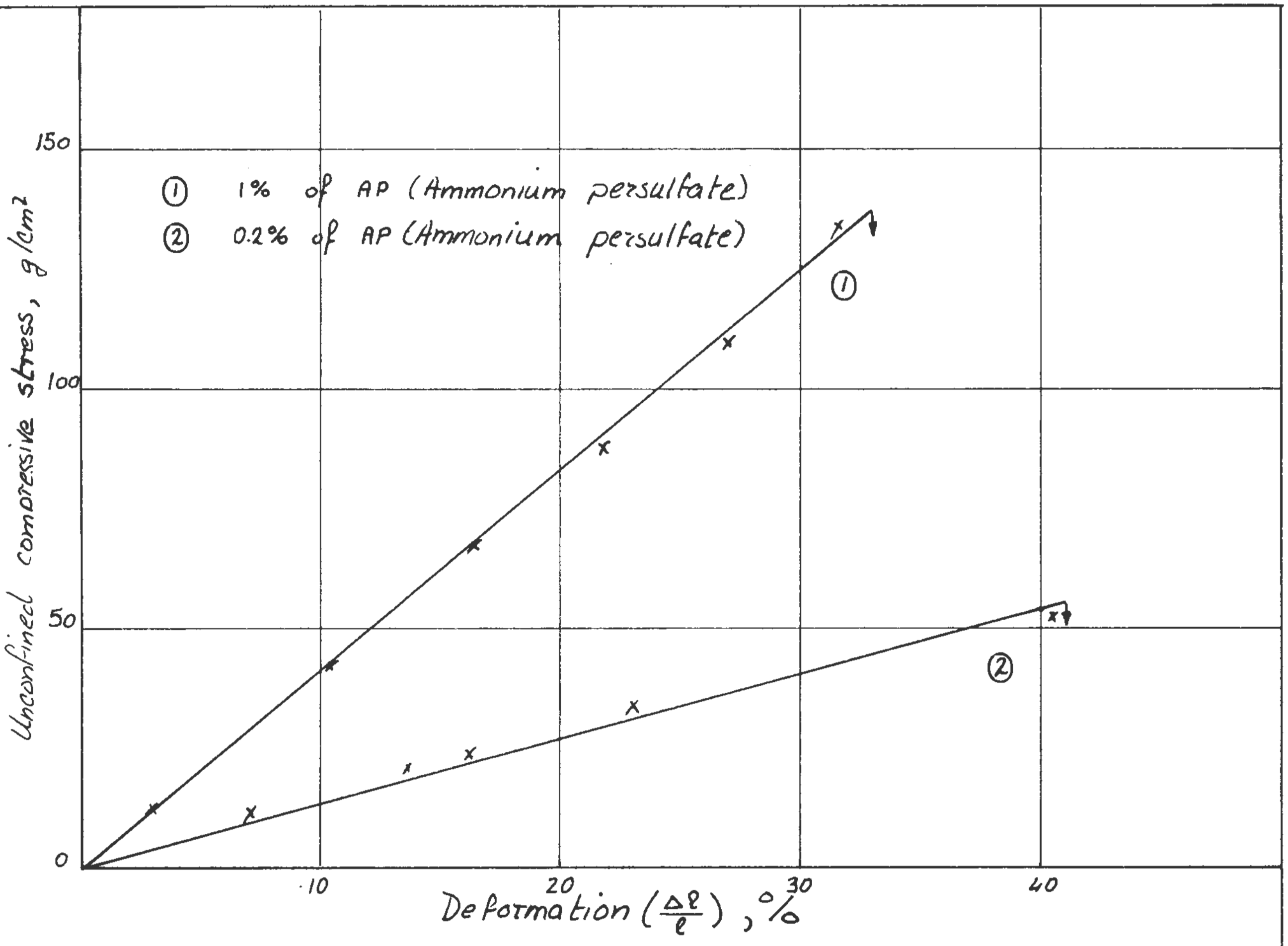


Fig. 108. Effect of AP Content on Stress/Failure Ratio in Compression of Polyacrylamide Grout

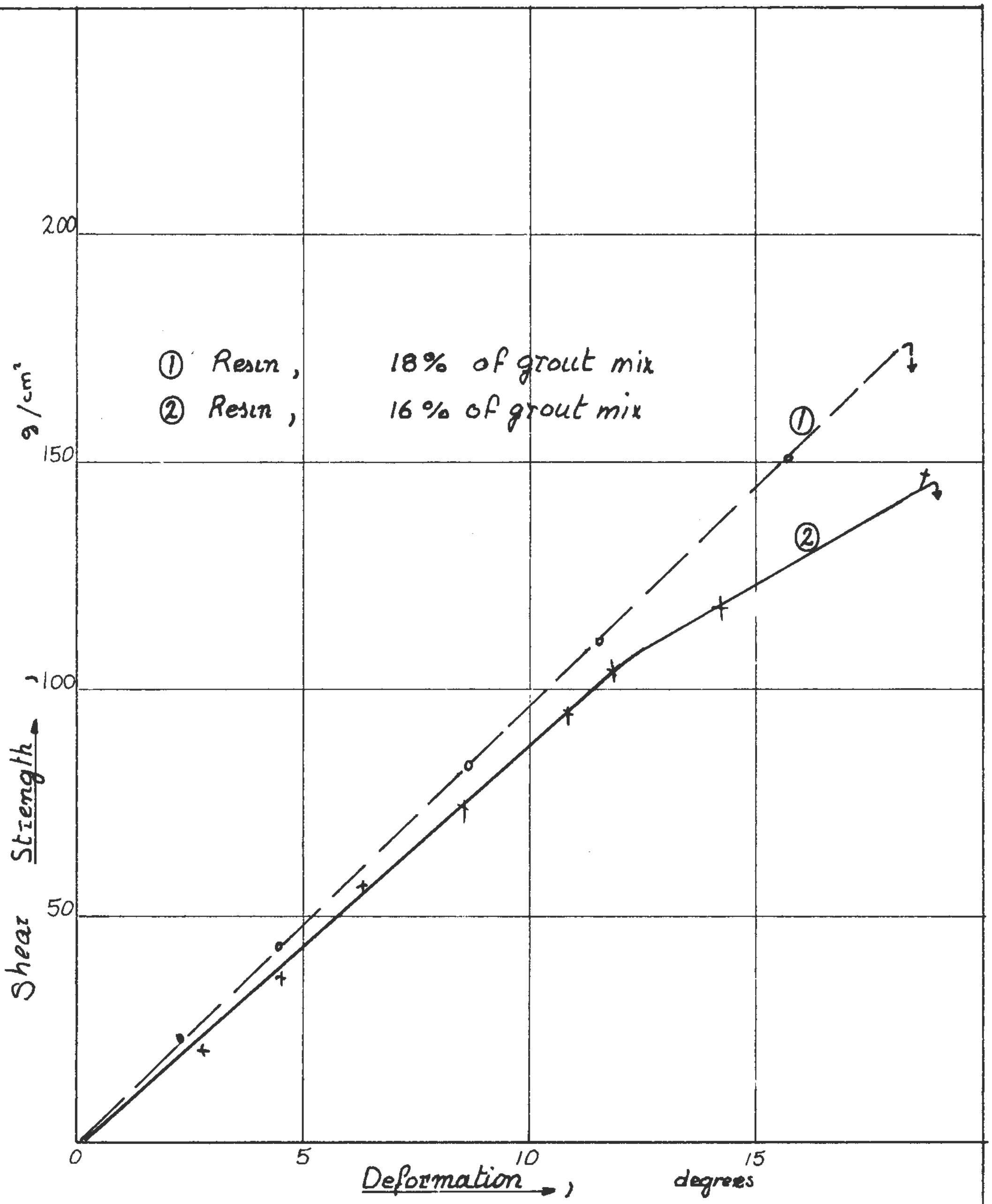


Fig. 109. Shear Stress/Deformation Ratio of Polyacrylamide Grout for Two Resin Concentrations

4. Strength of Treated Ground

At normal resin concentrations, pure polyacrylamide grouts have relatively low shear strengths, which would seem to indicate that these grouts do not perform well for consolidation. However, it appears that the glueing effect is paramount, so that treated ground may have sufficient strength for many consolidation applications, particularly in fine soil.

The range of strengths runs from 2 to 10 bars for normal acrylamide concentrations (5 to 15%) depending more on the rate of reticulation (ethylene diacrylamide or, sometimes, the proportion of catalyst) than on overall concentration. This triple effect is demonstrated in fig. 109.

It should be noted that at the same rate of reticulation, variations in resin concentration do not cause major variations in the strength of the treated ground. In fig. 110 , when resin concentration moved from 40 g/l to 150 g/l, strength only doubled. It should also be noted that the grout maintained its elastic character in the ground, so that the speed at which stress is applied will have very little effect on the treated ground's strength (table 31).

Table 31. Effect of Rate of Loading on Strength

Rate of Loading, mm/min.	Unconfined compressive strength of injected sand, bars
0.05	4.7
2	5.4
20	6.8
50	6.7

5. Durability

5.1 Airtight Mold Cure

Mechanical properties increase very rapidly after the grout sets, and a meaningful figure for final strength can be obtained at the end of a few hours. After 48 hours, strength will practically stabilize and will remain the same over time.

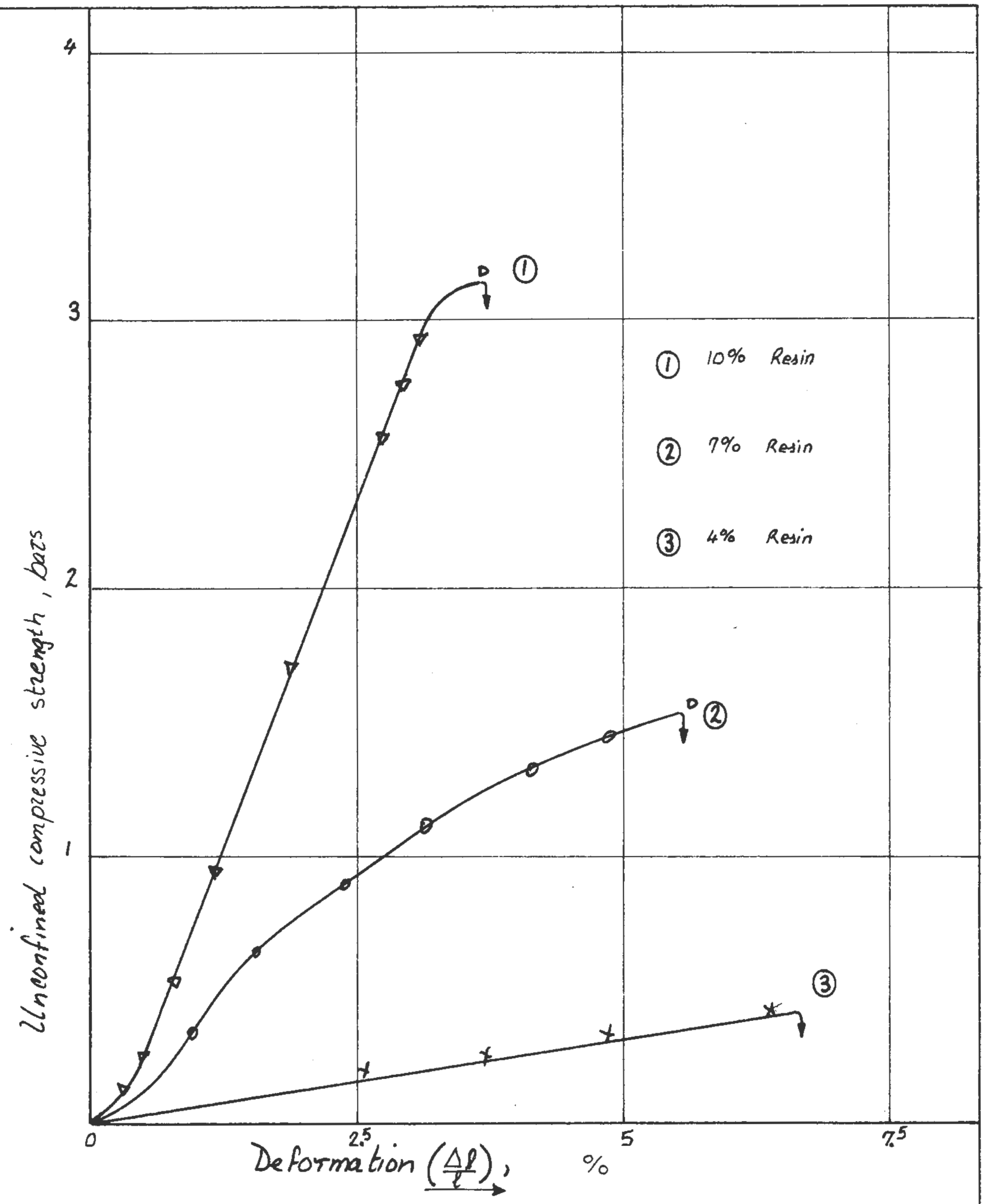


Fig. 110. Stress/Strain Curves for Mortars of Polyacrylamide Grout

5.2 Dry Cure

A remarkable property of these grouts is their ability to lose some of their water without causing any dislocation of the gel structure, in fine soil.

Under dry cure, this phenomenon enables mechanical properties to increase continually up to a point where the sample's water content is in equilibrium with the relative moisture of the ambient medium. Optimal strength will thus depend on the cure medium.

5.3 Wet Cure

Other than small amounts of catalyst which did not combine with the resin, a polyacrylamide grout's set will produce a substance which, sufficiently reticulated, is insoluble in water.

However, depending on the rate of reticulation, such a grout is likely to absorb water, which causes it to swell (fig. 111). In the long run, the swelling which occurs with the proper rate of reticulation can be observed to occur depending on the proportions of catalyst used (fig. 112). In the ground, wire reinforcement of the sand skeleton can check this swelling, but it can be assumed that exchanges with the cure medium would be more pronounced than those due to simple leaching.

The effect on strength will be negative for poorly reticulated systems. When test samples can swell, their mechanical properties drop off rapidly with the quantity of water absorbed, and in extreme cases the sand skeleton would no longer have any effect. Conversely, test samples with a high rate of reticulation have been cured by immersion in water without any modification in their characteristics (fig. 113).

Depending on the rate of reticulation, behavior upon contact with water will vary widely. To obtain figures which would be comparable with those obtained in situ, test samples would have to be placed in a confined medium similar to the groundso that swelling would be partially or totally checked.

In the presence of highly alkaline water, saponification occurs rather rapidly, causing a decrease in mechanical performance. The fact that a highly alkaline medium is very seldom present would indicate that in nearly all soils there is no risk of this phenomenon. However,

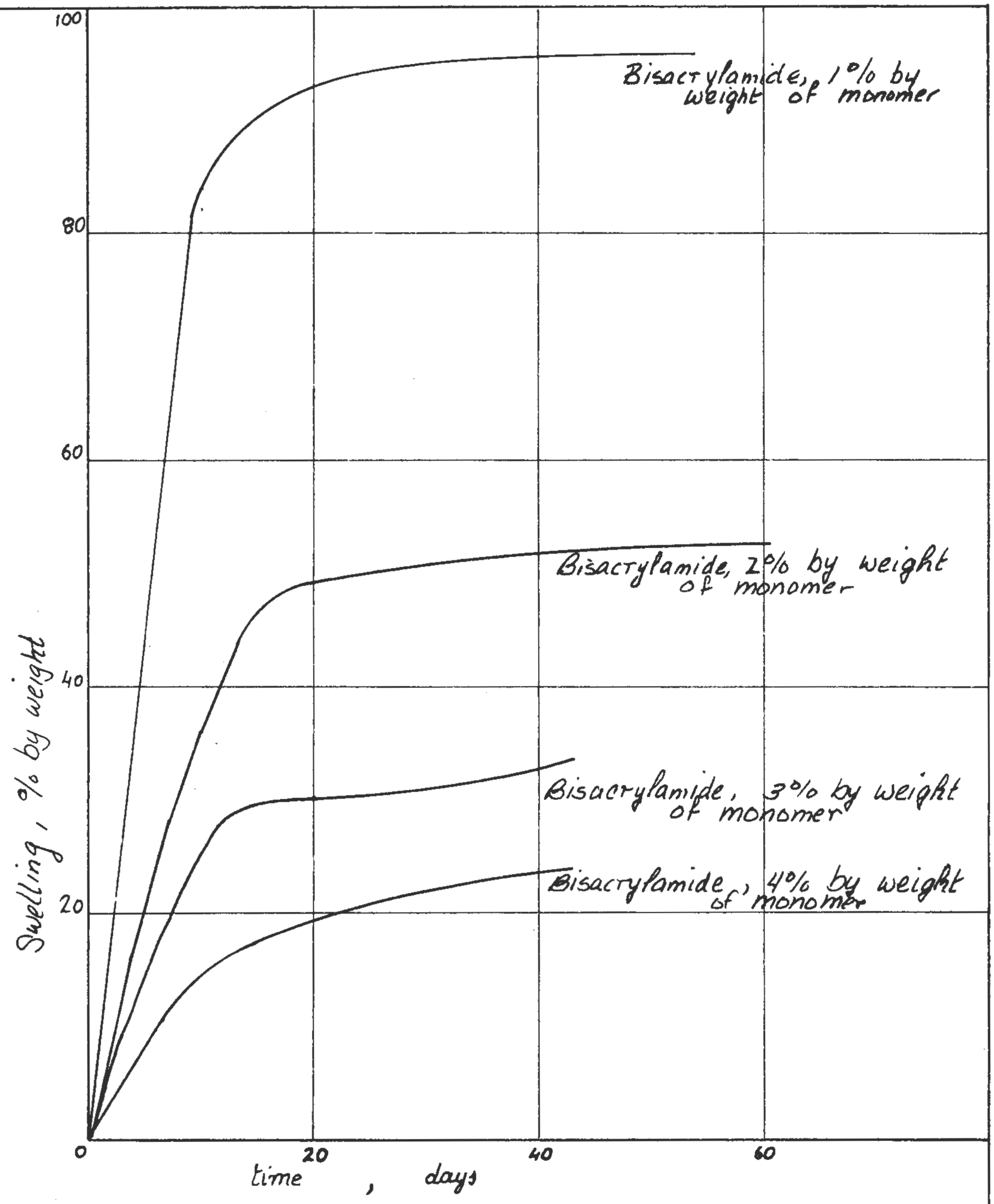
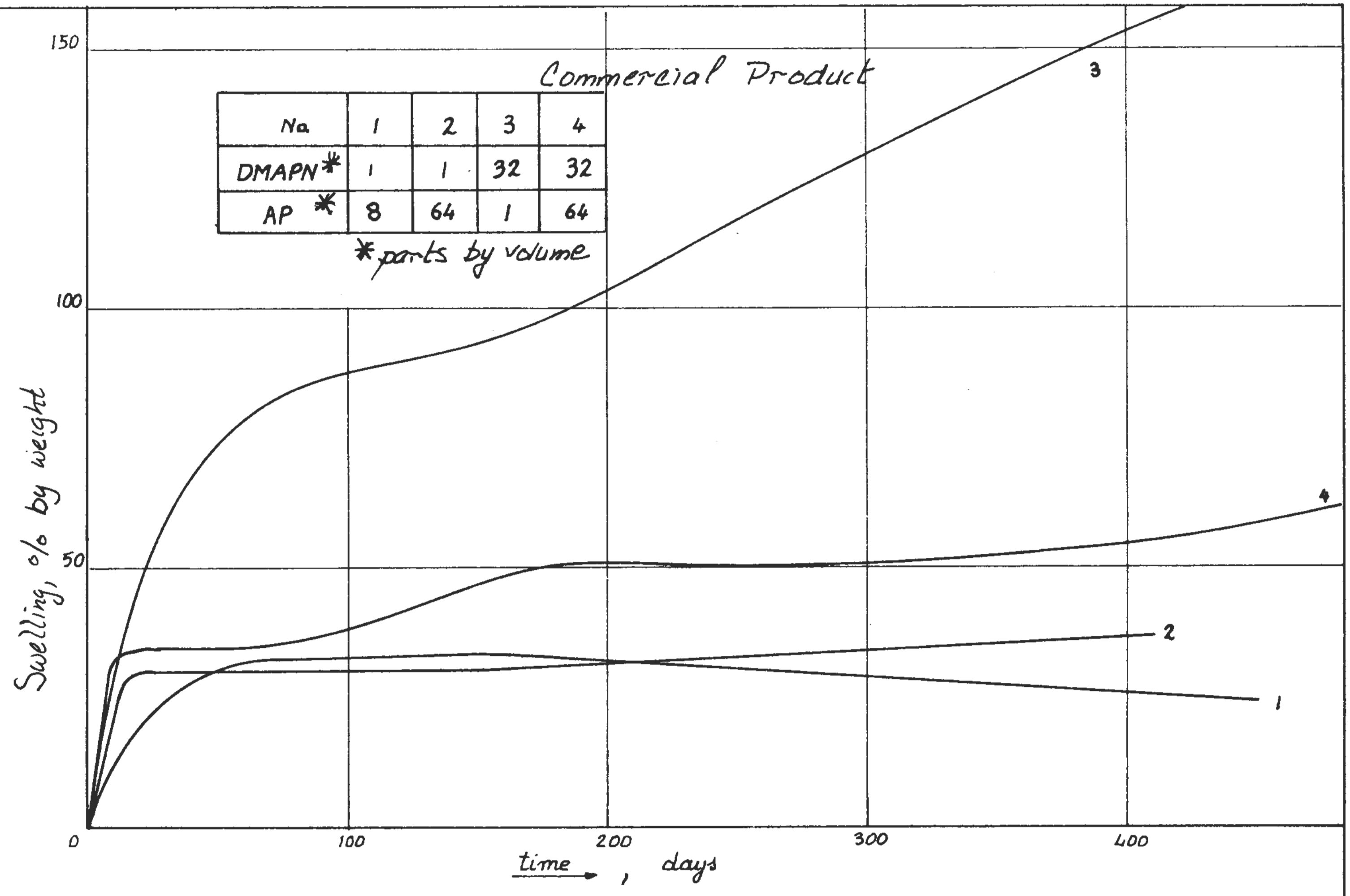


Fig. 111. Effect of Bisacrylamide Content on Swelling of Acrylamide/N N'methylene-bis-acrylamide



No.	1	2	3	4
DMAPN*	1	1	32	32
AP *	8	64	1	64

*parts by volume

Fig. 112. Swelling of Acrylamide Reticulated with 10% NN'methylene-bis-acrylamide

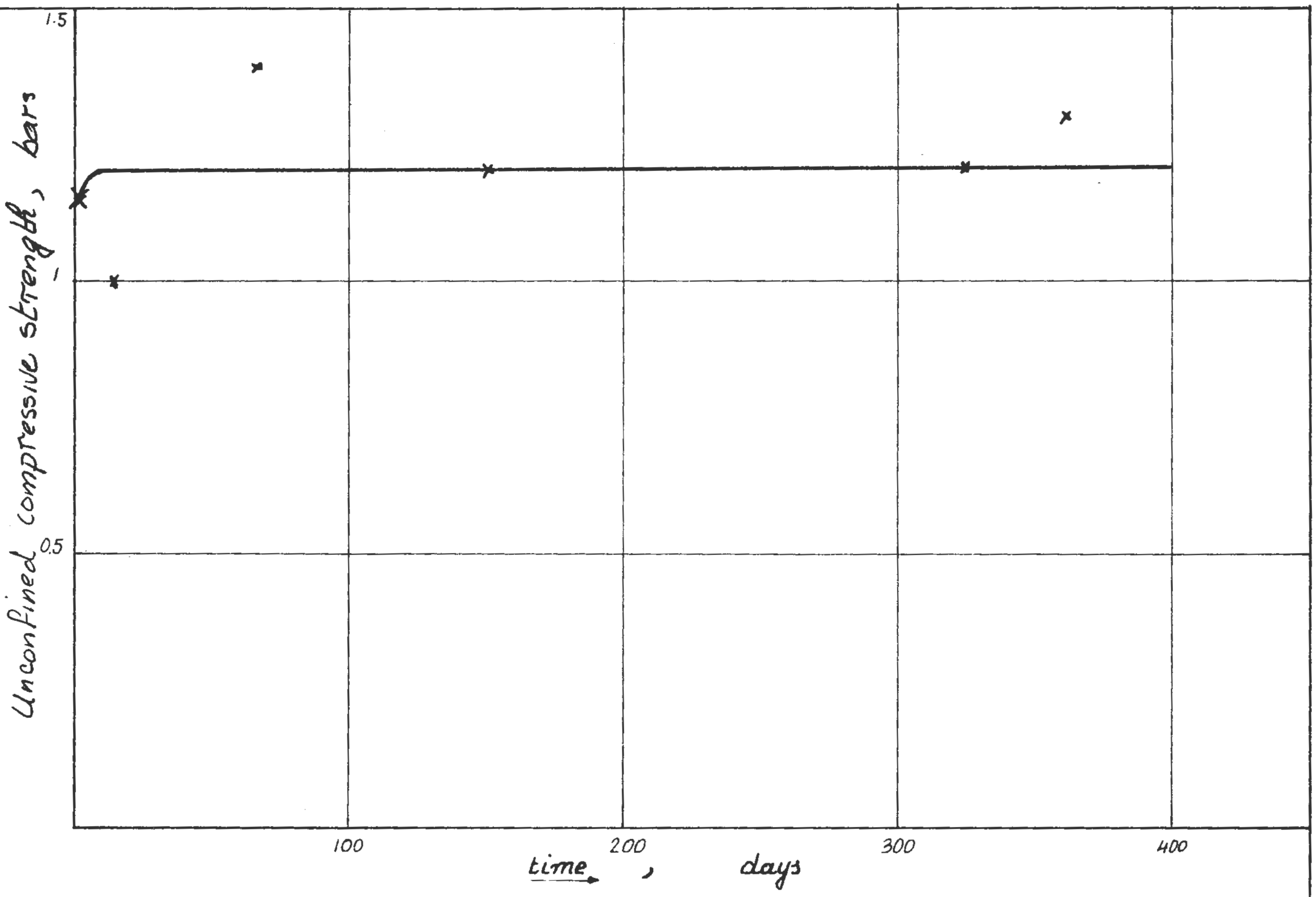


Fig. 113. Effect of Time on Unconfined Compressive Strength (Sand Treated with Polyacrylamide Grout and Cured in Water)

interface disturbances have been noted in the case of an acrylamide grout in contact with a highly basal material (cement, silica gel) at the time of injection.

5.4 Wetting-Drying Cycles

KAROL (57-01) describes the long-term behavior of these grouts in experiments where pure grout and grouted sand were analyzed after 13 years of cyclical wet-dry cure. The grouted sand suffered no disturbance over these cycles.

5.5 Cure with Water Percolating Under Pressure

One of the most representative durability tests uses water percolating under pressure, leaching out the grout if it is unstable. This test is the first in line for the criterion of durability.

But for leaching to take place, the water must be able to percolate in sufficient quantities through the test cell. On a well-grouted sample, residual permeability should be practically nil, 100 to 1,000 times lower than that for a compact clay. Thus, it is conceivable that, even at high rates of pressure (250), percolation flow would remain very low, most often not measurable or, at least, not representative. Any flow detected will far exceed the sample's own rate of flow.

For samples placed in a permeability cell which has been standardized and tested under a gradient of 250, percolation will amount to a few drops a day, and in these circumstances, it is obvious that the grout's behavior with regard to leaching will be excellent.

6. Toxicity

The distinction must be made between toxicity of the primary ingredients and the grout before it sets, and toxicity of the hardened grout.

6.1 Pre-Set Toxicity

All the basic ingredients on the market contain high proportions of acrylamide monomer whose industrial toxicity is well known (oral DL 50, 200 mg/kg). Strict industrial hygiene measures are thus indispensible to prevent accidents.

The American Cyanamid Co. has defined the precautionary measures which should be taken when using AM-9. The following should be noted in particular:

-a qualified technician should be present;
-AM-9 powder storage areas should be washed down;
-personnel should wear protective clothing (boots, raincoat, gloves, goggles);
-ventilation should be adequate.

Since additives to acrylamide grouts are used at worksites in very small amounts, the necessary precautions are easy to implement. It must be remembered, however, that some of these additives are more dangerous than the acrylamide itself, as shown in table 32.

Table 32. Toxicity of Acrylamide Grout Additives

Additive	DL 50 oral mg/kg	DL 50 ipr mg/kg	DL 50 scu mg/kg
perboric acid (Na salt)		538	
perchloric acid (Na salt)		596	
permanganic acid (K salt)	1,090		500
calcium acrylate	4,920		
trisodium phosphate			875

oral = orally
ipr = intraperitoneal
scu = subcutaneous
DL 50 = dose causing 50% mortality

6.2 Toxicity of Hardened Grout

Given the high toxicity of the acrylamide and its additives, it is absolutely imperative in the preparatory stage to have dependable equipment which would preclude any errors in dosages which might leave some acrylamide monomer or additives in the hardened grout. If this elementary precaution is observed and the grout is properly fabricated, there will be no notable toxicity in the polymer system. According to AMERICAN CYANAMID tests, the hardened grout will contain a maximum of 0.03% free acrylamide monomer, which can be absorbed by certain microorganisms in the soil.

Measurements taken at our request by the RHONE PROGIL laboratory, and using the operating procedure defined in the chapter on toxicology, confirm the opinion of AMERICAN CYANAMID:

Composition of Grout

ROCAGIL 1295	250 grams
ammonium persulfate (AP)	4 grams
diethylaminopropionitrile (DEAPN)	3 grams
water	750 grams

Appearance: a white gelatinous mass with cream highlights

Test Conditions

-CD rats (C.O.B.S.) [1] from the CHARLES RIVER Farm, France, weighing 150 to 185 grams, fasted 24 hours before the administration of the test substance, 10 rats (5 males, 5 females).

-Product put into suspension with a Teflon-headed grinder in a 10% gum arabic aqueous solution and fed through oesophageal tubes.

-Dosage: 15 g/kg p.o., two feedings at 3 hour intervals of 20 ml/kg of a 37.5% suspension.

-Length of observation period: 15 days, with animals weighed every 5 days.

-Sacrificed by intravenous injection of sodium pentobarbital the 15th day and autopsied for macroscopic examination of the principal thoracic and abdominal viscera.

Results

-mortality	none
-symptoms	none
-weight gain	normal
-autopsy	no anomaly

Conclusion: Taken orally, RHONE PROGIL 36 976 is not toxic to rats at a dosage level of 15 g/kg.

---

[1] Caesarian Originated, Barrier Sustained

VI. CATEGORY A-6 PHENOPLASTS

1. Viscosity

1.1 Initial Viscosity of Basic Resins

The majority of phenoplast resin-base grouts are easily comparable to the polyacrylamide resin-base grouts examined in the preceding chapter.

At concentrations commonly used, the viscosity of the resorcin-formaldehyde-base grouts examined is close to that of water (1.2 to 3 cP). Initial viscosity of some commercial products, using tannins for example, is much higher and can even exceed 20 cP. Fig. 114 shows the difference between a resorcin-formaldehyde-base grout and a commercial grout. This difference in viscosity can be quite pronounced since a commercial product often must be used in higher concentrations to produce the same mechanical performances as resorcin-formaldehyde. Thus, viscosity of some commercial products will be at least as high as that of a silica gel.

1.2 Effect of Addition of a Catalyst

In general, the addition of the catalyst does not increase viscosity (added to resorcin, in fact, it facilitates dissolution). However, some supplementary catalysts such as magnesium salts can have an immediate thickening effect.

1.3 Changes in Viscosity with Time

The behavior of resorcin-formaldehyde grouts from the time of preparation to the point of setting is identical to that observed in polyacrylamide grouts; viscosity remains practically constant until the grout begins to set (curve 1 and 1a in fig. 115).

With phenoplast-base commercial products, viscosity increases with time from the moment the catalytic system is introduced. The shorter the setting time, the faster these changes occur (example: curves 2 and 2a in fig. 115 should be compared with curves 1 and 1a, for the same setting time). In this case the grout quickly becomes so viscous that it cannot be easily injected into these very fine grounds for which it is intended. The rheological behavior of these grouts makes them comparable to silica and lignochrome gels.

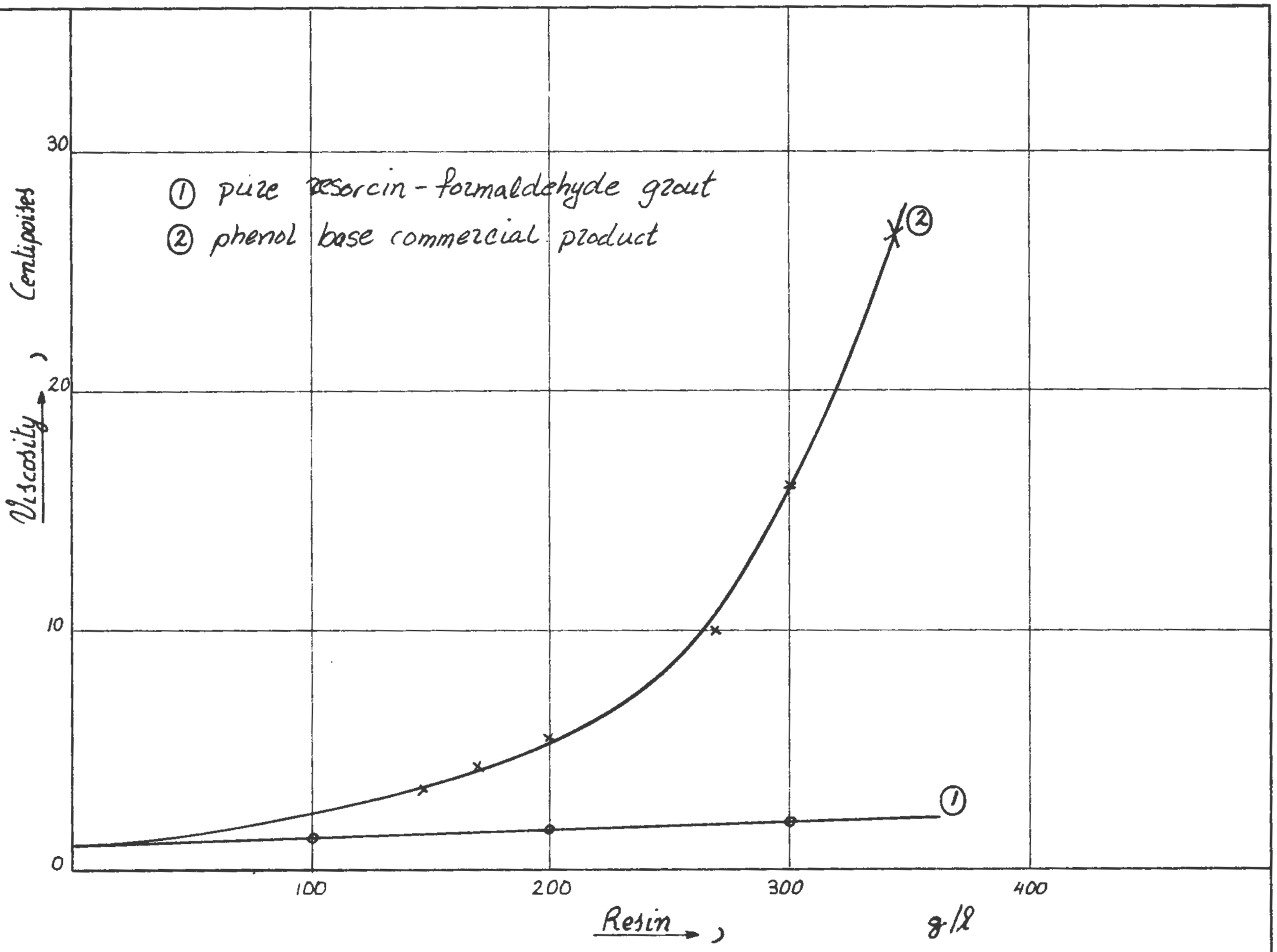


Fig. 114. Initial Viscosity of Two Phenoplast Grouts

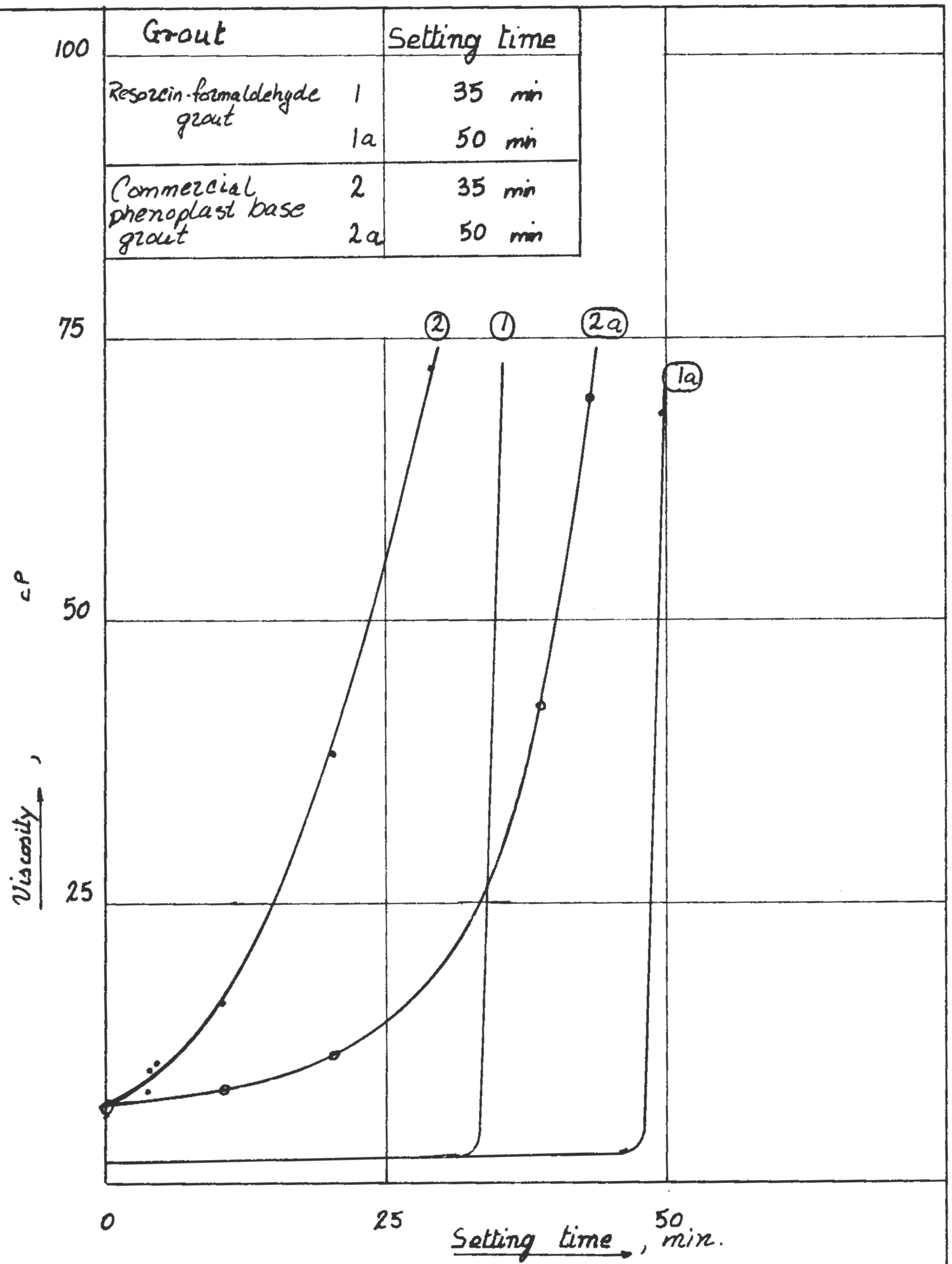


Fig. 115. Effect of Time on Viscosity of Different Phenoplast Base Grouts

2. Regulation of Setting Time

For a given temperature, setting time will depend on diluteness, the nature and proportion of catalyst used, and, finally, by the phenol/formaldehyde ratio.

The polycondensation of phenoplast resins is an exothermic reaction which increases the temperature of the medium undergoing reaction. The less dilute the medium, the more noticeable this rise in temperature will be (fig. 116). As a result, the setting time in adiabatic conditions will differ from that in isothermal conditions.

The ambient temperature has a distinct effect on the rate of set. The rate of change in setting time as a function of temperature is the same as with polyacrylamides. This time varies in a ratio of 2 when the mixture's temperature varies by about 7°C: that is, setting time is halved for every increase of 7°C (fig. 117). For commercial products, the coefficient is about the same (ratio of 2 for a variation in temperature of 6 to 7°C).

For the remainder of this section, all setting times will be given for 20°C.

2.1 Effect of Dilution

With the dosage of catalyst adjusted to an optimum level, the more dilute the mixture the longer the grout will take to set. If the mixture is highly dilute, the grout will set, but will take so long that its behavior will be uncertain, especially if there is water circulating underground.

Fig. 118 shows an example of changes in setting time in terms of dilution for a resorcin-formaldehyde formula and fig. 119 shows the same for a commercial product.

2.2 Effect of the Catalyst

Catalysis of phenoplast grouts occurs preferably in an alkaline medium. At constant concentrations, the nature of the catalyst will affect setting time (table 33), since these different bases are not all equally reactive.

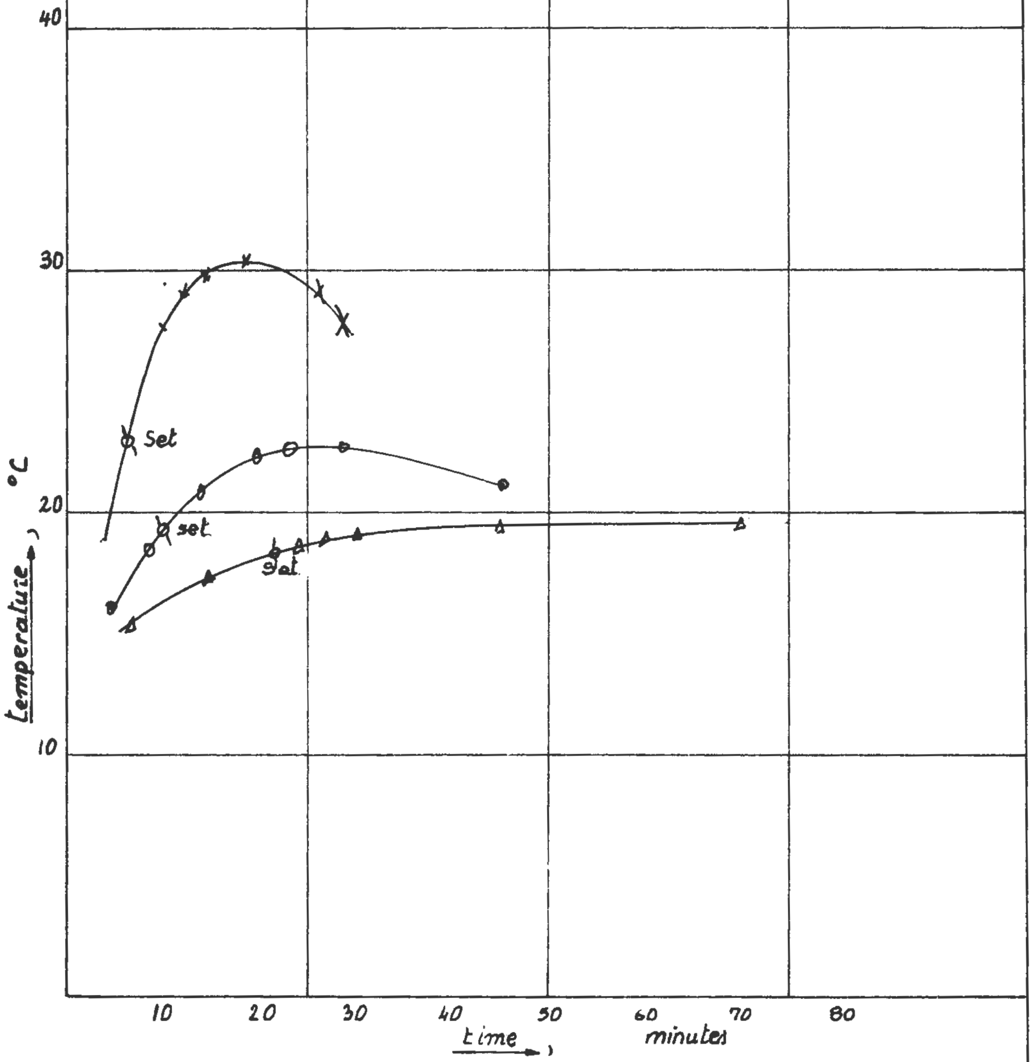


Fig. 116. Changes in Temperature of Phenoplast Grouts with Various Setting Times

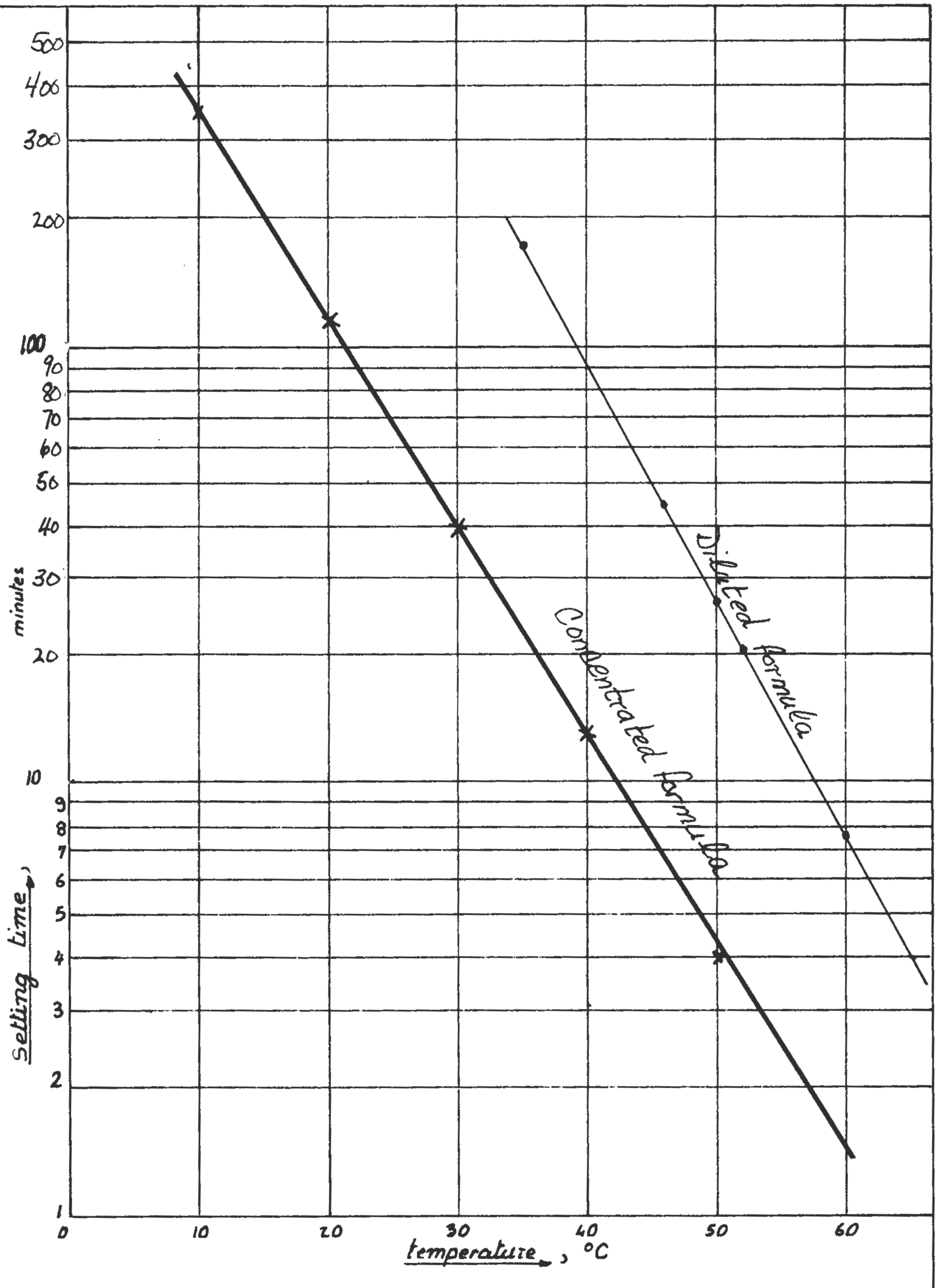


Fig. 117. Effect of Temperature on Setting Time

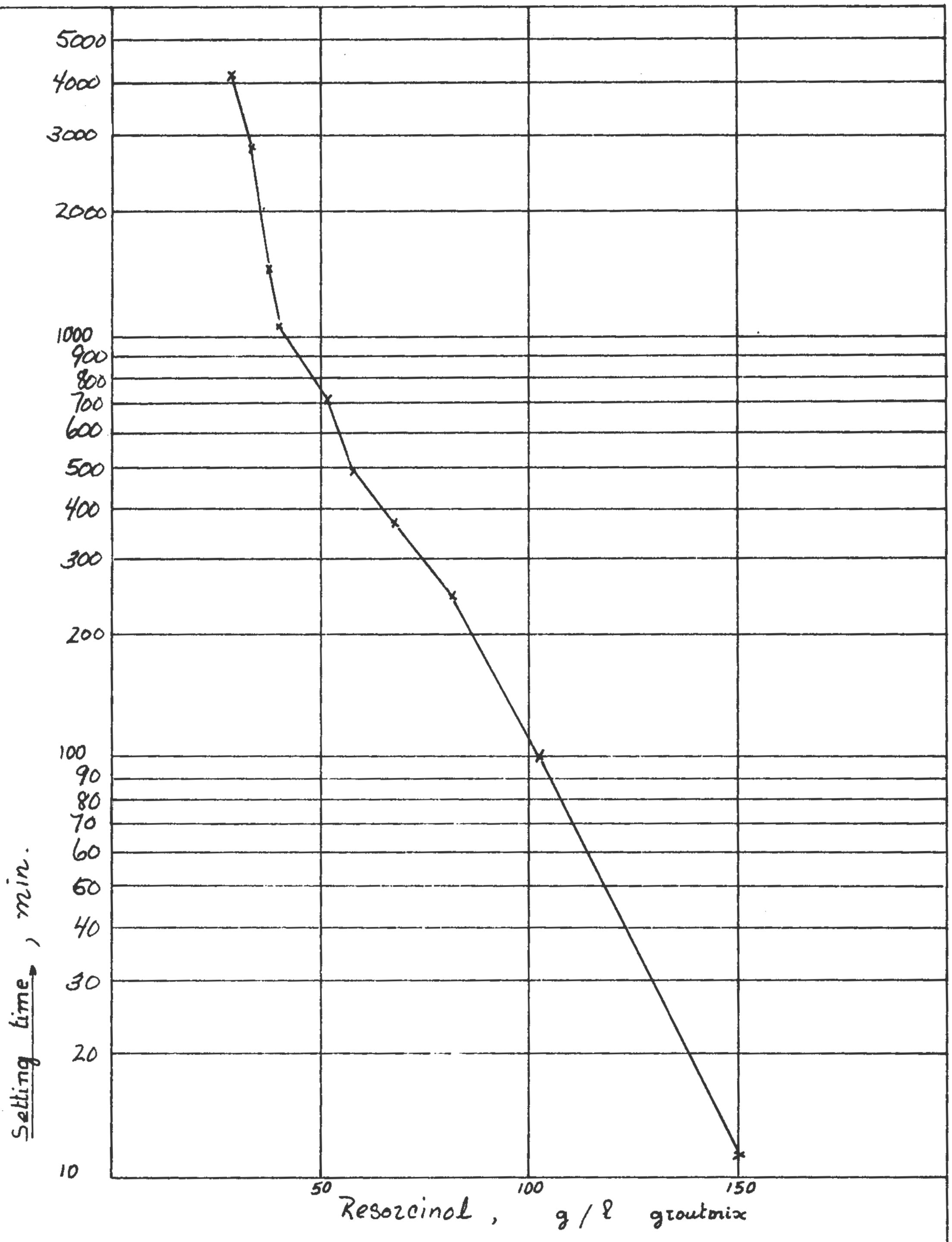


Fig. 118. Effect of Dilution on Setting Time
(Resorcin - Formaldehyde Grout)

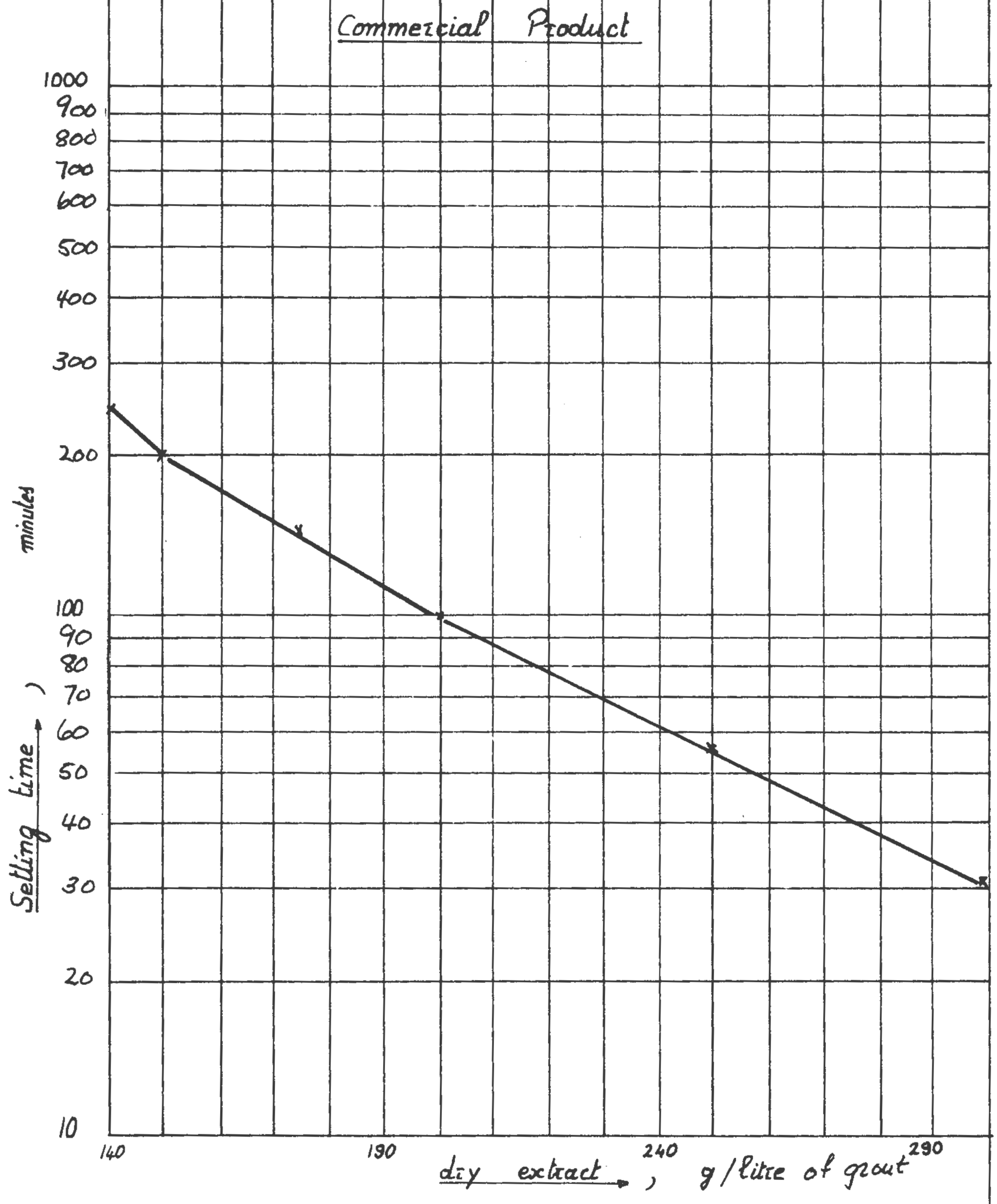


Fig. 119. Effect of Dilution on Setting Time (Commercial Product)

Table 33. Effect of Various Catalysts on Setting Time

Catalyst	Setting time in min.
Lithium hydroxide	25
Sodium hydroxide	20
Potassium hydroxide	60
Calcium hydroxide	20
Barium hydroxide	120
Lithium carbonate	50
Sodium carbonate	20
Potassium carbonate	20
Trisodium phosphate	1020

With each of these catalysts, setting time will depend on its concentration.

A systematic study was conducted with sodium hydroxide, the most commonly used catalyst at worksites, for a resorcin-formaldehyde grout. This showed that the shortest setting time was obtained with a pH of about 9.3, whatever the degree of diluteness (fig. 120). The catalyst dosage also has an effect on setting time with commercial products (fig. 121), the shortest setting time being obtained with a pH of about 9.5.

In both cases, minimum setting times will give the best mechanical characteristics. The term catalyst, although generally accepted, is thus a bit erroneous since a catalyst should affect only the speed of the reaction and not the grout's characteristics after polymerization.

2.3 Effect of the Phenol/Formaldehyde Ratio

Theoretically, another way of regulating setting time consists of modifying the phenol/formaldehyde ratio. With reference to the stoechiometric optimum, an increase in this ratio will extend the setting time, and a decrease will shorten it, but it harms the polymer's mechanical characteristics.

If specific mechanical properties are required, there can be no latitude in setting time without unbalancing the reaction, and thus incurring unfavorable economic circumstances.

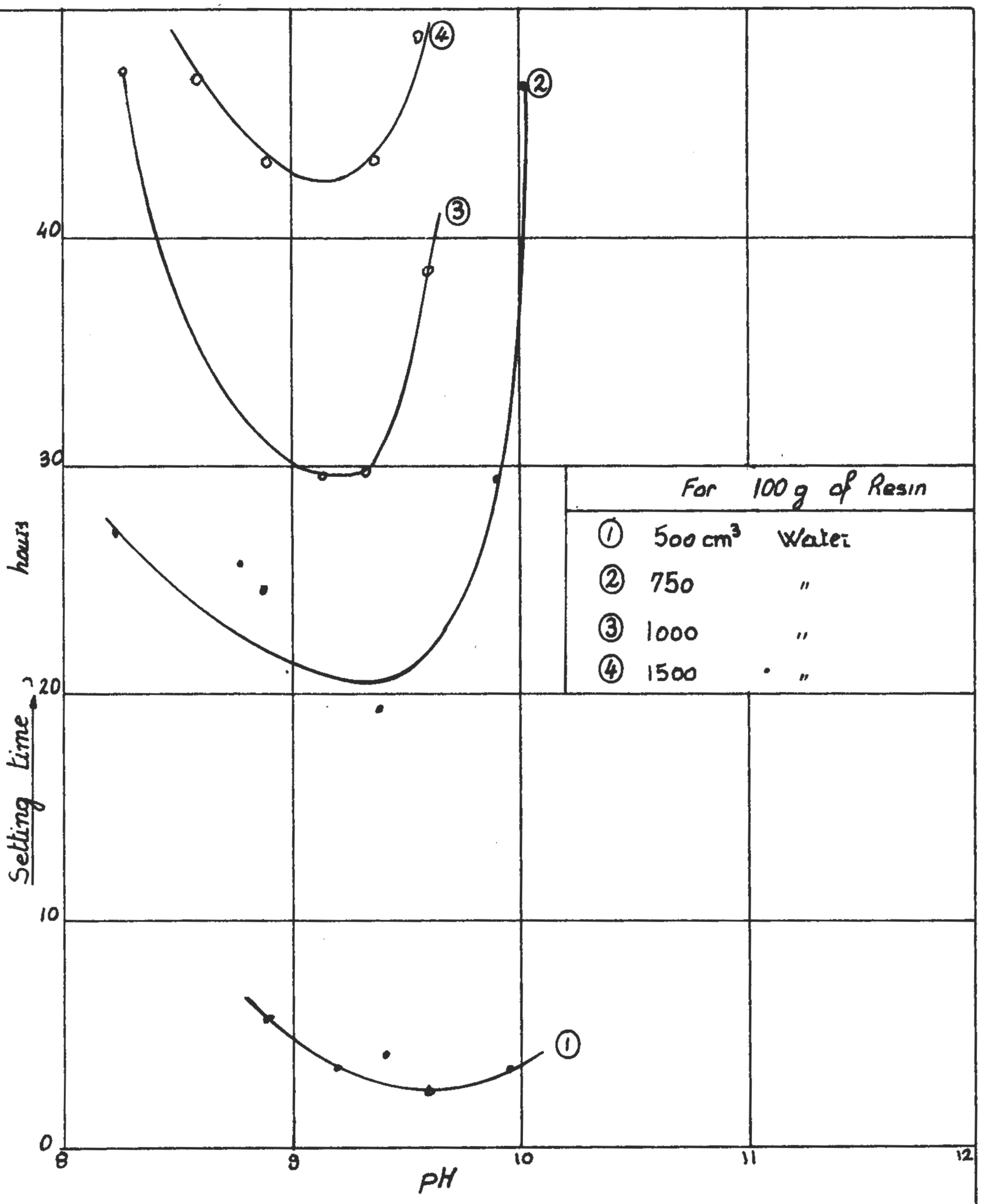


Fig. 120. Effect of pH on Setting Time for Different Dilutions

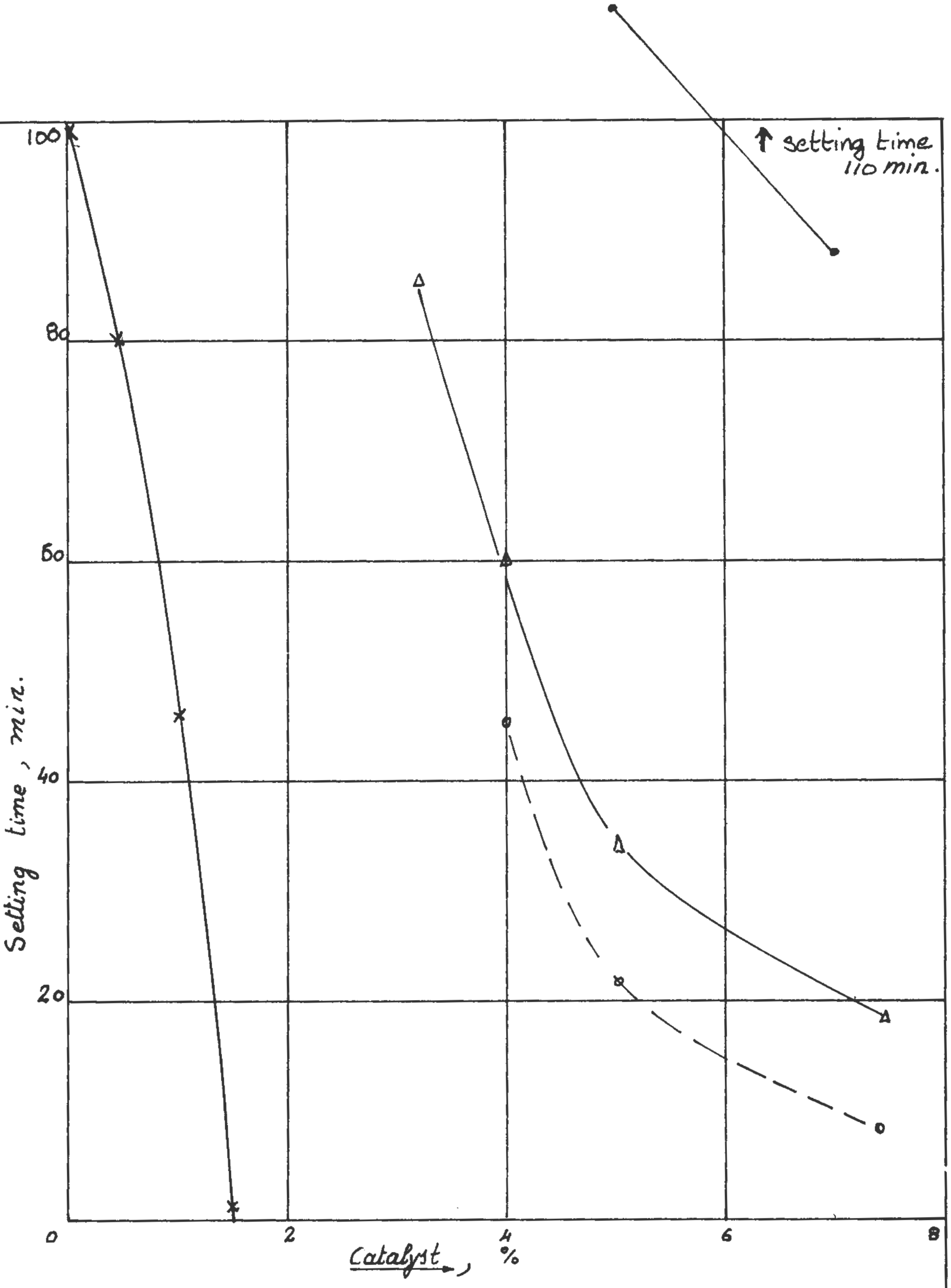


Fig. 121. Effect of Catalyst Content on Setting Time of Commercial Products at Different Concentrations

2.4 Conclusion

With both resorcin-formaldehyde and commercial grouts, the optimum phenol/formaldehyde ratio is sought. The optimum dosage of catalyst and regulation of setting time is much less flexible with phenoplasts than it is with polyacrylamides.

Very short setting times do not actually present a problem since they occur only with highly concentrated grouts whose strengths are unnecessarily high for most ordinary uses, and which are not normally used.

However, overlong setting times can be a problem. One solution is to incorporate small amounts of sodium silicate into the grout so that at the end of the desired setting interval there will be a pseudo-set which will fix the grout in the ground. The true set will occur only after the normal interval for the grout alone. An example of such a pseudo-set is given in fig. 122 .

3. Intrinsic Strength of Pure Grout

Strength of the grout will be affected by all the elements involved in the grout's formulation. As an illustration, fig. 123 clearly shows the effect of the proportion of sodium hydroxide on a resorcin-formaldehyde resin in varying degrees of dilution. There are similarities between these curves and those in fig. 121 which show changes in setting time under the same conditions.

To the extent that a well-balanced formulation is used (optimum dosages of formaldehyde and catalyst), shear strength of the pure grout will be affected only by its diluteness (fig. 124).

The behavior of resorcin-formaldehyde grouts is elastic (fig. 125), the ratio being perfectly linear. Because of this elastic behavior, shear speed has practically no effect on strength (table 34).

Table 34. Effect of Shear Speed on the Strength of a Resorcin-Formaldehyde Grout

Duration of shear stress in seconds	58	(1) 416	5280
Shear strength in g/cm^2	90	(1) 90.5	88

(1) Normal vane test shear speed

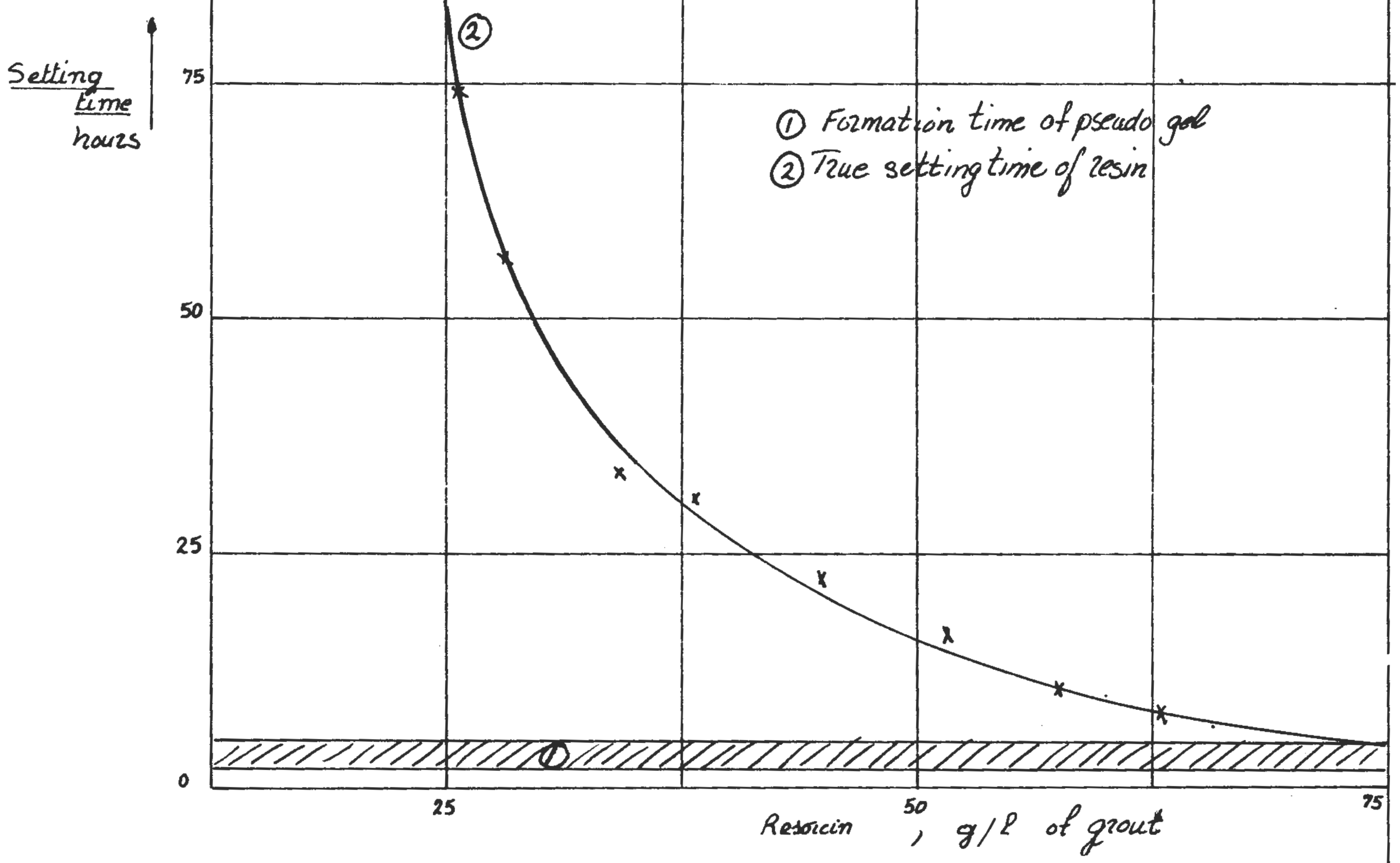


Fig. 122. Control of Setting Time By Use of Sodium Silicate

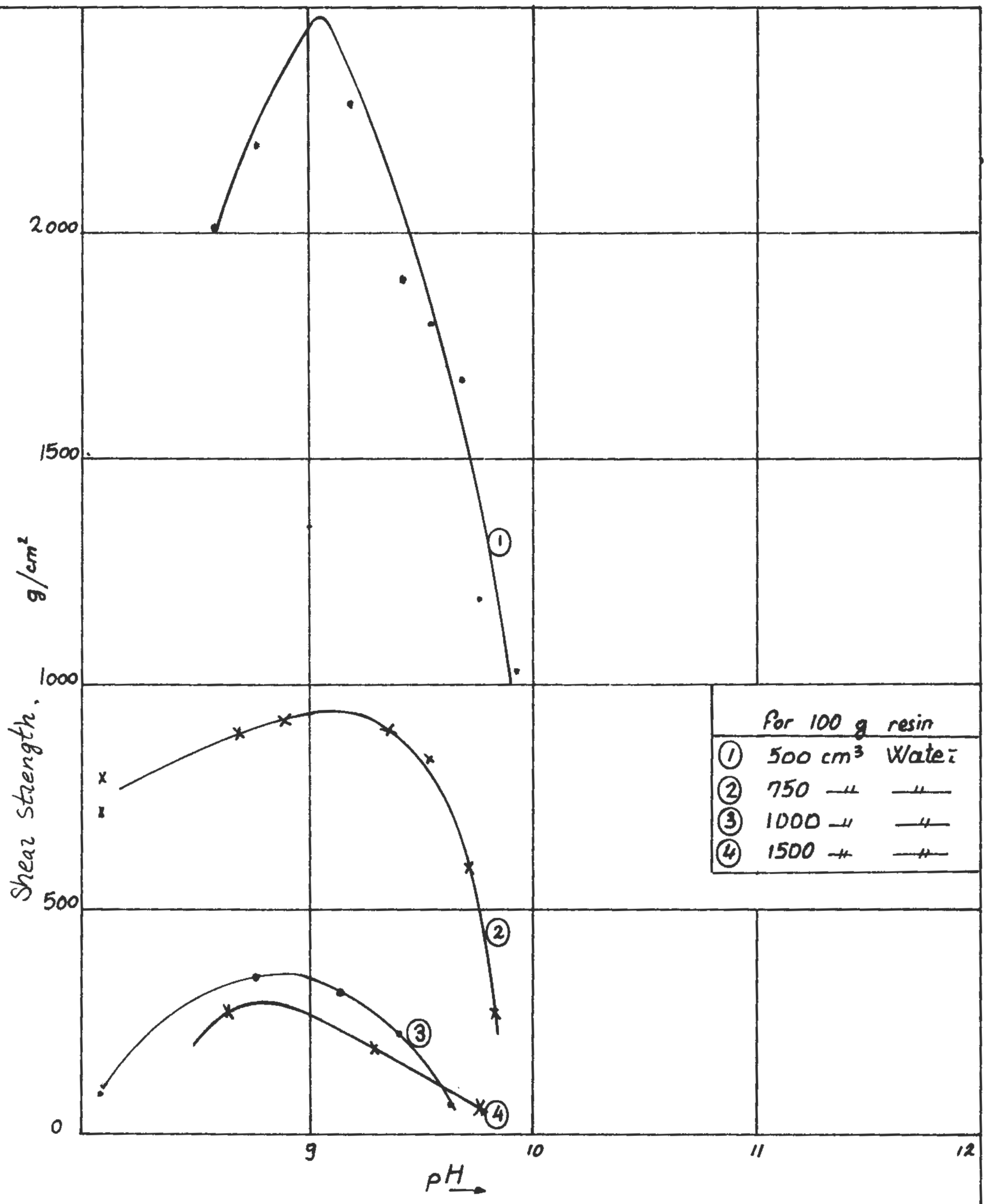


Fig. 123. Effect of pH on Shear Strength of Pure Resorcin-Formaldehyde Resin

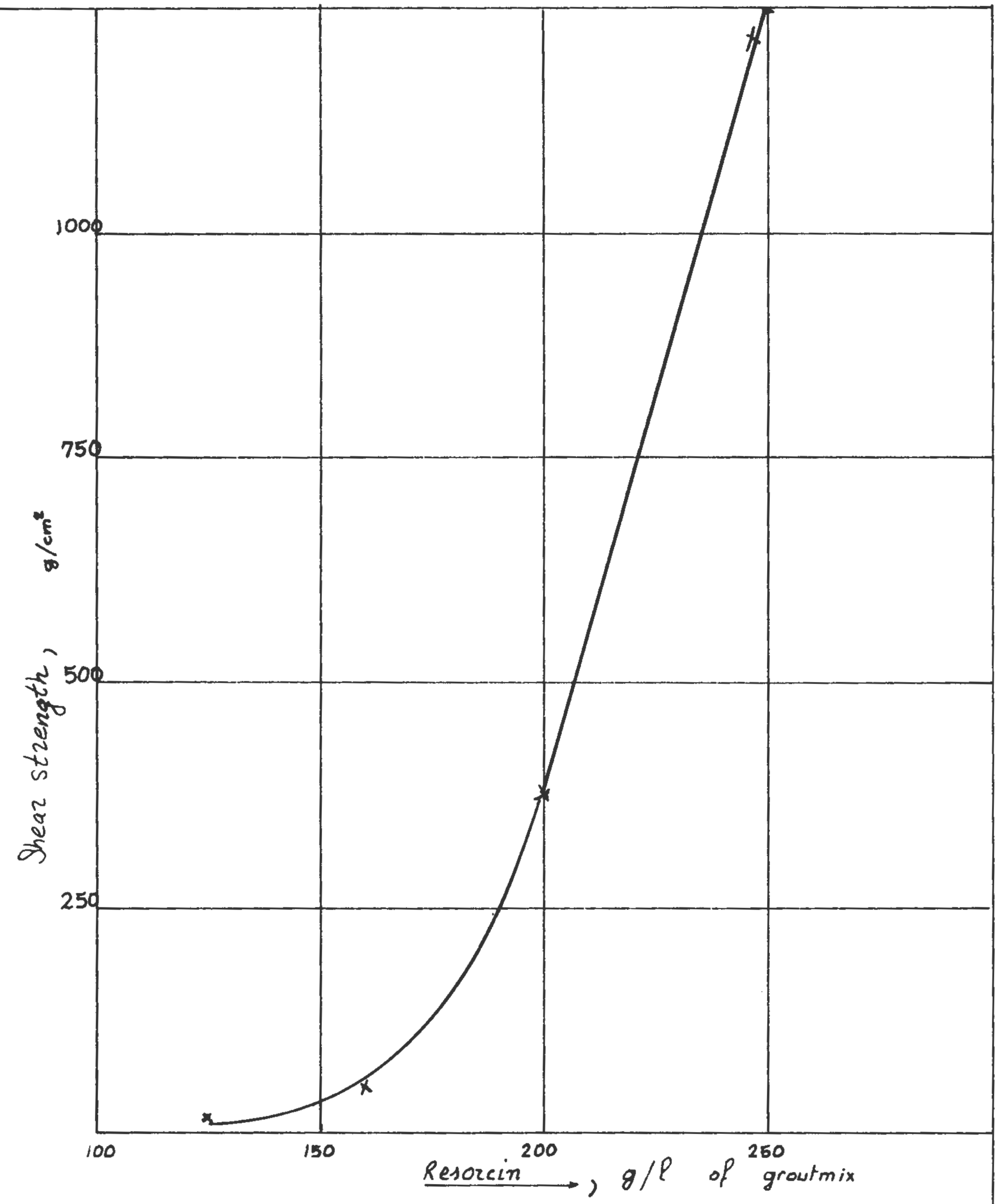
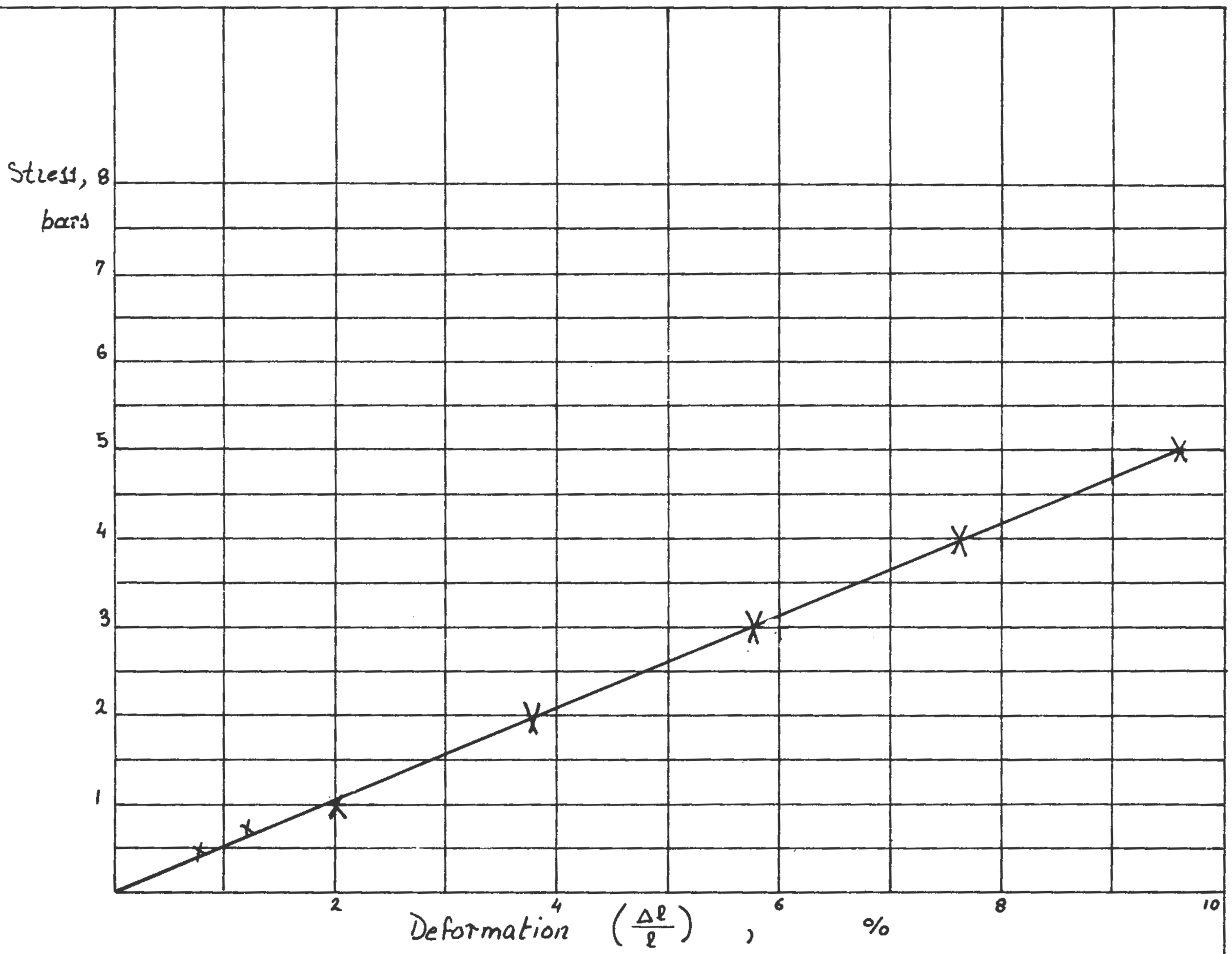


Fig. 124. Effect of Dilution on Shear Strength of Resorcin -Formaldehyde Grout



Stress at rupture 6.5 bars

Fig. 125. Stress-Deformation Relationship of Resorcin -Formaldehyde Grout

4. Strength of Treated Ground

Normal resin concentrations give relatively high shear strengths, so a whole range of strengths can be achieved in the treated ground and the desired degree of consolidation can be obtained (fig. 126).

Although some commercial products are quite comparable to resorcin-formaldehyde-base grouts, others give only mediocre results and should be used only for waterproofing irrespective of cost.

As is the case with polyacrylamide grouts, it appears that the speed with which stress is applied has less effect on the unconfined compressive strength of the sand-grout mixture than it does with silica gels, as shown in table 35 below and in fig. 127.

Table 35. Unconfined Compressive Strength of Resorcin-Formaldehyde Grout as a Function of Test Speed

Rate of deformation in mm/min		0.05	0.2	0.5	1	5	10	20	50
Unconfined compressive strength, bars	grouted sand	25	28.6	28.6	31.4	39.8		42.7	43.2
	mortar	20.7	22.3		24.1	27.5	28.5	31.2	31.1

This table also demonstrates the favorable effect on strength obtained by grouting the samples, rather than mixing sand and grout together to form a mortar.

5. Durability

Polycondensation of a properly formulated phenoplast grout will generally give a product which is insoluble in water; only the catalytic phase can remain partially free. For this reason, ground treated with a phenoplast grout is likely to behave well over time.

5.1 Hermetic Mold Cure

As with any resin, the mechanical properties of phenoplast grouts improve rapidly after the set. However, it should be noted that, depending on the formula used, these changes in mechanical properties can continue

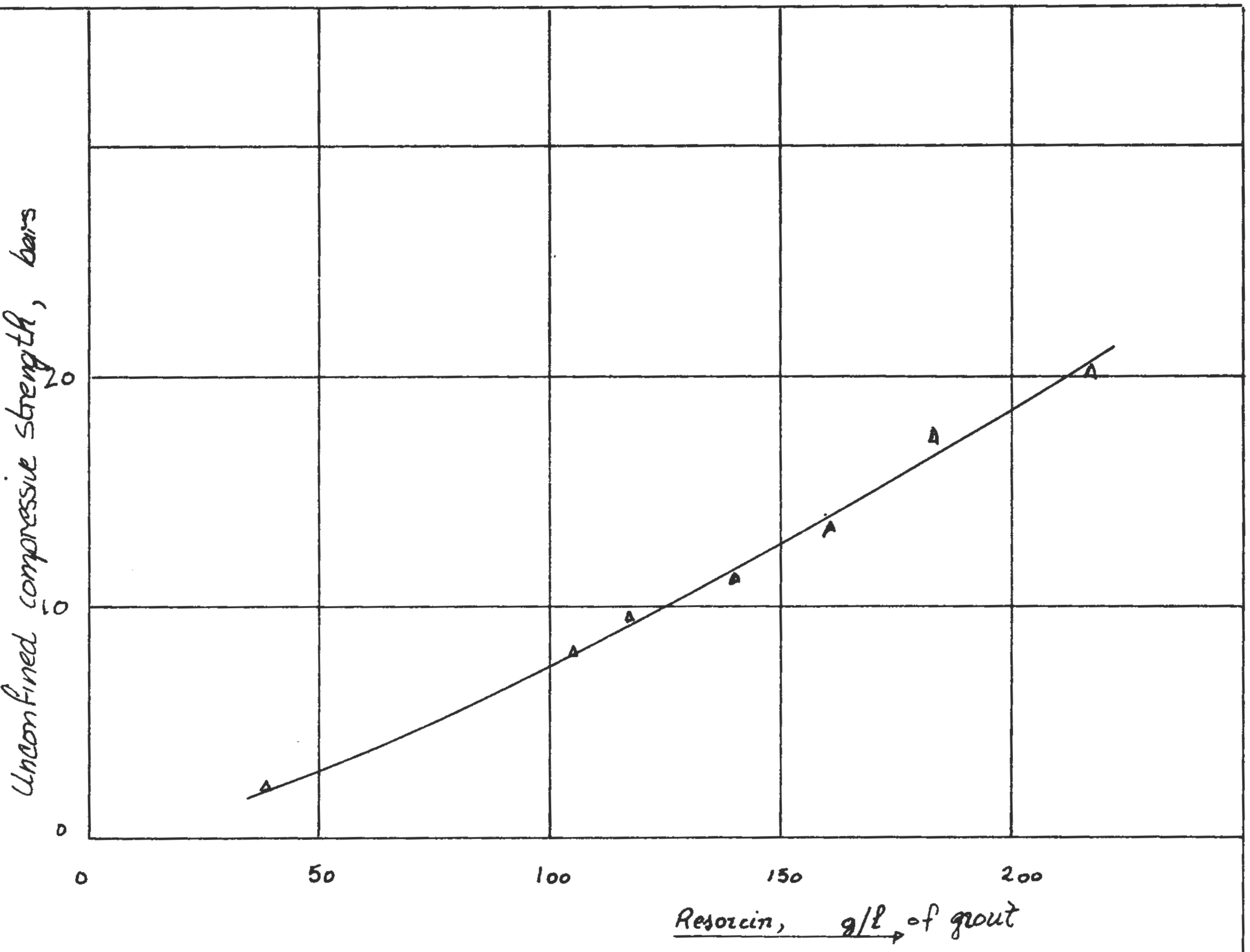


Fig. 126. Effect of Resin Content on Unconfined Compressive Strength of Phenoplast Grout

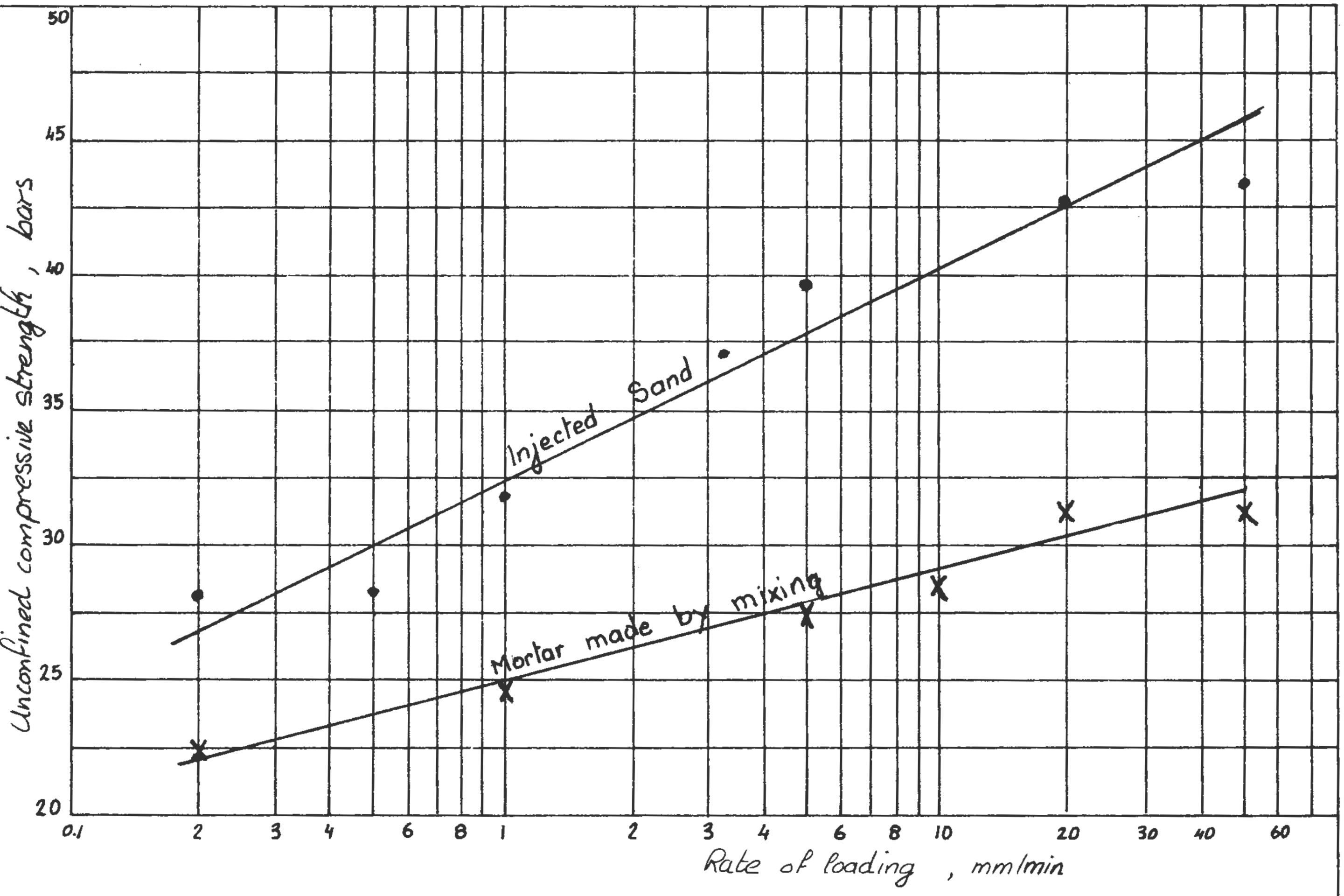


Fig. 127. Effect of Rate of Loading on Unconfined Compressive Strength of Phenoplast Resins

for some hours or for more than a week. For example, fig. 128 shows that about 10 days are needed for unconfined compressive strength to attain its maximum level. This is considerably longer than the interval needed for the corresponding pure grout to attain optimum shear strength (fig. 129).

In addition, the properties of some formulas, which are highly dilute or which use less reactive substitutes for resorcin, change gradually over several months. In general, however, the mechanical properties of soil treated with a phenoplast grout and cured in hermetic molds will stabilize at the end of about two weeks.

5.2 Dry Cure

Phenoplast grouts, as well as dry-cure grouted sand, tend to dehydrate with a dry cure, at first causing an increase in mechanical properties. But this loss of water involves internal tensions, whose intensity depends on the grout's formula, causing the treated ground to crumble. An example is given in fig. 130 for a mortar which has reached optimum strength in hermetic mold cure. This dehydration is practically irreversible and can ruin the sample as an equilibrium cannot be created with ambient moisture.

It is a matter of months before a sample can be considered ruined with this type of cure, and, in the context of an actual project, such an interval implies a measured risk, given the masses of ground grouted and the constant presence of moisture.

5.3 Wet Cure

WARNER (72-04) and others have demonstrated the good behavior of sands treated with phenoplast grouts and cured in water. WARNER's data and our results are shown in fig. 131.

A slight weakening occurs over a period of time, probably attributable to slow swelling of the resinous matrix. However, in some cases the performance of grouted samples cured in water is better than for those cured in hermetic molds.

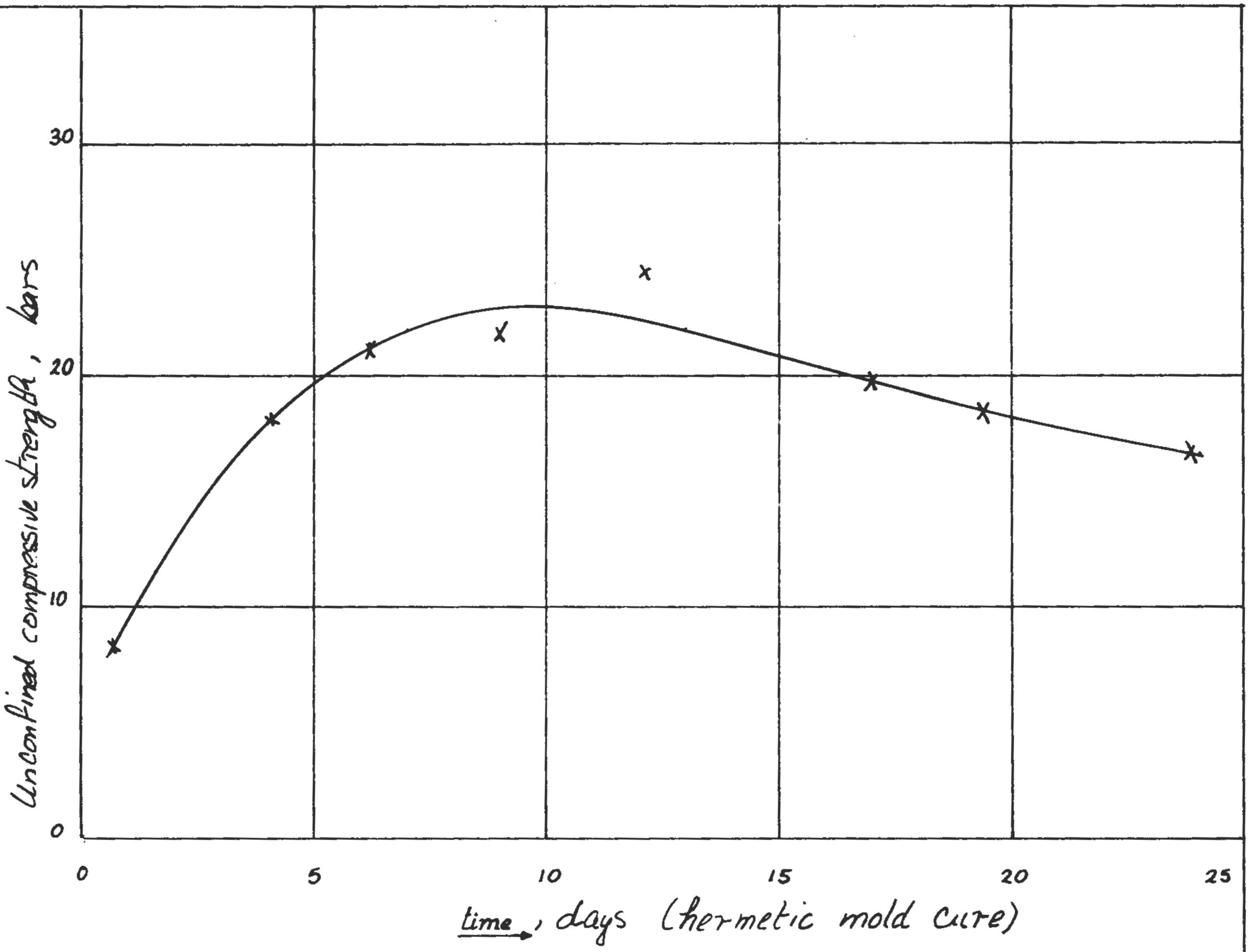


Fig. 128. Effect of Time on Unconfined Compressive Strength of a Sand Treated with Resorcin-Formaldehyde Grout

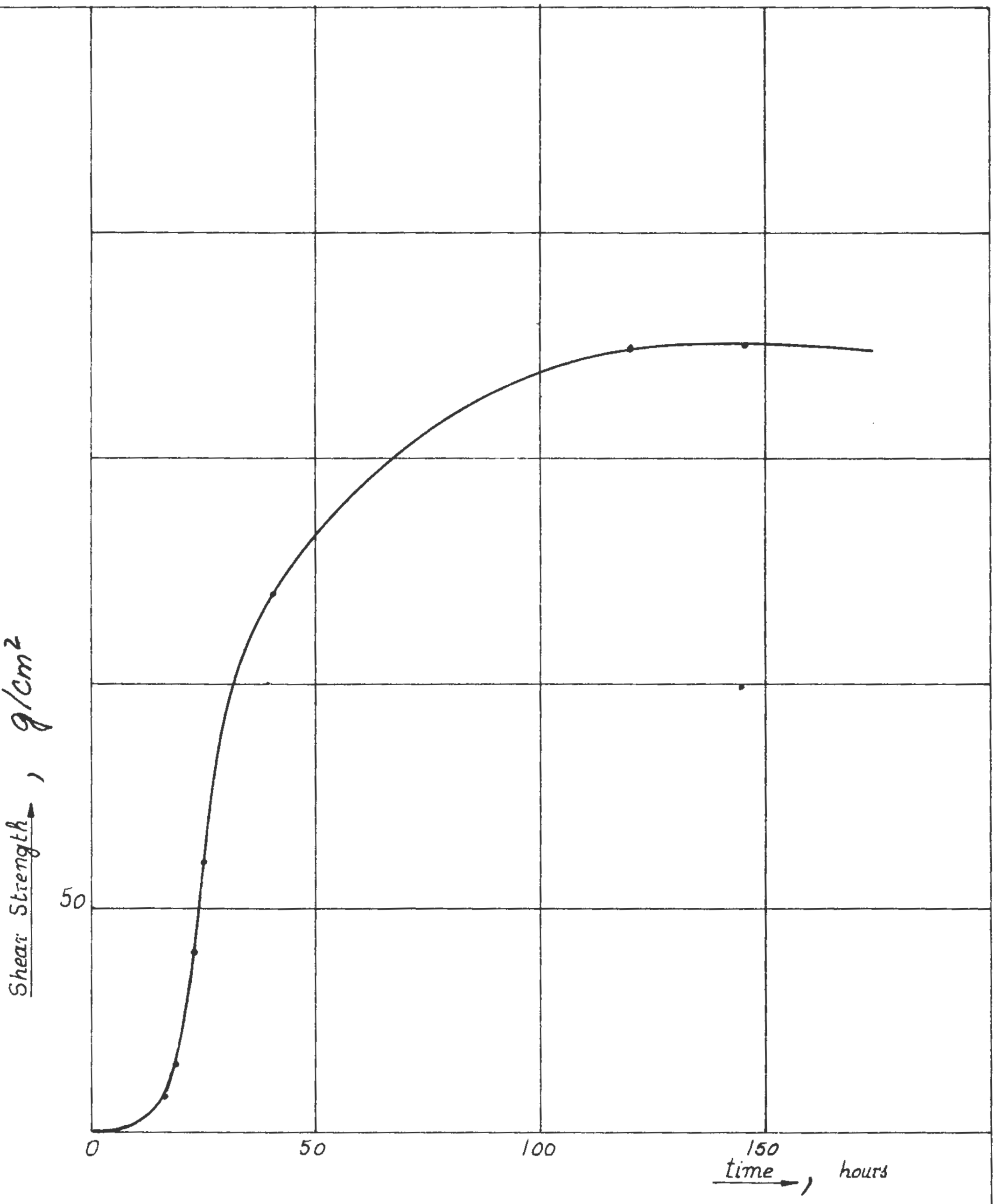


Fig. 129. Effect of Time on Development of Shear Strength for a Resorcin Formaldehyde Grout

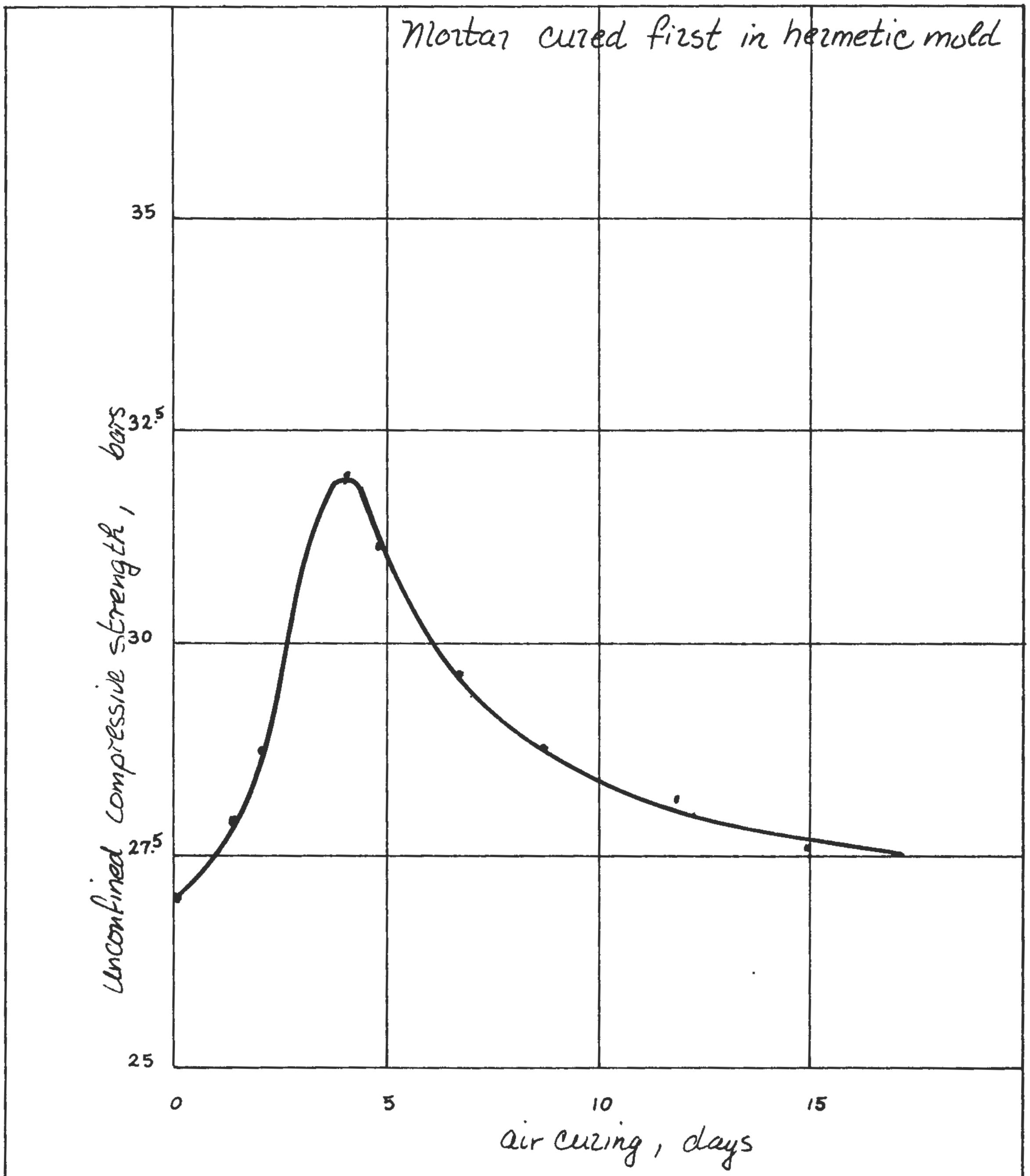


Fig. 130. Effect of Dry Curing on Strength of Resorcin-Formaldehyde Mortar

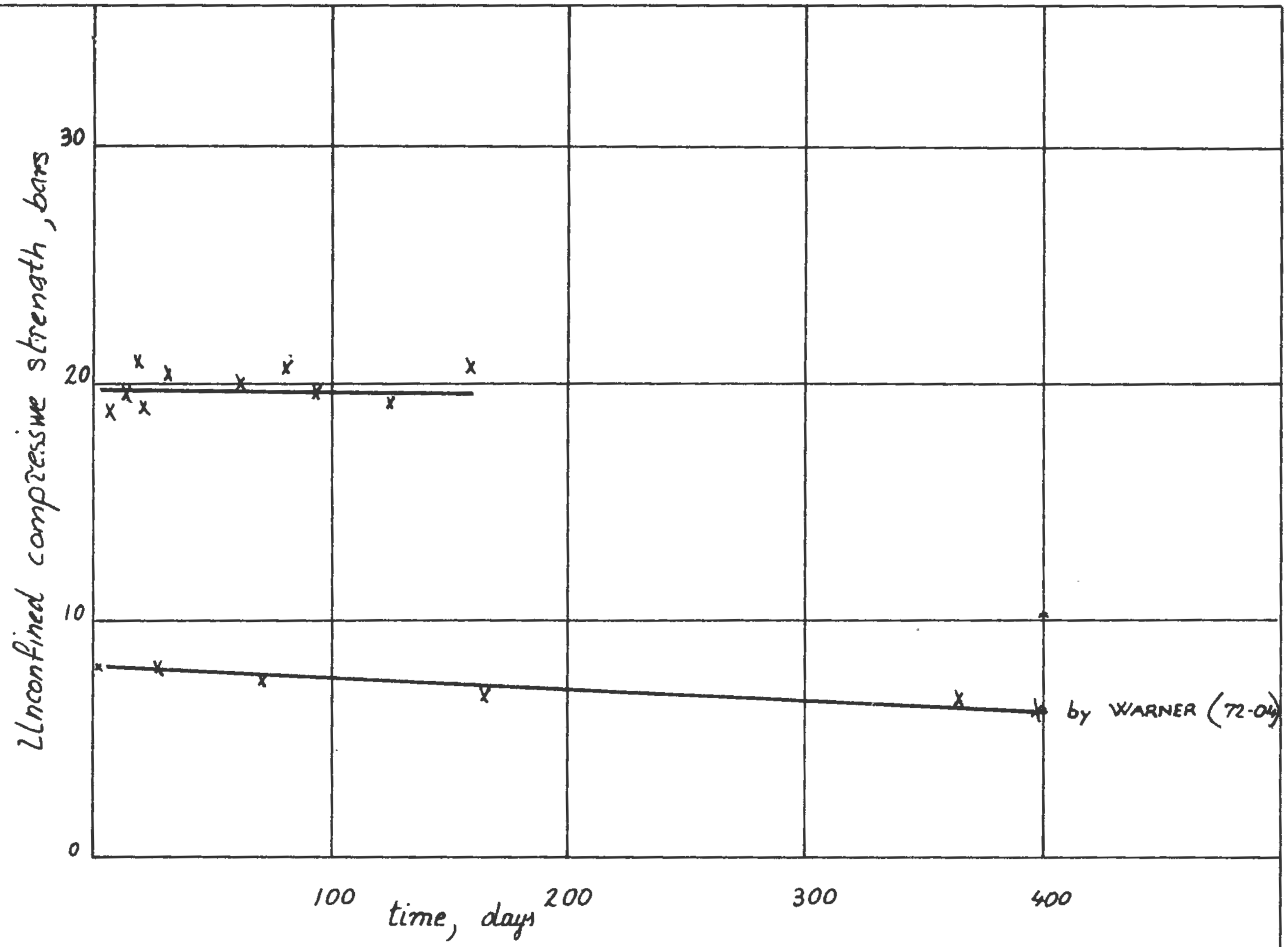


Fig. 131. Development of Unconfined Compressive Strength of a Sand Treated with Phenoplast Grout (Wet Cure)

5.4 Drying-Wetting Cycles

Fig. 132 shows an example of the effect of 2-day drying-wetting cycles on the long-term behavior of a phenoplast resin with average mechanical characteristics. These cycles are harmful, with the drying phase of the cycle largely responsible for this degradation.

5.5 Cure with Water Percolating Under Pressure

The percolation test is preferred for determining the durability of a grout in its sandy skeleton. In this test phenoplasts behave very well. As the permeability of samples grouted with phenoplast resin is well below 10^{-7} cm/s, the amount of percolation water is very slight even after several days on a steep gradient (250), and in these normal conditions, variations in permeability are undetectable in tests for erosion.

Observations of percolation water show that exchanges take place on the passive fraction of the grout (the catalyst) and thus do not alter the polymerized phase, either physical and mechanical properties.

5.6 Conclusion

The behavior of phenoplast grouts is very satisfactory with time, provided that dehydration does not occur.

6. Toxicity

As is the case with grouts as a whole, a distinction must be made between pre-set and post-set toxicity.

6.1 Pre-set Toxicity

A traditional formula for phenoplast grouts contains resorcin, formaldehyde, an alkaline base (generally sodium hydroxide). Taken individually, these ingredients are somewhat toxic or caustic, and commercial products of undefined formulas will be roughly the same. Although resorcin is less toxic and caustic than phenol itself, it remains a phenol and precautionary measures must be taken.

Although formaldehyde is in theory very dangerous, watering of the eyes and irritation of the throat and the mucous membranes and respiratory tract serve as warnings. However, if for any reason (dizziness, for example), a worker were to remain in an atmosphere where formaldehyde levels exceeded 40 to 50 ppm, there would be severe risk of

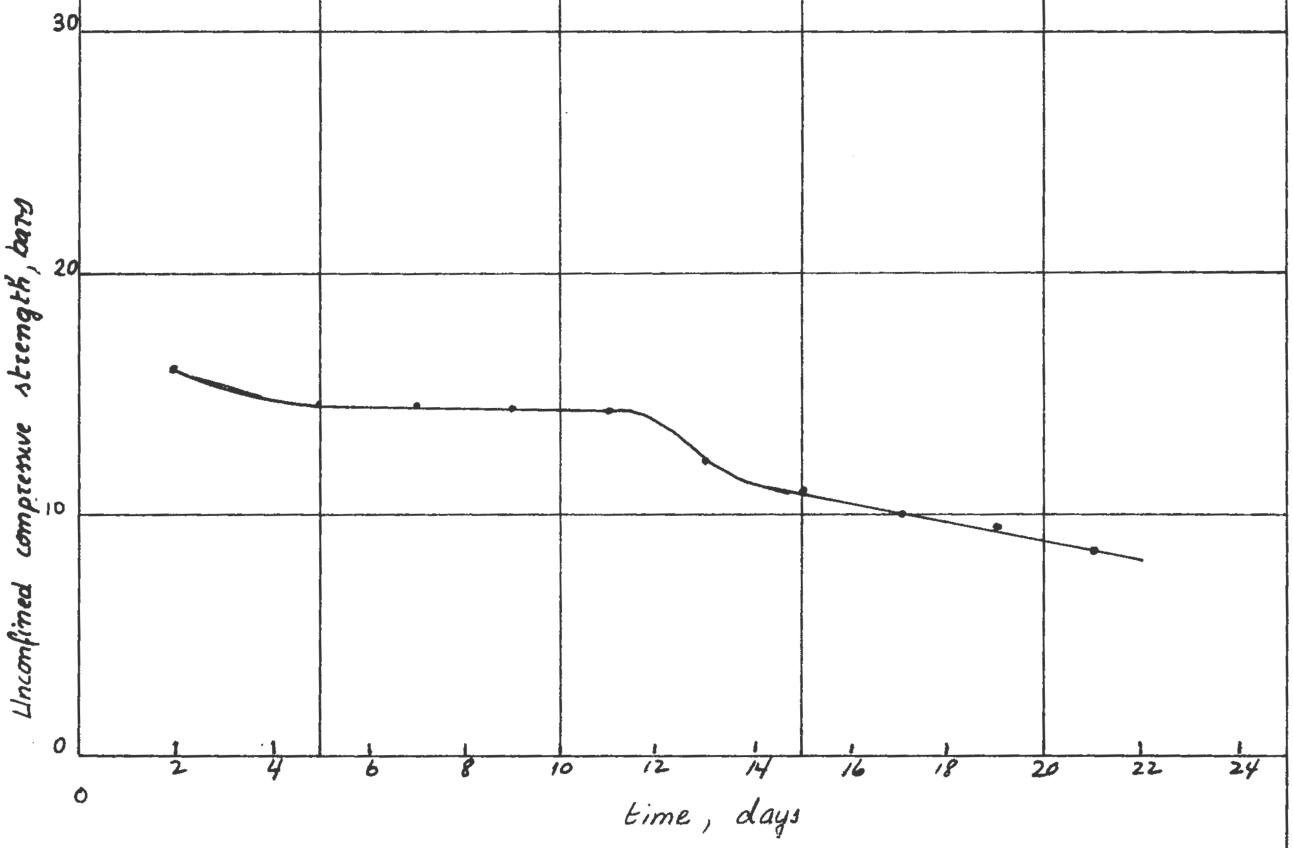


Fig. 132. Effect of Two Day Drying-Wetting Cycles on Strength for Resorcin-Formaldehyde Mortar

laryngitis, bronchitis, bronchial pneumonia, and even pulmonary edema, with hemorrhaging followed by necrosis of the affected area. In addition, repeated inhalation of low doses of formaldehyde leads to chronic irritation of the mucous membranes in the nose, eyes and respiratory tract (nasal catarrh, pharyngitis, laryngitis and, sometimes chronic bronchitis and asthma), and over the long run, dermatosis is possible. Since the catalyst is also highly caustic (generally sodium hydroxide precautionary measures must be taken for this product also.

Thus all precautions must be taken in the handling of the basic ingredients, the most dangerous being formaldehyde. However, its characteristic irritating odor constitutes the surest warning of its presence.

In contrast, because of diluteness and the almost instantaneous conversion of part of the resorcin into resorcinate and the rapid combination of the formaldehyde, the toxicity of the freshly-applied grout is much less than the basic ingredients.

The lethal dosages for the basic ingredients and the additives of phenoplast grout are shown in table 36. (Abbreviations used in the table are defined at the end of the table.)

6.2 Toxicity of Hardened Grout

The facilities where the grout is prepared should be equipped with a device to prevent any errors in proportioning. Thus, toxicity of the hardened grout will depend on the formula chosen. As far as possible, the formula should be designed to avoid leaving any resorcin and formaldehyde free, thus incorporating the optimum amount of catalyst and optimum resorcin/formaldehyde ratio (F/R ratio).

Fig. 133 shows that if the grout contains F/R ratios with an excess of formaldehyde, the latter can free itself after the set. This freeing of formaldehyde in a tunnel during excavation work could be bothersome and would necessitate ventilation. It should be noted, however, that the amount of free formaldehyde is limited, even if optimum dosages are exceeded.

Tests were conducted on rats using a hardened grout (well-balanced formula). The details follow.

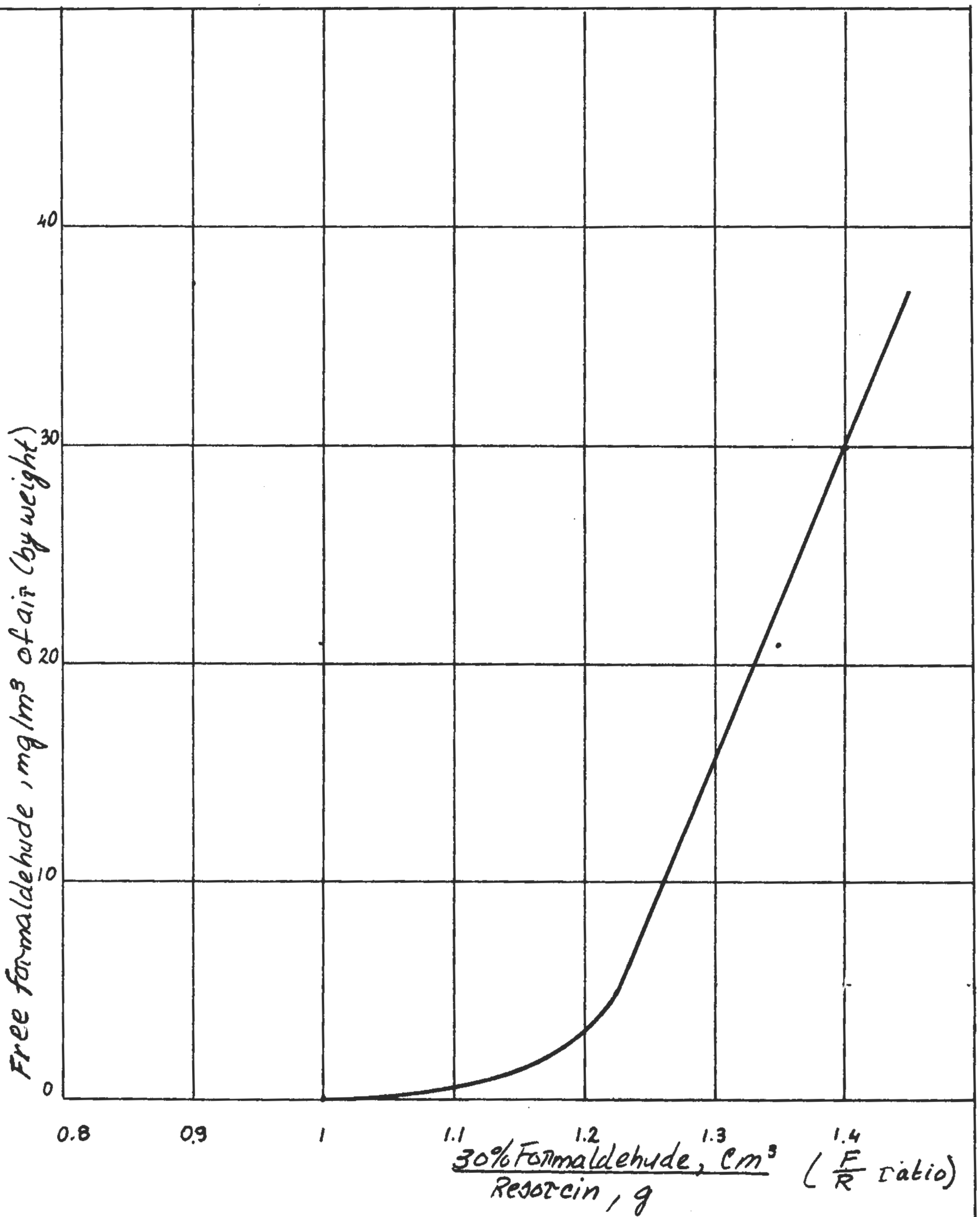


Fig. 133. Effect of F/R Ratio on Free Formaldehyde Content of a Treated Pulverized Soil

Table 36. Toxicity of Phenoplast Grout Ingredients

Ingredients		Toxicity		
		DL 50 oral mg/kg[1]		Miscellaneous
		rat	mouse	
<u>Basic ingredients</u>				
resorcin		301		
cresols	m – cresol	242		rabbit skin DL 50 2050 mg/kg
	o – cresol	121		rabbit skin DL 50 1380 mg/kg
	p – cresol	207		rabbit skin DL 50 301 mg/kg
xylenols	2,5-xylenol	444	383	
	2,6-xylenol	296	479	
	3,4-xylenol		400	oral rabbit DL 50 800 mg/kg
	3,5-xylenol	608	477	
phenols		414		rat skin DL 50 669 mg/kg
formaldehyde		800		guinea pig oral DL 50: 260 mg/kg
furfural		127		
<u>Additives and Catalysts</u>				
acids	acetic	3310		inhalation mouse LC 50: 5620 mg/kg
	boric	2660	3450	
	citric			ipr rat DL 50 975 mg/kg
	hydrochloric			M.A.C. (USA) 7 mg/m3
	formic	1210	1100	
	lactic	3730		guinea pig oral DL 50: 1810 mg/kg
	phosphoric	1530		rabbit skin DL 50 2740 mg/kg
	sulfuric	2140		
	sodium			M.A.C. (USA) 2 mg/m3
	potassium	365		
	ammonia	350		

---

[1] Abbreviations defined on page 265.

Table 36. Toxicity of Phenoplast Grout Ingredients (Continued)

Ingredients	Toxicity		
	DL 50 oral mg/kg		Miscellaneous
	rat	mouse	
aniline	440		rabbit skin DL 50 820 mg/kg
hydrazine	60		
dicyanodiamide			ipr rabbit DL 50 300 mg/kg ipr mouse DL 50 400 mg/kg
aminophenols para	1270		
meta	1660		
benzidine	309	214	
diphenylamine			hog oral DL 50 0.3 to 1.0 mg/kg
piperidine	520		rabbit skin DL 50 320 mg/kg
dimethylamine	698		
toluidine meta	974		
ortho	900		rabbit skin DL 50 3250 mg/kg
para	1285		
xylidines 2,3	933	1072	
2,4	467	250	
2,5	1297	841	
2,6	840	707	
3,4	812	707	
3,5	707	421	
ammonium bicarbonate			ivn mouse DL 50 245 mg/kg
calcium chloride	1000		ipr mouse DL 50 280 mg/kg
ammonium chloride	1650		ipr mouse DL 50 1300 mg/kg
stannous chloride			ipr mouse DL 50 66 mg/kg
sodium salicylate	1600	900	ipr rat DL 50 512 mg/kg ipr mouse DL 50 640 mg/kg
sodium thiocyanate	764		ivn mouse DL 50 484 mg/kg

Abbreviations:

DL 50 = Dose causing 50% mortality
LC 50 = Concentration in the air causing 50% mortality
ipr = Intraperitoneal
ivn = Intravenous
oral = orally
M.A.C. = Maximum allowable concentration in the air (U.S.A.)

Composition

water	770 cm^3
resorcin	100 g
formaldehyde	125 cm^3
sodium hydroxide	25 cm^3

Test Conditions

-CD rats (C.O.B.S.) [1]from the CHARLES RIVER FRANCE Farm weighing 150 to 185 grams, fasted for 24 hours before administration, 10 rats (5 male, 5 female).

-Product put into suspension (with a Teflon-headed grinder) in a 10% aqueous solution of gum arabic and administered by aesophageal tube.

-Dosage: 2 administrations at 3 hour intervals, 20 ml/kg of a 37.5% suspension.

-Duration of observation period: 15 days, with rats weighed every 5 days.

-Sacrificed with sodium pentobarbital given intravenously and autopsied on the 15th day for macroscopic examination of the principal abdominal and thoracic viscera.

Results

Mortality	none
Symptoms	none
Weight gain	normal
Autopsy	no anomaly

Conclusion

Administered orally to rats, this grout is not toxic in dosages of 15 g/kg.

---

[1] Caesarian Originated, Barrier Sustained

VII. CATEGORY A-8 COMBINED GROUTS

Two types of grout have been included in Category A-8: phenoplast-lignochrome combination grouts, and grouts combining silica gel and polyacrylamide resin.

For the first product, it would seem that it is not necessarily a matter of voluntary association, but that certain natural extracts can produce a grout having this mixed character. As noted in Volume I, there is nothing particularly remarkable about the grout's properties, which are half-way between those of a phenoplast and those of a lignochrome, with a tendency toward the one or the other, depending on the products used. For this reason, these grouts' characteristics will not be examined here.

By contrast, the silica gel-polyacrylamide combination grout is interesting because it adds new properties to those of its two basic components. These grouts are on the market, and RHONE-POULENC in particular sells its product in ready-mixed form under the name of SIPROGEL which is available in two solutions:

a) solution I contains in aqueous phase:

- polyacrylamide resin
- a hardener for the silicate
- an accelerator for the polymerization of the resin (DEAPN or DMAPN)

b) solution II contains:

- sodium silicate
- the resin's catalyst (ammonium persulfate)

Each of these concentrated solutions should be diluted by an equal volume of water when used. Formulations should be adjusted so that both solutions can be mixed in equal volumes when used. This type of grout is characterized by its resin and silicate concentrations.

The grout examined here, SIPROGEL 110-25, contains 11% acrylamide resin and 25% sodium silicate 30-32° Be. with a SiO_2/Na_2O ratio of 3.9.

1. Viscosity

1.1 Initial Viscosity

After solutions I and II have been mixed together, the initial viscosity of about 2 cP will be controlled primarily by the presence of the silicate.

1.2 Changes in Viscosity with Time

The silicate portion controls viscosity. This is discussed in Chapter II on silicate derivatives. This mixture produces a quick-setting diluted gel, and changes in viscosity occur rapidly.

2. Regulating Setting Time

One of the major disadvantages of a ready-mixed product such as SIPROGEL is that it is practically impossible to alter the setting time. According to the supplier, the setting process must follow a strict pattern: first, the silica gel forms and then the resin starts to set after the silicate has started, but before it has finished, setting.

Regulation of the setting time therefore is rather difficult. At most, a setting accelerator can be used which acts on both the silicate and the resin and allows setting time to be regulated by 1' or 2' and 50', depending on the dosage.

3. Strength of Pure Grout

The visco-plastic character of the silica gel formed is compensated by the purely elastic character of the polyacrylamide grout, thus shear speed has almost no bearing on strength readings (table 37).

It should be noted that the silica gel considerably strengthens these grouts in comparison with the basic grout.

Table 37. Effect of Shear Speed on Strength

Duration of shear stress in seconds	75	(1) 412	6375
Shear strength, g/cm^2	24	23.5	25.5

(1) normal shear speed

4. Strength of Treated Ground

Unconfined compressive strength tests conducted on a standard sand treated with this grout give strength readings on the order of 20 bars. These very satisfactory results justify the use of this more dilute grout. Measured by the direct molding method, strength is 14 bars.

The speed with which the stress is applied has practically no effect on the grouted sand's strength (table 38). This consistency in strength is unquestionably the remarkable parameter of this grout.

Table 38. Effect of Rate of Loading on Unconfined Compressive Strength

Rate of loading, mm/min.	0.05	0.2	0.5	5	10	20	50
Unconfined compressive strength, bars	14.8	14.3	14.0	14.0	15.2	14.9	15.1

5. Durability

Once set, the structure of this grout involves an overlapping of the inorganic silica gel into the organic polyacrylamide gel, with each component reinforcing the specific properties of the other.

5.1 Hermetic Mold Cure

Using this curing method, sand treated with silica gel-polyacrylamide grout attains unconfined compressive strength of 20 bars very quickly, in less than 24 hours. Strength continues to increase for a week, reaching 30 bars, and then drops back again to stabilize at around the initial value of 20 bars.

5.2 Dry Cure

Air-cured samples exhibit a considerable increase in strength for about 15 days, after which strength decreases. Optimum strength attained is very high, about 20 bars, and remains over 100 bars for about one month. Thus the grout is able to form a very resistant shell.

5.3 Cure in a Wet Medium

Once set, SIPROGEL is likely to absorb large amounts of water, up to 100% by volume, and the attendant swelling causes a loosening of the sandy skeleton. Tests on small unreinforced samples cured by immersion in water register a rapid drop in strengh.

5.4 Drying-Wetting Cycles

In this test, SIPROGEL's behavior is halfway between that of polyacrylamide grouts and that of silica gels. It can withstand these cycles for about a week without being particularly disturbed, then it begins to be disturbed by excessive swelling during the wetting phase.

5.5 Cure with Water Percolating Under Pressure

These grouts are comparable to polyacrylamide and phenoplast grouts and produce such a high degree of watertightness that it is impossible to measure the rate of seepage with normal test procedures.

5.6 Conclusion

The various behavioral tendencies in different media are shown in fig. 134.

6. Toxicity

6.1 Pre-set Toxicity

Information concerning toxicity of the basic ingredients, sodium silicate, acrylamide resin and hardeners, is available in Chapters II, IV and V.

The precautionary measures to be taken for personnel are primarily concerned with the handling of the acrylamide.

6.2 Post-set Toxicity

The data that follows on toxicity were obtained from the RHONE-POULENC toxicology laboratory for the hardened cured product, SIPROGEL 110-25.

Composition

-solution I	250 cm^3
-solution II	250 cm^3
-accelerator ACS	20 cm^3
-water	500 cm^3

Silicate setting time = 10 minutes
Resin setting time = 20 minutes

Ground with a pestle 24 hours after setting, appearance is a white gelatinous paste.

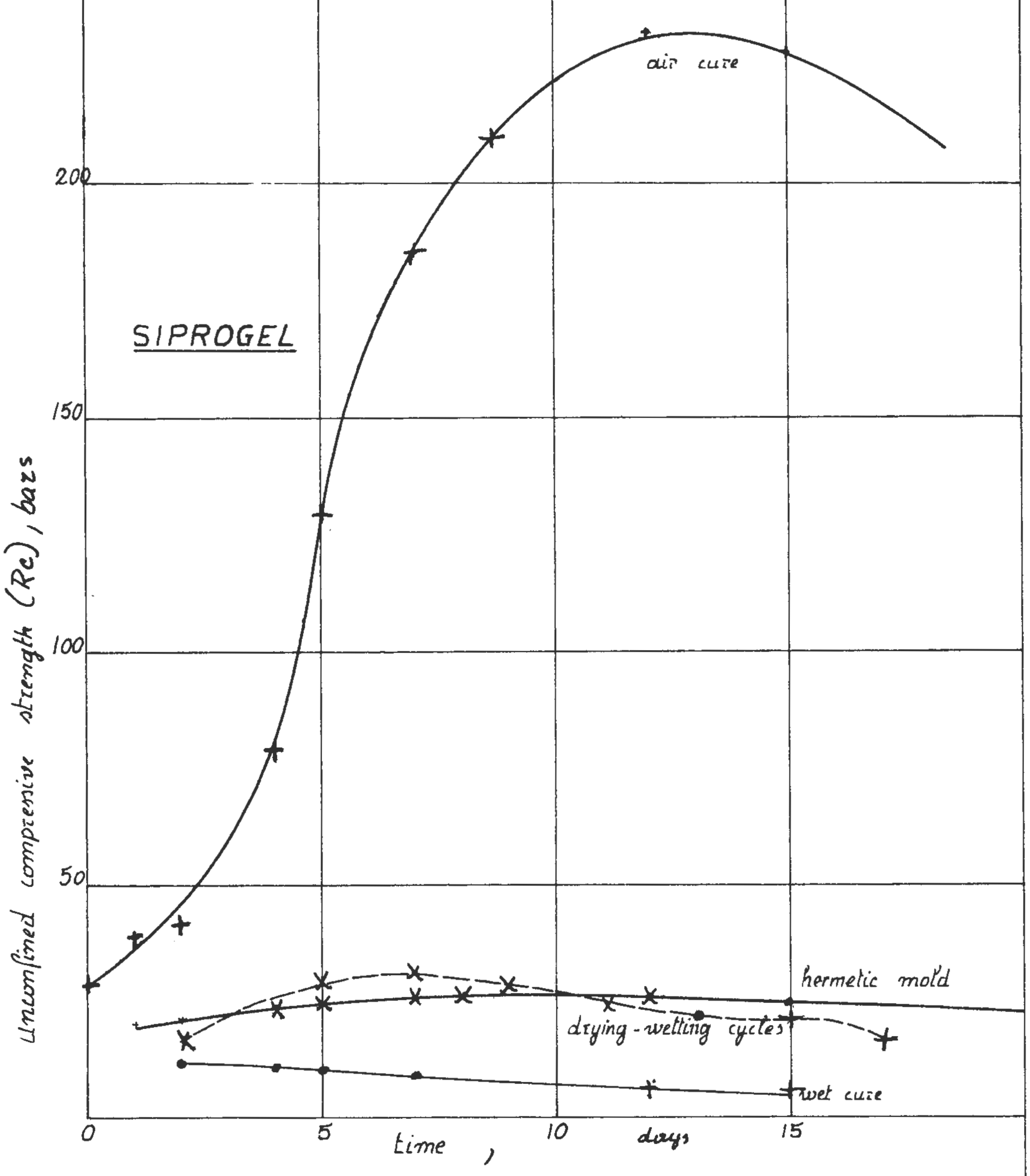


Fig. 134 . Effect of Curing Method on Strength (SIPROGEL)

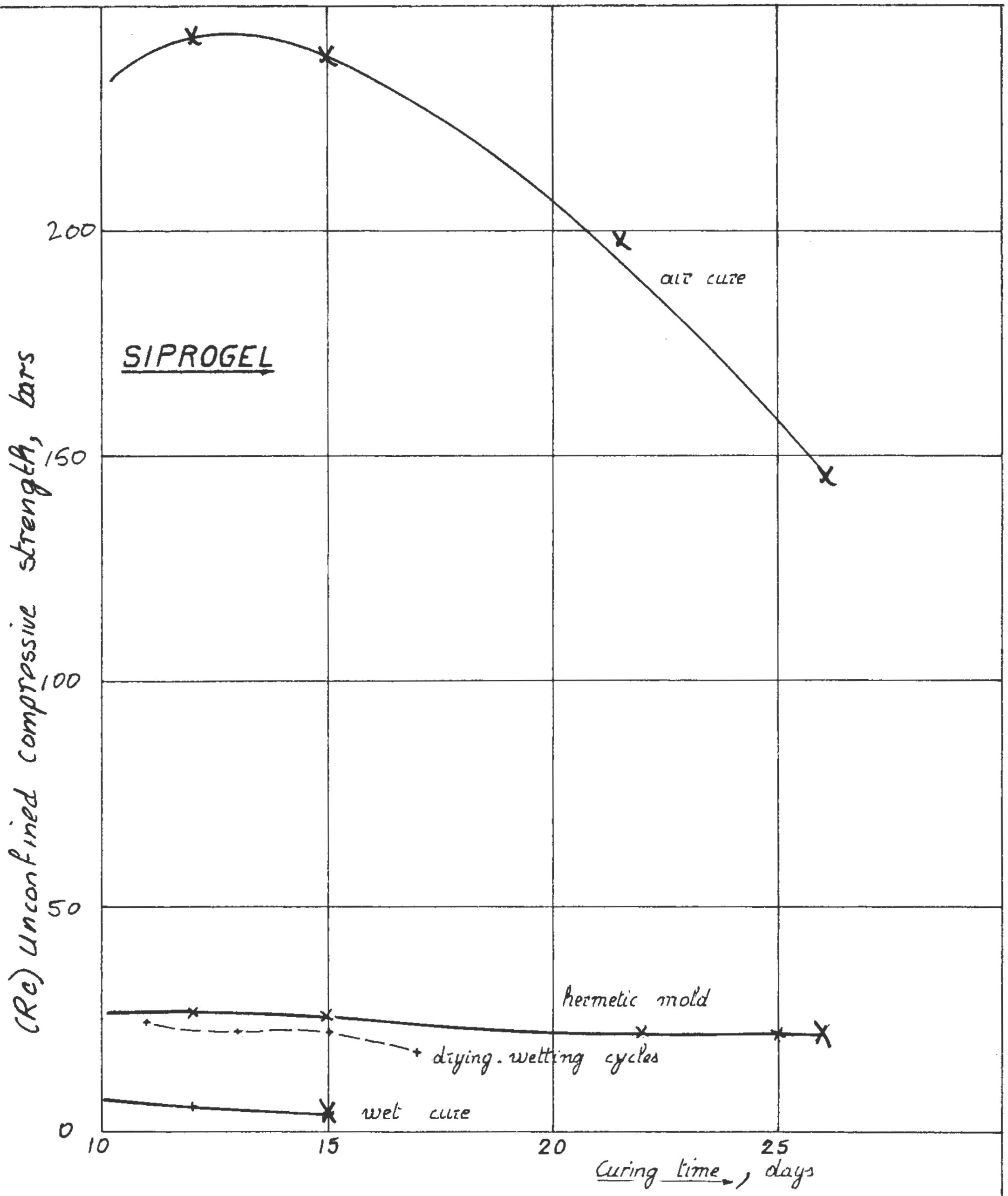


Fig. 134. Effect of Curing Method on Strength
(cont'd) (SIPROGEL)

Test Conditions

-CD rats (C.O.B.S.) [1]from the CHARLES RIVER FARM, France, weighing 160 to 190 g; 10 rats (5 male, 5 female)

-Product incorporated into "food pellets". Product impossible to dissolve or put into suspension in an adequate vehicle. The following pellet composition for one animal:

-36978 R.P.	3 g
-powdered milk	4 g
-honey	enough to make up pellet of 10 g

-Dosage: 15 g/kg per day, so a rat weighing 200 grams will ingest a pellet containing 3 grams of the product in a 24 hour period.

- Administration: after fasting for 32 hours, the rats are placed in individual cages and receive as their only nourishment for the following 24 hours a pellet containing 3 grams of product. At the end of this 24 hour period, the amount of pellet not consumed is weighed, and the rats, in groups of 5, receive their usual nourishment.

-Duration of observation period: 15 days, with rats weighed every 5 days.

-Rats are sacrificed by intravenous injection of sodium pentobarbital and autopsied on the 15th day for a macroscopic examination of the principal thoracic and abdominal viscera.

Results

Amount of pellet not consumed	negligible (1.5 g one rat)
Mortality	none
Symptoms	none
Weight gain	normal
Autopsy	no anomaly

Conclusion

Taken orally, RHONE PROGIL 36978 is not toxic to rats at a dosage level of 15 g/kg.

---

[1] Caesarian Originated, Barrier Sustained

VIII. CATEGORY B-2 INORGANIC COLLOIDS: BENTONITE GROUTS

1. Introduction

Bentonite grouts are different from silicate grouts (Category A-1) in four areas:

1) Bentonite grouts contain particles equal in size or smaller than one micron, provided that a peptizer has been added to keep the particles separate. These particles do not harm the grout's injectability, except in very fine terrain.

2) At rest, these grouts are highly rigid, unlike Category A grouts which are merely viscous.

3) As they are Binghamian fluids, their apparent viscosity is highly dependent on their speed of conduction, which will effect the injectability of this grout. At rest, they are rather highly rigid, and their apparent viscosity is high. At high speeds (injection by drilling, for example), rigidity disappears and apparent viscosity sharply decreases. A bentonite suspension then behaves as a fluid.

4) Finally, bentonite gels have very little strength and are used solely for waterproofing.

2. Viscosity and Rigidity

2.1 Initial Viscosity and Rigidity

Unlike Category A grouts, which become somewhat viscous as soon as their ingredients are mixed together, bentonite suspensions pass through a phase where the bentonite particles are hydrated, after which they acquire their final colloidal characteristics. Thus viscosity and rigidity of bentonite grouts can be defined only after the hydration phase is over.

Changes in viscosity and rigidity of bentonite suspensions at hydration can vary sharply depending on the nature of the material. These variations are shown schematically in fig. 135 for three different types of bentoites. The hydration of some bentonites occurs very rapidly (Curve 1), and their initial viscosity and rigidity stabilize after a few minutes; this very rapid hydration generally occurs in high yield bentonites. For other bentonites

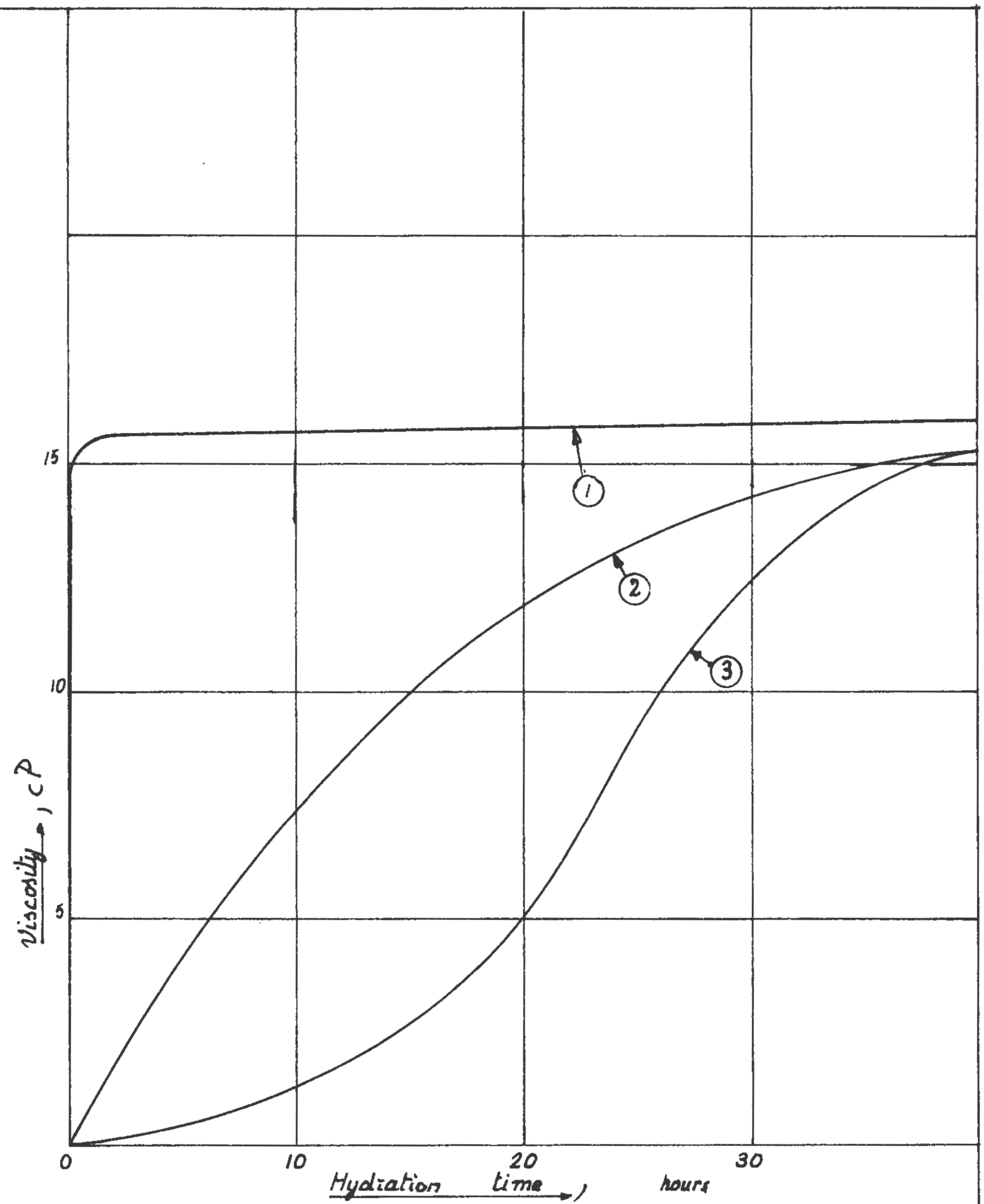


Fig. 135. Hydration of Three Bentonite Suspensions

hydration is very slow and can take up to 24 and even 48 hours (Curve 2). Finally, the shape of the curve for the third type of bentonite is between the two extremes (Curve 3). The addition of a peptizer to the grout alters the final figures, but not the shape of the curves.

Since a bentonite grout's shear strength is entirely secondary, the principal criterion is injectability, especially since bentonite gels are used only for waterproofing fine sands. A bentonite grout's initial viscosity also plays an important role in this respect. To ensure optimum injectability of the grout, initial viscosity is set at 15 cP ± 5 cP. Above this range, the gels become too viscous and injectability drops sharply; below it, there is a risk of sedimentation.

A Marsh viscosimeter, used by petroleum engineers, is often used to measure the viscosity of bentonite slurries. In this case, the figures given above would correspond in a Marsh cone to a 40 ± 5 second flow.

Expressed in terms of rigidity, this range of viscosity would correspond to values ranging from about 10 mg/cm^2. These very low values are measured with a highly sensitive rigidimeter.

As bentonite suspensions can be prepared using bentonites with widely differing colloidal power, the same initial viscosity of 15 cP can be attained with concentrations ranging from 35 to 90 kg of dry matter per m^3 of water.

2.2 Changes in Viscosity and Rigidity over Time

Once the bentonite is hydrated, the slurry's rheological characteristics will not change during the interval allotted for grouting. The viscosity and rigidity of a bentonite suspension increase slowly and almost indefinitely over time, but this increase is only marginal in the few hours following preparation, i.e. after hydration.

3. Setting Time

The setting time of bentonite gels cannot be regulated since no setting reagent is used. The grout will hold fast in the ground as soon as its rate of circulation becomes very low. As noted previously, bentonite gels are

Binghamian fluids, as shown in fig. 136a. Up to a certain level of stress, a bentonite slurry is not subject to displacement. If the stress increases, displacement becomes more and more rapid, and finally, in the third phase, speed of displacement becomes proportional to stress. In the first phase, the grout is comparable to a highly rigid gel, the second phase corresponds to a pseudo-liquid, the third phase to a fluid. The linear part of the curve (third phase) allows a determination of the gel's shear threshold, which is originally the abscissa. Fig. 136b shows the same phenomenon for apparent viscosity. The higher the grout's speed of circulation, the lower its apparent viscosity will be.

This rheological behavior, common to all inorganic colloids, has practical implications for injection. In injection by drilling, because the speed of circulation is high, the grout behaves as a fluid. In the ground, as the grout spreads out from the bore-hole, its circulation speed decreases at the periphery of the grouted area, and, consequently, its rigidity increases. This increase eventually causes the grout to stop moving in the ground.

If the injection pressure exceeds the shear threshold, the slurry will once again be subject to displacement. This phenomenon can reoccur, since the absence of a setting reagent in the system means that the bentonite slurry will not set. The only possible limitation to the slurry's injectability in a given terrain is thus determined by the injection pressure which can be exerted, given conditions at the worksite (the ground's particle size, weight of ground above the ground to be grouted, etc.).

Since the rheological characteristics of a bentonite grout vary depending on the nature of the bentonite, this will have an effect, however secondary, on injectability. Temperature also has some effect on the viscosity and rigidity of bentonite grouts: at low temperatures, there is a decrease in rigidity and an increase in viscosity, which appears in fig. 137 for a bentonite slurry examined with a FANN viscosimeter. This parameter can slightly alter the injectability of a bentonite suspension.

4. Intrinsic Strength of Bentonite Gel

As noted previously, a bentonite gel's shear strength is always very low, whatever the nature and dosage of the bentonite. Further, the adoption of a

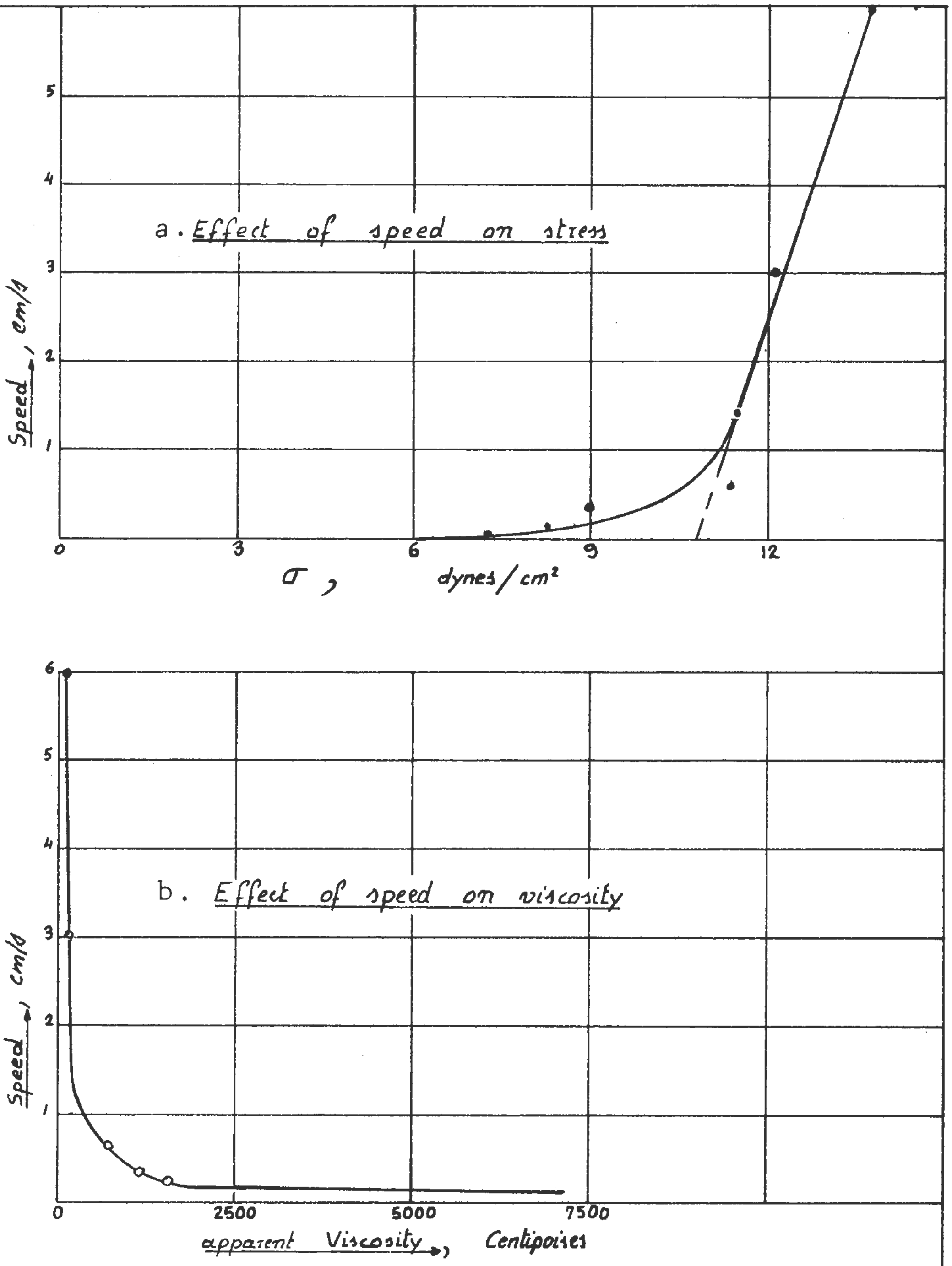


Fig. 136. Effect of Fluid Speed on Viscosity of Binghamian Liquids

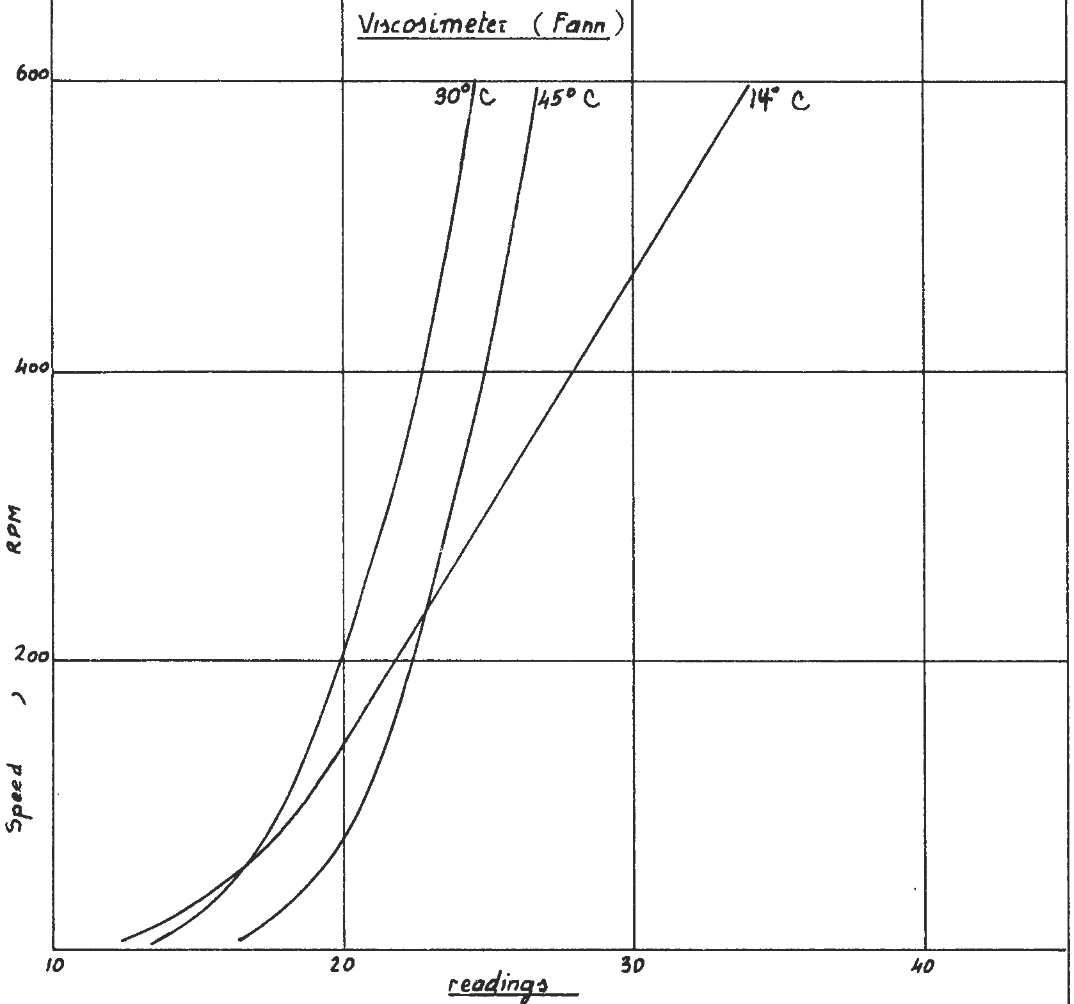


Fig. 137. Effect of Temperature on Rheological Characteristics of a Bentonite Mud (FANN Viscosimeter)

practically constant viscosity value corresponding to optimization of the bentonite gel's injectability also tends to narrow the differences in relative strength among the various gels.

Thus, with regard to preparation, one cannot speak of shear strengths of bentonite gels. At the most, the strength of grouts, whatever their nature, tends to increase with the proportion of dry matter. The same principle applies to bentonite suspensions. However, as the range of variations in dosage for a given bentonite is rather limited, this effect is marginal.

5. Durability

A bentonite grout's rigidity increases very slowly over time. Fig. 138 shows the rigidity of a grout cured in hermetic molds represented on a semi-logarithmic scale. Curing in a wet atmosphere does not disturb these grouts. Conversely, in dry cure the samples crumble into dust. However, this bad behavior in dry cure should not be a problem, since the bentonite grout will be used only to ensure soil watertightness in the form of grouted curtains, and will virtually always be in contact with water.

The type of cure of greatest interest is thus that of percolation under pressure, which allows testing of the material from two standpoints:

1. risk of washing out;
2. risk of erosion: the definition of its rheological characteristics indicates that a bentonite slurry, an unset material, can start to move again under strong pressure. In the ground that would mean erosion of the grouted curtain.

Because of the low strength characteristics, the percolation under pressure test was not conducted with the usual pressure of 1 bar, but only 0.1 bar. In fact, according to the ratio given by H. CAMBEFORT (67-12) in Chapter IV of Part One of this volume, there would have been some risk of erosion in a cell 10 centimeters high. During the entire test (28 days), no water was observed moving in the cell.

6. Toxicity

The basic ingredients (clays or bentonites) are absolutely not toxic. The same is true for the peptizers (generally polyphosphates). Since all products are in powder

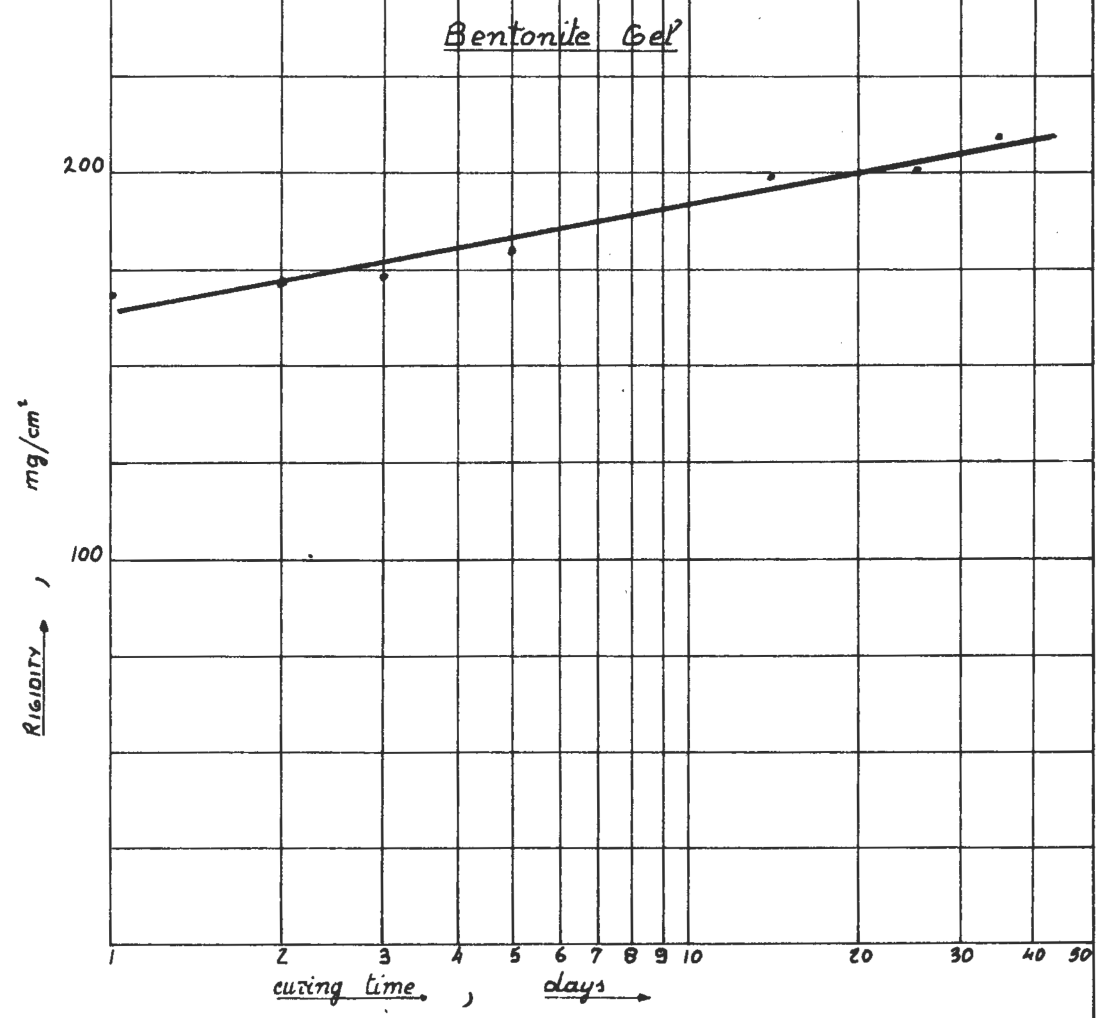


Fig. 138. Effect of Hermetic Mold Cure on Rigidity of a Bentonite Gel

form, the respiratory tract should be protected when prolonged handling is necessary. The injected grout is absolutely not toxic.

IX. CATEGORY F COMBINED SYSTEMS

1. Introduction

Only one grout is examined from Category F, a combination of a Category A grout (silicate derivatives) with a Category B-2 grout (inorganic colloids). This is a combination, with new properties, of a silica gel having a very low sodium silicate content and a colloidal bentonite suspension. Its strength is very low and it is primarily used for waterproofing.

CAMBEFORT (67-12) has drawn up a theoretical ratio linking erosion pressure with the injected grout's cohesion and the characteristics of the terrain. This ratio has been confirmed by very precise testing:

$$P = LSc(1-n)$$

where P is displacement pressure
S is the specific surface of the grouted curtain[1]
n is the ground's porosity
c is the grout's cohesion

Given a head of water of 50 metres (rather high for natural conditions), the cohesion of a grouted curtain 1 metre thick necessary to resist displacement pressure in fine standard sand (specific surface 380 cm^{-1}, porosity 0.386), according to this formula, will be about 2/10 g/cm^2.

The ground to be grouted is not of standardized sand. It may be much coarser, and some highly permeable areas may not be sufficiently treated by preliminary injections of clay-cement. Thus, although waterproofing chemical grouts are specific to the treatment of low-permeability terrain, one should take advance measures against the risk of erosion in coarse ground. Fig. 139 shows the degree of pressure which must be exerted to cause erosion of the grout in a 1 metre thick curtain injected into coarse sands of varying particle size. In this example, cohesion on the order of 1 g/cm^2 will be sufficient and give a good safety margin.

There will be a decrease in the strength of grouts subjected to prolonged stress, thus a safety coefficient should be adopted leading to a grout with an immediate shear strength of 5 to 10 g/cm^2.

---

[1] Specific surface = $\frac{\text{surface area of particle}}{\text{volume of particle}}$

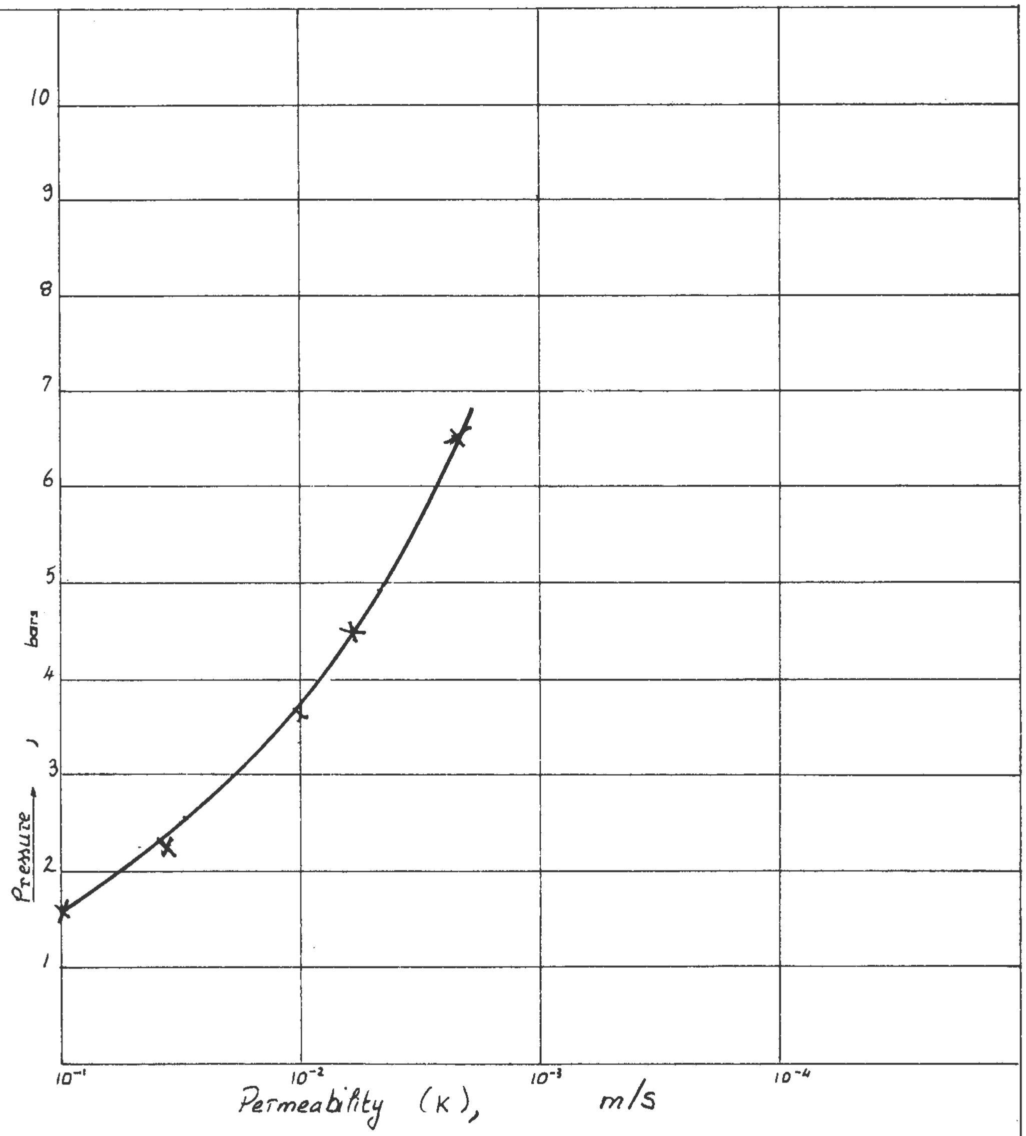


Fig. 139. Displacement Pressure for a Curtain 1 Metre Thick with Cohesion 1 g/cm^2 in Terms of Initial Permeability of the Ground

The classic Category A grouts, whether silica gels, lignochrome gels, or even organic resins, always surpass this minimal sufficient strength, even when used for waterproofing. This is no drawback, but can entail needless expense. With this grout, which combines a silica gel very low in sodium silicate content with a highly colloidal bentonite slurry, sufficient strength is attained for waterproofing.

This grout, called SUPERGEL, also offers the following characteristics:

-Injectability is maintained longer than with a classic silica gel, despite the presence of bentonite particles. This is caused by the incorporation in the grout of a deflocculating agent which keeps the bentonite particles separate from one another ($<1\mu$) as well as suppressing rigidity in the bentonite slurry which behaves like a Newtonian fluid during a major part of the setting process.

-Total absence of syneresis, because of the bentonite, helps develop better resistence to erosion than is the case with the classic waterproofing gels which have the problem of syneresis.

2. Viscosity

2.1 Initial Viscosity

2.11 Viscosity of Grout Before Addition of Silicate

With Supergel, the usual order of preparation consists of hydrating a highly colloidal bentonite slurry, then adding a strong peptizer or deflocculating agent (polyphosphate) and then a setting reagent for sodium silicate which will not flocculate the bentonite. The sodium silicate is added last, immediately before use. This is the reverse of the normal order of preparation for silica gels.

With Supergel, the initial grout mixture contains no sodium silicate. Such a grout is not rigid despite the presence of bentonite, for any rigidity is suppressed by the action of the polyphosphate used to peptize the bentonite. Similarly, as the amount of dry matter is very slight, apparent viscosity does not exceed 2 to 3 cP and the grout is thus very fluid.

2.12 Viscosity of Grout

The addition of sodium silicate on the order of 4 to 5 percent by volume only slightly increases viscosity. Viscosity rises to 3 or 4 cP, this slight increase being attributable to a double action:

1) viscosity of the sodium silicate itself;
2) instantaneous reaction of the sodium silicate with the inorganic setting reagent.

2.13 Changes in Viscosity as a Function of Time

Like slow-setting waterproofing gels, Supergel's viscosity increases gradually over about 2/3 of the time during which it is injectable (fig. 140). Because of the mixture's low silicate content, variations in temperature do not have a perceptible effect on changes in viscosity. Rigidity is only slightly perceptible at first (fig. 141).

3. Regulation of Setting Time

Supergel's setting time, like that of any other grout, should be adjustable according to:

1) ground conditions: these conditions, however, are relatively unimportant, since Supergel is used only for waterproofing fine sands or medium sands which have first been treated with a bentonite-cement grout; the risk of grout creeping beyond the area to be treated is thus limited. It should be possible to obtain rapid setting times if the degree of absorption is high and vice-versa.

2) ambient air and ground temperature: from this point of view, Supergel behaves like a silica gel and thus follows VAN'T HOFF-ARRHENIUS law. The setting time coefficient (for an increase or decrease in temperature of 10°C) is about 2, the same as for dilute silica gel using inorganic reagents, (see Chapter II, Part Three of this volume).

One way of regulating setting time is to modify the nature and dosage of the additives (peptizer, rigidifier). However, this should not be attempted at the actual worksite, because of the risk of having a poorly balanced mixture whose performance will be weakened.

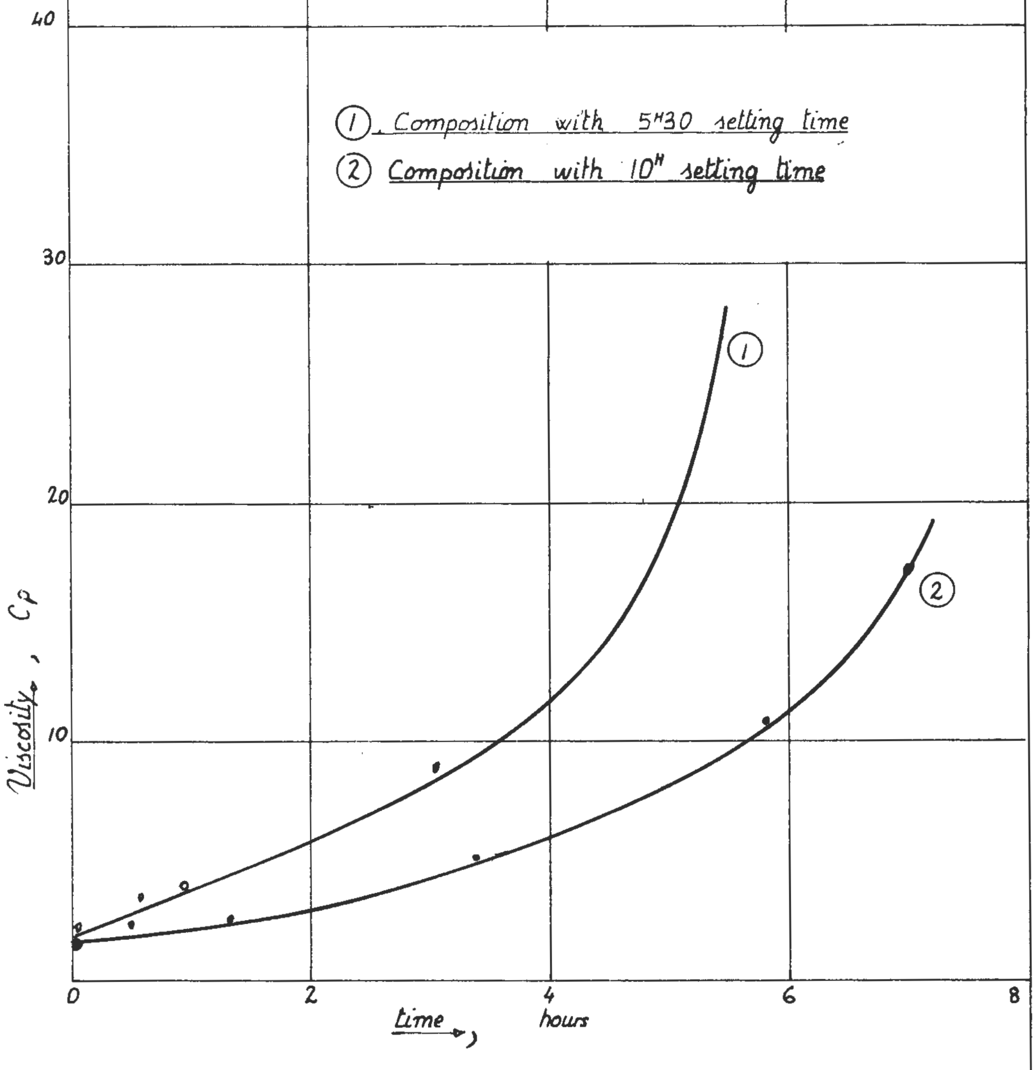


Fig. 140. Effect of Time on Viscosity of 2 Supergels

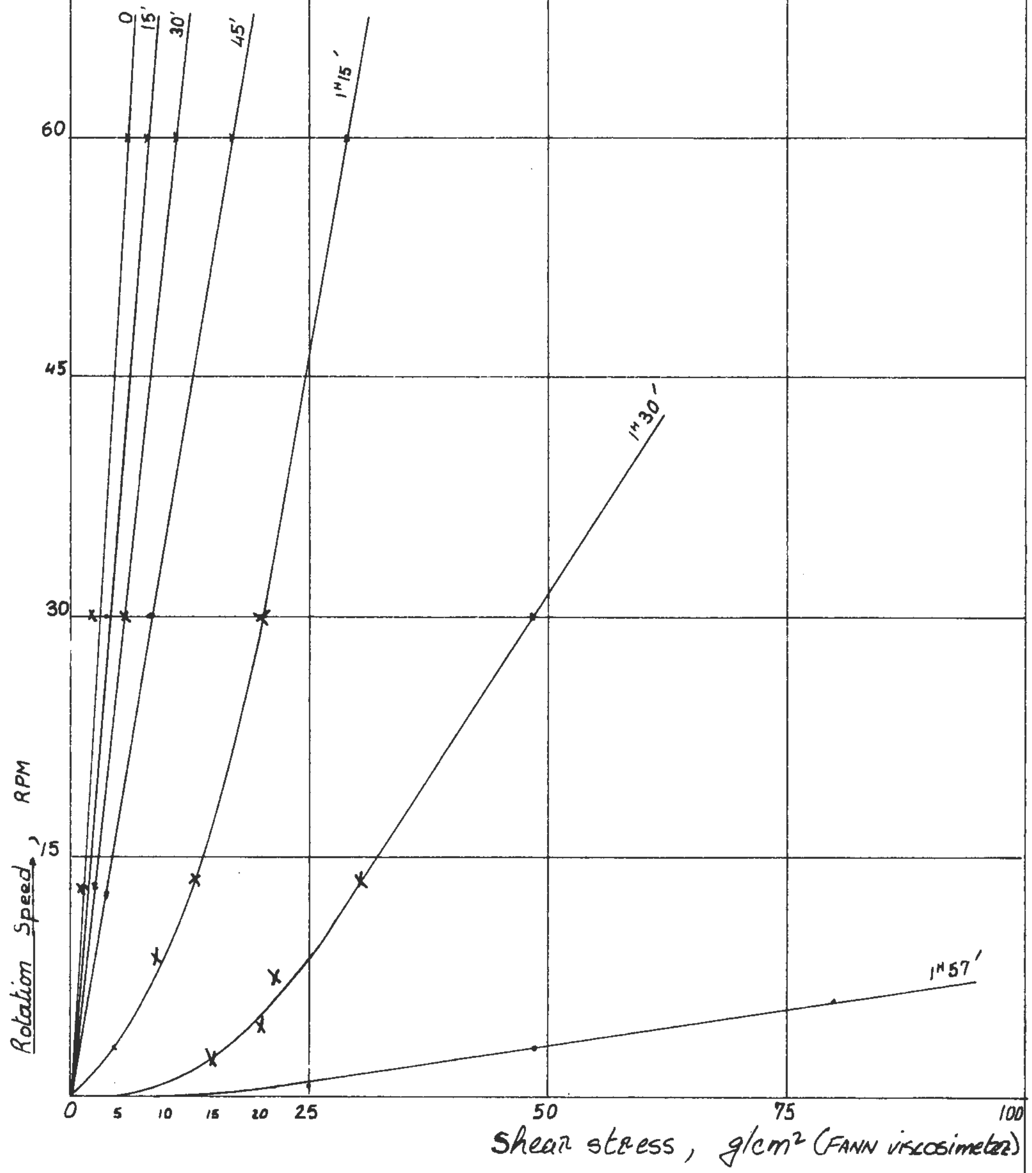


Fig. 141 . Reheological Behavior of a Supergel up to Set

Setting time can also be regulated by modifying overall dilution. Setting time is essentially a function of the bentonite/water ratio. As shown in fig. 142, a relatively slight increase of the bentonite content considerably hastens the setting (by fixing the water, the bentonite concentrates the mixture). Similarly , setting time is a function of the silicate/water ratio (fig. 143). However, if the silicate content is increased too much, there will be a retrogression in the curve for setting time.

Increasing the bentonite or silicate content improves the waterproofing characteristics, while decreasing injectability.

4. Shear Strength of Pure Grout

If the formula is well-balanced, the shear strength of Supergels should be around 10 g/cm^2. Theoretically, higher strengths can be attained by increasing the percentage of bentonite, but injectability then suffers (fig. 144).

In general, optimum strengths are obtained from minimum setting times. As with most grouts, shear speed alters the strength of pure gel. From this point of view, Supergel behaves like a waterproofing silica gel, as shown in fig. 145.

5. Durability

Supergel has been examined under the different curing methods described in Chapter 6, Part One of this volume.

5.1 Hermetic Mold Cure

Fig. 146 shows the perfect stability of this type of grout over time. The total absence of syneresis throughout the whole curing process gives Supergel a considerable advantage over waterproofing silica gels.

5.2 Dry Cure

Since Supergel contains a large amount of water, on the average 97% by volume, it is very sensitive to dessication. After 3 or 4 days of air cure there is severe cracking as well as shrinkage.

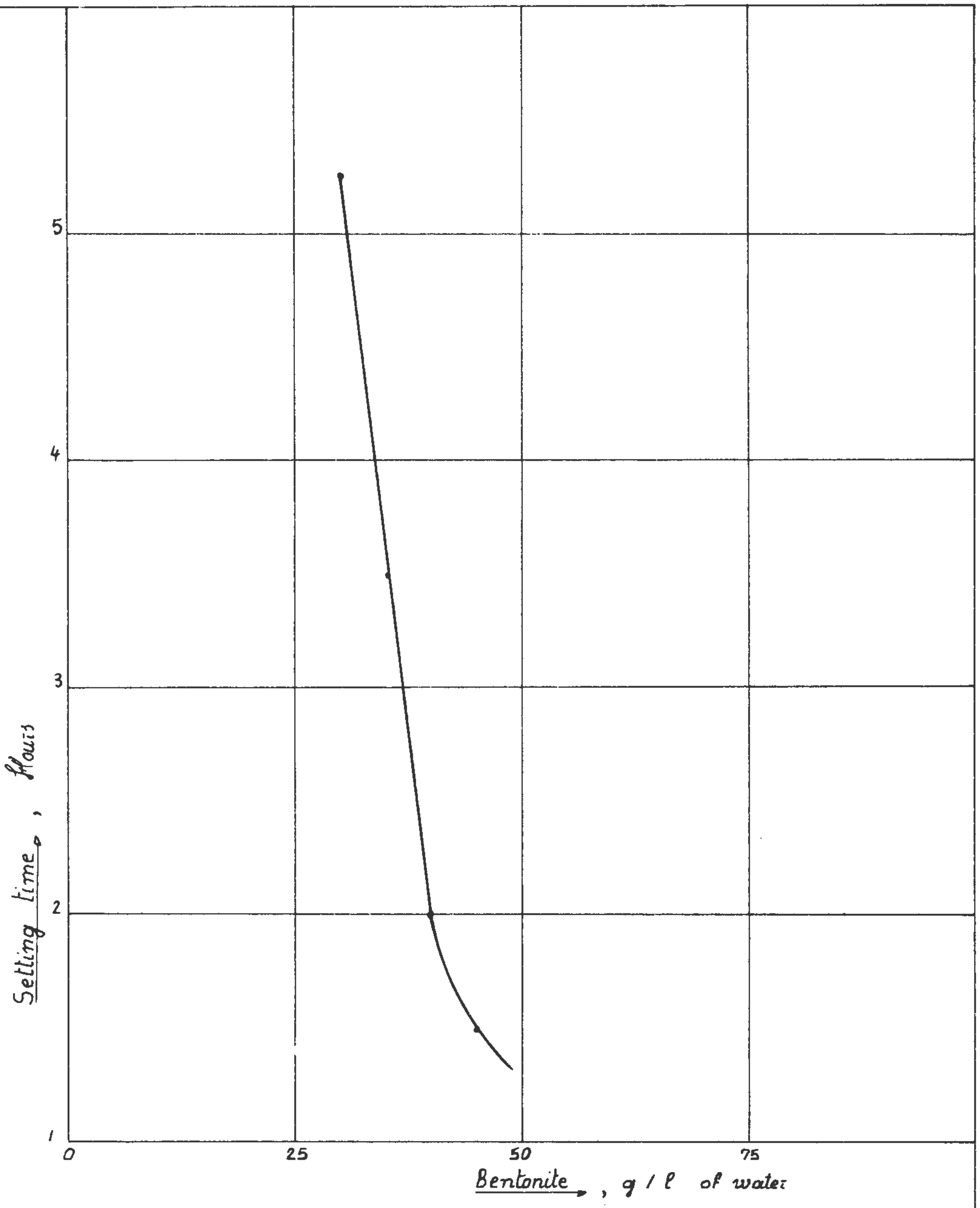


Fig. 142. Effect of Dry Matter Proportion on Setting Time of Supergel

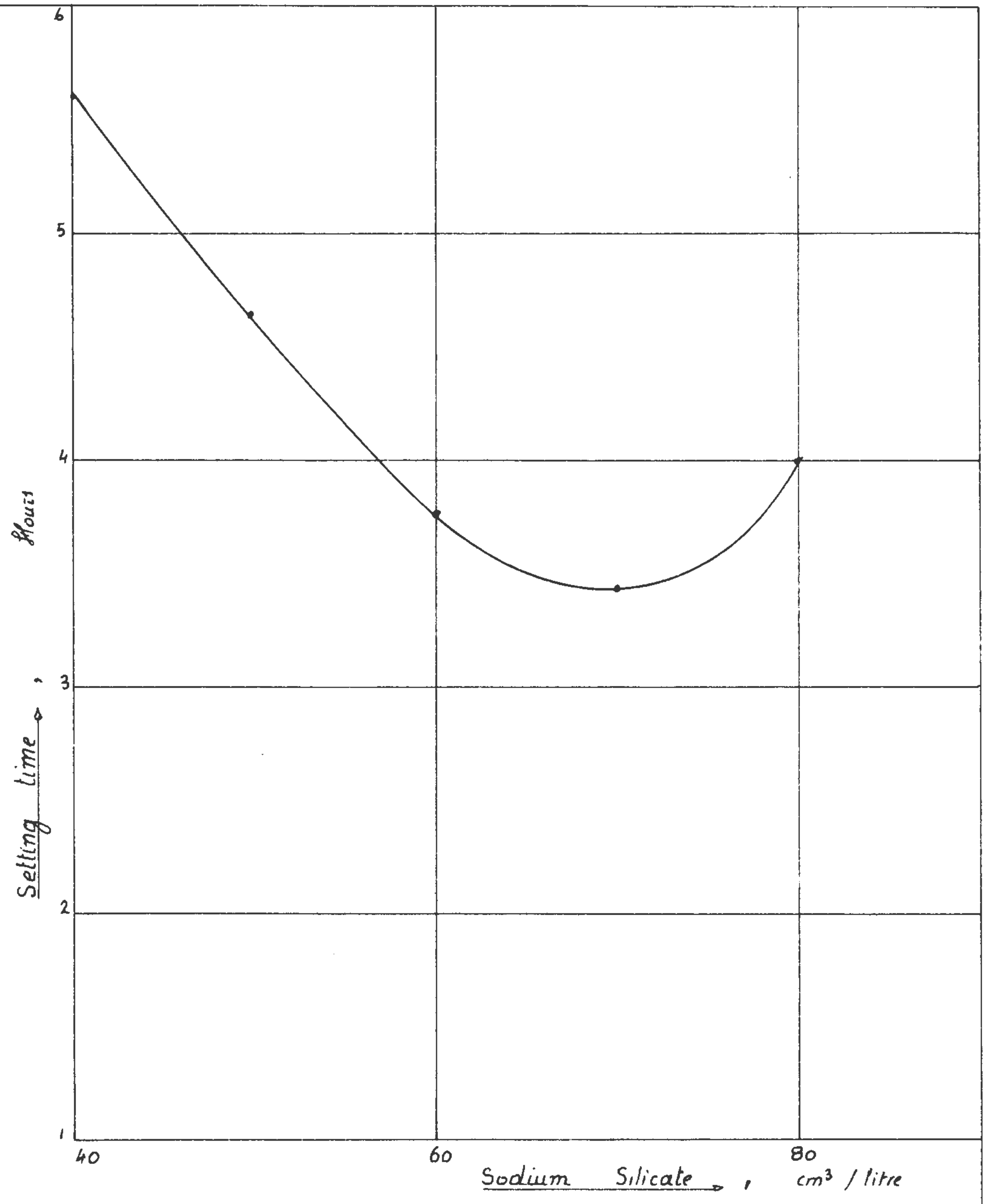


Fig. 143. Effect of Proportion of Sodium Silicate on Setting Time of Supergel

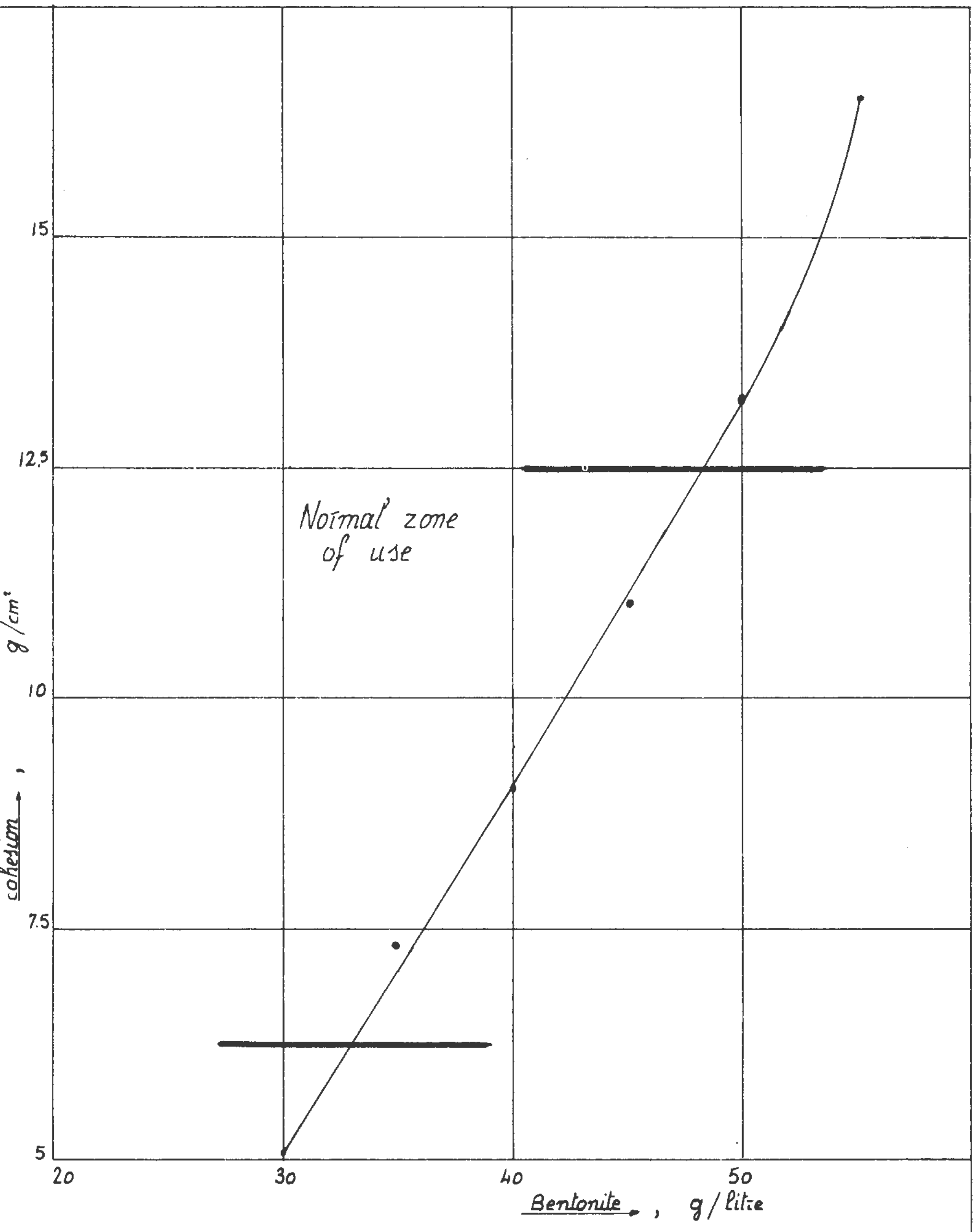


Fig. 144. Effect of Proportion of Bentonite on Cohesion of Supergel

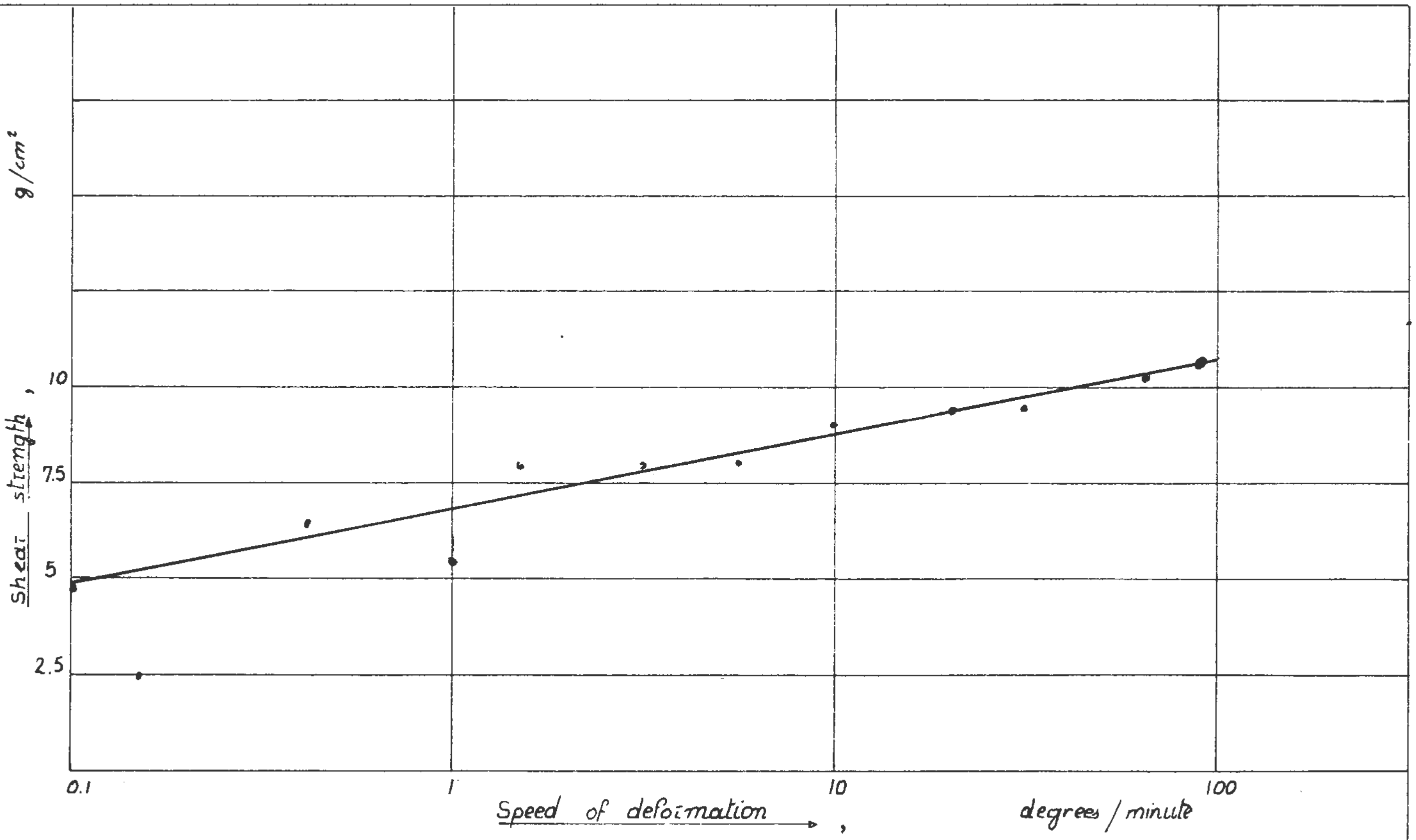


Fig. 145. Effect of Shear Speed on Strength of Pure Gel

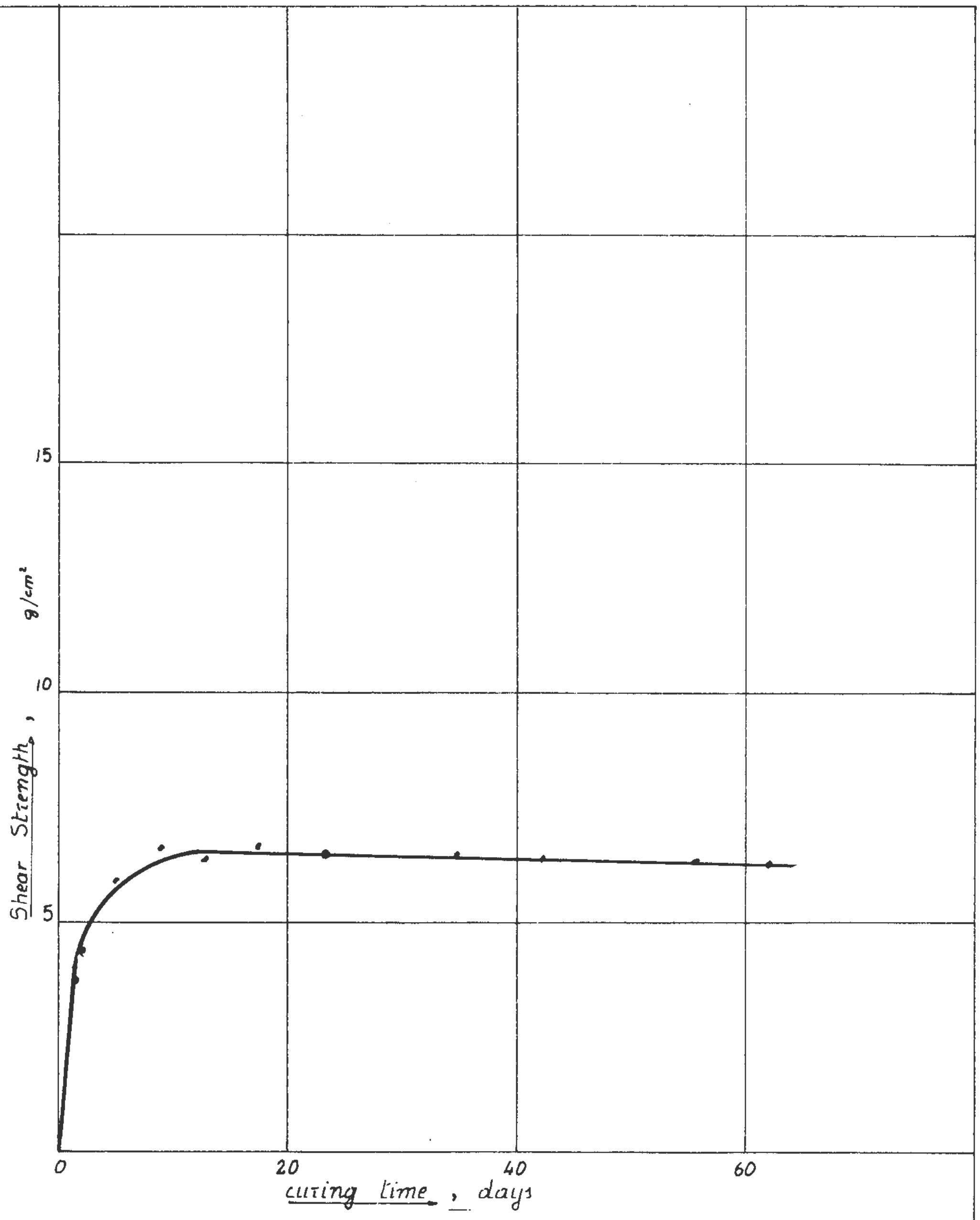


Fig. 146. Effect of Hermetic Mold Cure on Cohesion of Supergel

5.3 Wet Cure

Supergel behaves well in a wet medium. This is shown in fig. 147 for a grout of typical composition cured under water.

5.4 Cycles of Drying and Wetting

Wet-dry cycles, and particularly the drying phases, are unfavorable to Supergel. However, fig. 148 shows that the presence of the bentonite slightly retards decomposition. It is only after 5 complete cycles that the degradation of the Supergel begins, while a typical silica gel decomposes much faster.

5.5 Percolation Under Pressure

Fig. 149 shows Supergel's good stability with time, even under high percolation pressure. This is due to the total absence of syneresis as well as to a very high rate of destabilization with sodium silicate.

In conclusion, as a waterproofing material, Supergel is very stable under normal usage conditions.

6. Toxicity

6.1 Toxicity of Basic Ingredients

The toxicity of bentonite and sodium silicate have already been discussed in previous chapters. Bentonite, being a powder, poses a hazard to the respiratory tract during prolonged handling. The highly alkaline character of sodium silicate requires that the eyes be protected.

The phosphate-type peptizing agents are only slightly toxic and are used only in tiny doses (table 39).

Table 39. Toxicity of Supergel Peptizing Agents

Peptizing agent	Toxicity, DL 50
monosodium phosphate	ims rat: 250 mg/kg
sodium tetrapyrophosphate	ipr rat: 59 mg/kg
sodium pyrophosphate acid	scu mouse: 480 mg/kg

ims = intramuscular
ipr = intraperitoneal
scu = subcutaneous
DL 50 = dose causing 50% mortality

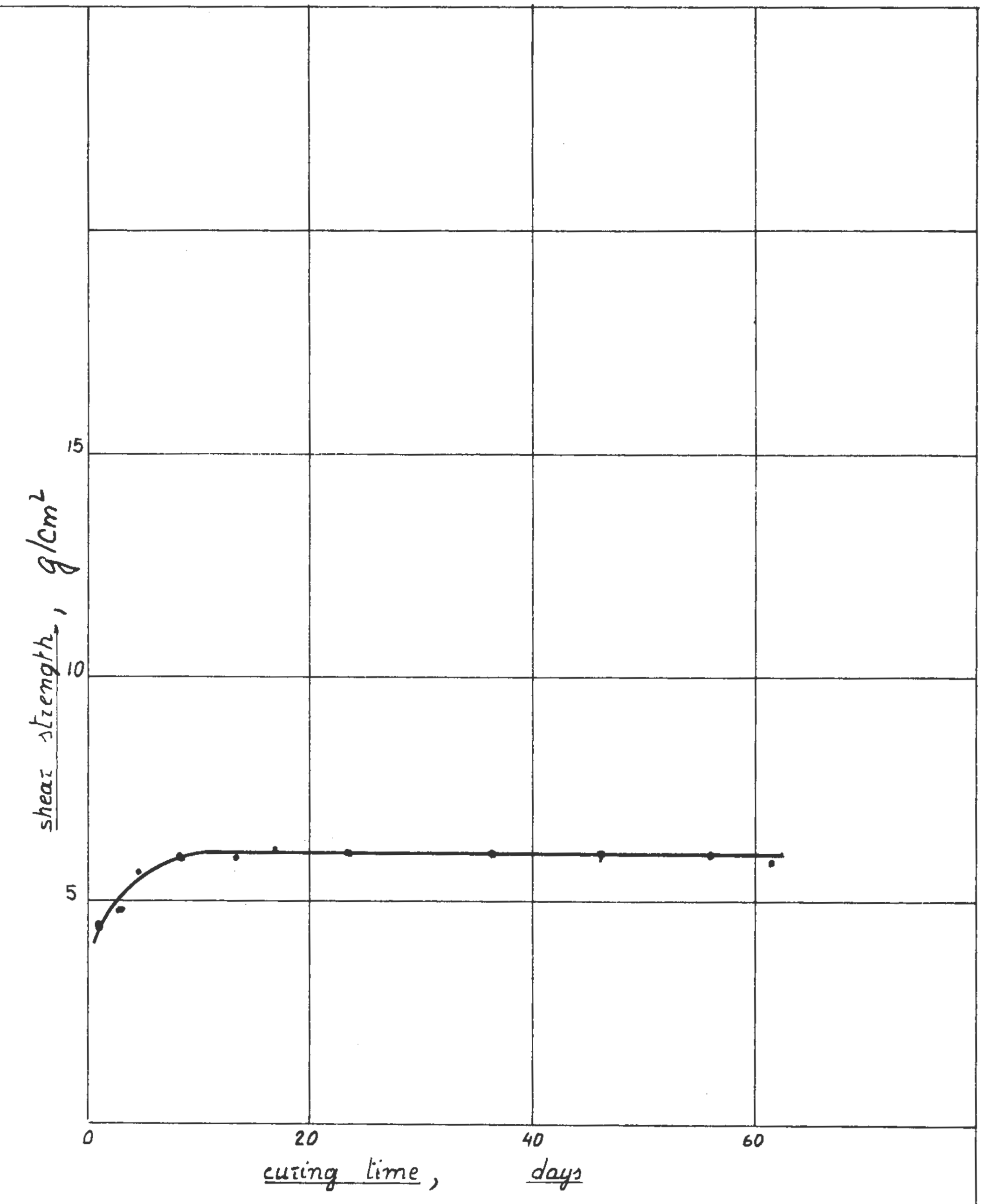


Fig. 147. Effect of Wet Cure on Cohesion of Supergels

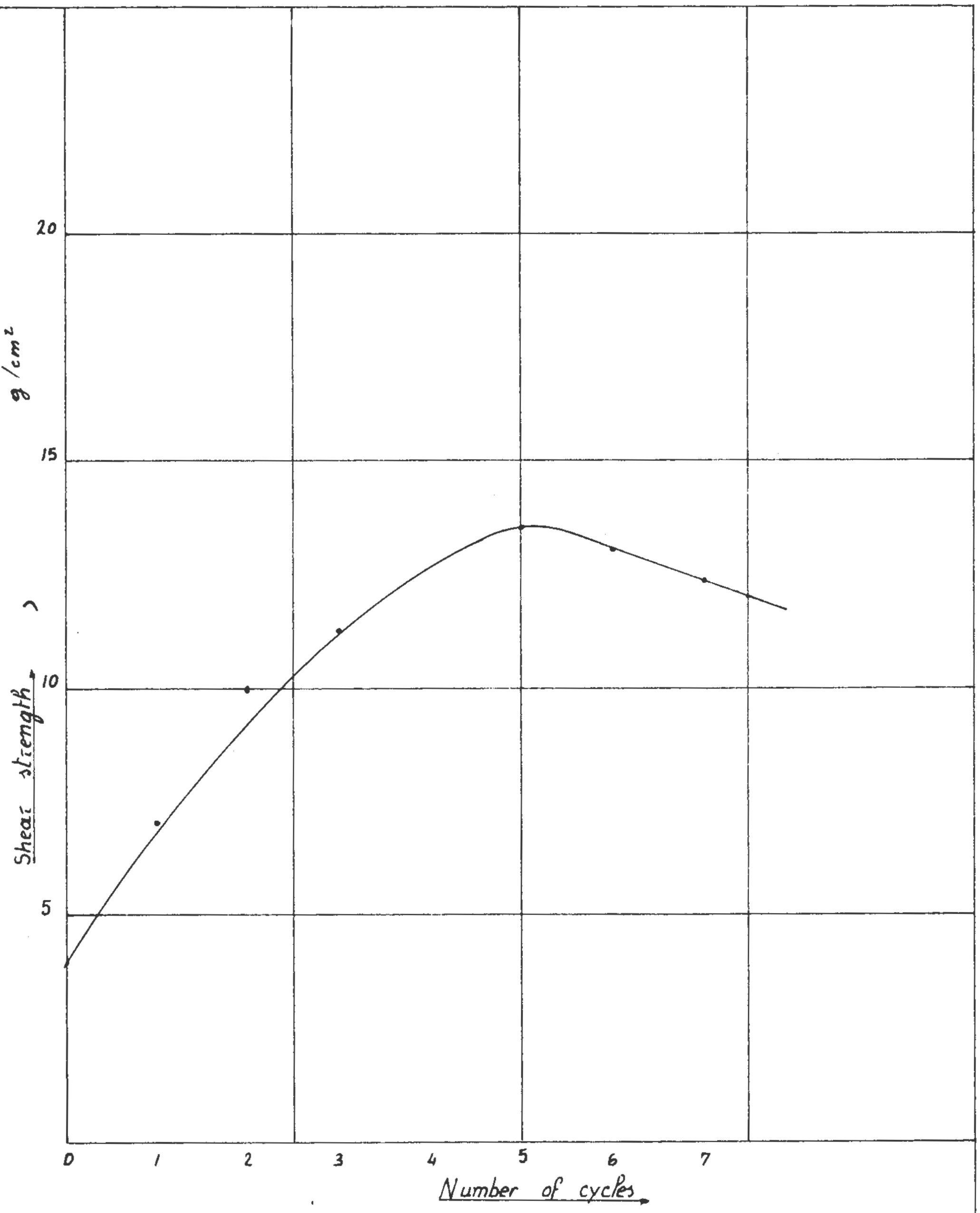


Fig. 148. Effect of Drying-Wetting Cycles on Cohesion of Supergels

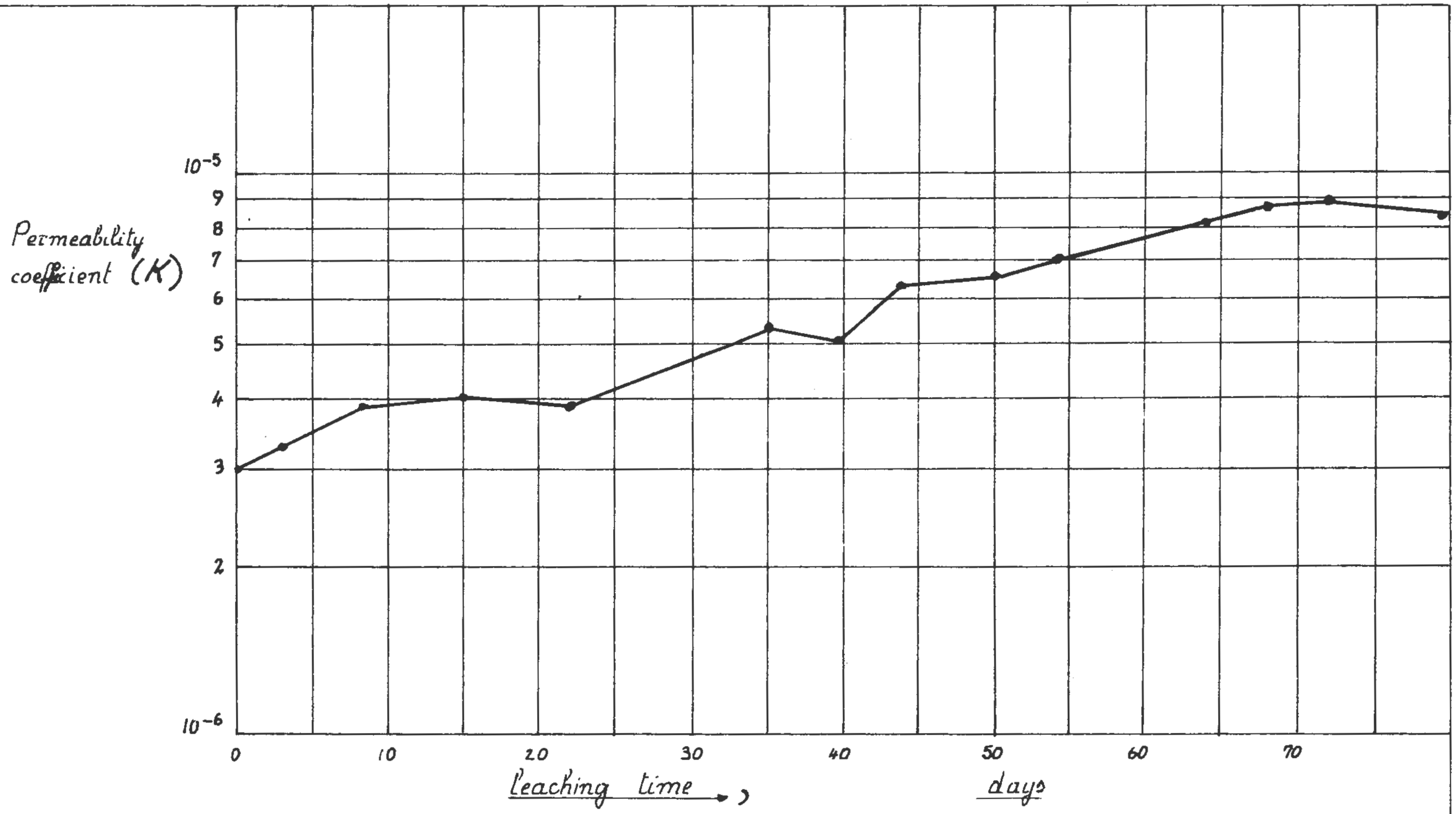


Fig. 149. Effect of Time on Permeability of a Supergel Grout

6.2 Toxicity of Fresh Grout

Before setting, Supergel is not toxic.

6.3 Toxicity of Hardened Grout

The hardened grout is not at all toxic. At most, surrounding water is made slightly basic for a while.

PART FOUR
EVALUATION OF PROMISING GROUT MATERIALS

CHAPTER I - Introduction

In its earliest stages of development, from 1910 to 1950, chemical grouting generally employed sodium silicate-base mixtures. At the present stage of development, numerous grouts, generally petrochemical derivatives, have been added. These products were listed in the general classification in Volume I, and the technical criteria were discussed in Part Three of this volume.

Volume I provides grout classifications in 19 categories and subcategories for the several hundred grouts available. About 90 percent of the reports in the literature refer to 7 types of grout.

-Silicate-base grouts (Category A-1) are by far the most widely used. The original procedure (JOOSTEN-JEZIORSKY) has been abandoned in favor of the one-shot procedure, which is easier to use and more reliable. Depending on the dilution of the silicate and the nature of the reagent, these procedures can produce gels for waterproofing or consolidation. For waterproofing, a gel-bentonite suspension combination (Category F) is of definite interest. For consolidation, acrylamide combinations (Category A-8) have been proposed and applied.

-For waterproofing or moderate consolidation, lignosulfite derivatives (Category A-3) have met with some success in the United States (under the name of EARTH FIRM) and especially in the U.K. (under the name of T.D.H.). Outside these countries, they are practically unused in Europe and are even forbidden in Germany, because of the toxicity of the residual Cr^6.

-Polyacrylamides, (Category A-5), first manufactured and developed by American Cyanamid under the name of AM-9, have met with great success in the United States. They have not become as established in Europe. In addition to being costly, they are accused of not giving good strengths, however high their monomer concentration. Over the last decade they have been extensively used in Japan. At present, they are being used less because of fears (probably unjustified) of toxicity.

-Depending on the dilution, phenoplasts (Category A-6) can solve waterproofing as well as consolidation problems (up to 100 bars in the treated ground). This type of grout has been extensively developed because it offers a wide range of possibilities. Several commercial formulas include combinations of tannin derivatives and phenol.

-Inorganic colloid-base grouts (Category B) have been developed to some extent for waterproofing. In addition to long-term stability, these substances offer very easy handling and a low price.

As they are widely used, these grouts have been the subject of research to determine their optimum use and their performances. Do these commonly used grouts merit additional research? Despite the work already done on them, the answer is yes, for new phenomena appear as they are more closely studied.

The other 15 categories of grouts, which are little used, and which, consequently, have been little researched, could also be improved significantly.

This study of chemical grouts indicated that the ingredients most often used were petrochemical derivatives. In fact, only six categories fall totally outside petrochemicals, three being inorganic (A-1, A-2, B-2), three being of plant origin (A-3, A-4, B-1). These six categories are the most promising because of the possibility that present petroleum sources might be exhausted in the future.

The research for improved grouts thus focused on the plant origin category. As the performances of plant colloid-base grouts are very limited and their quality/price ratio is much less favorable than those of Categories B-2 and F, no further examination of Category B-1 was made. Research was limited to Categories A-3 (lignosulfites) and A-4 (furfurans).

The lignosulfites are well known; they have been used in several countries. Thus additional research concerned the effect of the Cr^6 salt

The furfuran group is little known. The few existing references from Eastern Europe and the Soviet Union give little information about their characteristics. These grouts, whose base is of plant origin, merit wider recognition.

CHAPTER II

IMPROVING LIGNOSULFITE-BASE GROUTS

1. Problem

Lignochrome gels enjoy the advantage of using as their basic ingredient a residue (called black liquor or bisulfite liquor) which contains enough lignosulfite or lignosulfonate to be converted into a gel. This residue is in abundant supply and is inexpensive.

Less than one millionth of the available bisulfite liquor is used at present for grouting. As this is also the case with other uses of lignosulfite (additive for cement, hollow casting, etc.) which consume only marginal quantities, much of this interesting product is discarded, burned or discharged into (thus polluting) rivers.

As a raw liquor, this by-product is free. However, as this form is too dilute, it must be concentrated, which increases its price. It could possibly be used in less concentrated and thus less expensive solutions for grouting.

The economic advantages are counterbalanced by the fact that lignochromes use hexavalent chromium as an oxidizing agent for gelling, thus imparting a definitely toxic character to the mixture until it sets or even after setting, if Cr^6 salts remain free in the formula.

The purpose of this study is to try to replace the chromium 6 with a common and non-toxic oxidizing agent, or, at least, to minimize the dosage of chromium in the mixture so as to ensure that no Cr^6 remains free in the formula after the lignosulfonate has been oxidized.

2. Tests

2.1 Substitution of Another Oxidizing Agent for Dichromate

Since the hexavalent chromium, once it has oxidized the lignosulfite, precipitates it in the form of a heavy metal salt, it would seem that any combination of an oxidizer and a heavy metal salt could produce a gel. However, previous attempts of this sort in other laborabories have failed.

In order to obtain exact comparisons with the dichromate, we adopted a median reference formula using 300 g/l of lignosulfite and 60 g/l sodium dichromate, and then replaced the sodium dichromate successively with:

-sodium persulfate ($Na_2S_2O_8$)

-caro acid (H_2SO_5)

-hydrogen peroxide (H_2O_2)

As these oxidizers contain no heavy metal, it was added in the form of aluminum chloride ($AlCl_3$). As some of these oxidizers are acid and the aluminum chloride is also acid, the lignosulfite-sodium dichromate reference formula was acidified (pH moving from 3 to 5). For the results to be comparable, work had to be conducted within the same pH ranges since this factor has a paramount effect on the strengths of lignochromes (see Part Three, Chapter III). The control formula in the 3.5 to 4.5 pH range sets in less than one hour and its shear strength is 200 g/cm^2.

Taking into account the oxidation-reduction reactions of each product:

sodium dichromate:

$$Cr_2O_7{--} + 6\ e + 14\ H{+} \longrightarrow 2\ Cr^{3+} + 7\ H_2O$$

sodium persulfate: $S_2O_8{--} + 2\ e \longrightarrow 2\ SO_4$

caro acid: $SO_5{--} + 2\ e \longrightarrow SO_4{--} + \frac{1}{2}O_2$

hydrogen peroxide: $H_2O_2 + 2\ e\ 2H^+ \longrightarrow 2H_2O$

the following mixtures were tested (Table 40).

Table 40. Substitutes for Dichromate

Basic formula	Substitute formula		
Sodium dichromate	Caro acid	Hydrogen peroxide (110 v)	sodium persulfate
lignosulfonate Ca 300g	ligno Ca 300 g	ligno Ca 300g	ligno Ca 300g
$Na_2Cr_2O_7$ 60g	H_2SO_5 70 ml	H_2O_2 60 ml	$Na_2S_2O_8$ 144g
Acid variable	$AlCl_3$ 60 g	$AlCl_3$ 60 g	$AlCl_3$ 60 g
water 1000 ml	water 930ml	water 940 ml	water 1000 ml

None of the substitute formulas would set. The hydrogen peroxide destabilized as soon as the aluminum chloride was added.

In order to let the oxidation of the lignosulfonate take place slowly, the same tests were conducted while the mixture was allowed to rest: lignosulfite + oxidizer 6 days before the aluminum chloride was added. The results were no more encouraging. The same thing happened when the proportion of the ingredients was varied.

At present, pending more thorough research, it appears that the dichromate is indispensible for initiating the necessary reaction. Tests were conducted with low dosages of dichromate (5%), supplemented with the oxidizers listed above. These mixtures did not set.

Since the results were so discouraging, information developed in this research was used to develop formulas with adequate mechanical characteristics while keeping the dosage in dichromate below the 20% generally used and assuring that all the Cr^{6+} would be reduced to Cr^{3+}.

2.2 Lowering Proportion of Dichromate

The bibliographical study indicated the following:

-Calcium lignosulfonate is the most commonly used lignosulfite but there were few comparative studies indicating why this lignosulfite is of such interest.

-Strength increases in direct proportion to the dosage in lignosulfite.

-The pH has a marked effect on setting time and strengths in the pure gel, the oxidizing power of Cr^{6+} being practically nil at a pH of 7, and increasing with ambient acidity.

-For acidification, acids in varying strengths have been proposed along with acid salts. The nature of the acid ion probably has an effect on the characteristics of the hardened grout but there has been no comparative study on this topic.

-Strengths increase in direct proportion with the dosage in dichromate. For this reason, recommended formulas contained a minimum of 20% dichromate in relation to the lignosulfite. According to results obtained from the U.S.S.R. (52-17), there is some risk of toxicity if the dichromate proportion is 20%, while this risk disappears if that proportion is reduced to 10%.

2.21 Study Conducted with 15% Dichromate

In order to see if it might be possible to obtain suitable setting times and strengths of pure gel by limiting the sodium dichromate concentration to 15%, the following parameters were varied:

- nature of the lignosulfite
- lignosulfite concentration
- pH, with various acid additives.

A Setting Time

A.1 Effect of Nature of the Lignosulfite

Setting time varies with the nature and origin of the lignosulfite. With a lignosulfite concentration of 400 g/litre, we obtained the following results (table 41).

Table 41. Effect of Nature and Origin of Lignosulfite on Setting Time

Nature of Lignosulfonate	Setting Time, Hours
Acid lignosulfite, French	0.25
Calcium lignosulfite	
French	7
Swedish	13
English	12.5
Sodium lignosulfite	
French	no set
Swedish	10.5
English	28

A.2 Effect of Concentration in Lignosulfite

As the lignosulfite concentration is increased, the gel's setting time is shortened. Some examples are given in table 42.

Table 42. Effect of Lignosulfite Concentration on Setting Time

Nature of Lignosulfonate	Concentration, g/1	Setting Time, hours
Acid Lignosulfite	300	1
	400	0.25
	500	--
Calcium Lignosulfite, English	300	--
	400	12.5
	500	5
Calcium Lignosulfite, Swedish	300	--
	400	13
	500	6
Sodium Lignosulfite, English	300	--
	400	28
	500	20

A.3 Effect of Acid Additives

All these additives: orthophosphoric acid (fig. 150), monosodium phosphate (fig. 151), aluminum potassium sulfate (fig. 152), ferric chloride (fig. 153), and aluminum chloride (fig. 154), shorten setting time, except with acid lignosulfite, whose setting time is already short.

Otherwise, all lignosulfites, whatever their nature and origin, will have an appropriate setting time (about 1 hour) with a 15% dichromate concentration, provided that they are adequately acidified. In general, sodium lignosulfite (neutral or slightly basic) needs more acid than does calcium lignosulfite (originally slightly acid).

B. Agglomerating Power of Pure Gel

B.1 Effect of Nature of Lignosulfite

Marked variations in strengths of the grout were obtained from a solution of given concentration (400 g/1), depending on the nature and origin of the lignosulfite (table 43).

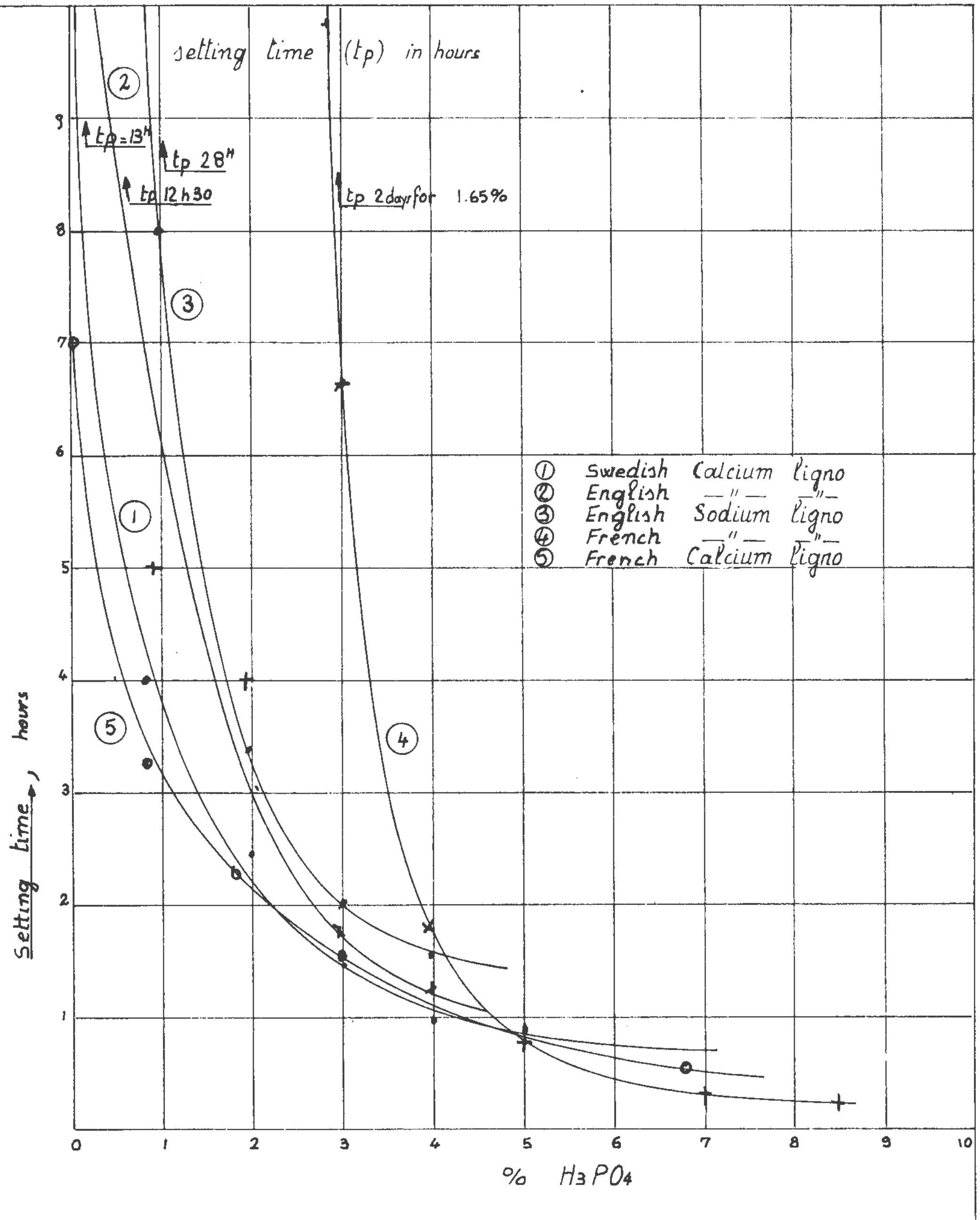


Fig. 150. Effect of Orthophosphoric Acid (75% Solution) on Setting Time of Various Lignosulfonates at 400 g/litre and 15% Dichromate

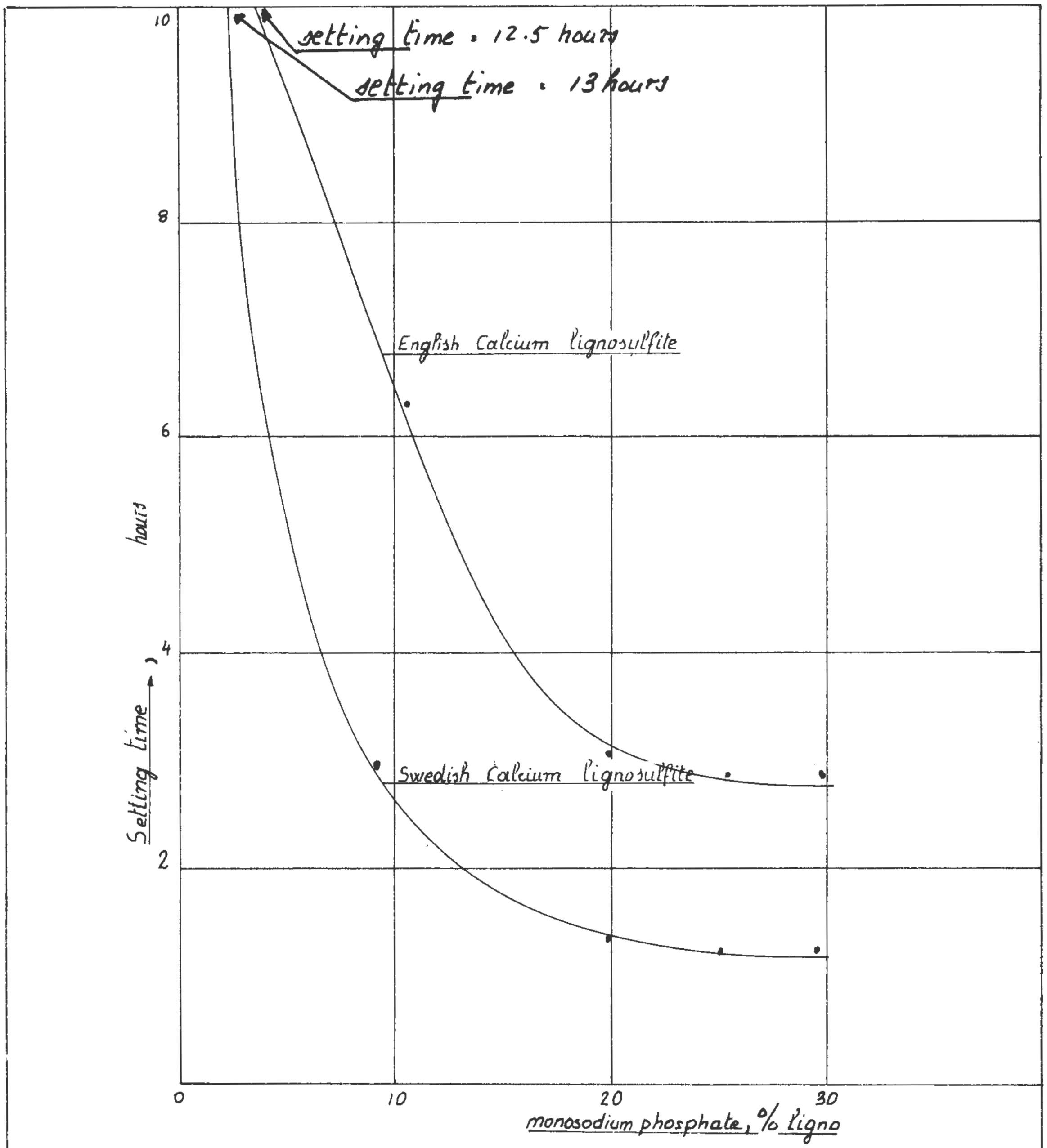


Fig. 151. Effect of Monosodium Phosphate Content on Setting Time of Various Lignosulfonates at 400 g/litre and 15% Dichromate

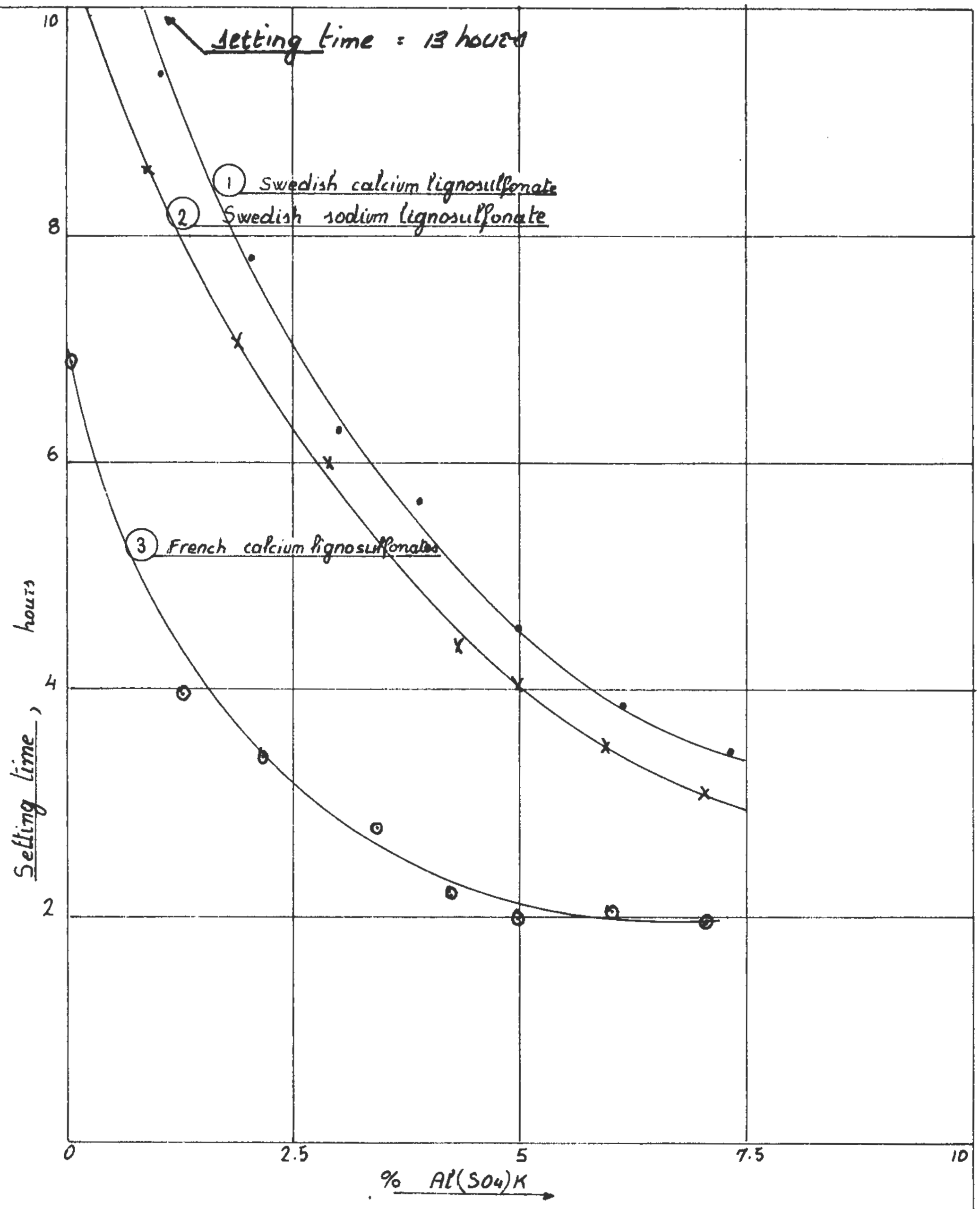


Fig. 152. Effect of Aluminum Potassium Sulfate on Setting Time of Various Lignosulfites at 400 g/litre and 15% Dichromate

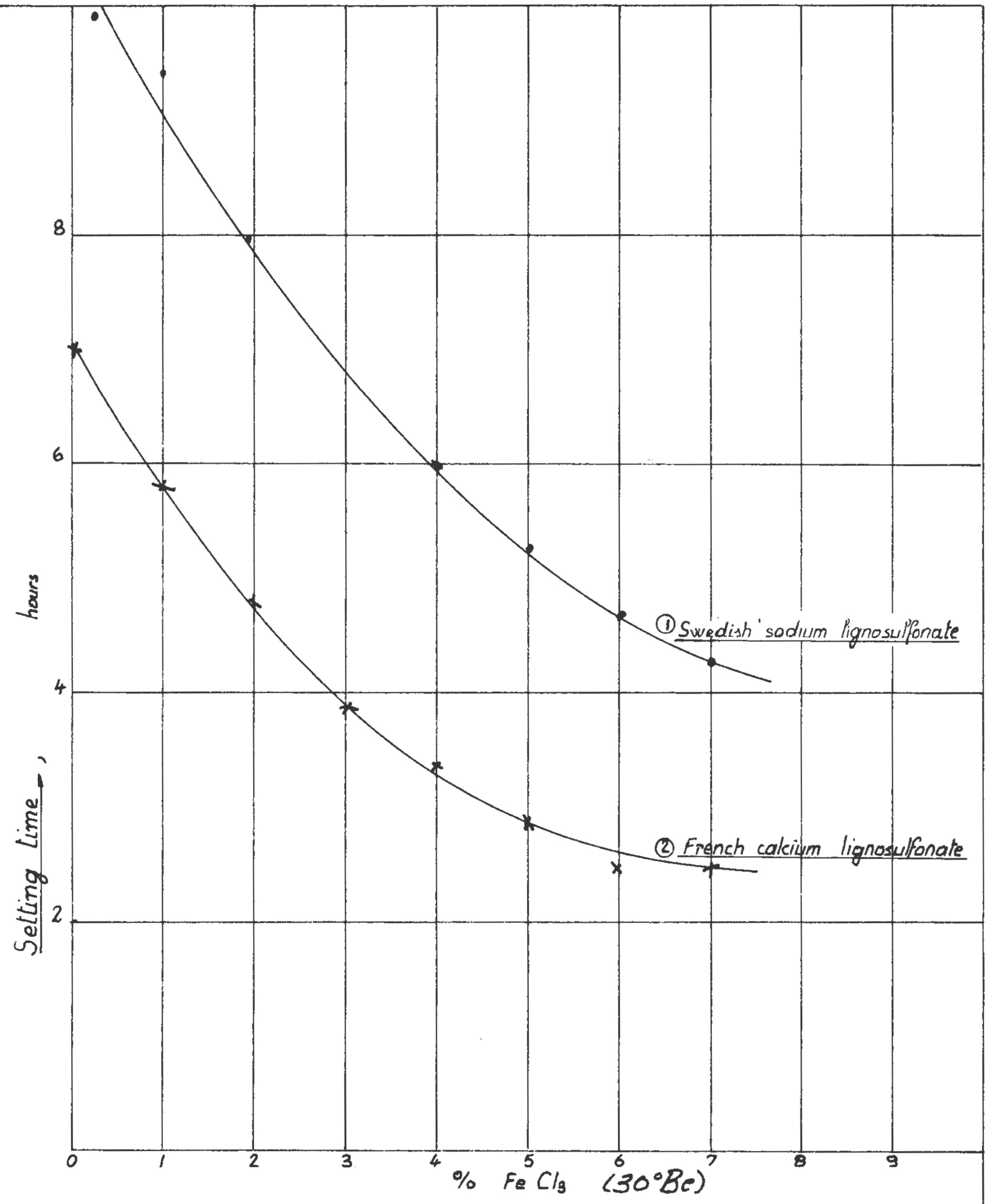


Fig. 153. Effect of Ferric Chloride on Setting Time of Various Lignosulfonates at 400 g/litre and 15% Dichromate

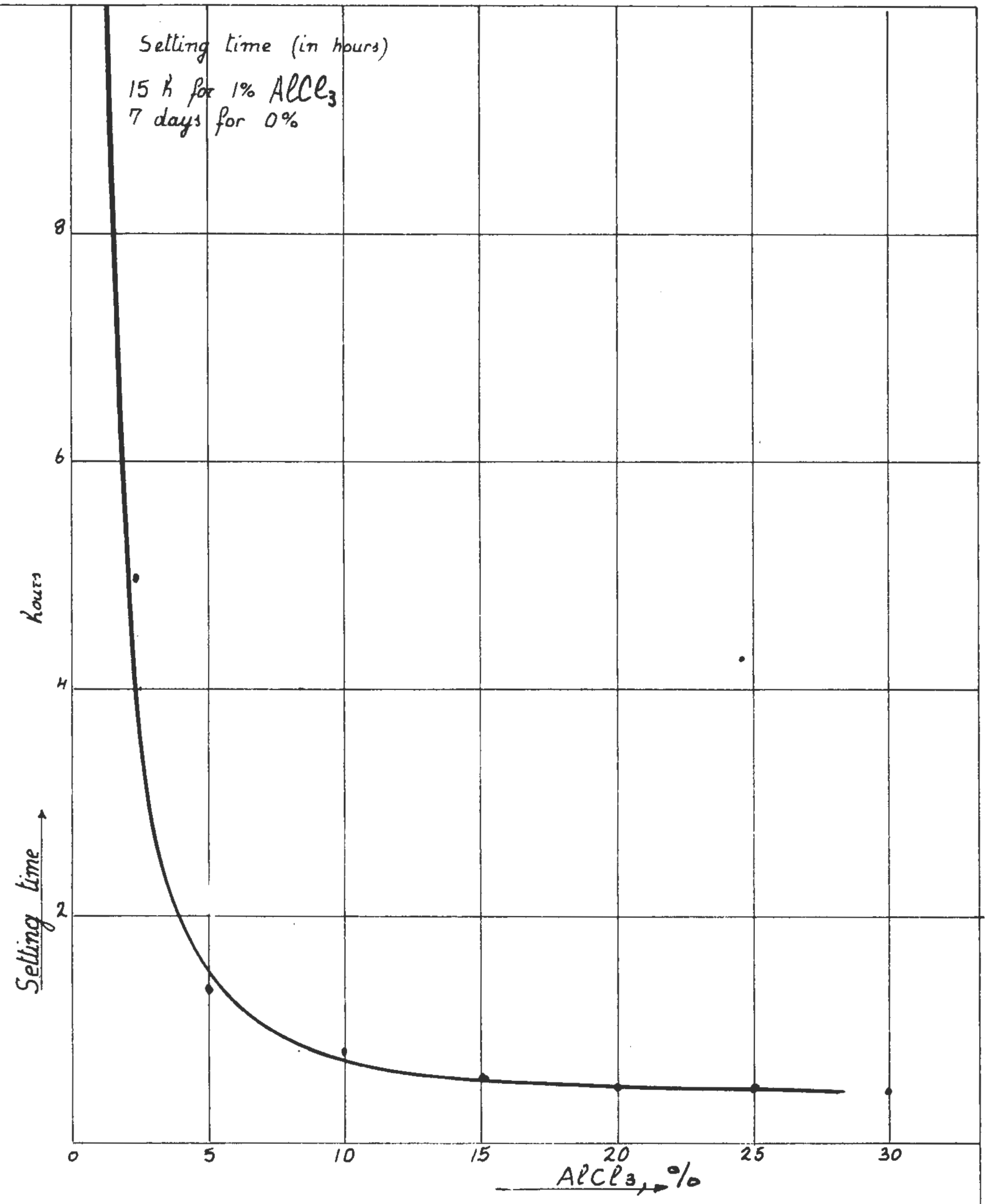


Fig. 154. Effect of Aluminum Chloride on Setting Time of a French Calcium Lignosulfite at 300 g/litre and 15% Dichromate

Table 43. Effect of Nature of Lignosulfite on Strength

Nature of Lignosulfonate (400 g/l)	Agglomerating Power of Pure Gel, g/cm^2
Acid lignosulfite, French	725
Sodium lignosulfite	
English	65
Swedish	62
French	0
Calcium lignosulfite	
English	85
Swedish	64
French	150

B.2 Effect of Concentration of Lignosulfite

Strengths doubled when the acid lignosulfite concentration was increased from 300 to 400 g/l and quadrupled when this concentration was increased from 400 to 500 g/l with Swedish and English sodium and calcium lignosulfites (table 44).

Table 44. Effect of Lignosulfite Concentration on Strength

Nature of Lignosulfite	Concentration, g/l	Agglomerating power, g/cm^2
Acid lignosulfite, French	300	385
	400	725
Sodium lignosulfite, English	400	65
	500	270
Calcium lignosulfite, English	400	85
	500	370
Swedish	400	64
	500	270

B.3 Effect of Acid Additives

a) orthophosphoric acid

Strengths were sharply improved (fig. 155)

b) monosodium phosphate

Increases in strength are comparable to those obtained with orthophosphoric acid, but the dosage must be higher, given the phosphate's pH (fig. 156).

c) aluminum potassium sulfate

Strength increases steadily as the dosage of aluminum potassium sulfate moves from 0 to 8% in proportion to the lignosulfonate (fig. 157).

d) ferric chloride

Strength increases until it reaches its optimum point at 6% ferric chloride and thereafter declines (fig. 158).

e) aluminum chloride

Strength increases sharply until an optimum point is reached at 15% aluminum chloride and thereafter declines (fig. 159).

C. Conclusion

It appears that with a 15% dosage in sodium dichromate, setting time can be brought into a reasonable range for grouting (15 minutes to 1 or 2 hours) so long as the medium is sufficiently acid. Thus sodium lignosulfites must be more acid than calcium lignosulfites. In these conditions, strengths are also adequate.

Strengths of 500 g/cm^2 and even 725 g/cm^2 can be attained by varying the lignosulfite concentration and assuring a good pH: an overly high pH is not suitable (thus, a sodium lignosulfite with a pH of 9.3, without the addition of an acid substance, will not set). Similarily, an overly low pH is not suitable. (Figs. 155, 156, 158, 159).

2.22 Study Conducted with 10% Dichromate: Choice of Acid Additive

As the results of tests conducted with a 15% concentration in dichromate were satisfactory, it seemed that

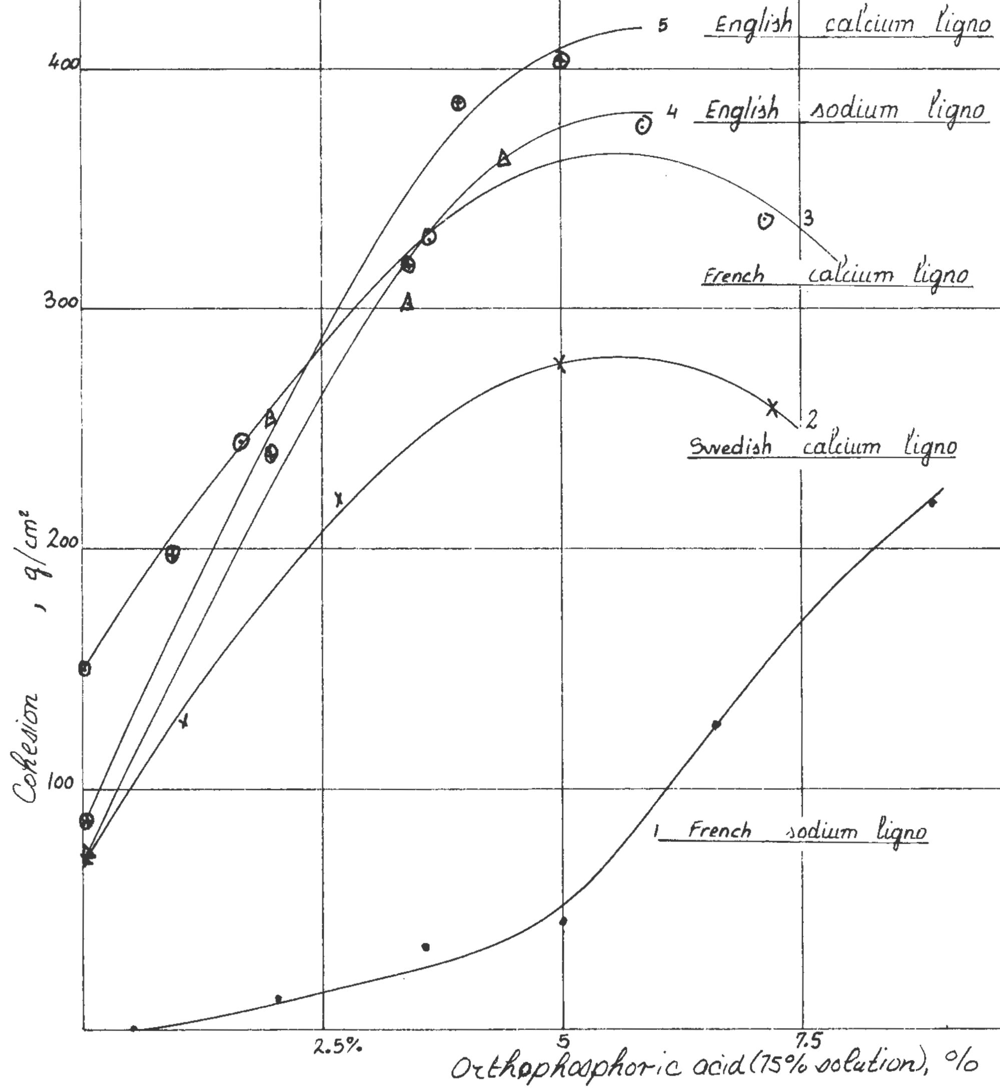


Fig. 155. Effect of Orthophosphoric Acid (75% Solution) on Cohesion of Pure Gel of Various Lignosulfites and 15% Dichromate

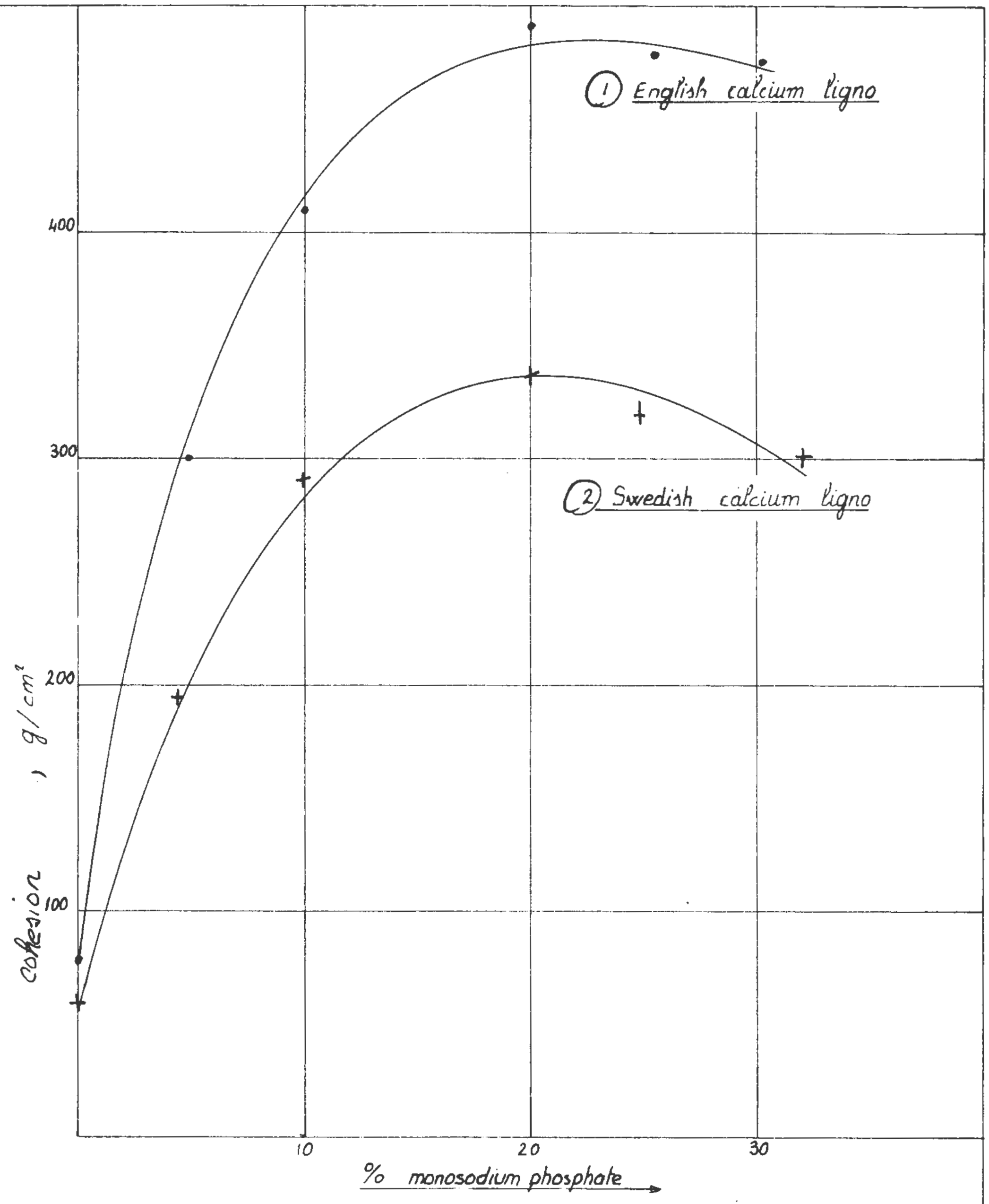


Fig. 156. Effect of Monosodium Phosphate Percentage on Cohesion of a Pure Gel of Various Lignosulfites at 400 g/litre and 15% Dichromate

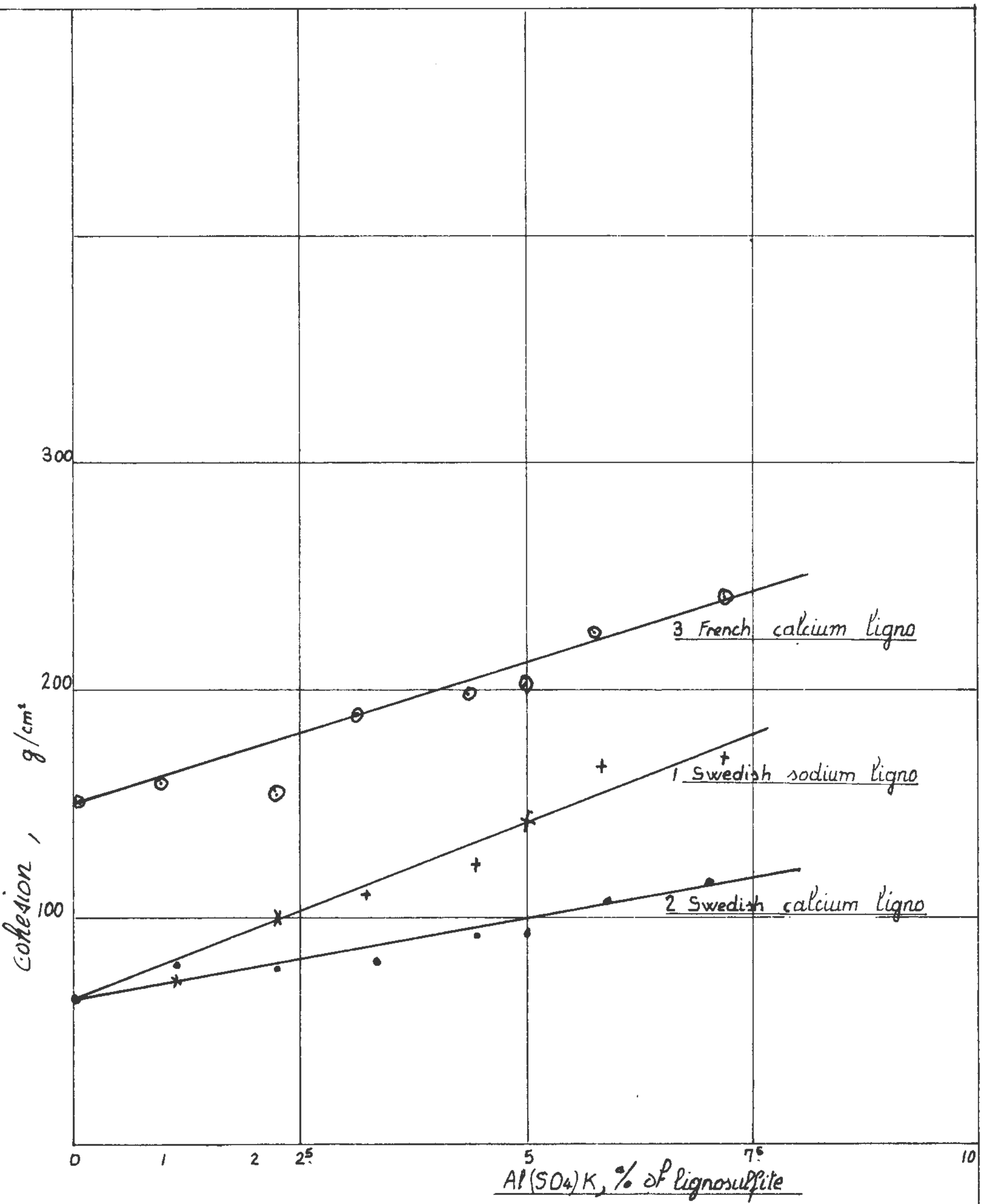


Fig. 157. Effect of Aluminum Potassium Sulfate Percentage on Cohesion of Various Lignosulfites at 400 g/litre and 15% Dichromate

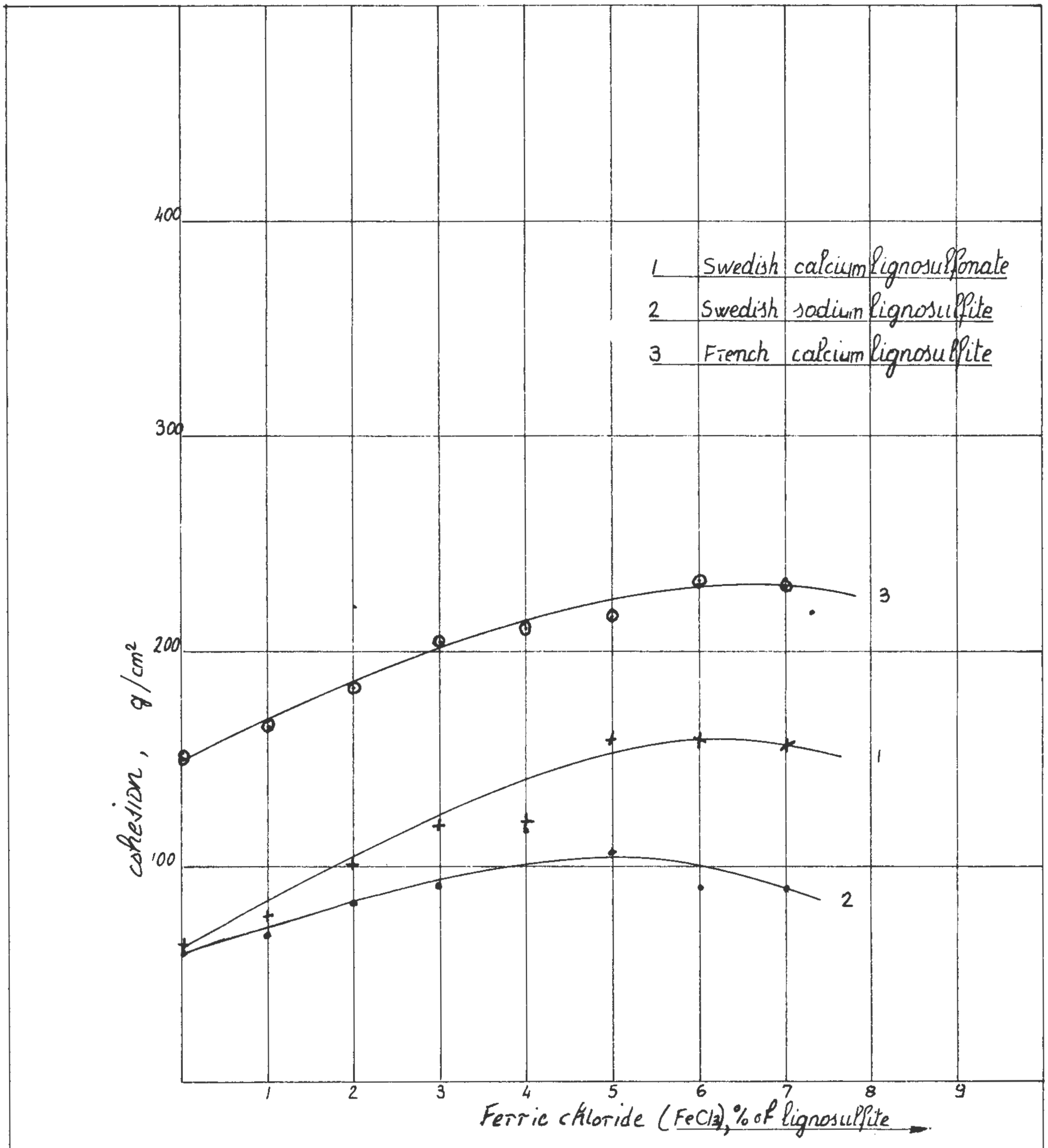


Fig. 158. Effect of Ferric Chloride Percentage on Cohesion of Pure Gel of Various Lignosulfites at 400 g/litre and 15% Dichromate

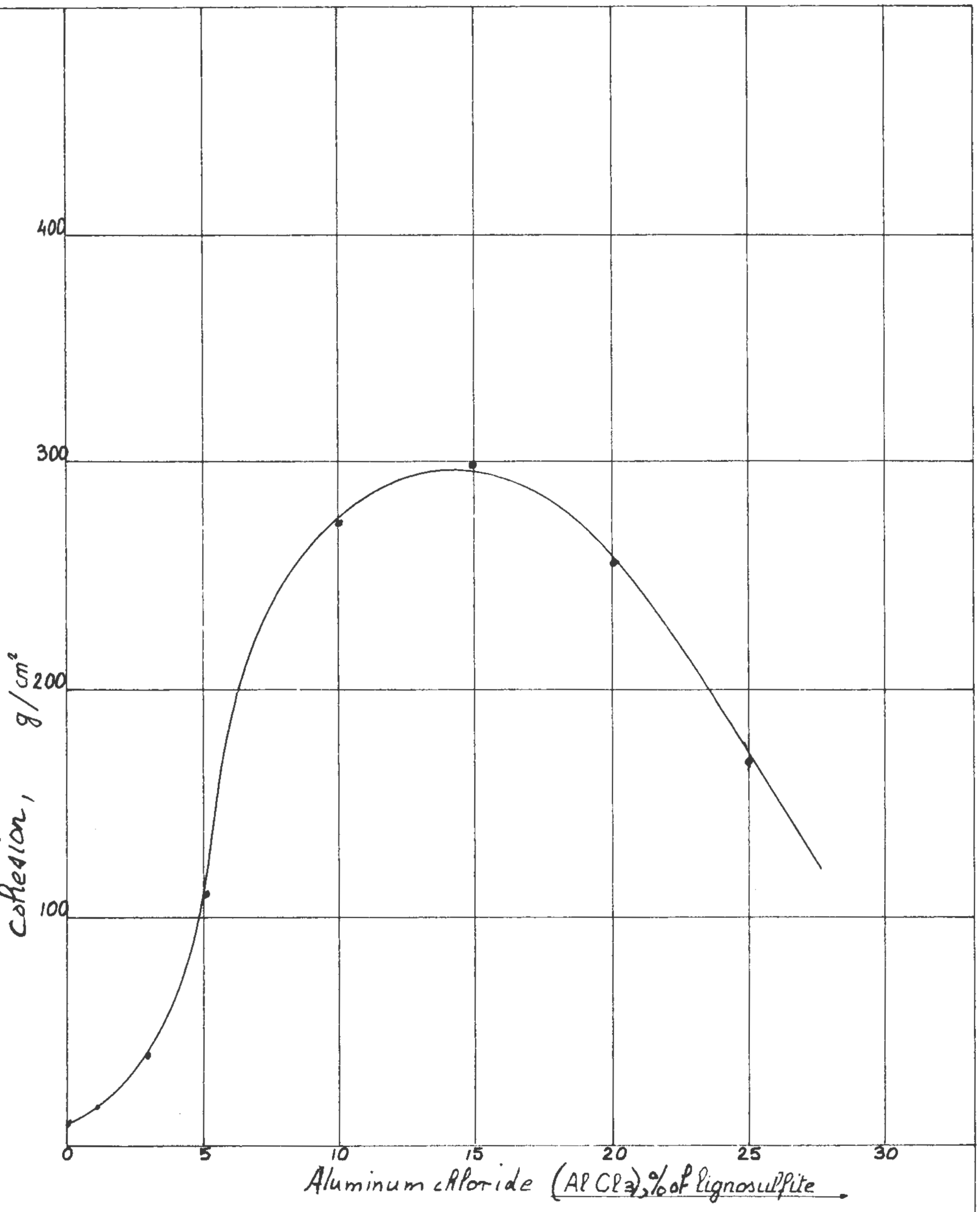


Fig. 159. Effect of Aluminum Chloride Content on Cohesion of Pure Gel of Calcium Lignosulfite at 300 g/litre and 15% Dichromate

a judicious choice of acid additive would allow the dichromate dosage to be lowered to 10%. Normally such mixtures will not set with only 10% dichromate (see Part Three, Chapter III, Lignosulfite Derivatives).

In order to eliminate the pH in each ingredient (lignosulfite, dichromate) as a factor, the pH of these ingredients was set at 7, and then varied with 3 acid products:

a) orthophosphoric acid, 75% solution;
b) ferric chloride in solution, at density 1.45;
c) aluminum chloride in solution, at density 1.26.

The lignosulfite used was a French calcium lignosulfite used in doses of 200 to 300 grams per litre of water.

It possessed the following characteristics:

i) appearance: fine powder
ii) solubility in water: about 99%
iii) average apparent density: 0.45
iv) pH in solution at 300 g/l: 5.7
v) maximum water: 5%
vi) calcium: 1.8%
vii) total sulfur: 6.8%
viii) carbohydrates expressed in glucose: 16 to 18%
ix) inorganic ash at 800°C: 5.3%

For these mixtures, setting time, agglomerating power of pure gel and pH were measured.

A. Setting Time

A.1 Orthophosphoric Acid

For a lignosulfite concentration of 200 g/litre, the mixture did not set when the proportion of acid was varied so that it corresponded to 0 to 30% of the lignosulfite. With the lignosulfite concentration at 300 g/litre, the mixture started to set with the acid at 7% and would no longer set with the acid at 20%. The setting time varied from 2 days to 2 hours (curve 1 on fig. 160).

A.2 Ferric Chloride

With the lignosulfite concentration at 200 grams per litre, the mixture would not set when the proportion of salt was varied so that it corresponded to 0 to 30% of the lignosulfite. With the lignosulfite at 300 grams per litre, the mixture would set when the ferric chloride was at 7.5 to 25% of the lignosulfite, the setting time thus vary-

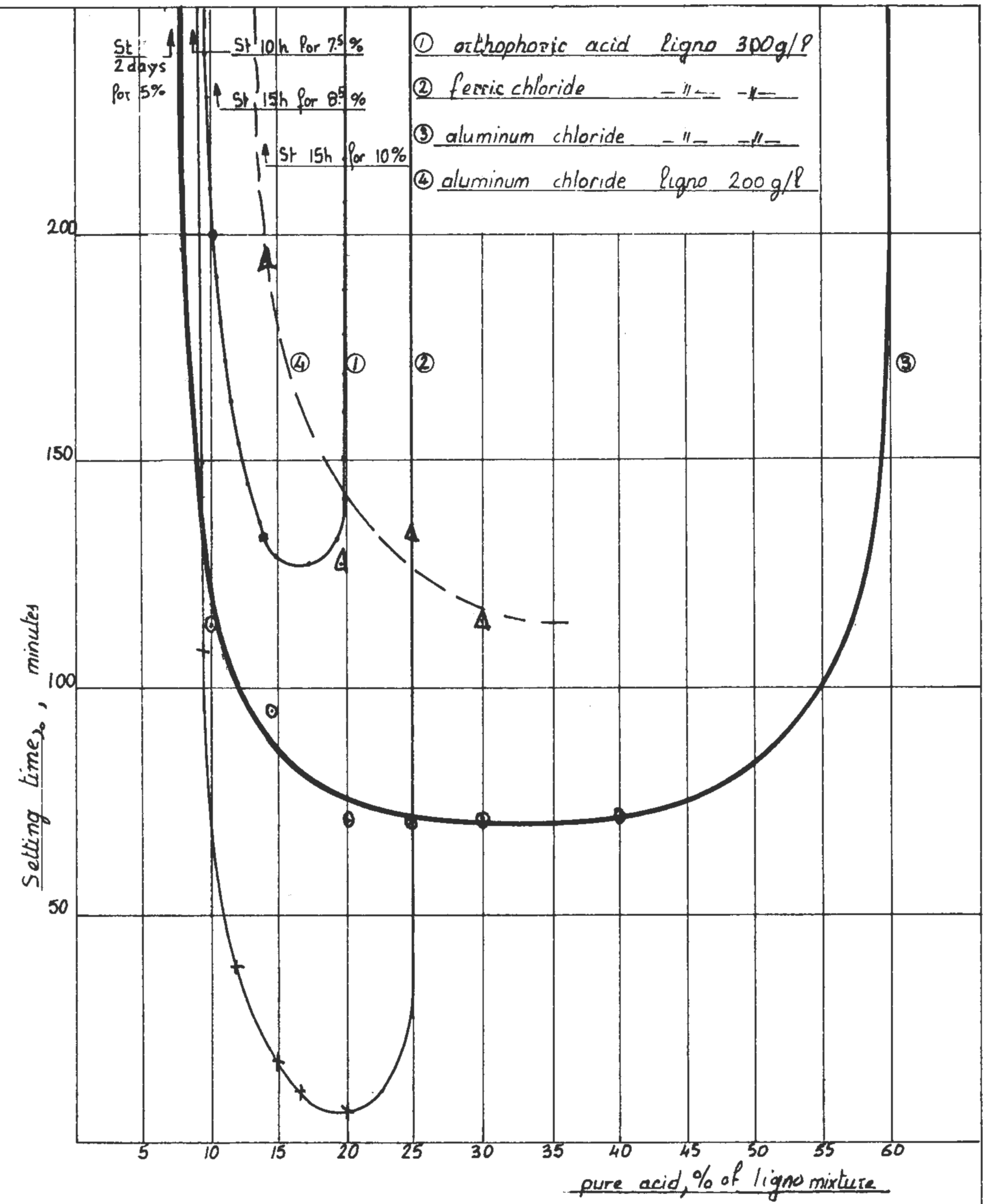


Fig. 160. Effect of Acid Content on Setting Time of a Calcium Lignosulfite at 300 g/litre and 10% Sodium Dichromate

ing from 10 hours (7.5% ferric chloride) to 5 minutes (17.5 to 20% ferric chloride). Above 20%, the setting time was longer (curve 2 on fig. 160).

A.3 Aluminum Chloride

With the two preceding products, the mixture would not set with only 200 grams of lignosulfite, however with the percentage of aluminum chloride ranging from 10 to 30, setting time varied from 15 to 2 hours.

Setting time varied from 2 days to 1 hour with 300 grams per litre lignosulfite and 5 to 30% aluminum chloride. It stabilized at about 1 hour up to 40% and then increased to a point where it would no longer set at about 60% aluminum chloride.

The setting time can thus be shorter than is the case with orthophosphoric acid, but much longer than with ferric chloride (curve 3 on fig. 160).

B. Agglomerating Power of Pure Gel

Fig. 161 demonstrates that orthophosphoric acid (curve 1) and ferric chloride (curve 2) give similar strengths (maximum about 15 g/cm^2) which are markedly lower than those obtained with aluminum chloride at 200 g/litre (curve 4) and at 300 g/litre (curve 3), the maximum strengths being about 30 g/cm^2 and 70 g/cm^2 respectively.

B.1 Role of pH and Conclusion

Figs. 162 and 163, for setting times and strengths in terms of pH, show that these characteristics do not remain constant for a given pH, that is, the pH is not the sole determining factor in the mixture, and each additive has its own role.

As aluminum chloride conferred noticeably higher strengths on the mixture than did the other additives, it was tested further, and more systematically with the results given below.

C. Systematic Study with Aluminum Chloride

C.1 Effect of Aluminum Chloride on Gel Characteristics

This series of measurements, taken with 200 to 300 g/litre of lignosulfonate and dichromate concentrations of 5, 10, 15 and 20% (with only 5% dichromate no gel will form),

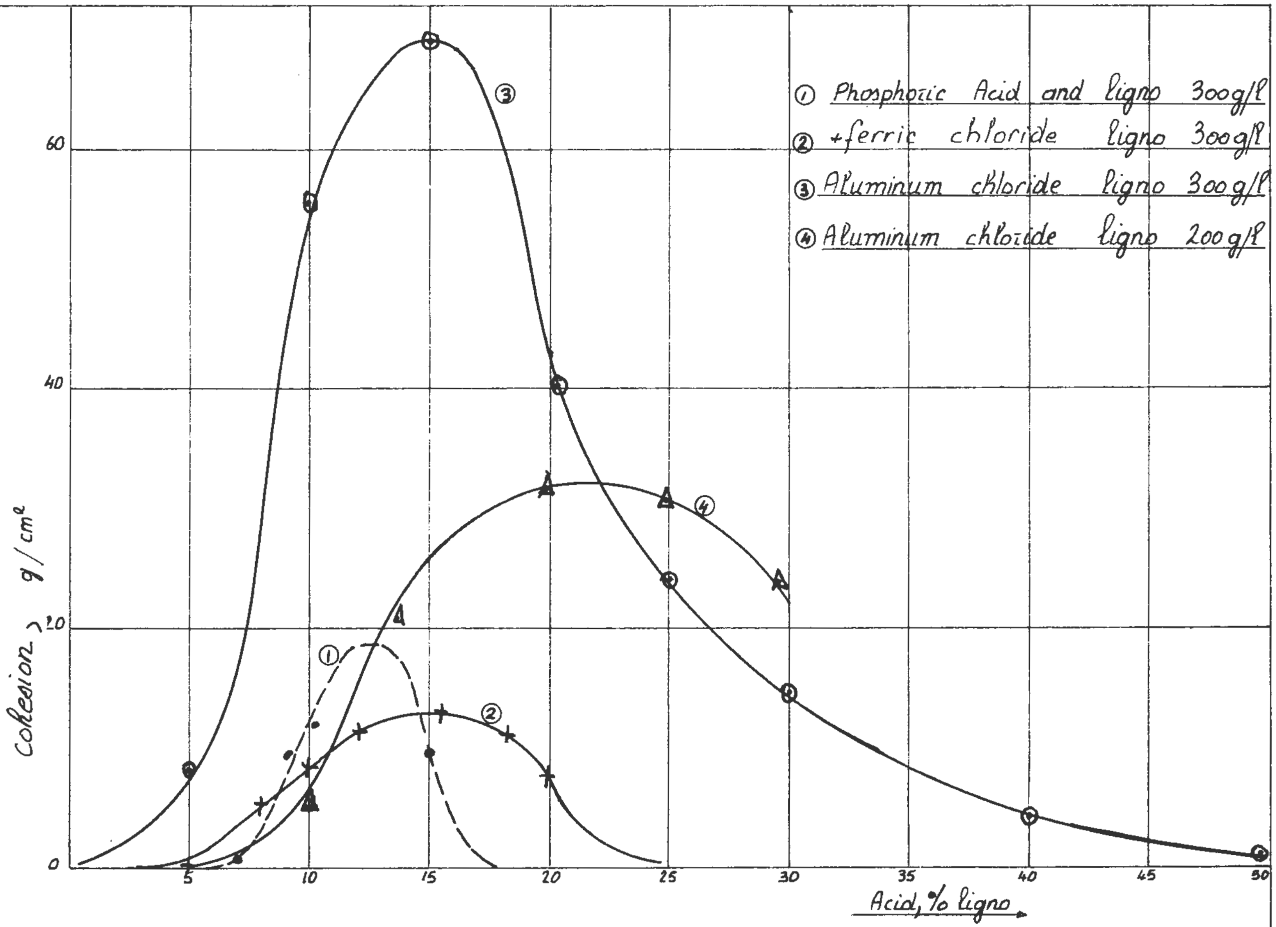


Fig. 161. Effect of Acid Content on Cohesion of a Pure Gel of Calcium Lignosulfite at 300 g/litre and 10% Sodium Dichromate

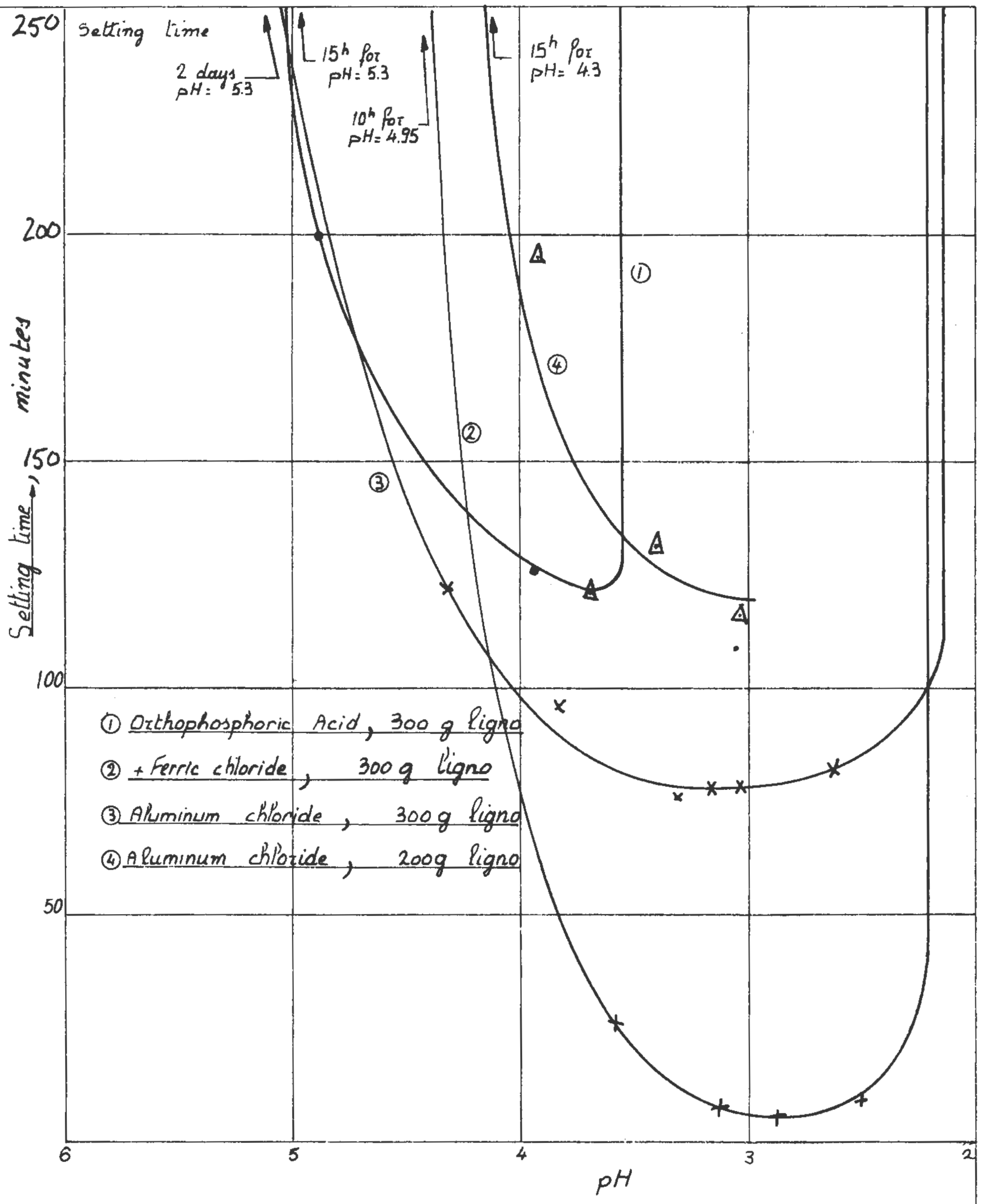


Fig. 162. Effect of pH on Setting Time of a Calcium Lignosulfite at 200 and 300 g/litre Lignosulfite and 10% Sodium Dichromate

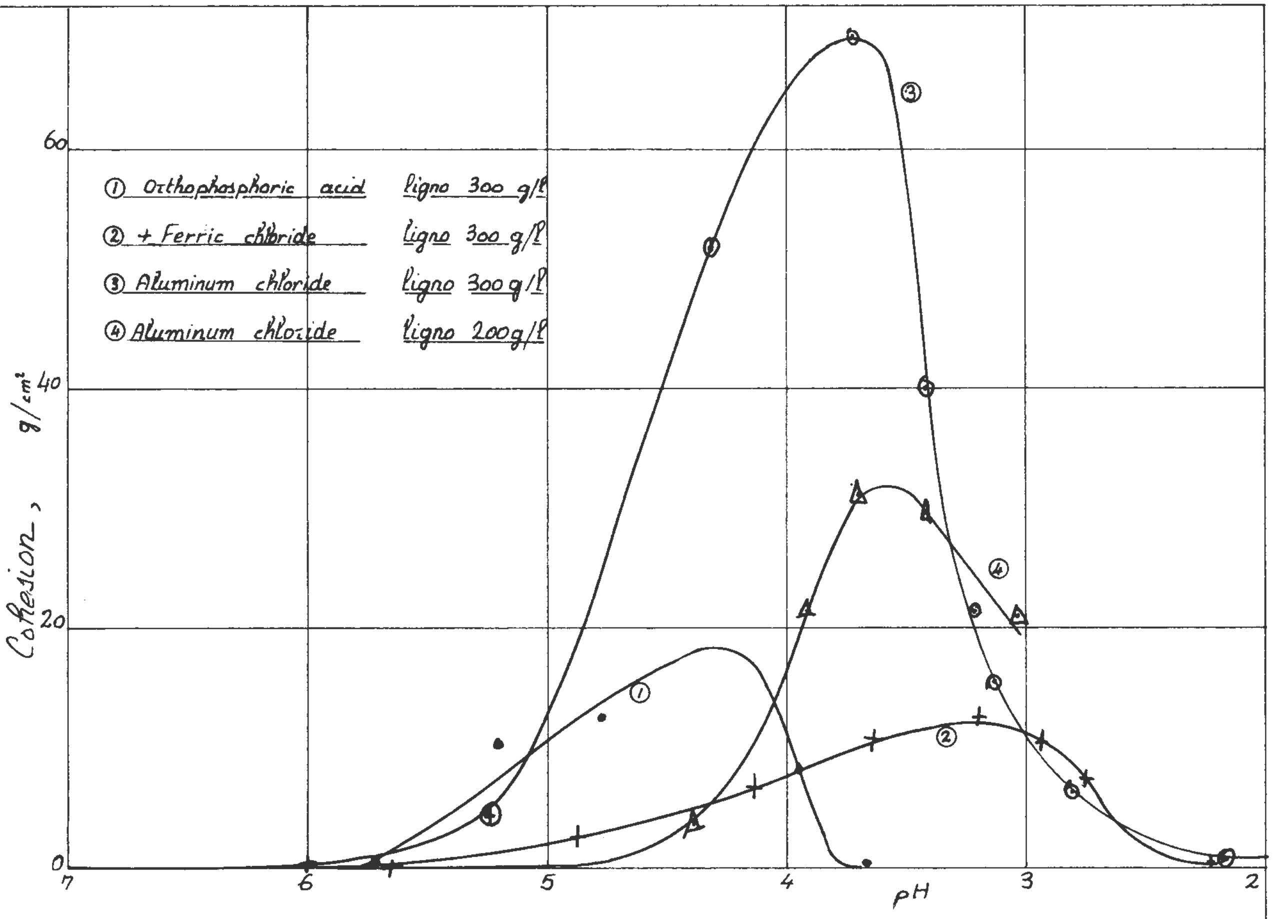


Fig. 163. Effect of pH on Cohesion of Various Additives at 200 and 300 g/litre Lignosulfite and 10% Sodium Dichromate

was intended to determine the grout's optimal intrinsic characteristics, independent of those factors which depend on the process of injection itself (setting time) or the ground (pH).

After neutralizing the lignosulfonate and the sodium dichromate and adding variable proportions of aluminum chloride, the following measurements were taken on the mixture:

i) pH
ii) FANN viscosity
iii) setting time
iv) cohesion after 7 days
v) strength after 7 days, measured on a mortar made up with Fontainbleau sand

C.11 Viscosity

For a given concentration in lignosulfonate, viscosity practically does not vary with different dosages of aluminum chloride. Viscosity is 3.5 cP for 200 grams of lignosulfonate per litre and 5.6 cP for 300 grams of lignosulfonate per litre.

C.12 pH (fig. 164)

Since aluminum chloride is a highly acid and only slightly basic salt, an increase in its amount will cause the pH to drop. As the lignosulfite and the dichromate had both been neutralized, the gel's pH would seem to be determined solely by the aluminum chloride. In fact, there are several interactions and one cannot obtain one single curve. However, all the pH values fall within a narrow range whose limits are:

for 5% $AlCl_3$	6.3 and 5.3
10%	5.2 and 4.3
15%	4.3 and 3.7
20%	3.8 and 3.4
25%	3.5 and 3.2
30%	3.2 and 3.1

C.13 Setting Time (fig. 165)

The setting times of the various mixtures ranged from 7 days to 7 minutes. In general, setting time decreases with the concentration in aluminum chloride, but differences tend to be minimized as the proportion of aluminum chloride approaches 20% (fig. 165).

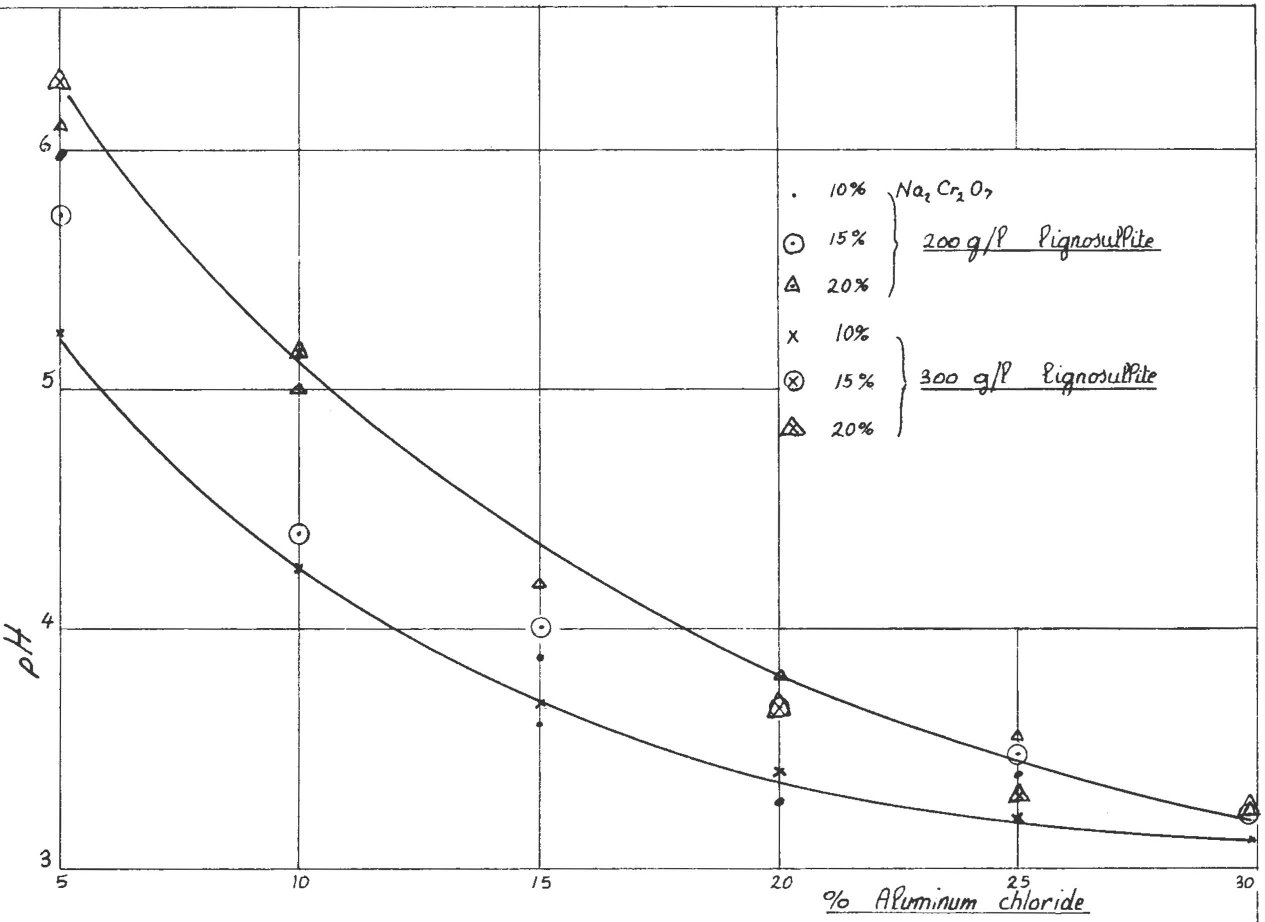


Fig. 164. Effect of Aluminum Chloride on pH of 200 and 300 g/litre French Calcium Lignosulfonate and 10, 15 and 20% Sodium Dichromate

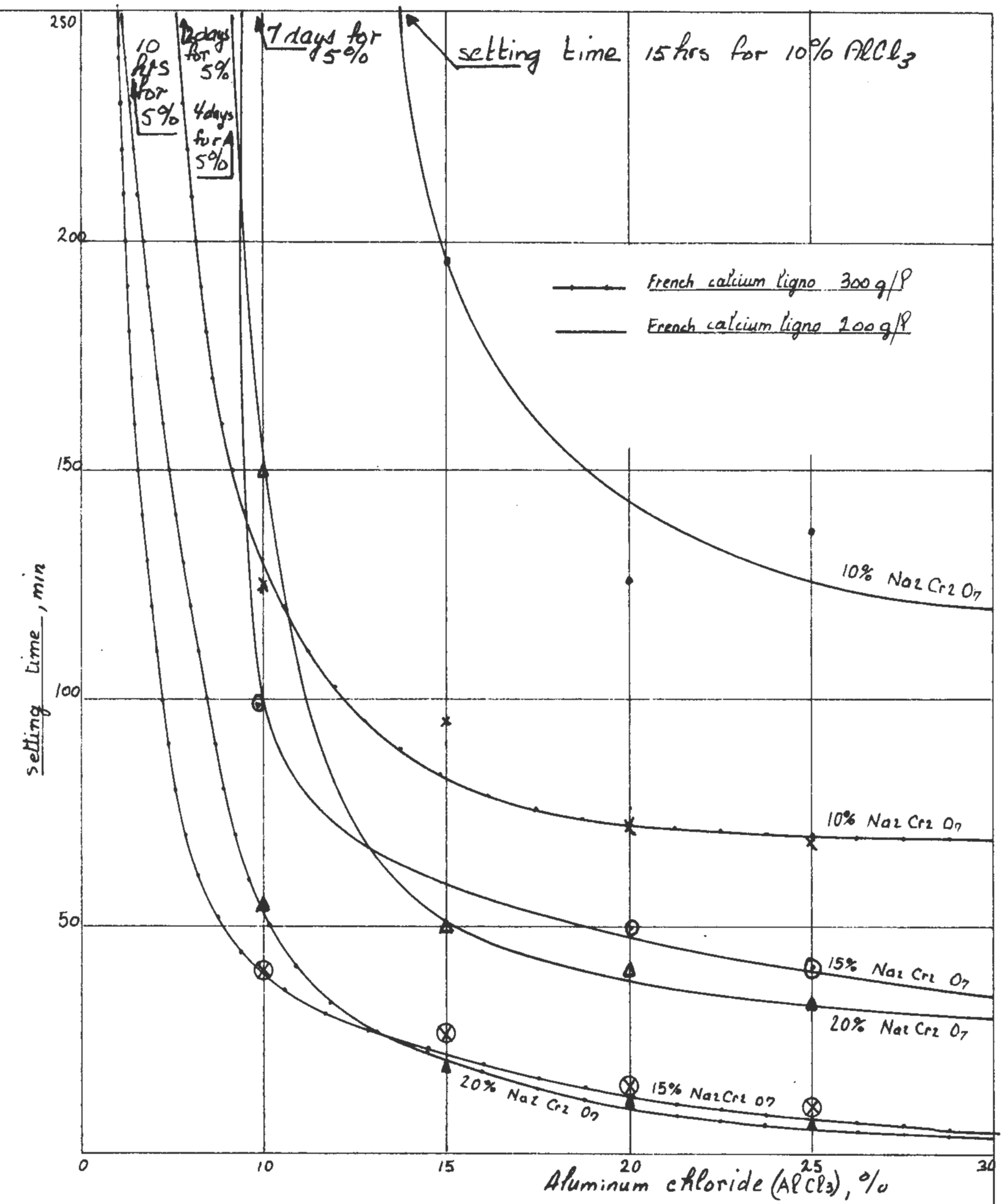


Fig. 165. Effect of Aluminum Chloride Content on Setting Time

C.14 Rigidity of Pure Gel after 7 Days

Rigidity increases with the dosage in aluminum chloride up to a maximum of between 20 and 25% (fig. 166), depending on the concentration in lignosulfonate, and thereafter decreases slightly. This phenomenon corresponds to the movement of the pH to the lower limit of reactivity for hexavalent chromium (pH < 3.5). In this series of measurements, maximum rigidity moves from 50 g/cm^2 to 1200 g/cm^2.

C.15 Strength of Mortar after 7 Days (fig. 167)

The changes in strength of a mortar made with Fontainebleau sand after 7 days on the whole follow the changes in rigidity (maximum attained with 20 to 25% aluminum chloride and decrease thereafter). Maximum strengths of the various formulas range from 1.8 bars to 14 bars, depending on the increase in the dosage of $AlCl_3$.

Those formulas with a high aluminum chloride content gave bad results on mortar, because of their very short setting times, while the results were good with pure gels tested for shear strength. Short setting times (under 15 minutes) entail rapid changes in viscosity and are incompatible with proper placing of the grout in the sand.

C.2 Effect of Lignosulfonate Content on Gel Characteristics

The preceding study seems to indicate that the optimal dosage in aluminum chloride is 20%; beyond this level the aluminum chloride harms the gels' mechanical characteristics and setting times are generally too short. However, given the conditions inherent in the fact that the ground to be grouted is usually calcareous, the concentration in aluminum chloride should be limited to 10% of the lignosulfite content. At this dosage, the mixture's pH will be in the neighborhood of 4.5, and at this pH level the carbonates in the ground will not decompose.

Using a constant proportion of aluminum chloride (10%), the effect of the lignosulfonate concentration will be examined by varying the concentration from 200 g/l to 250, 300, 350 and 400 g/litre.

C.21 Viscosity (fig. 168)

Viscosity practically does not vary with the dosage of sodium dichromate; on the other hand, it varies from 3.2 cP to 12.7 cP when the lignosulfonate content is increased from 200 g/litre to 400 g/litre.

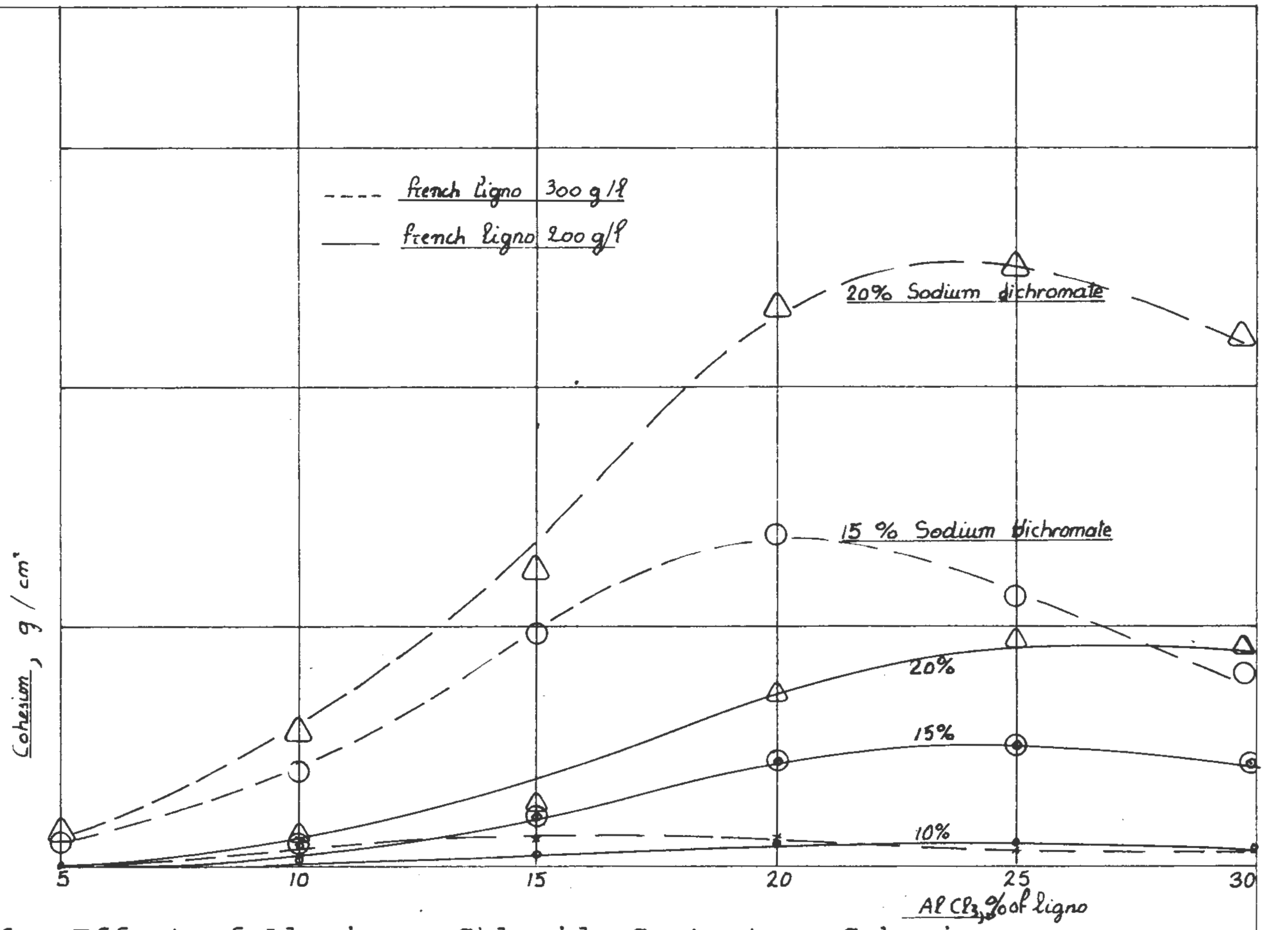


Fig. 166. Effect of Aluminum Chloride Content on Cohesion of Lignochrome Gels

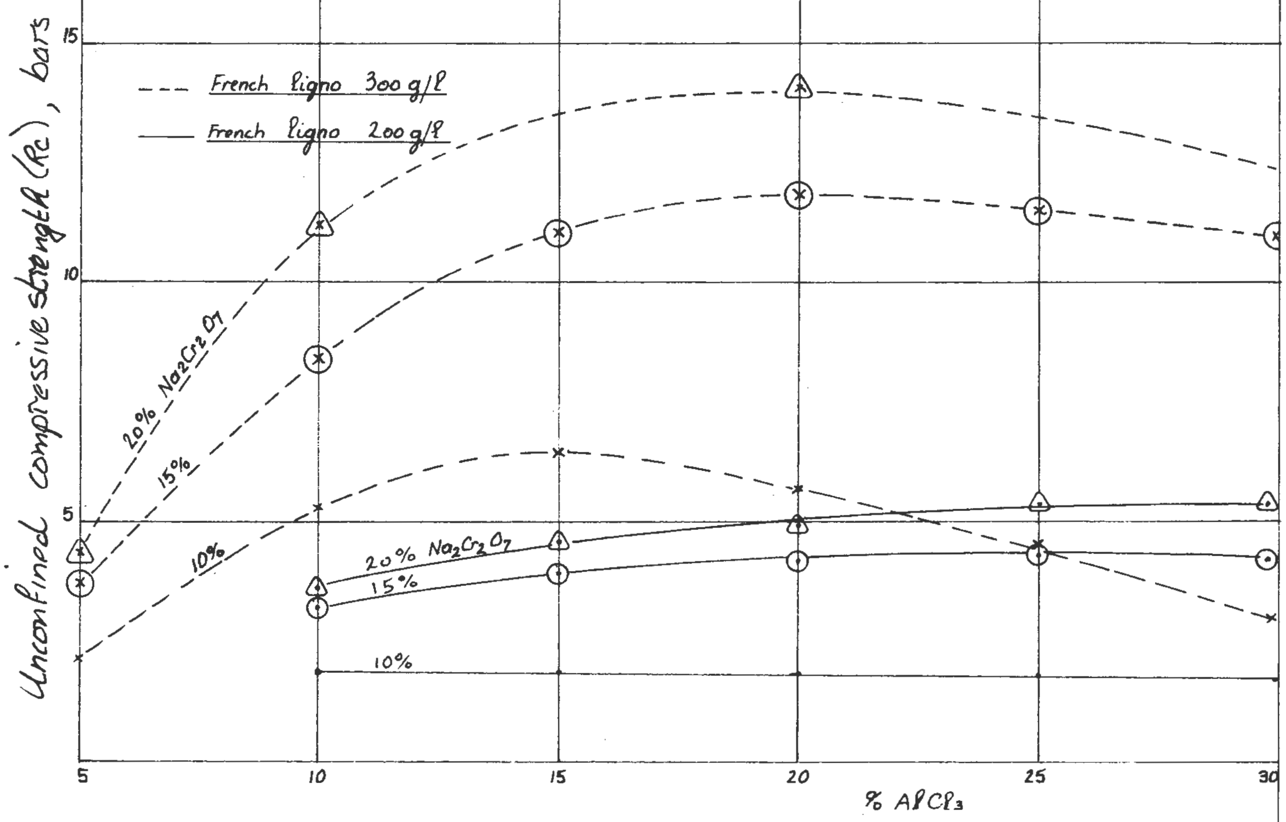


Fig. 167. Effect of Aluminum Chloride on Unconfined Compressive Strength After 7 Days

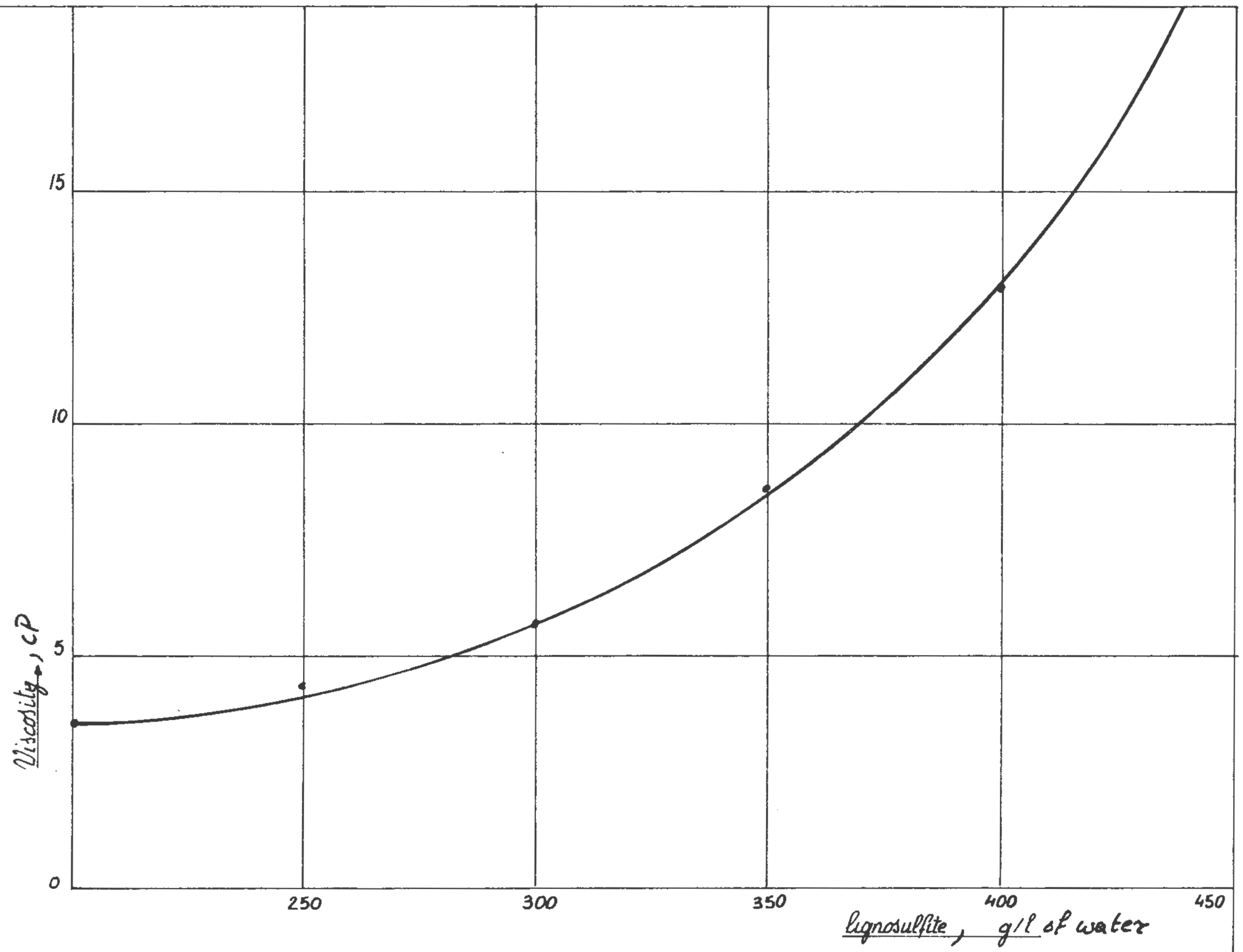


Fig. 168. Effect of French Calcium Lignosulfonate Content on Viscosity for 15% Dichromate and 10% Aluminum Chloride (Percentage of Lignosulfonate)

C.22 pH (fig. 169)

For a constant concentration in sodium dichromate, the pH varies very little:

4.3 to 4.5 for 10% dichromate
4.6 to 4.9 for 15% dichromate
5 to 5.2 for 20% dichromate

Thus, the pH falls between 4.3 and 5.2, an allowable pH range for calcareous terrain.

C.23 Setting Time (fig. 170)

Setting time decreases steadily as the lignosulfonate content moves from 200 g/litre to 400 g/litre. It also varies with the concentration in sodium dichromate, the difference between 10% and 15% being relatively pronounced, and much less marked between 15% and 20%. (Curiously, setting times with 20% dichromate are longer than they are with 15%).

C.24 Shear Strength (fig. 171)

If the proportion of dichromate remains constant, shear strength after 7 days increases steadily with the concentration in lignosulfonate. Thus, with 10% dichromate (the target proportion), it moves from 50 g/cm^2 with 300 g/litre of lignosulfite to 300 g/cm^2 with 400 g/litre.

D. Combined Method Using Aluminum Chloride and A Second Oxidizer

Given the favorable results obtained with aluminum chloride, this method was combined with the use of a second oxidizer. The purpose was to see whether the formulas in which the dichromate was limited to 10% (by weight of the lignosulfite) could thus be enhanced.

The following formula was used as a base:

calcium lignosulfite	300 g
sodium dichromate	30 g (10%)
aluminum chloride	60 g (20%)
water	1 litre

As previously explained, the pH of the lignosulfite and the dichromate was brought to 7.

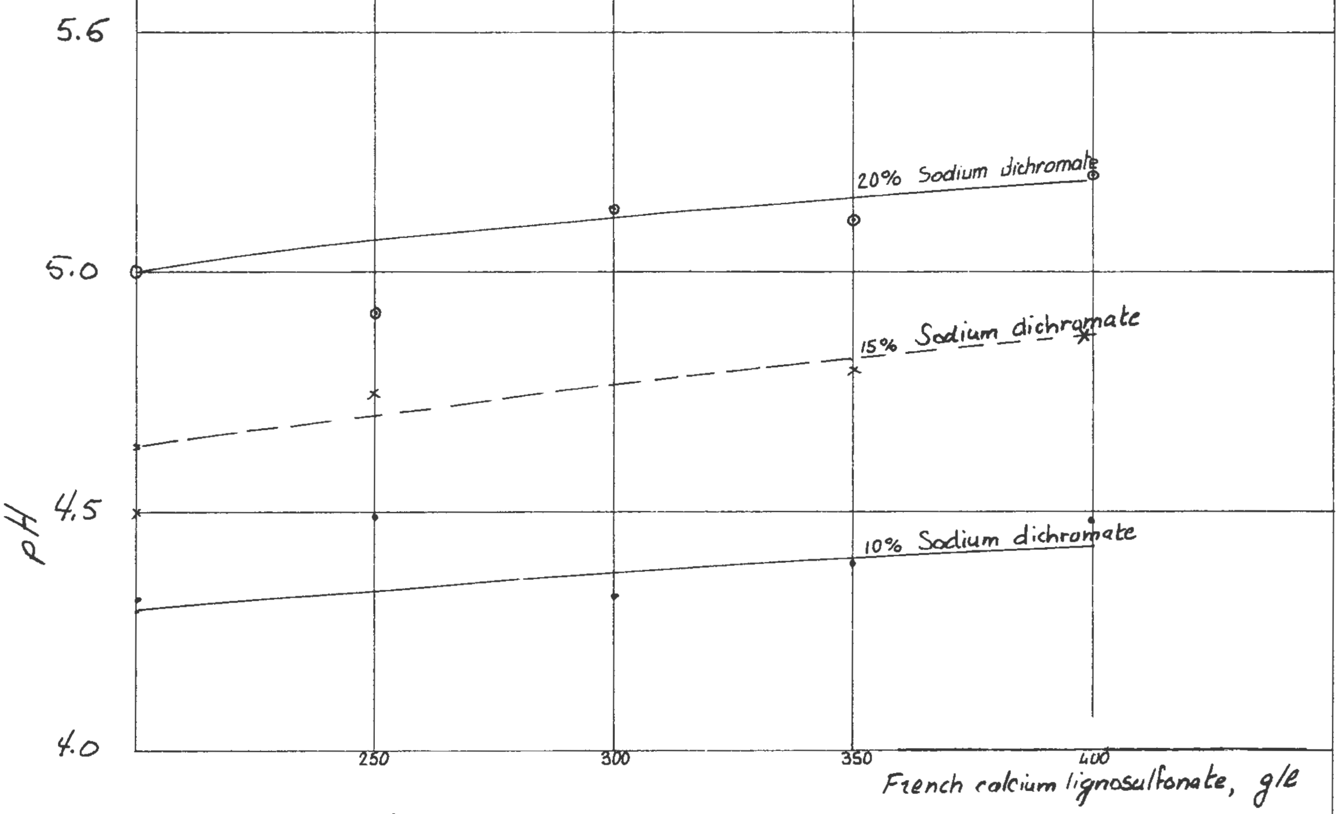


Fig. 169. Effect of Lignosulfonate Content on pH

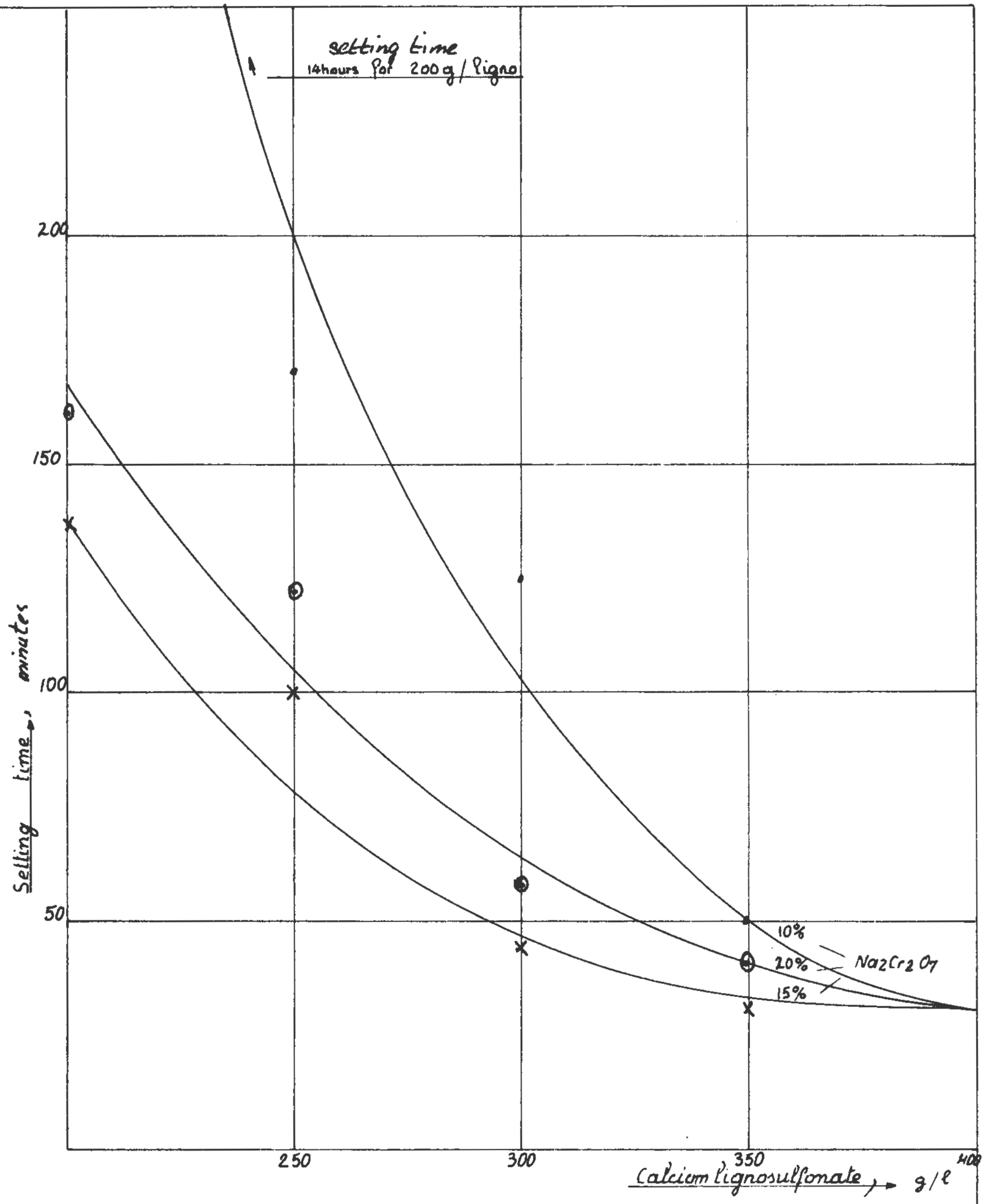


Fig. 170. Effect of Lignosulfonate Content on Setting Time of Various Concentrations of Sodium Dichromate

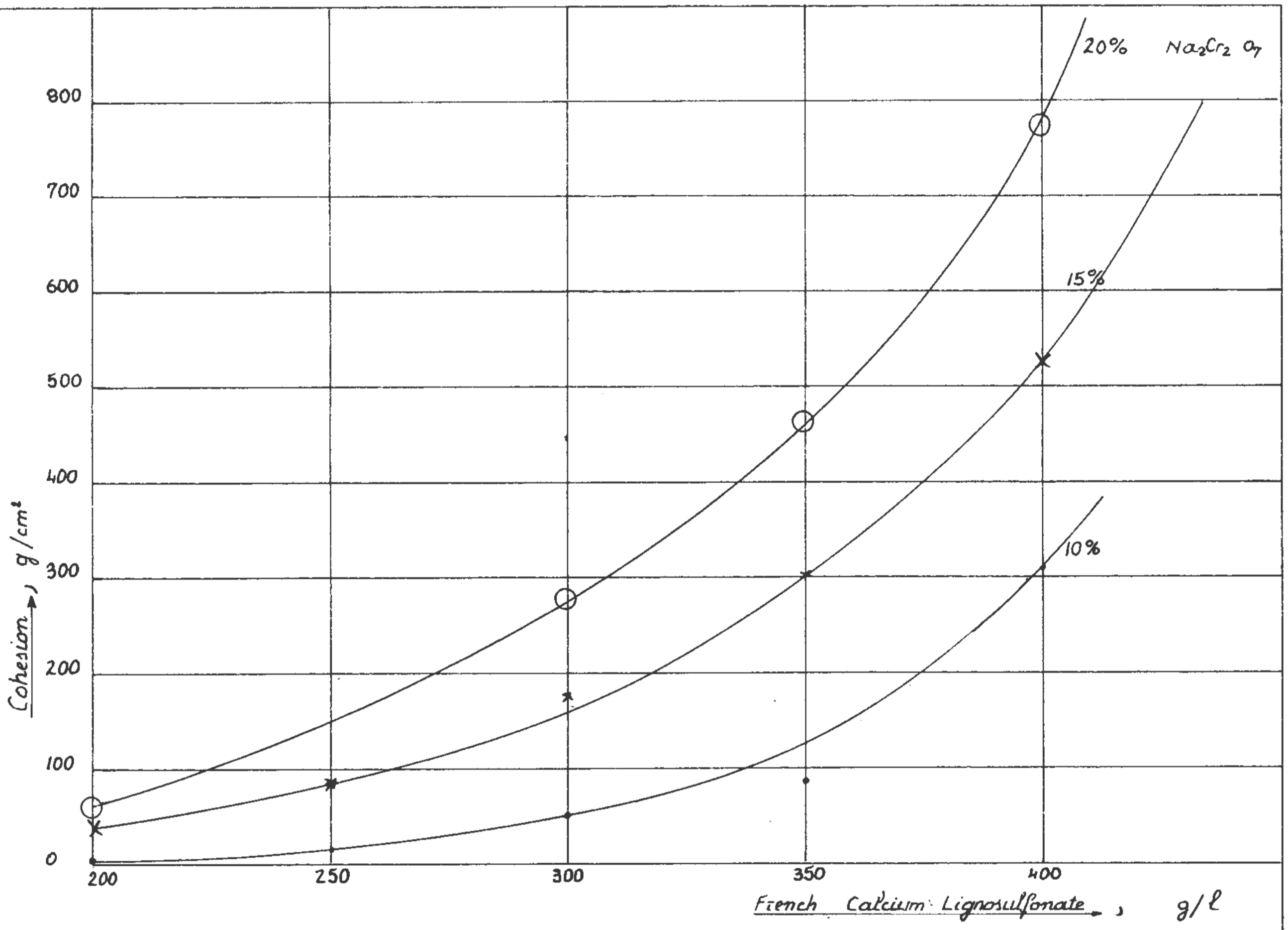


Fig. 171. Effect of Lignosulfonate Content on Cohesion of Pure Grout After 7 Days

The characteristics of the basic formula are as follows:

- i) setting time: 70 min
- ii) shear strength: 50 g/cm^2
- iii) unconfined compressive strength on standard mortar (direct mixing method): 5.5 bars

To this basic formula were added respectively: 30 ml of hydrogen peroxide, or 35 ml Caro acid, or 72 g sodium persulfate. The new characteristics are given in table 45 below:

Table 45. Changes in Characteristics With Added Ingredients

substances added	H_2O_2 30 ml (1)	H_2SO_5 35 ml	$Na_2S_2O_8$ 72g
setting time	60 min	60 min	45 min
agglomerating power after 7 days	around 0	4 g/cm^2	13 g/cm^2
strength of standard mortar after 7 days	around 0	2.4 bars	4 bars

(1) The hydrogen peroxide is destabilized at the moment when the sodium dichromate is added, the mixture is ejected from the container used to measure the gel's agglomerating power, while the formation of a cellular gel can be observed in the container used for mixing the various products.

Unless further study should prove otherwise, this route does not seem fruitful.

3. Conclusion

The attractiveness and, consequently, the applications of lignochromes in grouting are limited by the fact that their formulas include dichromate, which may entail some toxicological risk. Of course, the toxic Cr^{+6} is quickly reduced by the lignosulfite to non-toxic Cr^3, but with the dichromate dosages generally used, this conversion cannot be entirely complete and thus leaves some free Cr^{+6} in the hardened grout.

Attempts to replace the dichromate with another oxidizer connected with a heavy metal have not succeeded. On the other hand, we have been able to limit the dichromate content to much more reasonable doses: 15% and even 10%, while maintaining setting times and strengths which are suitable for both waterproofing and consolidation. This goal was achieved by precise regulation of pH to the exact decomposition limit of possible carbonates in the ground.

In addition to regulation of pH at the optimal level, this study has also demonstrated that the nature of the acid ion affects the mechanical characteristics of hardened grout. Of the 5 acid ions tested, aluminum chloride proved the best. It is altogether possible that still other ions might give even better results.

III. Improving Furfural Base Grouts

1. Problem

In an examination of Category A-4, it appeared that the most interesting products in this plant category were furfural and its derivatives.

Like lignosulfonate, the uses of furfural are far from being thoroughly developed. At present this product is extracted only from corncobs; more widespread collection could increase this production tenfold, and use of other sources such as bagasse, leaves, straw and even household garbage would allow another tenfold increase. However large the market may be in the decades to come, there is no risk of a lack of basic products containing furfural. Unlike petrochemicals, furfural manufacture (by distillation) does not require large industrial plants and can even be produced using simple equipment, as is done in China. It is at the level of collection that problems are encountered.

As opposed to these definite advantages, the following two drawbacks should be pointed out:

a) Although some furfural resins have been known for 30 years, research on this subject has been very limited. This field is vast and rich, but relatively unknown.

Following the bibliography on this subject in Volume I, we conducted further research in source material and were able to find and examine new texts and patents, notably on the manufacture of prepolymers and their uses as glue and binder in casting molds (virtually the only routine application of furfural polymers). These new sources are not included here since they have no bearing on the uses of furfural in grouts.

b) The second survey confirmed that an acid catalyst is always used for polymerization, thus ruling out this process for normal grouting. This study therefore seeks to increase knowledge of furfural resins and to explore the possibilities of basic systems.

Available literature lists four types of chemical reactions which have been used intermittently in public works:

1) an aniline-furfural reaction studied by WINTERKORN for the surface stabilization of fine sands.

2) the relatively complex two-shot process, patented by YOUNG, which uses a furfuryl alcohol prepolymer for grouting in connection with oil well drilling (thus the substance is heated) (65-21).

3) some types of concrete made with furfurylidene acetone-base resins (obtained through precondensation of the furfural on the acetone).

4) mixtures of urea-formaldehyde syrup (prepolymer) and furfuryl alcohol used in the Soviet Union for consolidation grouting of mines(50-21).

Only this last application was expressly for grouting and was therefore the formulation used as a reference. The reference material contained no indications as to the optimal urea-formaldehyde/furfuryl alcohol ratio, or performances.

2. Tests

2.1 Reference Formulation in Acid Medium: study of urea-formaldehyde (prepolymer)/furfuryl alcohol (monomer) combination.

2.11 Products Used

A. urea-formaldehyde prepolymer: NOBELAMINE 24 819 of HOECHST-NOBEL (active product content: 70%, density, 1.3; viscosity, 40 poises.

B. furfuryl alcohol monomer

C. various catalysts: sulfuric acid, hydrochloric acid, hydrochloric acid-ammonium persulfate mixture, phenol-sulfonic acid.

2.12 Compatibility

The urea-formaldehyde polymer and the furfuryl alcohol monomer are miscible in any proportions and are also miscible in water after being mixed together.

2.13 Choice of Acid Catalyst

Preliminary tests showed that although urea formaldehyde (UF) polymer-furfural alcohol (AF) monomer mixtures are compatible and miscible in any proportions, the mixture did not produce an unusually useful copolymer (with characteristics surpassing those of the basic UF prepolymer) unless the catalyst was employed in a definitely acid medium: $pH \leq 2$, obtained with a strong acid. The catalyst gives an exothermic reaction and the free formaldehyde in the UF prepolymer is combined.

Conversely, in a less acid medium, no heating effect is noted. The excess formaldehyde is not combined and the final mixture is more plastic than the control (pure UF). It can be concluded that the furfuryl alcohol has not reacted well.

The effect of the catalyst is quite apparent in table 46 below where the following proportions are used (by weight):

urea-formaldehyde prepolymer	100
water	60
furfuryl alcohol	20
catalyst	variable

Table 46. Effect of Catalyst on Strength

type of catalyst	catalyst dosage (%)	setting time (min)	Rc after 48 h (bars)	Rc after 28 days (bars)
hydrochloric acid (50% solution)	1	150	42	70
	1.5	40	73	100
	2	15	90	120
hydrochloric acid (10% solution) plus ammonium persulfate	2 + 1	10	93	173
	2 + 2	7	106	188
	2 + 3	4	116	226
	2 + 5	2	fissured	
phenol-sulfonic acid (50% solution)	1	45	63	103
	1.5	15	86	113
	2	14	73	106
	2.5	12	80	110
	3	10	86	115
sulfuric acid (20% solution)	1	25		105
	2	14		116
	3	11	69	160

Rc = unconfined compressive strength

It can be seen that the furfuryl alcohol reacts poorly with those mixtures containing more acid: after 28 days, strength barely exceeds 100 bars. Definitely acid systems give better performances since they set in less than 10 minutes. There is also a break in the curve for strength in terms of setting time at 10 minutes (fig. 172). However, setting time should not be unduly shortened since an excessively high dosage of acid will produce mixtures which are so exothermic that they crack (for example the mixture containing 2% hydrochloric acid and 5% ammonium persulfate).

For the rest of this survey, we have used 3% sulfuric acid.

2.14 Setting Time

Whatever the respective ratios of urea-formaldehyde prepolymer and furfuryl alcohol monomer, the sulfuric acid dosage was kept constant at 3%. For a given dilution, setting time is thus a relatively short constant: in the vicinity of 10 minutes for combinations at average dilution (60%), and even shorter for less dilute mixtures.

Thus, for purposes of grouting, it can be beneficial to extend the setting time by using the AF in prepolymer state. In practice, the proportion of catalyst can scarcely be changed at all for fear of decreasing strength. If setting time must be adjusted, the AF would have to be combined in monomer and prepolymer form.

2.15 Strength of Pure Grout

The reaction becomes exothermic as soon as the furfuryl alcohol is added, over 40% it is even violent, giving off free formaldehyde and causing the mixture to bubble wildly. For this reason, strength curves (for non-dilute grout) as a function of the respective percentages have been drawn only for 0 to 40% alcohol (table 47 and fig. 173). Thus, it is apparent that:

a) a final strength reading is available only after 28 days.

b) furfuryl alcohol is beneficial up to a level of 20%, at which point it will have combined all the free formaldehyde in the mixture, eliminating the formaldehyde odor. Above this level, the alcohol is harmful.

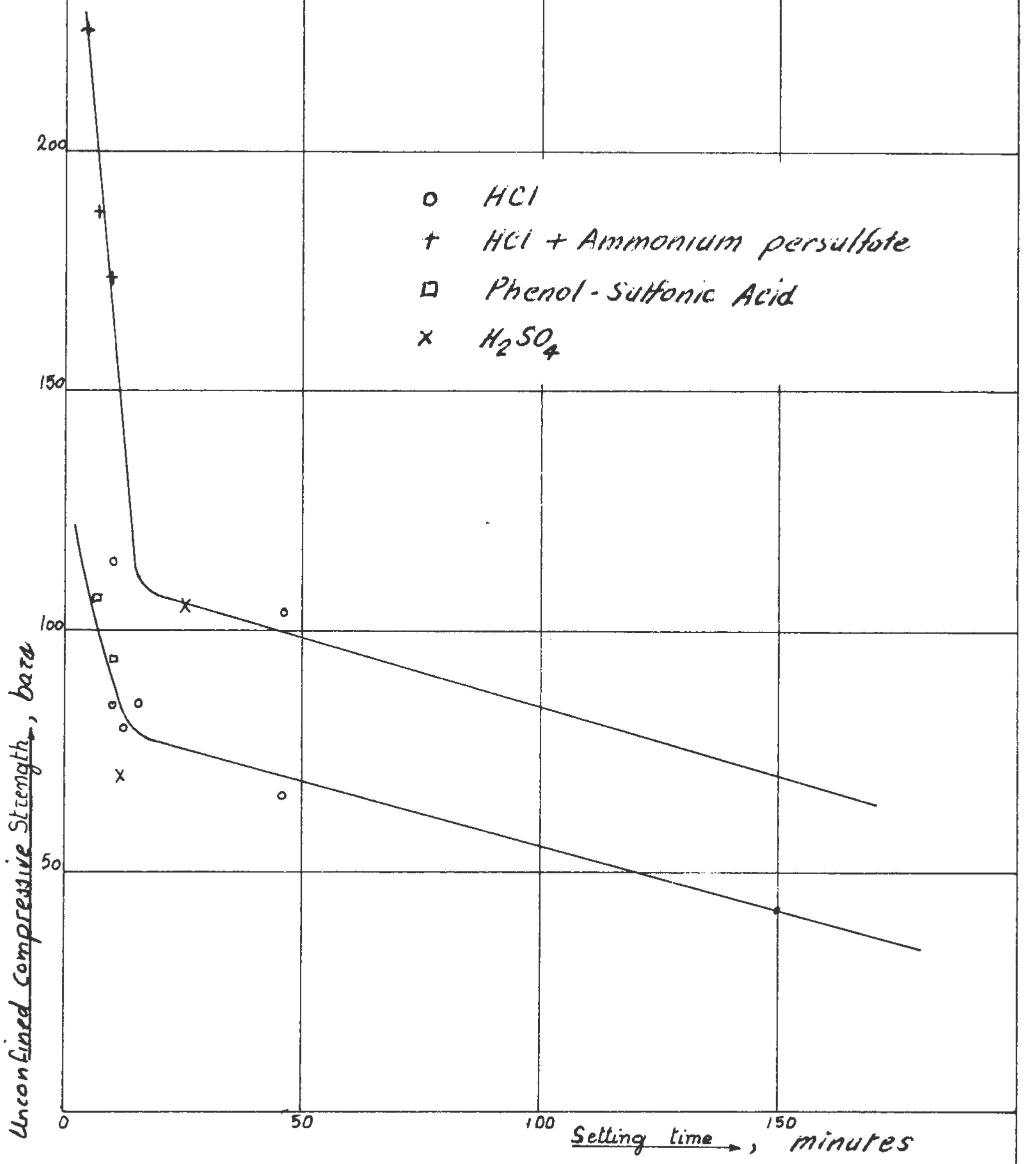


Fig. 172. Effect of Catalyst on Setting Time-Strength Relation

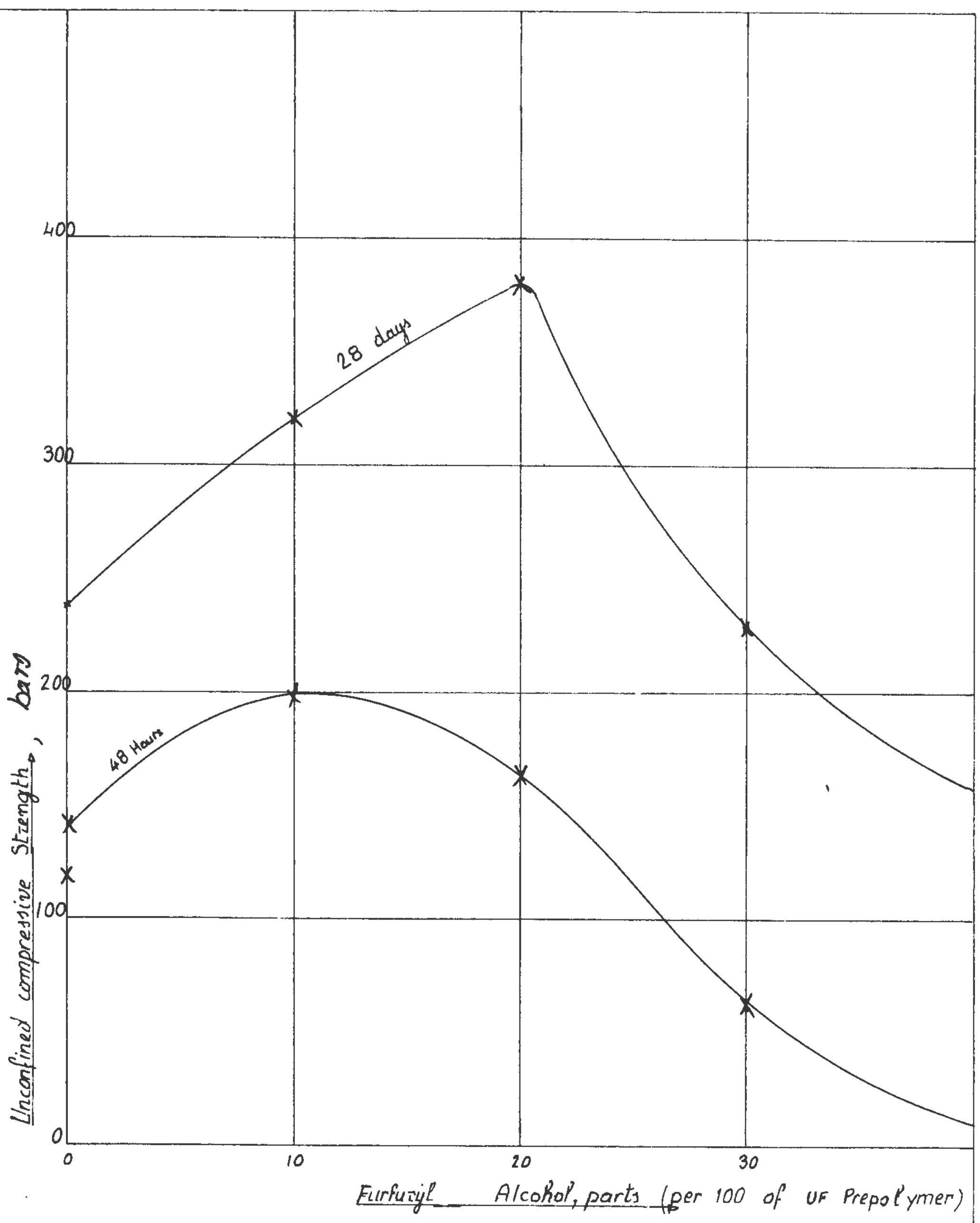


Fig. 173. Effect of Furfuryl Alcohol on Strength of Pure Grout (Nobelamine 24819)

Table 47. Effect of Furfuryl Alcohol Proportion on Strength

Catalyst H_2SO_4, 3%

parts alcohol per 100 of prepolymer	Rc after 48 hours (bars)	Rc after 28 days (bars)
0	140	233
10	200	320
20	166	380
30	63	230
40	10	150

Rc = unconfined compressive strength

In the first part of the curve, strength = furfuryl alcohol , the incline shows that this addition has been most effective. Thus, the addition of 20% alcohol to the UF prepolymer increases the price by 26% (based on 1976 prices), while strength has been increased by 60%. In addition to the economic factor, this modification renders the grout odorless, since the free formaldehyde in the UF has been combined.

The same findings have been obtained with dilute mixtures of UF prepolymer and furfuryl alcohol (table 48 and fig. 174). Once again 20% furfuryl alcohol gives optimum results after 28 days. The shape of the curves is altogether similar to that in fig. 173. Fig. 175 shows the effect of dilution on strength after 28 days.

2.2 Study of Basic System

The preceding tests show that UF/AF combinations, within certain ranges of proportions, can be considered for medium and strong grouting of non-calcareous ground. Thus, it was interesting to try to obtain the same performances in a medium compatible with calcareous sands, slightly acid or basic medium.

2.21 Preliminary Study

As indicated previously, whether based on furfuryl alcohol or a mixture of urea-formaldehyde and furfuryl alcohol, no useful compositions with a slightly acid medium (pH > 4.5) have been found which are compatible with calcareous sands.

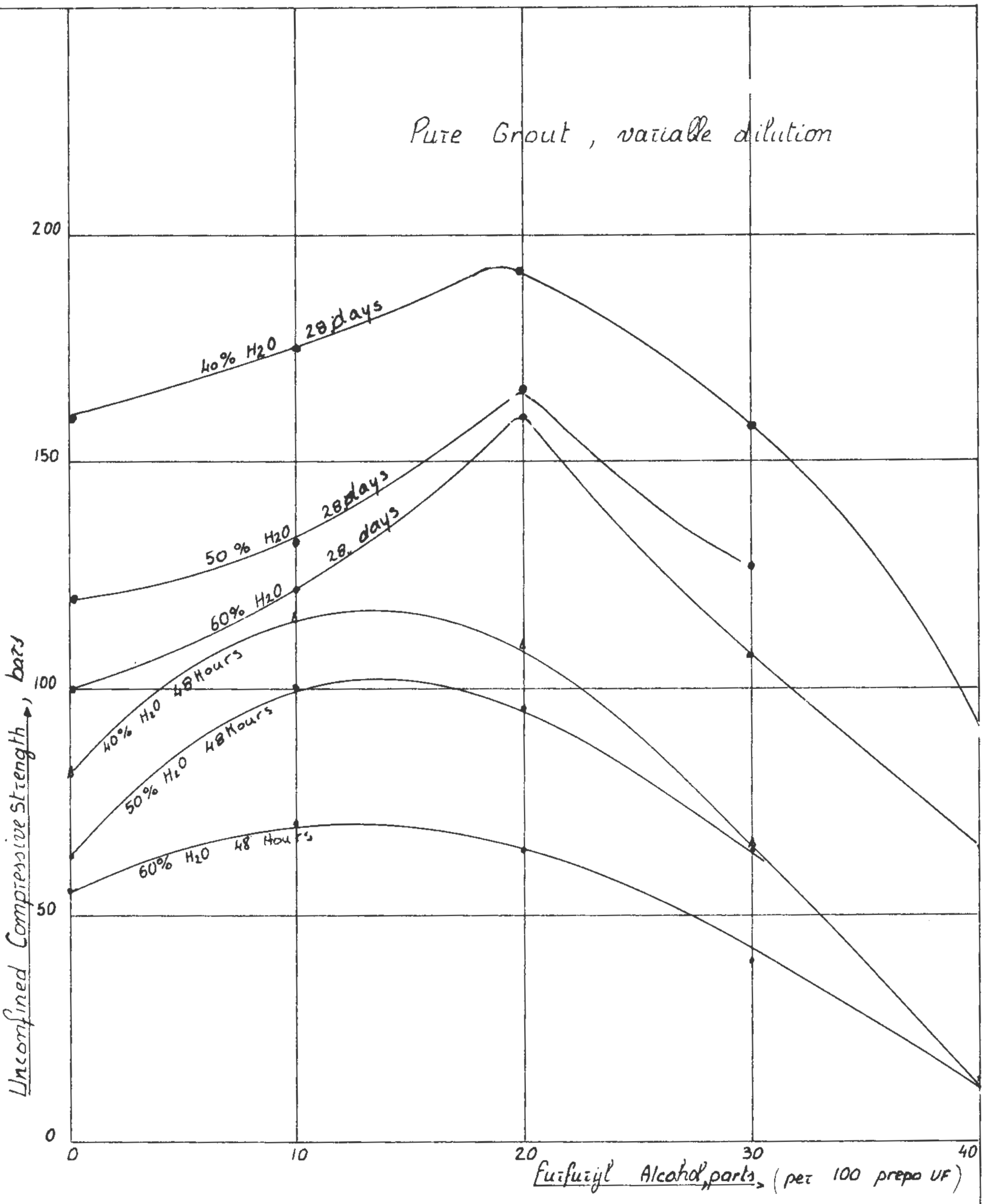


Fig. 174. Effect of Furfuryl Alcohol on Strength of Urea Formaldehyde Prepolymer (Nobelamine 24819)

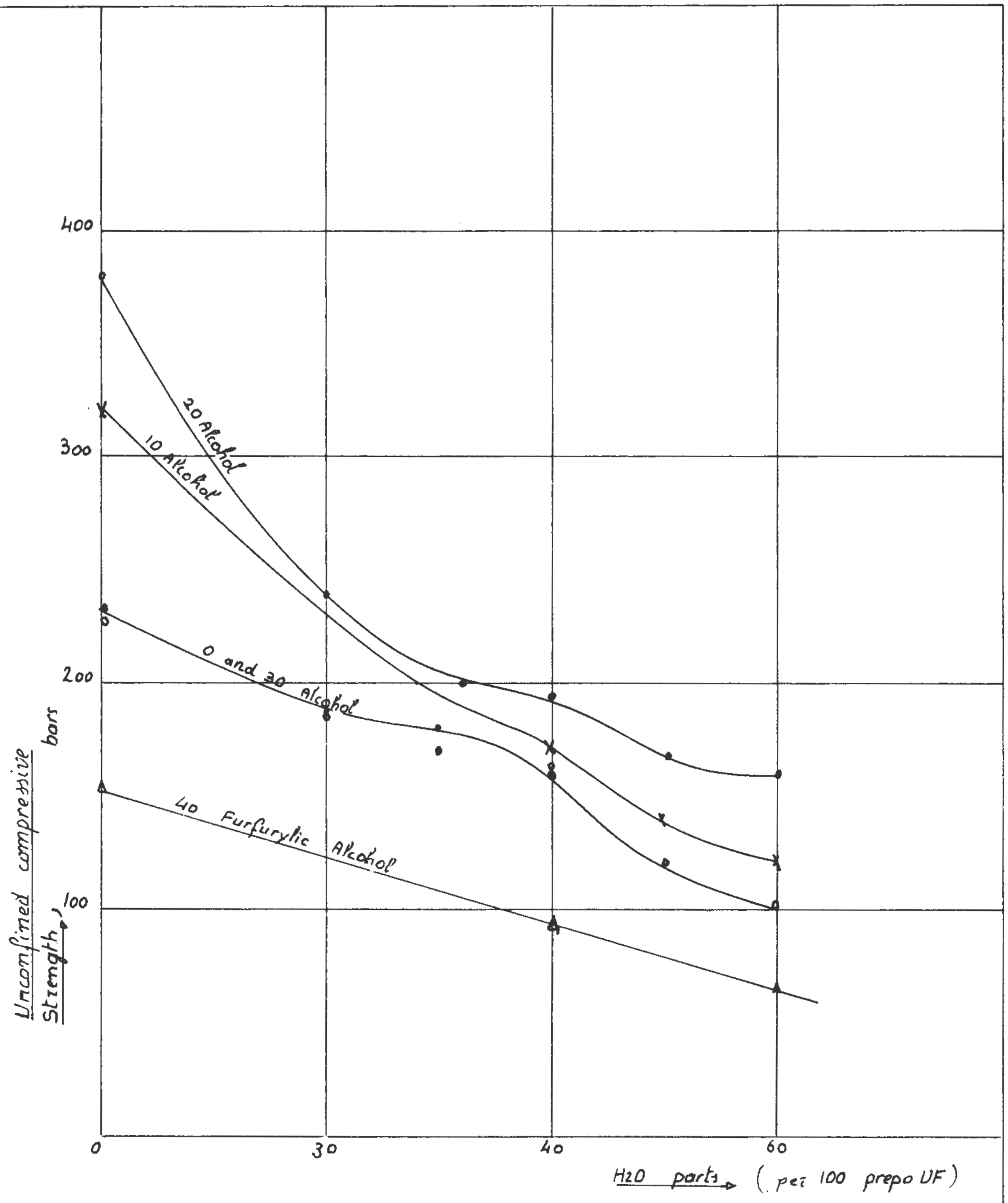


Fig. 175. Effect of Dilution on Strength of Pure Grout After 28 Days

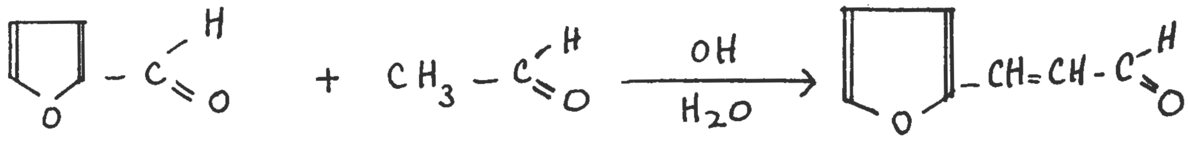
Table 48 . Effect of Dilution on Strength

Parts per 100 prepolymer UF	H_2O	AF	Rc 48 hours (bars)	Rc 28 days (bars)
8	20	20	133	233
13	20	30	66	186
9	30	20	100	200
14	30	30	76	170
24	40	0	80	160
28	40	10	116	166
10	40	20	110	193
15	40	30	66	160
18	40	40	10	93
23	50	0	63	120
27	50	10	100	133
11	50	20	96	166
16	50	30	66	127
22	60	0	56	100
23	60	10	70	120
12	60	20	69	160
17	60	30	40	107
19	60	40	13	66

Rc = unconfined compressive strength

More importantly, monomer or prepolymer furfuryl alcohol will not react in a basic medium. Similarily, combinations of furfural or furfuryl alcohol with amines, phenols, or alcohols, which are normal in an acid medium, are impossible in a basic medium.

To be sure, a reaction in a basic medium has been cited in the literature, in the LANTZ and WALTERS patent, "Synthetic Resin and Method of Making the Same from Furacrolien, Furfural, and Formaldehyde", U.S.A. 2,660,573, November 24, 1953. First, a furacrolein is formed by reacting acetaldehyde on furfural in a basic medium:



furfural acetaldehyde furacrolein

Then, a molecule of furacrolein is condensed with a molecule of formic aldehyde, this time in an acid medium.

Unfortunately, the basic precondensate is highly viscous and insoluble in water. The substance thus cannot be rendered less viscous by dilution with water with the result that this formula is unsuitable for grouting. The only furfural combinations found to work in dilute and basic media are those using resorcinol or resorcinol derivatives, such as ROCAGIL.

2.22 Study of Furfural-Resorcinol Polymer

This polymer is definitely analogous to the resorcin-formaldehyde combination examined in Category A-5. It is advisable to determine the optimal mix first for the furfural/resorcinol ratio, then for the catalyst (sodium) content.

The optimum furfural/resorcinol ratio, determined on pure grout, is 1.65 molecular, or 1.5 by weight (fig. 176). This ratio can be modified by 10% in either direction without any effect on strengths. Strengths are slightly increased when the sodium content is increased and an optimum is attained (fig. 177 , like the rest of the study, reflects a 36° B sodium solution). As this factor does not have a strong influence on the polymer's strength, this procedure provides an effective method for regulating setting time.

A. Regulation of Setting Time

As noted above, setting time is regulated by varying the proportion of sodium within that range having no effect on strength, between 6.5 and 16.4% of the furfural content. However, for consolidation mixtures with strong mechanical characteristics and over 40% resin, the setting times are too short, even if the sodium content is decreased to the minimum percentage. Thus, grouts containing 100 g of furfural and resorcin to each 150 g of water will set in 15 to 40 minutes when the sodium content varies between 16 and 8%.

It is also usually necessary to form a prepolymer. Sodium resorcin and part of the furfural are mixed in a concentrated solution and a prepolymer is formed as heat is given off. When the heat stops, the rest of the furfural is added to arrive at a F/R ratio of 1.5, and water is added for dilution.

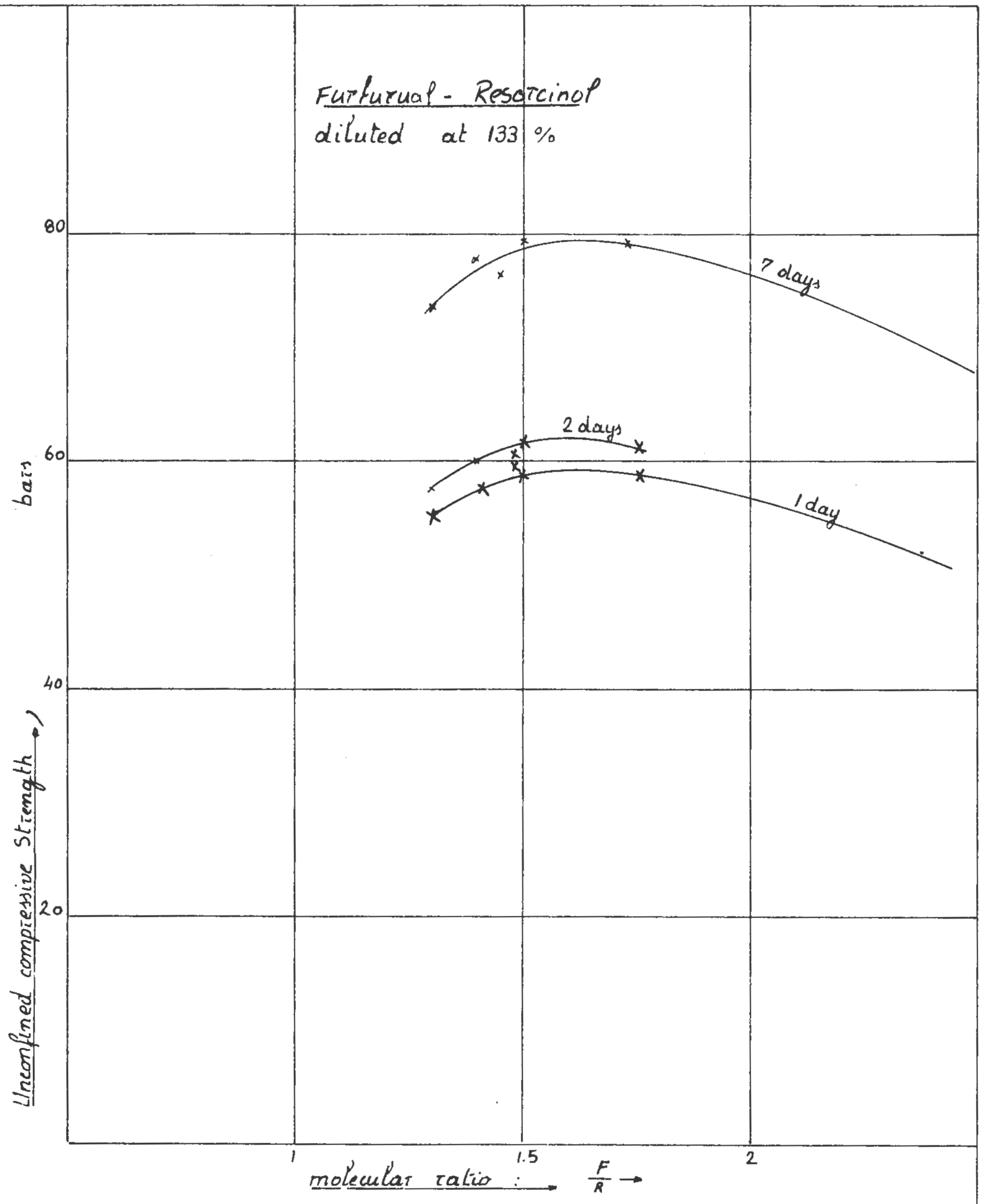


Fig. 176. Effect of Molecular Ratio, Furfural/Resorcinol, on Strength of Mortar

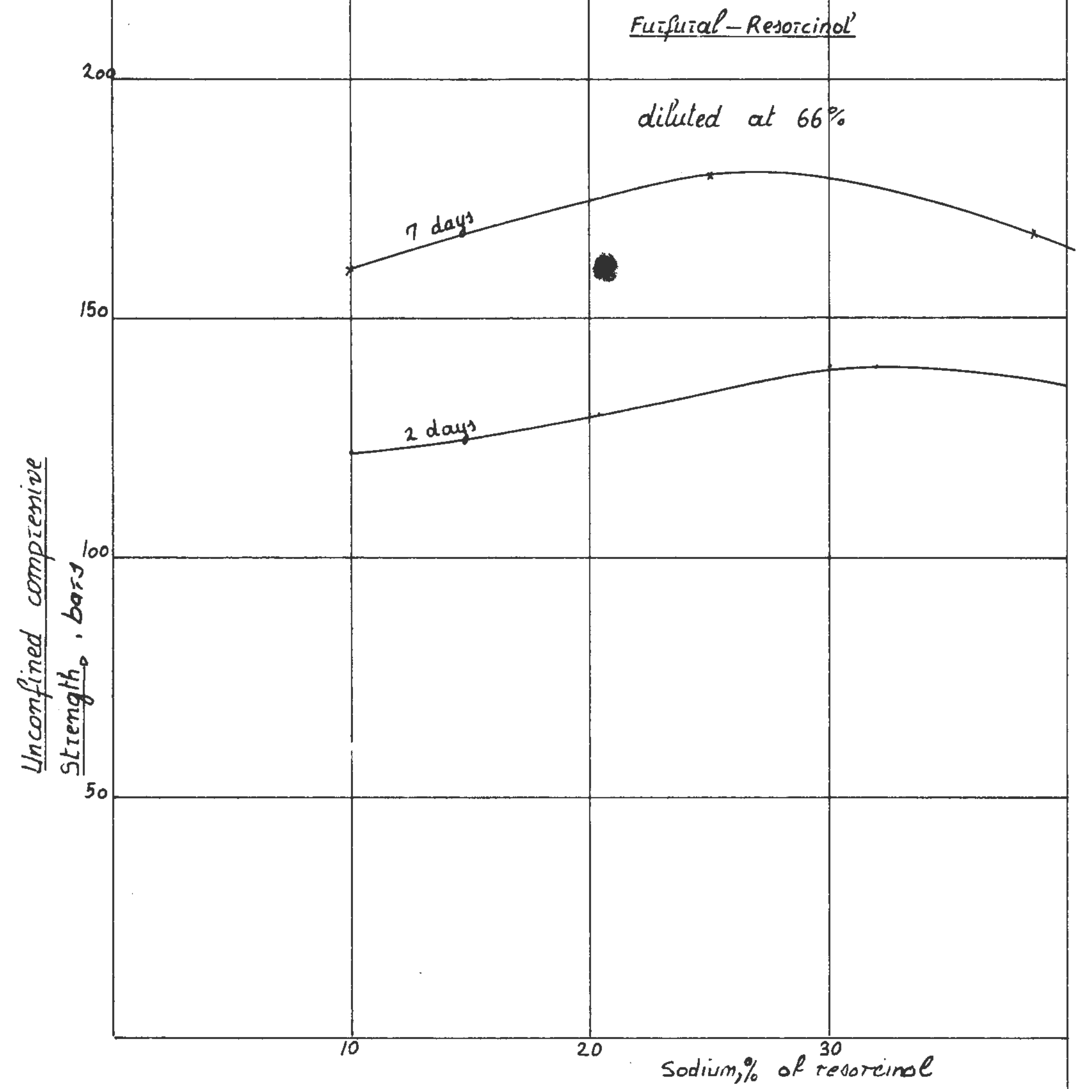


Fig. 177. Effect of Sodium Content on Strength of Pure Grout

With this method, the second reaction is less exothermic, and, consequently, setting time is lengthened. The more intense the propolymer, i.e. the greater the amount of furfural used in the first mixture, the longer the setting time will be (fig. 178). Setting time is then adjusted by varying the amount of sodium (fig. 179).

The prepolymer's viscosity is affected both by the amount of furfural and the proportion of sodium. Tables 49 and 50 below give examples of two prepolymers of different composition.

Table 49 . Effect of Prepolymer Composition on Viscosity

prepolymer ingredients	prepolymer 1	prepolymer 2
resorcin	100	100
water	100	100
furfural	50	40
sodium	variable	variable
additional furfural	100	110

Table 50 . Effect of Prepolymer Composition on Viscosity

Sodium content (%)	Viscosity (cP)	
	Prepolymer 1	Prepolymer 2
10	38	30
15	45	33
20	50	40
25	60	48

In each case, there will have to be a compromise between desired setting time and viscosity.

If the furfural in the prepolymer is limited to 40 to 50%, the final grout, after the addition of the rest of the furfural and water, will have a viscosity of less than 10 cP .

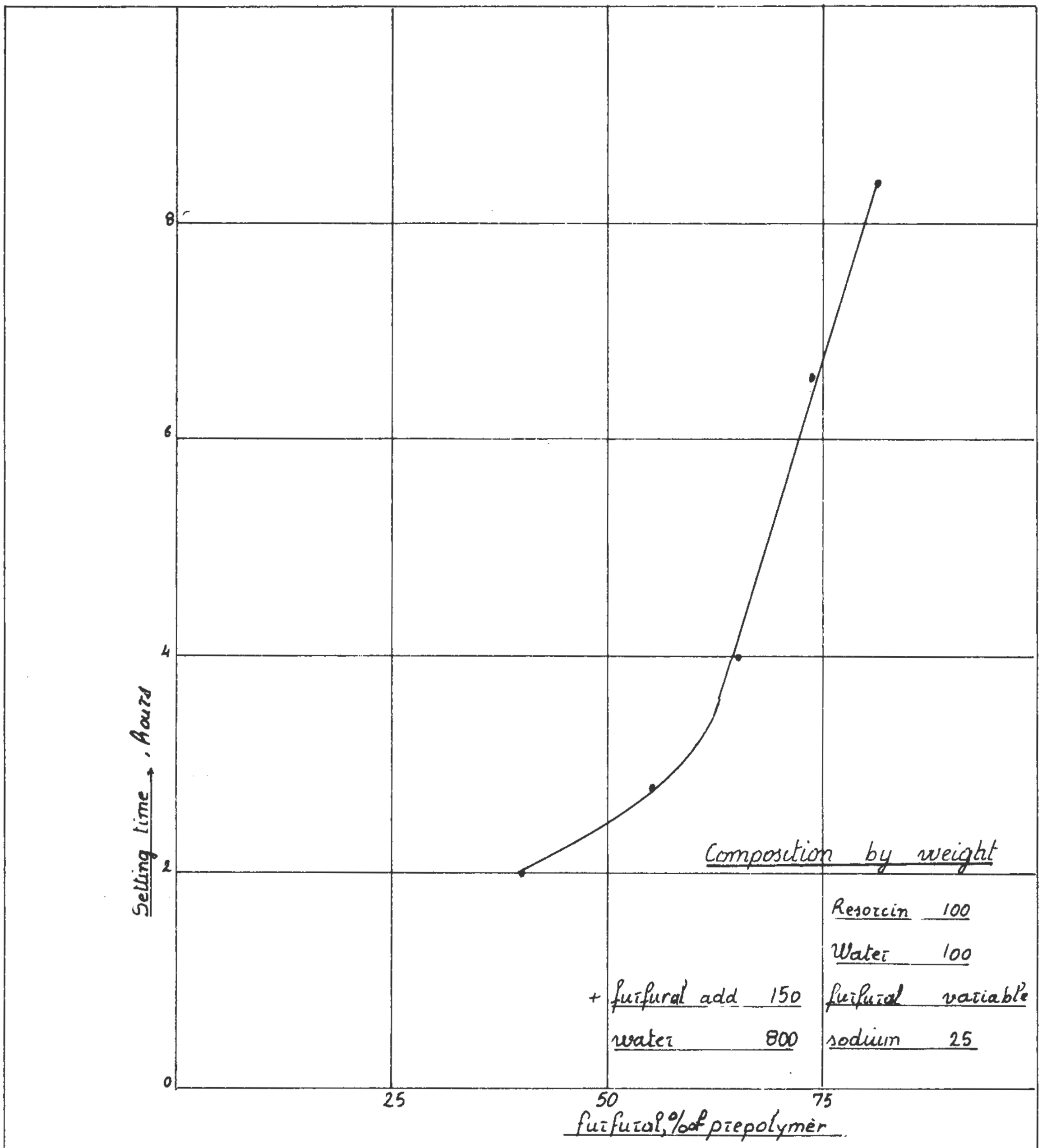


Fig. 178. Effect of % of Furfural in Prepolymer on Setting Time

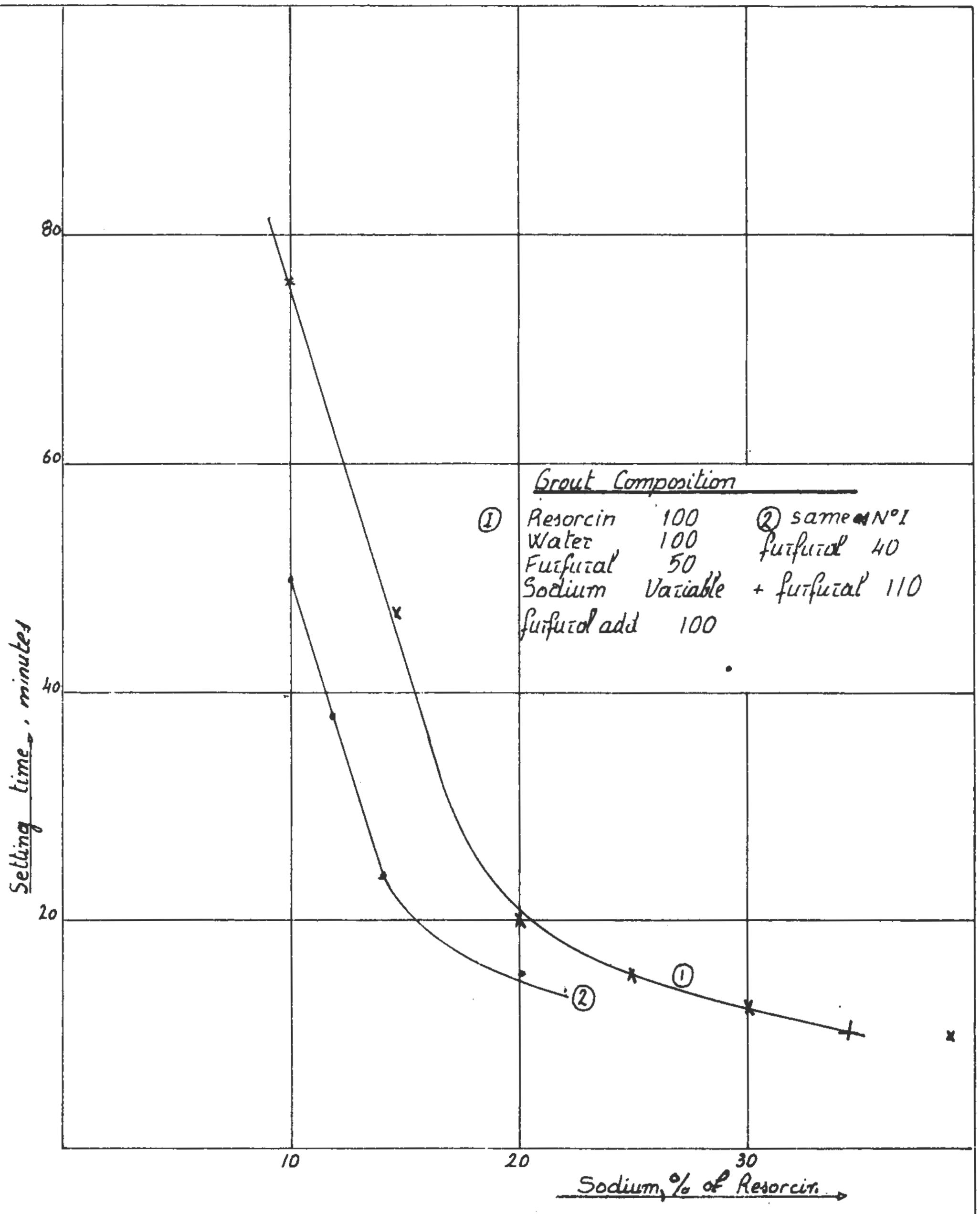


Fig. 179. Effect of % of Sodium in Undiluted Prepolymer on Setting Time

B. Strength

As noted previously, there is considerable latitude in the furfural/resorcinol and sodium furfural ratios without harming strength. This also applies to the prepolymerization of the resorcinol-furfural, so long as the furfural/resorcinol ratio in the prepolymer does not exceed 0.7. With higher ratios, the prepolymer's viscosity has a distinctly harmful effect on the mortar's strength. Strength can also be modified by the mixture's degree of dilution, as shown in fig. 180 for standard mortars made by direct molding.

2.23 Study of the Furfural Polymer ROCAGIL 3555

ROCAGIL is a phenolic syrup produced by the RHONE-PROGIL company and has the following general characteristics at 20°C:

a) appearance: reddish brown liquid, syrupy;
b) dry extract: active ingredients, 55%
c) volume at 20°C: 1.22 g/ml;
d) viscosity at 20°C: approximately 750 cP;
e) pH: 9.0 to 9.5;
f) degree of dilution in water: infinite.

According to the manufacturer's directions for normal use in grouting, the product must be diluted, the formaldehyde added, and when appropriate, the sodium.

Returned to a 15 to 35% dry extract, the grout sets to a hard gel after a variable and adjustable interval which, depending on dilution and dosage of sodium can range from about ten minutes to several hours. It was found that the H^+ in Rocagil can react on the OH^- in the furfural, and so the same research was conducted as with resorcinol, first determining the optimum furfural/Rocagil ratio and the effect of the pH (proportion of sodium).

The optimum furfural/Rocagil ratio by weight is 0.22 (or 0.40, discounting the water with which the Rocagil syrup is diluted). Fig. 181 shows that, as with furfural-resorcinol, the dosage can be varied 10% above or below the optimum without affecting strength.

The theoretical optimum sodium dosage (36° Baume sodium solution), which also applies with pure resin, is about 60% of furfural content, as shown in fig. 182. Once these two optimum dosages have been established, the resulting characteristics of a furfural-Rocagil grout are as follows:

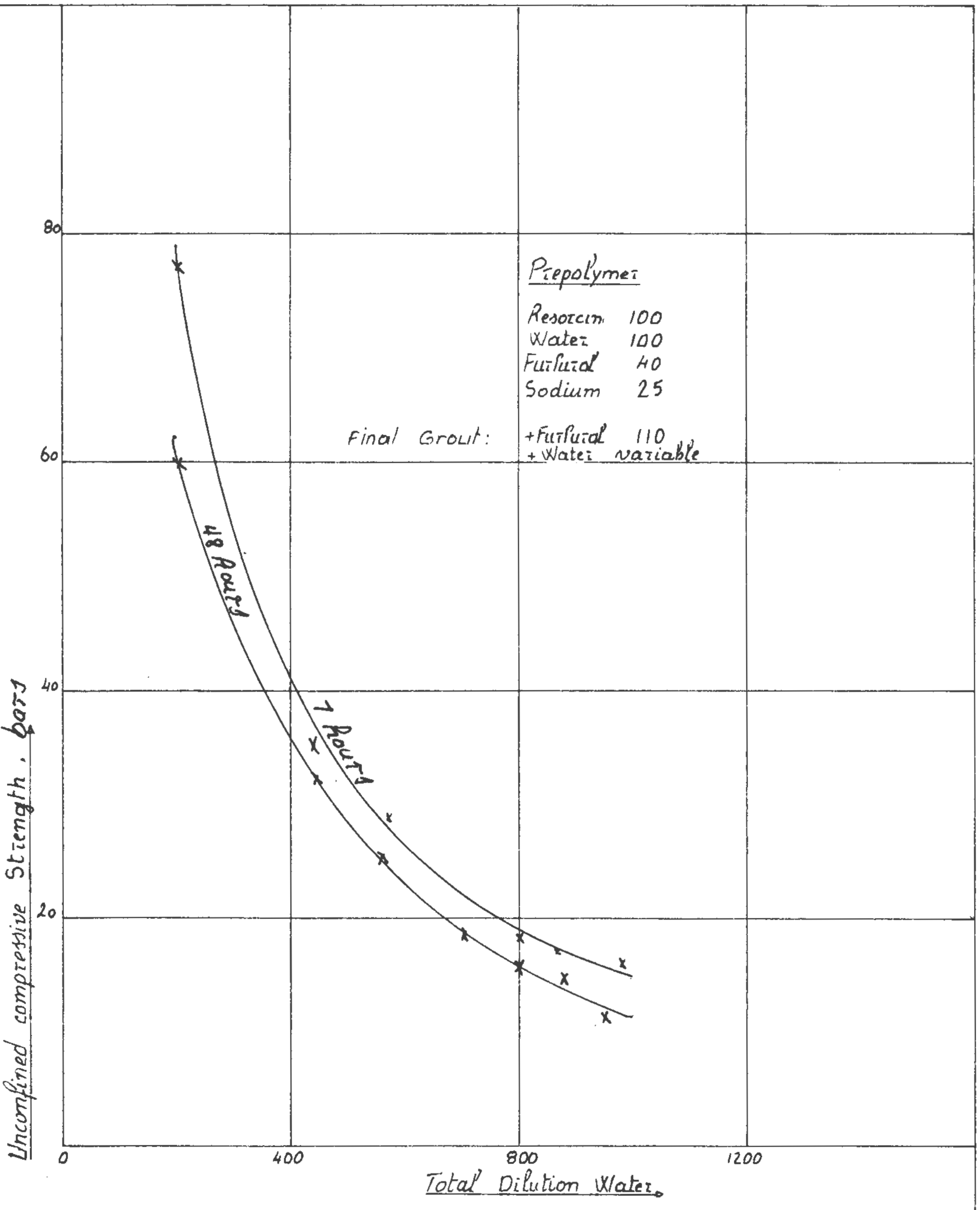


Fig. 180. Effect of Dilution on Strength of Mortar

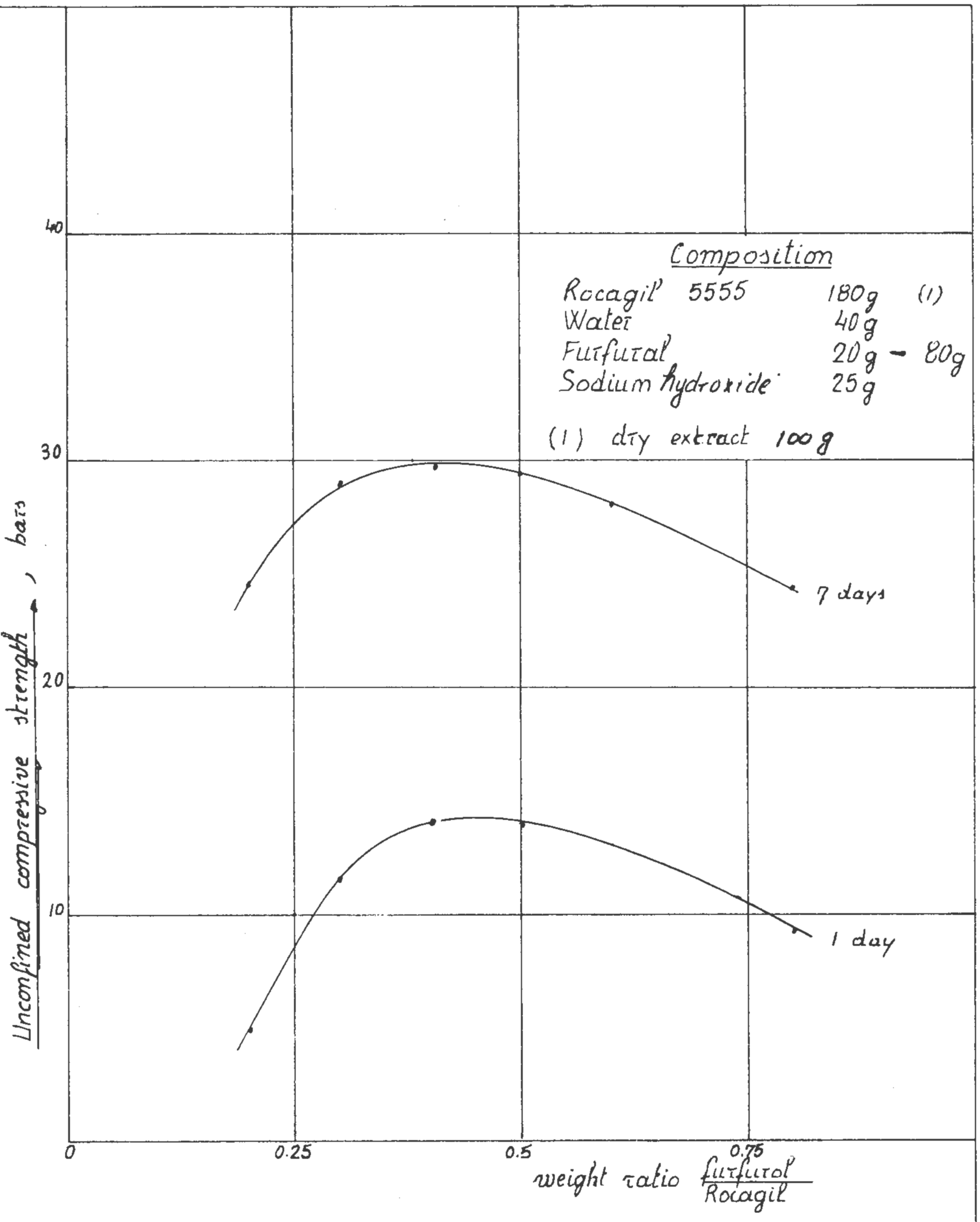


Fig. 181. Effect of Weight Ratio, Furfural/Rocagil on Strength of Pure Grout

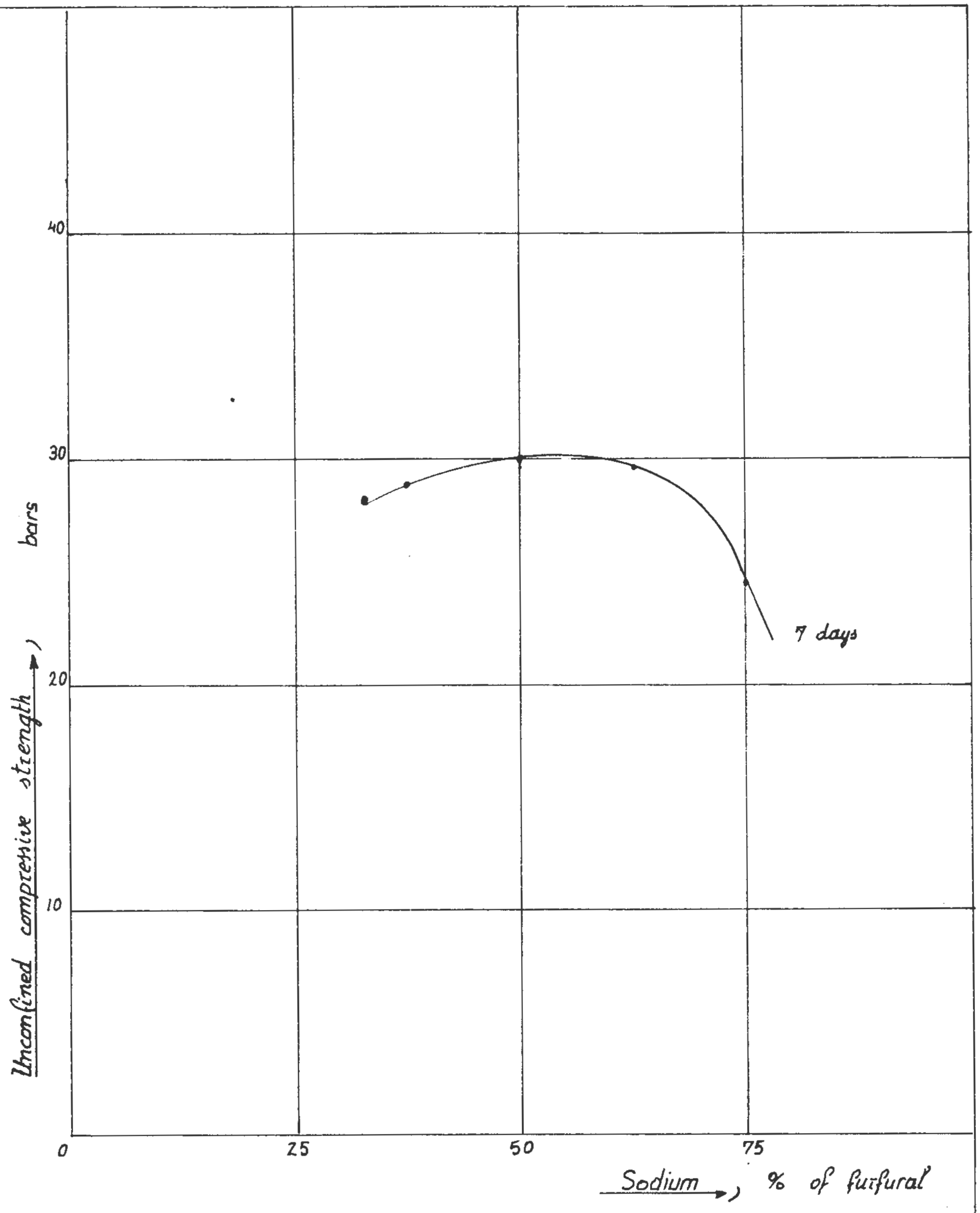


Fig. 182. Effect of Weight Ratio, Sodium/ Furfural, on Strength of Pure Grout

A. Regulation of Setting Time

Using the optimum dosages as specified above, setting time is determined solely by dilution. As Rocagil is less reactive than pure resorcin, the polymerization process gives off less heat, and thus setting times for most dilutions are appropriate for grouting. For proportions giving strengths of 10 to 20 bars, and therefore having 100 to 400 grams of water for 220 grams of furfural and Rocagil, setting times will range from 11 hours to 45 minutes (fig. 183).

Only highly concentrated mixtures have rather short setting times for grouting. Using the optimum furfural/Rocagil and sodium/furfural ratios as previously defined, setting time will be 8 minutes for a mix using 40 grams of water for 220 grams of furfural and Rocagil. The setting time can be extended by reducing these two ratios (tables 51 and 52).

Table 51. Effect on Setting Time of Furfural/Rocagil Ratio

Sodium content remains constant, sodium/furfural = 0.60

Ratio furfural/Rocagil	Setting time (min)
0.22 (control)	8
0.19	12
0.17	15
0.15	18

Table 52. Effect on Setting Time of Sodium/Furfural Ratio

Ratio sodium/furfural	Setting time (min)
0.60 (control)	8
0.50	10
0.30	15

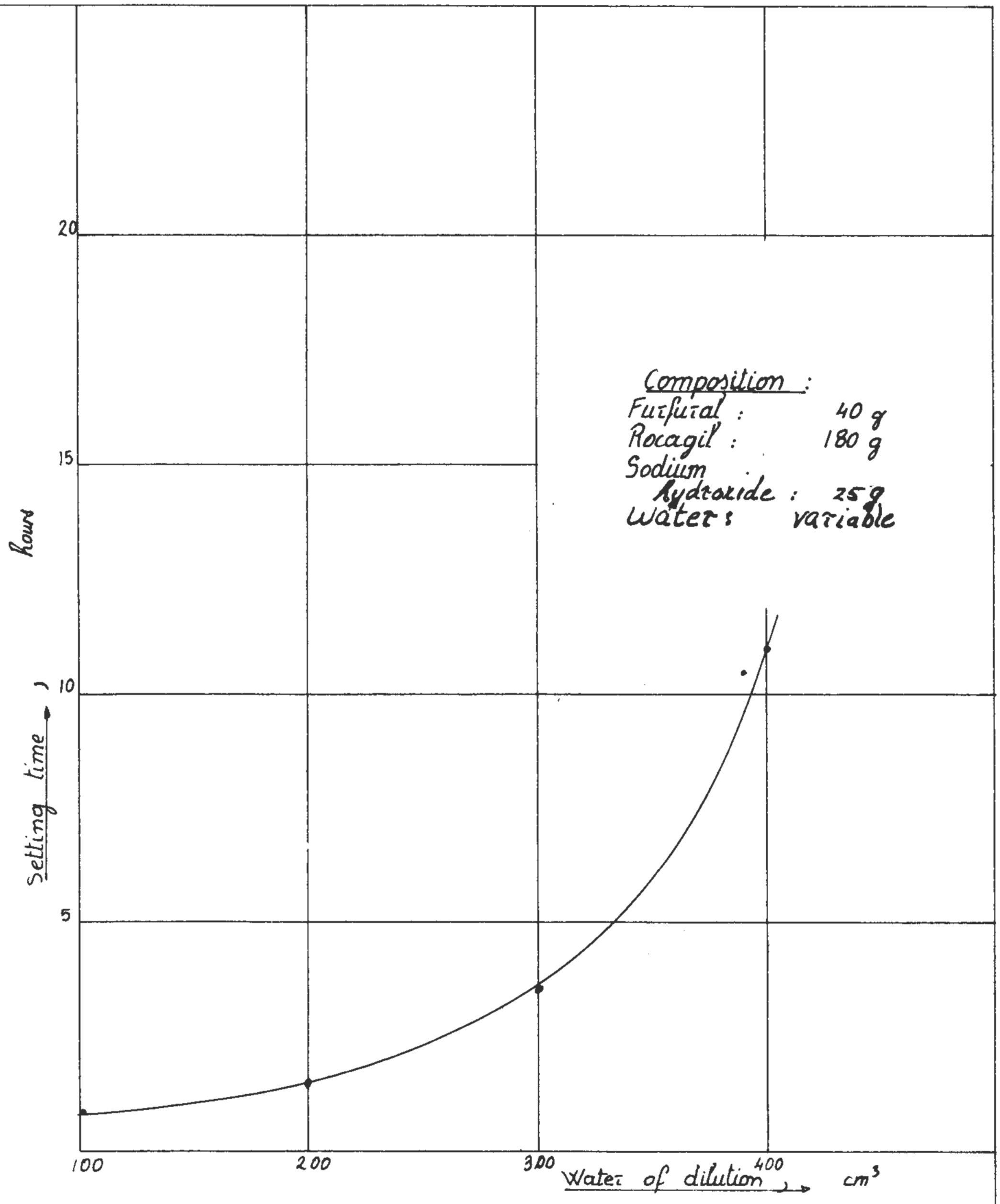


Fig. 183. Effect of Dilution on Setting Time

Finally, the two methods can be combined, simultaneously lowering the sodium/furfural and furfural/Rocagil ratios to attain a setting time of about 30 minutes.

C.2 Strength

Considerable latitude is possible in the furfural/Rocagil and sodium/Rocagil ratios without appreciable harm to strength. Strength can be regulated by adjusting the degree of dilution, as shown in fig. 184 for standard mortars (direct molding method).

3. Conclusion

It emerges from this study that furfural compounds offer interesting possibilities for grouting and might find numerous applications in construction and public works. These new possibilities merit further investigation:

a) In grouting, the frequent necessity of operating with a basic catalyst limits the reactive capacity of the furfural ring. Condensation of the OH in the furfural can take place only with highly directional H^+, such as are found in resorcinol or phloroglucinol. Unfortunately, the high cost of these two reagents limits the possible applications of such resins, although they have remarkable properties: perfect compatibility with dilution water, easily controlled setting times, ease of regulation of strength through degree of dilution, and non-toxicity.

The substitution of less highly processed phenols (such as Rocagil 3555) for the resorcin opens up interesting and less costly possiblities.

b) When an acid catalyst is used, a normal procedure for many industrial applications in construction and even in grouting in some cases, the reactive field of the furfural ring is greatly extended. The furfural ring is theoretically almost as rich as that of the aromatic compounds, but, while the latter has given rise to hundreds of synthetic plastic materials, the exploitation of the furfural ring is still in its infancy. With future shortages of aromatic derivatives, a shift toward plant derivatives, of which the furfural ring is a typical example, can be anticipated.

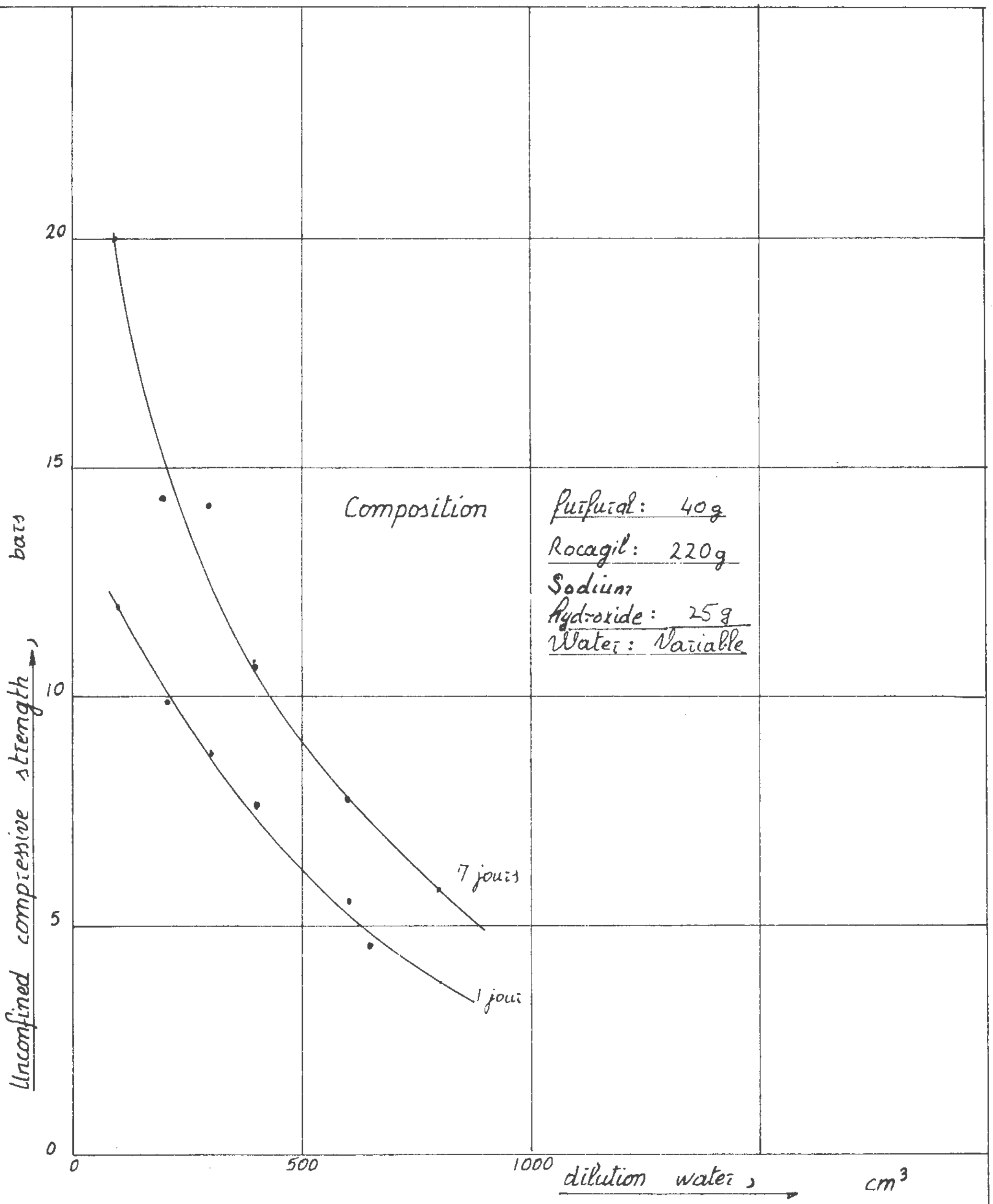


Fig. 184. Effect of Dilution on Strength of Furfural-Rocagil

Beyond the question of sources of supply, there is another interesting point with regard to the furfural ring. It can be used to produce non-flammable (or self-extinguishing) plastic materials, which is not generally the case with aromatic plastic materials. Given the number of recent serious accidents in construction, cellular resins might be used, where the non-flammable characteristic would be an important selection criterion, even if the present lack of knowledge about furfural compounds makes them more costly than the traditional petrochemical plastic materials.

c) Finally, furfural compounds coupled with traditional prepolymers definitely open up interesting possibilities. Only one combination was studied, and since it was a matter of an acid catalyst, it could be pursued no further. However, many other possibilities are available for research into the best quality/price ratios.

PART FIVE:
STUDY CONCLUSIONS AND RECOMMENDATIONS

I. Review of Survey and Summary of Results

1.1 The objective of this study has been to determine the feasibility of developing or improving chemical grouts, paying special attention to those not based on petroleum derivatives, for consolidating and/or waterproofing of ground, within the context of cut-and-cover work and soft-ground tunneling.

1.2 The various phases of the survey were conducted as follows.

1.2.1 A thorough review of all known chemical grouts in the form of:

a) a complete bibliographical review, including more than 800 items, about half of which were written during the last 20 years.

b) classification of chemical grouts, based on the nature of the major component, as shown in table 53.

1.2.2 An analysis of the grouts in each category in terms of seven physico-chemical criteria:

a) viscosity
b) setting time
c) permeability
d) strength of pure grout
e) strength of treated ground
f) durability
g) toxicity

Table 53 . Chemical Grout Classification Table

A	Aqueous Solutions	
	A-1	silicate derivatives
	A-2	other inorganic gels (alumina, magnesium oxide, etc.)
	A-3	lignosulfite derivatives
	A-4	other plant derivatives
	A-5	acrylamide derivatives
	A-6	phenoplasts
	A-7	aminoplasts
	A-8	systems combining above categories
B	Colloidal Solutions in Water	
	B-1	organic (alginate, etc.)
	B-2	inorganic (bentonite, etc.)
C	Non-Aqueous Systems	
	C-1	synthetic resins (polyester, polyvinyl, polyepoxide, etc.)
	C-2	vulcanizable oils
	C-3	asphalt and other heated compounds
	C-4	systems containing solvents
D	Emulsions	
	D-1	bituminous emulsions
	D-2	other emulsions (polyester, epoxide, vinyl, etc.)
E	Reaction with the Ground	
	E-1	reaction with the ground itself
	E-2	reaction with ground water
F	Combined Systems	

1.2.3 Provisional evaluation, in the form of ratings using the Delphi method, of the various categories of chemical grouts in terms of the following parameters:

1) cost
2) workability
3) effectiveness
4) durability

5) toxicity during preparation
6) toxicity after injection
7) non-dependency on petrochemical derivatives

These ratings could be assigned to only 10 of the 19 categories of products; the other types of products could not be rated for the following reasons:

a) They catalyze only in an acid medium (Categories A-4 and A-7).

b) They are impractical to use (necessity of heating for example, Category C-3).

c) Whatever their special merits, they are too costly for large-scale grouting (Categories C-1, C-2, C-4).

d) They are used only in very rare special cases (Category A-2).

e) They are not sufficiently reliable at the present state of the art (Categories E-1, E-2).

Finally, the ratings of these 10 categories (table 54) allowed a selection of seven categories with clearly higher ratings for in-depth examination. These include 7 waterproofing grouts and 5 consolidation grouts.

Some fragmentary bibliographical information indicates that the products in Category A-4 (furfural derivatives), known mainly for use in an acid medium and consequently not rated, might possibly be used in a basic medium. They were studied further in Part Four of this volume.

1.2.4 Recommended tests for evaluating the engineering characteristics of grouts was outlined in two parts:

a) The first part consisted of a detailed analysis of the various tests usually performed on chemical grouts for seven criteria: viscosity, setting time, permeability, strength of pure grout, strength of treated ground, durability, and toxicity. Then, for each criterion, with the exception of toxicity, the most suitable test method is described and recommended for standardization.

Table 54. Tentative Evaluation of Grouts

WATERTIGHTNESS												
CRITERION		MAX score	silicate A1	ligno A3	acryl A5	pheno A6	(A1-A5) A8	organic colloids B1	mineral colloids B2	bituminous emulsions D1	other emulsions D2	(A1-B2) F
1	COST	3	2.4	1.8	0.6	1.5	0.9	1.2	2.4	1.5	0.6	2.7
2	WORKABILITY	1	0.6	0.7	0.8	0.6	0.8	0.4	0.4	0.7	0.7	0.5
3	EFFICIENCY	1	0.9	0.9	0.9	0.8	0.9	0.5	0.5	0.5	0.5	0.9
4	DURABILITY	1	0.8	0.7	0.9	0.9	0.8	0.3	0.9	1	1	0.8
5	NON-TOXICITY (at preparation)	0.5	0.5	0	0.15	0.2	0.2	0.5	0.5	0.5	0.5	0.5
6	NON-TOXICITY (once injected)	1.5	1.05	0.9	1.05	1.05	1.05	1	1.5	1.5	1	1.5
7	NON-DERIVED from PETROLEUM	2	1.6	1.6	0.4	0.8	1	2	2	0	1.6	1.8
	TOTAL SCORE	10	7.85	6.6	4.8	5.85	5.65	5.9	8.2	5.7	5.9	8.7

Table 54. Tentative Evaluation of Grouts (Con't)

STRENGTHENING					
silicate A1	ligno A3	acryl A5	pheno A6	(A1-A5) A8	other emulsions D2
2.4	1.5	0.3	1.5	0.9	0.6
0.6	0.7	0.8	0.8	0.8	0.7
0.7	0.7	0.8	0.9	0.8	0.8
0.7	0.6	0.9	0.9	0.8	1
0.4	0	0.1	0.2	0.2	0.4
1.05	0.6	1.05	1.05	1.05	0.8
1.6	1.6	0.2	0.8	1	0
7.45	5.7	4.15	6.15	5.55	4.3

b) The second part consisted of an extensive laboratory study using the recommended tests as previously defined for the categories of grouts listed in table 55.

Table 55. Chemical Grouts Studied

Category	Name	Waterproofing	Consolidation
A-1	silicate derivatives	yes	yes
A-3	lignosulfite derivatives	yes	yes**
A-5	polyacrylamides	yes	yes**
A-6	phenoplasts	yes	yes
A-8	A-1/A-5 combination	yes*	yes
B-2	bentonite gels	yes	no
F	A-1/B-2 combination	yes	no

* = possible but not economical
** = possible but does not permit very strong consolidation

This laboratory study led to a more precise evaluation and comparison of the properties of the grouts studied and, as a result, a readjustment of the provisional ratings. Table 56 shows the final ratings for the grout categories above.

1.2.5 Examination of possibilities for improving the two categories of products deemed particularly promising by reason of their plant origin:

a) lignosulfite derivatives.
b) resins derived from furfural.

1.3 This study indicates that the number of cases where chemical grouting has been used, not just to rescue a structure, but as a normal construction procedure, shows that since about 1960, this ground waterproofing and consolidation technique has become a competitive and credible construction method. Chemical grouting is now at the industrial stage.

This study has also demonstrated that there is available on the market a vast range of chemical grouts, but has also pointed out the necessity of establishing a rational classification, using standardized tests in particular.

Table 56. Final Evaluation of Grouts

WATERTIGHTNESS

	CRITERION		silicate A1	ligno A3	acryl A5	pheno A6	(A1-A5) A8	mineral colloids B2	(A1-B2) F
1	COST	3	2.4	1.8	0.6	1.5	0.5	2.8	2.7
2	WORKABILITY	1	0.6	0.6	0.8	0.8	0.9	0.4	0.4
3	EFFICIENCY	1	0.9	0.9	0.9	0.8	0.9	0.5	0.9
4	DURABILITY	1	0.6	0.6	0.9	0.9	0.9	0.4	0.6
5	NON-TOXICITY (at preparation)	0.5	0.4	0.1	0.15	0.2	0.2	0.4	0.4
6	NON-TOXICITY (once injected)	1.5	1.05	0.9	1.05	1.05	1.25	1.45	1.4
7	NON-DERIVED from PETROLEUM	2	1.6	1.6	0.4	0.8	0.4	1.9	1.8
	TOTAL SCORE	10	7.55	6.50	4.80	6.05	5.05	7.85	8.20

STRENGTHENING

	CRITERION	silicate A1	ligno A3	acryl A5	pheno A6	(A1-A5) A8
1	COST	2.4	1.5	0.3	1.5	1
2	WORKABILITY	0.5	0.5	0.8	0.8	0.9
3	EFFICIENCY	0.7	0.6	0.8	0.9	0.8
4	DURABILITY	0.3	0.3	0.9	0.9	0.9
5	NON-TOXICITY (at preparation)	0.3	0.1	0.15	0.2	0.2
6	NON-TOXICITY (once injected)	1.05	0.6	1.05	1.05	1.25
7	NON-DERIVED from PETROLEUM	1.4	1.6	0.2	0.8	0.4
	TOTAL SCORE	6.65	5.20	4.20	6.15	5.45

The most developed chemical grouts are the pure or colloidal solutions injected by the "one-shot" process, which enjoy the advantage of being very easy to use and consequently are more dependable.

Aside from the chemical nature of the grout, viscosity is the fundamental characteristic which differentiates the products from one another. Waterproofing grouts are usually dilute and, whatever their nature, are generally of low viscosity. Consolidation grouts are not diluted to the same extent. The great differences in viscosity depend largely on the nature of the ingredients.

The development of recommended laboratory tests has demonstrated the fact that some factors have a significant effect on the values measured. These include the following:

a) The effect of temperature on measurements of viscosity (conditions of dissipation of the thermal energy released during the chemical reaction).

b) The effect of shear speed on measurements of shear strength.

c) The effect of crushing speed on the unconfined compressive strength of grouted soil samples.

d) The effect of the sample curing method on measurements of durability.

This study indicates further that some chemical grouts widely used could still be improved, for example, the silicate derivatives, whose durability could be improved. Research carried out on lignochromes and furans proves that these two grouts could be greatly improved:

a) For the lignochromes, it would be possible to lower the percentage of potassium dichromate by 10%, thus eliminating risks of toxicity posed by the Cr^{6+}.

b) For the furans, the addition of resorcin allows this grout to be used in a basic medium.

Without exception, the main principle of grouting is that the quality of any type of grouting operation depends on the perfect suitability of the grout to the ground to be treated. In heterogeneous ground, during the grouting process it will be necessary to change the nature of the grout, using a progressively more penetrating type in order to compensate for the gradual reduction of permeability in the ground. Three or four different types of grout might have to be used in succession over the course of the operation, but rupture and heave can be avoided by discontinuing use of a given type of grout at the point where it becomes ineffective, and using a more fluid grout with greater penetration.

The systematic use of very fluid grouts in all areas is not desirable either economically (needless expense is incurred) or technically. There is even the possibility that very fluid grouts, injected into highly permeable ground, will not remain in the treated area, moving downward through gravity. Furthermore, the durability of some of these fluid grouts (notably silica gels), although excellent in fine ground, becomes mediocre in coarse ground because of the syneresis phenomon.

The following conclusions concerning grout suitability have been drawn from this study of grouts:

1. There is available a series of grouts, of decreasing viscosity and perfectly suitable for a wide range of soils.

a) Binghamian-type materials, with cement or clay in suspension,are applicable to coarse ground.

b) Somewhat viscous colloidal solutions (silica or lignochrome gels, organic or inorganic colloids) are suitable for soils of average particle size.

c) Pure non-colloidal solutions (organic monomers in aqueous solution) are suitable for very fine ground.

2. Grout users must know how to place the grout where it is needed (distribution systems all derive to some degree from the "sleeve tube" process).

3. When using a series of grouts at one site, one must know when to change grouts. The right moment comes when the more viscous grout is no longer effective, penetrating the ground only through force and rupturing it. One must monitor the heave benchmarks precisely to define the moment to change grouts.

Grouting not only concerns the choice of a grout, but involves the technology used for injection. Both the grout and the injection technology must be adapted to the terrain. Large test sites must often be carefully evaluated for the purpose of such matching.

The controls used at the worksite ensure the matching of grout and injection technology to the site.

a) Concerning the grout, it should be verified that the specifications given by the manufacturer and by the operator are the same.

b) With regard to application, injection pressures, flow rates, ground movements, potential resurgences, etc., should be checked to ensure that the grout will penetrate the ground without ruptures.

II. New Directions for Research

2.1 The main purpose of this survey is to list, classify, compare, and standardize all current knowledge about grouting, including possible but untried products and techniques. In the process, some research was started in the specific field of grouts of plant origin. The results indicate that currently known grouts could be perfected.

It would be worthwhile to pursue this study of lignosulfite and furfural derivatives. Additional improvements could be obtained by combining existing products or through research on new systems. Such a study would concern consolidation grouts more than waterproofing grouts, since there is presently available a whole range of products for waterproofing which are generally inexpensive, non-toxic and non-polluting. The range of possibilities is more limited for consolidation: the silicate-base systems are not expensive, but have disadvantages, while the resin-base systems are currently expensive.

Emphasis should be placed on long-term strength, since this is the principal criterion for consolidation grouts. Even in pure waterproofing, measures must be taken to avoid the risk of long-term erosion. Drops in strength, in terms of the time during which the grouted mass was subjected to stress in laboratory tests, varies widely from one grout to another. The present lack of knowledge about long-term strength has led to grout formulations with highly excessive initial strengths (as a safety margin) for waterproofing as well as for consolidation. Grouts with elastic rather than plastic character should allow the use of much lower initial strengths, since maintenance of strength would be more dependable for any duration of stress application. The use of lower initial strengths should also be more economical since more dilute systems could be used, and as a corollary, these more dilute grouts would tend to pollute less.

2.2 With regard to the distribution of grout in the ground, the most common method throughout the world uses sleeve tubes or methods derived from it. Further research is recommended to improve grout distribution systems, since as previously stated, the overall quality of a grout treatment depends as much on grouting techniques as on the products used.

2.3 Finally, the precise moment to change to a more fluid grout must be defined. As fluid grouts are more costly than viscous grouts, a premature change can entail needless expense. A belated change can also cause needless expense, because the preceding grout will have penetrated by rupturing the ground, and thus be ineffective in filling the natural void space. There is at present no foolproof method for determining the exact moment to exchange one grout for another. It would be valuable to survey all methods currently used and their validity, with the purpose of improving them or developing others.

III. Conclusion

The treatment of ground by chemical grouting has become a common construction procedure, especially for cut-and-cover work and tunneling in urban areas. For example, between 1965 and 1976, construction of the new express line of the Paris Metro required the treatment of 300,000 m^3 of ground by chemical grouting (mainly with hard silica gels and phenoplast resins).

The development of this procedure has meant that, in addition to an improvement of knowledge about some traditional grouts, much research has been undertaken for the purpose of devising new, better performing and cheaper chemical grouts. This survey indicates the current status of knowledge of the properties and behavior of the various chemical grouts and gives some guidelines for the choice of the grout most suitable for specific purposes, as well as indicating some lines of research which appear promising, particularly for certain chemical grouts of plant origin which would be unaffected by price fluctuations or availability of petrochemical derivatives.

*U.S. GOVERNMENT PRINTING OFFICE : 1978 0-733-870/503