An Introduction to Chemicals for Grouting of Soils

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1. INTRODUCTION

1.1 PURPOSE. This discussion provides information and guidance for the investigation and selection of materials, equipment, and methods to be used in chemical grouting in connection with construction projects. Elements discussed include types of chemical grout materials, grouting equipment and methods, planning of chemical grouting operations, and specifications. Emphasis is placed on the unique characteristics of chemical grouts that benefit hydraulic structures. Uses of conventional portland-cement-based grouts and microfine-cement grouts are discussed in the technical literature.

1.2 CHEMICAL GROUT AND GROUTING.

1.2.1 CHEMICAL GROUTS. Chemical grouts are injected into voids as solutions, in contrast to cementitious grouts, which are suspensions of particles in a fluid medium. Chemical grouts react after a predetermined time to form a solid, semisolid, or gel. The distinction between chemical and cementitious grouts is arbitrary in that some particulate grouts are made up of suspension of microfine cement with particles generally less than 10 µm in diameter. The distinction is further complicated by the development of chemical grouts that have particles that are 10 to 15 nm in diameter. Grouts have been formulated that are mixtures of particulate materials in chemical grouts with the particulate materials themselves being capable of solidifying reactions. Grouts discussed in this manual are those in which the liquid and solid phases typically will not separate in normal handling and in which processes other than the introduction of solid particles and mixing are used to generate the grout. Mixtures of chemical and particulate grouts have the limitations of particulate grouts in terms of mixing, handling, and injection and so are best treated as particulate grouts.

1.2.2 CHEMICAL GROUTING. Chemical grouting is the process of injecting a chemically reactive solution that behaves as a fluid but reacts after a predetermined time to form a solid, semisolid, or gel. Chemical grouting requires specially designed grouting equipment in that the reactive solution is often formed by proportioning the reacting liquids in an on-

line continuous mixer. Typically, no allowance is made in chemical-grouting plants for particulate materials suspended in a liquid. Further, the materials used in the pumps and mixers are specifically selected to be nonreactive with the chemicals being mixed and pumped.

1.2.3 BACKGROUND. Chemical grouts were developed in response to a need to develop strength and control water flow in geologic units where the pore sizes in the rock or soil units were too small to allow the introduction of conventional portland-cement suspensions. The first grouts used were two-stage grouts that depended on the reaction between solutions of metal salts and sodium silicate. The goal in this work was to bond the particles of soil or rock and to fill in the pore spaces to reduce fluid flow. The technology has expanded with the addition of organic polymer solutions and additives that can control the strength and setting characteristics of the injected liquid. Chemical grouting has become a major activity in remediation and repair work under and around damaged or deteriorated structures. Much of the technology for large-scale grouting of rock or soil can and has been adapted into equipment for repairing concrete structures such as pond liners, drains, or sewers.

1.3 SPECIAL REQUIREMENTS FOR CHEMICAL GROUTS

1.3.1 GENERAL. In the selection of a grout for a particular application, certain chemical and mechanical properties should be evaluated. These include viscosity, durability, and strength. The following paragraphs serve to point out some of the more significant properties of grouts and grouted materials; however, these are not definitive guidelines for engineering design. In many cases, it may be advisable to construct a small field-test section to determine the handling and behavioral characteristics of the grout.

1.3.2 VISCOSITY. Viscosity is the property of a fluid to resist flow or internally resist internal shear forces. A common unit of measure of viscosity is the centipoise (cP). Viscosity is important in that it determines the ability of a grout to flow into and through the pore spaces in a soil. Thus, the flowability of the grout is also related to the hydraulic

conductivity (permeability) of the soil. As a rule of thumb, for a soil having a hydraulic conductivity of 10^{-4} cm/sec, the grout viscosity should be less than 2 cP. Grouts having viscosities of 5 cP are applicable for soils with hydraulic conductivity greater than 10^{-3} cm/sec, and for a viscosity of 10 cP, the hydraulic conductivity should be above 10-2 cm/sec.

1.3.3 GEL TIME. Gel time or gelation time is the interval between initial mixing of the grout components and formation of the gel. Control of gel time is thus important with respect to pumpability. Gel time is a function of the components of the grout, namely, activator, inhibitor, and catalyst; varying the proportion of the components can change gel time. For some grouts, viscosity may be constant throughout the entire gel time or may change during this period. Thus, it is important to know variation with gel time because of problems related to pumping high-viscosity liquids. After gelation, a chemical grout continues to gain strength. The time interval until the desired properties are attained is called the cure time.

1.3.4 SENSITIVITY. Some grouts are sensitive to changes in temperature, dilution by groundwater, chemistry of groundwater including pH, and contact with undissolved solids that may be in the pumps or piping. Sensitivity to these factors may influence gel time.

1.3.5 TOXICITY. Although most of the toxic grouts have been withdrawn from the market, personnel involved in grouting must maintain an awareness of the potential for certain materials to be or to become toxic or hazardous if not properly used. The basic approach should be to always follow the manufacturer's instructions in handling and disposing of such materials and to always follow safe practices in the field. Where large quantities of chemical grout are to be injected into the subsurface, it is prudent to consult the appropriate environmental regulatory agencies during planning.

1.3.6 DURABILITY. Durability is the ability of the grout after pumping to withstand exposure to hostile conditions. These include repeated cycles of wetting and drying or freezing and thawing that may occur as a result of changes in climatic or environmental

conditions. Certain chemicals in the soil or groundwater may also attack the grout and cause deterioration.

1.3.7 STRENGTH. Among other applications, grouts are injected into soils, primarily granular materials, to add strength to the soil matrix. The unconfined compression test on grout-treated samples offers an index of the strength of the material and may suffice as a screening test for the effectiveness of the grout. In many situations, the grout may be placed and remain under the water table, in which case the strength of the saturated material may be lower than that of a dry specimen. In all cases, the strength of the grouted soil in situ must be sufficient to perform its intended function.

1.4 ADVANTAGES AND LIMITATIONS OF CHEMICAL GROUTS

1.4.1 THE VISCOSITIES OF CHEMICAL GROUTS can be very low, and except for fillers that may sometimes be used, chemical grouts contain no solid particles. For these reasons, chemical grouts can be injected into foundation materials containing voids that are too small to be penetrated by cementitious or other grouts containing suspended solid particles. Chemical grouts can therefore be used to control water movement in and to increase the strength of materials that could not otherwise be treated by grouting. Chemical grouts have been used principally in filling voids in fine granular materials; they have also been used effectively in sealing fine fissures in fractured rock or concrete. Chemical grouts have been frequently used for stabilizing or for increasing the load-bearing capacity of fine-grained materials in foundations and for the control of water in mine shafts, tunnels, trenches, and other excavations. Chemical grouts have also been used in conjunction with other void-filling materials for curtain grouting under dams constructed over permeable alluvium and for other treatments such as area grouting or joint grouting.

1.4.2 CHEMICAL GROUTS suffer from the disadvantage that they are often more expensive than particulate grouts. Large voids are typically grouted with cementitious grout, and chemical grouting is done as needed. Chemical grouts are also restricted in

some circumstances due to potentially toxic effects that have been observed with some of the unreacted grout components. Potential groundwater pollution is a major consideration in the selection of the type of grouts to be used in many cases.

2. CHEMICAL GROUT MATERIALS

2.1 TYPES OF CHEMICAL GROUT. Several kinds of chemical grouts are available, and each kind has characteristics that make it suitable for a variety of uses. The most common are sodium silicate, acrylate, lignin, urethane, and resin grouts. A general ranking of grouts and their properties is presented in Table 2-1. Typical applications of chemical grouts are presented in Table 2-2.

2.2 FACTORS AFFECTING PENETRATION. Penetration of grout in any medium is a function of the grout, the medium being injected, and the techniques used for grout injection. Typically, grouts that gel quickly have a limited range of treatment and require close spacing of injection holes and rapid injection rate. Low-shear-strength grouts are frequently useful in extending the range of treatment to times beyond initial gelation. Rapid times of setting are of use when a variety of different strata with different permeabilities are being treated and in situations where groundwater flow may displace the grout during injection. When gelling occurs before pumping is halted, the last injected grout typically moves to the outside of the grouted mass, and both large and small openings are filled. Methods of injection are also of importance. Typically, grouts that are continually moving will gel less quickly, and penetration from continuous injection will be greater than that from the same volume of grout used in batch injection.

2.3 SODIUM SILICATE SYSTEMS. Sodium silicate grouts are the most popular grouts because of their safety and environmental compatibility. Sodium silicates have been developed into a variety of different grout systems. Almost all systems are based on reacting a silicate solution to form a colloid which polymerizes further to form a gel that binds soil or sediment particles together and fills voids.

2.3.1 REACTANTS. Sodium silicate solutions are alkaline. As this alkaline solution is neutralized, colloidal silica will aggregate to form a gel if the sodium silicate is present in concentrations above 1 or 2 percent (by volume). Three types of alkaline silicate grouts are recognized based on reactants used with silicate solutions.

2.3.1.1 ACID REACTANT (phosphoric acid, sodium hydrogen sulfate, sodium phosphate, carbon dioxide solution).

2.3.1.2 ALKALINE EARTH AND ALUMINUM SALTS (calcium chloride, magnesium sulfate, magnesium chloride, aluminum sulfate).

2.3.1.3 ORGANIC COMPOUNDS (glyoxal, acetic ester, ethylene carbonate formamide).

2.3.2 PROCESSES. Sodium silicate and a reactant solution can be injected as separate solutions, or the sodium silicate can be premixed with the reactant to form a single solution that is injected.

2.3.2.1 TWO-SOLUTION PROCESS. The two-solution process is sometimes referred to as the Joosten two-shot technique. In this approach, the sodium silicate solution is injected into the material to be grouted. The reactant solution, usually a solution of calcium chloride, is added as a second step. The two solution approach is reported to produce the highest strength gain in injected soils but is considered to be the most expensive technique that is employed.

2.3.2.1.1 THE TWO-COMPONENT TECHNIQUE can be made to form gel very rapidly. This near-instantaneous hardening can be very useful in shutting off water flow. An additional advantage is the permanent nature of the hardened grout. Testing done on 20-year old, grouted foundations showed no apparent deterioration.

2.3.2.1.2 THE RAPID HARDENING that occurs in the two component technique restricts the volume of soil or sediment that can be treated from a single injection point. It typically is not possible to control the mixing of the silicate and reactant in the subsurface. Some unreacted grout components should be expected when the two-component system is employed.

2.3.2.2 ONE-SOLUTION PROCESS.

2.3.2.2.1 THE ONE-SOLUTION PROCESS involves the injection of a mixture of sodium silicate and a reactant (or reactants) that will cause the silicate to form a gel. The separate solutions are prepared and mixed thoroughly. The one-solution process depends on the delay in the onset of gelation. This process offers the advantages of more uniform gel formation, improved control to gel distribution during injection, and reportedly strong grout.

Type	Penetration in Grouted Units	Durability	Ease of Application	Potential Toxicity	Flammability of Materials	Relative Costs
Portland-cement-based grouts	L[1]	H	M	L	N	L
Silicates	H	M	H	L	N	L
Acrylates	H	M	H	M	L	H
Lignins	H	M	H	H	L	H
Urethanes	M	H	M	H	H	H
Resins	L	H	M	H	M	H

[1] N = non-flammable; L = low; M = moderate; H = high.

Table 2-1
Ranking of Major Grout Properties

Application	Sodium Silicate	Acrylate	Lignin	Urethane	Resins
Adding strength	C[1]	C	C	R	R
Reducing water flow	C	C	C	U	R
Concrete repair	U	U	U	C	C
Sewer repair	U	U	U	C	C
Load transfer and support	U	U	U	C	U
Installation of anchors	R	R	R	U	C

[1] C = commonly used; U = used; R = rarely used.

Table 2-2

Ranking of Chemical Grouts by Application

2.3.2.2.2 REACTANTS USED IN THE one-solution process neutralize the alkalinity of sodium silicate in a way similar to the two-solution system, but the reactants are diluted and materials that react slowly (such as organic reagents) are used. Sodium bicarbonate and formamide are common reactants. One customary formulation involves mixing formamide, sodium aluminate, and sodium silicate. The formamide causes gelation, and sodium aluminate accelerates the gel formation after the initiation of gelation.

2.3.2.2.3 THE SILICATE SOLUTION concentration that may be used in grouting may vary from 10 to 70 percent by volume, depending on the material being grouted and the result desired. In systems using an amide as a reactant, the amide concentration may vary from less than 1 to greater than 20 percent by volume. Generally, however, the amide concentration ranges between 2 and 10 percent. The amide is the primary gel-producing reactant in the one-solution process. Concentration of the accelerators is determined by gel time desired. The viscosity of a silicate grout is dependent on the percentage of silicate in the grout; a high silicate concentration is therefore more viscous than a low silicate concentration and has less chance of entering small voids. The viscosity of a particular

one-solution silicate is relatively low in concentrations of 60 percent or less. Viscosity versus concentration is tabulated below:

Sodium Silicate Concentration, percent	Viscosity (as Compared with Water) Factor
10	2.5
20	3.2
30	3.5-4.5
40	4.0-6.0
50	5.2-12
60	8.0-20
70	92

2.3.3 STRENGTH AND PERMEABILITY. Sodium silicate grouts have been used to cut off water flowing through permeable foundations and to stabilize or strengthen foundations composed of granular materials and fractured rock. Granular materials that have been saturated with silicate grout develop quite low permeability if the gel is not allowed to dry out and shrink. Even though shrinkage may occur, a low degree of permeability is usually obtained. Treatment with sodium silicate grout will improve the strength and the load-bearing capacity of any groutable granular material coarser than the 75-µm sieve. Factors that influence strength are grain size, particle-size distribution, particle shape, absorption, the ability of the grout to adhere to the particle surfaces, moisture content, curing environment, and method of loading.

2.3.4 DURABILITY. Grouts containing 35-percent or more silicate by volume are resistant to deterioration by freezing and thawing and by wetting and drying. Grouts containing less than 30-percent silicate by volume should be used only where the grouted material will be in continuous contact with water or for temporary stabilization.

2.3.5 SILICATE SYSTEMS. One widely used silicate-grout system contains sodium silicate as the gel-forming material, formamide as the reactant, and calcium chloride, sodium aluminate, or sodium bicarbonate in small quantities as an accelerator. Accelerators are used individually in special situations, not together; they are used to control gel time and to impart strength and permanence to the gel. The effect of the accelerator is important at temperatures below 37 °C and increases in importance as the temperature decreases. Excessive amounts of accelerators may result in undesirable flocculation or formation of local gelation, producing variations in both the gel and setting times that would tend to plug injection equipment or restrict penetration, resulting in poorly grouted area. The accelerator is usually dissolved in water to the desired concentration before the addition of other reactants, and the subsequent combination of this mixture with the silicate solution forms the liquid grout. The reactant and accelerator start the reaction simultaneously; however, their separate reaction rates are a function of temperature. At temperatures below 34 °C, the reaction rate of the accelerator is greater than the reaction rate of the reactant. The reverse is true above 37 °C. Generally, when high temperatures are experienced, an accelerator is not required.

2.3.5.1 SILICATE-CHLORIDE-AMIDE SYSTEM. A silicate-chloride-amide system can be used where there is a need for an increase in the bearing capacity of a foundation material. This system has been successfully used for solidification of materials below the water table. It is a permanent grout if not allowed to dry out, and with 35-percent or more silicate concentration by volume, the grout exhibits a high resistance to freezing and thawing.

2.3.5.2 SILICATE-ALUMINATE-AMIDE SYSTEM. A silicate-aluminate-amide system has been used for strength improvement and water cutoff. Its behavior is similar to the silicate-chloride-amide system but is better for shutting off seepage or flow of water. The cost is slightly greater, and this system can be used in acidic (3) Silicate-bicarbonate-amide system. A silicate-bicarbonate-amide system can be used for semi-permanent grouting and for various surface applications when the stabilization requirement is for relatively short periods of time.

2.3.5.3 SILICATE SALT OF A WEAK ACID (MALMBERG SYSTEM).

2.3.5.3.1 THE MALMBERG SYSTEM is based on the production of a silicic acid gel by the mixture of a solution of sodium silicate with a solution of the salt of a weak acid. This system differs from other similar two-solution systems since they are based on a precipitate and differs from acid reaction systems by maintaining an alkaline pH. This system has a delayed silicic acid gel formation.

2.3.5.3.2 REACTANTS USED IN THIS SYSTEM include acid, alkali, or ammonium salts of weak acids such as sulfurous, boric, carbonic, and oxalic acid. Specific salts include sodium bisulfite, sodium tetraborate, sodium bicarbonate, potassium hydrogen oxalate, potassium tetraoxalate, and sodium aluminate. These salts will yield differences in performance. For optimum effect, the salt should be chosen on a basis of all of the factors of application. All of these salts will perform adequately for many strengthening or water-shutoff applications.

2.3.5.3.3 THE PROPORTIONING OF THE SODIUM SILICATE to the total volume of grout can range from 10 to 75 percent by volume with most work being done in the 20- to 50-percent range. The liquid silicate may be used as a diluted stock solution or mixed with water during the reaction with the acid-salt stock solution. There are a variety of sodium silicate products on the market, and it is important to use the correct concentration.

2.3.5.3.4 THIS SYSTEM HAS A SMALL corrosive effect on light metals such as aluminum; however, the effect is not strong enough to warrant anything other than conventional equipment in mixing and pumping.

2.3.5.3.5 FOR FAST GEL TIMES, a two-pump proportioning system is desirable, as with some other systems; however, for slow gel times, batch mixing can be employed. Compressed-air-bubble mixing or violent mixing that introduces air should not be used because of the reaction between the solutions and carbon dioxide.

2.3.5.3.6 THE GEL TIME CAN be controlled with this system, as with other systems, by varying solution concentrations. Increasing the sodium silicate concentration retards gel time; increasing the acid-salt concentration decreases gel time; increasing temperature decreases gel time, and vice versa. Gel times are also influenced by the chemistry of the formation being treated. Acid soils, or soils containing gypsum, frequently accelerate gel time, whereas alkaline soils may decrease or even prevent gelation.

2.3.5.3.7 SANDS STABILIZED WITH the Malmberg system have shown a permeability in the range of 10-8 cm/sec, and when allowed to dry out, the permeability often increases to 10-5 cm/sec with the sample still having good strength characteristics. This means that this system is useful for water shutoff below the water table or where there is sufficient moisture to continually replace water lost due to evaporation. This system should not be used for water shutoff in rock or other open fissures due to a large degree of syneresis.

2.3.5.3.8 THIS SYSTEM IS PERMANENT above the water table, if some unreacted sodium silicate is present, and in most applications below the water table. Limited field experience has shown this system to perform satisfactorily under such conditions as thin surface applications in the Nevada desert.

2.3.5.3.9 FINE SANDS with up to 10 percent passing a 75-μm sieve can be penetrated by a grout containing up to 50 percent, by volume, of sodium silicate if a surfactant is used. On one project, a 25-percent, by volume, sodium silicate grout was successfully injected in a sand with 22 percent passing a 75-μm sieve.

2.3.5.3.10 LUBRICITY AND VISCOSITY are two important factors in the penetration characteristics of this system. For example, when mixed with the proper surfactant, a 10-cP Malmberg-system grout is reported to penetrate materials not penetrated by a 3-cP system. For a grout with a given lubricity, the less viscous will penetrate better than the more viscous.

2.3.6 PENETRATION. A 30-percent silicate solution has a lower practical limit of penetrability for material passing a 106-µm sieve with not more than 50 percent passing a 150-µm sieve or not more than 10 percent passing a 75-µm sieve. Gel time can be controlled from minutes to hours at temperatures ranging from freezing to 21 °C. The stability of the grout is excellent below the frost line and the water table, and poor when subjected to cycles of wetting and drying or freezing and thawing. Grout penetration is influenced by the following factors: depth of overburden, allowable pressure, void ratio and permeability of material being grouted, distribution of particle sizes, etc. The most fluid silicate grout (i.e., the silicate grout with the lowest silicate concentration) has the ability to penetrate materials coarser than the 75-µm sieve. One of the most viscous (i.e., 70-percent silicate concentration) silicate grouts commonly used will penetrate materials coarser than the 300-µm sieve or not more than 25 percent passing the 106-µm sieve or not more than 25 percent passing the 75-µm sieve.

2.3.7 PHYSICAL PROPERTIES AND FACTORS AFFECTING GEL TIME.

2.3.7.1 FIGURE 2-1 SHOWS THE RATE of strength development for various concentrations of sodium silicate grout injected into sand of unknown grading in which a 30-percent solution of calcium chloride was used as the reactant. The tests were conducted on laboratory prepared specimens, and a two-solution system was employed.

2.3.7.2 FIGURE 2-2 IS A PLOT OF GEL TIME versus temperature for a 20-percent silicate concentration in the silicate chloride- amide system, and Figure 2-3 is a plot of gel time versus accelerator concentration for a 20-percent silicate concentration in the silicate-aluminate-amide system. Both Figures 2-2 and 2-3 are for one concentration of silicate.

2.3.7.3 THE FOLLOWING FACTORS affect the gel times of the one-solution silicate grout:

2.3.7.3.1 AN INCREASE IN SILICATE concentration increases the gel time if other ingredient concentrations are held constant.

2.3.7.3.2 AN INCREASE IN THE REACTANT concentration decreases the gel time.

2.3.7.3.3 AN INCREASE IN THE CONCENTRATION of the accelerator, within limits, decreases the gel time.

2.3.7.3.4 GEL TIMES ARE DECREASED with an increase in temperature. Up to 48 °C, no special precautions are necessary.

2.3.7.3.5 THE pH OF THE MATERIAL to be grouted has little effect except where large amounts of acid are present. When acid is present, silicate grout containing aluminate should be used.

2.3.7.3.6 THE PRESENCE OF SOLUBLE SALTS such as chlorides, sulfates, and phosphates in the medium to be grouted has an accelerating effect on the gel time depending upon their concentration.

2.3.7.3.7 IMPURITIES OR DISSOLVED SALTS in some waters may have an effect on gel time; hence, the gel time should be determined using water from the source that is to be used in the final product.

2.3.7.3.8 DIRECT SUNLIGHT HAS no effect on gel time.

2.3.7.3.9 FREEZING HAS LITTLE effect on silicate-grout ingredients; however, freezing must be avoided during placement.

2.3.7.3.10 SOME FILLER MATERIALS such as bentonites and clays have little effect on gel time. However, if moderate to high concentrations of fillers are used, the temperature

will vary, which would change the gel time. If reactive materials are used (such as portland cement) their effect on gel time and on the final product should be checked.
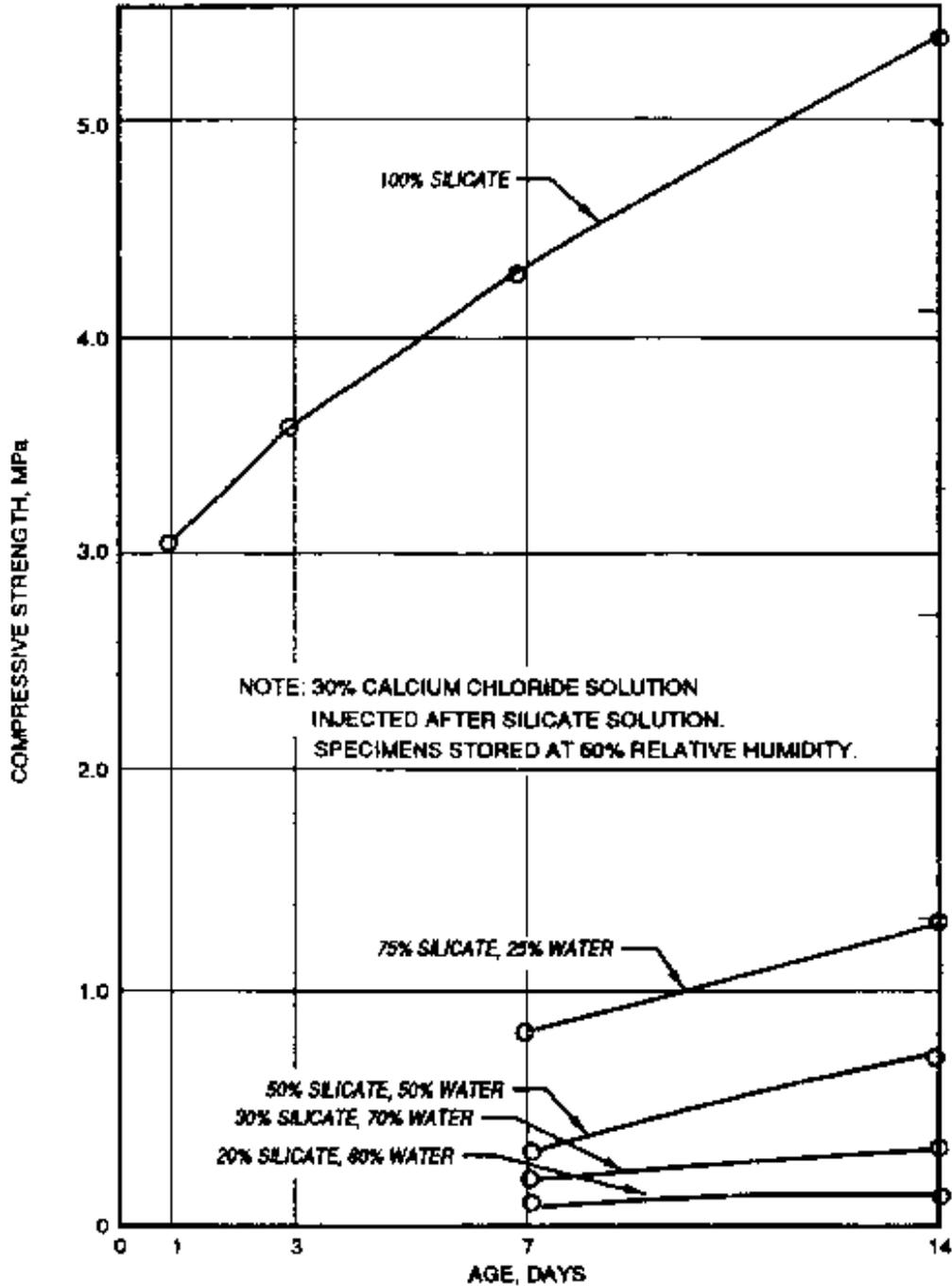

Figure 2-1

Effect of dilution of silicate grout upon compressive strength of solidified sand
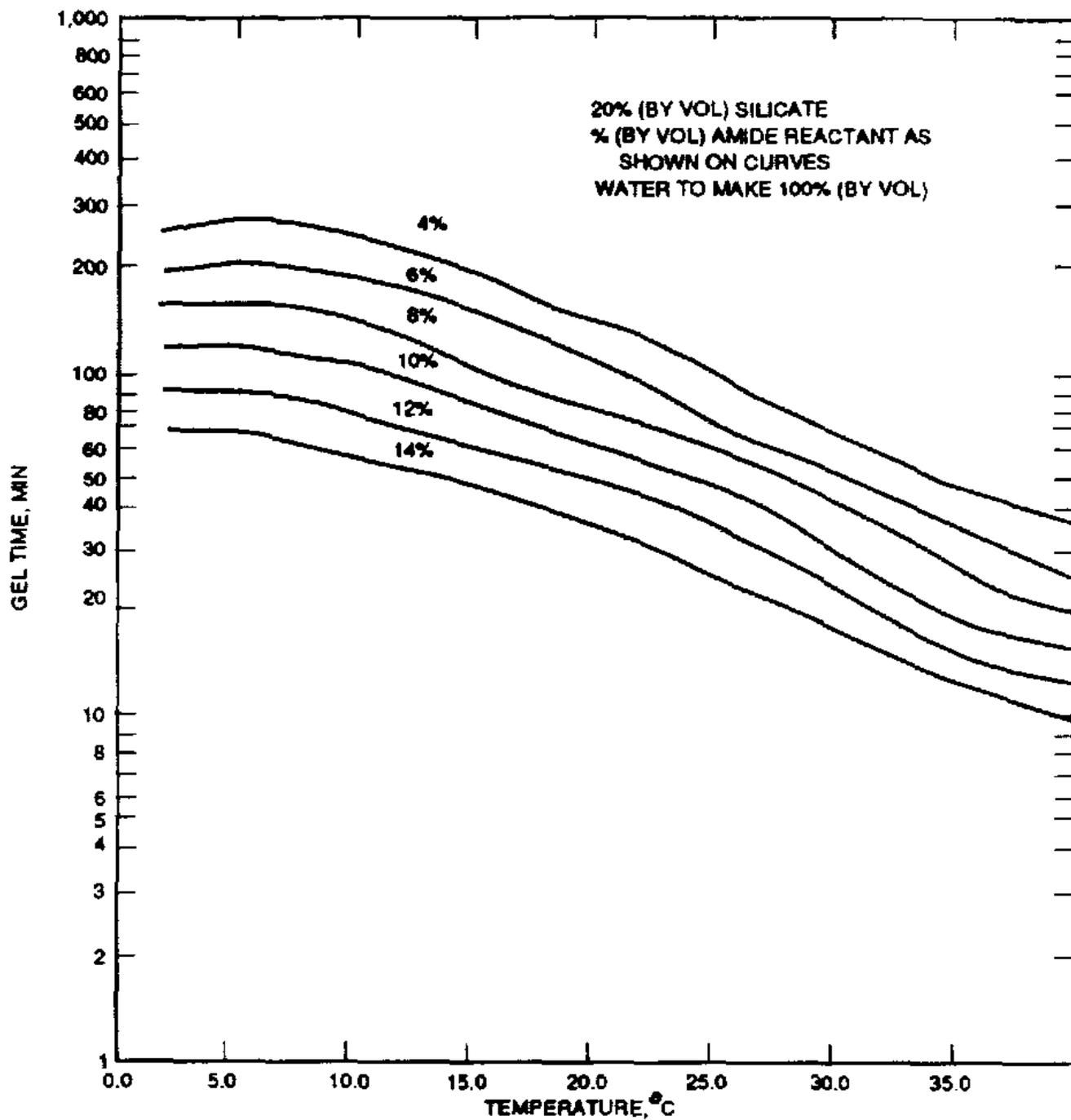
Figure 2-2

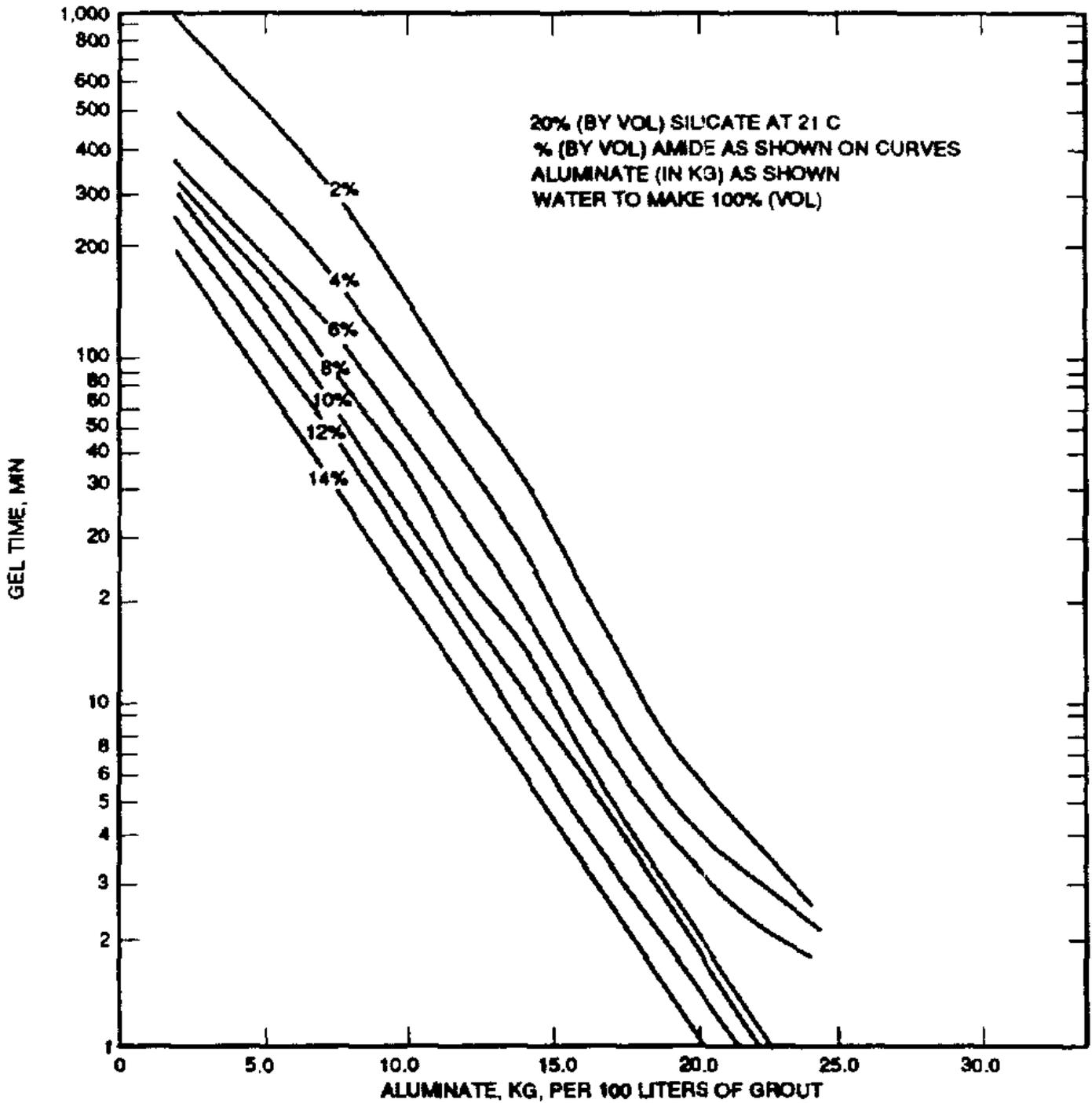Gel time versus temperature, silicate chloride- amide system

Figure 2-3

Gel time versus accelerator concentration, silicate-aluminate-amide system

2.3.7.4 SODIUM SILICATE IS NONCORROSIVE TO METALS. Reactants such as amide and their water solutions will attack copper and brass, but they are noncorrosive to aluminum and stainless steel. The chloride solutions are not corrosive to iron and steel in the sense that acids are; however, if steel in a chloride solution is exposed to air, rusting will occur at the junction of the liquid and air. Bicarbonate is noncorrosive.

2.3.7.5 GENERALLY, THE STRENGTH AND LOAD-BEARING capacity of any groutable granular material coarser than 75-μm sieve can be improved when treated with a silicate grout. Table 2-3 gives some general guidelines as to what unconfined compressive strengths can be expected from materials grouted with sodium silicate.

2.3.7.6 THE STRENGTH OF A GROUTED granular material is primarily a function of grout concentration and relative density of the formation. In grouted loose material, strength is governed by the gel and only slightly modified by the material itself. The angle of internal friction can be increased from that of the unstabilized state. For dense, compacted grouted material, strength is governed primarily by the material.

Material	Compressive Strength, kPa, of Material After Grouting
Very loose granular material saturated with a silicate grout, cured dry	4,000-7,000
Very loose granular materials saturated with a silicate grout, cured at 80-100% relative humidity	2,800-3,500
Very loose granular materials saturated with a silicate grout, cured underwater	700-2,800
Average field conditions with one injection (incomplete saturation)	700-2,800
Compact, medium-grain granular materials saturated with a silicate grout, wet subsurface	200-4,000

Table 2-3

Unconfined Compressive Strengths of Various Materials Treated with Silicate Grout

2.3.7.7 TESTS INDICATE THAT 40-PERCENT and stronger silicate grouts have high durability and are permanent, with the exception of the grouts containing bicarbonates. Tests and observations have indicated silicate grouts to be permanent under freeze-thaw conditions, dimensionally stable to temperature, and resistant to acidity, alkalinity, salinity, bacteria, and fungi. Granular materials or rocks that are completely saturated with grout are essentially impermeable if the gel is not allowed to dry out and shrink.

2.3.8 PORTLAND CEMENT-SODIUM SILICATE COMPATIBILITY.

2.3.8.1 PORTLAND CEMENT CAN BE USED as a filler in silicate grouts but acts as an accelerator. Extremely short gel times have been experienced when portland cement was used, making this system very useful for cutoff of flowing water or water under pressure. Strong bonding properties to the in situ materials have been reported when silicates were combined with portland cement. This system has been used in grouting below a water table and produces a high-strength, permanent grout if not allowed to dry out. Gel or set times in the range of 10 to approximately 600 sec with strengths as high as 7,000 kPa have been reported, with these short gel times being obtained by increasing the amount of cement. Finely ground portland cements are typically most useful with sodium silicates.

2.3.8.2 SODIUM SILICATE GROUT can be injected more easily than a silicate-portland-cement grout, which, in turn, can be injected more easily than portland-cement mixtures. Silicate-portland-cement grout can be injected more easily than portland-cement mixtures apparently because the cement particles are lubricated by the silicate.

2.4 ACRYLATE GROUTS. Acrylates were introduced as less toxic alternatives to the toxic acrylamide compounds that are no longer available as grout. Acrylate grout is a gel formed by the polymerization of acrylates. The gelling reaction is catalyzed by the addition of triethanolamine and ammonium or sodium persulfate to a metal acrylate (usually magnesium acrylate). Methylene-bis-acrylamide is used as a crosslinking agent. Potassium ferricyanide is used as an inhibitor if long times of setting are required.

2.4.1 PRINCIPAL USES. Acrylates have replaced acrylamide as the usual grout for forming water stops around sewer systems. Acrylate is typically not used in areas where it is subject to wetting and drying or freezing and thawing.

2.4.2 STRENGTH AND PERMEATION. Acrylates typically form soft gels. Standard sand samples grouted with acrylates can obtain strengths as high as 1.5 MPa. Acrylate grouts

can be prepared with viscosities as low as 1 cP. The low viscosity and ability to develop long gel times (up to 120 min) make acrylate grouts useful in fine sediments.

2.4.3 MODIFIED ACRYLATE GROUTS. Specialized acrylate grouts have been developed by using acrylate grout in a two-part injection technique with each injected solution a monomer (silicate or acrylate, for example) and the catalyst for the other monomer. This type of special application grout is restricted to use at temperatures between 5 and 30 °C.

2.5 URETHANES. Urethane grouts are available in several different forms, but all depend on reactions involving the isocyanates cross-linking to form a rubbery polymer. One-part polyurethane grouts are prepolymers formed by partly reacting the isocyanate with a cross-linking compound producing a prepolymer with unreacted isocyanate groups. The one-part grouts react with water to complete polymerization. The grouts will typically gel or foam depending on the amount of water available. Viscosities range from 50 to 100 cP. The two-component grouts employ a direct reaction between an isocyanate liquid and a polyol and produce a hard or flexible foam depending on the formulation. Viscosities range from 100 to 1,000 cP. Factors that affect the application of urethanes include the following:

2.5.1 TOXICITY. Isocyanates typically are toxic to varying degrees depending on the exact formulation. The solvents used to dilute and control the viscosity of the urethane prepolymers are also potential groundwater pollutants. There are additional safety problems related to combustion products produced if the grout is exposed to flame. Some grouts are highly flammable before and after setting.

2.5.2 ADAPTABILITY. Urethane grouts have provided very versatile materials. They can be injected directly into flowing water as a water stop and can be used for seal openings as small as 0.01 mm. Rigid foams have found applications in distributing loads in underground structures.

2.6 LIGNINS. When combined with a oxidizer such as sodium dichromate, lignin, a by-product of the sulfite process of making paper, forms an insoluble gel after a short time. Viscosities of various lignin solutions can be obtained over a range that makes the lignins capable of being injected into voids formed by fine sands and possibly coarse silts. Lignins are generally not acceptable if chromium compounds are used due to the toxicity of chromium.

2.6.1 TYPES OF LIGNIN-BASED GROUTS.

2.6.1.1 LIGNIN-BASED GROUTS are injected as a one-solution single-component system, the reactant or reactants being premixed in the lignin-based material. Gel times with the precatalyzed lignosulfonate system are easily adjusted by changing the quantity of water. This precatalyzed lignosulfonate is reported to be a dried form of chrome lignin.

2.6.1.2 TWO-COMPONENT SYSTEMS of lignosulfonates are also commercially available. The reactants of this system are mixed separately as with a proportioning system, and the total chemical grout is not formed until immediately prior to injection. Advantages of this system are closer control of gel time and a wider range of gel times coupled with elimination of the risk of premature gelling.

2.6.1.3 THE MATERIALS USED IN LIGNIN GROUTS are rapidly soluble in water, although mechanical agitation is recommended. The lignin gel in normal grout concentrations is irreversible, has a slightly rubbery consistency, and has a low permeability to water. Short-term observations (less than 2 years) show that for grouted materials protected against drying out or freezing, the grout will not deteriorate.

2.6.2 USES. Lignin grout is intended primarily for use in fine granular material for decreasing the flow of water within the material or for increasing its load-bearing capacity. These grouts have also been used effectively in sealing fine fissures in fractured rock or concrete. Their use in soils containing an appreciable amount of material finer than the 75-μm sieve generally is unsatisfactory and is not recommended because material this

fine will not allow satisfactory penetration. However, lignin grout of low viscosity injected at moderately high pressures may be effective in fine materials.

2.6.3 REACTANTS.

2.6.3.1 VARIOUS REACTANTS used with lignin-based grouts include sodium bichromate, potassium bichromate, ferric chloride, sulfuric acid, aluminum sulfate (alum), aluminum chloride, ammonium persulfate, and copper sulfate. The bichromates have been the most widely used and apparently are the most satisfactory, but now are considered a potential grout-water pollutant.

2.6.3.2 AMMONIUM PERSULFATE has also been used as a reactant in the lignin-grout system, but the ultimate strength is approximately 40 percent of that of a similar grout mixture in which sodium bichromate is used as a reactant.

2.7 RESINS. Resin grouts consist essentially of solutions of resin-forming chemicals that combine to form a hard resin upon adding a catalyst or hardener. Some resin grouts are water based or are solutions with water. Injection is by the one-solution process. The principal resins used as grouts are epoxy and polyester resins. The terms epoxy and polyester resins apply to numerous resin compounds having some similarity but different properties. Various types of each are available, and the properties of each type can be varied by changing the components. Resins can be formulated to have a low viscosity; however, the viscosities are generally higher than those of other chemical grouts. A large amount of heat is generally given off by resins during curing. They retain their initial viscosity throughout the greater part of their fluid life and pass through a gel stage just before complete hardening. The time from mixing to gel stage to hardened stage can be adjusted by varying the amount of the hardening reactant, by adding or deleting filler material, and by controlling the temperature, especially the initial temperature.

2.7.1 EPOXIES. Epoxy grouts are generally supplied as two components. Each component is an organic chemical.

2.7.1.1 NORMALLY, THE TWO COMPONENTS are a resin base and a catalyst or hardener; a flexibilizer is sometimes incorporated in one of the components to increase the ability of the hardened grout to accommodate movement. Tensile strengths generally range in excess of 28 MPa in both filled and unfilled system. A filled system is one in which another ingredient, generally material such as sand, has been added. An unfilled system refers to the original mixture of components. Elongation may be as much as 15 percent. Flexural strength in both filled and unfilled systems is generally in excess of 40 MPa with considerably higher strengths reported in some instances with filled systems. Compressive strengths greater than 70 MPa are attainable and may reach 270 MPa in a filled system. Water adsorption is approximately 0.2 percent or less and shrinkage, by volume, is 0.01 percent and lower.

2.7.1.2 EPOXY RESINS, in general, also exhibit the following characteristics: resistance to acids, alkalies, and organic chemicals; a cure without volatile by-products (therefore, no bubbles or voids are formed); ability to cure without the application of external heat; acceptance of various thixotropic or thickening agents such as special silicas, bentonite, mica, and short fibers such as asbestos or chopped glass fiber; and capability of being used in combination with various fillers to yield desired properties both in hardened and unhardened state.

2.7.1.3 EXAMPLES OF EPOXY fillers are aluminum silicate, barium sulfate, calcium carbonate, calcium sulfate, and kaolin clay, which act as extenders; graphite, which aids in lubricating the mixture; and lead for radiation shielding. These fillers are generally added to reduce the resin content and in most instances reduce the cost. Fillers reduce heat evolution, decrease curing shrinkage, reduce thermal coefficient of expansion, and increase viscosity. The tensile strength, elongation, and compressive strength are adversely affected by the addition of granular fillers.

2.7.1.4 IN GENERAL, EPOXY RESINS are easier to use than polyesters, exhibit less shrinkage, develop a tighter bond, and are tougher and stronger than polyesters. Epoxies

are thermosetting resins; hence, once they have hardened, they will not again liquefy even when heated, although they may soften.

2.7.1.5 EPOXY RESIN GROUTS have been used for grouting of cracked concrete to effect structural repairs; more recently, for grouting fractured rock to give it strength; and in rock bolting.

2.7.2 OTHER RESINS.

2.7.2.1 AQUEOUS SOLUTIONS of resin-forming chemicals. A commercially available resinous grouting material has been investigated for possible use in grouting in sandstone to reduce water flow. The resin solution has a viscosity of 13 times that of water and is hardsetting. Two aqueous solutions of resin-forming chemicals compounded with accelerators and retarders are employed in this grout. The two resin-forming materials solidify upon addition of the catalyst to form a hard plastic. Investigations have shown that the time of setting of this grout can be accelerated by chemicals in the sandstone. Waterflow pressure tests before and after grouting have shown that a reduction in flow through test specimens was obtained.

2.7.2.2 WATER-BASED RESIN. A water-based-resin grouting material having an initial viscosity of approximately 10 cP is commercially available. This grout has an affinity for siliceous surfaces and attains a hard set. Tests on a clean, medium-fine sand grouted with this resin have shown compressive strengths of approximately 8 MPa. This grout is used in grouting granular materials, presumably to reduce water flow. Sandy soils containing as much as 15 percent in the coarse silt range (0.04 mm) can be treated with this material. In calcareous materials, this grout will not set properly. The gelled grout is not affected by chemicals generally present in underground water. The neat gel has a compressive strength of 5.5 MPa in 3 hr; has a low permeability to water, oil, or gas; and is stable under nondehydrating conditions; however, when water is lost, shrinkage will occur with an accompanying strength loss. Medium-fine sands (0.5 to 0.1 mm) injected with this material have compressive strengths in the 10.3-MPa range. In laboratory

studies, sands treated with this material showed no deterioration under wet conditions at the end of 1 year.

2.7.2.3 CONCENTRATED RESIN. Concentrated resins are marketed and are intended for use where strength and waterproofing are necessary. These resins are used in sand, gravel, and fractured and fissured rock. Presumably, they could also be used in fractured concrete. Laboratory tests with both a 50- and an 80-percent concentration (50:50 and 80:20, by volume, resin to water) of resin indicated that fractures as small as 0.05 mm could be grouted. These tests were performed by injecting grout between two pieces of metal separated by appropriate size shims. Approximately 7 MPa was required to inject both concentrations into the 0.05-mm spacing. Tests on spacings smaller than 0.05 mm were not performed. The viscosity of the concentrated resin ranges between 10 and 20 cP for normal concentrations used and temperatures encountered in the field. The base material is liquid diluted with water and reacted by a sodium bisulfate solution. Gel times are controllable and with normal concentrations (50:50, by volume, resin to water) reach a firm solidification set within 24 hr. Strengths of stabilized sand after curing have reached 3 to 35 MPa. Strength is a function of amount of mixing water used and decreases with an increase of water. If strength is not a consideration, the base material may be diluted with up to twice its volume of water to provide temporary water control. If used in this manner, viscosities will be lower and gel times longer. Soils and rock masses can attain permeabilities on the order of 1×10^{-7} cm/sec. Gel time varies as a function of solution temperature and reactant concentration. Stainless steel should be used throughout the reactant side if the proportioning system of pumping is employed.

2.8 OTHER GROUTS. The five groups of chemical grouts discussed previously are not the only chemical grouts that have been or can be used. Some of the other chemical grouts include a cationic organic-emulsion using diesel oil as a carrier, a resorcinol-formaldehyde, an epoxy-bitumen system, a urea-formaldehyde, and a polyphenolic polymer system. Most of these grouts are no longer used due to toxicity. A variety of special application grouts have also been developed for structural repair and for installation of anchors. These include thermo-setting grouts such as molten sulfur and

molten lead. Additionally, special epoxies and acrylates have been developed as bolt anchoring and concrete patching kits.