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CHEMICAL GROUTS FOR POTENTIAL USE IN BUREAU OF RECLAMATION PROJECTS

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16. ABSTRACT

This report consists of a review of literature related to chemical grouting. Attention focuses on the sources of technical literature and the state of the art for chemical grouting. The chemical behavior of the most prominent chemical grout classes is also discussed. A survey of chemical grout use within the Bureau indicates that chemical grouts are seldom used. Suggestions for their increased use are given.

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UNITED STATES DEPARTMENT OF THE INTERIOR ★ BUREAU OF RECLAMATION

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PURPOSE OF THE STUDY

The purpose of this study is to determine where chemical grouts could be used in Bureau (Bureau of Reclamation) operations, the state of the art, and what would be necessary to implement the use of chemical grouts in a manner most beneficial to the Bureau.

SCOPE

The investigation is centered on the collection and study of pertinent literature to determine the state of the art. However, other sources of information are used, such as discussions with authorities on the subject and case histories.

The remainder of the program, which is laboratory work, will be restricted to two areas: (1) establishment of test methods and facilities with which grouts can be systematically evaluated, and (2) evaluation of selected grouts by the test methods developed. No field work has been planned; however, any opportunity for field observation will be used to supplement laboratory studies.

APPROACH

This report involved collecting literature, studying the literature, and attending training courses, seminars, etc., to establish the state of the art for the purpose of determining what further effort would be required. In addition, some laboratory work was performed for the purpose of becoming familiar with the behavior of certain types of chemical grouts, and a survey questionnaire was circulated among potential users within the Bureau to determine current usage.

HISTORY AND DEFINITIONS

In the United States, portland cement grout has been used since the turn of the century and is still the cheapest and most widely used grout. However, cement is not a true solution, but a particulate suspension, and the voids it can enter are limited by the size of the cement particles. It is widely accepted that cement cannot be injected when void apertures are less than three times the diameter of cement particles.

Chemical grouts are true solutions made up of reacting species that form gels after injection. Although they are true solutions and will penetrate soils that would not admit cement, a given chemical grout will be limited by its viscosity. In some cases, the viscosity of water is approached, but in others the viscosity limits application.

It should be made clear at this point that all types of grouts are used for either of two reasons: (1) to stop water movement, or (2) to strengthen soil. The latter case is most commonly encountered where excavation might cause cave-ins in loose sands or alluvium or to prevent shifting of a nearby structure.

The first chemical grouts to be used were silicate preparations (as early as 1886). Silicates are still the most widely used and are the cheapest. However, they have relatively high viscosity, making injection into fine-grained soils impossible, and some silicates are subject to a form of shrinkage called syneresis. In spite of these facts, silicates are by far the most widely used grouts in the United States. Seventy to eighty percent of grouts used in the United States are silicates, depending on who is making the estimate. Of this percentage, most are used for strengthening soils.

Limitations of silicates led to the introduction of organic polymers, starting about 1950. Since that time, a number of organic chemical grouts have been introduced, and many have fallen into disuse because of unfavorable characteristics or concern with possible toxic effects.

Until recently, a novice attempting to get acquainted with the use of chemical grouts would almost certainly experience complete confusion. Very little authoritative literature was available. Most of it consisted of narratives of use initiated by individuals with different backgrounds and widely varying problems. Manufacturers, of course, published information on the use of their products, but data were hard to compare and, in some cases, misleading. Often, the information consisted of little more than directions on how to mix the components. Grouting contractors were probably the most knowledgeable in the use of chemical grouts, but they had little incentive to publish any of their knowledge. There was no single work that comprehensively covered all aspects of chemical grouting including injection technology, relevant geotechnical considerations, and comparison of characteristics of the various grout classes.

Today, that situation is changing rapidly. Several manuals have been prepared by the Department of Transportation [1, 2, 3, 4, 5, 6, 7, 8][1] and a good text by R. H. Karol [9] has been published.

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[1] Numbers in brackets refer to entries in the bibliography.

ASTM (American Society for Testing and Materials) Committee D18.16 is devoted to standardization of tests and has so far produced three test standards for chemical grouts. A conference on grouting in general, which attracted participants with papers and case histories from all over the world, was held in New Orleans in 1982. A book containing the presentations, many of which are devoted to chemical grouting, has been published [10].

STATE OF THE ART

Insofar as injection technology and relevant geotechnical matters are concerned, chemical grouting is well developed and well documented.

The bibliography contains a list of comprehensive, recent Government publications dealing with chemical grouting [1, 2, 3, 4, 5, 6, 7, 8], which may be obtained from the National Technical Information Services, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The text by R. H. Karol, *Chemical Grouting,* [9] is an excellent, up-to-date work.

Papers presented at the New Orleans Conference in 1982 can be obtained from the American Society of Civil Engineers and copies are available in the Bureau Library.

The works cited above generally describe the state of the art quite adequately. Thus, it would be redundant if this study were to repeat what has already been accomplished, and no attempt will be made to do so. Instead, problem areas in the state of the art will be pointed out.

The first problem that will be discussed is the definition of grout and its specialized meaning in engineering circles. A ''preliminary glossary of terms'' relating to grouting prepared by the ASCE[2] (American Society of Civil Engineers) is recommended for initiates to the subject. This greatly reduces misunderstandings, but problems in terminology still persist, particularly in chemical terminology. The section entitled ''Chemistry of Chemical Grouts'' in this report covers these discrepancies.

Other terms that are used with ''grout'' and cause confusion are ''caulk'' and ''sealant.''

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[2] *Journal of the Geotechnical Engineering Division,* 15581, GTF, July 1980.

The term ''caulk'' apparently arises from the early days of the shipbuilding industry when cracks in the wooden hulls of ships were closed with pitch or other viscous materials. Thus, the term caulk refers to the sealing or closing of a crack or joint, a particular geometric configuration. Caulk implies a viscous material because otherwise it would flow out of the crack before setting. However, this description is not adhered to rigorously and the words ''sealant'' or ''grout'' may be used instead.

To ''seal'' means simply to limit or prevent access. Thus, tombs, letters, and boxcars are sealed. Likewise, an object may be sealed specifically to prevent the entry of water. Without clarification, the word ''sealant'' does not necessarily refer to making a body watertight and says nothing about the configuration of the sealed space. However, from the context of a discussion, such points are usually clear.

The problem is that the word ''grout'' is used to include both caulking and sealing. The spaces between bathroom tile are ''grouted'' and certain materials referred to as ''chemical grouts'' are also used to close cracks. ''To grout'' actually means to fill any void or space without reference to geometric shape or purpose. The preliminary glossary of terms relating to grouting, however, narrows this definition by restricting grouting to the filling of voids or spaces in ''soil or rock for the purpose of altering physical properties'' of the grouted body, the only two properties being strength and permeability. This definition restricts grouting to limited application and purpose in use, but since the same word is used by the uninitiated in referring to other cases, it can become confusing.

The term ''chemical grout'' refers to a particular class of grouts but, here again, confusion can arise. In soil grouting, the term refers to any compound mixed with water to obtain low viscosity and which gels or polymerizes after injection to provide soil stability or reduced permeability. There are a number of such materials on the market. Most of them are organic, but one class, the silicates, are inorganic.

The confusing part arises because many other substances are often specifically referred to as chemical grouts or they are considered in works with titles addressing chemical grouts. For the most part, these are organic substances that polymerize without being mixed with water (non-aqueous). They are much more viscous and are unsuitable for soil grouting in the engineering sense previously described. They are used extensively to repair cracks in concrete. Two of the more common materials are epoxies and urethanes. However, the urethanes cure by reaction with water. They can be injected undiluted into a leaking concrete crack where they mix with water and set, forming a hard rubber-like material, which may be foamed or dense depending on the amount of water present. But certain formulations of urethanes can be mixed with water before injection to reduce viscosity. In this case, a gel is formed that has considerable strength. The urethanes can be used to grout soil and may be classed as chemical grouts in the engineering sense.

To clarify where problems exist, it is probably best to examine the steps involved in a soil grouting operation as follows.

Soil Testing

This includes boring of test holes, soil testing, and in situ pumping tests. Technology for this step is well documented in the literature previously cited and in many other works.

Selection of Grout Candidates on the Basis of Penetrability

This step considers only the penetrability of a grout into the given soil classification. This is a function of viscosity. Selection is made from a penetration chart such as the one shown on figure 1.

The idea is simple, but in practice there are several problems. Penetration charts have been developed by various authors and manufacturers, but they vary in the range of soils and materials included. The viscosity of almost any chemical grout can be reduced to permit greater penetration simply by adding water. However, this reduces the strength of the grout and affects other properties such as shrinkage. Consequently, penetration capability is not totally reliable unless concentration is known.

The presence of a particular chemical grout on a penetration chart does not ensure its availability. Older charts list materials no longer in production.

Another way to select grouts is on the basis of soil permeability (*k*) versus viscosity as indicated in table 1 given by Karol [9].

Selection on the Basis of Characteristics

After having selected a grout that could be injected, a number of other factors must be considered to make a final decision. In reading the literature, the most striking feature is that there is never any positive statement regarding which grout is best for a given application. It would be desirable if there were explicit rules such as "use silicates for structural strength" or "use urethanes for

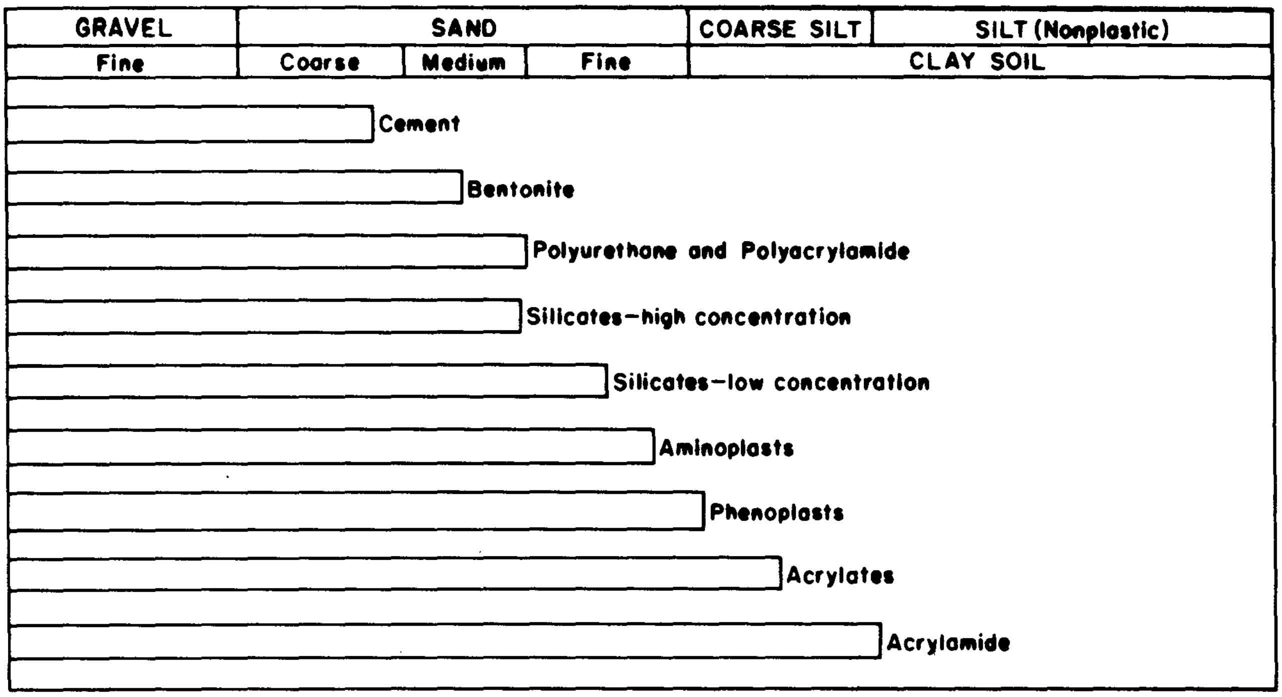

Figure 1. – Penetrability of various grouts.

Table 1. – Groutability based on permeability (*k*). From [9].

$k = 10^{-6}$ or less:	Ungroutable
$k = 10^{-5}$ to 10^{-6}:	Groutable with difficulty by grouts with under 5-cP viscosity and ungroutable at higher viscosities
$k = 10^{-3}$ to 10^{-5}:	Groutable by low-viscosity grouts but with difficulty when viscosity is more than 10 cP
$k = 10^{-1}$ to 10^{-3}:	Groutable with all commonly used chemical grouts
$k = 10^{-1}$ or more:	Use suspended solids grout or chemical grout with a filler

cracks in concrete." Unfortunately, nothing of the sort is to be found. The variability in cost, job requirements, and site conditions would make any such rule extremely difficult to establish.

Karol [9] has listed a number of qualities that would come very close to characterizing an ideal grout:

1. A powder readily soluble in water (this eliminated the expense of transporting a solvent, and water is the least expensive solvent)
2. Inexpensive and derived from chemicals in abundant supply
3. Stable at all anticipated storage conditions
4. Nontoxic
5. Noncorrosive
6. Nonexplosive

And the grout solution should be:

7. A low-viscosity solution, preferably that of water
8. Stable under all normal temperatures
9. Nontoxic, noncorrosive, nonexplosive
10. Catalyzed with common, inexpensive chemicals, meeting the criteria of 8 and 9 (above)
11. Insensitive to salts normally found in ground water
12. Of stable pH on the positive side (so that it may be used in conjunction with cement)
13. Readily controlled for varying gel times
14. Able to withstand appreciable dilution with ground water

And the end-product should be:

15. A permanent gel
16. Unaffected by chemicals normally found in ground water
17. Nontoxic, noncorrosive, and nonexplosive
18. Possess high strength

Karol [9] goes on to comment that no such grout exists. Furthermore, a particular project might not require an ideal grout. Consequently, selection of grout beyond penetrability is largely a matter of finding a grout that meets the requirements at the least possible cost. Thus, before selection can be made, the requirements must be firmly established.

A more specific list of possible factors for consideration follows:

1. Toxicity
2. Permeability after grouting
3. Strength
4. Viscosity testing
5. Gel time
6. Durability
    a. Freeze-thaw cycling
    b. Wet-dry cycling
    c. Shrinkage of any sort
    d. Creep
    e. Extrusion
    f. Chemical instability
7. Cost

Each of these are discussed in following paragraphs.

Toxicity. – This is probably the most misunderstood factor in the selection of a grout. Many grouts are not used because of fear of toxic effects. However, few, if any, have been banned in the United States (the author knows of none).

A classic example of the problem occurred with a product called AM9, an acrylamide, marketed by American Cyanamid Company. It was perhaps the nearest thing to an ideal grout according to many grouters and was used extensively from about 1955 until 1978, when American Cyanamid stopped production. No explanation for the cessation was given, but there has been speculation that it was prompted by several cases of neural disorder in Japan arising from careless use of an acrylamide.[3] The use of acrylamides as a grout was banned in Japan in 1974, but not in the United States (see "Federal Register," December 23, 1977, part VI). Indeed, the Japanese product that was banned, Nitto SS (currently marketed as AV 100) continued to be marketed in the United States and is still available along with similar products from France. The availability of acrylamide grouts is evidenced by the fact that these materials are included in brochures from a number of grouting contractors.

Practically all grouts, as Karol points out, are potentially toxic if mishandled. If this potential is considered without qualification for handling, practically all chemical grouts would be unusable. If properly handled with due consideration for possible contamination of drinking water, chemical grouts can be used, as they currently are being used, without harm. AM9 was used for a considerable number of years without incident, and acrylamides are not banned by the EPA although they are under investigation.

The key to the question of toxicity is to be found during the selection process and planning. If drinking water, especially ground water near wells, is involved, chemical grouts should not be used. No matter how well a grout is mixed, excesses of one ingredient or another will remain after the grout has set. These excesses will migrate through the soil at a rate that depends on the presence of water and permeability of the grouted body.

In addition, in all projects, proper handling precautions and availability of protective clothing and equipment should be ensured along with good ventilation.

Permeability Testing after Grouting. – Methods of testing soil permeability are well established in engineering. It is generally recognized, however, that such tests are not entirely reliable because

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[3] W. B. Jaques, "Stopping Water with Chemical Grout," *Civil Engineering*, p. 59, December 1981.

it is difficult to remove soil without disturbing it, at least to some extent, and because permeability is not uniform in all directions. These effects do not play such a significant role after a grout has been installed, and it is possible to obtain test results that give a reasonably accurate estimate of the level to which permeability can be reduced using a particular grout of given concentration. As yet, no agreement has been reached for a standard ASTM test.

Strength. – A standard test, ASTM D 4320, has also been established for measuring unconfined compressive strength. A standard triaxial test has not been established. Here there is also no deficiency in the state of the art, but it should be noted there is considerable difference between wet and dry strength. Aqueous chemical grouts contain large amounts of water. When dried, they gain strength. At times, manufacturers' data refer to dry strength; whereas, it is the wet strength that exists in a grouted soil and is of interest.

Viscosity. – ASTM D 4219 standardizes viscosity measurements.

Gel Time. – There is no ASTM test designed specifically for measurement of gel time. However, the viscosity test indicates how to measure gel time using a viscometer. The principle is quite simple; when viscosity increases rapidly, gelling is taking place and is recorded on a strip chart. Reasonably accurate gel time can be determined if the gel time is short by tilting a container of the grout at timed intervals and observing when the grout ceases to flow.

Durability. – In all the previously discussed characteristics, there are virtually no deficiencies in the state of the art that cannot be corrected in future phases of this study. Essentially, the state of the art for getting the grout into a soil is very good. However, the question of how long it will stay there, the permanence, is not equally well established. This uncertainty is associated primarily with chemical behavior in the presence of soil and soil-water substances that may be present. Other factors related more to physical circumstances also affect the durability of a grout, but these are generally more predictable and can be avoided in many cases.

The deficiency in the state of the art is that tests for the various causes of failure over time have not been devised or standardized. Furthermore, prediction of life expectancy is still largely a matter of approximation or estimation from case histories. The factors known to affect the permanence of chemical grouts are listed below and discussed in the paragraphs that follow.

- Freeze-thaw and wet-dry cycling
- Shrinkage of any sort
- Creep
- Extrusion
- Chemical instability

Freeze-thaw and wet-dry cycling effects are well-known phenomena, and all aqueous chemical grouts are affected by them. Little can be done about these effects except to avoid circumstances where they occur. In most circumstances, grouted soils carry enough water to prevent wet-dry effects at depths of several feet. Likewise, grouted soils below the frost line are not affected.

Shrinkage does occur in aqueous grouts, but the most detrimental cases occur in connection with water loss. If pure gelled grout is placed in a container with no soil and is exposed to the atmosphere, the shrinkage upon drying is alarming. Aqueous grouts are largely water (as much as 80-90%). Upon removal of the water, severe shrinkage is to be expected. However, if drying is prevented, shrinkage occurs for other reasons that will be discussed in the section on the chemistry of grouts. In most cases, these other forms of shrinkage are not unacceptable and are often quite negligible.

Creep, according to Karol (p. 45 of [9]), has not been determined for all chemical grouts, but all should be suspect. Although no tests have been standarized, it is presumed that ordinary engineering tests for creep can be used. Creep is a function of loading and, if loading is not involved, creep is not a factor as would be the case where only reduction of permeability is of interest.

Extrusion from the soil caused by hydrostatic pressure could occur. This would most likely occur where a grout curtain is used. Karol claims (p. 13 of [9]) that a curtain of 6 to 12 inches is sufficient to withstand unbalanced hydrostatic heads of several hundred pounds per square inch. Although no supporting experimental data have been discovered, the limited number of case histories reviewed thus far seem to support his claim.

Chemical instability is the most difficult aspect of durability to evaluate. Furthermore, there seems to be no standard method of evaluation or testing. Major reliance seems to be based on trial-and-error case histories.

Cost comparison requires no particular technical skill and constitutes no deficiency in the state of the art. However, there is a tendency to reject a candidate grout solely on its price per gallon, which can be as high as $45.00. However, chemical grouts can be diluted considerably so that the injection cost per gallon is much less. Furthermore, the severity of a problem sometimes warrants a high price.

Installation

Once a grout has been selected, the next stage is its installation. Techniques for injection, injection equipment, and knowledge of flow behavior are all well established, and the literature previously cited documents these processes quite well.

The case of water flowing through concrete joints or cracks requires a material with qualities different from those for soil grouting or ordinary caulking. The material should have higher viscosity than for soil grouts, where very low viscosity is desired, yet the material cannot be as viscous as most caulks. Water should not affect its adhesion to concrete, a quality many caulks do not possess. Such a grout may be required to react very rapidly, sometimes in seconds, to stop flowing water. In the case of very fine cracks, reduced viscosity would usually be a requirement. However, this requirement can be reduced considerably where urethanes are used. They gas and force the grout into very small cracks or voids.

In this study, the term ''crack grouting'' is used. However, in the literature there is no such term as ''crack grouting'' nor any single term that addresses cracks or joints specifically. There are, however, numerous works under ''concrete repair'' that are concerned with the repair of cracks or joints. However, concrete repair includes general surface restoration and the use of cement mortars to restore entire sections of concrete. Literature is also found under the names of the compounds used, for example ''epoxy repair of concrete.'' The term ''sealant'' may also be used. The term ''crack grouting'' refers specifically to the repair of cracks or joints, but not to general surface repair.

Grouting Services

Despite the advances that have been made, the chemical grouting industry in the United States is segmented. In Europe, grouting is often considered an integral part of a general civil engineering firm. Many firms have their own capability for grouting. There is direct coordination between grouting operations and other engineering activities. Thus, knowledge and experience are accumulated over a broad range. However, in the United States, grouting is not usually handled by general civil engineering organizations. Any grouting considered necessary is subcontracted to grouting specialists. This produces a severance between general civil engineering and grouting.

Furthermore, U.S. grouting contractors tend to specialize. Some deal exclusively with cement, others primarily with silicates for structural strength, and still others cover a range of materials.

There are also those who specialize in what is called crack grouting in this study; they seal dams, sewer systems, and other concrete structures.

It would seem that such specialization would provide excellent services, and it probably does. However, one most be sure to contact the appropriate specialist with the specific grouting experience required.

CHEMISTRY OF CHEMICAL GROUTS

General

The chemistry of chemical grouts has not been sufficiently addressed in the literature. One exception is the manual on available materials [3], but even it is not entirely adequate. It appears that in most cases this has had minimal effect in grouting operations, except with the silicates where there seems to be some disagreement and misunderstanding. There are also some problems with terminology that can cause misinterpretations. For these reasons, this section of the report is devoted to the chemistry of grouts.

Although there are a number of chemical grouts on the market today, the oldest class, the silicates, remains the workhorse, constituting 80 to 90 percent of the market, depending on who is making the estimate. They are the most economical, but they are used mostly in structural applications.

A second class of chemical grout, a variety of organic polymers, has appeared more recently. Some of these have not survived in the United States because of their toxic effects or failure to perform competitively. The organics tend to be more costly, often substantially so. Their appearance seems to have been the result of inadequacies of the silicates. Unfortunately, the organic polymer that probably came closest to being an ideal grout, AM9, has fallen into disfavor.

The chemistry of grouts will be broken into two categories: (1) silicate grouts, and (2) organic grouts. This is necessary because, as will become apparent, there is considerable difference in their behavior.

Definitions

Before discussing relevant chemistry, several points of terminology should be clarified. It has been noted in the engineering literature that certain terms are not used in the same sense as in chemical circles. This can lead to misunderstandings. The following terms are defined according to chemical terminology and will be used exclusively in this report.

Polymers. – Huge molecules formed from smaller chemical units. They may be either chains or three-dimensional networks of chains that are hooked together. The simple chain-type polymers are not used in chemical grouting, only networks are used.

Figure 2 depicts a portion of such a network in oversimplification. The protruding lines are chains extending to other connecting points to form one huge molecule, usually referred to as a gel.

Water and water-soluble material can fill the space between connected chains. All chemical grouts with low viscosity are formed in water so that the bulk of the network is filled with water. In some cases, 80 to 90 percent is water. The more water involved, the weaker the structure, and the more unstable it will be. If exposed to the atmosphere, the water will evaporate out and cohesive forces between the chains will draw them together causing the body to shrink considerably. If submerged in water, the dried polymer may take the water back in and restore some, if not all, of its original volume. Other factors, such as temperature, pressure, pH, and ion content, can also cause volume changes [3]. In most cases, these variations will be minimal because the installation will be in water-saturated bodies (at least in water control applications) where temperature variation is small.

Gel. – Gel is formed when the particles of a colloidal suspension (colloids are particles large enough to cause the scattering of light) coalesce, usually through temperature reduction, as with jello, but also through attractive electrical charges or poles on the particles. The distinction is that there is no permanent covalent bond. Water is entrapped between the particles giving a jelly-like composition. This is a longstanding description of a gel but, as knowledge of polymer chemistry has developed over the last 50 or so years, network polymers with included water (or other liquids

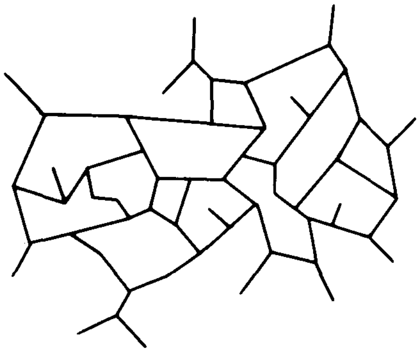


Figure 2. – A polymer network (in two dimensions).

in general) have also been referred to as gels. The distinction of this case is that permanent chemical bonds are formed at chain connection sites and cannot be dissolved except through a chemical reaction. Temperature changes will not disperse the gel unless it is so severe that decomposition occurs. In chemical grouting literature, no distinction is made between the two cases. Organic materials form networks; whereas, silicates (inorganic) tend to form gels through attractive charge effects, but some permanent bonding may also be involved.

Reactants. – These are the chemical subunits that combine to form a new compound. In the case of polymers, these subunits are usually referred to as monomers unless water is the reactant. The word reactant is rarely used in grouting literature. It appears that in some cases one of the reactants is considered to be a catalyst; however, this is erroneous.

Catalyst. – This is a substance used to increase reaction rate. However, it is not a reactant because it will not become a part of the product; it merely increases the rate. The rate will vary with the concentration of the catalyst. When the reaction is complete, the catalyst remains unused and could be recovered, although that might be physically inconvenient in practice. In some cases, it is asserted that when the catalyst is diluted out of a gel, the reaction reverses – causing the gel to decompose into its monomeric subunits. However, this is erroneous. Certain reactions can reverse, but not because the catalyst is removed. Many chemicals are synthesized through catalysis, and upon completion of the reaction, the catalyst is removed but the reaction does not reverse. Undoubtedly, authors of such statements did indeed witness decomposition and possibly reversal did occur, but not because of catalyst dilution.

Accelerator. – This is just a synonym for catalyst. However, in some cases it appears that an author has used this term to refer to one of the reactants. Chemical reactions are rate-dependent on concentration. If $A + B \rightarrow C$, then increasing the concentration of A, or B, or both increases the rate of production of C. One could in all justice regard B as an accelerator by virtue of what happens, but it would also be true for A, so there is no reason to consider B an accelerator any more than A. Furthermore, a reader could more reasonably think a third material, a catalyst, is being referred to.

Inhibitors. – These are materials used to slow a reaction when it proceeds faster than desired. Usually, inhibitors poison or temporarily react with one of the reactants.

Initiators. – An initiator is a third material required by certain reactions to get started. Many free radical reactions require initiators. Adding one reactant to a second also initiates a reaction, but the term initiator refers to a third substance, not one of the reactants. In some cases, it appears an author is referring to one of the reactants, not a third substance required to initiate the reaction.

Silicate Grouts

Despite the much greater experience with silicate grouts in chemical grouting, they are still poorly understood for two reasons. First, the chemical behavior of silicate grouts is complex and can lead to unforeseen events. Secondly, there is little evidence that any attempt has been made to distinguish between formulations of the silicate grouts. Although gelling can be brought about in a number of ways, it appears the final products are thought to be the same and have the same behavior. Although the author cannot entirely refute this notion, there is good evidence that it is erroneous; it will be discussed later. For an excellent description of gel behavior see [11].

Silicate Chemistry

Reliance has been placed almost exclusively on the works of three authors: Vail [12], who is widely recognized and mentioned by many authors as an authority on the subject of silicates, Iler [13], who has produced an exhaustive work on the subject, and Eitel [14].

Silica refers to the compound silicon dioxide (SiO_2), but this brief description can be quite misleading. Without further explanation, the formula SiO_2 implies silica is composed of molecules consisting of one atom of silicon and two of oxygen. But this is not the case at all. Actually, silica in the solid state can be considered as one giant molecule in which both oxygen and silicon are bonded together. If one were to count all silicon and oxygen atoms in such a body, it would be found that there are two oxygen atoms for every silicon, but that does not mean that individual molecules of one silicon and two oxygen atoms exist.

The most striking feature of silicon is that it has a valence of four. That is, it can combine with four other atoms. The traditional method of depicting this structure is by means of a tetrahedron, with silicon at the center and the four vertices representing the atoms to which silicon is bonded, as shown on figure 3.

Viewing the tetrahedron from the top, as on figure 4, provides a different and more useful picture.

The dots in figures 3 and 4 represent atoms to which silicon, the circle, is bonded. The lines do not represent bonds, but merely show the tetrahedron formed by the bonded atoms around silicon. The bonds would appear as on figure 5.

In SiO_2 and the silicates, the bonded atoms are oxygen, which has a valence of two. This means that each of the oxygen atoms must be bonded to some other silicon atom besides the indicated silicon. As a result, the tetrahedra may be connected together through oxygen to form giant molecules, as shown on figure 6. Note that for each silicon atom, there are two oxygen atoms; thus, one may write SiO_2 to indicate the proportions of silicon and oxygen, but the molecule could contain far more than one silicon and two oxygen atoms. It would appear the oxygen atom above silicon and at the end of the chain on figure 6 is being neglected, but it is a member of another series of connected tetrahedra above those shown on the figure.

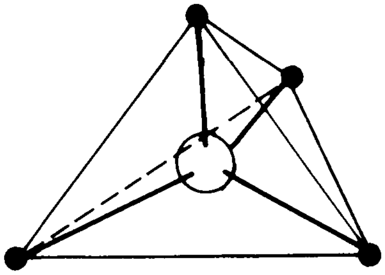


Figure 3. – Tetrahedral structure of silicon.

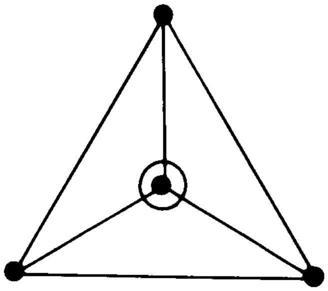


Figure 4. – Top view of tetrahedral structure of silicon.

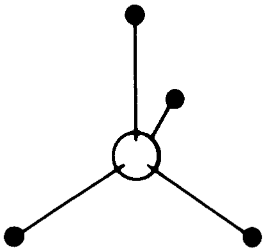


Figure 5. – Silicon bonds.

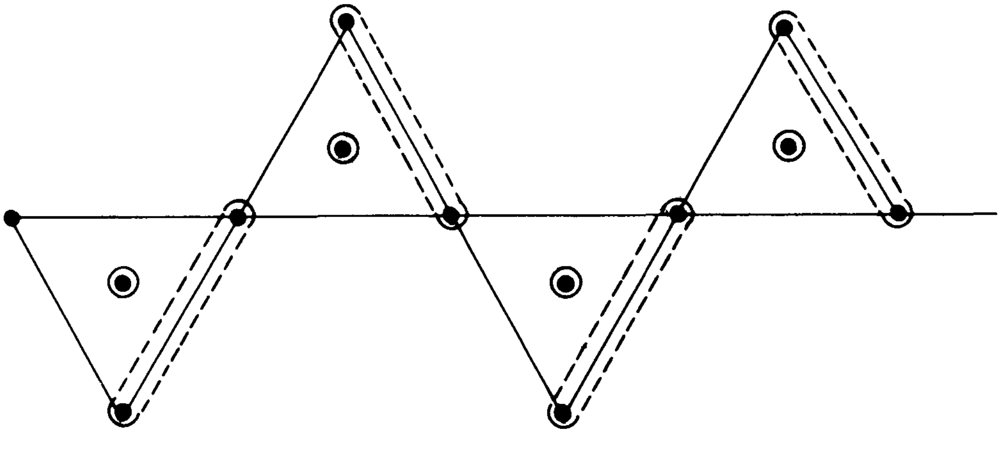


Figure 6. – Portion of a giant SiO_2 molecule.

The reader may wonder why there is such concern with silica when silicate grouts are formed from sodium silicate, a different compound. The answer is that sodium silicate is a derivative of silica and the behavior of silica explains much of what happens with sodium silicate.

It is said that silica can dissolve in water. However, it is well known that a sand composed largely of silica in the form of quartz is not very soluble. The extent of solubility is quite small at ordinary pH, about 6 or 7. Furthermore, the silica does not dissolve in the sense that SiO_2 molecules dissociate from the solid phase and distribute themselves in water, as would be the case for a compound like sugar. A reaction occurs that produces H_4SiO_4, silicic acid. The reaction is complex and not entirely understood. Without going into a more detailed description, that reaction is:

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4$$

However, since silica does not exist as discrete SiO_2 molecules, it is obvious that the given reaction does not reflect all that occurs. Nonetheless, the product is H_4SiO_4 and is referred to as silicic acid.

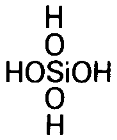
There are several crystalline forms of silica and an amorphous form that has no regular or crystalline form. Each of these forms dissolve to a different extent. Furthermore, there has been considerable disagreement as to extent of dissolution for the various structures. These differences are small and of no consequence in grouting. The form that will be of greatest interest to grouters is the amorphous form. Table 2 indicates a reasonable estimate in p/m (parts per million) [14].

It can be seen from table 2 that solubility is a function of pH. Above pH 10.6, dissolution is even greater. Solubility also increases with temperature. The presence of certain materials (mostly metal ions) in the case of soil-water can retard or increase solubility.

Silicic acid exists in the tetrahedral form previously shown. At each of the vertices there is a hydroxyl group (oxygen bonded to hydrogen). This is more easily shown by the following diagram:

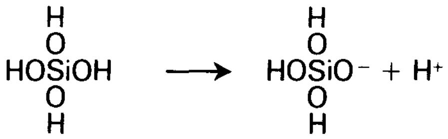
Table 2. – Solubility as a function of pH.

pH	Solubility, p/m
6 to 8	120
9.0	138
9.5	180
10.0	310
10.6	876



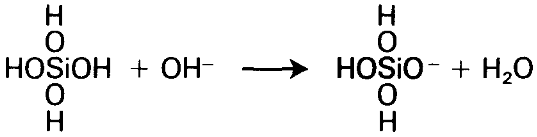
$$\mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{OH}$$

The hydrogens of silicic acid can become ionized:



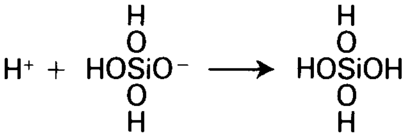
$$\mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{OH} \longrightarrow \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{O}^- + \mathrm{H}^+$$

This occurs in solutions with elevated pH or excess hydroxyl ion (OH^-) so that a more realistic equation would be:



$$\mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{OH} + \mathrm{OH}^- \longrightarrow \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{O}^- + \mathrm{H_2O}$$

In acid solution, the reverse occurs:

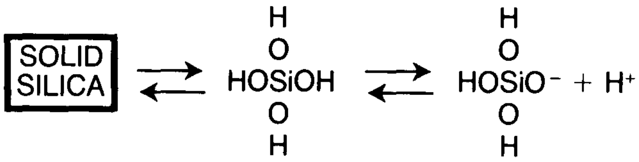


$$\mathrm{H}^+ + \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{O}^- \longrightarrow \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{OH}$$

The un-ionized form is witnessed by the fact that it will not migrate to the positive pole in an electric field and will not salt out with metal ions, as is true with ionized silicic acid.

The process of dissolution is shown on figure 7.

As the silica dissolves as H_4SiO_4, it further ionizes as indicated. As the temperature or pH is increased, the extent of dissolution increases.



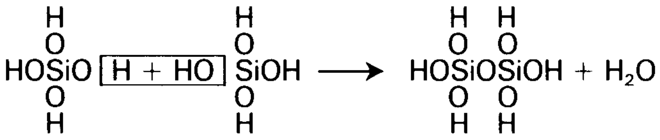
$$\boxed{\begin{array}{c}\text{SOLID}\\\text{SILICA}\end{array}} \rightleftarrows \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{OH} \rightleftarrows \mathrm{HO}\underset{\substack{\mathrm{O}\\\mathrm{H}}}{\overset{\substack{\mathrm{H}\\\mathrm{O}}}{\mathrm{Si}}}\mathrm{O}^- + \mathrm{H}^+$$

Figure 7. – Process of dissolution of solid silica.

At a given pH and temperature, the process continues until it reaches equilibrium. The rate of forward reaction equals the rate of the reverse reaction so that concentration of all species remains constant. Thus, at ordinary ambient temperatures for each pH, there is a specific amount of silica in solution. If concentration is below its equilibrium value, dissolution proceeds until equilibrium is reached.

If the pH is reversed (reduced) slowly, the dissolved silica will tend to deposit on the solid phase. Likewise, if the concentration is increased above its equilibrium value (by evaporation), the same thing occurs. Conceivably if temperatures were reduced, equilbrium concentration would also be reduced and, thereby, cause deposition. But at ordinary temperatures normal fluctuations would have only negligible effects.

In contrast, if no solid silica is present or if changes in pH, temperature, or concentration are made very rapidly, deposition on the solid cannot occur. Instead, silicic acid molecules react with one another.



$$\mathrm{HO\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{Si}}O}\boxed{\mathrm{H + HO}}\mathrm{\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{Si}}OH} \longrightarrow \mathrm{HO\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{Si}}O\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{Si}}OH} + H_2O$$

The dimer thus created can then react with itself or other silicic species. The conglomerates are of small proportions and remain suspended in solution. They are referred to as polysilicic acid or colloidal silica. Polysilicic acid can ionize by losing a hydrogen ion in the same way shown for silicic acid.

Pure silicic acid has never been isolated because any attempt to remove water and to concentrate the silicic acid results in the formation of polysilicic acid.

Metals can also be compounded with silicic acids. When this occurs, the grouping SiO_4 is found universally. Compounds with this grouping are called silicates.

At this point, it becomes convenient to introduce two terms commonly used in silicate chemistry. The symbol SiOH is referred to as a silanol group. The other three bonds of silicon indicate connection to other unspecified atoms. The SiOSi group is referred to as a siloxane bond. These are the bonds found in silica and the silicates.

This process of forming larger molecules from smaller ones essentially constitutes the well-known process of polymerization. However, the analogy with organic polymerization is not justified. There are considerable differences, as stated by Iler (p. 247 of [13]):

> "Because the most obvious behavior of a silicic acid solution is that it increases in viscosity and finally forms a gel, its polymerization was generally assumed to be an aggregation process or a polymerization by which smaller molecular units linked together into larger ones. The nucleation and growth of discrete particles prior to the stage where aggregation begins have not been recognized by many workers, who held to the idea that $Si(OH)_4$ polymerized into siloxane chains which then were branched and cross-linked as in many organic polymers. Even now attempts are still made to apply the idea of monomer functionality and condensation polymerization theory of organic chemistry to the silica system. In fact, there is no relation or analogy between silicic acid polymerized in an aqueous system and condensation-type organic polymers."

The key here is that particles are formed before silicate gelling takes place; whereas, organic polymerization proceeds directly from monomer units. Figure 8 shows how the process works:

The A branch on figure 8 indicates a silica solution in the pH 7 to 10 range after preparation with no metal ions present. It consists of a range of particles formed by the reaction:

$$\mathrm{SiO}\boxed{\mathrm{H + HO}}\mathrm{Si} \longrightarrow \mathrm{SiOSi} + \mathrm{H_2O}$$

The particles are essentially silica spheres whose outer surface contains unreacted silanol groups, as shown on figure 9. This occurs only if the silica has a concentration greater than its maximum solubility, roughly 100 p/m. Below 100 p/m, the silica is stable and has no tendency to aggregate.

In a pH 7 to 10 range, there is an excess of OH^- ions, which extract hydrogen:

$$\mathrm{SiOH} + \mathrm{OH^-} \longrightarrow \mathrm{SiO^-} + \mathrm{H_2O}$$

This creates negative sites on the surfaces and an overall charge develops on the particles so that they repel one another, but the unreacted silanol groups can still react with small molecular units. Thus, a dynamic sol is established wherein bonds are being made and broken, but the particles remain dispersed, and there is a distribution of particle sizes that eventually drift to larger more uniform sizes.

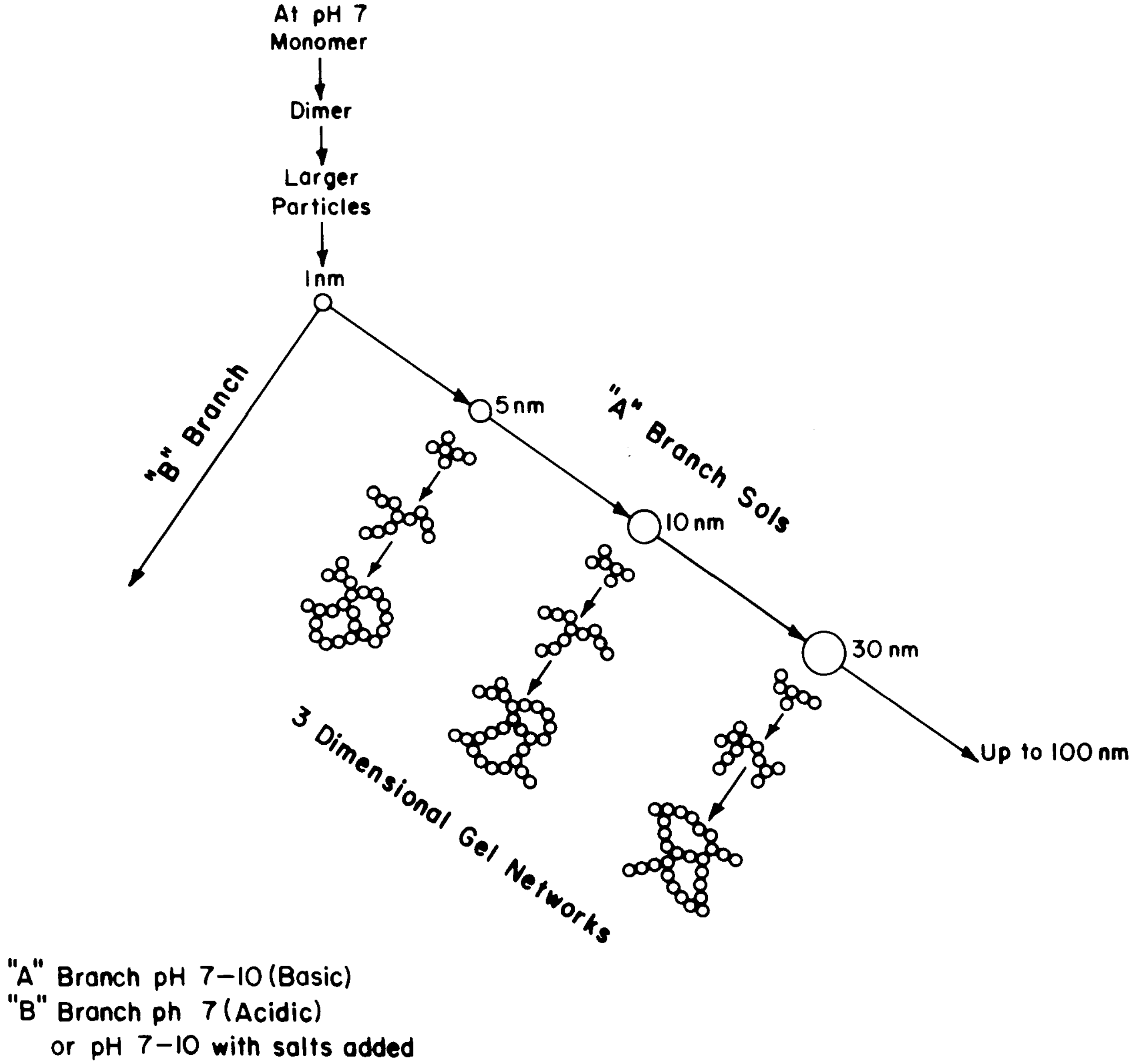


Figure 8. – Polymerization of silica.

Considering next the B branch, either of two possibilities may exist:

(1) pH < 7, meaning acid is added
(2) pH 7 to 10, with a metal salt added

Either of these processes result in gelling. The silica particles are joined together in loose chains that enclose water. See figure 10.

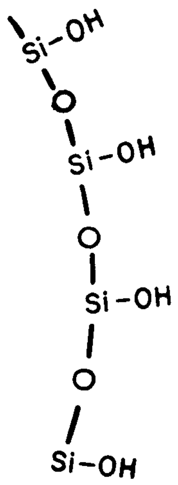


Figure 9. – Surface of a colloidal particle.

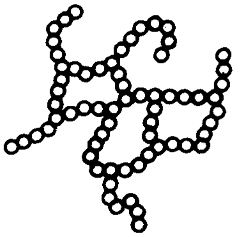


Figure 10. – Distribution of particles in a gel.

In the first case, by adding acid, an excess of hydrogen ion, H^+, is established and the negative sites are neutralized:

$$SiO^- + H^+ \longrightarrow SiOH$$

This reduces repulsion due to charge, and the large particles come together more readily to form siloxane bonds that hold the particles together. This is not a stable situation. After initial gelling, the process continues and the chains of particles form more and more siloxane bonds. This draws the chain particles closer to one another and forces water out of the bulk. The overall result is a particular type of shrinkage referred to as syneresis. The bulk of a gelled silicate grout may be reduced by as much as 80 percent through syneresis, depending on the concentration. Figure 11 shows the effects of syneresis. However, the sample shown was probably too dilute for grouting operations, and the syneresis was probably more severe than that in a normal grout.

The second case involves the addition of a metal salt. Almost any soluble salt of a metal ion such as calcium (Ca^{+2}), iron (Fe^{+3}), copper (Cu^{+2}), or aluminum (Al^{+3}) will cause what appears to be a gelling process. However, the processes involved are not entirely clear and the term coagulation

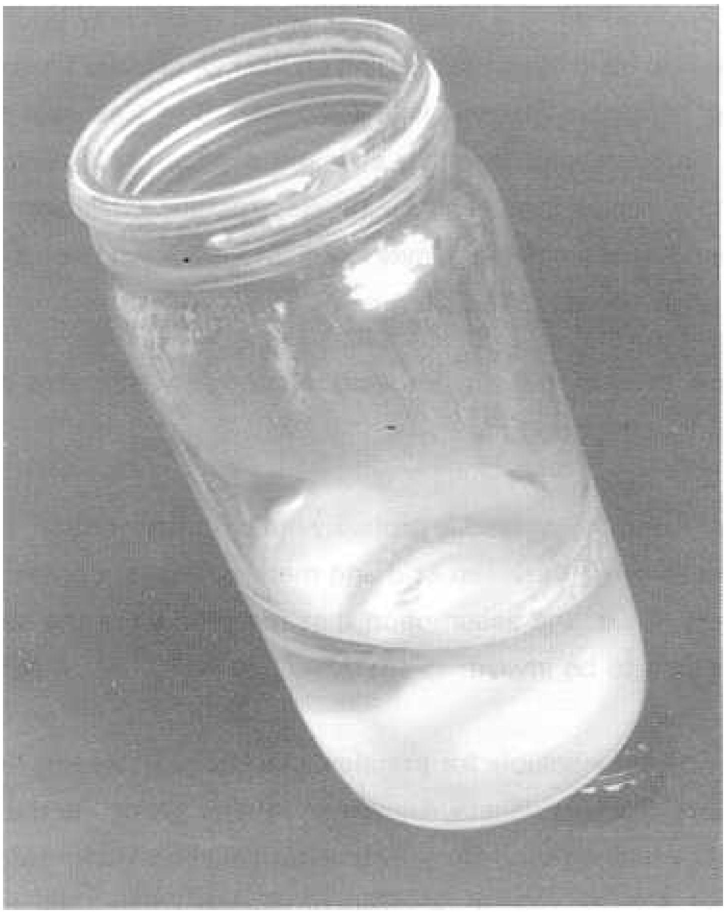


Figure 11. – Effects of syneresis. The solid silicate portion contracts leaving a supernatant liquid. P801–D–81032.

probably better describes this situation. Iler [13] classifies a silicate gel as one in which silicate particles hook together throughout the solution so that unless one considers an exceedingly small volume, there is no essential change in silicate concentration, and water is trapped and held between limbs of the network. Coagulation, in contrast, draws the particles together and results in a change of concentration of silicate particles at different points in the mix. To make the distinction clear, if acid is added to solution A equal in silicate concentration to solution B to which a metal salt is added, their behavior would be quite different. Solution A would solidify into a jelly-like substance throughout its volume and each portion would appear the same as any other portion. Solution B would aggregate into clumps that would settle. This difference would be noted only if the equal solutions were sufficiently dilute. On the other hand, if the concentrations were high enough, solution B would not show much evidence of settling and it would be difficult to distinguish gelling from coagulation.

The difference is that specific siloxane bonds are formed in the acid-treated gel; whereas, in the case where metal ions are added, the particles are drawn closer together by different mechanisms.

The type of bonding involved when a metal ion is added is still only poorly understood. Several types of bonding appear to be involved depending on mixing, pH, and ionic charge. In some cases, metal silicate bonding appears to be involved ($\equiv SiOMOSi\equiv$) at least to some extent where divalent ions such as Ca^{+2} are used. Another scenario depicts the hydrated ions as holding negatively charged silicate particles together through electrostatic attraction. Another hypothesis is that the added metal ion forms a polymeric hydroxide (this is known to occur) that holds the silicate particles together through Van der Waals forces.

There is good evidence for all of these hypotheses. However, which ones predominate as circumstances vary is not well understood.

In grouting, which mechanism is involved is probably not of much interest. The point of significance is that bonding is quite different between acid and metal salt gels. Consequently, one can expect behavior to be different. Thus, the assumption that the product is the same regardless of how gelling is obtained appears to be invalid.

Most silicate compounds are insoluble for practical purposes. However, two, sodium and potassium silicate, are soluble. Sodium silicate, known as "water glass," is the one normally used for grouting. It is prepared by heating sand (actually any form of silica, diatomaceous earth for example) with Na_2CO_3 at around 900 °C. CO_2 is released producing sodium silicate $Na_2O \cdot xSiO_2$ (with x depending on the ratio of Na_2CO_3 and SiO_2 used). Heated to 1200 to 1400 °C and poured slowly into water, the molten glass hardens and sinters and, upon rolling in a closed drum, it dissolves. The solution as usually prepared is viscous, but may be diluted to all concentrations. If not exposed to air, it will remain in solution indefinitely.

Water glass composition is customarily expressed as the ratio $Na_2O:SiO_2$. When dissolved in water, the solution is basic, depending on the ratio $Na_2O:SiO_2$. When the ratio is high, the glass is said to be alkaline; when the ratio is low, the glass is said to be acidic. Unfortunately, the ratio has been expressed in different orders, depending on the author. Consequently, care must be taken to ascertain which ratio is being used, $Na_2O:SiO_2$ or $SiO_2:NaO_2$. Diamond Shamrock, a major producer of sodium silicate, expresses a commonly used ratio 3.22:1, meaning $SiO_2:Na_2O$.

Again, it is necessary to be cautious about assigning a simple chemical formula to water glass. It is better to think of it as a mixture of polysilicic acids whose pH has been adjusted by addition of NaOH, and existing as particles as previously described for the B branch of figure 8. Gelling behavior described for additions of acid or metal salts indicates what is occurring in silicate grout systems.

Gelling of water glass is obtained in the same way as for dissolved silica. That is, acids or metal salts are added to obtain gelling. There are, however, some differences in behavior. Water glass has a large amount of sodium ion present. The sodium appears to be the cause of differences in behavior. The most notable difference is that gelling occurs at higher pH. Even though an acid is added to obtain gelling, the excess liquor is alkaline ($pH>7$). If a sand cylinder grouted with an acid-formed gel is placed in water, the water will become alkaline. Gels formed by adding metal salts are also alkaline.

Karol (p. 59 of [9]) states that sand cylinders formed with silicate grouts and placed in water become weakened and in some cases fall apart. He makes no statement, however, on how the grout was formed nor the concentrations involved.

In summary, there are two generalizations that seem to hold true. First, the presence of sodium causes gelling at a higher pH than for a pure polysilicic acid. Secondly, the literature gives evidence that decomposition occurs when the sodium is diluted with water.

Actually, neither acids nor metal salts are added directly to obtain gels. The reactions are so rapid that injection would be impossible. The earliest silicate grout process did indeed do this by means of a two-shot process called the Joosten method. In this method, sodium silicate was first injected followed by a second injection of a solution of calcium chloride ($CaCl_2$), a metal salt that brought about gelling. From the literature, it appears to have worked fairly well, but grout holes had to be placed very close together because the calcium solution would not travel far before gelling prevented movement. Ungrouted regions or holes were fairly common. Today, the Joosten process is hardly used, if at all.

In current practice, the acid or metal salt reactions are slowed or altered by processes that permit gel time control and one shot injection. Acids are not added directly; instead esters are used. Esters hydrolyze (react with water) slowly and release an acid slowly enough that gel time can be controlled. Terraset produced by Celtite, Inc., uses this process.

Metal salts are added along with formamide ($HCONH_2$) in a product called "Siroc" suggested by Diamond Shamrock, a producer of sodium silicate. They do not sell the other ingredients (either calcium chloride or sodium aluminate plus formamide); they merely give the formulation and sell the sodium silicate.

Undoubtedly, many variations could be developed and there are probably some that have not yet come to the attention of the author, but the two processes previously described (acid or metal salt) will be involved in some way.

There are several problems with silicate grouts. Probably the most striking is syneresis. This behavior can be quite alarming if one prepares an acid gel in pure form, such as that shown on figure 11. However, when injected into a porous soil in the laboratory, the effects of syneresis are not so readily apparent. All that is witnessed is a hardening of the sample over a period of several weeks to a month. The soil cannot shrink and the gel cannot migrate through the soil; therefore, syneresis appears to be toward the pore walls. Because much of the soil is silicious, bonding to soil particles is to be expected and explains the hardening. If the gel is essentially drawn to the walls of the soil pores, it would be expected that the permeability would increase.

Individuals active in silicate grouting or research have indicated in conversations that permeability does indeed increase after installation.

In summary, what appears to be a thoroughly unacceptable condition when observing the pure grout is not necessarily detrimental. If strength is a desired quality, the effects of syneresis appear to be slightly beneficial. The increase in permeability is not desirable, but several authors indicate that it may be acceptable, depending on requirements.

In the literature, the author has not discovered any distinction made between acid gels and metal salt gels. In the grouting industry, the final product appears to be considered the same regardless of reaction class. However, it is the author's opinion that there is considerable difference. This is based on the assumption that there is considerable difference between the bond strength and solubility of siloxane bonds and metal silicate bonds.

There is more than a theoretical assumption to support this contention. In experiments conducted by the author, two products demonstrate the difference at least in terms of syneresis: Terraset, an acid gel produced by Celtite, Inc., and Siroc 142, a metal ion gel or coagulant. Figure 12 shows the difference. Terraset underwent syneresis and reached its current appearance about 3 months after gelling. Siroc 142 remained essentially unchanged after more than 2 years.

The durability of silicate grouts seems to be in question among various participants in the grouting industry.

Baker, a competent grouting engineer, makes the following comment:

> "Silicate grouts may provide excellent waterproofing characteristics and low strength structural improvement for temporary works up to several months. They should not be considered to be permanent with a lifetime of several years, unless the particular silicate catalyst system has been shown to be permanent under the expected service conditions."

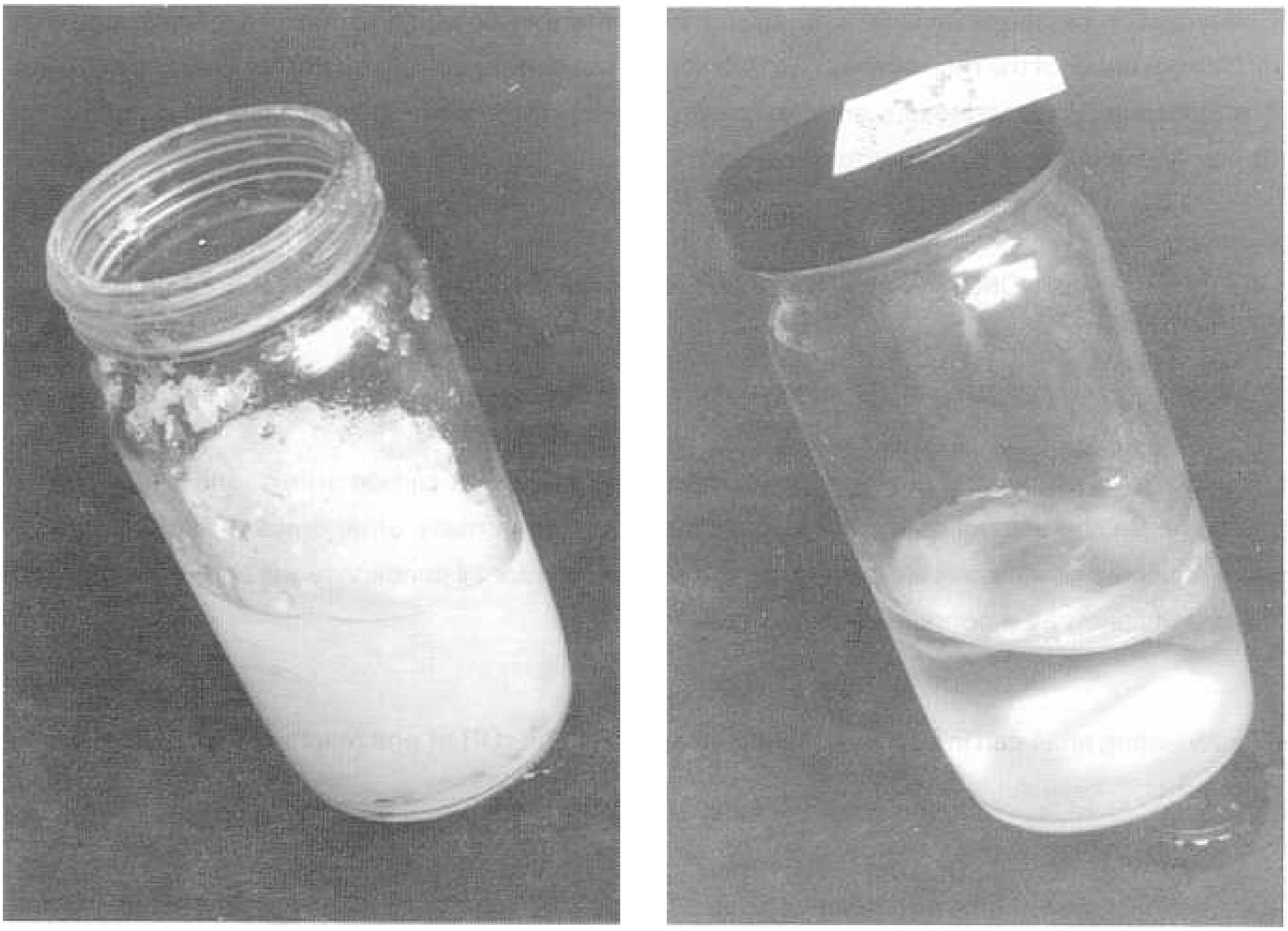


Figure 12. – Difference in syneresis effects. Left – an acid gel that displayed severe effects of syneresis within about 3 months. P801-D-80134. Right – Siroc 142, a metal ion gel that remained virtually unchanged for 2 years. P801-D-81033.

In contrast, Bowen [15] claims that silicate grouts excavated from under the Thames River in London had retained their properties after 20 years of service.

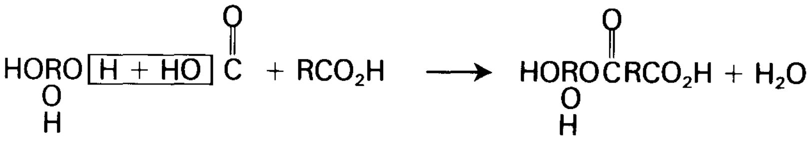
Organic Grouts

The term "organic grouts" has not been noted in the literature. This is a term coined by the author of this study. Polymer grouts would also have been a good description.

Regardless of the adjective to be used, the point of distinction is that organic gelling processes are quite different from those of silicates. Furthermore, organic polymerization is better understood and more predictable.

There are essentially two classes of polymerization: addition and condensation

Condensation reactions involve two unlike monomers that combine to form repeating units that differ from either of the monomers. This definition is not entirely complete, but for grouting activities it is sufficient. Polyacetate is a good example. These polymers are formed from the combination of a polyalcohol with a polycarboxylic acid.



$$\mathrm{HO}\underset{\underset{\mathrm{H}}{\mathrm{O}}}{\mathrm{R}}\mathrm{O}\boxed{\mathrm{H + HO}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}} + \mathrm{RCO_2H} \longrightarrow \mathrm{HO}\underset{\underset{\mathrm{H}}{\mathrm{O}}}{\mathrm{R}}\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{RCO_2H} + \mathrm{H_2O}$$

Alcohol + Carboxylic acid ⟶ Ester

"R" can be any organic grouping often composed of numerous carbon atoms, and it may not be the same for the alcohol as for the acid. In this case and in many other condensation reactions, water or some other molecule is released. This is not true for all condensations and is not required for classification as a condensation reaction.

The repeating units can in turn react with one another. The $^{-}$OH of one reacts with the CO_2H group of another.

If each monomer has only two reactive groups (OH or CO_2H in this case), straight chains are formed with no connections between them. At least some of the monomers must have three or more reactive groups. The alcohol shown above has three OH groups. It can form a side chain that could link to another chain at a point of trivalency. The result is that a three-dimensional network can be formed.

A three-dimensional network is essential for polymers used in grouting. Most polymers are very costly and so viscous that injection would be impossible except into relatively large voids. Thus, they are mixed with water to reduce viscosity and provide bulk. The water remains trapped in the chains of the network. Thus, low viscosity is obtained and cost is reduced, but at the expense of strength. If only straight chains were available and soluble in water, there would be nothing to hold them together.

The second type of polymerization is referred to as an addition reaction. All that was said regarding condensation polymers is true for addition reactions with several important exceptions. First, the monomers are the same. That is, there is no difference among reactants such as alcohol and carboxylic acids.

The addition reaction process is also quite different from the polymerization process. But this will not be discussed because it is rather involved and, more importantly, because the author has not encountered the use of such a polymer in grouting.

The most notable difference between silicate and organic grouts is that silicates go through a preliminary process in which spherical particles are formed from the monomer silicic acid. Gelling occurs when the particles hook together. In contrast, organic grouts are formed from single-molecule monomers.

Bonds between silicate particles are reversible, at least to some extent, as a function of pH. Furthermore, in the case where metal ions are used to obtain gelling, bonding is not entirely covalent. Instead, Van der Waals and electrostatic forces appear to be more prevalent. Such conditions invite instability. This is witnessed in syneresis and by the instability noted by at least some grouters. In contrast, the organic grouts form covalent bonds, which are more stable.

Shrinkage in organics occurs for altogether different reasons than the syneresis noted in silicates. Because organic grouts are networks that are more flexible and hold large amounts of water, several factors can cause the grout to shrink. The most obvious factor is evaporation. As water disappears, the chains are drawn together through attractive forces resulting in volume reduction. Furthermore, temperature can, in theory, cause considerable variation in volume. In addition, ground water carrying various ions can move into or out of the network. The degree of attraction to the polymer chains can also cause volume changes (p. 247 of [13]).

Desiccation is the greatest cause of shrinkage in organics. Shrinkage caused by other factors is small. Data published by manufacturers indicates that shrinkage is in the 5 to 7 percent range.

Desiccation of silicate grouts exposed to the atmosphere also occurs, and some shrinkage can be expected, but the reduction in volume is not so much as might be imagined. A rather fragile, crustlike framework remains. On the other hand, if not exposed to the atmosphere, shrinkage for the reasons cited for organics is minimal compared with syneresis, which is due to the ongoing reaction or instability of the gel.

COST OF CHEMICAL GROUTS

In this study, no deliberate effort has been made to determine the prices of chemical grouts. There has been some exposure to them in connection with other activities. Sodium silicate has been purchased at $95.00 per 55-gallon drum. Because it can be diluted about 1:1, or slightly more, the cost with other reagents would probably be in the range of $1.15 per gallon or possibly less for large volumes. Urethane grouts can run as high as $45.00 per gallon, although in the case studied, the producer claimed to be giving a discount. This of course sounds expensive, but the type of application can cause wide variation in cost. For soil grouting, dilution can be as high as 15:1 when urethanes are used. For cracks in concrete, neat urethane grout is usually pumped, but the material foams to varying degrees upon reaction with water. An expansion of twofold would probably be a minimum. The expansion plus the fact cracks involve relatively small volume makes the cost acceptable.

In summary, it suffices to say that chemical grouting is considerably more costly than cement grouting. This probably limits its use where large volumes are used. In one case where a chemical grout (AM9) was used in a dam foundation (not a Bureau dam), it was used as a supplement to cement grout. The Chinese have used urethanes to produce grout curtains for seepage problems following construction of dams. The Hayward Baker Company pumped a million gallons of silicate grout, but this was to stabilize soil during a subway excavation in Pittsburgh. These cases seem to represent the upper limit of usage. More commonly, chemical grouts are used in relatively low volume where cement cannot be used.

CURRENT BUREAU OF RECLAMATION USE OF CHEMICAL GROUTS

From the scant information available at this time, it appears that chemical grouts have been used by the Bureau of Reclamation from time to time, and this use is expected to continue. The technology is available, and there are contractors and consultants available to guide and assist in the work. However, there are a number of factors that discourage the use of chemical grouts.

The first problem is concerned with the acquisition of knowledge and experience with a range of chemical grouts. Ordinarily, one would simply refer to the literature, at least for starting information in an unfamiliar subject. However, the literature is a mix of information. Some of the literature is concerned with materials that have lost popularity for various reasons and are no longer available; some of it was not very informative to begin with; and some, mingled among this bulk, are very good works. Even with computerized literature searching, the task of acquiring the literature, digesting it, and separating the meaningful material from the other is very time consuming.

Alternatively, one could approach contractors or consultants without relying on the literature only to meet more confusion. As previously mentioned, the field is segmented and experience and materials used are varied so that it would be difficult for the novice to gain any clear picture or to make an informed decision among the various possibilities.

Much of this problem is a matter of organization and commitment of resources. As it stands, most work done in the regions remains isolated. There is a problem with lack of pooling of experiences or knowledge gained. Thus, knowledge over a broad range of chemical grouts is rarely achieved in any region or body within the Bureau. To change this would require a commitment of resources on a continuing basis, which has not consistently taken place.

Because there is little experience with chemical grouts in the Bureau, and because it is time consuming to establish experience on the subject, in the author's estimation there is usually a reluctance to use chemical grouts except as last resort. The fact that chemical grouts are expensive also discourages their use.

Lack of information does not seem to be restricted to the Bureau. At a recent ASTM meeting, a representative from an engineering consulting firm remarked to the group that his firm was specifying the use of grouts (not necessarily chemical), but had little understanding of what was taking place onsite.

Before embarking on a program of research on any subject, there should be a well-defined need for the results. In the author's opinion, the need or demand for chemical grouting was a questionable point. To establish the fact that there is indeed demand, a questionnaire letter was circulated among the regions. The text of the letter and the specific questions follow:

> In the research study of DF-22, several chemicals have been identified which appear to be promising for use in various grouting problems. This study will be more effective if possible applications can be identified. Assistance is requested to ensure that we are aware of as many uses as possible.
>
> Since it is generally assumed that the cost of chemical grouts restricts their use to cases where portland cement grouts cannot penetrate, a first step in determining where chemical grouts could possibly find use lies in determining where portland cement *cannot* be used.
>
> Please indicate on the attached questionnaire where cement grouts *cannot* be used to alleviate water seepage problems that you have experienced. Your prompt action in returning the questionnaire would be appreciated.

The following are examples of situations where some material other than portland cement might be used:

1. Foundation grouting of dams (use space for comments).
2. Postconstruction periods where seepage is occurring through soil or alluvial deposits from impounded water bodies as reservoirs or dams.
3. Seepage or flow through cracks or joints of a dam or other concrete structure.
4. Any other situation not mentioned above.

Twelve replies were received from the regions and from several sections in the E&R Center. The questions were interpreted widely. In several cases, the first three questions were not answered at all; the respondents made all remarks under the fourth question. Some answered the first, but were obviously referring to cases that would have more appropriately fallen under the second question. In several cases, the respondents seemed to be suggesting where research is needed as opposed to actual conditions requiring the use of something beyond portland cement grouts.

Response to the first question was mixed. Six respondents did not answer at all. Three cited cases where chemical grouts could have been used. One expressed concern regarding toxicity. Only one said that chemical grouts might be considered in upcoming construction.

The most striking feature was that no one cited a case where chemical grouts had been used. Three suspected where it might have been used in hindsight, and only one realized potential use and would at least consider chemical grouts for a project.

It must be concluded that the use of chemical grouts in construction of foundations has been virtually nonexistent. The possibility of using chemical grouts has been recognized in a few cases after consideration, but this has not led to its use.

From conversations with several individuals in the field of grouting, the author is aware that, at least in some cases, it is thought that if cement grouting during foundation construction does not reduce seepage entirely, the remaining seepage problem is not worth the expense of chemical grouting.

The second question drew more positive answers. Five respondents did not answer, and one claimed a preference only for very fine cement produced in Japan. The remaining six gave conditions where chemical grouts could be used in postconstruction remedial work. Of these six respondents, two named a total of 11 sites.

The conclusion for the second question must be that there is somewhat more awareness of potential use, but there was only limited indication of use; one case history was cited, Hart Butte Dam in 1954.

Response to the third question was the most decisive of all. Only one respondent said he knew of no cases where cement grouts could not be used. Another did not respond, but the question did not apply to his line of work. Of the remaining 10 respondents, 4 simply stated conditions where cement could not be used, 4 named nine specific sites where cement could not be used, and 2 named a total of five case histories where chemical grouts had been used to seal cracks. One of the respondents who named sites where cement could not be used also cited a case of chemical grouting that had failed.

It is also noteworthy that a pilot program to determine the effectiveness of a polyurethane grout produced by 3M Corporation has been initiated at Deadwood Dam in Idaho.

The conclusion must be that leaking cracks in cement draw more attention than other circumstances, and it is customary to attempt to seal them. This attention may be due to the greater visibility of the effects and the possible critical nature of the leakage. The efforts follow, because the volume requirements and costs are lower than those for soil and rock grouting.

The fourth question drew only limited response. Anchor bolts were mentioned twice and containment of oil leaks was also mentioned. No conclusions were drawn regarding the fourth question.

This survey cannot be regarded as entirely representative. Undoubtedly, not all previous cases of chemical grout use were known or reported by current personnel, and interpretation of the questions was varied. Nonetheless, it is reasonably clear that chemical grouts in soil and rock grouting are not used much within the Bureau. Although there seems to be a realistic demand for the sealing of cracks in all sorts of concrete structures (tunnels, pipes, dams, retaining walls, etc.) the use of chemical grouts was not widespread.

The experience of the author substantiates the survey. Individuals seeking information on grouts are often referred to the author's office. All inquiries thus far have been related to sealing cracks in concrete. There has never been an inquiry on chemical grouts for use in soil or rock grouting.

CONCLUSIONS

- With regard to the state of the art, the field of chemical grouting is well established. What is lacking are details on the various grouts. Details include case histories to provide an estimate of durability, limits on use caused by toxicity, prices, and physical and chemical characteristics that influence or limit use. Further knowledge and experience can be gained to the extent that chemical grouting is used by the Bureau.

- Use of chemical grouts has been restricted to applications where cheaper materials could not be used. Cheaper materials include cement grouts and, possibly, certain caulks or sealants. Use in dam foundations during construction has been very seldom. This is true for several reasons: cement grouts usually suffice, costs of chemical grouts are high, and the need for a chemical grout is not always recognized at the time of construction. The greatest demand for chemical grouts seems to arise in connection with visible leaks through concrete structures of all sorts: dams, tunnels, pipelines, retaining walls, etc. Soil grouting does not appear to be much in demand now, but there are indications that certain problems might be remedied through the use of soil chemical grouting. Such use can normally be expected as a corrective measure after construction. Silicate grouts are widely used to stabilize soils during excavation, but work in the Bureau does not involve such problems very often.

- There appears to be considerable misunderstanding on the durability of silicate grouts and on the differences among their various formulations. It is possible that much of this can be reduced through discussions with consultants in the chemical grouting field. In any event, a number of questions must be answered before informed use can be made of silicate grouts.

- Chemical grouts have been used in the Bureau but on a very limited scale. The causes appear to be lack of information and experience, absence of test facilities, and cost.

- It seems likely that underutilization of chemical grouts will continue unless there is a commitment of resources to remedy the underlying causes.

- The commitment of resources that would be necessary are:
  (1) Laboratory facilities and equipment for testing chemical grouts. Much of this is already available.
  (2) An individual assigned to keep abreast of the field of chemical grouting and to provide information and testing services for field personnel considering use of a chemical grout. Such duty would be in addition to other responsibilities.

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Mission of the Bureau of Reclamation

The Bureau of Reclamation of the U.S. Department of the Interior is responsible for the development and conservation of the Nation's water resources in the Western United States.

The Bureau's original purpose "to provide for the reclamation of arid and semiarid lands in the West" today covers a wide range of interrelated functions. These include providing municipal and industrial water supplies; hydroelectric power generation; irrigation water for agriculture; water quality improvement; flood control; river navigation; river regulation and control; fish and wildlife enhancement; outdoor recreation; and research on water-related design, construction, materials, atmospheric management, and wind and solar power.

Bureau programs most frequently are the result of close cooperation with the U.S. Congress, other Federal agencies, States, local governments, academic institutions, water-user organizations, and other concerned groups.