Engineering properties of silicate-R100 ester chemical grouts

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For the stabilisation of sands and sandy gravels around major excavations, shafts and tunnels, chemical grouting is an established engineering expedient for both soil impermeabilisation and strengthening. Many chemical systems are available and the environmental qualities of ‘one shot’ sodium silicate-based grouts, coupled with a versatile range of engineering properties, ensure their widespread use for ground improvement.

The objective of developing the silicate-R100 ester grout was that both chemical constituents would be produced by one supplier and as a result, Crosfield were able to provide a detailed quality manual for the grout, field test procedures, a fully equipped field laboratory, training of laboratory technicians, and the conduct of performance tests on production grout for quality assurance and regular auditing of site procedures to ensure that appropriate standards were maintained. This is considered to be a quite unique service and the overall package was designed to provide a high quality product in the most cost-effective way.

At London Underground's Jubilee Line Extension Contract 102, silicate-R100 ester grouts have been employed to reduce the residual permeability of the Terrace Gravels prior to the sinking of shafts and when tunnelling in close proximity to these gravels, and also to strengthen the gravels beneath foundations where appropriate. Further examples of ground water-tightening using Crosfield silicate based grout include the ABM bank, Amsterdam, the Netherlands; River Yare Crossing, Yarmouth, UK; the Susten Tunnel, Switzerland; and currently the WMATA Metro Extension, Washington DC, US.

Following an introduction to the manufacture of soluble silicates and their chemical and physical properties, the purpose of this paper is to describe the basic rheological and stiffening characteristics of silicate-R100 ester grouts, the unconfinied compressive strengths of silicate grouted fine sands and how such properties can be varied over a wide range by changing the proportions of silicate and hardener in the grout formulations.

Soluble silicates

Soluble silicates are inorganic and environmentally benign. When heated, they emit only water vapour. In effluent and surface waters, they rapidly disperse to form insoluble silica and soluble metal salts, similar to compounds which comprise a high percentage of the earth's crust.

Two processes are used for the manufacture of basic silicates, the furnace route and the hydrothermal process.

In the furnace route, a sodium silicate glass is produced which is then dissolved in water to form a solution. The glass is manufactured by the direct fusion of precisely measured proportions of silica sand and soda ash at a temperature of about 1400°C. This temperature is needed to ensure complete fusion, and low enough viscosity to ensure a continuous stream of molten glass from the furnace. The proportion of sand and soda ash fed into the furnace determines the molar ratio of silica to alkali in the glass product, which in turn influences the properties of the final solution.

The hydrothermal process involves the direct dissolution of sand in caustic soda, to produce a silicate solution in one precisely controlled step. The reaction takes place at elevated temperatures and pressures in specially designed autoclaves.

Silicate solutions made by either process can be mixed, diluted or concentrated in a computer controlled blending plant to give end products that satisfy application parameters such as molar ratio, density and viscosity. The use of specialised vacuum filtration techniques during manufacture ensures that silicate solutions are clear products, free from suspended solids and other sources of turbidity.

The nature of the application of sodium silicate in soil stabilisation places stringent demands on quality and consistency of supply. In the UK, sodium silicate should be manufactured in conformance with the quality assurance requirement of BS5750 PTII/ISO 9002.

Chemical and physical properties of sodium silicates

Sodium silicates are essentially combinations of an alkali metal oxide (sodium) and silica, usually with some water. The general formula is represented as:

\[ \times \text{SiO}_2 : \text{Na}_2\text{O} \]

where \( \times \) is the molar ratio (moles SiO_2/moles Na_2O).

The ratio of a silicate solution can also be expressed on a weight basis. For example, a silicate solution containing 36% SiO_2 and 18% Na_2O is said to have a weight ratio of 2:1. Since the molecular weights of Na_2O and SiO_2 are similar, the difference between weight and molar ratios for sodium silicate solutions is small and insignificant. For grouting applications, silicates with a molar or weight ratio greater than three are normally used, in order to obtain low viscosities and practical setting times.

For chemical grouting applications the sodium silicate is generally diluted and mixed with a hardener prior to injection. Once the grout has permeated the soil to be treated, its components react to form a silica gel matrix, filling the voids and bonding the soil particles together to achieve the desired improvement.

The properties of the grout are thus linked to the characteristics of the sodium silicate, which in turn are controlled by the proportions of its various constituents:

- \( \times \text{SiO}_2 \) content influences the mechanical properties of a gel, higher silica levels resulting in stronger gels;
- \( \times \text{Na}_2\text{O} \) is the constituent which is neutralised to cause gelation; and
- total solids content, i.e. \( \% \text{SiO}_2 + \% \text{Na}_2\text{O} \), controls the density and viscosity.

In the UK, the density of a sodium silicate solution is normally expressed in terms of degrees Tweddell, (°Tw), and in continental Europe in degrees Baumé (°Be). These parameters are related to specific gravity as follows:

\[
\begin{align*}
SG &= 1 + (°Tw/200) \\
SG &= 1.45 (145 - °Be)
\end{align*}
\]

A precise relationship exists between the density of a silicate solution and its solids content. For a known molar ratio, measurement of

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The diagram shows the viscosity of a silicate solution at 20°C as a function of the weight ratio of SiO_2 to Na_2O. The graph illustrates how the viscosity changes with varying molar ratios.
the density allows the solids content to be calculated directly.

The viscosity of a silicate solution is important because of its influence on ease of handling and the injection pressure required during a grouting operation. Viscosity is usually quoted in centipoise (cp) or millipascal seconds (mPa.s) and is influenced by weight ratio, total solids content and temperature as follows:

- $\text{SiO}_2: \text{Na}_2\text{O}$ ratio - viscosity increases as weight ratio increases for a given solids content
- total solids content - viscosity increases as solids increase for a constant weight ratio
- temperature - viscosity decreases as temperature increases.

Figure 1 shows the relationship between viscosity and weight ratio for solutions of constant solids at 20°C.

Figure 2 shows the relationship between viscosity and temperature for a number of standard grades of sodium silicate with a constant weight ratio of 3.3.

**Engineering properties of silicate-based chemical grouts**

Single shot silicate based grouts usually contain three main components, namely sodium silicate, a hardener and dilution water.

In UK grout formulations, the hardener is usually organic in nature and capable of producing strong gels. After dispersion in the silicate solution the hardener slowly hydrolyses and, after a predetermined time, causes the liquid to set in the form of a white mass of silica gel.

Injected as a low viscosity liquid, the grout permeates the soil and then solidifies in situ, conferring on the ground formation the required residual permeability and strength. The strength of the soil can be controlled over a wide range by modifying the proportions of silicate, dilution water and hardener in the grout.

When the nature of the ground has been assessed with particular reference to permeability and porosity, and the requirements of the ground treatment have been specified, e.g. residual permeability or strength, a number of factors have to be considered in the formulation of an appropriate silicate based grout. These include:

- initial grout viscosity and viscosity development with time;
- setting or gelling time of the grout;
- effect of temperature;
- degree of neutralisation of the gel;
- chemical composition of groundwater; and
- syneresis.

**Grout viscosity**

For a given temperature, the initial viscosity of a silicate grout depends on type of silicate used (weight ratio, total solids content %), the silicate/water ratio and amount of hardener used.

For a given grade of silicate and hardener, viscosity increases as the silicate : water ratio increases (ie as the grout becomes more silicate rich), and as the amount of hardener increases (ie as the degree of neutralisation increases, see below).

The initial viscosities of silicate grouts tend to lie in the range 2cP-30cP (see Table 1).

The rate of grout permeation into a soil is estimated using Darcy’s law, and assuming a Newtonian fluid, the flow is primarily a function of grout viscosity, soil permeability and grout injection pressure. In the UK injection pressures are normally carefully controlled to ensure permeation, and not hydrofracture, of the ground.

Figure 3 shows the relationship between injection pressure and soil permeability for a range of grout viscosities. The need to carefully control injection pressure, coupled with the inherent viscosity of a particular grout formulation, defines the range of soil permeabilities that can be treated satisfactorily with silicate. Typically the initial soil permeability range exploited by silicate grouting is $10^{-3}$m/s to $10^{-5}$m/s approximately (see Figure 4).
Setting time

The setting time of a grout is important as it often determines the time over which injection is possible. A typical viscosity profile is shown in Figure 5 where the setting time is taken as the time for the viscosity to reach 100 cP. For practical purposes, the time over which a grout can be injected is about 75-80% of the setting time. Clearly, grout formulations displaying very small viscosity increases during injection followed by a rapid gelation provide the greatest flexibility in practice. Figure 6 shows typical setting times at 20°C for different proportions of silicate and hardener.

The setting time depends on:
- **Nature of the silicate**: the lower the weight ratio the longer the setting time. Silicates with high solids concentrations will generally give rise to shorter setting times, assuming a constant degree of neutralisation.
- **Concentration of silicate in the grout**: at constant volumetric proportions of hardener, the setting time increases with increasing silicate levels. However, at a constant degree of neutralisation higher silicate levels result in shorter setting times.
- **Type of hardener used**: several different hardeners are commercially available, some of which have retarded setting times for use in hot tropical climes.
- **Concentration of hardener**: as the proportion of hardener in a grout formulation is increased the degree of neutralisation also increases and the setting time decreases.
- **Grout and soil temperatures**: the rate of reaction of hardener and silicate increases as the temperature increases and decreases as the temperature decreases, shortening and lengthening the setting time, respectively.
- **Nature of the soil**: acidity in the soil or ground water tends to shorten setting times while significant alkalinity tends to lengthen them. High levels of calcium or magnesium can cause premature gelation due to the formulation of highly insoluble silicate salts.

Effect of temperature

As the temperature decreases, the rate of hydrolysis of the traditional organic type of hardener decreases and so the setting time of a silicate group increases. Figure 7 illustrates the typical effect of temperature for a 40% silicate-5% R100 formulation.

Degree of neutralisation

After addition of the organic hardener to the silicate solution, a hydrolysis reaction slowly transforms the active components into diacids. These diacids then partially or completely neutralise the alkali component of the silicate resulting in the formation of the silica gel. The amount of alkali neutralised depends on the amount of hardener

![Figure 6. Typical setting times at 20°C of silicate - R100 ester grout.](image)

![Figure 7. Effect of temperature on setting time for a 40% silicate 5% R100.](image)

![Figure 8. % neutralisation for different proportions of sodium silicate 3.3 wt ratio and R100 ester hardener.](image)

![Figure 9. Syneresis of pure silicate - R100 ester gel samples tested after one month.](image)

![Figure 10. Variation of syneresis as a function of grain size; 60% silicate-ethylacetate gel (after Caron).](image)

![Figure 11. Particle size distribution of Leighton Buzzard sand (grade 14/25).](image)
added to the grout.

The concept of degree of neutralisation is extremely important as a number of properties of the treated soil, e.g., strength and durability, depend upon it.

For a given silicate concentration, increasing the degree of neutralisation by an increase in the level of hardener improves the strength of the treated soil.

In general terms, the greater the level of silicate in the grout then the harder will be the resulting silica gel and the stronger will be the treated soil. Low silicate levels, e.g., 20-30%, give rise to weak gels suitable only for waterproofing purposes under low hydraulic gradients. Higher silicate levels, e.g., 60-70%, give rise to high strength gels suitable for long-term strengthening applications.

The durability of the treated soil, in terms of resistance to ground-water, depends on the degree of neutralisation; more precisely, on the level of alkali left unneutralised.

The degree of neutralisation may be calculated from the following equation:

\[ \text{degree of neutralisation} = \frac{V_h \times S_g H \times 6200}{(V_s \times S_g S \times N_a) \times M_h} \]

where:
- \( V_h \) = volume of hardener (litres)
- \( S_g H \) = specific gravity of hardener (typically 1.0 to 1.10)
- \( V_s \) = volume of silicate (litres)
- \( S_g S \) = specific gravity of silicate (typically 1.35 to 1.40)
- \( N_a \) = weight % alkali (Na₂O) in silicate
- \( M_h \) = molecular weight of hardener (typically 160 to 180)

Most organic hardeners commercially available in the UK are mixtures having molecular weights in the range 160-180.

**Figure 8** illustrates the relationship above for a range of silicate and R100 hardener contents.

**Effect of ground water**

The presence of water and/or other materials in the ground can influence the performance of chemical grouts. The presence of significant levels of metal salts may result in reduced setting times and the degree of alkalinity or acidity in the soil may also respectively lengthen or shorten the expected gel time.

These factors should be taken into account when deciding on the most appropriate grout formulation for a particular situation. Tests can also be conducted under representative conditions in order to confirm acceptable grout characteristics.

**Syneresis**

Syneresis is a phenomenon that affects pure silica gels. It is the progressive extrusion of significant quantities of water by the gel. This loss of water leads to shrinkage and distortion of the gel structure. The degree of syneresis refers to the weight of water extruded from the gel expressed as a percentage of the initial weight of the gel sample.

Many factors contribute to the degree of syneresis observed for a particular gel, however, most important are the influence of silicate ratio, degree of neutralisation and the \( \text{SiO}_2 \) content of the grout formulation.

For a given silicate level and degree of neutralisation, syneresis decreases with increasing silicate ratio. Syneresis also reduces with increasing degree of neutralisation and increases with increasing level of silicate in the grout formulation, peaking at about 60% silicate by volume.

**Figure 9** shows the extent of syneresis observed on a series of gels based on Crosfield silicate (at levels from 20-70%) hardened by a typical commercial ester over the range 50-100% neutralisation.

It should be noted that the data referred to above were obtained for pure gels. Syneresis is much less apparent for silicate gels permeated into sands. The influence of soil grain size is shown in **Figure 10** (after Caron, 1975).

**Compressive strength of grouted sand**

In order to predict the compressive strength of treated ground and to compare the effects of different grout formulations, it is important to conduct tests on samples prepared under carefully controlled laboratory conditions. For the test results reported in this paper a uniform medium dense, medium sized Leighton Buzzard sand Type 14/25 (see **Figure 11**) was employed where the voids ratio attained was within the range 0.60 to 0.65. This sand has the following characteristics (SG = 2.66; emin = 0.51; emax = 0.84; D60 = 0.80mm; D10 = 0.48mm; coefficient of uniformity = 1.67).

**Figure 11** illustrates the permeation apparatus where the grout was injected by gravity displacement into saturated sand contained in stainless steel moulds, 38mm diameter and 300mm long, which could be split into two halves longitudinally to facilitate sample removal with minimal disturbance. The sand filled moulds were injected from the base at a low constant pressure to ensure permeation (relative density = 70%; injection pressure = 20kPa; rate of advance = 13 to 17mm/s). In addition, injection was only stopped when excess grout, equivalent to 120% of the pore volume had passed through the sample.

The unconfined compressive strength development characteristics of a typical grout formulation (30% silicate/6% R100 hardener) when used to consolidate this standard sand are shown in **Figure 12**. Presentation of this strength profile as a 'band' depicts the typical spread of results obtained under laboratory conditions (±20%) and should highlight to the specifier the need to build in an appropriate safety factor. The graph clearly shows the development of strength dur-
ing the early period (up to seven days) after which there is little change at an ambient temperature of 20°C. In such circumstances, seven day strength may be used as an acceptable criterion for comparing grout formulations (Figure 14). However, where unconfined compressive strength of permeated sand is specified in practice, it may be necessary to obtain 28-day strengths where temperatures are low (eg 10°C), because of the slower rate of hydrolysis.

Test data
To facilitate the design of grouted ground, general data are often required for grouts based on silicate levels ranging from 30-60% silicate and from 4-10% R100 hardener. "At a glance" summary charts defining degree of neutralisation, setting time and compressive strength as a function of grout composition are illustrated in Table 2. The Crystal 9AG silicate used to generate the test data was a standard 3.3 ratio product of density 75° Tw (SG = 1.375).

References

Acknowledgments
The authors wish to thank the Jubilee Line Extension Project and Balfour-Beatty AMEC Joint Venture for permission to publish this paper.