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Effect of Long-term Aggressive Environments on the Porosity and Permeability of Granular Materials Reinforced by Nanosilica and Sodium Silicate

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ABSTRACT: Colloidal nanosilica is a kind of new chemical grout materials for filling small pores of fine-grained soil. Compared to traditional sodium silicate material, the advantages and disadvantages of colloidal nanosilica should be studied. In this paper, laboratory tests were conducted to study pure gels and sand-gel mixtures of the two materials in terms of long-term volume stability. Samples of Fontainebleau sand injected by nanosilica and sodium silicate were conserved in dry air, water, salt solution and acid solution for 8 different time periods. The shrinkage of pure gels was measured firstly, and then the porosity and permeability were analyzed to evaluate the effectiveness of pore-filling in terms of types of material immersed environments and conserving times. The results show that pure gel of nanosilica is much more stable than pure gel of silicate sodium in all environments studied; from results of porosity, nanosilica does not has manifest advantages compared with sodium silicate; from results of permeability, nanosilica sand has more stable capacity of water-blocking in all environments.

KEYWORDS: Nanosilica, Sodium silicate, Shrinkage, Porosity, Permeability

1. INTRODUCTION

Soil reinforcement by chemical materials is among the most widely used techniques in civil engineering to improve the characteristics of soil (Cambefort 1977, Karol 1990). One of the main objectives of chemical reinforced soil is sealing land, minimize or completely stop seepage in and around existing structures by reducing the porosity and permeability (Karol 2003, Persoff 1999, Saiyouri 2011). Lots of studies on soil treatment with chemical binders have been published during the past years, including the method of treatment, the choice and development of materials etc. However, environmental factors should also be considered as the soil chemical materials maybe affected, while chemical material could affect the local ground atmosphere, the nontoxic chemical material needs to be developed (Hewlett 1983). Meanwhile, the local soil environment must be considered for choosing chemical binders for better application effects (Bakharev 2003, Bakharev 2004, Gaboriaud 1999, Hamouda 2014, Kristensen 1993).

The use of chemical pure solution to alter the physical properties of fine-grained soil has developed since 1950s. The most common materials are sodium silicate, acrylate, lignin, urethane and resin grouts, but it should be studied that which one is the ideal choice depends on the properties of permanence, penetrability, strength, safety, easy of handling, availability, and cost (Karol 1983). In general, sodium silicate grout is a typical defense against fast flows (Olaniyan 2011), but because of its sensitive setting time, low strength, durability concerns and shrinkage, it is unsuitable for providing permanent seepage barriers against high flow/high head conditions (Bruce 1997)..

In the early 90s, a new generation of chemical grout held the opinion that colloidal silica was a kind of product nontoxic to environment (Karol and Oka 2003, Noll 1993). This colloid composed of SiO_2 which are dispersed in an aqueous solution by electrostatic repulsion. The suspension becomes hard gel in the presence of electrolyte by reducing the soil's porosity and enhancing its properties. Unlike other chemical materials such as sodium silicates, colloidal silica in gel form is physically stable and exhibits no shrinkage or small shrinkage in a saturated environment (Bolisetti 2009 and Guefrech 2010). The physical-chemical properties and hydraulic properties after mixing with soil should be deeply studied and compared with traditional materials.

The gel stability of soils is not clear when they are exposed in natural media to aggressive conditions like atmosphere, acidity, ionic load in water, pollution, etc. (Brauns 2001, Tognonvi 2009, 2012) and the effect of filling the pores of the soil will also change. There are few studies about the stability of sand-binder in aggressive environments.

In this study, the stability of pure gel of new material (nanosilica) and traditional material (sodium silicate) was measured and compared in various environments. Then the porosity of sand-gel mixture was compared, which is a very important indicator for evaluating the effect of pore-filling. Finally, the permeability was measured; it is of significant interest to relate the permeabilities of gel mixed sand to parameters that control the development of microstructure. As a consequence, a variety of investigations have been carried out to elucidate possible relationships between pore structures and permeability in these materials (Bosl 1998, Dullien 1992). On the basis of the experiments, empirical relationships between characteristics of the media (e.g. permeability and porosity) can be established to study the filling effect of chemical binders in soil pore.

2. MATERIALS AND METHODS

2.1 Materials

Fontainebleau sand (FBS) which is a fine material silica (SiO_2>98%) was adopted. The grain size is between 50 μm and 400 μm (the same sand used by Muresan 2011). Its particle and bulk densities are 2600 kg/m^3 and 1450 kg/m^3 respectively. The internal friction angle is between 30 and 35°. The coefficient of curvature (Cc) is 1.09, and coefficient of uniformity (Cu) is 1.87.

The solution of colloidal silica is a kind of liquid composed of dispersed colloidal amorphous silica (SiO_2) diluted and mixed with a reagent. This reagent is generally a salt solution (NaCl solution used in this test) which causes the irreversible gelation of the solution. In this study, the nanosilica used is Levasil 300/30%. The main characteristics of Levasil 300/30% are given in Table 1.

The stability of colloidal silica according to pH and nature of the salt has been extensively experimental studied (Allen 1969, 1970; Depasse 1970, 1997, 1999; Iler 1979; Mlilonjic 1992). The work of (Iler 1979) presented the mechanism of coagulation of silica presence of monovalent and divalent cations such as sodium. Iler (1975) proposed the hypothesis of bonds formation between silica particles through cations. In an aqueous solution, water molecules are adsorbed against sodium by their oxygen atoms. Figure 1 shows coagulation of silica particles in presence of cations.

When sodium is adsorbed to the surface of a particle, the oxygen atoms of water molecules are replaced by those of the silanol groups. Thus, a direct bond between the silanol groups of silica particles is prepared by means of sodium (Figure 1). Several "points of contact" can form between particles and silica suspension begins to coagulate to form a solid and compact gel.

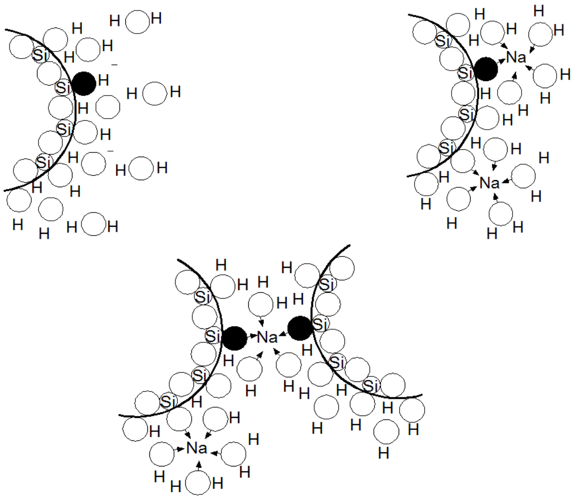


Figure 1 Coagulation of silica particles in the presence of cations: large circles are oxygen atoms (Guefrech 2010)

Table 1 Parameters of nanosilica-Levasil 300/30%

Physical and chemical properties	Descriptions and quantities
Density (kg/m^3)	1316
Size (diameter/nm)	12
Concentration (weight)	30%
pH	10
Charge de surface	anionique
Viscosity (mPa.s)	Max 7
Conductivity (mS/cm)	5.54

A traditional material-sodium silicate was also used in this study to compare with nanosilica. It is an alkaline, colloidal aqueous solution, when mixed with reagent solutions, the mixture changes in viscosity over time to produce a gel (U.S. Army Corps of Engineers 1995). The properties of sodium silicate were as Table 2.

Table 2 Properties of sodium silicate (Molecular ratio of 2.4)

Physical and chemical properties	Descriptions and quantities
Density (kg/m^3)	1336
Size (diameter/nm)	14.84
Molar ratio($Na_2O\cdot mSiO_2$)	3.3
Be'	36.3
pH	11.33
Viscosity (mPa.s)	78.9
Conductivity (mS/cm)	14.38

Sodium aluminate was used as hardener. The reaction equation is:

$$3(Na_2O \cdot nSiO_2) + Na_2O \cdot Al_2O_3 \rightarrow Al_2(SiO_3)_2 + 4Na_2O + 3(n-1)SiO_2 \qquad (1)$$

Actually, this kind of sodium silicate was chosen because it has the similar characteristics with nanosilica apparently: inorganic, true solution, low viscosity, method of grouting, nontoxic, friendly to environment etc.

2.2 Sample preparations and testing methods

2.2.1 Environments conditions

Four kinds of conservation environments were controlled (favorable or aggressive to the binders): for samples conserved in air, the relative humidity is 50%, actually, dry atmosphere might unfavorable to the stability of silica and silicate gel because of evaporation of water; for samples conserved in water, 15ml of water was added in the bottle after gelling, and this environment could be favorable because of humidity retention or unfavorable because of gel dissolves; for samples conserved in saline solution, NaCl solution concentration was 1g/L, and this environment was studied in case that ground soil reinforced by chemical binders perhaps immersed in seawater, chloride ion could be aggressive to binders; for samples conserved in acid solution, pH was adjusted to 4 by using sulfuric acid, and this case was for studying acid environments which were in contrast with the proprieties of alkaline gel. During these tests, the temperature of all the environments remains at 20 °C, while for water used in all solutions, distilled water was adopted.

2.2.2 Choice of binder formulas and preparation of gel

In order to compare the two kinds of binders in terms of volume stability, pore-filling effect and hydraulic properties, the option of formulas was based on the gel time and mechanic properties.

The gel time was fixed to 30 to 60 minutes, as noted bellow. The sand-gel mixtures were made to columns, and then the simple compression test was conducted to measure the compression resistance of all the columns. The NN1 was noted NN1 for formula1: nanosilica+NaCl (75g/L), while NN2 for formula2: nanosilica+NaCl (95g/L) and similarly SA1 for formula3: sodium silicate + sodium aluminate (3% by volume), SA2 for formula4: sodium silicate + sodium aluminate (4% by volume and SA3 for formula5: sodium silicate + sodium aluminate (5% by volume). The formulas NN1 and SA1 were chosen based on the same value of compression resistance, while the formulas NN2 and SA3 were chosen with the same value of compression resistance.

Preparation of the two kinds of binders as follows.

(1) For nanosilica

Sodium chloride-NaCl was used activate Levasil 300/30%. A constant volume ratio of 1/4 between saline solution and nanosilica was kept. Two concentrations of saline solutions were prepared to control the gelling time: 75g/L and 95g/L which were diluted by water. The choice of the two concentration of NaCl solution was depending on the mechanic properties and the setting time. The setting time was 60minutes (C_{NaCl}=75g/L) and 30 minutes (C_{NaCl}=75g/L) at 20°C respectively.

(2) For sodium silicate

Sodium aluminate was adopted as the hardener, 20% of mass was used to dilute sodium aluminate powder. The order of mixing should be firstly water (75-77% of total volume), then sodium silicate (20% of total volume) and the hardener (3-5% of total volume). A mixer was used with temperature adjustment to ensure complete mixing. The setting time was 75minutes ($V_{Aluminate}$=3% of total volume), 47 minutes ($V_{Aluminate}$=4% of total volume) and 25 minutes ($V_{Aluminate}$=5% of total volume) at 20°C respectively. The gelling time of sodium silicate is not easy to control and could be changed with the impact of the external environment, which is the reason that three formulas were chosen in this study.

2.2.3 Shrinkage of pure gel

Most of the silicate sodium gel will, upon standing, exude water and shrink (Yoshida 2001). This phenomenon is called syneresis and occurs at a decreasing rate. After gelation time, the gel network continues to reform, causing the gel strength to increase gradually.

As the system approaches equilibrium, the gel shrinks and expels the liquid it contains (Dhafeeri 2008). The first systematic investigation of such syneresis in silicic acid gels by (Holmes et al. 1919). Brinker and Scherer (1990) discussed syneresis and the factors affecting it in detail from the literature. They found that syneresis is generally attributed to the formation of new bonds (siloxane bonds) during gel development by condensation of two silanol groups (–Si–OH). Gel shrinkage occurs because the siloxane bond formed takes less space than the two individual silanol groups from which it derived. Ferguson and Applebey (1930), who studied the kinetics of silicic acid gels and found that the more rapidly the gel sets, the larger are the initial syneresis rate and the volume of expelled liquid.

Syneresis also takes place in the voids of stabilized soil masses. Generally, in soil whose voids were completely filled with new gel, the shrinkage accompanying syneresis results in an increase in residual permeability after several weeks.

The samples were kept in an environment of 20 °C. The volume of the storage bottle is 40ml. We putted 20ml of gel in each bottle (see Figure 2(a)).

Eight periods of 1, 3, 7, 15, 30, 90, 180 and 365 days were set to measure the values of shrinkage rate (Figure 2).

(a) Initial state; (b) Progressive volumetric shrinkage; (c) Cracks after 3 months

Figure 2 Shrinkage and crack of pure gel

The original volume (V_0) of gel sample was measured firstly in the initial time, and then a volume (V_1) at a time point was measured. The volume of gel was measured with a cathetometer and the shrinkage rate (φ) is:

$$\varphi = \frac{V_0 - V_1}{V_0} \times 100\% \tag{2}$$

2.2.4 Porosity test sand-binder mixture

After learning the volume stability of pure gel, the porosity of sand-gel mixture was further measured to see whether the syneresis phenomenon was the same as pure gel. The porosity of sample is a measurement of how much of its volume is pore space, expressed as a percentage of the sample's total volume. By learning the porosity, we can see how much is the syneresis of the binder when mixed with sand and how this phenomenon affects the pore-filling result.

There are at least 4 common methods of measuring porosity: Buoyancy, Helium porosimetry, Fluid saturation and Mercury porosimetry (ASTM 2011). According to our sand-binder mixture characteristic (low mechanical resistance, granular material), vacuum saturation method was adopted to measure the porosity.

Firstly, the volume of binder was calculated: The original density of FBS was 1450kg/m^3, the original porosity of FBS was 0.44. The proportion of the pore filling is 25% by volume: 3.32ml of gel mixed with 43.5g of sand, making the same sample volume of 30 ml.

After preparing these formulas of binders, 5 minutes should be waited before the setting time, and then the binders were mixed with sand by a mixer. The columns are prepared by successive layers of 1 cm height are groomed successively. The tamping is performed by dropping a circular with weight of 120g to obtain a uniform density of 1600kg/m^3 at each level (see as Figure 3). The porosity of sand-gel mixture was 0.3293 before immersed in environments for periods.

Then samples were conserved in four environments: Air, water, saline solution and acid solution (Figure 3). The size of each sample-storage bottle was: 10cm high by 2.6cm diameter. The material of storage bottles for containing the samples was Teflon, which did not react with our materials.

The porosity n is a fraction of the volume of voids over the total volume:

$$n = \frac{V_p}{V_t} \tag{3}$$

The total volume of all the samples remained at 30ml.

The volume of the pore space (V_p) was measured by vacuum saturation method:

(1) For samples conserved in air, they were saturated with pure water with vacuum pump (Figure 4) and weighed by balance to get M_1, then dried in the dryer at 80° temperature during 48 hour (Figure 4) and weighed by balance to gel M_2, the masse difference before and after drying (M_1-M_2) is noted as ΔM, V_p is calculated as: $\Delta M / D_{solution}$, in which $D_{solution}$ is the density of solution.

(2) For samples conserved in solutions, they were dried in the dryer at 80° temperature during 48 hour (Figure 4) and weighed by balance, the masse difference before and after drying is noted as ΔM, V_p is calculated as: $\Delta M / D_{solution}$, where $D_{solution}$ is the density of solution.

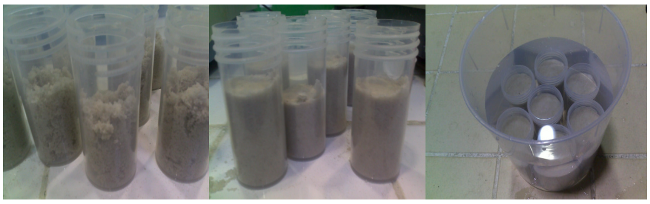


Figure 3 Sample preparation and conservation

Figure 4 Drying chamber of $80°C$ and vacuum pump

2.2.5 Permeability test sand-binder mixture

Porosity and permeability are related properties, the permeability is a measurement of how easily liquid flows through a material (Beard 1973, Ghrieb 2014). The porosity and permeability are two primary factors that limit the movement and the amount of water retained in the sand-binder mixture. The permeability is a very important indicator to evaluate the soil combination effect and to estimate the anti-seepage effect after using the chemical material.

As the permeability of our sand (2.85×10^{-3} cm/s) is larger than 10^{-4}cm/s, constant head test method was adopted to measure the hydraulic conductivity (ASTM 2006, Katz 1986, Tidwell 1997).

The preparation of samples was as same as the test of porosity, while the size of sample was 5.2cm of the diameter and 10cm in height. The columns were prepared by successive layers of 2cm after compaction. The compaction was done by dropping a circular with mass of 256.5g to obtain a homogeneous density of 1600kg/m^3 at each level. The material of sample molds and storage bottles for containing the samples was Teflon, which did not react with our materials, and a thin layer of silicone was coated on the inner wall of mold.

Then the columns were stored in four different environments: a dry atmosphere (50% of humidity), water, saline solution and acid solution. The preservation time is 1, 7, 15, 30, 90, 180 days before each measurement the permeability.

The system of measuring permeability was showed as Figure 5. Opening the inlet valve slightly for the first run to conditions that the flow in steady state was with no changes in hydraulic gradient, delayed measurements of quantity of flow and heat until a stable head condition without appreciable drift in water manometer levels was attained.

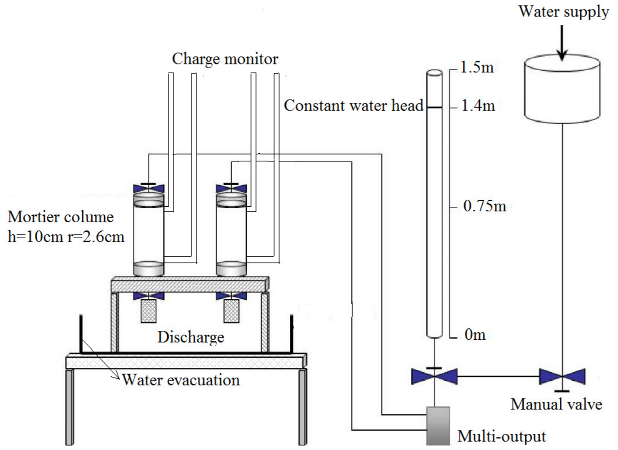


Figure 5 Schematic of permeability test equipment

Then measure and record the time-t, head-h (the difference in level in the manometers), quantity of flow-Q and water temperature-T. Repeated test runs at heads increasing by 0.5 cm in order to establish accurately the region of laminar flow with velocity-v (where v = Q/At), directly proportional to hydraulic gradient-i (where i = h/L). When departures from the linear relation became apparent, indicating the initiation of turbulent flow conditions, 1-cm intervals of head might be used to carry the test run sufficiently along in the region of turbulent flow to define this region if it was significant for field conditions. At the completion of the permeability test, drain the specimen and inspect it to establish whether it was essentially homogeneous and isotropic in character. Any light and dark alternating horizontal streaks or layers are evidence of segregation of fines. The coefficient of permeability k was then calculated, the results were given in terms of intrinsic permeability expressed in m^2 as follows:

$$k = \frac{Q \cdot L \cdot \mu}{A \cdot t \cdot h \cdot \rho \cdot g} \qquad (4)$$

Where:

K is the coefficient of intrinsic permeability,
Q is the quantity of water discharged,
L is the distance between manometers,
A is the cross-sectional area of specimen,
t in the total time of discharge,
h is the difference in head on manometers,
μ is the dynamic viscosity of water at 20° C, μ water=10^{-3}Pa.S,
ρ is the density of the fluid (kg/m^3),
g is the acceleration due to gravity (m/s^2).

2.3 Results and Discussions

2.3.1 Shrinkage of pure gel

The shrinkage rate of the same formula in different environments is analyzed (Figure 6-7 and Figure 8-10). The shrinkage rate of all the formulas conserved after 365 days is also analyzed (Figure 11).

The volume shrinkage rate of nanosilica pure gel hardened by NaCl solution (75g/L) in four environments for one year is shown in Figure 6. Generally, the shrinkage rate of nanosilica is very small (no more than 1.5% of total volume of pure gel), nanosilica can be defined as a very stable binder from point view of volume stability.

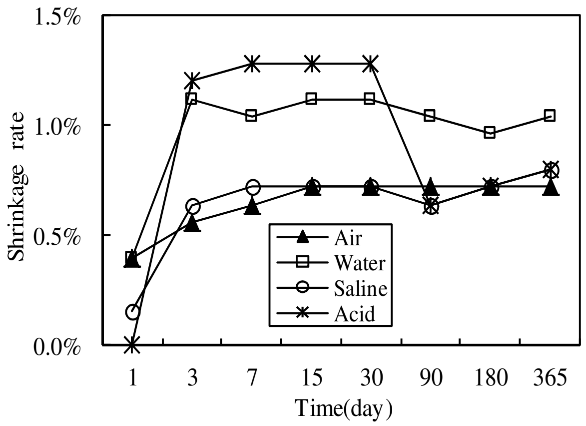


Figure 6 Shrinkage rate of the pure gels of nanosilica hardened by NaCl solution (75g/L of concentration)

Firstly, the shrinkage of gel in each environment is analyzed with time passing. The shrinkage rate increases greatly in the first 3 days, during this period, the gel is not stable yet, when exposed to these four different medias, certain degree of loss and damage take place, the greatest shrinkage of gel is in the acid solution, following by the environment of water, the shrinkages of gel in salt environment and in dry air are much smaller than the other two environments. From 3 to 30 days, the shrinkage process tends to very slow four all the environments. The gel in air, water and saline solution keeps stable after 30 days, while volume expansion happens in acid solution instead of shrinkage. The phenomenon of volume expansion of gel in acid conserving solution can be explained by the reaction between gel and solution, large amount of hydrogen ions surrounds the gel particles and reverses the reaction, and this phenomenon should be considered when used as grout material.

Secondly, in terms of different environments, the maximum syneresis is the case of immersed in acid solution (about 1.3% of total volume of pure gel column), following by environment of water (about 1.1% of total volume), the shrinkages of gel in salty solution and dry air are similar (about 0.7% of total volume of pure gel column). From point view of volume stability, this formula of nanosilica hardened by NaCl solution (75g/L of concentration) has the ability of resistance to different environments with the following order: Air > Saline solution > Water > Acid solution.

Figure 7 shows the syneresis of pure gel of nanosilica hardened by NaCl solution (95g/L) in four environments for one year.

The shrinkage rate of nanosilica is also very small (no more than 2.0% of total volume of pure gel), nanosilica can be defined as a very stable binder from point view of volume stability. Comparing the two formulas, we can see that with the increase of concentration of NaCl solution, the shrinkage rate increases, gel becomes more plastic. The choice of concentration of hardener and its proportion should depend on the request of gel time and subsequent stability. The maximum shrinkage occurs in saline solution, which is different from formula of nanosilica hardened by NaCl solution (75g/L). With the increase of concentration of hardener (NaCl solution), the volume stability of gel in salty solution is worse, this effluence is significant, even more than the change of environments.

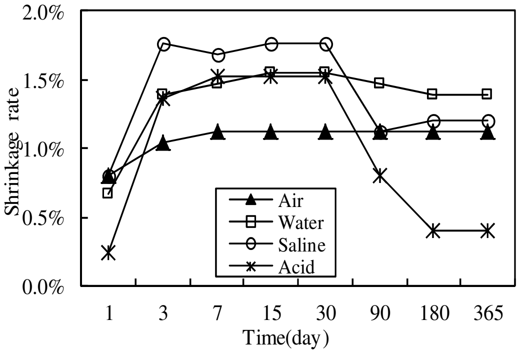


Figure 7 Shrinkage rate of the pure gels of nanosilica hardened by NaCl solution(95g/L of concentration)

The shrinkage rate increases greatly in the first 3 days, same as formula of case (NaCl solution of 75g/L as the hardener). After this period, the pure gel kept in air and water did not shrink, which meant this kind of gel was stable in air and water, no matter what concentration of hardener was adopted.

The gel volume expanses in the saline and acid conserving solutions after 30 days, the most extent of expansion occurs in the acid solution. For these two environments, the phenomenon of volume expansion of gel can be explained by the reaction between gel and solution, large amount of hydrogen ions surrounds the gel particles and reverses the reaction, and also excess amount of sodium ions makes the coagulation reverse. After long-term immersion in aggressive environments, the gel loses its effect and gradually deteriorates. This result should be considered when it is used as pore filling material.

The Shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (3% of total volume) in four environments during 1 year is shown in Figure 8

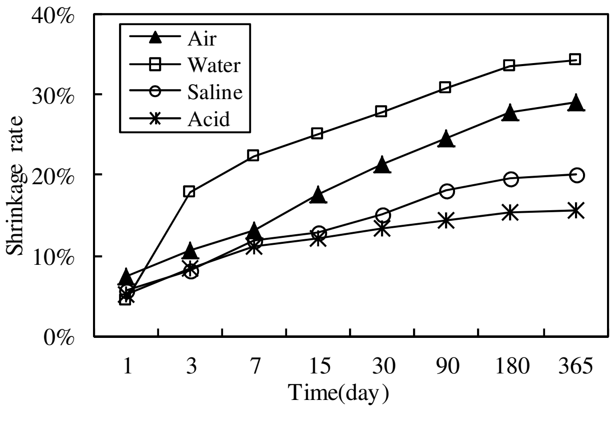


Figure 8 Shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (3% of total volume)

Compared with nanosilica, the syneresis of sodium silicate is much greater than nanosilica, the maximum shrinkage value of formula SA1 is 35% of total volume of pure gel column, 15 times more than formulas of nanosilica, the volume of SA1 gel after 1 year's conservation remains only 2/3 of original volume, this result is very important during the usage of pore filling. It is obvious that sodium silicate is much less stable than nanosilica, and from this point of view, nanosilica has its absolute advantage.

The shrinkage of SA1 in all the environments develops gradually from 1 day to 365 days. Unlike nanosilica, it does not exist phenomenon of volume expansion.

After 1 day's conservation, the volume shrinkage of SA1 in all environments arrives about 5% of total volume, this value is already bigger than the total value of nanosilica. In the first 7 days, SA1 in air, saline and acid solution shrink had a similar value, while gel immersed in water shrinks had a much greater value. After 7 days, SA1 in water remains its greatest value of shrinkage, SA1 in air shrinks less than in water but more than in environments saline and acid. After 30 days, SA1 in water and in air has the same rate of shrinkage, following by the case of salty environment, while SA1 in acide solution has the smallest shrinkage rate. After 180 days' conservation, SA1 in four environments tends to stop shrink.

Shrinkage rate of SA1 in four environments after 365 days' immersion in descending order is Water > Air > Saline solution > Acid solution.

Figure 9 shows the shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (4% of total volume) in four environments during 1 year.

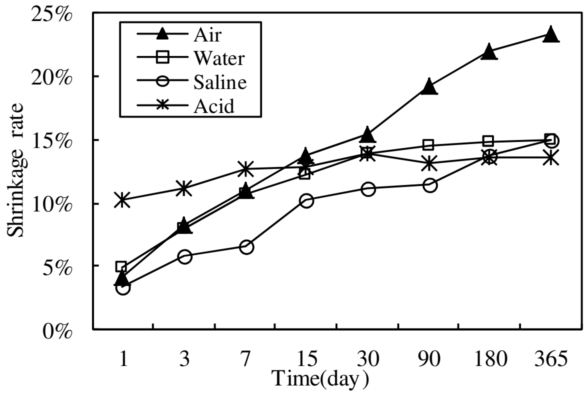


Figure 9 Shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (4% of total volume)

The maximum syneresis occurs in the case of air, reaching 23% of total volume, and the shrinkage does not stop after 365 days, this phenomenon can be explained by evaporation of water and dry cracking in dry atmosphere. In other three environments, the maximum syneresis is about 12.5% in volume. The syneresis tends to stop after 90 days in case of water and acid environments, while the syneresis tends to stop after 180 days in case of saline environment. Comparing with the pure gel of sodium silicate hardened by sodium aluminate (3% of total volume), the syneresis is much smaller. When immersed in air water solution, the two formulas (3% aluminate and 4% aluminate) exhibit completely different behaviors. When the quantity of sodium aluminate is 3% of total volume, sodium silicate is not perfectly hardened, after the gel is immersed in water, it dissolves in water, the failure phenomenon does not occur in saline solution and acid solution, this can be explained by the interference ions Na^+, Cl^+ and H^+.

As shown in Figure 10, the Shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (3% of total volume) in different environments seems similar during the observation time. The maximum shrinkage occurs in acid solution which is different from the other two formulas

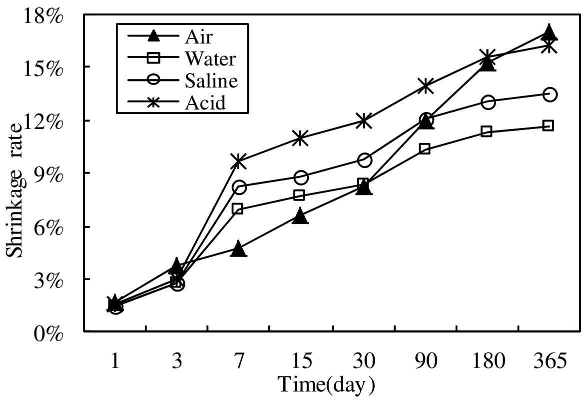


Figure 10 Shrinkage rate of pure gels of sodium silicate hardened by sodium aluminate (5% of total volume)

This can be explained by the increase of amount of sodium aluminate in this formula, as the pH of sodium aluminate (14) is bigger than sodium silicate (11.33), the more quantity that sodium aluminate used, the more fragile the gel becomes when immersed in acid solution. Generally, with the increase of sodium aluminate, the shrinkage rate is smaller in all the environments, the maximum shrinkage rate of this formula is about 17% of total volume of pure gel column.

From Figure 6-10, we can summarize the volume stability of all the formulas as following:

It is manifest that the syneresis of nanosilica is much smaller than sodium silicate in all environments, the characteristic of constant volume is an absolute advantage for grout materials, especially for the objective of filling pore and anti-seepage. For nanosilica, with increase of NaCl concentration, the shrinkage increases slightly. Conversely, for sodium silicate, with the increase of the sodium aluminate, the shrinkage is smaller.

In dry atmosphere, the syneresis tends to stop of formula NN1, NN2 and SA1. For formulas SA2 and SA3, the gel keeps shrink even after 365 days.

Compared with dry atmosphere, the differences of shrinkage rate of formulas of sodium silicate become greater when immersed in water. That is because, in addition of syneresis of gel itself, the interference of water dilution and dissolution also affect the results.

For all formulas in saline solution, the syneresis tends to stop after 180 days. For nanosilica, with increase of NaCl concentration, the shrinkage is slightly larger for the first 90 days, and then the syneresis of the two nanosilica formulas tends to stop. For silicate, formula SA1--sodium silicate + sodium aluminate (3% by volume) has a greater value of syneresis, formulas SA2 and SA3 have similar syneresis rate after 7days.

The difference of shrinkage rate of sodium silicate hardened by sodium aluminate in acid solution is smaller than in other environments after 7 days. This can be explained by the reaction between gel and acid solution, no matter how much the amount of sodium aluminate used, the effluence of chemical reaction makes syneresis of all gels to converge. For all the formula, the syneresis tends to stop after 180 days. Gel of nanosilica and gel of sodium silicate both behave instable in acid solution, but generally, nanosilica is much more stable than sodium silicate.

After 365 days, the shrinkage rate of all formulas is summarized in Figure 11.

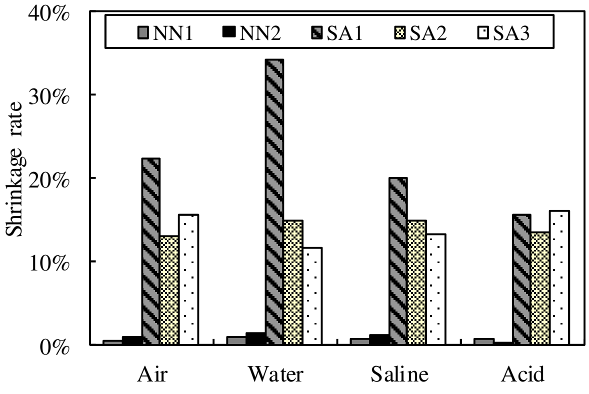


Figure 11 Shrinkage rate of pure gels after 365 days' immersion in four environments

It is shown that the syneresis of nanosilica is much smaller than sodium silicate in all environments after long-term immersion, and nanosilica gel is much more stable than sodium silicate gel. This property is very important when the gels are used in soil as pore filling material. For nanosilica gel, the final shrinkage of NN2 is slightly bigger than NN1 in environments air, water and salty solution after 1 year, while the final shrinkage of NN1 is a little more than NN2 in acid solution after 1 year. For sodium silicate gel, after immersed in pure water and salty solutions during 365 days, with the increase of quantity of sodium aluminate, the shrinkage rate is smaller. However, the cases in air and in acid solution are different. In dry atmosphere, formula SA1 has the greatest shrinkage, following by SA3, and formula SA2 has the smallest shrinkage. In acid environment, formula SA3 has the greatest shrinkage, following by SA1, and formula SA2 has the smallest shrinkage, but the shrinkage difference between the three formulas in acid solution is very small.

The syneresis of gel is depending on the temperature, concentration of nanosilica and sodium silicate, particle size of gel, gel volume, bonding at the gel-matrix interface, hydrogen ion concentration, sodium ion concentration, pH etc. (Jeffris 1995). The difference of syneresis between nanosilica gel and sodium silicate gel is a result of combination of these factors.

The shrinkage was measured by pure gel; the results can be a reference to learn more about the physical properties of the gel. After injection or mixing with soil, the phenomenon may be different. From the following two sections, we study the physical and hydraulic properties of sand-binder mixtures from aspect of porosity and permeability.

2.3.2 Porosity of sand-binder mixture

The porosity of the same formula in different environments was showed in figure 12-13 and figure 14-16. The porosity of all the formulas conserved in four environments after 365 days is also summarized and analyzed (Figure 17).

Figure 12 shows the monitoring of porosity of sand samples mixed with nanosilica hardened by NaCl solution (75g/L of concentration). The amount of gel used is 25% of the pore volume, but the testing result shows that the filling percentage cannot arrive 25% of the pore volume.

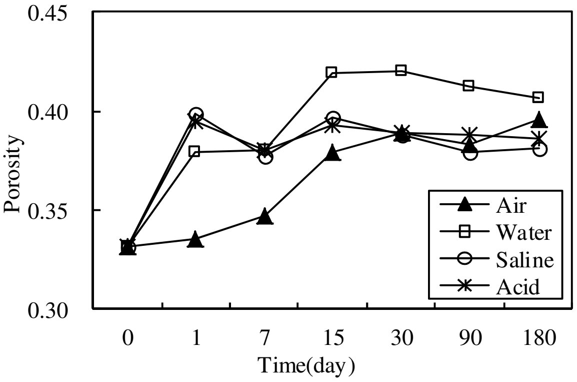


Figure 12 Porosity of sand samples mixed with nanosilica hardened by NaCl solution(75g/L of concentration)

After the samples were immersed for 1 day, the porosity of sample in air increases a little, but the porosity in the liquid solutions increases significantly, this can be explained by the instability of gel, the gel has been dissolved by the solution with a large part. After samples immersed for 7 day, the porosity of sample in air is little bigger than samples for 1 day, but the samples immersed in solutions for 7 days seem more stable, the porosity is smaller than samples for 1 day. From 7 days to 15 days, the porosity increases for all the immersed conditions, that indicates the shrinkage of gel or the loss of effectiveness of partial gel. After 15 days, the porosity of formulas decreases slightly for the conditions of solutions, which means more effectiveness of gel; conversely, the porosity of samples in air continues increasing, that means the gel keeps shrink in air.

Figure 13 shows the monitoring of porosity of sand samples mixed with nanosilica hardened by NaCl solution (95g/L of concentration). Comparing the two formulas of nanosilica, when the concentration of the NaCl increases, the porosity is more stable and takes shorter time for stabilization. After immersed 1 day, the porosity in the liquid solutions increases significantly, this is explained by the instability of gel, the gel has been eroded by the solution. After 7 days, the porosity of samples in solutions remains stable with small amplitude fluctuations. The porosity of samples kept in air increases with the time passing until 30 days, then the porosity tends to stable. After immersed in four environments for 180 days, all the samples have very similar porosity, and the effective pore-filling percentage is 16.7%.

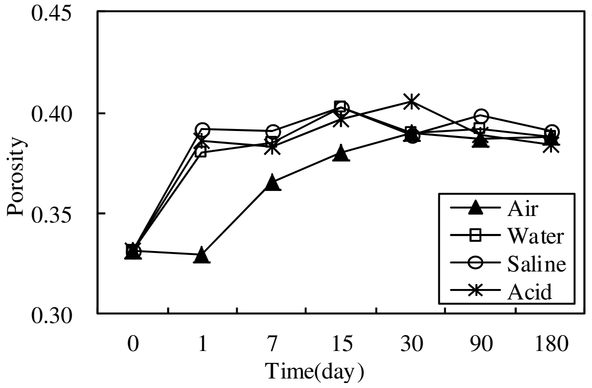


Figure 13 Porosity of sand samples mixed with nanosilica hardened by NaCl solution(95g/L of concentration)

Generally, the stability of nanosilica in four environments in a descending order as: Saline solution> acid solution>water>air. As shown in Figure 14, for formula (Sodium aluminate of 3% by volume), after the samples were immersed for 1 day, the porosity in liquid solutions increases significantly, the most great increasing porosity occurs for sample immersed in saline solution.

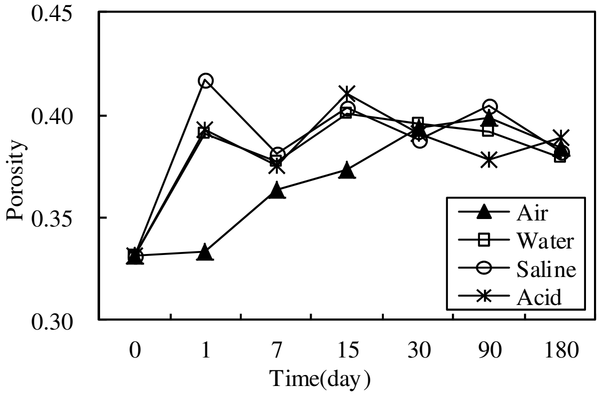


Figure 14 Porosity of sand-binder samples of sodium silicate hardened by sodium aluminate(3% of total volume)

After 1 day, the porosity of samples immersed in solutions fluctuates, the value changes between 0.375-0.42. There exist the competition of shrinkage and loss of particle of gel with the combination of gel and solutions. The porosity of sample in air keeps increasing until 90 days, which can be explained by shrinkage, but the shrinkage rate of silicate gel after mixing with sand is not as great as pure gel, the combination of sand-gel makes the particles of gel dispersing to smaller parts, which inhibit the shrinkage.

The difference between nanosilica and sodium silicate in aspect of porosity is not as great as imagined after learning the shrinkage of the two kinds of gels. The physical-chemical properties of gel before and after mixing with sand is different, before using grout materials, it is necessary to test the materials from two aspects-pure gel test and soil-gel mixture test.

For formula (Sodium aluminate of 4% by volume), as shown in Figure 15, the porosity tends to stable after 30 days for all environments, which means that with the increase of amount of hardener, the gel becomes more stable when mixed with sand, this phenomenon is corresponding with the shrinkage study in section 2.3.1. For 1 day's conservation, the porosity of samples immersed in solutions increase a lot, which indicates the loss of invalid part of gel, the case of acid solution is the most manifest.

For 7 days' conservation, the porosity of samples immersed in solutions is smaller than 1 day's conservation, and the value of porosity of sample in all solutions remain the same.

For 15 days' conservation, the porosity of samples in four environments varies again, the maximum value return to the case of acid solution. The porosity of samples kept in air increases with the time passing until 30 days, then the porosity tends to stable.

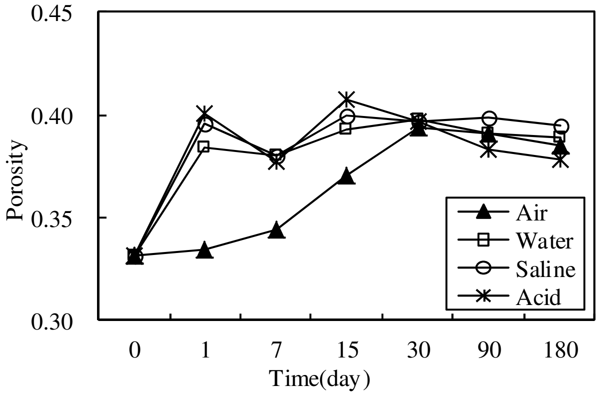


Figure 15 Porosity of sand-binder samples of sodium silicate hardened by sodium aluminate(4% of total volume)

The porosity of sand-binder samples of sodium silicate hardened by sodium aluminate (5% of total volume) is shown in Figure 16. Compared with the above 2 formulas, the value of porosity is bigger, varying between 0.33 and 0.43 after 1 day, for samples immersed in solutions, the porosity is around 0.4, this result means that the pore-filling effectiveness of odium silicate hardened by sodium aluminate is not good, the gel in sand pore loses a lot of its volume.

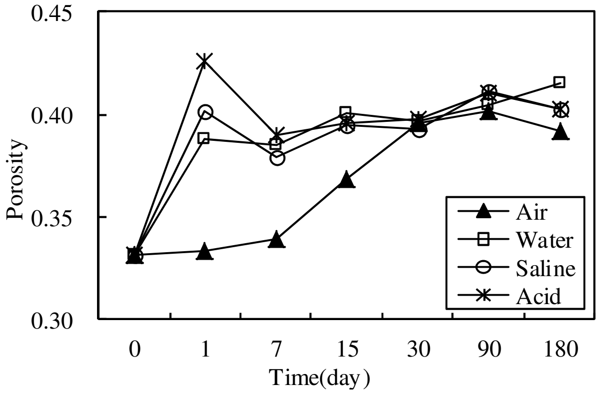


Figure 16 Porosity of sand-binder samples of sodium silicate hardened by sodium aluminate(5% of total volume)

In section 2.3.1, the pure gel of sodium silicate hardened by sodium aluminate (5% of total volume) has less shrinkage rate when comparing with the formulas (sodium aluminate of 3% and 4% in volume), in accordance with the reasoning, this formula should have better pore-filling effect, but as analyses above, we get an opposite conclusion. This results tell us that the physical-chemical properties of gel before and after mixing with sand is different, and before using grout materials, it is necessary to test the materials from two aspects-pure gel test and soil-gel mixture test. Generally, the stability of sodium silicate in four environments in a descending order as: Water>saline solution> acid solution>air.

From Figure 12-16, we can summarize the porosity of all the formulas as following:

With time increasing, the porosity of all formulas conserved in air increases gradually, it is a processes of shrinkage and loss of humidity of gel. The porosity of sand-binder samples conserved in water increases greatly in the first day, and then changes with slight value. The changing law of porosity of formulas NN2, SA1 and SA2 seems similar, while formulas NN1 and SA3 perform differently.

From the results of porosity of all formulas in pure water, the following regular patterns are obtained: for formula NN1, the maximum porosity arrives 0.427, the gel volume decreases a lot after mixed with sand, and this phenomenon is different from pure gel; for formula SA3, the porosity increases from the beginning to the end of observation, changing from 0.329 to 0.418, the volume of gel SA3 keeps reducing for reason of shrinkage or instability with the effluence of water; for formulas NN2, SA1 and SA2, the porosity increases significantly in first day, this is explained by the instability of gel, the gel has been eroded by the solution, after 7 days, the porosity of samples remains stable with small amplitude fluctuations.

For all the formulas in saline solution, the porosity increases significantly in first day, then remains stable with fluctuations. For 1 day's conservation, SA1 has the biggest porosity, which means the gel volume decreases the most, this result is corresponding with the test of pure gel. The final porosity in a descending order is: SA3> SA2> NN2> NN1 & SA1.

For acid environment, the gel is more stable when mixed with sand, after a great increase in the first day, the porosity changes very slightly. It is worth mentioning that, for formula SA3, in which the quantity of sodium aluminate is bigger, the porosity is greater than the other formulas, this phenomenon can be explained by the instability of higher alkaline gel under the effluence of H^+ in acid solution.

After 180 days' conservation in four environments, the shrinkage rate of all formulas is summarized in Figure 17.

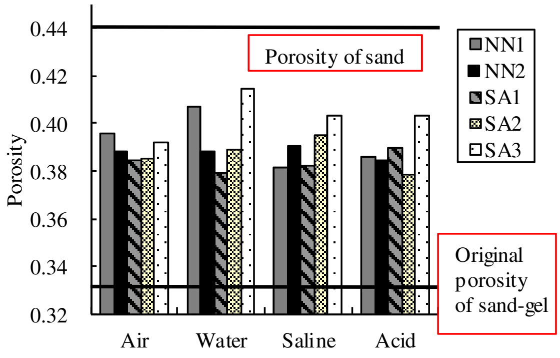


Figure 17 Porosity of sand-binder samples in four environments after immersed for 180 days

Analyses of porosity of sand-binder samples after 180 days' immersion (e.g. Figure 17) show that, the difference between the two kinds of gels-nanosilica and sodium silicate in aspect of porosity is not as manifest as pure gel, with the influence of sand particles, the gel exhibits different physical properties, the gel has been separated by sand particles, with the gel volume decreases largely to micro echelle, the syneresis decreases also. Especially in dry atmosphere, the porosity difference of all formulas is very small.

The final effective pore-filling percentage is about 16% with an initial pore-filling percentage of 25% in dry atmosphere.

In practice, this phenomenon should be account into consideration. The greater remain porosity is, the more loss of gel volume in sand, which means the pore filling effectiveness of the great remain porosity is worse. For formulas of sand-nanosillica, with the increase of concentration of hardener (NaCl of 75g/L and 95g/L), the porosity decreases in environments (air, water and acid solution), while the porosity increases in salty solution. This result is corresponding with the result of pure gel analyses. For formulas of sand-sodium silicate, with the increase of quantity of hardener (Sodium aluminate volume of 3%, 4% and 5% to the total gel volume), the porosity increases in environments (air, water and salty solution). In acid solution, we have not observed this rule, the porosity after 180 days' immersion in acid solution of SA3 is the biggest, and following by SA1, the smallest porosity is the case of formula SA2. This result is corresponding with the result of pure gel analyses.

The porosity of sand is 0.44, while the original porosity of sand-gel mixture is 0.3293, the gel volume is 3.32ml for 30ml of sand-gel column. After 180 days, the porosity of all formulas in four environments varies from 0.37 to 0.416. After calculating the porosity to gel volume in sand pore, we can get that the gel volume in sand pore is 2.1ml to 0.72ml. The loss of gel volume in sand pore varies from 36.7% to 78.3% of original gel volume. The loss of gel volume can be explained by two reasons: the gel shrinkage (for this reason, the shrinkage of pure gel studied in section 2.3.1 can be referenced); the combination of gel with sand particles, large amount of gel has wrapped around the sand particle surface, this effect should be studied further, for example, erosion test can be adopted to examine the combination of sand with gel.

2.3.3 Permeability of sand-binder mixture

Through analyzing the porosity of all formulas in four environments under long-term conservation, we have got basic conceptions about the new binder material-nanosilica and its properties in aspect of volume stability, and by compared with traditional binder material-sodium silicate, the advantages and disadvantages of the two kinds of binders have been initially noted in terms of volume stability.

In order to further study the volume stability of gel after mixing with sand, the permeability with constant water head was measured. Though measurement of permeability, the effectiveness of gel to fill the sand pore is examined, furthermore, by testing the ability of allowing water through the sand-gel structure, we can evaluate the soil combination effect and to estimate the anti-seepage effect after using the chemical material.

In this section, formula NN1 and formula SA2 were chosen to be analyzed. The permeability of all the columns was analyzed: The same formula in different environments was showed (Figure 18 and Figure 19); Comparison between the two formulas conserved in the same environment was also analyzed (Figure 20-23).

Figure 18 shows the permeability of sand samples mixed with nanosilica hardened by NaCl solution (75g/L of concentration) under four environments for 1 to 180 days. For short time of conservation in four environments (results of 1 day, 7 days and 15 days), the permeability of nanosilica in acid solution is greater than in the other environments, following by nanosilica in saline solution. After 90 days, the permeability of nanosilica in air is greater than in the other environments. The higher permeability means weaker ability of anti-seepage, the gel is not well combined with particles of sand, during the processes of permeability measurement, and the gel is also lost along with outflow.

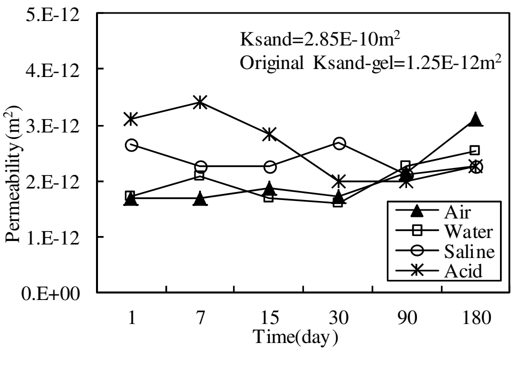


Figure 18 Permeability of sand samples mixed with nanosilica hardened by NaCl solution(75g/L of concentration)

Figure 19 shows the permeability of sand samples mixed with sodium silicate hardened by sodium aluminate (4% of total volume) under four environments for 1 to 180 days. With time passing, the permeability of sample conserved in air remains the same until 30 days, and after 30 days, the permeability increases greatly, this means the gel in sand begin to lose its volume stability, larger passage for water forms.

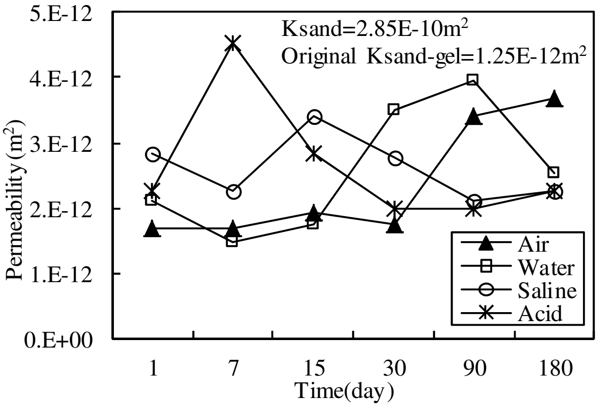


Figure 19 Permeability of sand samples mixed with sodium silicate hardened by sodium aluminate(4% of total volume)

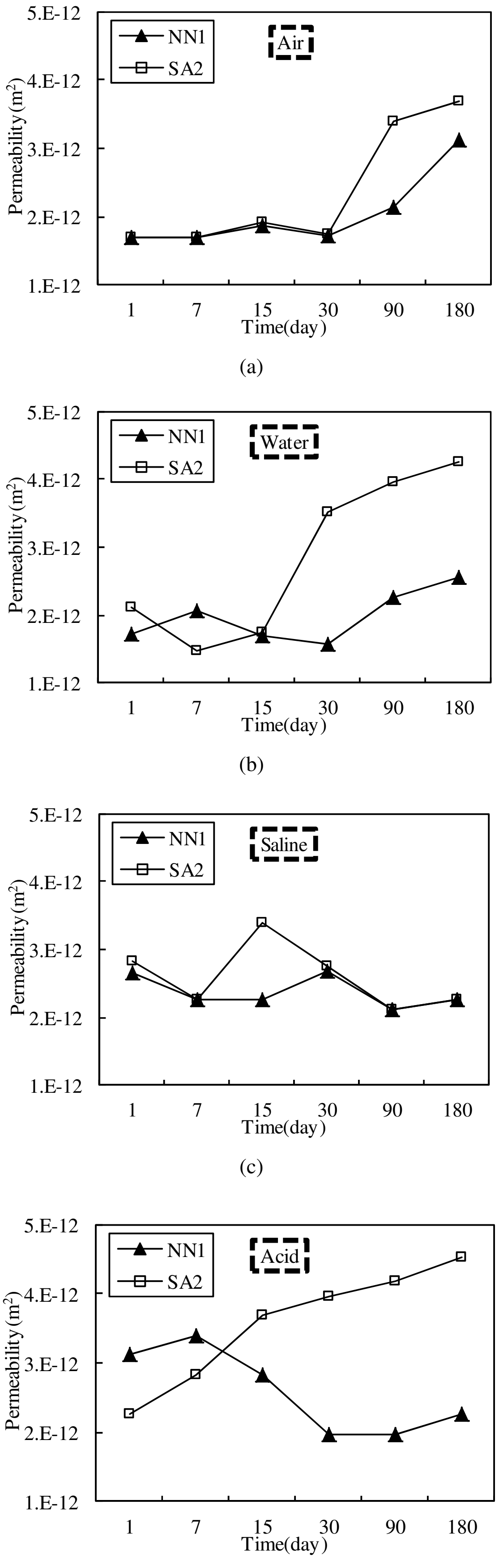
The permeability of sample conserved in water remains stable until 15 days, and then increases greatly until 90 days, after that, the permeability decreases. In the beginning of conservation in acid solution, the permeability is greater than the other environments, this means the loss of unsolid gel, from 7 days to 30 days, the permeability in this case begins to decreased, and after this period, the permeability increases with a slight value. When samples were immersed in saline solution, the permeability changes with small extend comparing with other environments, which means the gel is more stable in this environment.

To compare the permeability of the two kinds of binders in each environment, we get Figure 20.

It is clear from Figure 20 that the permeability of formula nanosilica is much smaller than formula silicate after a period of time. In dry atmosphere, the two formulas have almost the same permeability during the first 30 days, then the permeability of silicate increases with a higher value to nanosilica. This law is similar in water, and the difference between the two formulas begins earlier (since 15 days). Generally, the two types of formula have similar ability of reducing permeability in saline solution, and the fluctuation of permeability is very small. The permeability in the beginning and after 30 days of the two formulas remains the same. For 15 days' conservation, the permeability of SA2 is much bigger than NN1. For environment of acid solution, in the beginning 7 days, NN1 has a greater permeability than SA2. After 15 day's conservation, the permeability of SA2 is much bigger than NN1. To sum up from a long-term point view, the sand-nanoslica sample is much more stable of reducing permeability than sand-silicate sample.

Finally, the link of porosity and permeability is tried to be revealed in Figure 21.

For pure sand, the relationship between permeability and porosity is linear (Beard 1973). After mixing with gel, we can see that the development of permeability has discrepancy with suspect from the porosity law in section 2.3.2, this can be explained by: Firstly, the difference of stability static and dynamic. The monitoring of porosity judges the volume stability of gel in sand under a static state, while the monitoring of permeability indicates the stability of gel in sand under a dynamic state; Secondly, the permeability also change with the factors of pore shape and connection mode of pores, gel that completely displace the fluid in the soil pores form a continuous but open and non-uniform latticework that binds the grains together.



(a)

(b)

(c)

(d)

Figure 20 Comparison of permeability of sand-binder samples in each environment : (a) Air; (b) Water; (c) Saline; (d) Acid

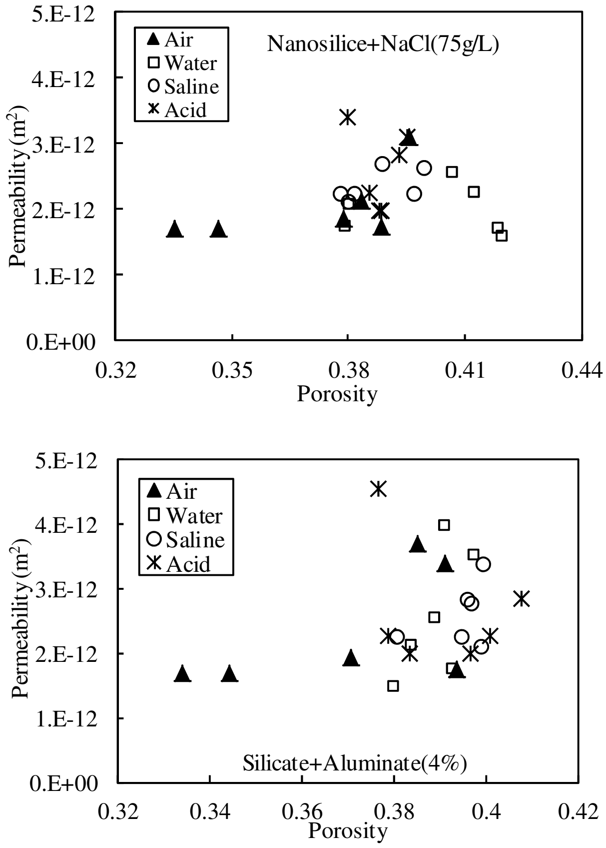


Figure 21 Permeability-porosity of the two kinds of sand-gel mixtures

3. CONCLUSION

In this work, usual techniques are adopted to provide practical and direct information on the effect of the reinforcement of sand with new material-nanosilica and traditional material-silicate binder in terms of volume stability.

The pure gel of nanosilica is much more stable than sodium silicate after long-term immersion in all four environments.

The difference between nanosilica and sodium silicate in aspect of porosity is not as great as imagined after learning the shrinkage of the two kinds of gels. The physical-chemical properties of gel before and after mixing with sand are different as gel has changed from macro echelle to micro echelle.

From results of permeability, the sand-nanosilica has more stable capacity of water-blocking compared to sand-sodium silicate. The permeability-porosity of sand after mixing with gel is not linear as pure sand, and this can be explained by the difference of stability static and dynamic. The monitoring of porosity judges the volume stability of gel in sand under a static state, while the monitoring of permeability indicates the stability of gel in sand under a dynamic state. Meanwhile, the permeability also changes with the factors of pore shape and connection mode of pores.

The amount of gel is 25% of the pore volume, but the actual filling rate is about 16-18% of the pore volume initially, this result can be a reference for practical use of the material. After a period of using, the filling rate varies in terms of environment, the stability of gel etc.

Generally, there is not much different on the stability of nanosilica among four environments. While the stability of sodium silicate in four environments varies in a descending order is: Water>saline solution> acid solution>air.

Compared with silicate sodium, nanosilica is much more stable in all environments, which means that this new material has advantages of long-term stability of reducing soil pore. This study can be a reference for calculating the original quantity of grout which should be used in order to achieve a final effectiveness. The new material can be used for water shut off, anti-seepage and anti-erosion in many kinds of hydraulic structures exposed in aggressive environments. Besides of its volume stability, the new material has other advantages, such as: low viscosity, small particle size, easy-controlled setting time and respect for environments, which should be studied further of this new kind of binder.

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