



# An analytical model for the control of silica grout penetration in natural groundwater systems



M. Pedrotti\*, C. Wong, G. El Mountassir, R.J. Lunn

University of Strathclyde, Department of Civil and Environmental Engineering, James Weir Building, Level 5 75 Montrose Street, Glasgow G1 1XJ, UK

## ARTICLE INFO

### Keywords:

Colloidal silica  
Grouting  
Groundwater chemistry  
Viscosity  
Gel time

## ABSTRACT

Over the last three decades, colloidal silica has been investigated and more recently adopted as a low viscosity grouting technology (e.g. for grouting rock fractures within geological disposal facilities nuclear waste). The potential of colloidal silica as a favourable grouting material exists due to: its initial low viscosity; its low hydraulic conductivity after gelling (of the order of  $10^{-7}$  cm/s); the very low injection pressures required; its controllable set/gel times (from minutes to several days); the fact it is environmentally inert; its small particle size (less than hundreds of nanometres) and its cost-effectiveness. Despite the documented success of colloidal silica based grouts for hydraulic barrier formation, research has not translated into widespread industrial use. A key factor in this limited commercial uptake is the lack of a predictive model for grout gelling which controls grout penetration: whilst data are available to underpin design of a grouting campaign in laboratory conditions, little research has been done to underpin applications in natural environments. Here we develop and validate an analytical model of colloidal silica gelling in groundwaters with varying pH and background electrolyte concentrations. This paper presents an analytical model that accounts for changes in pH, electrolyte concentration, cation valency and molar mass, silica particle size and silica concentration giving predictive capability without the need for site-specific calibration. The model is validated against experimental observations for gel times of 32–766 min, the model accurately predicts the log(gel time) with an average error of 4% which corresponds to an  $R^2$  value of 0.96.

The model is then applied to a hypothetical case study to demonstrate its use in grout design, based on published in-situ groundwater data from the Olkiluoto area of Finland. The model successfully predicts the required accelerator concentration to achieve a grout gel time of approximately 50 min, taking into account the cations already present within the synthetic groundwater.

## 1. Context

With increasing use of underground space, and redevelopment of subsurface infrastructure, comes the requirement for adequate groundwater control. For example the construction of a geological disposal facility will require very fine aperture fractures down to  $10\ \mu\text{m}$  to be sealed (Butrón et al., 2010). In the tunnelling industry, in-situ water ingress reduction often requires finer grouts than micro-cement ( $d_{95} < 30\ \mu\text{m}$ ) and ultrafine cement ( $d_{95} < 15\ \mu\text{m}$ ), especially when a pre-injection strategy is adopted (Bahadur et al., 2007). The penetration of traditional cementitious grouts is limited by their particle size and high viscosity (Eklund and Stille, 2008). Although chemical grouts can penetrate finer fractures and have lower viscosities than cement grouts (Karol, 1982), they are often expensive (Karol, 1968), exhibit syneresis and may contain toxic components (Magill and Berry, 2006).

Over the last three decades, colloidal silica has been investigated, and more recently adopted, as a low viscosity grout due to: (i) its initial low viscosity (close to water) (Moridis et al., 1995), (ii) its low hydraulic conductivity after gelling (of the order of  $10^{-7}$  cm/s) (Moridis et al., 1996a), (iii) the very low injection pressures required (Moridis et al., 1995), (iv) its controllable set/gel times (from minutes to several days) (Iler, 1979; Yates, 1990), (v) the fact it is environmentally inert (Moridis et al., 1995), (vi) its small particle size (less than hundreds of nanometres) (Persoff et al., 1995; Moridis et al., 1995; Iler, 1979; Yates, 1990) and (vii) its cost-effectiveness (Tsuji et al., 2014).

As a grout material, colloidal silica has been intensively tested both at laboratory and in-situ scale by the Lawrence Berkley National Laboratory and the Brookhaven National Laboratory (Persoff et al., 1995, 1999; Moridis et al., 1995, 1996a, 1996b, 1999; Hakem et al., 1997; Manchester et al., 2001) with an overall aim of creating hydraulic

\* Corresponding author.

E-mail addresses: [matteo.pedrotti@strath.ac.uk](mailto:matteo.pedrotti@strath.ac.uk) (M. Pedrotti), [christopher.wong@strath.ac.uk](mailto:christopher.wong@strath.ac.uk) (C. Wong), [grainne.elmountassir@strath.ac.uk](mailto:grainne.elmountassir@strath.ac.uk) (G. El Mountassir), [rebecca.lunn@strath.ac.uk](mailto:rebecca.lunn@strath.ac.uk) (R.J. Lunn).

<http://dx.doi.org/10.1016/j.tust.2017.06.023>

Received 8 December 2015; Received in revised form 15 May 2017; Accepted 21 June 2017

0886-7798/© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

barriers to control radionuclide migration at nuclear sites.

The potential for colloidal silica to be deployed as a low pH grout within nuclear waste repositories in crystalline rock has been investigated by the Chalmers University of Technology (Axelsson, 2006; Funehag and Fransson, 2006; Funehag and Gustafson, 2008; Butrón et al., 2009). In the tunnelling and underground construction industry, it has been successfully applied for preventing water ingress, mainly as a second stage injection (following a first micro-cement injection) (e.g. Butrón et al., 2010; Bahadur et al., 2007). It has also been successfully used as a fluid-flow control system within the petroleum industry (Jurinak and Summers, 1991) and for passive site remediation as a non-disruptive mitigation technique to sites susceptible to liquefaction (Gallagher, 2000).

Despite the documented success of colloidal silica based grout for hydraulic barrier formation, research has not translated into widespread industrial use. A key factor in this limited commercial uptake is the lack of a predictive model for grout gelling (Lakatos et al., 2009): whilst data are available to underpin design of a grouting campaign in laboratory conditions, little research has been done in natural groundwater systems. In the past, the difficulty of predicting the gelation time for in-situ conditions has prevented the exploitation of colloidal silica in grouting campaigns, (e.g. Dounreay shaft isolation project, Donaldson Associates Ltd, 2006 or Jurinak and Summers (1991)). Where the groundwater presents elevated salinity, two issues have inhibited grout use: first, if local untreated water is employed for grout preparation, there is an inability to control the grout gel time, second, even where grout is prepared with imported fresh water, interactions with local groundwater at the injection front may cause premature gelling of the grout front, compromising barrier emplacement and performance.

Furthermore, the lack of a predictive model for grouting gelling is also restricting the manner in which colloidal is currently being deployed in practice. At present, colloidal silica for grouting purposes is sold as two components, which are mixed together on site to give a gel time set by the manufacturer. The model presented herein could be used by grouting contractors to design their own mix of the components to achieve their desired gel time, for example reducing the colloidal silica content in order to increase the gel time and hence achieve greater penetration. This would greatly extend the engineering applications in which colloidal silica could be deployed.

This paper presents an electrochemically inferred model that (i) is able to predict the gelation time and the change in viscosity for a given pH, electrolyte, silica particle size and silica concentration, and (ii) forms a useful tool for the design of grout mixes using colloidal silica that accounts for in situ groundwater conditions. Experimental data investigating a wide range of pH, electrolyte and silica concentration are presented in order to calibrate and validate the model. By way of example, the model is then applied to demonstrate grout design using published in-situ groundwater data from the Olkiluoto area of Finland (Ollila, 1999).

## 2. Material and experimental method

Colloidal silica is an aqueous dispersion of silica particles, which are generally uniform in size (ranging from several to hundreds of nanometres). Upon destabilization siloxane bonds are formed and the colloids gel. The gelation rate, and gel time can be controlled by varying several factors that influence the process including: particle size, particle concentration, pH, electrolyte concentration and valency and temperature (Iler, 1979).

Colloidal silica grout consists of two components: a colloidal silica suspension (Meyco MP320) and an electrolyte accelerator. According to the manufacturer specifications Meyco MP320 has a viscosity (20 °C) ~10 mPa s, density (20 °C) 1.3 kg/l, pH 9.5 to 9.8 and silica concentration (by mass)  $40 \pm 1$ . Silica particle size was calculated by means of specific surface area measurements following the procedure

by Sears (1956). Particle size was found to be 17 nm.

NaCl, CaCl<sub>2</sub>, and KCl were each investigated as electrolyte accelerators at concentrations ranging from 0.1 to 2.0 M. To investigate changes in pH conditions, HCl and NaOH were used to adjust the grout solution pH to values between 3 and 9. All experiments were carried out in a temperature controlled laboratory at 20 °C. Grout solutions were prepared in a 5:1 ratio of colloidal silica to accelerator by volume respectively. A set of samples were prepared at 37% of silica concentration by diluting the 'as-delivered' silica with distilled water before being mixed with the accelerator.

For viscosity tests, 200 ml of colloidal silica were each time mixed with 40 ml of the desired accelerator. Viscosity was measured in the temperature controlled laboratory (at 20 °C) with a Brookfield digital viscometer model LVT DV-II. The viscosity tests were performed with spindle number 3 of the LV Series and the rpm was set to be 30. With this configuration the maximum readable viscosity is 4010 mPa s. Viscosity was recorded every second during the test. To calculate gel time, viscosity (mPa s) is plotted against time (s) and the gel time is given by the intersection between the linear regression of all the points at viscosity higher than 2000 mPa s and the x-axis (Bergna and Roberts, 2005).

## 3. Experimental results

30 samples were tested at different pH and NaCl concentrations. The pH of the solutions ranged from 3 to 9 and the NaCl concentration from 0.5 to 2.0 M (initial concentration of accelerator prior to mixing with colloidal silica). In Fig. 1a the experimental data are reported. For each set of NaCl concentration the gel time showed a non-monotonic trend when plotted against pH. In the alkaline pH range, increasing the NaCl concentration reduces the gel time (i.e. faster gelation). In contrast, in the acidic pH range, the gel time is unaltered by any variation in the NaCl concentration.

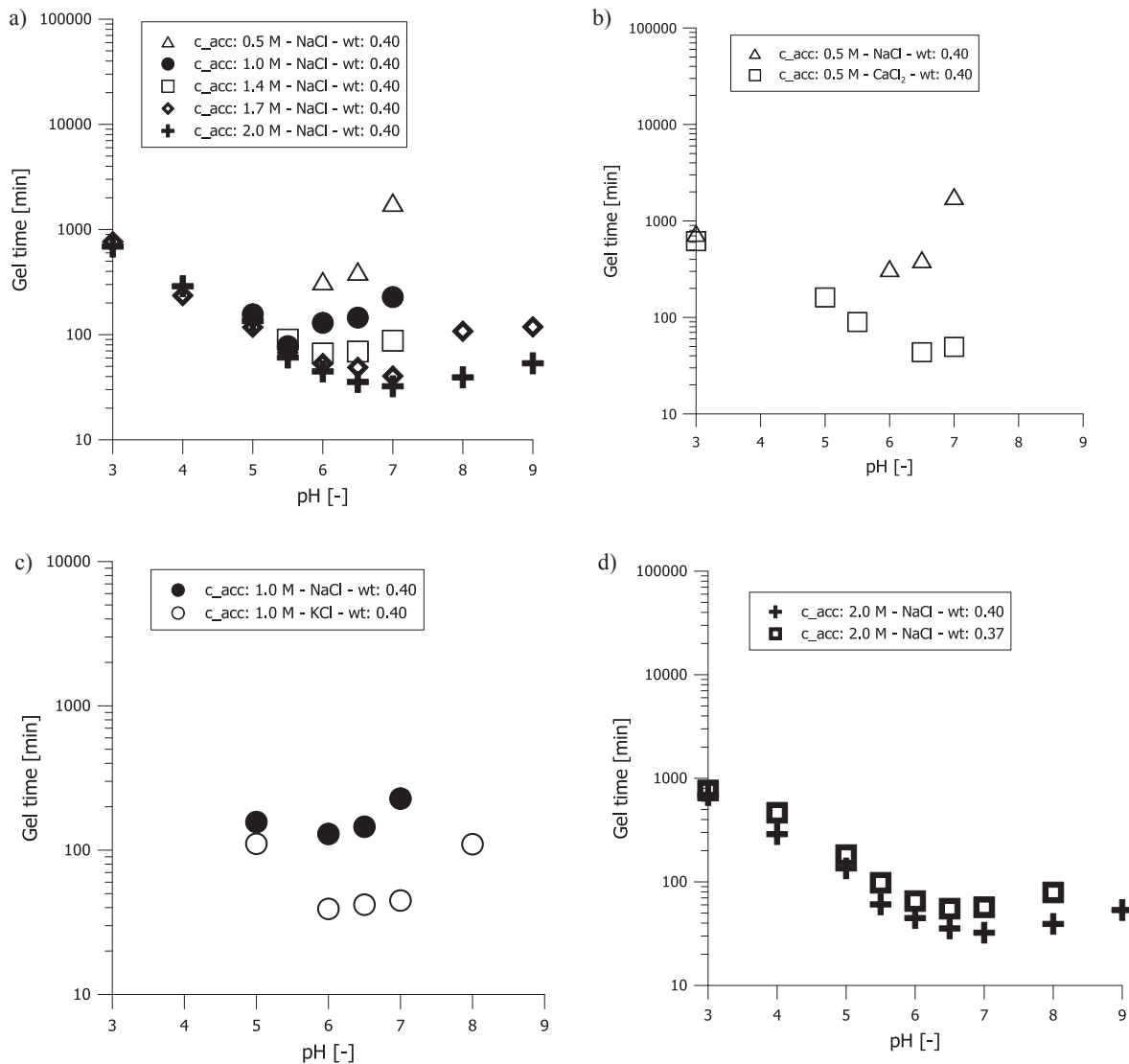
To illustrate the effect of adding cations with a different valency, Fig. 1b shows silica gel times for 3 different values of pH (pH 3, 6 and 7) using 0.5 M calcium chloride as an alternative to the NaCl accelerator shown in Fig. 1a. Also plotted in Fig. 1b are the corresponding gel times for 0.5 M of NaCl solution. Although the molar concentration is the same, the resulting gel time is greatly reduced when the accelerator contains divalent cations (Ca<sup>2+</sup>) as expected.

To investigate the effect of molar mass for accelerators of the same valency, 5 samples were tested using a 1.0 M KCl solution as the accelerator instead of a NaCl solution. Different values of pH were tested (from 5 to 8), and compared with the respective NaCl solution (Fig. 1c). Although Na<sup>+</sup> and K<sup>+</sup> have the same valency and the molar concentration was the same, the two sets of tests show different gel times under alkaline conditions. Samples tested with a KCl accelerator, which has a larger molar mass, resulted in faster gel times.

To illustrate the effect of silica particle concentration on gel time a further 7 samples were tested at a silica concentration of 37% by mass using a fixed accelerator concentration of 2.0 M NaCl and varying the pH conditions from 3 to 9. The results are compared to the same tests using 40% silica concentration in Fig. 1d. It is evident that lowering the silica concentration increases the time needed for gelation to occur.

## 4. Model development

In order to propose an analytical model capable of predicting the gel time for given conditions, the effect of these factors must be fully investigated. The model proposed here considers gel time as the sum of two different terms, (described below) term 1 and term 2 ( $t_{gel} = \text{term 1} + \text{term 2}$ ). Term 1 dominates in acidic pH conditions (left-hand side of the curves in Fig. 2) whilst Term 2 dominates in alkaline conditions (right-hand side of the curves in Fig. 2).



**Fig. 1.** Experimental results for Meyco MP320 colloidal silica. (a) Gel time vs pH for different NaCl concentration of the accelerator. (b) Gel time vs pH for 0.5 M electrolyte concentration of the accelerator prepared with different cations: NaCl and CaCl<sub>2</sub>. (c) Gel time vs pH for 1.0 M electrolyte concentration of the accelerator prepared with different cations: NaCl and KCl. (d) Gel time vs pH for different silica concentration (0.40 and 0.37) of grout prepared with a NaCl concentration of the accelerator of 2.0 M.

#### 4.1. Effect of pH

It is well-known that pH alters the electrical charge of the surface of silica particles. Silanol bond (compounds containing the Si-O-Si group) formation is promoted by the presence of OH<sup>-</sup> anions in solution. Silanol bonds condense to form siloxanes. When siloxane bonds start to form, gelation begins. The higher the pH, the more negative the electrical charge is, resulting in repulsion between particles, a low rate of silanol bond formation and longer gel times.

Experimental data for the gel time of colloidal silica prepared at 1.0 M NaCl concentration are plotted in Fig. 2a and b. Considering acidic conditions (Fig. 2a) the data are well fitted by an exponential function with a negative argument (Term 1). By contrast, for alkaline conditions (Fig. 2b), the data are fitted by an exponential curve with a positive argument (Term 2). A1, B1 and C1 are fitting parameters: A1 and B1 have dimensions of time (minutes) whilst C2 is dimensionless.

#### 4.2. Effect of the electrolytes

When an electrolyte is added to colloidal silica, the repulsion between particles is reduced, leading to an increased collision rate of silica particles and hence reduced gel times, because the presence of cations

depresses the double layer interaction.

Electrolyte is added as an accelerator in order to control the gel time, but cations are also already present in-situ and in the water used in grout preparation. Since different cations may be found, the electrolyte must be studied in terms of concentration, molar mass and valency. In Fig. 2c and d gel time data are plotted against the NaCl concentration for acidic (pH 3, 4 and 5) and alkaline conditions (pH 6, 6.5 and 7) respectively. Since no clear trend is shown, for acidic conditions term 1 can be considered as a constant, whilst for alkaline conditions term 2 depends on the electrolyte concentration with an exponential law. A2, B2, C2 and D2 are fitting parameters. A2 and B2 are expressed in minutes, C2 is the inverse of a molar concentration (L/mol) and D2 is a molar concentration (mol/L).

To model gel time with electrolytes of differing molar mass and valency, the concept of an equivalent electrolyte concentration can be introduced. Equivalent electrolyte concentration,  $c_{eq}$  [mol/L], is defined in Eq. (1), where  $c_{acci}$  is the molar concentration (mol/L) in the accelerator for cation,  $i$ .  $M_i$  is the molar mass of cation,  $i$ , and  $M_{Na}$  is the molar mass of the Na, that is taken as a reference cation. The term  $r$  is defined in Eq. (2) as the ratio of the volume of silica suspension,  $V_{coll}$  [m<sup>3</sup>] to the volume of grout  $V_{grout}$  [m<sup>3</sup>], where the volume of grout is the sum of the volume of the colloidal silica suspension and the volume

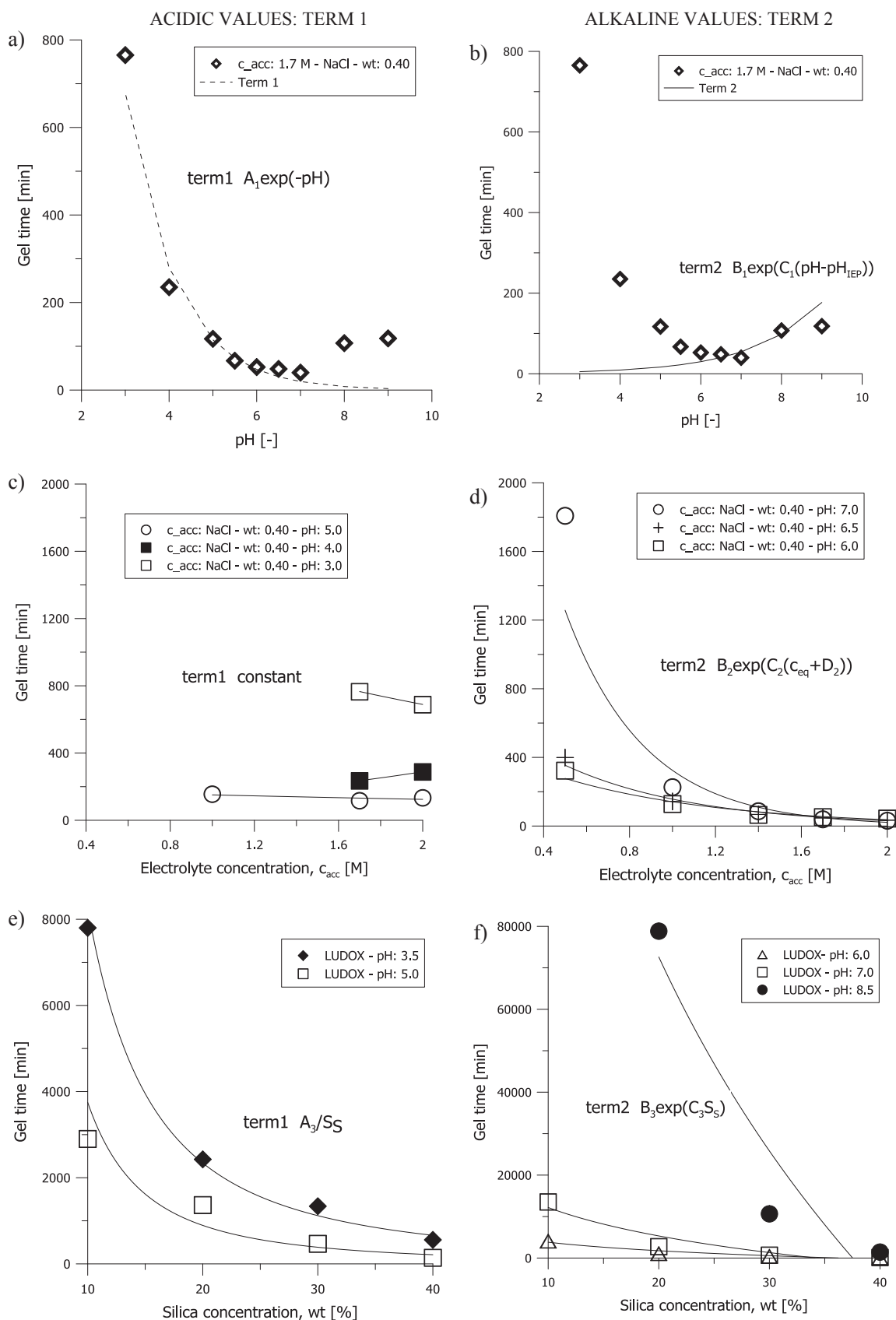


Fig. 2. Trends of factors controlling the gel time. (a) Meyco MP320 colloidal silica: gel time vs pH. (b) Meyco MP320 colloidal silica: gel time vs pH. (c) Meyco MP320 colloidal silica: gel time vs  $c_{acc}$ . (d) Meyco MP320 colloidal silica: gel time vs  $c_{acc}$ . (e) Ludox HS colloidal silica: pH vs silica concentration in terms of weight. (f) Ludox HS colloidal silica: pH vs silica concentration in terms of weight.

of the accelerator,  $V_{acc}$  [m<sup>3</sup>],  $V_{grout} = V_{coll} + V_{acc}$ .

$$c_{eq} = \sum_i c_{acc_i} (1-r) \cdot v_i \cdot \frac{M_i}{M_{Na}} \quad (1)$$

$$r = \frac{V_{coll}}{V_{grout}} = \frac{V_{coll}}{V_{coll} + V_{acc}} \quad (2)$$

#### 4.3. Effect of the total specific surface

The specific surface of the colloidal silica,  $S_{coll}$  [m<sup>-1</sup>], is defined as the ratio between the surface area of the silica particles ( $A_{Si}$  [m<sup>2</sup>]) present in a given volume of colloidal silica suspension and the volume of the colloidal silica suspension itself, (Eq. (3)). On the other hand, the specific surface of the silica present in the grout,  $S_{grout}$  [m<sup>-1</sup>], is defined as the ratio between the surface area of the silica particles ( $A_{Si}$  [m<sup>2</sup>]) present in a given volume of grout and the volume of grout itself, (Eq. (4))

$$S_{coll} = \frac{A_{Si}}{V_{coll}} \quad (3)$$

$$S_{grout} = \frac{A_{Si}}{V_{grout}} = \frac{A_{Si}}{V_{coll}} \cdot \frac{V_{coll}}{V_{grout}} = S_{coll} \cdot r \quad (4)$$

By considering the colloidal silica suspension only (without the accelerator), from the definition of silica concentration (expressed in terms of volume),  $\phi$ , it is possible to infer the relationship between the number of particles present in a volume  $V_{coll}$  and the particle size,  $d$  (Eq. (6)). The concept of specific surface is embedded in both the silica particle size,  $d$ , and the silica colloid concentration,  $\phi$ . From the definition of silica colloid concentration,  $\phi$ , it is then possible to rewrite Eq. (6) to give the number of particles in a given volume  $V_{coll}$  and as a function of the particle size  $d$  (Eq. (6)).

$$\phi = \frac{V_{Si}}{V_{coll}} \rightarrow V_{Si} = \phi \cdot V_{coll} \quad (5)$$

$$V_{particle} = \frac{1}{6} \pi d^3$$

$$V_{Si} = n \cdot V_{particle}$$

$$n = \frac{\phi \cdot V_{coll}}{\frac{1}{6} \pi d^3} \quad (6)$$

By substituting the expression for the number of particles into the definition of total surface area,  $A_{Si}$ , the relation between  $A_{Si}$  the silica colloid concentration,  $\phi$ , and the particle size,  $d$ , can be written as (Eq. (7)).

$$A_{Si} = n \cdot A_{particle} = n \cdot \pi d^2 = 6 \frac{\phi}{d} V_{coll} \quad (7)$$

Combining Eqs. (3) and (7) the relationship between the colloidal specific surface,  $S_{coll}$ , the silica concentration,  $\phi$ , and the particle size,  $d$ , can then be expressed as (Eq. (8)).

$$S_{grout} = \frac{A_{Si}}{V_{coll}} \cdot \frac{V_{coll}}{V_{grout}} = \frac{A_{Si}}{V_{coll}} r = 6 \cdot \frac{\phi}{d} r \quad (8)$$

Since in the concentration of colloidal silica is generally expressed in terms of weight concentration as a ratio between the mass of silica and the mass of the colloidal suspension,  $wt = \frac{M_{Si}}{M_{coll}}$ , it is preferable to rewrite the concentration by volume,  $\phi$ , in terms of weight:

$$\phi = \frac{V_{Si}}{V_{coll}} = \frac{M_{coll}/\rho_{coll} - M_w/\rho_w}{M_{coll}/\rho_{coll}} = 1 - \frac{M_{coll} - M_{Si}}{M_{coll}} \frac{\rho_{coll}}{\rho_w} = 1 - (1-wt) \frac{\rho_{coll}}{\rho_w} \quad (9)$$

where  $M_{coll}$  [kg],  $M_w$  [kg] and  $M_{Si}$  [kg] are the mass of the colloidal suspension, the mass of the water and the mass of silica that are present in the colloidal suspension respectively.  $\rho_{coll}$  [kg/m<sup>3</sup>] and  $\rho_w$  [kg/m<sup>3</sup>]

are the density of the colloidal suspension and the water respectively. Therefore, Eq. (8) can be rewritten as follows:

$$S_{grout} = 6 \cdot \frac{r}{d} \left[ 1 - (1-wt) \frac{\rho_{coll}}{\rho_w} \right] \quad (10)$$

The effect of the specific surface is different when the pH of the solution is acid or alkaline. In order to investigate the effect of silica particle concentration, data from Yates (1990) (cited in Bergna and Roberts (2005)) have been considered. In Fig. 2e and f data for colloidal silica ‘‘Ludox HS’’ in acidic and alkaline condition respectively are shown. The silica solutions of Yates (1990) were prepared using a NaCl concentration of 0.1 M and with colloidal silica concentrations by mass of 10, 20, 30 and 40%. For alkaline conditions, the three sets of data are all well fitted by an exponential law, which is a function of the specific surface. The data for pH 3.5 and 4.0 show the gel time is inversely proportional to the specific surface SS. A3, B3 and C3 are fitting parameters. A3 has dimensions of time over length (minutes/meters), B3 has dimensions of time (minutes) and C3 is a length (meters).

## 5. The analytical model

### 5.1. Gel time prediction

The effects of pH, electrolyte type and concentration, silica particle size, silica particle concentration can all be combined into a single analytical model of gel time. By rearranging each of the two terms as a function of three variables (pH, SS and  $c_{eq}$ ) and 4 parameters (A, B, C and D) we can obtain the following relationship for the gel time,  $t_{gel}$ :

$$term\ 1 \rightarrow A \cdot \frac{1}{S_S} e^{-pH}$$

$$term\ 2 \rightarrow B \cdot e^{(-CS_S c_{eq} + D) \cdot (pH - pH_{IEP})}$$

$$t_{gel} = term\ 1 + term\ 2 = A \cdot \frac{1}{S_S} \cdot e^{(-pH)} + B \cdot e^{(-CS_S c_{eq} + D) \cdot (pH - pH_{IEP})} \quad (11)$$

In Eq. (11),  $t_{gel}$  is expressed in minutes,  $c_{eq}$  in mol/L, SS in 1/m and pH is dimensionless. The parameters A (minutes/meter), B (minutes), C (the inverse of a molar concentration times meter, mL/mol) and D (dimensionless) are all constants.

### 5.2. Viscosity prediction

The rate of change of viscosity (post gel time) was found to depend upon the gel time itself by a power law (data are reported in Fig. 3)

In order to have a smooth transition from the plateau at constant viscosity, the trend of the viscosity of the silica grout has been assumed to be a quadratic Bézier curve. The two reference curves of the Bézier curve are reported in Eq. (12):

$$for\ t < t_{gel}\ v = v_0 \quad (12)$$

$$for\ t > t_{gel}\ v = v_0 + \left( \frac{\Gamma}{t_{gel}} \right) \cdot (t - t_{gel})$$

In Eq. (12), viscosity,  $v$ , is expressed in mPa s, time  $t$  and gel time  $t_{gel}$  in minutes [min], and  $\Gamma$  is expressed in mPa s.  $\Gamma$  was found to be 11,991.

## 6. Model calibration and validation

### 6.1. Calibration

The proposed model was calibrated on the limited set of experimental data shown in Fig. 1a: i.e. Meyco MP320, for pH ranging from 3 to 9 and NaCl as the accelerator with concentrations ranging from 0.5 and 2.0 M and a silica concentration of 40%. The calibrated values for

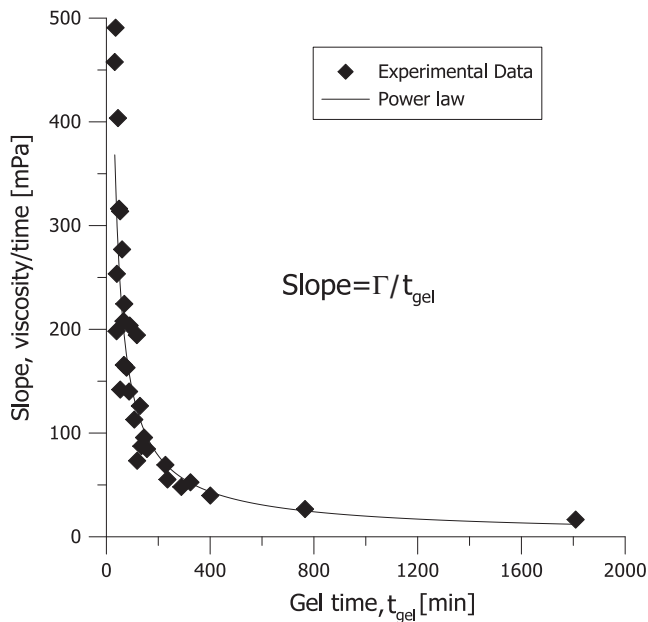


Fig. 3. Colloidal silica viscosity evolution: slope vs gel time.

A, B, C and D in Eq. (9) were found to be 994.5 [min/m], 0.8947 [min], 55.92 [mL/mol] 1.763 respectively.

For comparison, the experimental data are plotted alongside the analytical model prediction in Fig. 5a over a full range of pH values. Fig. 5b shows the same data but with the predicted gel time plotted against the experimentally observed gel time; a perfect fit would lie on the straight line  $y = x$ . The model fit is generally good, with an average error of 4% (calculated on the logarithmic scale) over a range of gel times from 32 min to 766 min. This corresponds to an  $R^2$  value of 0.96.

The calibrated model was then used to predict the evolution of viscosity with time. Model predictions are plotted alongside experimental observations in Fig. 4 for 4 different values of pH, each with the same electrolyte concentration of 2.0 M NaCl. In general, the fit is excellent; deviations between the model and the experimental data are observed at the onset of gelling for grouts with a prolonged gel time (i.e. > 100 min).

6.2. Model validation

The analytical model, using the calibrated parameters, was

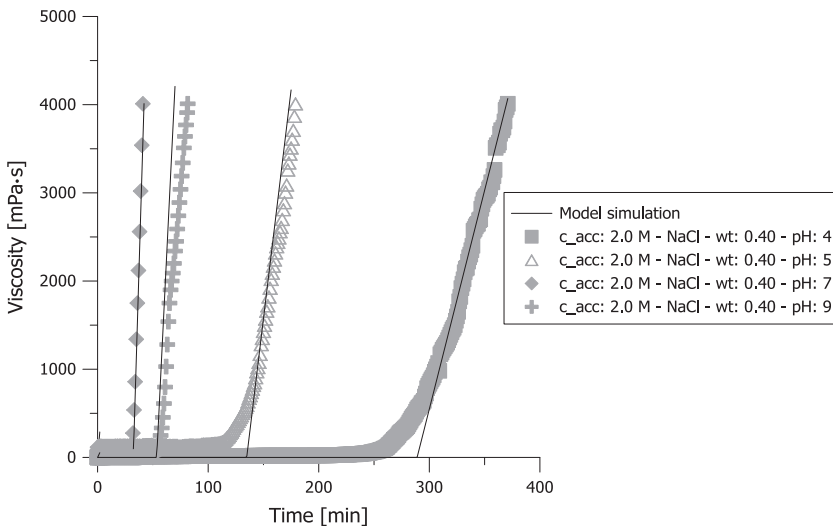


Fig. 4. Viscosity prediction.

validated against experimental data by comparing model predictions with experimental observations using different electrolytes and electrolyte concentrations. Experimental gel time results for colloidal silica grouts prepared with electrolytes of different valency and atomic mass are shown in Fig. 5c and d respectively. These data were not used in the calibration process and model predictions compare well with experimental observations.

As a final validation of the model, predictions of gel time were compared with experimental observations for silica grouts with different values of silica concentration (Fig. 5e). Fig. 5f shows the experimental data plotted against the model data, demonstrating an excellent fit.

7. Model applications

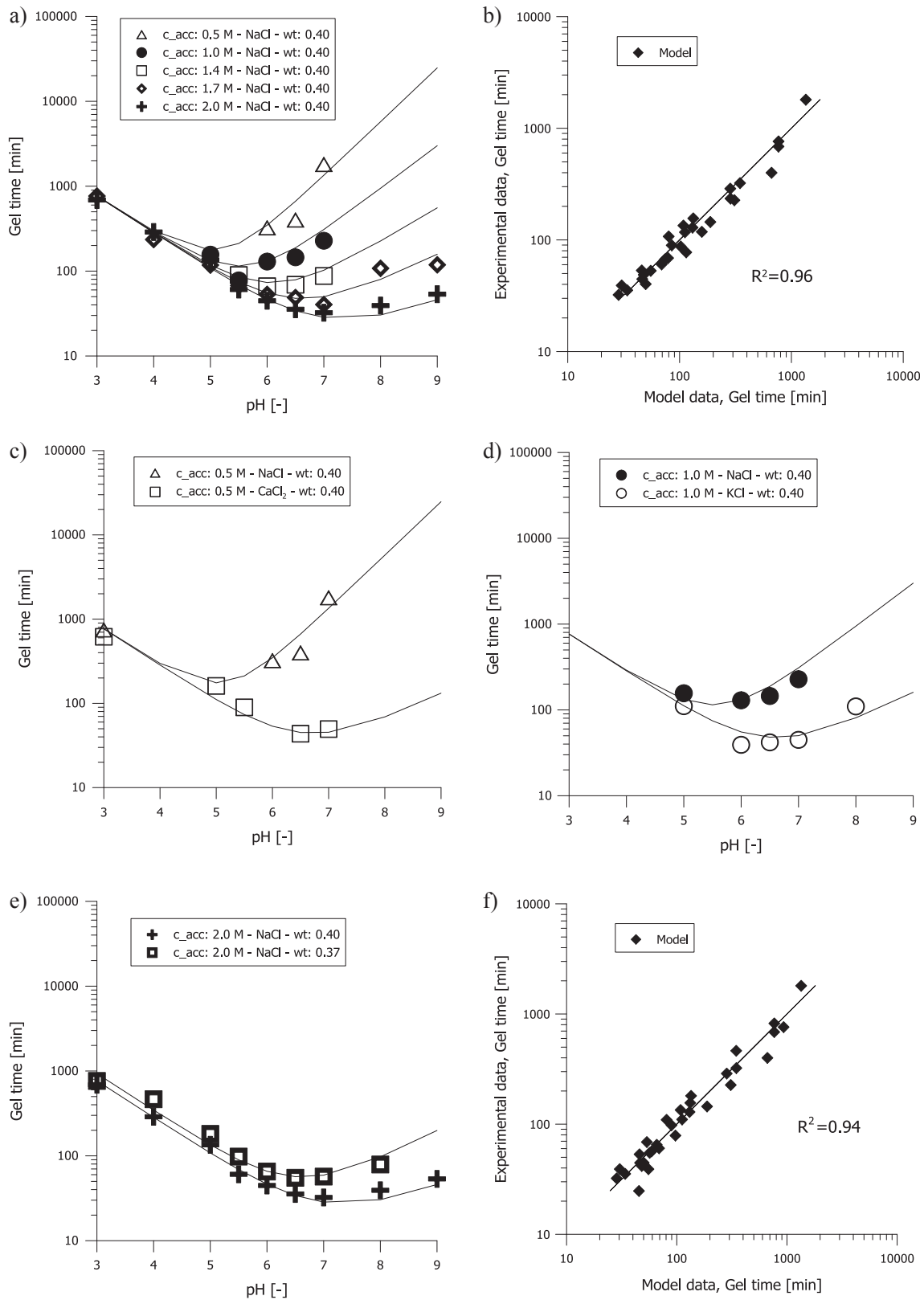
7.1. Prediction with mixed cations: case study

The above model was applied here to determine the appropriate accelerator concentration to use when preparing the accelerator with in-situ groundwater. The groundwater composition was, purely for demonstration purposes, chosen to be that published for the Olkiluoto area; the site for disposal of spent nuclear fuel in Finland. The composition of groundwater at Olkiluoto has been well studied (Ollila, 1999). The main composition was found to be 209 mM  $Na^+$ , 100 mM  $Ca^{2+}$  and 2.3 mM  $Mg^{2+}$  and average pH equal to 7.

For the grout design, Meyco MP320 colloidal silica was chosen with a colloidal silica-accelerator ratio of 5:1. The required gel time for the simulation was chosen to be 50 min; within the normal range of set times used in commercial grouting campaigns. The accelerator was found to be 1.7 M NaCl when distilled water is used, and 1.1 M when the synthetic saline water is considered. Three hypothetical cases were considered:

- (i) Accelerator concentration of 1.7 M of NaCl mixed with distilled water.
- (ii) Accelerator concentration of 1.7 M of NaCl mixed with the synthetic groundwater.
- (iii) Accelerator concentration of 1.1 M of NaCl mixed with the synthetic groundwater.

The model prediction of viscosity evolution with time for a 50 min gel time is plotted alongside the experimental data for each case in Fig. 6. As expected, for case 2 the gelling is premature, since the cations already present in the groundwater are ignored in the accelerator concentration calculation. This represents the current predicament of



**Fig. 5.** Model calibration and validation. (a) Gel time at different NaCl concentration fitting. (b) Model prediction vs experimental data. Model validation. (c) Gel time vs pH for 0.5 M electrolyte concentration of the accelerator prepared with different cations: NaCl and CaCl<sub>2</sub>. (d) Gel time vs pH for 1.0 M electrolyte concentration of the accelerator prepared with different cations: NaCl and KCl. (e) gel time vs pH for different silica concentration (0.40 and 0.37) of grout prepared with a NaCl concentration of the accelerator of 2.0 M. (f) Experimental data vs model prediction.

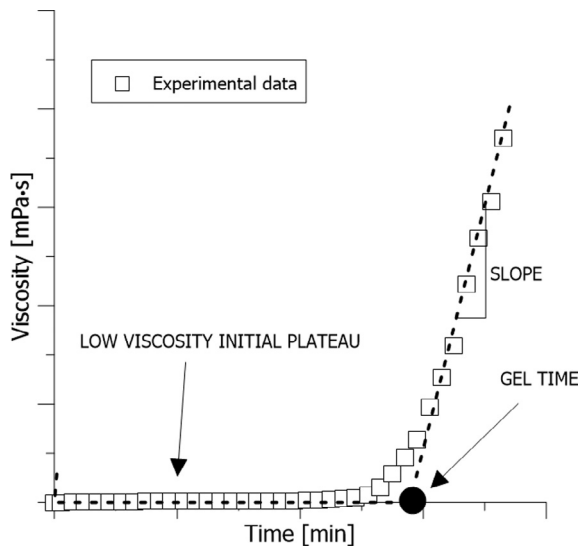


Fig. 6. Viscosity evolution. Experimental data for case 1, 2 and 3 compared with as “designed” viscosity.

grouting contractors wishing to apply colloidal silica in saline or complex environments, where without having a tool to enable them to adjust their grout mixes based on the local groundwater conditions, current practice may result in poor control of colloidal silica gelling on-site and thus impact grout penetration. Fig. 6 illustrates that the desired gel time and predicted viscosity evolution can be achieved (deviation of 3 min) for the simple scenario of preparing the accelerator using distilled water (case 1) and for case 3 where the presence of multiple cations present in the synthetic groundwater were taken into account in the accelerator design calculations using the model. These results validate the use of the model for the design of grouting campaigns for injection at sites with saline or complex groundwater.

## 7.2. Further considerations

The model presented here uses a single set of parameters that have been calibrated for an ambient temperature of 20 °C. These parameters would require recalibration for a change in the ambient temperature. As an alternative to recalibration, the effect of temperature on gel time has been well studied (Bergna and Roberts, 2005; Iler, 1979); as temperature increases, the gel time reduces and vice versa. In general, (Tung and Dynes, 1982; Enns and Gillham, 1983; Roller, 1975) the change in gel time with temperature is modelled by means of the well-known Arrhenius equation (Arrhenius, 1889) which describes the temperature dependence of a chemical reaction by means of an exponential equation for the reaction rate. Both the analytical model proposed here and the Arrhenius equation are exponential in nature and, hence, can theoretically be combined without the introduction of additional fitting parameters. To validate a combined model, an additional experimental campaign would be required in which temperature can be controlled to take the range of values likely to be encountered in ground engineering applications.

The above case study shows that, for a fixed temperature, the model accurately predicts the gel time of the colloidal silica grout (under simultaneous variations in pH, electrolyte concentration, cation valency, cation molar mass, silica particle size and silica concentration) without requiring parameter re-calibration. This makes it a powerful tool for enabling bespoke design of a grouting campaign. For example, when injecting into a saline aquifer, the difference in salinity between the groundwater and the advancing grout front could significantly alter the gel time of the grout at the front, incurring a risk of premature gelling. In high pressure injection of viscous grouts such as cement, cation diffusion at the grout front is generally considered negligible. Colloidal

silica, however, has a density and viscosity similar to water and is mainly proposed for injections at low pressure or at higher pressures to achieve greater soil or rock mass penetration (i.e. longer gel times). Under these conditions, mass transport due to cation diffusion may occur at the grout front. To eliminate this risk, the accelerator could be designed so that the concentration of each individual cation present within the groundwater is less than that within the final grout mix, thus inhibiting inward diffusion of cations at the grout front.

## 8. Conclusions

This paper presents the first generic model for gelling of colloidal silica based grout that accounts for changes in pH, electrolyte concentration, cation valency, cation molar mass, silica particle size and silica concentration. The model gives good predictive capability without the need for parameter re-calibration for multiple cations with differing molar mass and valency, at a range of pH and silica concentrations.

The developed model is applied to calculate appropriate accelerator concentrations for a given gel time (and hence penetration distance) for use in hydraulic barrier formation in saline groundwaters. Using synthetic groundwater, based on data from the proposed site for spent fuel disposal in the Olkiluoto area of Finland (Ollila, 1999), the model successfully predicts the required accelerator concentration to achieve a grout gel time of approximately 50 min, taking account of cations already present within the synthetic groundwater.

## Acknowledgments

The authors gratefully acknowledge the financial support of the Research Councils' UK Energy Programme under grant EP/L014041/1, “Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories (DISTINCTIVE), and for the additional support provided by our key industry partners, NDA, NNL and Sellafield Ltd.

## References

- Arrhenius, S., 1889. Über die Dissociationswärme und den Einfluss der Temperatur auf den Dissociationsgrad der Elektrolyte. *Z. Phys. Chem.* 4, 96–116.
- Axelsson, M., 2006. Mechanical tests on a new non-cementitious grout, silica sol: a laboratory study of the material characteristics. *Tunn. Undergr. Space Technol.* 21, 554–560.
- Bahadur, A., Holter, K., Pengelly, A., 2007. Cost-effective pre-injection with rapid hardening microcement and colloidal silica for water ingress reduction and stabilisation of adverse conditions in a headrace tunnel. In: *Underground Space-The 4th Dimension of Metropolises, Three Volume Set + CD-ROM: Proceedings of the World Tunnel Congress 2007 and 33rd ITA/AITES Annual General Assembly, Prague, May 2007*, 2007. CRC Press, p. 297.
- Bergna, H.E., Roberts, W.O., 2005. *Colloidal Silica: Fundamentals and Applications*. CRC Press.
- Butrón, C., Axelsson, M., Gustafson, G., 2009. Silica sol for rock grouting: laboratory testing of strength, fracture behaviour and hydraulic conductivity. *Tunn. Undergr. Space Technol.* 24, 603–607.
- Butrón, C., Gustafson, G., Fransson, Å., Funebag, J., 2010. Drip sealing of tunnels in hard rock: a new concept for the design and evaluation of permeation grouting. *Tunn. Undergr. Space Technol.* 25, 114–121.
- Eklund, D., Stille, H., 2008. Penetrability due to filtration tendency of cement-based grouts. *Tunn. Undergr. Space Technol.* 23, 389–398.
- Enns, J.B., Gillham, J.K., 1983. Time-temperature-transformation (TTT) cure diagram: modeling the cure behavior of thermosets. *J. Appl. Polym. Sci.* 28, 2567–2591.
- Funebag, J., Fransson, Å., 2006. Sealing narrow fractures with a Newtonian fluid: model prediction for grouting verified by field study. *Tunn. Undergr. Space Technol.* 21, 492–498.
- Funebag, J., Gustafson, G., 2008. Design of grouting with silica sol in hard rock—New design criteria tested in the field, Part II. *Tunn. Undergr. Space Technol.* 23, 9–17.
- Gallagher, P.M., 2000. *Passive Site Remediation for Mitigation of Liquefaction Risk* (Ph.D.). Virginia Polytechnic Institute and State University.
- Hakem, N., Al Mahamid, I., Apps, J., Moridis, G., 1997. Sorption of cesium and strontium on Savannah River soils impregnated with colloidal silica. In: *International Containment Technology Conference*. Petersburg: [sn], pp. 652–657.
- Iler, R.K., 1979. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*. John Wiley & Sons.
- Jurinak, J., Summers, L., 1991. Oilfield applications of colloidal silica gel. *SPE Prod. Eng.* 6, 406–412.



- Karol, R.H., 1968. Chemical grouting technology. *J. Soil Mech. Found. Div., Am. Soc. Civ. Eng., United States*, p. 94.
- Karol, R.H., 1982. Chemical grouts and their properties. *Grouting Geotech. Eng. ASCE* 359–377.
- Lakatos, I.J., Medic, B., Jovicic, D.V., Basic, I., Lakatos-Szabo, J., 2009. Prevention of vertical gas flow in a collapsed well using silicate/polymer/urea method. In: *SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers.
- Magill, D., Berry, R., 2006. Comparison of Chemical Grout Properties, Which Grout Can be Used Where and Why. Webster, Texas, Avanti International.
- Manchester, K., Zaluski, M., North-Abbott, M., Trudnowski, J., Bickford, J., Wraith, J., 2001. Grout selection and characterization in support of the colloidal silica barrier deployment at Brookhaven National Laboratory. In: *Proc. 2001 International Contain. and Remed. Technol. Conf. and Exhib.*, 10–13 June, 2001. Orlando, FL.
- Moridis, G., Apps, J., Persoff, P., Myer, L., Muller, S., Pruess, K., Yen, P., 1996a. A field test of a waste containment technology using a new generation of injectable barrier liquids. *Medium: ED; Size: 16p*.
- Moridis, G., James, A., Oldenburg, C., 1996b. Development of a design package for a viscous barrier at the Savannah River site. Lawrence Berkeley National Lab., CA (United States). Funding organisation: USDOE Office of Environmental Restoration and Waste Management, Washington, DC (United States).
- Moridis, G., Persoff, P., Apps, J., Myer, L., Pruess, K., Yen, P., 1995. A field test of permeation grouting in heterogeneous soils using a new generation of barrier liquids. *Committed To Results: Barriers for Long-Term Isolation*. ER, 95.
- Moridis, G.J., Finsterle, S., Heiser, J., 1999. Evaluation of alternative designs for an injectable barrier at the Brookhaven National Laboratory Site, Long Island, New York. *Water Resour. Res.* 35, 2937–2953.
- Ollila, K., 1999. Dissolution of unirradiated UO<sub>2</sub> fuel in synthetic groundwater—Final report (1996–1998). Posiva Rep 99-24.
- Persoff, P., Apps, J., Moridis, G., Whang, J.M., 1999. Effect of dilution and contaminants on sand grouted with colloidal silica. *J. Geotech. Geoenviron. Eng.* 125, 461–469.
- Persoff, P., Finsterle, S., Moridis, G.J., Apps, J., Pruess, K., Muller, S.J., 1995. *Injectable Barriers for Waste Isolation*. Lawrence Berkeley Lab, CA, United States.
- Roller, M., 1975. Characterization of the time•temperature•viscosity behavior of curing B-staged epoxy resin. *Polym. Eng. Sci.* 15, 406–414.
- Sears Jr., G.W., 1956. Determination of specific surface area of colloidal silica by titration with sodium hydroxide. *Anal. Chem.* 28, 1981–1983.
- Tsuji, M., Funehag, J., Kobayashi, S., Sato, T., Mikake, S., 2014. Comparison of grouting with silica sol in the Äspö Hard Rock Laboratory in Sweden and Mizunami Underground Research Laboratory in Japan. In: *ISRM International Symposium-8th Asian Rock Mechanics Symposium*. International Society for Rock Mechanics.
- Tung, C.Y.M., Dynes, P.J., 1982. Relationship between viscoelastic properties and gelation in thermosetting systems. *J. Appl. Polym. Sci.* 27, 569–574.
- Yates, P.C., 1990. Kinetic of gel formation of colloidal silica sols. In: *200th National meeting: Abstract*.