A Silicate Based Process for Plugging the Near Well Bore Formation

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HAL Id: hal-01740288
https://ifp.hal.science/hal-01740288

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Abstract

A method for treating the surrounding of a well using a reactive suspension is studied, using silicate based solutions. They present the following key qualities: high performance, long term chemical stability, good injectivity, little environmental impact. We present an experimental investigation of the precipitation of commercial low-cost potassium silicate solutions, using a weak acid to lower the pH. Experiments were performed between 20°C and 60°C, by adding a non-hazardous acidic compound to the silica based solution. Bulk gelation times were estimated between a few minutes to 4 days. A coreflood injection experiment was then performed on an analog sandstone sample, representative of CO_2 formation, by using an optimum mixture with viscosity close to water. After a few days, a breakthrough experiment was performed by increasing gradually the differential pressure across the sample. Preliminary results indicate a very large strength of the order of 600 bar/m.

1. General principles

A large number of methods can be used to treat the surrounding of a well [1]. The objective here is to inject a solution around the well in a selected depth interval (a few meters) in order to plug the formation, i.e., reduce porosity and permeability ideally down to zero. Hence, CO_2 flow at this depth interval cannot occur. Schematically, the envisioned process is such that the porosity should be filled with a solid, and this solid is the result of the precipitation of some components of the injected solution.

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Some key requirements are:
- long term stability (one year or more),
- injectivity: the solution should not be too viscous, nor contain too large particles,
- reactivity: the solution should not react outside the geologic formation, and especially in the well during injection; i.e., the reaction should not be too fast for practical reasons.

Beside other possibilities such as cement or resins, a first initial choice was to select a process among two main categories: the precipitation of carbonate or silicate alkaline solutions. For example, using a lime solution:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

or using a silicate solution (water glass):

$$Na_2O.3SiO_2 + 2H_2O + 2CO_2 \rightarrow 2NaHCO_3 + 3SiO_2(am) + H_2O \tag{2}$$

In the latter, amorphous silica is formed when the pH is low enough, for example at the plateau value of solubility (other solids are formed at intermediate pH values). The difference can be viewed in terms of the solubility of calcium and silica in alkaline solutions (Figure 1). As a function of pH, the solubility of silica is much higher and potentially, the amount of solid that can be formed is much higher. Another strong argument in favour of silicates is related to their stability: indeed, below a pH of about 9 (Figure 1), no dissolution occurs and a plateau of solubility is present. This is not the case for carbonates for which the solubility is still evolving around a neutral pH and below. In a geological formation containing CO_2, the pH could still change as a function of the brine-rock-CO_2 equilibrium but there is no known process able to bring pH values back to 9 and above. Hence, the generated solids plugging the porous media are fundamentally stable when the initial solution is diluted and the pH drops down below 8.
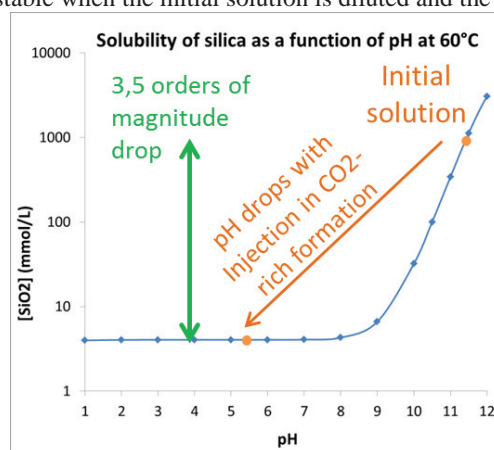

Figure 1: Solubility of Ca and SiO_2 as a function of pH

The efficiency of carbonate vs. silicate solutions has been investigated recently [2] by performing experiments in a bead pack. The reduction of the apparent permeability to CO_2 after precipitation of the injected solution is one order of magnitude larger for silicate solution compared to a lime solution. These observations confirm our reasoning.

2. Literature brief overview

Silicates are used in the petroleum industry but also for other applications related to soil consolidation and civil engineering (e.g. [3]). Besides these two domains, systems made of silica and an alkali metal (e.g. NaOH, KOH) are heavily used in chemical engineering to produce silica particles by precipitation, and nanoporous solids as catalysis support. For this domain, the related knowledge can be found (at least) in two reference books on the subject [4,5].

An overview of the general mechanisms involved in the precipitation processes to form particles is given in Figure 2. Starting from a liquid state containing various complexes (described later), the decrease of pH induces the formation of oligomer, followed by the growth of primary particles. If the concentration of these particles is high enough (as the pH is further decreased), the growing aggregates percolate and form a gel. The gel may precipitate to form solid silica-based porous nano-particles. The sodium silicate chemistry is rather complex and still not fully understood. Quite surprisingly, new precipitation processes to produce silica particles are still being developed nowadays [6]. Unfortunately, as will be seen, some important aspects of interest for our application cannot be found.

Silicates are used for conformance control in the petroleum industry [7–9]. Processes based on pure silicate solution (our situation) have been evaluated by Lakatos et al. [9]. We list below a series of advantages and disadvantages noted by these authors:

Advantages:
- Low viscosity,
- Short to moderate pumping time before onset of gelation,
- Flexible chemical mechanisms,
- Good chemical stability,
- Excellent thermal and mechanical resistivity,
- Easy gel breaking in case of technical failures,
- Simple and cost effective surface technology,
- Environmentally friendly material, prone to form precipitates instead of gel

Disadvantages:
- Rigid gels prone to fracture
- Syneresis effect (shrinkage and water expulsion) inducing potentially a time dependant blocking effect,
- Solution penetration may be short if buffer capacity of the rock is high
- Setting time difficult to control
- Initiation of intensive ion exchange
- Modify interfacial properties

The setting time (or gelation time) is indeed a critical issue because silicates are very reactive products.
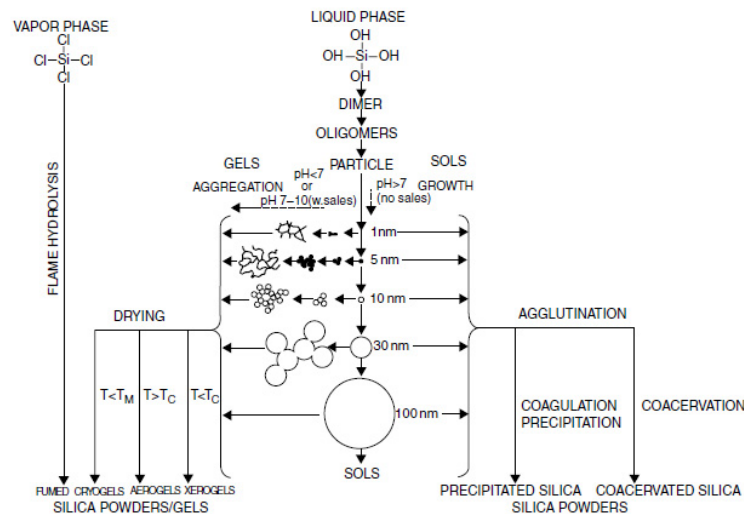

Figure 2: General overview of polymerization and precipitation of alkaline silica solution [5].

2.1. Gelation time

The gelation time is typically measured using a rheometer (as detailed later), or by visual observations of the sol-gel transition; therefore it varies from one author to another. For conformance control, the gelation time was measured as a function of both the pH and the Na concentration (Figure 3, [10]); the initial sodium silicate solution at pH=11.4 was first diluted with distilled water and then hydrochloric acid was added to lower the pH and initiate a reaction. All the data can be described nicely using exponential functions. As the Na-Si concentration increases, the gelation

time becomes very short below pH=10 (a few minutes), suggesting that the gelation may be quasi-instantaneous when using a concentrated solution. A more comprehensive explanation of gelation is given by Tognonvi et al. [11]. The gelation time of an alkaline silica solution ([Si]=3.7 mol/l) diluted in HCl has been studied and the results reported either at a constant Si concentration or at a constant pH to observe the effect of these two parameters independently. The increase of gelation times for increasing pH is interpreted as a competition between poly-condensation reactions and the formation of silicate species due to the dissolution of particles. The decrease of gelation times for increasing concentration is due to a dilution effect, poly-condensation effects becoming more difficult when particles are more dispersed.
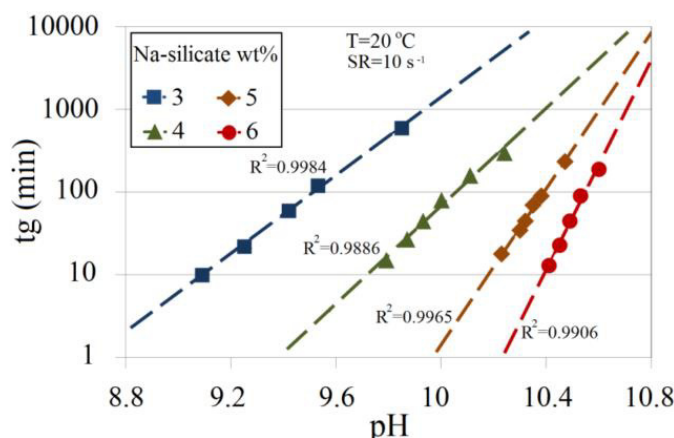

Figure 3: Gelation time tg for Na silicate solutions [10].

Effect of temperature

The temperature effect on gelation times can be described by a Arrhenius type relationship - exp(Ea/RT) - where Ea is an activation energy (J/mol), R is the gas constant (8. 314 J/mol/K) and T is the temperature in Kelvin. Above 40°C, it was found [10] that the gelation time decreases with Ea=70 kJ/mol, in agreement with other work (when gathering all works, the range is 60-80 kJ/mol). Similarly for the precipitation rate, an Arrhenius relationship was also chosen with an activation energy of -49.8 kJ/mol in the range of temperature relevant for geologic storage [2]. With such a high activation energy, gelation time may increase by a factor of 5 between 40 and 60°C, and the precipitation rate by a factor of 11.

Effect of salinity

Similarly to clay suspensions, the presence of salt affects the gelation time or may even generate a gel. In general, dissolved salts tend to reduce repulsive forces between particles, depending also on their surface charges. It was found [12] that the gelation time may be severely affected by dissolved salts in the usual range of interest in geological formations. However, in this case, the studied system is a suspension of non-porous silicate particles of size around 10 nm, in brines with different salinities. The gelation time decreases by several orders of magnitude. It was also observed that divalent ions (Ca^{2+} or Mg^{2+}) impact the gelation time compared to NaCl brines [10]. In addition, simple NaCl solution can be used to initiate a reaction without adding acid [13].

2.2. Viscosity

Viscosity and density can be found in individual studies. Charts showing general trends are available since 1952 [14]. For viscosity (Figure 4), we observe a sharp decrease in a narrow range of Na_2O content for Na silicate

alkaline solution diluted in water. Since the pH is not very sensitive to water dilution unless one uses very large dilution ratios, these diluted solutions are all stable.
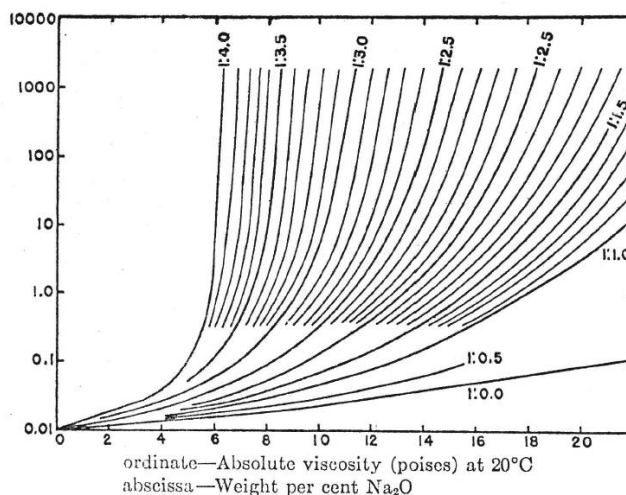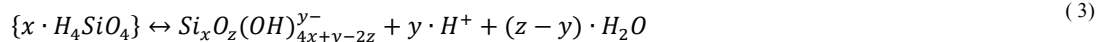

Figure 4: Viscosity chart at 20°C for constant Na$_2$O /SiO$_2$ ratio (by weight) as a function of Na$_2$O content; the solution is diluted with water [14].

2.3. Chemical characterization, speciation and gel type

Whereas diluted solutions (< 0,01 M Si) contain only the mono-silicic acid $H_4SiO_4(aq)$ and its associated anions $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, silico-alkaline solutions SAS with high concentrations of SiO$_2$ and Na$_2$O contain a variety of oligomers $\{x \cdot H_4SiO_4\}$, with x up to 8, and their conjugated anions [15] :

$$\{x \cdot H_4SiO_4\} \leftrightarrow Si_xO_z(OH)_{4x+y-2z}^{y-} + y \cdot H^+ + (z-y) \cdot H_2O \tag{3}$$

A general framework for the polymerization/precipitation process is available [4] but more detailed descriptions have only become available recently using ^{29}Si NMR spectroscopy. Oligomers are described as purely Si-O-H structures in all the publications we could refer to, except Tognonvi et al. [16,17] who introduced Na-Si-O-H structures to account for the observed gels that appear from Na-Si waterglass (Figure 5). Their approach combined small-angle X-ray scattering (SAXS) to ^{29}Si NMR spectroscopy. The concentrated sodium solution had the following characteristic: pH=11.56, [Si]=7mol/l, Si/Na atomic ratio=1.71. Initially at the highest pH (11.56), the identified species is a Si$_7$O$_{18}$H$_4$Na$_4$ neutral complex (Figure 5). As the pH decreases with water dilution, the above neutral complex is dissociated progressively into (Si$_7$O$_{18}$H$_4$Na$_{4-n}$)$^{n-}$ and Na$^+$ ions. The same authors also studied the complexes formed during dilution with hydrochloric acid [11]. In particular, in the pH range 9-10.75 and Si concentration between 0.2-2.9 mol/l, irreversible gels are formed and solids are generated. According to this interpretation, the Si$_7$O$_{18}$H$_4$Na$_4$ complex and its associated anions contain the major part of the dissolved silica in concentrated SAS at high pH.
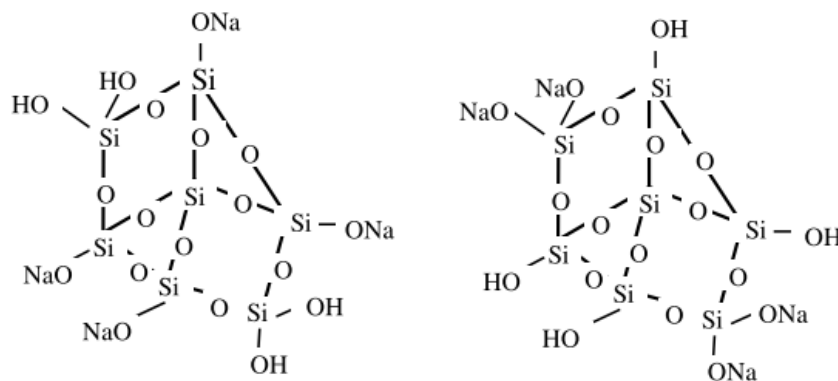
Figure 5: Structure of two possible $Si_7O_{18}H_4Na_4$ complexes compatible with the NMR and SAXS measurements [17].

Solution speciation, i.e., the distribution at equilibrium of concentrations and activities of dissolved species, can be calculated at conditions (temperature T, pressure P, concentration) for which equilibrium constants are available. Provided that relevant data are known, it is the most straightforward and rigorous way to predict pH and composition evolution when mixing the SAS with other solution, and to calculate saturation with respect to solid phases, e.g., a silica phase likely to precipitate when the SAS is acidified, or a mineral phase with which the SAS is in contact in a reservoir. An example of common species distribution is represented in Figure 6. Gaboriaud et al. [15] used these values to simulate acidification of 6 distinct SAS, which they also performed experimentally by incremental addition of 0,5 ml of 1 M HCl to 10 ml SAS, and found an agreement between simulations and experiments. However, there is some uncertainties whereas this approach can be applied to our concentrated solutions and the possible existence of more complex species as described above, for which equilibrium constants are not available.
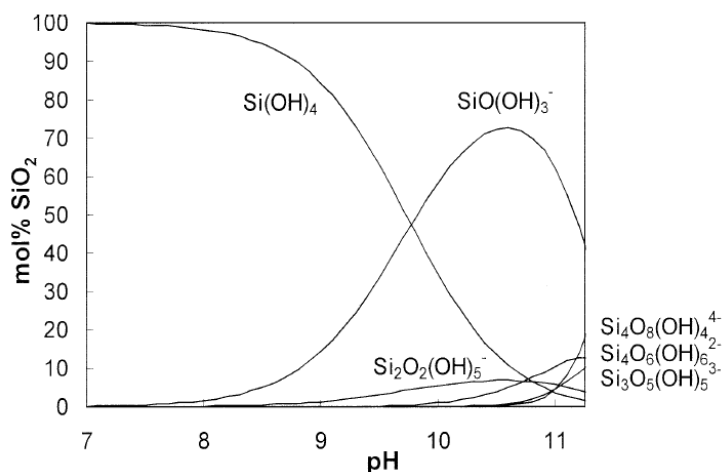

Figure 6: Distribution of the most abundant silicic species, at 25°C and at equilibrium with amorphous silica [18].

Finally, the type of gels or precipitates is of primary importance. For Na silicate solutions, gel types were mapped as a function of pH and Si concentration (Figure 7, [16]). Several domains were evidenced:

- **Domain A :** limpid, stable solution ;
- **Domain B :** gelling, transparent gel, stable except if T increase, or agitation, or water dilution ;
- **Domain C :** gelling, white gel, stable except if T increase or water dilution, ripening with time to form white grains that settle down ;
- **Domain D :** gelling, ripening irreversibly to solid.
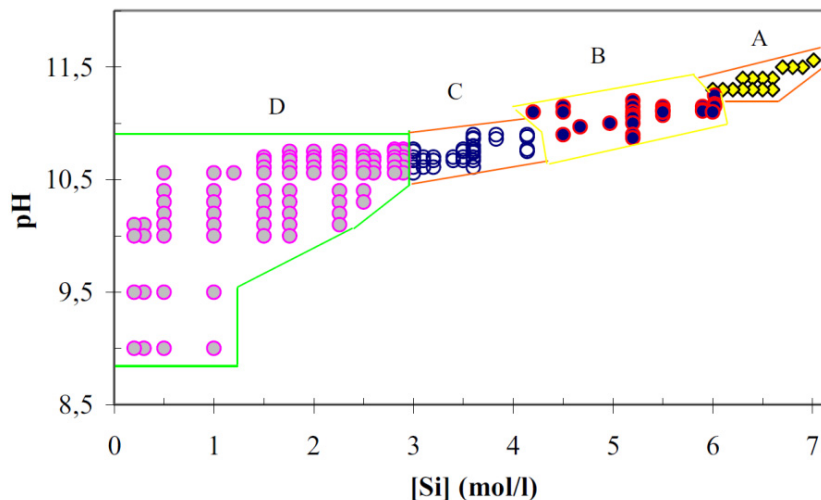

Figure 7: Various behavior of SAS observed at varying Si concentration and pH [16]. Domain A : limpid, stable solution ; Domain B : gelling, transparent gel, stable except if T increases, or agitation, or water dilution ; Domain C : gelling, white gel, stable except if T increases or water dilution, ripening with time to form white grains that settle down ; Domain D : gelling, ripening irreversibly to solid.

For our application, the target is to create irreversible gels and solids.

3. Description of the process and results

3.1. Choice of solution and characterization

There is a very large number of parameters to consider in designing a solution that is expected to precipitate and plug a porous media. A compromise must be found between several contradictory effects. First, to decrease porosity, one should choose the highest possible Si concentration such that precipates will occupy the largest possible volume. However, when the Si concentration is high, the viscosity may too important, gelling time may be too short or too difficult to control (Figure 3), and the gel type may not be irreversible (Figure 7). After a screening performed on various solutions, detailed studies were performed around an optimum one.

The silicate solutions were provided by Woellner, a leading manufacturer of silicates (Table 1). Among the 4 main products available, we chose a potassium silicate with the lowest viscosity, BetolK28T (Table 2). Diluted at 50wt%, the viscosity is reduced to 1.1 cP at 40°C, with a density of 1.11 g/cm^3 (Table 3).

Table 1: Characterization of Woellner solutions.

Product Name	SiO$_2$ %	Na$_2$O %	K$_2$O	Molar ratio	Viscosity (cP)	Density	pH (*)
Ligasil 39	27.5	8.3	0	3.47	100	1.37	11.3
NaSil HK35	26.1	7	0	3.85	150	1.32	11.3
Betol K35T	23.9	0	10.9	3.43	55	1.32	11.0
Betol K28T	20.5	0	8.2	3.92	28	1.25	10.8

(*) at a dilution of 10% in water

Table 2: Characteristics of the silicate solution provided by the manufacturer (Woellner).

Betol K28 T solution	
SiO$_2$ content	20.5 wt% 2.645 mol/L
SiO$_2$/K$_2$O	3.92
K$_2$O	8.2 wt%
pH	11.62
Specific density	1.25 g/cm^3
Viscosity	28 mPa.s at 20°C

Table 3: Characteristics of the diluted solution

Potassium silicate solution Betol K28 T / Water solution 50 : 50 by weight	
SiO$_2$ content	1.90 mol/L
pH	11.41
Specific density	1.11 g/cm^3 at 20°C
Viscosity	1.20 mPa.s at 29.7°C
	1.08 mPa.s at 41.9°C
	0.99 mPa.s at 63.6°C

3.2. Preliminary test with CO$_2$ at a gelling agent

Preliminary tests were performed with a sodium silicate solution provided by Sigma-Aldrich (SiO$_2$ content: 6.04 mol/L, SiO$_2$/Na$_2$O=2.2). Several batch experiments were performed to see if precipitates are generated in contact with CO$_2$. In a reactor maintained at 40°C, different diluted solutions were placed in contact with CO$_2$; the reactor is then closed and the pressure recorded. The run products (Figure 8) for one dilution (10% water, 90% water glass solution) are about 4 wt% heavier than the initial solution introduced in the reactor, which indicates that CO$_2$ has been trapped in the solid run products. It indeed appears that solid carbonate phases are formed as well as amorphous silica gel, as it is indicated by the presence of a solid white precipitated product surrounded by the transparent silica gel. This observation have been confirmed by XRD data, which indicate the presence of two different sodium carbonates, one being hydrated and having thus a higher molar volume.
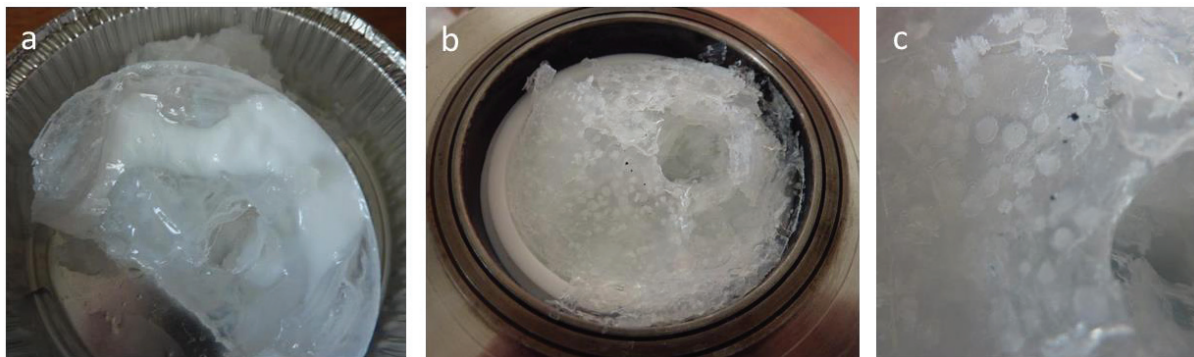
Figure 8: (a) Run products of experiment 2; silica gel is observed around a more solid white phase, formed of carbonates. (b)-(c) Run products of experiment 4. White centimeter-sized phases, which we identify as carbonates, can be observed in the silica gel.

Under the same pressure of CO_2 (50 bar), a more diluted solution (50%/50%) showed an increase of mass of 10%. Since this experiment had less Na available to form Na-carbonates than the previous experiment, the excess amount of trapped CO_2 must have been dissolved in the gelified water of the solid silica phase.

To quantify the degree of hydration of the solid phase with a rudimentary method, 26.4 g of solid was placed over 24h at 60°C in an anhydrous environment. Only 6.75g remained after 24h. After 48h, 6.67 g. After a week, 6.52 g. In other words, it appears that around 75 wt% of the formed phase was composed of water. Since water actually represented around 83.5 wt% of the initial mixture (50% water glass solution, 50% pure water), it represents around 75.9 wt% of the run product incorporating trapped CO_2. This suggests that the residue remained feebly hydrated (0.9 wt%) and that the carbonates formed remain stable.

Using CO_2 to precipitate silica is an efficient means to form various solids at high CO_2 pressure. However, the reaction kinetics are fast and difficult to control. In addition, there is no theoretical basis to predict the run products and the amount of CO_2 trapped in the solid phase. In practice, the injection of such a solution in the formation around a well may be difficult due to fast reactivity yielding a short penetration. Based on these observations and especially in view of the lack of possible control of the kinetics of precipitation, it was decided to explore a different option: use of a weak acid to initiate a precipitation, the kinetics of which are compatible with field operations.

3.3. Gelation using acetic acid

The solution used in these experiments is Betol K28T diluted with water (50wt%). Following the methodology of Tognonvi [16], a screening was first performed with several mixtures of diluted Betol and acetic acid (1M, similar to vinegar). Precipitation was qualitatively observed for various fractions of diluted solution and acid at 40°C (Figure 9). When enough acid is present, solid precipitates are observed after a variable time and these solids cannot be dissolved again back into water. If the acid content is too low (not shown), the gel is weaker and reversible. These tests allowed 3 acid concentrations to be tested in more detail using rheological and NMR measurements, as described in the next section.
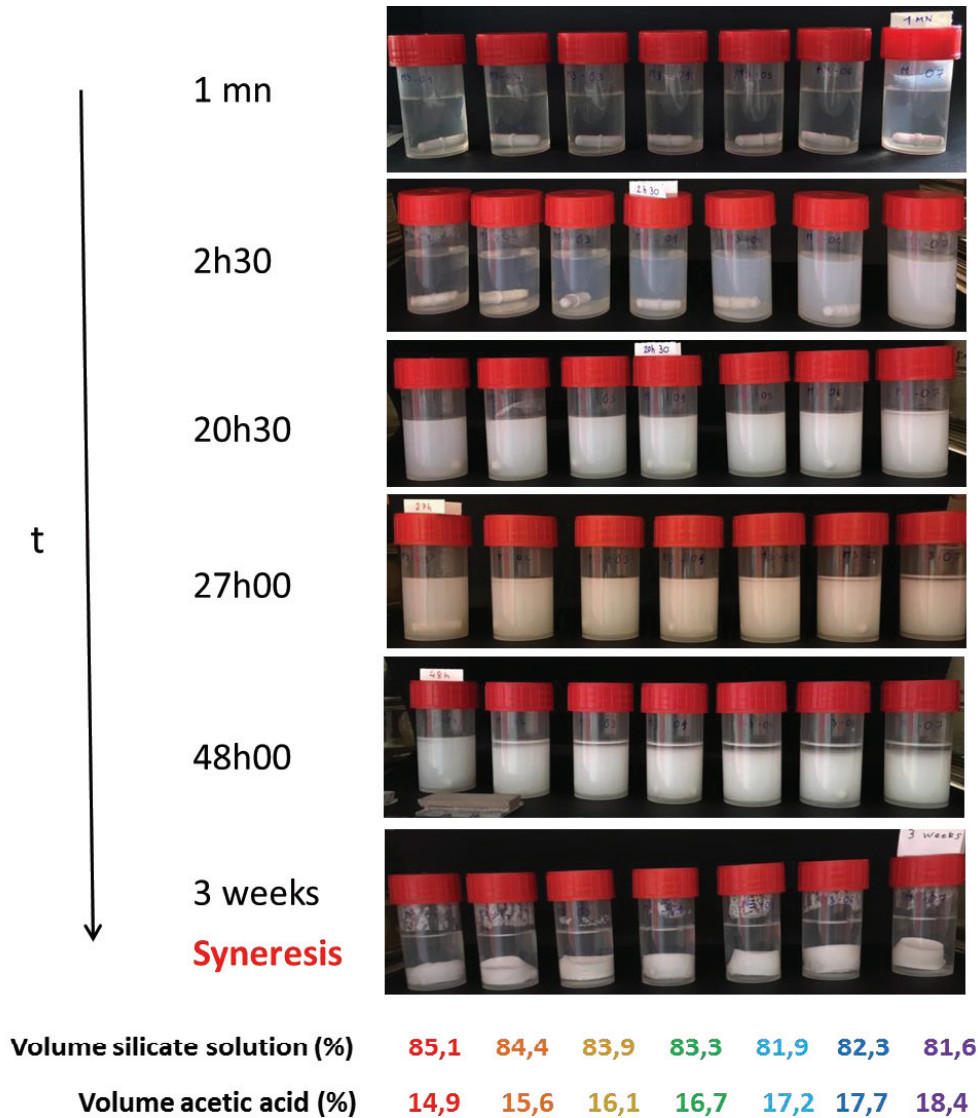
Volume silicate solution (%)	85,1	84,4	83,9	83,3	81,9	82,3	81,6
Volume acetic acid (%)	14,9	15,6	16,1	16,7	17,2	17,7	18,4

Figure 9: Precipitation experiments with acetic acid (1M) at different times. Solution: BetolK28T diluted with water (50wt%).

The gelling times can be obtained very precisely from rheological measurements. The instrument used is a MCR300 from Physica. The geometry is a cone-plate maintained at 40°C using a Peltier set-up, together with a system minimizing evaporation and contact with air. The rheometer was operated in an oscillating mode at low frequency (1Hz) and small oscillating angle (<10°), yielding a shear rate as small as possible. Such protocol are common when studying polymers.

A typical result is shown in Figure 10. The purpose of the graph is to show the sudden increase in viscosity after 500 minutes, defining precisely the gelling time t_g (in this case 510 min); note that the viscosity value before gelling may not be accurate and it has been measured using another geometry (exact values are given in Table 3).
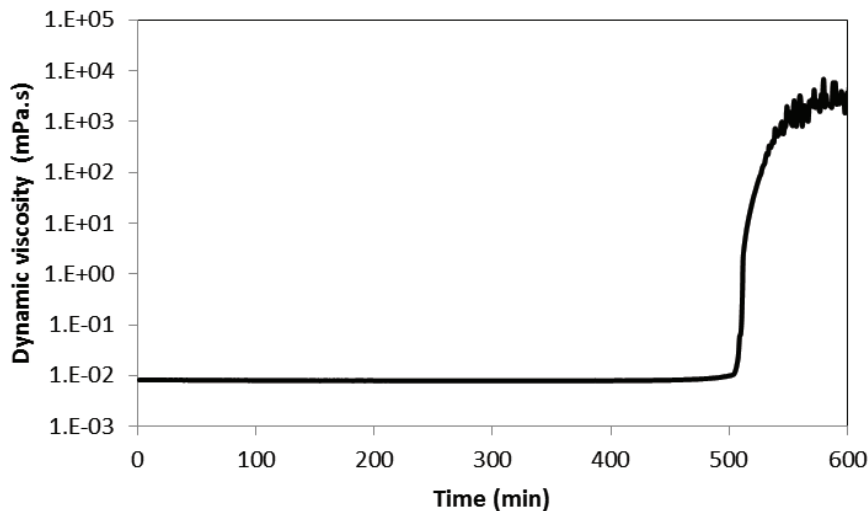
Figure 10: Evolution of the viscosity of a mixture diluted Betol K28T with 15.7wt% of acetic acid 1M. Temperature: 40 °C.

The viscosity measurements tend to indicate that no change in the mixture occurs before tg but this is not true. Another useful method is to study the evolution of the water interactions within the mixture, and this is given by the NMR relaxation measurements as a function of time (Figure 11, performed with a 23 MHz apparatus from Oxford Instrument); the T_2 relaxation time characterizing the mixture decreases progressively from the initial and maximum T_{2m} down to a plateau value T_{2p}. By comparing several viscosity and NMR measurements, we established that the abrupt change of viscosity corresponds to the time at which the relaxation time $T_2(t=tg)$ is such that the relative variation of relaxation times is 0.235, i.e.,

$$\frac{T_2(t = t_g) - T_{2p}}{T_{2m} - T_{2p}} = 0.235 \qquad (4)$$

The NMR relaxation time is a measure of the local interactions of water with the oligomers but the long range collective effects between oligomers yielding a gel structure and a sharp increase of viscosity cannot be detected because water molecules are not trapped within the gel and can diffuse almost freely [19]. Using NMR relaxation, we have been able to observe the syneresis effect occurring after a much longer time, and the expulsion of water leading to a bimodal relaxation time distribution instead of a unimodal distribution.
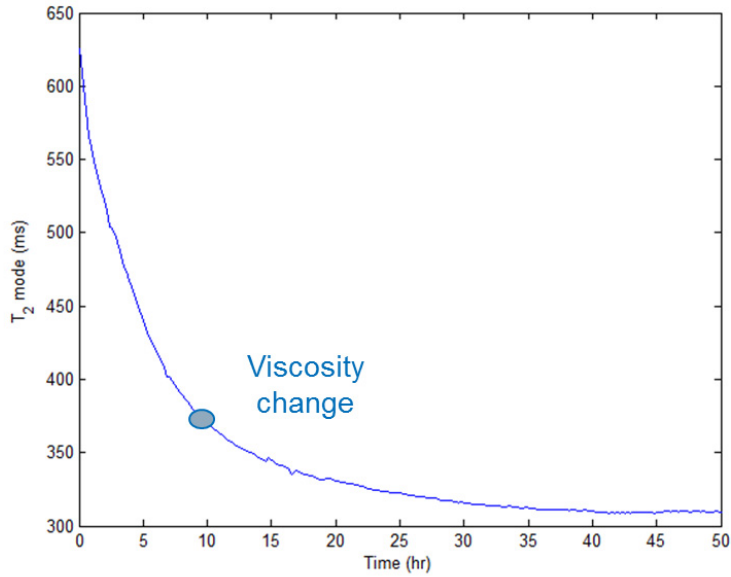
Figure 11: Evolution of the T_2 relaxation time for the same mixture as in Figure 10. The circle indicate the gelling time t_g (abrupt change of viscosity).

To study the effect of temperature on gelling times t_g, we use NMR measurements and the relationship between rheological and NMR relaxation measurements described above. In practice, NMR measurements are much more convenient to use at high temperature and provide more information. The sensitivity can be described using an Arrhenius law (Figure 12):

$$t_g \propto \exp(-\frac{E_a}{RT})$$

(5)

where Ea is an activation energy (J/mol), R is the gas constant (8. 314 J/mol/K) and T is the temperature in Kelvin. From the data, we found Ea=80kJ/mol (Figure 12). Such a value is in agreement with literature as discussed earlier. Expressed in more practical units, such an activation energy means a strong dependence with temperature. For example, at 40 °C, we have a gelling time of 510 min (8.5 h), at 50°C, 193 min (3.2 h) and at 60°C , 77 min (1.3 h).
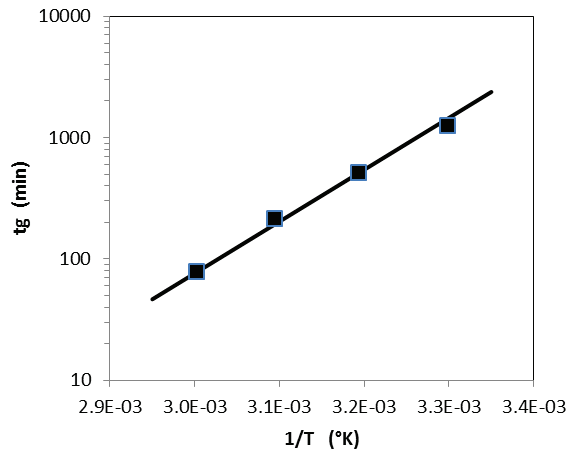
Figure 12: Gelling times determined by NMR as a function of temperature (data points at 30, 40, 50 and 60°C). BT28 solution diluted with 50wt% water. Acetic acid content: 15.7wt%.

Increasing the acid fraction above 15.7% decreases the gelling time by a factor of about 4.5 (Figure 13) but it is not possible to increase the gelling time by lowering further the acid fraction. Hence, it appears that, using acetic acid, a maximum and ideal value is reached (about 15.7%).
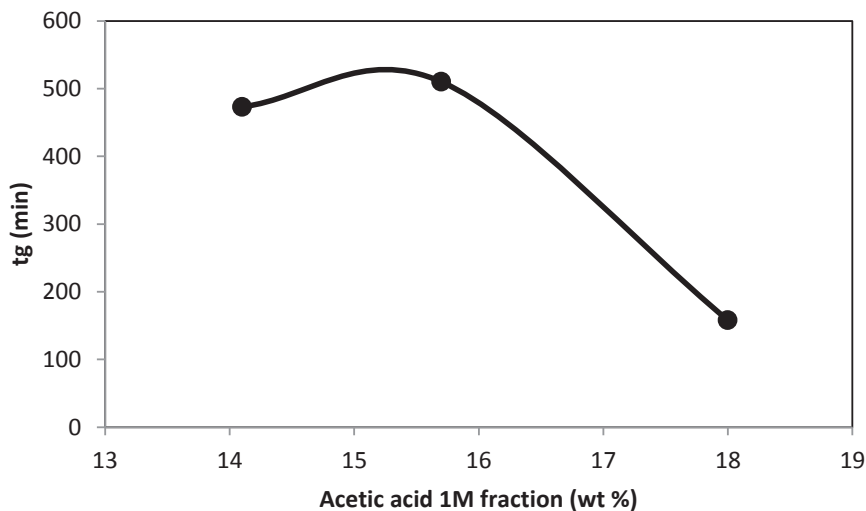

Figure 13: Gelling times as a function of acetic acid fraction at 40°C. Lowering the amount of acid in the solution does not increase the gelling times.

3.4. Results in porous media

The strength of the gel was tested in a porous media in a flooding cell (Figure 14). In a similar way to CO_2 injection experiments, we injected the mixture in different porous media. The samples are small plugs 2 cm in diameter and 3 cm long. The applied confining pressure was 80 bar, and the pore pressure was 20 bar. The protocol was the

following:

- - After saturation with 20 gr/l NaCl brine, measure the permeability to brine,
- - Inject the reactive solution into the plug and monitor the pH at the outlet; stop when the pH has reached the value of the injected solution,
- - Flush all tubing and end-pieces with brine,
- - Wait for 24 hours or more,
- - Inject brine through the tubing and end-pieces to verify that they are not plugged,
- - Try to inject brine through the porous media.

This protocol was performed at 40°C. Several experiments of this type were performed and they all indicate that the porous media was severely plugged. For example, a pressure differential of about 20 bar could be applied to the plug before measuring a significant flow rate. Since the plug length was 3 cm, these tests give therefore a gel strength of the order 600 bar/m. This test was also performed with several differential pressure steps applied for longer period of times and it gave similar results. The tests were performed on a Vosges sandstone (50 mD) and a sample from the Becej field (5mD) [20].
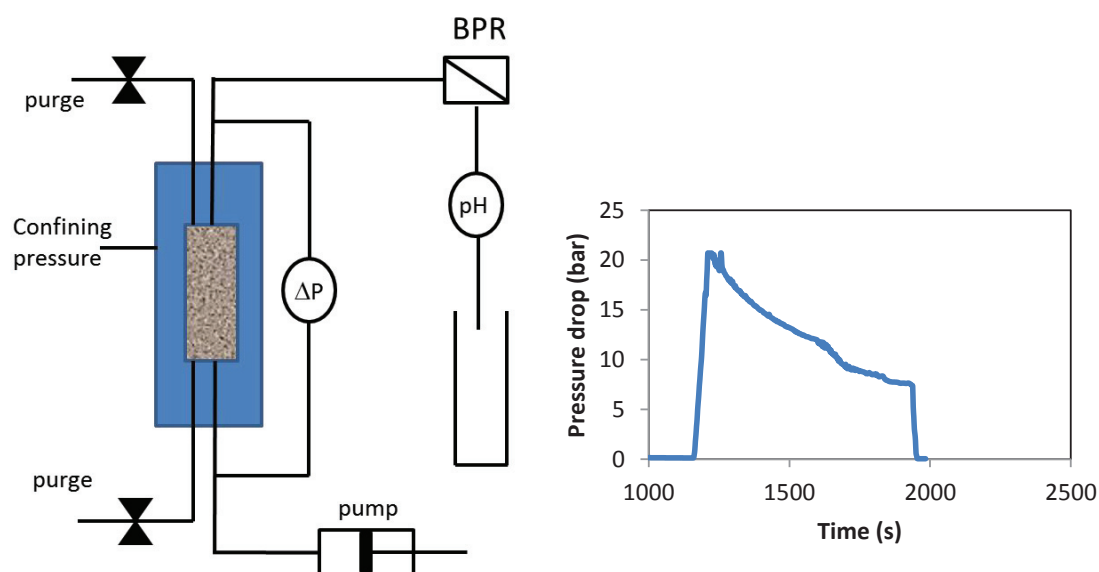

Figure 14: Simplified schematic of the experimental set-up for testing reactive solutions in porous media (left). The cell allows flushing all the tubing and end pieces to remove the reactive solution after flooding the porous media. The graph shows that a pressure differential of 20 bar could be applied before the gel breaks and allows brine to flow through the porous media.

4. Conclusion

In the framework of the MiReCOL three-year European project, a method for treating the surroundings of a well using a reactive suspension is studied. Among many possible choices, a high concentration potassium silicate solutions was selected. The process has a long term chemical stability (w.r.t. acid), good injectivity (low viscosity and no particles) and no or little environmental impact.

An experimental investigation of the precipitation of a commercial low cost potassium silicate solutions using a weak acid to lower the pH has been performed. Preliminary results using CO_2 indicate that the reaction kinetics are too fast and the plugging too strong to permit practical field implementation. Hence, laboratory experiments were

performed testing various concentrations of acetic acid added to the commercial silica based solution, and estimating the bulk gelation times before the mixture became too viscous for injection. The impact of temperature was determined by performing experiments at 20, 40 and 60°C, with gelation times estimated between a few minutes up to 4 days. To follow the kinetics, several complementary techniques were used: rheological visco-elastic properties to observe the gel onset and NMR relaxation time measurements to follow the gradual increase of water interactions within the gel.

The ability of the precipitates to plug a porous media was tested on a sandstone samples representative of CO_2 storage formations, as well as a sample from the Becej field (Serbia). With a viscosity close to water and no particles present in the liquid, injection of such products is possible in almost any permeable media. Using an optimum mixture tuned as described above, the solution is simply injected through the porous media and then left at constant temperature (e.g. 40 °C) for precipitation. After a few days, a breakthrough experiment performed by increasing gradually the differential pressure across the sample, indicate that the gel strength was 20 bar over a sample length of 3 cm (600 bar/m).

A field-test injection in a well not reported here has been performed and confirmed the ability of such product to plug a formation.

Acknowledgements

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