A silicate based process for plugging the near well bore formation

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IFP Energies nouvelles

In the framework of the MiReCOL three-year European project [1], a method for treating the surrounding of a well using a reactive suspension is studied. Among many possible choices, silicate based solutions were selected due to the following key qualities: high performance, long term chemical stability (w.r.t. acid), good injectivity (low viscosity and no particles) and no or little environmental impact.

Silica-alkaline solutions are aqueous solutions containing high concentrations of SiO\textsubscript{2} and A\textsubscript{2}O, where the alkaline element A is generally sodium (Na) or potassium (K). Commercial stable solutions exist with high molar ratio SiO\textsubscript{2}/A\textsubscript{2}O, spanning from 1.6 up to 3.9 with pH values above 11.5. When the pH is lowered either in contact with CO\textsubscript{2} or using an acid, silica precipitates to form particles [2]. Below a pH of approximately 9 according to the solubility curve, the particles formed are stable and no back-dissolution is possible unless the pH is increased again. Hence, one expects a long term stable chemical stability. Under certain circumstances, when induced in a porous media, this process has the potential to plug the formation around a well, to prevent gas or liquid flow through the treated formation. Although known for a long time [2], some details of the polymerization/precipitation process useful for quantitative prediction are only partially available recently, and systematic experimental investigation is required. Renewed interest for this type of product is also present in the oil industry for conformance issues. A key aspect is to control the gelation/precipitation kinetics in order to be able to inject the solution into the formation without plugging surface equipment or the well itself.

We present an experimental investigation of the precipitation of commercial low cost sodium and potassium silicate solutions using a weak acid to lower the pH. Laboratory experiments were performed testing various concentrations of an environment-friendly concentration of a socially acceptable and non-hazardous acidic compound, adding it 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. Multiple characterization of the run products were performed using high resolution physico-chemical techniques. To follow the kinetics, several complementary techniques were used: rheological visco-elastic properties to observe the gel onset, NMR relaxation time measurements to follow the gradual increase of water interactions within the gel, infrared spectroscopy to observe the gradual formation of Si-O-Si bonds within the fluid. In addition, the syneresis process (expulsion of water from the gel) was also studied as a function of time and temperature.
The ability of the precipitates to plug a porous media was tested on analog sandstone samples representative of CO₂ storage formations. 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 is performed by increasing gradually the differential pressure across the sample. The results obtained so far indicate a very large strength of the order of 600 bar/m. SEM imaging (Figure 1) of the plug has been performed to verify the obstruction of the pore network by the solidified gel. A field-test injection in a well is currently being considered, in order to test the efficiency of the developed method on a large-scale geological setting.

Figure 1: SEM image of the porous media after injection and precipitation of the silicate solution.

[1] Part of the research reported in this abstract has been conducted with funding from the European Commission FP7 project MiReCOL (www.mirecol-co2.eu), Grant Agreement no. 608608, 2014-2017.