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New Gel Systems To Remediate Hydraulic Short-Circuits In Heterogenous Or Fractured Heat Reservoirs

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ABSTRACT

The increasing interest for geothermal operations in highly heterogeneous or fractured reservoirs (such as EGS) highlights the effects of thermal short-circuits between injection and production wells, detrimental to the process efficiency. Remediation methods involving aqueous gels, similar to those implemented for oil production in Conformance Control Operations, are being investigated. A major challenge for adapting these methods to geothermal lies in the impact of high and varying temperatures on gelation kinetics and gel performances. Indeed, operations where short-circuits issues arise often involve deep reservoirs, with higher temperatures than oil reservoirs and significant temperature gradients in circulating fluids. This study introduces a new type of gels made of sulfonated polyacrylamide polymers and inorganic crosslinkers. As gelation requires interactions between crosslinkers and acrylate monomers that are not initially present in the polymer's structure, these systems remain in the sol phase during injection. This means that there is no risk of injection well plugging. When the sol self-propagates in the high conductivity fractures, it is exposed to increasing temperatures: acrylamide hydrolysis leads to formation of acrylates, enabling gelation over the entire fracture width. As gelation kinetics is controlled by both the temperature and the ratio between acrylamide and sulfonated units, these versatile gel systems are well adapted for geothermal operations even if the temperature gradient and fracture properties are not precisely known. The experimental study presented includes a set of parametric gelation tubes tests and coreflood experiments performed in artificially fractured plugs, where gelation kinetics, gel parting pressure and gel aging are investigated.

1 INTRODUCTION

Several types of geothermal systems relying on well doublets, such as those producing hot water from aquifers, those aimed at seasonal energy storage in aquifers (Aquifer Thermal Energy Storage, ATES), and especially those coupling heat production and lithium extraction in which the heat transfer water is injected from the surface to great depths into a fracture network (Enhanced Geothermal Systems, EGS), are likely to see their efficiency reduced by the effects of rapid hydraulic contact between injection and production wells. These effects, known as “short-circuits”, originate from preferential flows in highly permeable zones or in fractures with large openings and/or limited branching. In EGS, they compromise both the heat transfer from the rock to the water and the dissolution of lithium from the rock into the water. In conventional well doublets and ATES, they increase the risk of contact between the cold bubble and the hot bubble in the aquifer. Physical modeling of short-circuit effects has been proposed based on thermo-hydro-mechanical approaches. A notable study (Gee et al., 2021), using finite elements calculation methods and based on flow modeling in planar fracture networks between injection and production wells, showed that an initial uniform flow distribution across all fractures can gradually evolves into a configuration where the flow is dominated by a single channel. Another study (McLean and Espinoza, 2023), implementing three-dimensional modeling of the fracture network, examined the impact of temperature changes on the evolution of stress distribution in the network and showed that short-circuits are more likely to occur in areas where initial stresses are low and fractures are less compliant. Regarding field operations, short-circuit effects have been proposed to explain several observations of reduced efficiency in geothermal systems, both in heterogeneous aquifers (heat production and ATES) (Bodvarsson, 1972; Fergusson, 2007; Galgaro and Cultrera, 2013) and in EGS operating in hot dry rocks (Parker, 1999; Tenma et al., 2008). In the case studied by the Tenma group, that of the Hijiori EGS in Japan, a particularly clear correlation was observed between a drop in injection pressure and a decrease in production temperature. Such observations are consistent with the occurrence of short-circuits, which cause an increase in the permeability of the fracture network. In the United States, where geothermal energy (particularly EGS) and geothermal lithium extraction are rapidly developing, this issue was deemed significant enough to prompt a public call for research projects in 2021 (US Department of Energy, 2021).

In a remediation approach to the effects of short circuits, methods inspired by techniques known as Conformance Control, Profile Control, or Water Shutoff from the petroleum sector are being considered. These techniques, implemented since the 1980s (Sydansk, 1988; Seright, 1995 & 1997; Seright and Lee, 1999), aim to limit the flow of brine through preferential pathways in reservoirs or near wells, in order to reduce the amount of water produced. They essentially involve injecting hydrogels into the reservoir, including aqueous polymer gels (which are easily injectable and whose gelation or swelling kinetics can be controlled) or silica gels. These systems are commonly used in the field and are regularly improved (see, for example, the review by Lei et al., 2022). While the analogy with the issue of short circuits in geothermal energy is evident, two major differences mean that the technologies implemented in the petroleum sector cannot be directly transposed to geothermal energy.

The first, obvious difference is temperature: while it rarely exceeds 120°C in oil reservoirs, it can range from 80°C to over 250°C in geothermal operations. This means that high-temperature-resistant hydrogels must be developed. The second difference, which concerns only Enhanced Geothermal Systems (EGS), relates to temperature gradients. Indeed, unlike the petroleum context, where rapid water circulation between injection and production wells is never desired (whether for pressure maintenance or hydrocarbon sweeping), the water injected into an EGS must circulate between the two wells in a controlled manner. This means it must move slowly enough to have time to heat up and become enriched in lithium, but quickly enough to ensure sufficient heat and lithium production at the surface. As a result, the water circulating in-depth is subjected to significant temperature gradients, and the hydrogels must be adapted to this situation. Thus, since the temperature at which gelation is desired is likely to be reached relatively close to the producer in a short-circuit situation, the gelation kinetics at the target temperature must be rapid to ensure that the gel forms properly in the reservoir. However, at the injection point temperature, the kinetics must also be as slow as possible to avoid the risk of clogging the injection well.

Pioneering works aimed at developing hydrogels adapted to geothermal conditions have recently been carried out by the groups of Baojun Bai (Darko et al., 2024; Liu et al., 2024) and Dongmei Wang (Wang et al., 2023). These authors have presented encouraging results, proposing “trial-and-error” approaches for hydrogel formulations already developed for the petroleum sector. Bai and coworkers investigated Preformed Particle Gels (PPG), i.e., aqueous polymer gels of partially hydrolyzed and/or sulfonated polyacrylamide prepared in reactors, then dried and ground before being injected into fractures, where the clogging effect results from the progressive swelling of the gel during its rehydration. The main challenge with PPG is that this technique requires a relatively precise knowledge of fracture opening sizes (to ensure both good in-depth propagation of the particles before their swelling and effective clogging by the particles once swollen), which seems difficult to achieve in the geothermal context, where the fracture network evolves over time. Techniques based on the injection of sol phases appear more promising, as the gel, once formed in the fracture network of the reservoir, occupies the entire volume of the fracture into which it was placed. Wang and coworkers investigated such sol-gel systems, focusing on biopolymer-based formulations. These formulations can involve hydroxyethyl cellulose, scleroglucan or starch. A challenge with this approach is the control of the properties of the bio products in industrial batches and the potential presence of impurities that could entail unwanted clogging in the near wellbore area.

The objective of the present study is to lay the ground to enable the use of high-temperature synthetic polyacrylamide polymer-based sol-gel system for application in EGS or other geothermal operations in fractured reservoirs. New formulations, involving sulfonated polymers that are initially acrylate-free and a proven zirconium crosslinker are proposed and evaluated in tube tests and in coreflood tests with artificially fractured outcrop rock plugs. The conditions for the study are that of a reference Rhine-Graben case, where heat generation is associated to lithium production and where the temperature ranges from 85°C at the injection point to 170°C at the production side.

2 MATERIALS

2.1 Brine

All experiments were performed with a synthetic brine representative of the Rhine Graben case considered. Its composition is presented in Table 1. It is a lithium-rich high salinity brine with a fairly high hardness parameter of 0.23 (defined as the ratio of the mass concentration of calcium and magnesium cations over the mass of concentration of sodium, potassium, calcium and magnesium cations).

2.2 Rock

The coreflood tests were performed with Trias aged Buntsandstein outcrop sandstone from the Loegel Rothbach quarry (Rothbach, France), with permeability ranging from a few tens to a few hundred millidarcies. These rocks

are representative, at least in terms of mineralogy, of the sedimentary formation that constitutes, with the basement rock below, the reservoir for the case considered.

Table 1: Composition of the synthetic brine.

Ion	Concentration (mg/L)
Na^+	25 450
K^+	3 245
Ca^{2+}	8 000
Mg^{2+}	144
Li^+	173
Sr^{2+}	424
Cl-	57 411
Total Dissolved Solids	**94 847**

2.3 Crosslinker

A zirconium type inorganic crosslinker was used in the formulations investigated. It was preferred to chromium type crosslinker as it represents a less toxic and more environment friendly option (Chauveteau et al., 1999). The sample used was an aqueous solution of a zirconium lactate (ZrLa) complex purchased from Dorf Ketal under the commercial name reference "Tyzor 217" at 5.4 wt-% concentration. Such industrial crosslinkers are easily available for industrial field operations as they are frequently employed in near wellbore plugging and fracturing operations by oil operators (Zhu et al. 2017 and Hamza et al. 2019).

2.4 Polymers

The polymers employed where "SPAM" type polymers, namely polymers with a polyacrylamide base, bearing sulfonated units (ATBS type) in order to ensure their stability in high temperature, high salinity and high hardness reservoirs (Al-Mayyan et al., 2025a). The following three polymers were investigated (the ATBS contents and molecular weights, "MW", are estimates provide by the vendor):

- a SPAM with approximately 25 mol-% ATBS and MW ≈ 10-15.10^6 g/mol (AN125VHM from SNF);

- a SPAM with approximately 50 mol-% ATBS and MW ≈ 12.310^6 g/mol (Superpusher SAV 55 XV from SNF);

- a SPAM with approximately 70 mol-% ATBS and MW ≈ 12.310^6 g/mol (Superpusher SAV 37 XV from SNF).

The gelation mechanism is traditionally described (Sydansk, 1988) between partially hydrolyzed polyacrylamide polymers and metal ion complex inorganic crosslinkers (such as zirconium or chromium). It involves the formation of ionic bounds between the positively charged crosslinker complexes and the carboxyl groups from the acrylate units. The decision in this study to investigate SPAM polymers, which have already been proposed for conformance control (Pinho de Aguiar, 2020), with initially no acrylate units, was made in order to achieve a delayed gelation in high temperature environments. Namely, gelation still involves acrylate units, but they are to be created by the progressive hydrolysis of acrylamide groups into acrylate groups. As the kinetics of hydrolysis is highly temperature dependent (the higher the temperature, the faster the hydrolysis, see for example Muller et al., 1980), polymers with high ATBS contents, and hence low acrylamide contents, were investigated in order to further delay the gelation in high temperature by reducing the amount of candidate units for creating bounds with the crosslinker. As an additional advantage, high ATBS contents provides enhanced stability at elevated temperature. Overall, the approach proposed is expected to allow the formulation to remain in the sol state in the relatively low temperature environment of the near wellbore long enough to avoid any potential injectivity loss, and to undergo gelation where the short-circuits need to be plugged (which can be either at relatively short distance of the near-wellbore or in-depth the reservoir, depending on the case), triggered by both residence time and progressive increase of temperature.

3 METHODS

3.1 Temperatures

The experiments in this study were performed at 3 temperatures: 85°C, which is the typical temperature at the injection point for the case considered and served as the reference temperature for the study, and also 110°C and 130°C, to investigate temperatures experienced deeper in the reservoir.

3.2 Tube tests

The gel preparation method was as follows: (a) preparation of a 12 g/L polymer solution in the synthetic brine, (b) transfer of about 10 mL of the polymer solution in a tube with a closed screw cap (the volume of polymer solution introduced in the tube was adjusted to reach 10 g/L as a final polymer concentration, for all the ZrLa concentrations investigated), (c) introduction in the tube of the desired amount of ZrLa solution at 5.4 wt-% in deionized water (the dilution effect of the salts was neglected given the low amount of high concentration ZrLa solution introduced), (d) soft stirring at ambient temperature with a motorized rotary device allowing to slowly shake the tube upside down for 1 hour, (e) introduction of the tube in an oven set at the desired temperature of 85, 110 or 130°C (initial time noted "t_0"). In this study, the pH of the solutions was not adjusted, either before or during the tests. The ovens were also not set in an anaerobic environment: it was assumed that the presence of crosslinks in the gel allowed neglecting the impact of polymer chain rupture events (as compared to non-crosslinked polymer solutions).

The solutions were then submitted to the Sydansk qualitative gel strength assessment test (Sydansk, 1988), typically twice a day during the first days to investigate the gelation kinetics, then less frequently to investigate the long-term stability of the gels. The gel strengths were determined visually as per the scale presented in Figure 7. The observations were made immediately after taking the tubes out of the oven, which means that the structural properties of the gels were still the ones achieved at the oven's temperature.

Extensive series of tests were performed at 85°C with the three polymers and, for each polymer, with 12 individual ZrLa concentrations, ranging from 62 mg/L to 6000 mg/L (hence covering two orders of magnitude), the long-term stability being assessed for up to 140 days. For the higher temperatures of 110°C and 130°C, only the short-term gelation kinetics was investigated, over about 3 days.

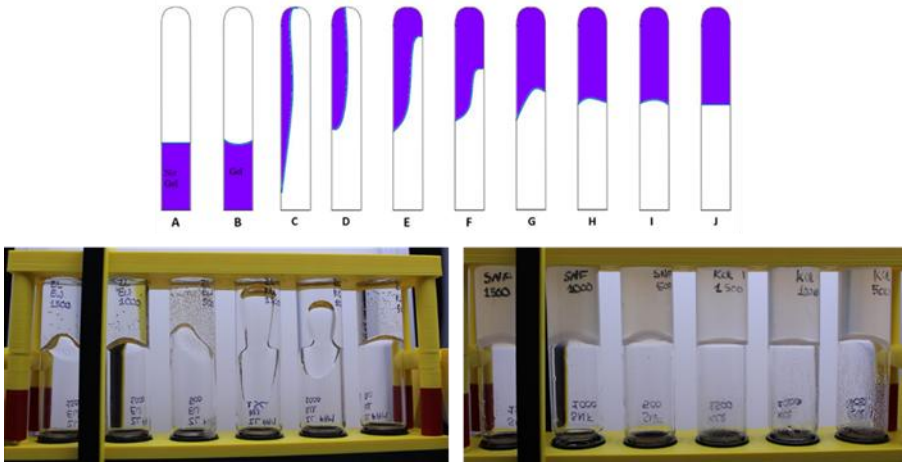


Figure 1: Sydansk gel strength code (top) with examples of weak (bottom left) and strong (bottom right) gels.

3.3 Coreflood tests

The coreflood tests were performed with plugs of Buntsandstein rock in their initial state, then after the creation of an artificial fracture and before and after placement of gel in this fracture. A conventional Hassler-type core holder was employed, with the confining pressure set to 60 bars and the pore pressure to 5 bars. The objectives were to determine if, for a candidate gel formulation selected based on the outcomes of the tube tests, gelation takes place at conditions representative of the Rhine Graben case considered and also to provide first data regarding the stability of the gel versus time and temperature variations. The procedure was as follows: (a) determination of the matrix permeability of the selected 20 cm long and 4 cm diameter Buntsandstein plug, (b) cutting of the plug in two halves along its main axis using a wire saw (Figure 2, left), (c) installation of "spacers", namely strips of PEEK with a thickness of 200 µm, (Figure 2, right) to ensure that the fracture remains open under pressure during the experiment; (d) determination of the permeability of the plug with open artificial fracture, (e)

injection of the candidate formulation inside the fracture at 85°C using a syringe, (f) circulation of synthetic brine over the upstream and downstream pistons and tubings (using dual openings at the piston's tips, allowing to circulate brine at the plug's inlet and outlet faces) to ensure that the formulation remained only inside the fracture, (g) shut-in time at 85°C to allow the formulation to age at reservoir temperature (duration was set to be representative of the time needed to reach a strong gel as per the tube tests), (h) injection of synthetic brine, first at low rate (set, by convention, to 3 mL/h, corresponding to an interstitial velocity v_i of 0.3 m/day, representative of in-depth flow conditions) to check if the fracture is plugged by a gel and then at variable rates (up to 200 mL/h, corresponding to v_i of 21 m/day, which should be representative of the maximum velocities experienced near wellbore) to determine permeability and (i) new determinations of permeability at variable time or temperature steps.



Figure 2: Cutting of a Buntsandstein outcrop plug with a wire saw (left) and example of the same plug cut, set in the Viton sleeve with spacers to maintain the fracture open, before pressurization (right).

Two coreflood tests were performed: test reference "A8-1" with a plug of 51 mD initial matrix permeability and 18.7% porosity and test reference "A9-1" with a plug of 320 mD initial matrix permeability and 18.6% porosity. The difference in permeability between the two plugs, which were extracted from neighboring locations in the same block, are due to fine scale bedding that were evidenced by CT-scan observation of the plugs and could not be made perfectly parallel to the plugs axis.

4 RESULTS AND DISCUSSION

4.1 Tube tests

The results of the tube tests performed at 85°C are presented in Figure 3, showing, for each of the three polymers, the short-term gelation kinetics results (up to 3 days) on the left side and the long-term results (up to 140 days) on the right side.

The first major outcome is that the ATBS contents plays a major role in controlling the gelation kinetics: whereas strong gels (letters H, I, J) and moderate gels (E, F, G) can be obtained after 3 days with, respectively, the 25% ATBS and the 50% ATBS polymers, no gels at all are obtained after 3 days with the 70% ATBS polymer. This outcome is in line with the expectations based on the molecular gelation mechanism: the more ATBS monomers are present, the less candidate acrylamide monomers remain for hydrolysis. As a result, a "critical" amount of hydrolyzed acrylamide to allow for the formation of ionic bounds with ZrLa takes more time to be achieved with 50% ATBS than 25% ATBS and with 70% ATBS than 50% ATBS. For field operations, it means that formulations with high ATBS contents polymer are safe in terms of injection well clogging risks. Over the long-term, the results show that gels are obtained at 85°C will all three types of polymers. Those obtained with the 70% ATBS polymer have a very slow gelation kinetics and hence do not reach "strong" gels state in all configurations. However, it clearly appears that, once strong gels are formed at adequate ZrLa concentrations, they are very stable over the entire window of observation, namely up to 140 days.

The concentration in ZrLa has a non-monotonous impact on the gel formation kinetics, as already observed in our previous work (Al-Mayyan et al., 2025b). Namely, when ZrLa concentration is too low (62, 125 and 250 mg/L) gels can quickly form with the 25% ATBS polymer but are not stable (for example, the formulation with 250 mg/L ZrLa reaches letter H within 3 days, before collapsing to letter B after 100 days), whereas for 50% and 70% ATBS polymers the gelation kinetics is only extremely slow. Two mechanisms, potentially acting in conjunction, could explain the gel degradation with the 25% ATBS polymer: (i) interaction with divalent cations of the "free" acrylates left when not enough zirconium ions are present, (ii) oxidative degradation when not enough crosslinks are present, the system being more sensitive to individual chain breakage. The very slow kinetics with the 50% and 70% ATBS polymers seems to be only due to a lower probability of forming ionic bounds, given that only few ZrLa complexes are present to interact with the few formed acrylates.

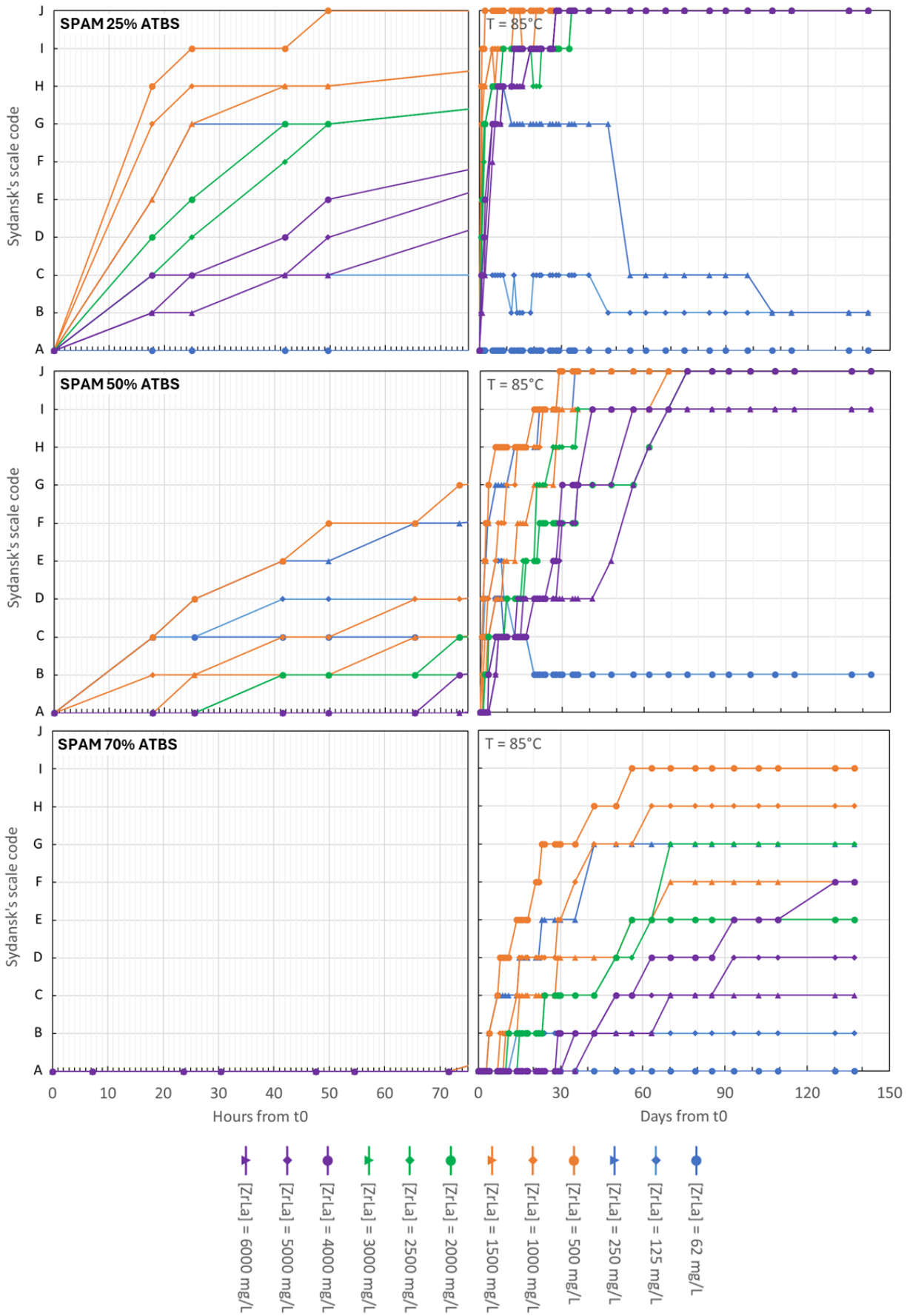


Figure 3: Gel strengths as per Sydansk's scale for tube tests over short time (70 hours or 3 days, left) and long time (140 days, right) for the 3 polymers with variable SPAM contents and ZrLa concentrations ranging from 62 to 6000 mg/L at 85°C.

The results also show that increasing ZrLa concentration accelerates the gelation kinetics up to an optimum and then slows it down. This is observed with all 3 polymers, the optimum ZrLa concentration being always 500 mg/L. A potential lead to explain this behaviour could be, at high ZrLa concentration, a competition between zirconium ions for creating crosslinks. A satisfactorily interpretation would require detailed investigations at the molecular scale, for example with X-ray or neutron scattering.

The results regarding the impact of temperature on the gelation kinetics (namely over 3 days) with the 70% ATBS polymer are presented in Figure 4. As expected, based on what is known of the impact of temperature on the acrylamide hydrolysis reaction (see section 2.4), increasing the temperature has a massive impact on gelation kinetics. Namely, strong gels (letters H, I, J) are achieved before 3 days at 130°C. Interestingly , increasing the temperatures seems to shift the optimum ZrLa concentration: from 500 mg/L at 85°C, it becomes 1000 mg/L at 110°C and then 1500 mg/L at 130°C. This spectacular behavior stands as a positive insight for applying gel-based temperature-activated short-circuits remediation techniques. Namely, in reservoirs with strong temperature gradient, a formulation could easily flow past the relatively low temperature near-wellbore area because it would remain in the sol phase and then become a strong plugging gel deeper in the reservoir where temperature is high enough.

Unfortunately, given the design of the tubes that could not stand high-pressures to prevent water boiling, long-term behavior could not be investigated in this work at 110°C and 130°C. Such investigation are of course very important and need to be performed in further works, as syneresis effects are known, for example, to affect hydrogels over the long term (see for example Zhang et al, 2015).

Based on the results of the tube tests, the formulation made of the 25% ATBS polymer and 500 mg/L ZrLa was selected for the coreflood tests performed at the reference temperature of 85°C.

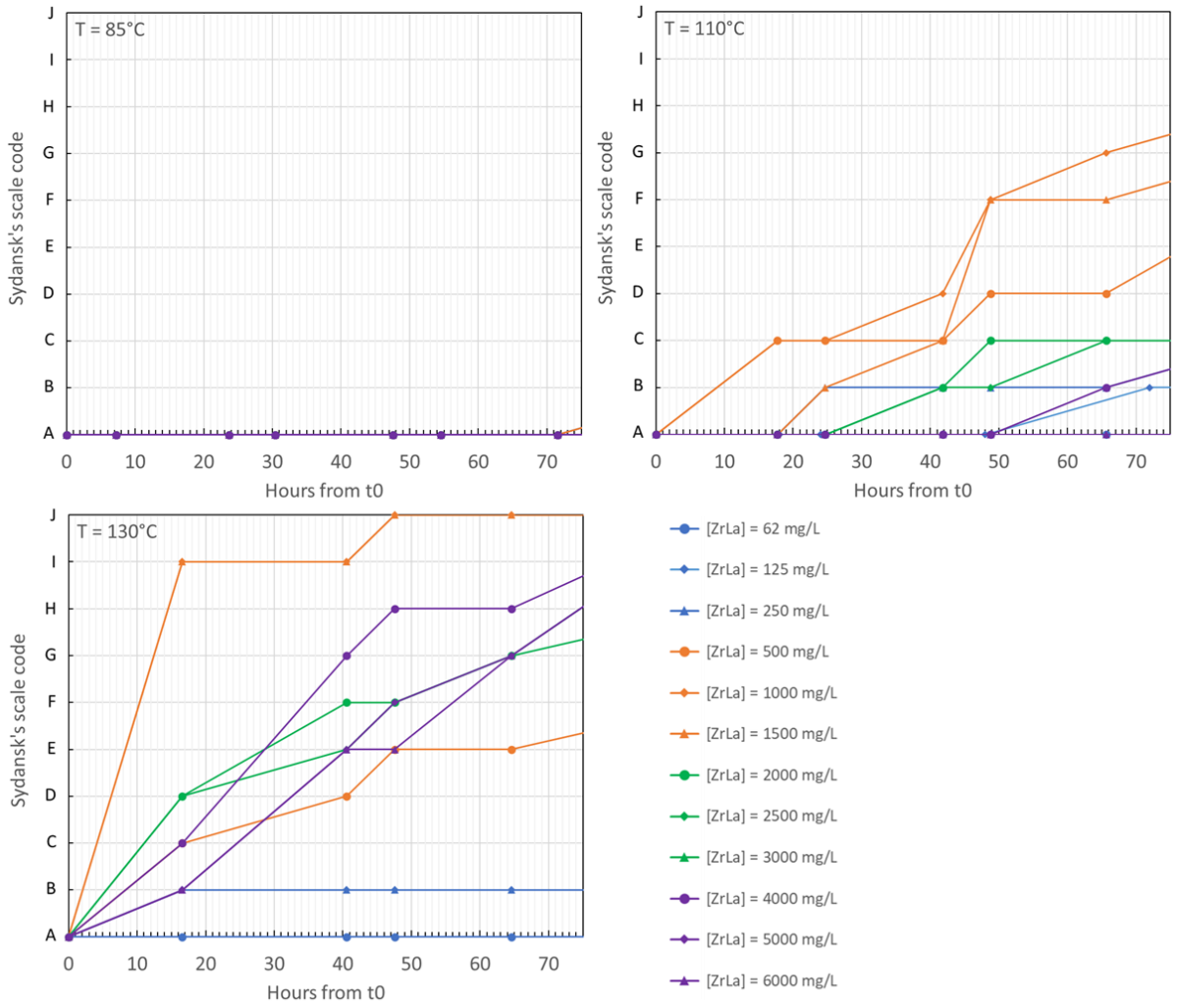


Figure 4: Impact of temperature on gelation kinetics over the short time (70 hours) for the SPAM polymer with 70% ATBS and for ZrLa concentrations ranging from 62 to 6000 mg/L.

4.2 Coreflood tests

The results in terms of permeability changes à 85°C for the three base steps (initial matrix condition, fractured plug with open fracture and fractured plug post gel placement, after 3 days for A8-1 and after 1 day for A9-1) of the two coreflood tests are presented in Figure 5. As evidenced by the logarithmic scale on the y-axis, the open fracture permeability is 150 (for A8-1) to 25 (for A9-1, due to the initial bedding in this plug) times higher than the matrix permeability. It clearly appears than the gel plays its intended role: in A8-1, the permeability post gel placement is very close to the initial matrix permeability, and, in A9-1, it is even lower, close to that of A9-1, probably because the gel has plugged the streak responsible for the higher initial permeability in A9-1. The fact that the gel performances are the same after 3 days at rest (in A8-1) than after 1 day at rest (in A9-1) shows that, based on the outcomes of the tube tests, reaching a I letter grade gel is enough to achieve an effective plugging effect. These results demonstrate that, in representative conditions, namely in confined conditions and under pressure, SPAM polymer and ZrLa formulations can efficiently play their role as fracture plugging agents.

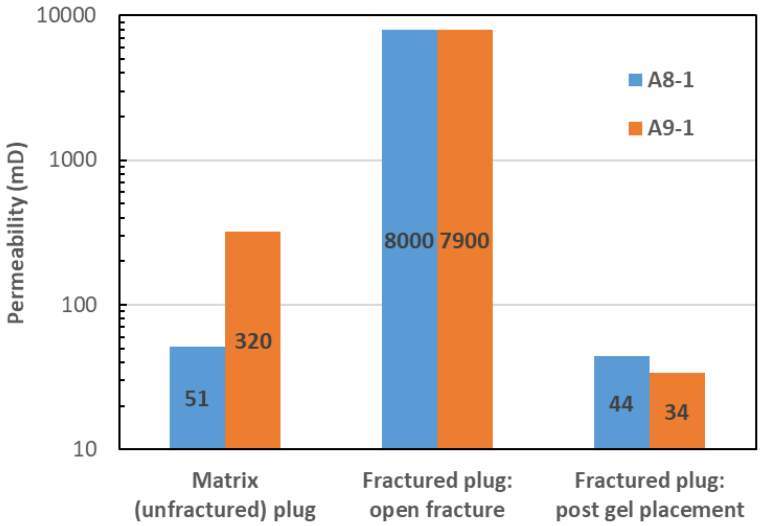


Figure 5: Permeability of the two plugs determined at 85°C in the initial "matrix" (unfractured) state and after fracturation with the open fracture then after gel placement.

Figure 6 shows the permeability variations versus time elapsed after the placement of the formulation in A9-1. The temperature was kept to 85°C until day 5 and then abruptly increased to 110°C. In addition to the first measurement taken after 1 day, permeability was assessed at intervals up to 34 days.

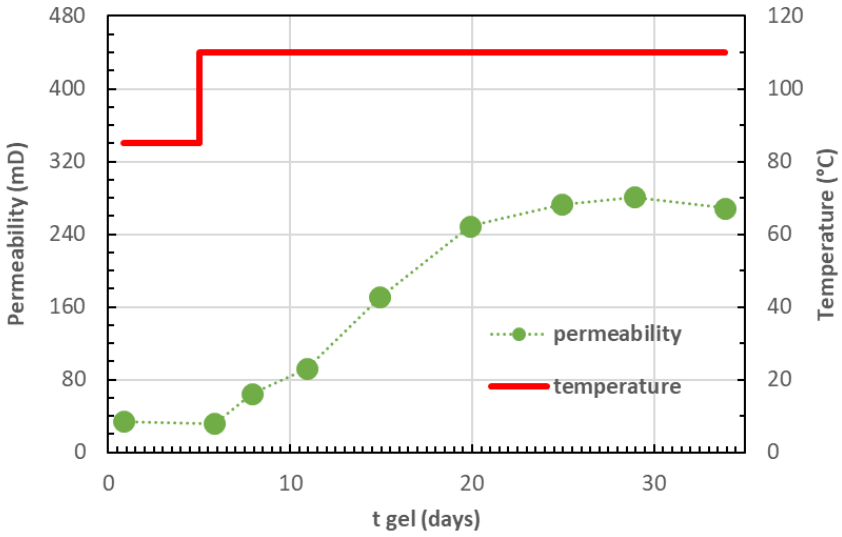


Figure 6: Permeability of the fractured plug A9-1 determined over time after gel placement at 85°C for the first 5 days and then at 110°C until 34 days.

It appears that the gel placed in the fracture remains remarkably stable over 5 days at 85°C, with a plug permeability of about 32 mD, and then undergoes changes when the temperature is increased to 110°C until reaching a stable state after about 20 days, with a plug permeability of about 270 mD. As the permeability remains 30 times lower than the open fracture permeability after 34 days, the results show that the fracture plugging effect holds at 110°C, which means that the gel seems to remain in place within the fracture volume and does not undergo massive degradation such as syneresis. However, the permeability obviously increases for 85°C to 110°C: this means that structural evolutions of the gel occur, that will need to be better characterized. A potential lead to that end would be to perform coreflood tests under a CT-scan or micro-CT scan equipment to visualize the interface between the gel and the rock surface.

It should however be stressed that better performances at 110°C are expected with the polymers with higher ATBS content. These are to be evaluated in further tests. Furthermore, gel stability needs to be evaluated over much longer timespan, of the order of a few months, to make the results valuable in view of field applications. To that end, dedicated experimental methods that are the same time more representative than tube tests (in terms of pressure and confinement) and more flexible than coreflood tests (to allow for parametric studies, which is not possible in coreflood as multiple experimental rigs cannot be mobilized for months) need to be developed.

5 CONCLUSION

This exploratory study shows that versatile polymer/crosslinker temperature-activated gel formulations can be designed to meet the operational constraints of short-circuits remediation operations in geothermal systems, particularly EGS where significant temperature gradients are present. Beyond the better understanding of the physicochemical mechanisms at play that is desirable, the design of field application ready formulations and procedures will require: (i) further experimental work involving coreflood tests to assess for gelation kinetics elevated temperature and long-term stability tests in conditions representative of the reservoir, in order to select formulations with adequate performances and (ii) dynamic reservoir simulations based on relevant characterization of the temperature gradients and transport velocities in the fractures network in order to define the gel injection flow rate, volume and the shut-in period.

These goals seem achievable in the short term. Hence, in the same way as for conformance control in the oil industry, enhanced operational methods to support the long-term economic viability of geothermal and lithium extraction systems are likely to emerge and to see successful field applications in the near future.

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