The effect of CO₂ reinjection on silica scaling in geothermal reservoirs

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ABSTRACT

The capture and reinjection of the non-condensable gases (NCG) that are associated with geothermal brine production is a key technology to ensure that geothermal energy remains a sustainable part of Aotearoa's transition to a low carbon economy. Whilst several pilot schemes are underway to trial the viability of NCG reinjection, its potential effects on reservoir geochemistry are not well understood. Here, we present a combined experimental and modelling approach to investigate the effect of the incorporation of CO_2 (the primary component of the NCG fraction in NZ geothermal brines) into reinjected brines.

Four experimental reinjection simulations were performed in high-PT flow-through reactors under geochemical conditions relevant to New Zealand geothermal reservoirs, with varying levels of added CO_2. The empirical observations collected as part of these experiments were used to constrain the rate parameters of a reactive transport model built using PFLOTRAN that can accurately reproduce the geochemical behaviour of the experiments. This numerical model can then be used to extend our investigation to the relevant spatial and temporal scales required to understand the long-term reservoir response to NCG reinjection. We show that for acid-dosed brines, addition of CO_2 can significantly reduce the rate of silica scaling in reservoir. This has significant implications for reducing the injectivity decline of reinjection wells, which may help realise previously underappreciated cost savings achieved by NCG reinjection technologies. We demonstrate a framework whereby this combined experimental-modelling approach can be used to quantify the effect on silica scaling for any brine-reservoir rock combination, with the aim of helping to de-risk and accelerate the deployment of NCG reinjection technologies across the NZ geothermal sector.

1. INTRODUCTION

The extent to which geothermal energy can play a part in the global transition to a low carbon future will be dictated by the industry's ability to minimize lifecycle carbon emissions whilst remaining economically competitive with other renewable sources. The use of geothermal resources is not inherently carbon neutral, due to the dissolved non-condensable gases emitted during the production of geothermal brines (Arnorsson, 2004). These emissions also incur a cost under emissions trading schemes and other carbon taxes.

The precise determination of the lifecycle CO_2 emissions of a geothermal plant is complicated because they are usually situated in areas of high background emissions (Ármannsson et al., 2005). Different geological settings can also greatly impact the amounts of CO_2 and heat present, meaning that geothermal plants can have a wide range of CO_2 emissions intensities. Fridriksson et al. (2017) present an overview of fuel cycle CO_2 emissions from geothermal plants worldwide. These range from 20 to 750 g kWh^{-1} with a weighted average of 122 g kWh^{-1}. For comparison, the average emission from the natural gas power plant is 550 g kWh^{-1} (Mclean et al., 2020).

The obvious solution to mitigate the emission of greenhouse gases at geothermal power stations is to recombine the non-condensable gas phase with the condensate and residual brine before reinjection into the reservoir, as brine reinjection is already standard practice in the industry. Whilst this approach does not necessarily aim to sequester carbon in the subsurface over geological timescales as in conventional carbon sequestration and storage technologies, the retention of the CO_2 in the geothermal reservoir rather than accelerating its release to the atmosphere would still have a significant impact on local CO_2 emissions (Kaya & Zarrouk, 2017). There have been a number of attempts to deploy this technology in geothermal reservoirs with variable success (e.g. Kaieda et al., 2009; Clark et al., 2020), and it is expected to be a key technology in the drive to lower carbon emissions associated with geothermal power generation in New Zealand.

An additional concern during brine reinjection is the precipitation or scaling of minerals due to water-rock reactions within the reservoir. Amorphous silica scaling is the most common issue, as geothermal fluids are often rich in SiO_2 which becomes supersaturated when the fluid is flashed and cooled at the surface (Angcoy, 2006). Silica scaling in geothermal reservoirs reduces porosity and permeability, resulting in injectivity declines that can significantly limit the lifetime of injection wells (Goto, 2000).

Silica precipitation rates decrease with decreasing pH, and dosing with acid is effective at slowing scaling in plant infrastructure (Von Hirtz, 2016). However, this technique is ineffective within the reservoir, where the brine can react with minerals within the reservoir rock, neutralizing acidity, and raising the pH. Well reworking and downhole acid treatments have been partially successful at alleviating injectivity decline, but do not address the root cause of the issue and are costly (Flores-Armenta and Ramírez-Montes, 2010; Lim et al., 2011). Ultimately, new reinjection wells must be drilled which means that any geochemical effect that reduces silica scaling could provide a strong incentive in terms of cost reduction to operators.

The effect of CO_2 reinjection on the rate of downhole silica scaling is an important unknown when considering cost analyses for the potential deployment of any NCG reinjection schemes. If any beneficial effects on the rate of silica scaling can be quantified, it should accelerate the uptake of a technology which otherwise may be seen as prohibitively expensive. Recent experimental results

collected at GNS suggest that the presence of CO_2 in reinjection fluids can significantly inhibit silica scaling, especially in formations that contain calcite. Here, we present a reactive transport approach to further investigate these experimental results, intending to fully quantify the effects of CO_2 on silica scaling rate. We also outline how this technique could be used to take the high quality experimental data from reinjection simulations, and use it to maximum effect by incorporating it into reservoir-scale flow models in a general sense.

2. METHODOLOGY

In this study, we use a reactive transport modelling approach to build on previous work carried out at the GNS Experimental Geochemistry Lab on the effect of CO_2 incorporation into acid-dosed brines during reinjection simulations.

Full methodology and discussion of the underlying experimental work is reported separately (Mountain et al., *in press*), but a summary is presented here for reference. Four silica antiscaling experiments (SAE 1-4) were carried out to simulate the reinjection of a New Zealand geothermal brine with a typical Taupo Volcanic Zone (TVZ) reservoir rock (greywacke) over 30 days at 150 °C. The experiments were conducted using a high temperature and pressure hydrothermal flow simulator (Coretest Systems Ltd) which allows continuous single-pass flow of fluid through rock substrates. The brine was flowed through the reactors at 5 ml/hr and the effluent was sampled daily for major element chemistry. After each experiment, the reactor vessel was opened and the reacted substrate was analysed with SEM to determine the nature and extent of any mineral dissolution/precipitation.

A suite of four experiments were performed with varying configurations of substrate and solution, designed to demonstrate the effect of CO_2 addition to reinjection fluids in a typical New Zealand geothermal reservoir. The configurations for each experiment are summarized in Table 1.

EXPERIMENT	SUBSTRATE	SOLUTION
SAE1	greywacke	unmodified brine
SAE2	greywacke + 1.5wt% calcite	unmodified brine
SAE3	greywacke + 1.5wt% calcite	brine + ~2000ppm CO_2
SAE4	greywacke + 1.5wt% calcite	brine + ~600ppm CO_2

Table 1. Substrate and fluid compositions for reinjection simulation experiments SAE 1-4.

The control experiment SAE1 showed minor silica loss in the collected effluent, and minor amounts of amorphous silica were observed on the rock surface after the experiment, indicating the occurrence of silica scaling. Experiment SAE2 displayed elevated pH in the collected effluent throughout the experiment, due to the dissolution of the added calcite. There was also significant silica scaling as evidenced by depleted SiO_2 in the effluent and the presence of thick amorphous silica on the reacted rock. The first experiment to include added CO_2, SAE3, showed dramatically decreased rates of silica scaling compared to SAE2. There was no appreciable amorphous silica present after the experiment, and pH levels throughout the experiment were much lower than in SAE2. Experiment SAE4 also had added CO_2, although at a lower level than in SAE3. The extent of silica scaling was still significantly reduced when compared to SAE2, although not as strongly as in SAE3.

Overall, the experiments provided a robust demonstration that adding CO_2 to acid-dosed brines will effectively reduce the rate of silica scaling, particularly in reinjection formations that contain calcite. However, while these results can be used to understand the fundamental geochemical behaviour of the system, there are a number of potentially useful questions that are difficult to answer satisfactorily with a limited suite of four experiments. For example, exactly how much CO_2 is required to effectively inhibit silica scaling sufficiently in a reservoir setting? How would this process be affected by different reservoir temperatures? How would the behaviour change over timescales of longer than 30 days? In order to address these questions, we developed an approach combining the robust empirical data with a reactive transport modelling implementation.

2.2 Reactive transport model implementation

The reactive transport model was built using PFLOTRAN, an open-source reactive flow and transport model with inbuilt parallel scalability (Hammond et al., 2014). The experimental apparatus was simulated as a 1D model, with an input cell matching the known input brine composition and flow rate.

The mineral species considered in the model are calcite, albite, kaolinite, amorphous silica and amorphous aluminous silica. Whilst there are certainly a greater range of minerals participating in dissolution/precipitation reactions within the experiment, we found that we were able to satisfactorily reproduce the overall geochemical behaviour of the system using this assemblage.

The kinetic behaviour of mineral precipitation/ dissolution in the SAE experiments was constrained using the parameter estimation software PEST (Doherty, 2015). The daily effluent chemistry data from SAE 1-4 were used to tune the kinetic parameters in the model to reproduce the experimental observations as closely as possible. The model fit was weighted such that the key parameters required for the model to reproduce in the effluent chemistry were pH, and concentrations of SiO_2, Ca^{2+} and Al^{3+}. All four sets of experimental data were considered at once such that the tuned parameters are applicable across the range of geochemical conditions of the experiments.

Mineral kinetic parameters were taken from the compilation of Palandri & Kharaka, 2004, and in general taken to be fixed, except for selected key parameters such as

the dependence of amorphous silica precipitation on H^+ abundance. Otherwise, the precipitation dissolution rates were controlled by mineral specific surface areas, which were allowed to vary, along with the parameters controlling the relationship between surface area and volume fraction for each mineral.

3. RESULTS & DISCUSSION

3.1 Model fits to experimental data

After the mineral kinetic and surface area parameters were tuned using PEST, we can run simulations that match the conditions of experiments SAE1-4 to validate that our model is correctly reproducing the emergent geochemical behaviour of the system. In Figures 1 and 2, we plot the measured pH and SiO_2 time-series data of the collected effluent samples for each experiment, alongside a dashed line representing the corresponding model simulation.

It should be noted that for the first three days of experimental data shown for each experiment, the reaction vessel is kept at ambient temperature, before being raised to the operating temperature of 150 °C for the rest of the experiment. These first three data points are therefore excluded from the model training dataset. The last ten days of the SAE2 experiment are also excluded, as there appears to be an artificial reduction in calcite dissolution rate attributed to an armouring effect of silica scale on the calcite crystals. We do not anticipate that this armouring effect would occur in a natural system and so do not want to attempt to force the model to reproduce this behaviour.

Figure 1 shows that the models closely reproduce the effluent pH values across the four experimental configurations. As pH is a key driver of a number of other geochemical processes in the model, it is important to capture its behaviour. In each experiment the pH in the effluent is consistently higher than the initial 4.7 at input, due to the dissolution of calcite within the reaction vessel. In experiment SAE1 the pH drops off during the experiment, likely due to the fact that the little calcite naturally present in the greywacke has been mostly removed. The added calcite in experiment SAE2 results in a much higher effluent pH. This remains relatively constant until the last ten days, where the slight drop in pH is attributed to the armouring effect described above and not considered in the model. The model closely reproduces the magnitude and trend of the pH behaviour in experiments SAE3 and SAE4, save for a slight overestimation of the pH in the latter half of SAE3.

Figure 2 shows the SiO_2 concentrations observed in the effluent samples. Comparison of the effluent observations with the 820 ppm concentration of the input brine allows an indirect calculation of the extent of silica scaling occurring within the reaction vessel by mass balance. As the rate of silica scaling is one of the key science questions of this study, it is crucial that the model closely reproduce these observations. The model provides a good fit across the four experiments, correctly displaying the much higher rate of scaling in SAE2, when compared to the experiments containing added CO_2 in SAE3 and SAE4. Whilst the model outputs are not as constant for SAE3, and slightly underestimate the rate of silica scaling in SAE4, the overall pattern matches closely.

Other geochemical behaviours that are reproduced in the model but not plotted here are the loss of dissolved

Al^{3+} within the reaction vessel, which is primarily precipitated as amorphous aluminous silica, with minor kaolinite precipitation. Ca^{2+} increases in the effluent are also reproduced due to calcite dissolution.

3.2 Model application to experimental simulations

As discussed in the introduction, an important advantage of the reactive transport approach is the ability to quickly run models to simulate experiments over a range of different configurations that would be impractical to investigate thoroughly in the lab. We demonstrate two such applications here.

In Figure 3, we show the results from a series of 100 model simulations of experiments with the same setup as SAE2-4, with the CO_2 concentration in the input brine ranging from 4.4 to 4400 ppm, with logarithmic spacing. These models are run using the mineral kinetic parameters determined in the previous section. The points corresponding to the actual CO_2 concentrations used in the SAE2-4 experiments are shown on the graph for reference. Using the completed model simulations, we are able to calculate the total silica scaling occurring for each pCO2 value. Using these results, we can easily answer how effective CO_2 is at inhibiting silica scaling for any given value of pCO2. An operator may be able to use this information to quickly determine how effective this process might be in a given reservoir, without having to rerun time consuming and costly experiments each time. It would also allow targeted business decisions to be made as the diminishing returns of additional CO_2 are clear at levels over 100 ppm, and exactly how much CO_2 is required to reduce silica scaling to the desired level can be easily found from these results.

In Figure 4, we explore the effects of different temperature on the results from experiment SAE4. As the experiments were run at a constant temperature of 150 °C, it is not immediately clear how applicable the results of the experiments would be to a real geothermal reservoir at a higher or lower temperature. As the laws controlling the temperature-dependence of the reactions considered in our model are well constrained, we believe that using our tuned model to extrapolate the results to temperatures outside those used in the experiments is valid. Here, we show that small temperature changes can have a significant effect on silica scaling rate, as well as the potential for added CO_2 to mitigate it. While ground-truthing these kinds of results with real experimental data will always be preferable, here we can quickly get an indication that silica scaling will be highest at around 140 °C.

3.3 Extension to reservoir time and length scales

A further application of this reactive transport approach is to investigate time and/or length scales that are impossible to fully investigate in a lab setting. As one of the biggest uncertainties in reservoir injectivity declines is the long term response over many years, it is clear that a 30 day experiment may have some limitations in applicability. However, using our tuned models, we can effectively simulate an experiment that continues indefinitely, or interacts rock and brine over a volume of many cubic kilometres.

In Figure 5, we show results from a simple 2-dimensional reservoir model example. Both panels show the results of a 1-year flow simulation through a hypothetical reservoir of 25 m extent, using the tuned geochemistry

parameters derived in the previous sections. Brine is injected into the bottom left of the domain, and outflow is to the top right. The left-hand panel shows a base case with an unmodified input brine, and the right-hand panel shows the results with a brine containing an added 600 ppm of CO_2. The colour indicates the volume fraction of amorphous silica at the end of the model run. It can be seen that the base case results in high levels of silica scaling close to the reinjection well, where it would have the highest effect on injectivity. In the case with added CO_2, the silica scaling still occurs, but due to the slower kinetics it occurs over a much wider area, and so would have a smaller impact overall on porosity and permeability. This example shows that the reactive transport approach can be used to investigate in-depth questions about the timing and location of silica scaling occurrence in geothermal reservoir examples.

4. CONCLUSION

In this submission, we present the results of a reactive transport model designed to replicate the geochemical behaviour of a suite of high pressure-temperature water rock interaction experiments. We demonstrate that we can use parameter estimation techniques to constrain the numerical implementation of the mineral kinetics. We then show potential applications of this technique in order to maximise the knowledge value gained from experiments of this kind, and its utility in addressing key questions in understanding geothermal reservoir behaviour.

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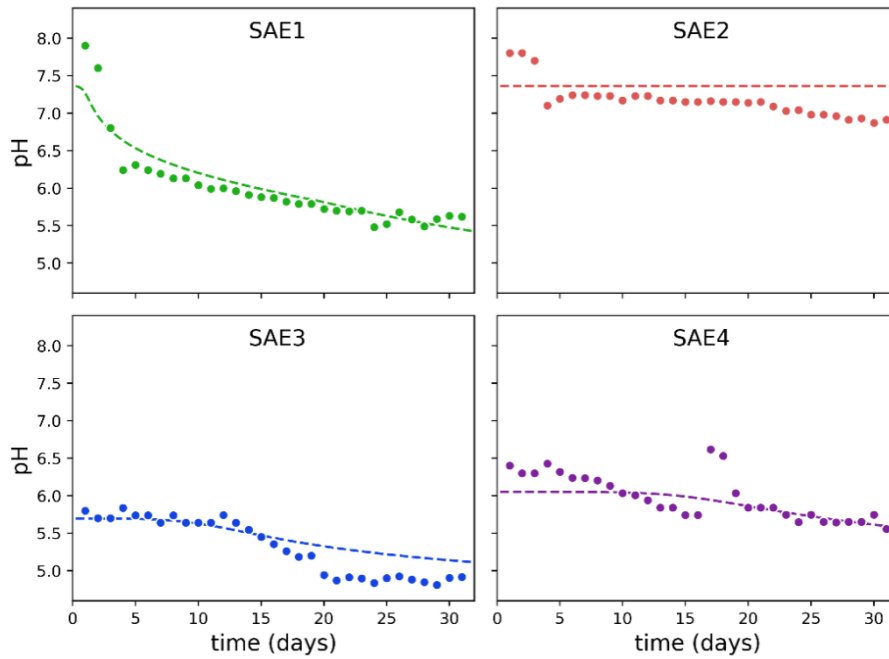
Figure 1. Comparison of measured effluent pH between experimental observations (dots) and model simulations (dashed lines) against time for experiments SAE1-4. The input pH of the brine used in all experiments is 4.7 and increases from that value seen here in the effluent can be attributed largely to calcite dissolution. As silica precipitation rate is strongly pH dependent this is a key control for silica scaling.
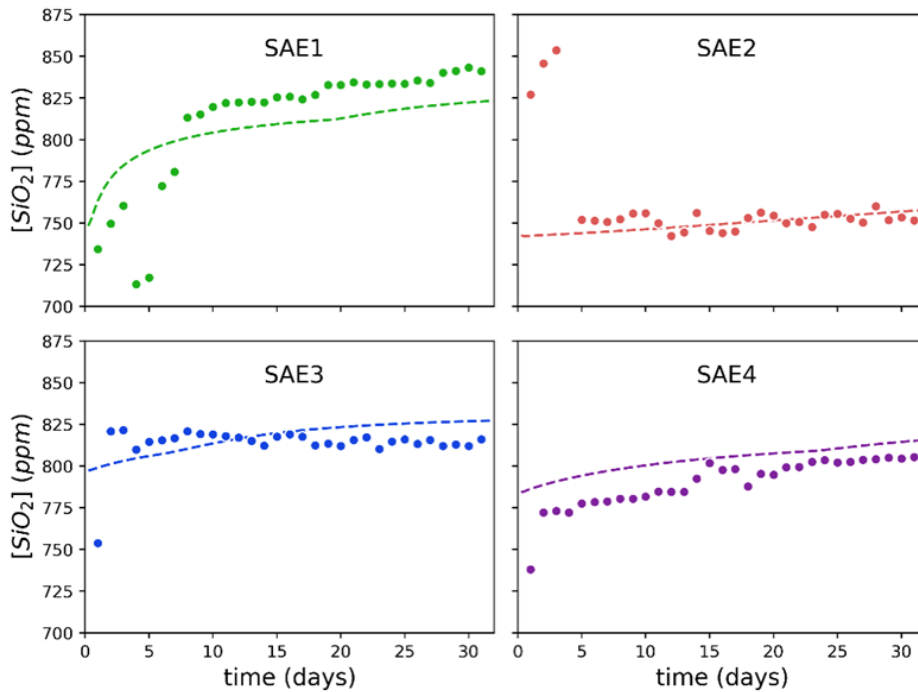

Figure 2. Comparison of measured effluent SiO_2 concentration between experimental observations (dots) and model simulations (dashed lines) against time for experiments SAE1-4. For each experiment the initial concentration of SiO_2 in the input brine is 820 ppm, and any deficit observed in the effluent corresponds to amorphous silica precipitation occurring within the reaction vessel. Here, it is clear that silica precipitation is greatest in SAE2, with the addition of CO_2 in SAE3 and SAE4 reducing this effect.
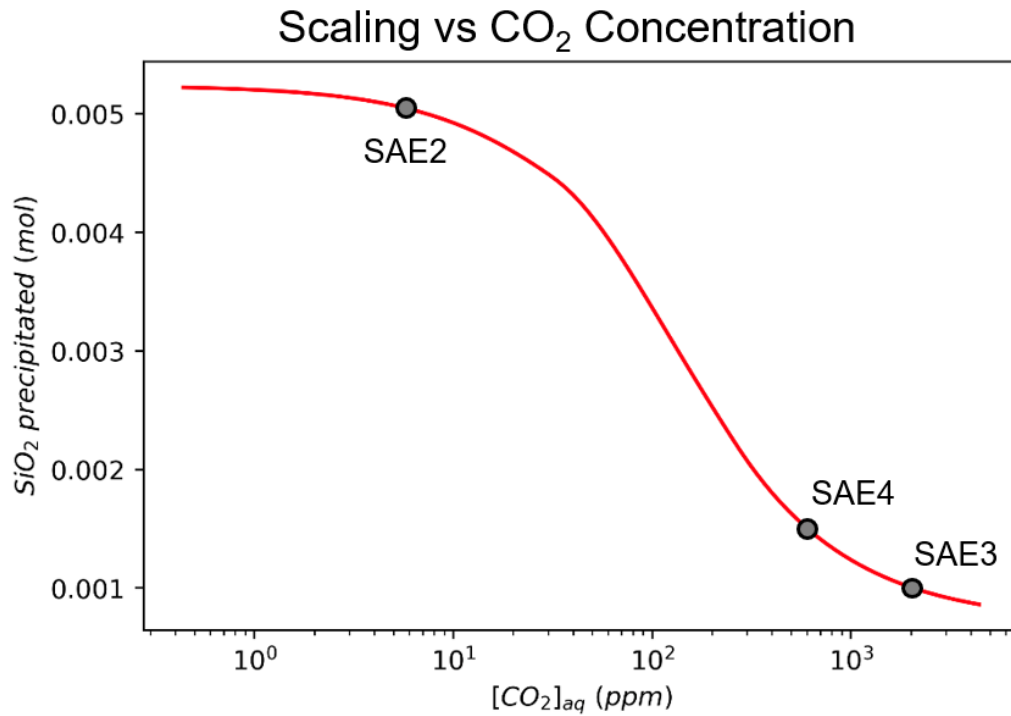
Figure 3. Results compiled from 100 model simulations reproducing the SAE experiments with variable concentrations of CO_2 in the input brine. Here, we can clearly see the relationship of CO_2 concentration with total silica precipitated within the experiment, and observe that the rate of silica scaling reduction is greatest at a CO_2 concentration of around 100 ppm.
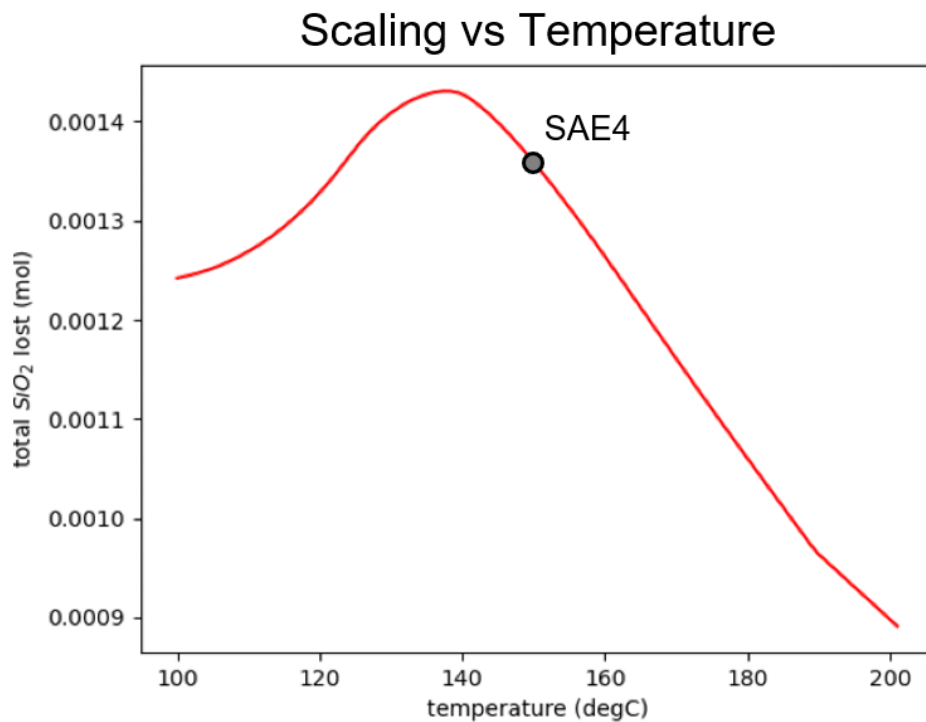

Figure 4. Results compiled from 100 model simulations, reproducing experiment SAE4 over a temperature range from 100 – 200 °C, with the original experiment (conducted at 150 °C) indicated. The y axis denotes the total SiO_2 precipitated within the experiment as amorphous silica, calculated by mass balance between the input and effluent. It can be seen that the model predicts that silica scaling will be greatest at around 140 °C, and drops off significantly at higher or lower reservoir temperatures.
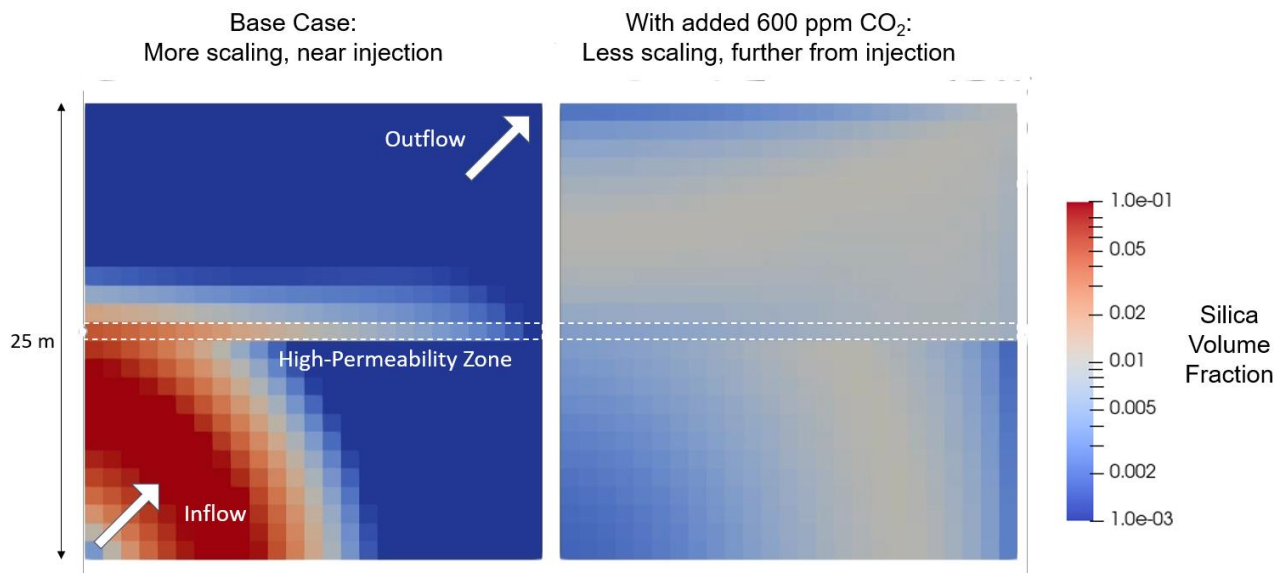
Figure 5. Results from a 2-dimensional reservoir model example. The left-hand panel shows a simple 2-dimensional flow model with injection in the bottom left point and outflow in the top right. There is a high-permeability zone in the middle and the geochemical behaviour is modelled using the tuned results from the SAE experiment model. In the right hand panel the physical parameters of the model are identical, but there is 600 ppm of CO_2 added to the input brine. The colour indicates the volume fraction of silica after 1 year of flow. The base case shows high levels of silica precipitation close to the injection well, which would dramatically decrease injectivity. In the example with added CO_2, the silica precipitates over a much wider area.