Effect of of Min-eral Scaling on Geothermal Wells

Ullas Rajvanshi

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by

Ullas Rajvanshi

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Thesis committee: Prof. dr. ir. P. Vardon,   TU Delft, supervisor
                                    Prof. dr. D. Voskov,   TU Delft

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Preface

The thesis was written as a part of bachelor studies of Applied Earth Sciences at Delft University of Technology under the supervision of Prof. Phil Vardon and Prof. Denis Voskov. During my eight weeks work, I extensively made use of PHREEQC for batch simulation reactions. During my first weeks I did a literature study to get an idea before starting the project. The literature study was focused on fro basics of geothermal energy to scaling in the wells while understanding the chemical and thermodynamic processes. Scaling is a potential problem since it can slow down the well and hence the production and use of the geothermal energy. A lot of research data worldwide has been used in this report.

I would like to first of all thanks my supervisors Prof. Phil Vardon and Prof. Denis Voskov who were available in the summer and helped me with the thesis throughout by providing their valuable feedback. They helped me in understanding the process and the problem in a brief and constructive manner. I would also like to thank my study counsellor Mr. Pascal de Smidt, who has provided me with all the guidance in order to get my thesis done in the right time.

Moreover, I would also like to thank my friends and family with their love and support which also made it possible for me to finish my thesis on time.

Ullas Rajvanshi
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Contents

1

Introduction

In this chapter an introduction to the geothermal wells along with an introduction to scaling and its effects is given followed by some relevant chemical reactions and their properties.

1.1. Introduction to Geothermal Wells

As of 2040, Energy Information Administration (EIA) expects an increase of 28% in world energy consumption. The majority of this consumption is projected to account from developing countries such as India, China and other third world countries since the economy is increasing rapidly. [3]

In order to overcome this fast increase, the human kind cannot rely only on fossil fuels and other sustainable technologies like solar, wind, geothermal are required. However, the emmision of CO_2 is also increasing from 6000 million metric tons carbon in year 2000 to 10000 million metrics tons in 2010. That's why many countries such as Denmark, Norway, Germany, The Netherlands etc., are moving away from traditional fuel sources to the new energy. One of these energy is Geothermal energy.

As the name suggests, *Geothermal* comes from the greek work, *geo*: which means Earth and *therma* meaning heat. Geothermal energy is the fraction of the natural heat of the Earth that is transported by the magma flow, conduction or/and convection from the Earth surface to the drilling range of the surface. The heat comes from the decay of the natural radioactive material that is transmitted to the surface from the molten core in the earth. It has been estimated that about 42 million megawatts of power flow from earth's interior by conduction.[9]

It is important to mention that there are mainly two types of geothermal resources: Low Temperature and High Temperature Resources. Low temperature resources are less than 180 degree C and are enough to supply only heating whereas high temperature resources (more than 180 degree C) are hot enough to generate electricity. The High Temperature resources supply about 99% of its geothermal energy and are considered in this report. [8]

1.2. Introduction to Scaling

Despite the fact that geothermal is one clean energy and almost CO_2 free, it does have some major drawbacks mainly, scaling and corrosion. Moreover, thats not the only problem associated with this. Scaling is site specific which is a major problem in the wells.

To get a more detailed understanding of the effect we need to understand how does geothermal reservoir works. In the reservoir, fluid with certain chemical composition is available which is then brought to the surface by production well. Upon reaching the surface the heat is lost to heat exchangers. As a result of which there is a change in temperature which then causes the change in chemical composition. which then leads to mineral scaling and clogging of the piping of the power plant. The same happens when the fluid is reinjected into the reservoir, which changes the temperature and hence chemical composition. Despite the fact that

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scaling is site specific, a statistical approach with a geochemical simulation using PHREEQC, an approach can be attempted to solve and estimate the effect in the lifetime of geothermal well.

Scale formation is generally divided into these main classes:

- Carbonate

- Silica and Silicates

- Sulpahte and Sulphides

Carbonate and Silicates are the most common scaling mechanisms which can occur in a geothermal reservoir followed by sulphate and sulphides. However due to the much higher complexity of silicates, they are not discusses here. For the sake of simplicity and the level of this report, the main focus is on carbonate scaling.

As mentioned earlier, scaling is very site specific, hence understanding the mechanism behind the formation can change from site to site. In order to understand this situation better, a geothermal reservoir (in this location)???? is used for simulations and modelling. However, typical thermodynamicals conditions in geothermal power plants have been considered.

1.3. $CaCO_3$ Scaling

Henry Law states that the amount of dissolved gas is proportional to its partial pressure in the gas phase. Since all geothermal reservoirs contains dissolved CO_2, and this carbon dioxide present in water solution should then be proportional to partial pressure of CO_2 in equilibrium according to the Henry's law. It is important to mention that the concentration of the dissolved carbon dioxide also includes carbonic acid H_2CO_3 and the exploitation of the geothermal reservoir starts with a constant and statitc CO_2 charged liquid with no vapour phase. As the production starts, there is a shift in equilibrium from left to right due to the decrease in pressure.[2]

$$2HCO_3^- <=>> H_2O(g) + CO_2(g) + CO_3^{--}(liq.) \tag{1.1}$$
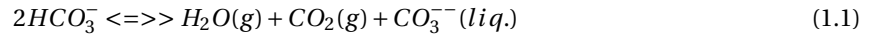
The concentration of the CO_3^{--} ions increases which results in the precipitation of the $CaCO_3$ because of the solubility product of $CaCO_3$

$$(Ca^{2+}).(CO_3^{2-}) = K_p \tag{1.2}$$

Since during flashing the $CO3^{2-}$ concentration increases, precipitation of $CaCO_3$ begins with flashing. As a result of which scaling can occurs depending where the flashing is more porminent. If flashing occurs in part of the productive well, in-hole scaling is to be expected. However, formation plugging can occur is the flashing begins in the formation. Finally, if flashing begings at the surface equipment encrustations is expected in the equipments. [2][7]

using the equilibria equation of the above mentioned equation and the partial pressure of CO_2, it is found that the ocncentration of calcium ions (Ca^{2+} depends upon:

- Temperature

- Partial Pressure of CO_2

- Ionic Strength, I

Using these, saturation index I_s can then be defined as the ratio between the measured Ca^{2+} concentration in equilibrium condition as:

$$I_s = logF_s \tag{1.3}$$

where F_s is

$$F_s = \frac{[Ca^{2+}].Alk^2.k_{HCO_3}.\gamma_{Ca^{2+}}.\gamma_{Alk.}^2}{k_{H_2CO_3}.k_{CO_2}.P_{CO_2}} \tag{1.4}$$

In Figure. 1.1 calcite scaling can be observer in a 3"bore where the calite is over saturated and is deposited in around three weeks. [1]
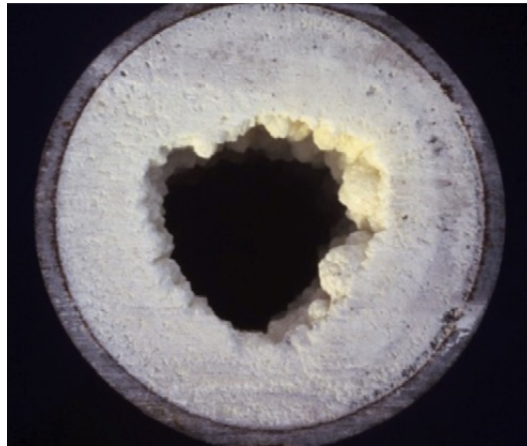
Figure 1.1: Calcite scaling in a well after three weeks [1]

1.4. Prevention: CaCO$_3$ scaling

In order to prevent calcium carbonate scaling, prevention menthods can be designed and tailored depending upon the site and the conditions at the site. There are mainly three ways to avoid calicum carbonate scaling:

- acting on CO$_2$ partial pressure

- acting on the pH of the solution

- using chemical additives

However, it is important to emphasize that prevention is not been considered into an extent for this research project since it was out of scope for this report.

1.5. Silica Scaling and prevention

Silica scaling is often found in high-temperature resources mainly in the wells and the re-injection lines. There are two types of common silica scaling: amorphous silica and quartz and are often found especially in countries like Italy and El Salvador with high geothermal gradient. As for carbonate scaling, calcite, aragonite and dolomite were considered to be in equilibrium with the geothermal fluid, however for silica scaling quarts is considered to be in equilibrium with the fluid. As the amount of quartz increases with temperature the solubility of quarts is independent of pH. [2]

As mentioned, silica scaling can be reduced or even eliminated by changing the pH of the solution by adding either HCl or NaOH to the brine fluid. However,this can lead to a huge cost investment and may not be a prefered solution in this case.

Due to the complexity of the kinetics of silica polymerization, they are not considered in the report.

1.6. Other types of scaling

Apart from carbonate and silica, sometimes heavy metal sulphade scaling is observed in production wells which arises due to the sudden pressure decrease of the brine solution which in turn also changes the pH. Again, these are not discussed in this report for the sake of simplicity.

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Conceptual Model

In the previous chapter, a general introduction to geothermal reservoir was given along with a brief understanding of scaling. In this chapter, a conceptual model for the geothermal reservoir will be discussed along with the boundary conditions set which will then be used to implement in PHREEQC.

2.1. Diagram

In the Figure 2.1, the conceptual model has been designed. At the reservoir, the hot water present with cer-
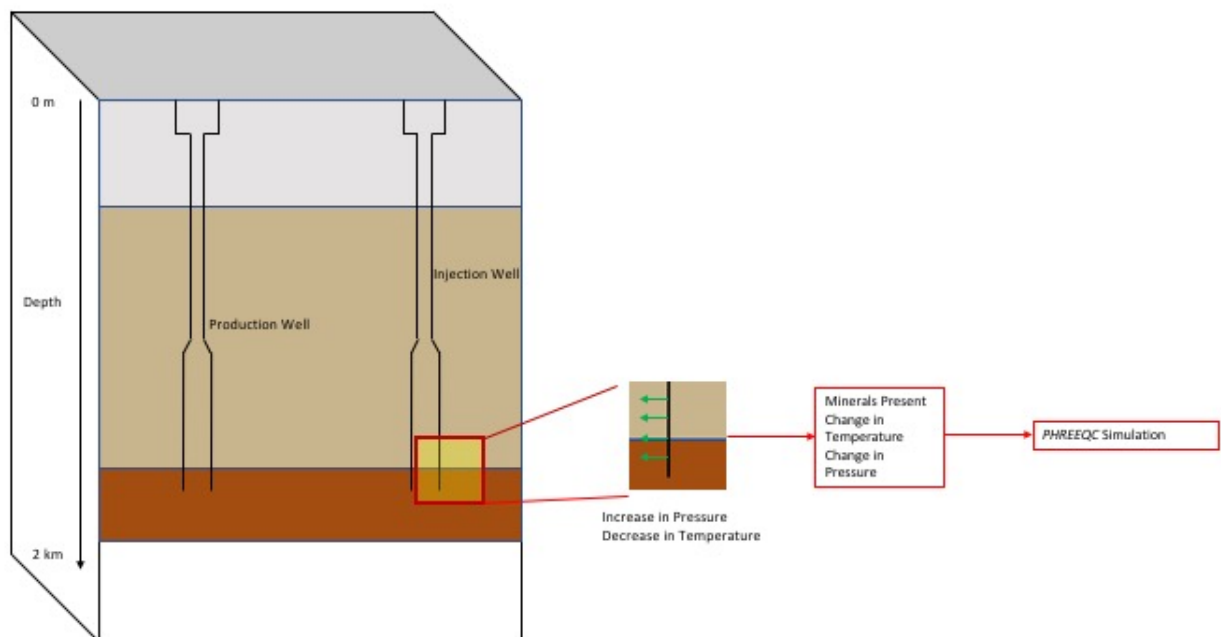

Figure 2.1: Conceptual Model

tain chemical composition is available and is brought to the surface by the production well. When, the fluid reaches the surface it loses heat to heat exchangers. The change in temperature causes a change in the chemical composition of the fluid to change, which eventually leads into scaling of the pipe. Later, the fluid is then condensed and re-injected into the reservoir which again causes a change in the chemical composition which then leads to scaling. See Fig. 2.1

In the figure, a macroscopic, meso-scropic and microscopic model has been structured. In the right side of the figure, i.e., the injection well there is an increase in the well pressure and a decline in the temperature. In the left side, the production well there is only decline in pressure.This chance in pressure or temperature as mentioned earlier leads to scaling and further change will lead to continuous scaling of the well or the pipe.

Due to the scaling, there is then a change in the mineral composition of the fluid and hence we obtain a new pore fluid. In this paper, about saturation indices of 22 minerals are considered and modelled in PHREEQC. A list of these minerals with their chemical formula can be found in Appendix 1. Moreover, we are considering both the change in production well and the injection well along with considering re-injection in the doublet,

To summarize the idea behind the conceptual model, it can be established that:

In the mentioned model, the boundary condition is set up at the production well, the injection well and the condenser:

	Pressure (bar)	Temperature (Celsius)	Presence of Oxygen	Phase of Liquid
Production Well	1 - 30	150 - 400	No	Two phase or super saturated
Reinjection Well	20 - 300	50 - 150	Possible	Liquid or possible bubbles
Condenser	0.08 - 0.12	25 - 35	Yes	Liquid Dissolved (CO_2 and H_2S)

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Hydrogeochemical Modelling

Since the conceptual model is now set up, the idea can now be implemented inside PHREEQC. In order to find the change in the chemical composition of the geothermal fluid due to the changes in the temperature and pressure, PHREEQC has been used extensively.

It is important to mention that the modelling has been done without considering the gas phase and only saturation indices of carbonate minerals is considered. The minerals with their chemical formula are present in Table 3:

Mineral	Chemical Formula
Aragonite	$CaCO_3$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$

Moreover, geothermal water selected for this batch simulation The idea behind checking the change in composition will be to look at the saturation index of the minerals. The saturation index is an index which can tell whether water will precipitate out as a particular mineral or will dissolve. The sign indicated whether the mineral is dissolved (if negative) or whether it is precipitated (if positive) or when water and mineral are in equilibrium (if zero) [5]

A change in temperature is only observed in the reinjection well, where the temperature can vary upto 150 degree celsius. As explained in the conceptual model, first the temperature of the fluid is maintained at 150 degree Celsius from the ground to the the re-injection well at a certain depth. There is a pressure drop from 500bar to about 200 bar. This is because of the fact that the well has less pressure than the ground. Once that is done, the same fluid composition is then carried out with an upward flow, where the temperature changes from 150 degree celsius to 25 degree celsius and pressure from 200 bar to 1 bar. A conceptual design is presented in 3.1. However,these properties of raw geothermal water can help in determining the intensity of the scaling phenomena which can exist on the surface of the nanofiltration membrane and can have an influence on total efficiency of the process. [4][6]

In the batch simulation process PHREEQC was used in order to simulate the mentioned conceptual model. The mentioned model is used with the help of using REACTION TEMPERATURE and REACTION PRESSURE were used extensively in order to work with the change in temperature and pressure. The chemical composition changes when it is cooled and when it is reinjected and hence the simulations are done at surface and reservoir temperature.

It is important to mention about the composition of solution considered at 1 atm and 25 degree Celsius for a general solution present in The Netherlands. The data has been collected from a thesis done by another student at Delft University of Technology under supervision of Prof. Timo Heimovara at TU Delft. [11] The geothermal water selected is set to be highly conductive with a very high hardness level by increasing the amount of calcium sulphates and magnesium. Some values which were found to be a bit absurd were taken

from other resources and were then average in order to achieve a better result. [10]

Sample	Concentration (Mg/kg)
Ba	0.25
C	249.59
Ca	1350
Cl	4713 charge
K	74
Fe(2)	0.49
Li	2.44
Mg	18
Mn	1.28
Na	1670
S(6)	95.32
Sr	22
Zn	1.53
Si	1.3

The idea behind solving this problem was to use first pure water in equilibrium with calcite and aragnoite in equilibrium with them. This was then by setting up an equilibrium using PHREEQC function EQUILIB-RIUM PHASES as shown below:

```
SOLUTION 1 Pure Water
pH 7.0
temp  25.0
EQUILIBRIUM_PHASES
Aragonite 0.0
Calcite 0.0
    Dolomite    0.0
```

The solution was then mixed with the chemical composition mentioned in Table **??** with a varieties of ratio such as 7:3, 3:7, 5:5 where the first term is pure water and the second is chemical composition of the mentioned minerals in Table **??** in order to change the phase of the composition. A phase with completely hard water solution has also been considered with only 1% pure water. [12][6] This was achieved with the use of MIX function in PHREEQC where SOLUTION 1 which is pure water and SOLUTION 2 with the chemical composition. For example for a ratio of 7:3, this can be declared like:

```
   MIX
   1   7.0
   2   3.0
```

Finally the temperature and pressure were changed as mentioned in the conceptual model. This can also be seen from the Figure 3.1 where the injection pressure is set at 300 bars considering that the reservoir pressure at 200 bars. This was achieved by using REACTION TEMPERATURE and REACTION PRESSURE functions of PHREEQC. For the injection well, the steps used are:

```
REACTION_TEMPERATURE 1
25 150 150 150
REACTION_PRESSURE   1
1 300 300 200
```

Using the same concept for production well, the changes were estimated as well, however REACTION TEMPERATURE was not considered due to the fact that there is no change in temperature observed:

```
   REACTION_PRESSURE 1
   200 100 100 1
```
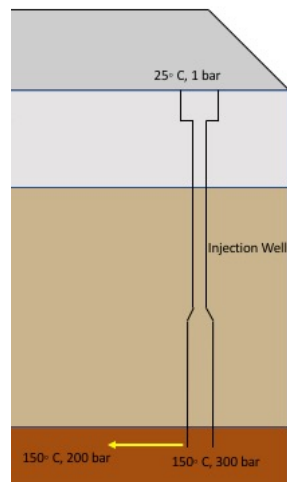
Figure 3.1: Conceptual Design for Modelling input into PHREEQC for injection well

As already mentioned earlier, PHREEQC didn't provide that good results for production well. Due to the fact that most of the changes were in-situ conditions only, no scaling was found during the PHREEQC simulations, due to the fact that PHREEQC is sensitive on temperature and not on pressure this makes sense.

4

Results

In the previous chapter, it was explained how the modelling was to be done. In this chapter, the results obtained from the simulation will be evaluated. The evaluation was done by obtaining the results of PHREEQC simulation and processing them into software package like MATLAB to obtain graphical results for clear understanding. As mentioned, the idea was to focus on three main minerals: Aragonite, Calcite and Dolomite. However, when using the results of Dolomite they were interfering with the values and hence were disregarded. A solution with Dolomite is attached in Appendix A.
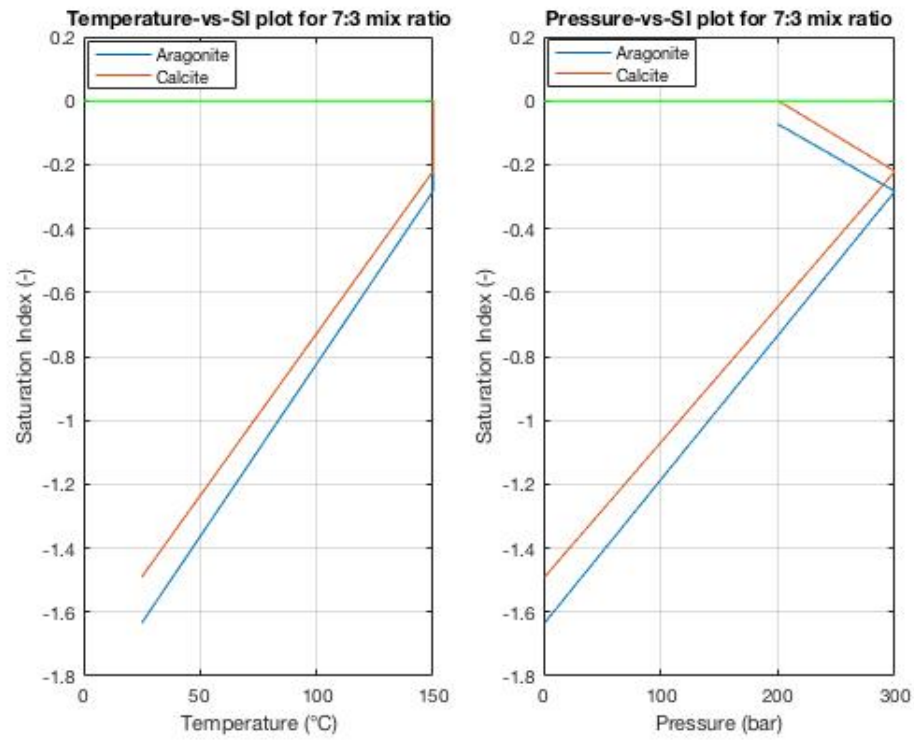
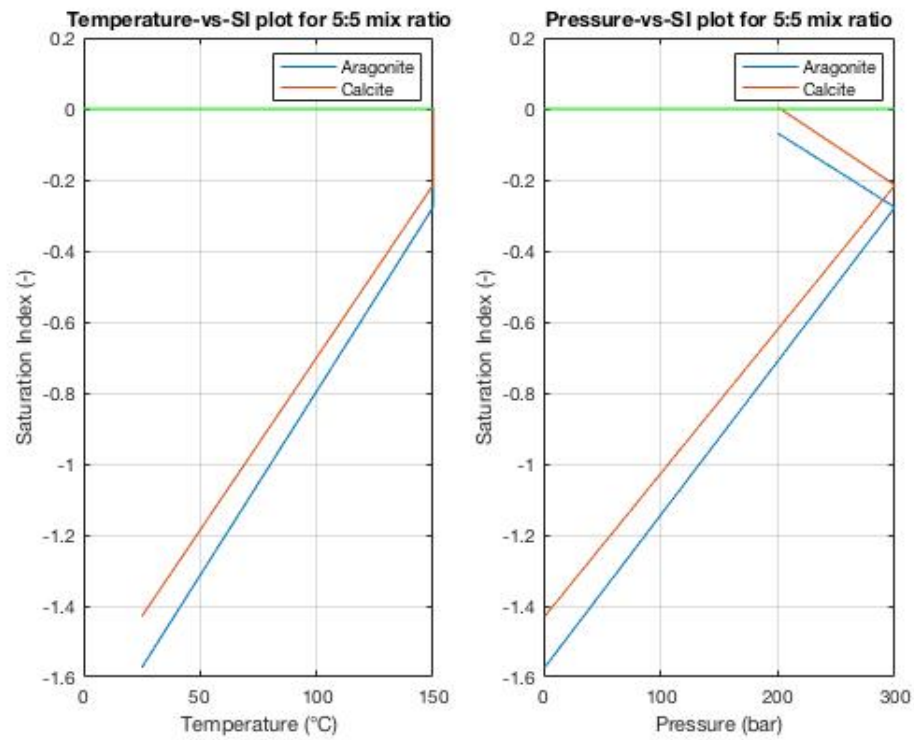Figure 4.1: Change in SI with Temperature and Pressure for 7:3 mix

Figure 4.2: Change in SI with Temperature and Pressure for 5:5 mix
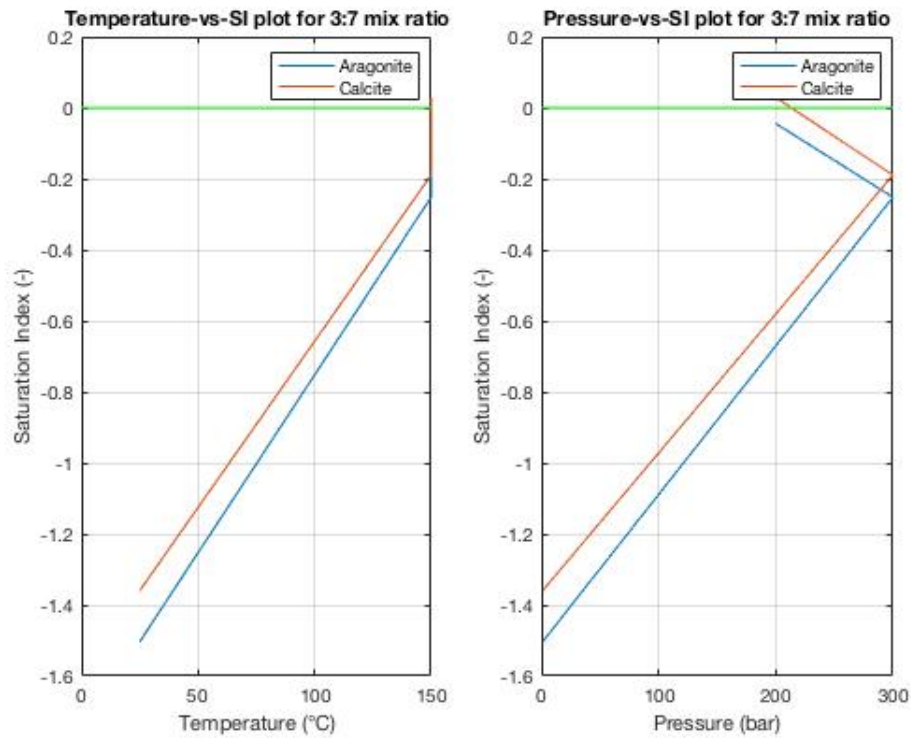
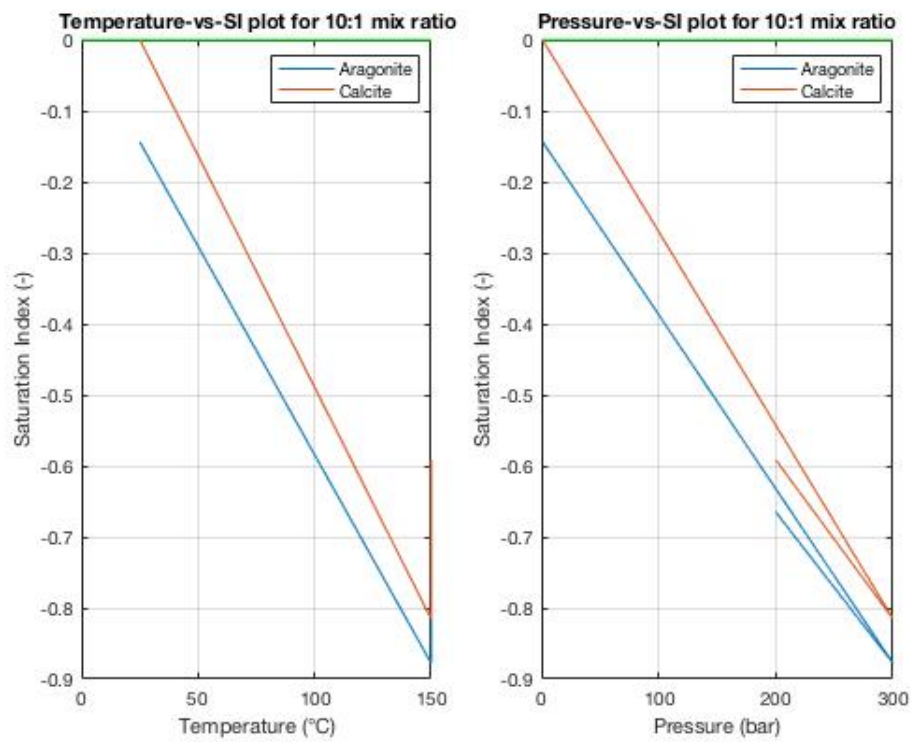Figure 4.3: Change in SI with Temperature and Pressure for 3:7 mix

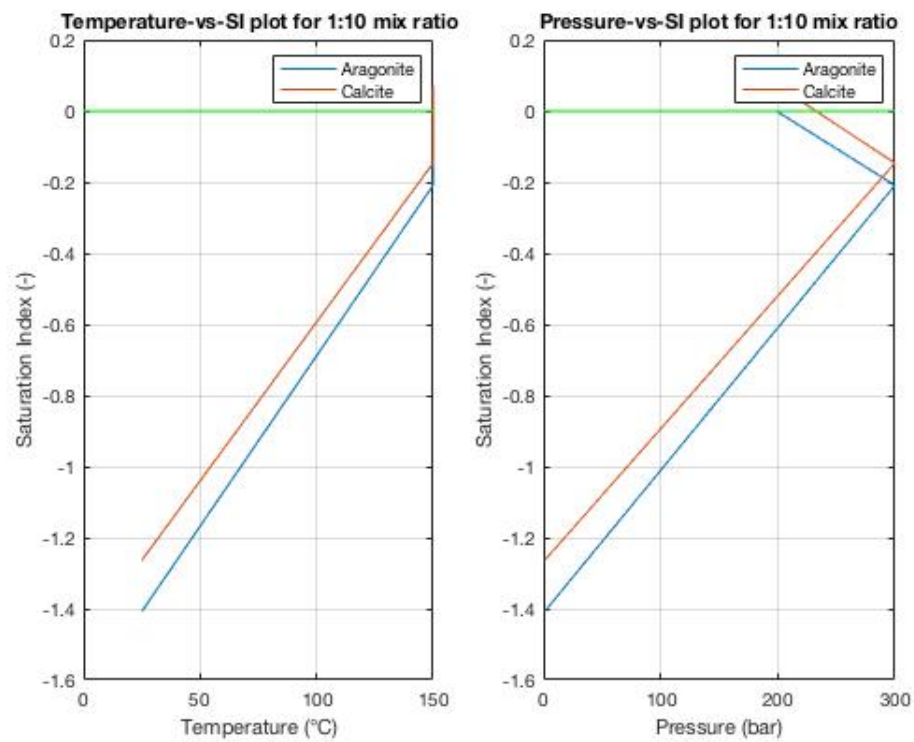Figure 4.4: Change in SI with Temperature and Pressure for 10:1 mix

Figure 4.5: Change in SI with Temperature and Pressure for 1:10 mix

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