

Review of the Current State of the Geothermal Industry with a focus on The Netherlands

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Energy demands are rising while fossil fuels are depleting at faster rates. Coupled with environmental problems such as global warming and climate change the need for green, sustainable, renewable energy has been highlighted. Geothermal energy looks to be a future player in the energy industry. Methods of heat extraction and electricity production are examined as well as the potential and state of the geothermal industry in the Netherlands. Problems faced by the industry include corrosion and scaling which is studied in great detail using the PHREEQC geochemical program. The program simulates a 1-D geothermal system and models mineral and gas solubility to see its affect during fluid transport in a system. It is found that there is significant scaling and corrosion during pressure drop especially at 10 bar of pressure. Temperature drop also leads to significant scaling. Knowledge can be used for future operations in prevention and inhibition of corrosion and scaling thus improving system efficiency and reducing operational costs. Improvements are required in the databases by experimental solubility data. Furthermore, understanding can be improved by gathering information from operators at the geothermal plants via standardized methods of sampling and analysis.

Methods,
Potential, and
Problems

1. Introduction.....	4
- Renewable Energy	
- Classifying Geothermal Energy	
- Geothermal Exploration	
2. Commercial Geothermal Energy.....	8
- Heat Transfer	
- Thermodynamic Properties of Water and Steam	
- Commercial Geothermal Plants	
- Commercial Geothermal Methods	
- Geothermal Heat Pumps	
3. Geochemical Theory of Minerals and Water.....	17
- Equilibria and the Solubility of Minerals	
- Equilibria Thermodynamics	
- Pressure on Chemical Reactions	
- Solid Solutions	
- Kinetics of Geochemical Processes	
- Hydrolysis and Redox Reactions	
4. Corrosion & Scaling.....	21
- Types of Corrosion and Scale	
- Formation of Scale	
- Rate of Scale Formation	
- Interrelation between Scaling and Corrosion	
- Effects of pH, CO ₂ Partial Pressure & Temperature	
- Ca ²⁺ and Mg ²⁺ in Scaling and Corrosion	
- Calcite in Corrosion and Scaling	
5. Geothermal Energy in The Netherlands.....	31
- A Developing Energy Resource	
- Dutch Geothermal Platform and DAGO	
- Localities	
- Sub-Surface Conditions in The Netherlands	
- Lead Formation in Doublets	
6. Economics.....	38
7. Actions For Corrosion and Scaling.....	40
- Removal and Disposal	
- Prevention/Inhibition	

- Predicting Corrosion and Scaling
- Monitoring

8. Methods.....	49
- Sampling and Procedures	
- Minimizing Discrepancies	
- Understanding Modelling and Using Models	
9. PHREEQC Simulations.....	52
- Databases	
- Standard Model Setup	
- Mineral and Gas Solubility	
- Model Validation	
10. Conclusion.....	63
11. Literature References.....	64
12. APPENDIX.....	67

1. Introduction

Mankind has depended largely on fossil fuels as a source of energy since the industrial revolution approximately 200 years ago. These fossil fuels consist of coal, petroleum, and natural gas and are a non-renewable source of energy since these fossil fuels are being used faster than nature is able to replenish them. As energy demands continue to rise, coupled with ever drying non-renewable energy sources, turning to renewable sources of energy is an increasingly popular phenomenon. Additionally, the need for renewable energy has been strengthened due to the negative consequences of using fossil fuels, highlighted numerous times in various research journals. This recent shift of focus to renewable sources of energy consists of resources that are able to be naturally replenished on a human (micro) timescale and includes wind, sunlight, tides/waves and geothermal heat. These sources of energy are so called green energies, with minimal impact on global warming and climate change. These renewable energies are able to replace fossil fuels in four major areas: heating, electricity generation, motor fuels, and rural energy services. Currently, renewables contribute to only 19% of our total energy consumption in 2012 while in 2013, renewables contributed to 22% of our global electricity generation (REN21, 2014). Worldwide investments in renewable technologies reached over US\$214 billion in 2013 with the United States and China as the biggest investors (REN21, 2014).

One form of renewable energy that replaces fossil fuels in two major areas, electricity generation and (direct) heating, is geothermal energy. This is a great source of energy that is sustainable, clean, and replaceable. The temperature of the Earth's core is approximately 4000°C, and as a result, there is a heat flow outwards through the mantle and the crust. The temperature gradient at the Earth's surface is around 30°C/km, i.e. for every kilometre in depth, there is an increase of 30 degrees Celsius. This heat flow is continually maintained from the original formation of the Earth (20%) as well as from radioactive decay of isotopes (80%). There are many geologically active parts of the world where the interfaces of tectonic plates provide naturally occurring steam jets and hot springs as a steady source of thermal energy. Furthermore, in regions that are geologically stable, geothermal energy can still be extracted using advanced technologies and intricate methods which will be discussed later. In general a geothermal field is a geographical definition which indicates an area of geothermal activity at the earth's surface. This can also indicate the area at the surface which corresponds to all the subsurface components if there is lack of a surface installation. Geothermal energy can be used for generating electricity through water and steam or directly for heating (to housing projects, greenhouses and/or commercial buildings).

Overall, geothermal energy has the potential to remain CO₂ free, as long as the input electricity is from a green source. It is considered to be renewable because the amount of heat extraction that can occur is small compared to the Earth's heat content. Furthermore, the Earth has an internal heat content of 10³¹ joules, which was nearly 100 billion times the worldwide annual energy consumption in 2010 (Ingvar, 2008). Since the Earth is naturally cooling down on geologic timescales, any human extraction of heat taps only a minute fraction of the total outflow and therefore does not accelerate cooling (Ingvar, 2008). Additionally, geothermal power is considered sustainable due to its power to sustain the ecosystems on Earth, as well as allowing future generations to use their own resources to the same amount that those energy sources are presently used (Ingvar, 2008). Lastly, geothermal energy has great potential for mitigating global warming due to its low emissions

in carbon dioxide. Nevertheless, as beneficial as geothermal energy may be, it is still important to monitor heat extraction so as to avoid local depletion. Reservoirs with water can also face a reduction in overall water, but can be replaced if water is injected back. It is possible for wells to slowly decrease local temperatures over a long period of time especially if the surrounding temperature has no time to equilibrate (injection of water is always at a lower temperature than when it was extracted). Lastly, geothermal energy has yet to reach its full potential as a source of energy around the world.

This research paper will describe the current state of the geothermal industry both around the world and within the Netherlands by looking at the various available technologies, methods of heat extraction, and problems faced from exploitation. Furthermore the report will provide a sound understanding in geothermal operations including the physical and chemical theory of such operations. Lastly, it will look at ways to tackle the problems faced during heat exploitation through identification, prevention, inhibition, and disposal. The last section will create models to aid in prediction methods to prevent future problems from arising.

1.1 Classifying Geothermal Energy, Systems, and Reservoirs

Geothermal systems and reservoirs can be classified in terms of: their reservoir enthalpies, their reservoir temperature, its physical state, or its geological setting and nature. Geothermal systems refer to all parts of the hydrological system involved such as the recharge zone, the seepage zone, subsurface components, and outflow of the system. On the other hand the geothermal reservoir refers to the part of the geothermal system that can be directly exploited, usually the hot and permeable reservoir rock.

Classification by its reservoir enthalpy (geothermal environment in which the reservoir operates in), leads to two types: low enthalpy and high enthalpy. Low enthalpy environments are defined as having reservoir fluid enthalpies less than 800 kJ/kg, which correspond with temperatures less than 190°C (Saemundsson, 2009). High enthalpy environments are defined with reservoir fluid enthalpies greater than 800 kJ/kg (Saemundsson, 2009). Initially, it was common for geothermal plants were to operate in high enthalpy environments for electricity generation purposes. These environments included areas of high seismic/volcanic activity with steep geothermal gradients, greater than the average of 30°C km⁻¹. Overtime with increase in technology and methods of operating, low enthalpy environments became more popular, usually on a small scale as a form of direct heating to housing and commercial buildings. These environments tend to draw heat from the general heat flow of the Earth's crust. Reservoir temperature can be classified into three: *low temperature* (systems with reservoir temperature at 1km depth below 150°C that are often characterized by boiling springs); *medium temperature* (systems with reservoir temperature at 1km depth between 150°C-200°C); and *high temperature* (systems with reservoir temperature at 1km depth above 200°C, usually characterized by steam vents, high altered ground, mud pools, and fumaroles) (Saemundsson, 2009).

When classifying the geothermal system by its physical state, there are three categories: liquid-dominated, two-phase, and vapour-dominated. Liquid-dominated reservoirs are composed of water that is at or below the boiling point for the prevailing pressure, and the water phase controls the pressure within the reservoir (Saemundsson, 2009). They can be found near young volcanoes, rift zones, and in hot-spots. Most commonly these systems are

used to generate electricity by converting the liquid into steam. Two-phase reservoirs are where water and steam co-exist, while the temperature and pressure follow the boiling point curve (Saemundsson, 2009). Vapour-dominated reservoirs are at temperatures well above the boiling point for water (or the liquid in that system) at the prevailing pressure. In this case the steam phase controls the pressure in the reservoir (Saemundsson, 2009). Both liquid-dominated and vapour-dominated reservoirs can have minor amounts of steam and liquid in the system respectively.

Defining the geothermal system by its geological setting and nature, of which there are three classifications (convective, volcanic, sedimentary), overlaps with previous definitions, but nevertheless is worth mentioning to further understand geothermal systems as a whole. In convective systems the heat source is from the hot crust at depth in tectonically active areas where there is above average heat-flow (Saemundsson, 2009). Geothermal water would have circulated to great depths (greater than 1km) via vertical fractures while extracting heat from the rocks. In volcanic geothermal systems, as the name suggests, are associated in some way to volcanic activity. The heat sources for these systems primarily arise from hot intrusions or magma. They are often located inside, or close to, volcanic complexes within or close to plate boundaries or hot spots (Saemundsson, 2009). Fault zones, permeable fractures as well as permeable strata (including sediments, lavas or ignimbrites) control the flow of water in volcanic geothermal systems (Saemundsson, 2009). Sedimentary geothermal systems are alternating layered sequences of permeable and impermeable strata. Water tends to be interstitial, while temperature varies depending on depth of permeable rocks. Natural circulation of the geothermal fluids is minimal and thus pumping is required. Sedimentary systems are the most common type worldwide (Saemundsson, 2009).

It is important to note that many examples of geothermal fields¹ around the world are classed either into either high-temperature geothermal fields or low-temperature geothermal fields. High-temperature fields include rift zones (mid ocean ridges, oceanic rifts, continental rifts, hotspot volcanism, and flank zone volcanism) and compressional regimes (arc volcano's and inter-arc basins, micro-continental arc volcanoes, continental margin arc volcanism, and batholiths driven geothermal systems).

1.2 Geothermal Exploration

This is exploring the subsurface for a viable, active geothermal region and includes a wide range of disciplines such as geophysics, geology, geochemistry and engineering. An active and suitable geothermal region will be characterized by: Heat source, reservoir, geothermal fluid, and a recharge area. Not only does it have to be suitable for mining, it also must take a cost effective approach, since about 42% of all expenses is attributed to exploration (Jennejohn, 2009). The greatest advancements in this industry can come from developments in exploration techniques and technologies (Jennejohn, 2009). Methods of exploration include drilling, geophysics and geochemistry studies.

¹ As mentioned previously, the definitions have distinguished between geothermal fields (surface locality), geothermal systems (subsurface components/locality), and geothermal reservoir (thermal exploitation zone). All possible classifications have been presented and are interchangeable; the classifications used vary according to research paper/person/group etc. Some classifications may not be used anymore, or have been refined.

Drilling during the exploration phase will provide the most accurate information, but is very costly. Thermal gradient holes (TGH), exploration wells, and full-scale production wells provide the most reliable information on the subsurface (Jennejohn, 2009). These will give information on thermal pockets, temperature gradients and any other geothermal characteristics. Geothermal exploration never reaches more than 4 kilometres in depth, with many wells at 2 or 3 km in depth (at approximately \$400 per foot). The first production well has a success rate of 25%, which increases to a range between 60% and 80% after further analysis and studies (Jennejohn, 2009). Geophysics and geochemistry studies are important for determining a potential field, as well as for minimizing costs by successful drilling. Methods such as seismology (waves that propagate and interact with subterranean components and respond accordingly), gravity (changes in densities to characterize subsurface properties), magnetic studies (depth of the Curie point), isotopic ratios, elemental ratios, and CO₂ concentrations used in geothermal exploration, are methods also used in the oil and gas industry.

2. Commercial Geothermal Energy

The concept of geothermal power has existed for many hundreds of years, but it is only in relatively recently in the 20th century where the demand for (cleaner) electricity led to widespread use of geothermal power. This section provides a basic understanding of the energy science behind geothermal energy, as well as current commercial geothermal plants and systems.

2.1 Heat Transfer

Heat is the primary energy when dealing with geothermal energy. Heat transfers itself in three ways if a suitable physical pathway is available: convection, conduction, and radiation. Convection is the transport of heat due to the bulk motion of a fluid; the fluid has a density ρ , a temperature T that moves with a velocity u . The mass flow per unit area per second is ρu and the thermal energy per unit mass is cT (Andrews and Jelley, 2007). The product of ρu and cT gives the rate of flow of heat per unit area by convection, thus:

$$Q/T = (\rho u)(cT) = \rho ucT$$

A cold fluid that flows over a hot surface will have a greater rate of heat transfer from the hot surface to the fluid than that of a stationary fluid. Since the temperature gradient at the hot surface is very large, the layer of fluid adjacent to the wall is heated rapidly by conduction. The hot fluid mixes with the cold material in the bulk of the fluid and the net heat transfer is much larger than that by heat conduction alone (Andrews and Jelley, 2007). With forced convection, the rate of heat transfer per unit area can be expressed accordingly:

$$Q/A = Nu \frac{k(T_s - T_\infty)}{L}$$

Where T_s the surface temperature, T_∞ is the temperature in the body of the fluid, L is a characteristic length, and Nu is a dimensionless parameter known as the Nusselt Number. The Nusselt number is a function of two other non-dimensional parameters: Prandtl number² and the Reynolds number³ (Andrews and Jelley, 2007).

Convection is the most important process of transfer in geothermal systems; however, conduction and radiation are worth mentioning. Conduction is the transfer of internal energy via microscopic diffusion and collisions of particles within a body. This takes place within a body or when two bodies are in contact with one another. The heat flows due to a temperature gradient existing between a hotter body and a colder body, thus the heat flows from hot to cold. Conduction plays a small role when a hot fluid loses heat due to the colder surroundings during fluid flow. Radiation is the transfer of heat energy in the form of particles or waves through a material medium or even through space. This plays a minimal role in geothermal systems.

² This is a dimensionless number defined as the ratio of momentum diffusivity (kinematic viscosity) to thermal diffusivity, i.e. $\frac{\text{viscous diffusion rate}}{\text{thermal diffusion rate}} = \frac{c_p \mu}{k}$

³ A dimensionless quantity used to predict similar flow patterns in different fluid flow situations. Defined as the ratio of momentum forces to viscous forces and therefore quantifies the relative importance of the momentum and viscous forces for given fluid flow conditions

2.2 Thermodynamic Properties of Water and Steam

Convictional geothermal plants have water as the working fluid, which changes phase from water to a two-phase mixture of both water and steam, to dry steam, and back to water again at various stages in the cycle. By looking at the thermal properties of water and steam we can gain a valuable theoretical understanding of plant operations. The Temperature T and the entropy s are the most important thermodynamic variable in these plants. Figure 1 below shows the temperature-entropy diagram for water and steam.

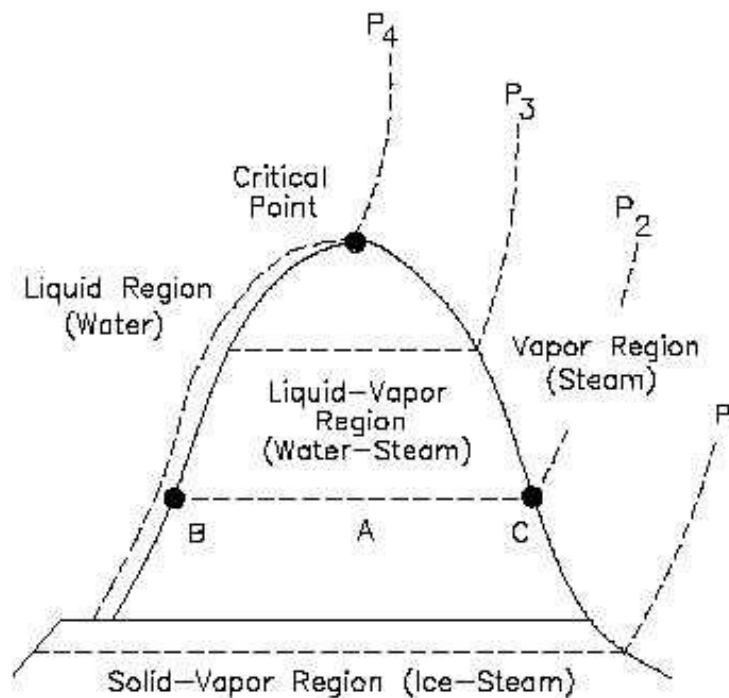


Figure 1: Three regions can be distinguished: a liquid region inhabited only by water, a liquid-vapour region inhabited by water and steam, and a vapour region inhabited only by steam. The bell shaped curve represents the phase boundary while the solid lines are isobars (constant pressure). The dashed lines in the liquid-vapour region are lines of constant steam quality x , i.e. the fraction by mass of steam in the two-phase mixture. Superheated fluid (where the temperature of the steam is above the boiling point) is represented by the line CB. Here the temperature of the dry steam rises at a constant pressure as more heat is supplied. The properties of water in the liquid region and dry steam in the vapour region can be obtained from steam tables. Source: (Andrews and Jelley, 2007)

2.3 Commercial Geothermal Plants

There are a number of geothermal plant types that are in use for commercial or energy purposes. The main distinction lies in those power plants used to generate electricity and those plants used for direct heating. Three types of geothermal power plants for electricity production exist:

1. **Dry Steam Power Plant (Figure 2):** This directly uses steam generated inside the earth to create power. Since this eliminates the need to change water into steam to generate power, there is no need for additional heating boilers and boiler fuel. The steam fills the wells and goes directly to a turbine. This causes rotation of the turbine and consequently activates a generator so that electricity is produced. This is one of the world's oldest geothermal power plants, and overall is not a commonly used plant as dry steam in natural reservoirs is rare (California Energy Commission, 2008).

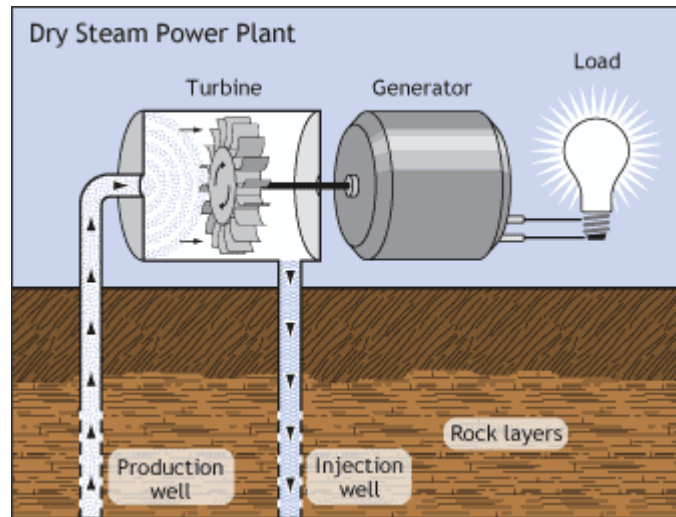


Figure 2: Dry Steam Power plant. Source: California Energy Commission, 2008

2. **Flash Steam Power Plant (Figure 3):** This power plant uses hydrothermal fluids with temperatures greater than 182°C (360°F) to produce electricity (California Energy Commission, 2008). This type of plant is commonly used in geothermal operations and it works by collecting fluid in a tank that is held at a much lower pressure than the fluid. This causes most of the fluid to rapidly vaporize, or ‘flash’, and the resulting vapour drives a turbine to produce electricity. Remaining liquid is sometime flashed a second time for maximum extraction of energy. The remaining condensed steam is injected into the reservoir.

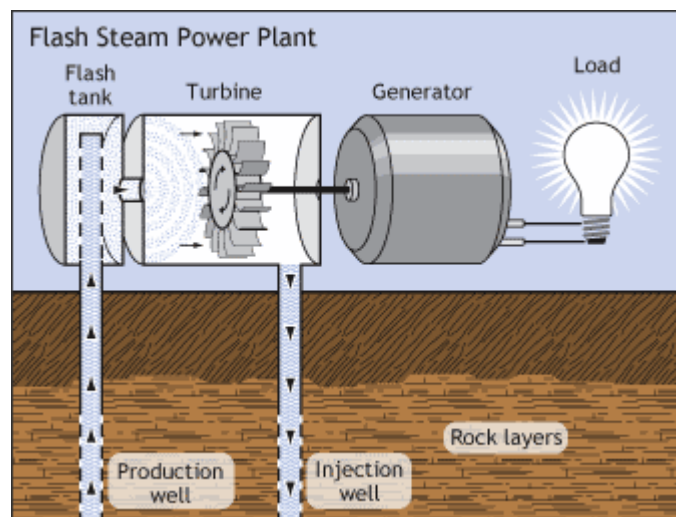


Figure 3: Flash Steam Power plant. Source: California Energy Commission, 2008

3. **Binary Cycle Power Plant (Figure 4):** This type of plant uses moderate-temperature geothermal fluid as well as a secondary fluid which has a lower boiling point than water. As the geothermal fluid passes through a heat exchanger, it causes the secondary fluid to flash to vapour which then drives the turbine (California Energy Commission, 2008). As a closed loop system there are no emissions into the atmosphere. Also both fluids never come into contact with one another.

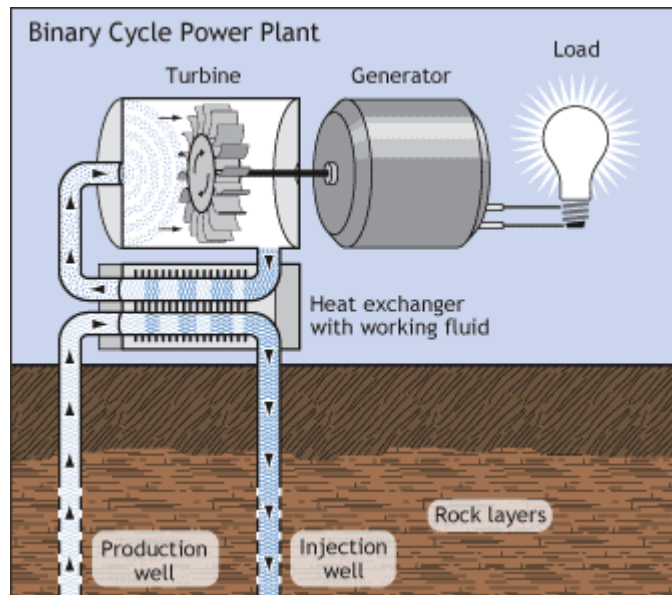


Figure 4: Binary Cycle Power plant. Source: California Energy Commission, 2008

Hot water from geothermal resources is not only used for electricity generation but also for direct heating purposes for buildings, districts, greenhouses, water for fish farms, or industrial processes. A well is drilled into a suitable reservoir to provide a continuous stream of hot water. This water is brought up through the well and a mechanical system, consisting of piping, a heat exchanger, and controls, delivers the heat directly for its intended use turbine (California Energy Commission, 2008). Another well will take the cooled water and inject it back into the reservoir, or may even dispose of it on the surface. The geothermal fluids in this case tend to be at lower temperatures than used for electricity generation. A typical system configuration for direct geothermal heating is shown in Figure 5.

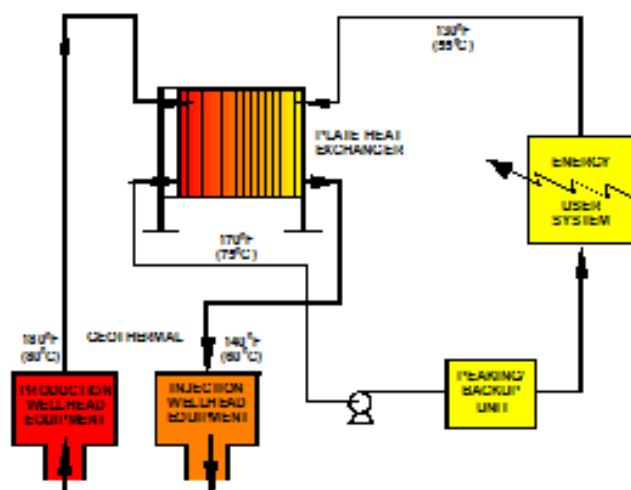


Figure 5: Shows the well head (in red) with incoming heat at 80 degrees Celcius, after which it travels through the plate heat exchanger. It then leaves at the other well head (in orange) at 60 degrees Celcius. The yellow boxes indicate the users system which can control the heat. Source: Geothermal Energy Association, <http://geo-energy.org/Basics.aspx#ways>

2.4 Commercial Geothermal Methods

There are a number of methods used for mining geothermal heat, usually dependent on the geological subsurface conditions. The methods of heat mining presently used in a number of countries include hot dry rock (HDR), hot wet rock (HWR), enhanced geothermal system (EGS), and aquifers. As technology and research continues to improve in this field, new methods are slowly being developed, and these include depressurized reservoirs and magma resources.

AQUIFERS

This is a layer of water-bearing porous rock that is trapped between two layers of impermeable rock such as granite, marble, or slate, usually tens of meters in thickness. Aquifers tend to be shallow in depth; reaching a maximum of 2-3km with temperatures typically reaching 60-90 degrees Celsius (Andrews and Jelley, 2007). Those aquifers close to the surface can provide large reservoirs of water that has been collected after rains. Cold water is usually injected into the aquifer via a borehole, and as the water flows through the permeable rock, it absorbs heat from the rock. This hot water is then removed via a second borehole.

Heat conduction from the impermeable rock above and below the aquifer is usually negligible over the timescale for heat extraction from an aquifer (Andrews and Jelley, 2007). Thus for simplicity we can use a 1-D fluid flow model to demonstrate the theory for heat extraction from an aquifer (Figure 6).

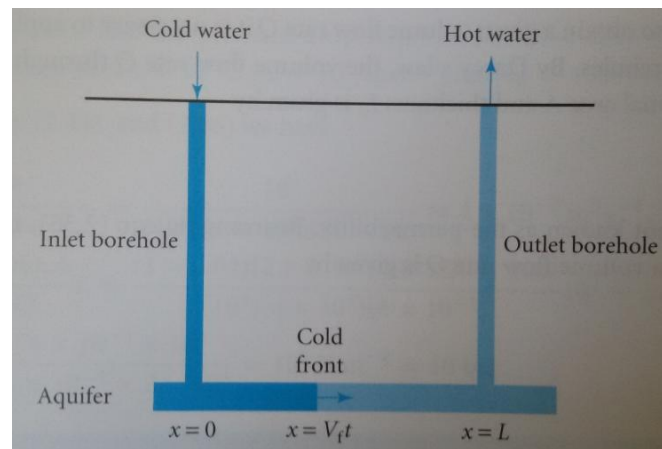


Figure 6: Twin borehole system for heat extraction from an aquifer. At the inlet borehole $x=0$ cold water is injected, while at outlet borehole $x=L$ hot water is extracted. Source: Andrews and Jelley, 2007.

If the inlet is taken as temperature T_0 , and the aquifer is initially taken as T_1 , the heat available per unit volume from the rock is $p_r c_r (T_1 - T_0)$. The product of the volume flow rate Q , and the heat per unit volume gained by the water, i.e. $p_w c_w (T_1 - T_0)$, gives the power output of the system. As the cold water passes through the aquifer it begins to absorb heat from the hotter porous rock; during the lifetime of the system a cold front moves from the inlet borehole to the outlet borehole. The speed of the moving cold front v_f is:

$$v_f = \kappa_w$$

where $\kappa = p_w c_w / [(1 - \phi) p_r c_r]$ is a dimensionless parameter and $v_w = Q/A$ is the bulk velocity of the water in the aquifer (Andrews and Jelley, 2007). The porosity, or fraction of

the volume occupied by pores, is φ . The lifetime of the system is the total time it takes for the cold front to move from the inlet borehole to the outlet borehole, and is given by:

$$t_{life} = \frac{L}{V_f} = \frac{(1 - \varphi)p_r c_r AL}{p_w c_w Q}$$

Consequently, for a long lifetime is attainable when there is a large spacing between the two boreholes, a low porosity, a large cross-sectional area of aquifer, large heat capacity per unit volume, and a low volume flow rate. Since the total amount of thermal energy available from the system is fixed, the choice of volume flow rate and the lifetime of the system are determined by the economics of the system (Andrews and Jelley, 2007). Ultimately, a pressure drop Δp must be applied between the two boreholes so a given volume flow rate Q can be obtained. Using Darcy's law the volume flow rate Q through a slab of porous rock of thickness L and cross-sectional area A is given by:

$$Q = kA \frac{\Delta p}{L}$$

Here k is the permeability which is a known constant. This can then be re-arranged to calculate the pressure drop for a given volume flow rate, which is given as: $\Delta p = \frac{QL}{kA}$

HOT DRY ROCK (HDR)

HDR is the most abundant geothermal resource that is available for energy extraction. A vast amount of thermal energy is stored in the impervious crystalline basement rocks that are both extremely hot and dry (no hydrothermal fluids of any kind). These rocks tend to have natural fractures, joints and cracks. Water is pumped from the surface down to the reservoir and through the narrow gaps in the hot, dry rock formations under high pressures. The fluid injected into the reservoir absorbs thermal energy from the high-temperature rock surfaces and then serves as the vehicle for transporting that heat to the surface for practical use (Ito and Kaieda, 2002). It is important to note that injecting the water 'creates' a so-called reservoir. As the reservoir forms by the pressure-dilation of the joints, the elastic response of the surrounding rock mass results in a region of tightly compressed, sealed rock at the periphery (Brown, 1993). This essentially makes the HDR reservoir a closed and confined system/loop. One benefit of HDR is the fact that the operating parameters (production temperatures, injection and production pressures) as well as the physical characteristics (depth, size) can be controlled carefully and pre-planned. Suitable rock types for HDR is granite in blocks of 10-100m in dimension. One advantage granite has is its slightly higher temperature gradient.

Heat is lost by unsteady heat conduction from the surrounding rock (Figure 7). Over time the heat flux to the water will decrease, as the layer of cooled rock thickens. Similar to the aquifer, a cold front moves from the inlet to the outlet, but the temperature behind the front is more diffuse because some heat continues to be supplied from the walls behind the cold front (Andrews and Jelley, 2007). Using a binary cycle to generate electricity is possible in these situations if the temperature is between 100-150 degrees as steam forms and turns the turbine.

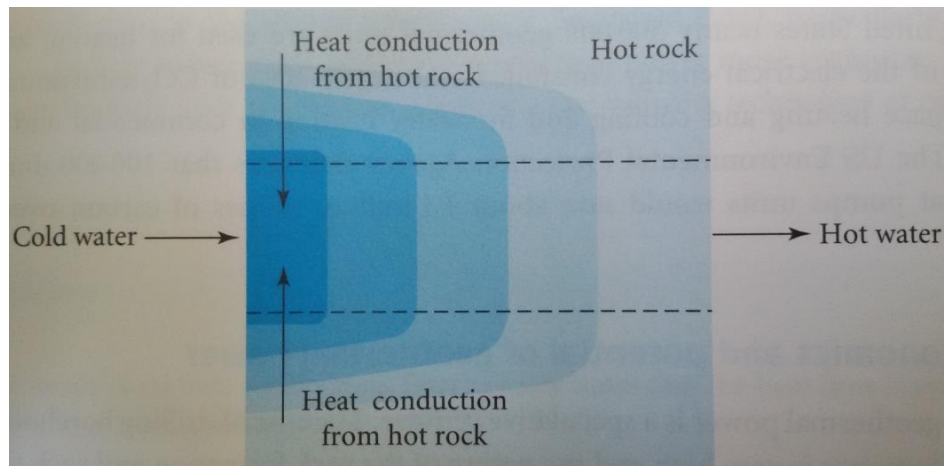


Figure 7: Heat extraction from hot dry rock. One well injects the cold water (on the left side), and another well extracts the resulting hot water (on the right side) as the liquid moves through the porous dry rock. Source: Andrews and Jelley, 2007.

ENHANCED GEOTHERMAL SYSTEM (EGS)

This is very similar to the HDR geothermal mining in that it creates geothermal resources in HDR via 'hydraulic simulation'. Since HDR can only be exploited where naturally occurring heat and rock permeability are sufficient to allow energy extraction, EGS seeks to improve or enhance energy exploitation in areas that do not allow for economic flow rates. This usually means in areas where natural cracks and joints have a weak permeability and therefore are not cost effective. EGS works by pumping high-pressure cold water down an injection well into the rock which increases the fluid pressure in the naturally fractured rock, mobilizing shear events that enhance the system's permeability (Sass and Robertson-Tait, 2002). The heated water is transported to the surface and used directly or flashed. The now cool water is then injected back into the reservoir to be heated up again. A continuous circulation eliminates the need to maintain the fractures. EGS wells are expected to have a useful life of 20 to 30 years before the outflow temperature drops about 10 degrees Celsius and the well becomes uneconomic (Sass and Robertson-Tait, 2002). Recent studies have looked at the possibility to use supercritical CO₂ instead of water as the geothermal working fluid since it has a number of advantages such as: Greater power output, carbon sequestration, minimized parasitic losses from pumping and cooling, and reduced water used. The best locations for EGS are over deep granite that is covered by a 3-5 kilometer layer of insulating sediment that reduces heat loss (Pierce, 2010).

HOT WET ROCK (HWR)

This is basically hydrothermal energy, in which thermal energy is exploited from hot fluids already in place within the Earth's crust. Water can naturally seep below the surface where it is trapped above impermeable rock. At great depths the rock is hot which causes the water to heat up. Sometime the water is heated when it comes into close contact with magma (molten rock) in volcanically active regions. If the water is heated enough it can become superheated. This builds steam pressure which can cause the water to naturally seep to the surface either explosively or slowly. Sometimes drilling down to extract the water in a closed loop system is another way to exploit HWR. The water will usually leave the outlet borehole due to high subsurface pressures, and the cooled water is returned into the reservoir.

GEOPRESSURIZED RESERVOIRS and MAGMA RESOURCES

A large amount of research has been focusing on new methods for geothermal energy exploitation for commercial uses and this coupled with advances in engineering over the last two decades has made it possible to exploit geothermal resources that was not otherwise feasible. Two areas of focus are in magma resources and in geopressurized reservoirs. Geopressurized reservoirs contain methane-rich fluids which are co-produced with steam and/or hot water. “Geopressurized” reservoirs have yet to be commercially developed, but the US government supported production engineering studies in the Gulf Coast Region to simultaneously generate electricity from the geothermal fluids as well as to produce natural gas (Gallup, 2009). Magma resources are a method in which heat is directly extracted from cooling magma on active volcanoes. Ideally this works in areas where magma is closer to the Earth’s surface than usual. A recent breakthrough in Iceland has essentially created the world’s first magma-EGS system. As part of the Iceland Deep Drilling Project (IDDP), a borehole was drilled at Krafla in 2008 and 2009, and as is well known, it ended in a molten magma at 2100 m depth, with a temperature of 900-1000 °C (IDDP, 2014). The hole was lined with a steep casing most of the way down except at the section closest to the magma. Tests were carried out by pumping cold water down to the rocks beside the magma. This created high- pressure steam for months at temperatures over 450 °C, which beat the world record for geothermal heat (IDDP, 2014). Furthermore, this well was the hottest in the world and one of the most powerful which could lead to an energy revolution for geothermal resources in high-temperature or high-enthalpy areas.

2.5 Geothermal Heat Pumps

Commonly known as ground source heat pumps (GSHP) in the Netherlands, it serves as a central heating/cooling system by transporting heat to and from the ground. It is more of an energy conservation system as opposed to extracting geothermal resources deep into the earth’s crust. Additionally, GSHP tends to receive most of its heat from the sun and only a minor amount of heat from the ground. It uses the earth both as a heat source (for the winter months) and as a heat sink (for the summer months). The design of GSHP’s (Figure 8) takes advantage of the fairly stable temperatures in the ground to reduce heating and cooling costs. Depending on latitude, the temperature beneath the upper 6 metres of Earth’s surface maintains a nearly constant temperature between 10 and 16 °C (Hanova, 2007).

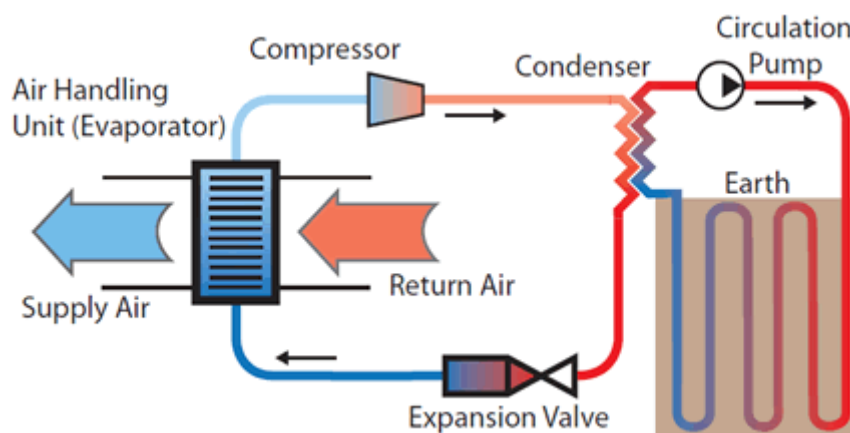


Figure 8: Ground Source Heat Pump. The use of a heat pump can transfer heat against the natural flow direction or enhance the natural flow direction. The compressor and expansion valve aid the heat pump; compressor helps with warm air (creating denser air) while the expansion valve aids with cool air (creating less dense air). Source: Hanova, 2007.

GSHP can be used to keep a building at a constant temperature all year round since in winter, the ground temperature is warmer than the air temperature, and in summer the ground temperature is cooler than the air temperature. It is important to note that the ground will contain two separate storage areas for the warm and cold water. A ground source heat pump thus extracts ground heat in the winter, for heating, and transfers heat back into the ground in the summer for cooling (Hanova, 2007). GSHP are very energy efficient technologies for heating, ventilating, and air conditioning.

In some circumstance it is necessary to extend to lifetime of a geothermal reservoir using sustainable methods. For example in The Geysers project, production has depleted fluid mass from the reservoir more efficiently than extracting the heat stored in rock mass (Gallup, 2009). A technique was developed where treated waste water from local communities was carefully injected into the reservoir. This has increased steam production at the reservoir and prevented the decline of The Geysers field.

3. Geochemical Theory: Minerals and Water

3.1 Equilibria and the Solubility of Minerals

Any form of equilibria in water can be described by the law of mass action which states that for a generalized reaction type $aA + bB \leftrightarrow cC + dD$, the distribution at equilibrium of the species at the left and right side of the reaction is given by:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K is the equilibrium constant while the bracketed quantities signify effective concentration or activity. Important is that the law of mass action is only valid for the activity of ions, which is the measured total concentration corrected for the effects of electrostatic shielding and for the presence of aqueous complexes (Appelo, 2005). This law applies to any type of reaction including mineral dissolution, dissolution of gas in water, formation of complexes between dissolved species, among others. For mineral dissolution the activity of a solid phase is taken as 1, which means the equilibrium constant is left as $K = [C]^c [D]^d$. An example is the dissolution of gypsum: $CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$ where the solubility product $K_{Gypsum} = [Ca^{2+}][SO_4^{2-}] = 10^{-4.60}$ at 25°C (Appelo, 2005). A logarithmic plot can show the equilibrium condition between gypsum and the solution, denoted as a straight line. Plots for fluid analysis below the line indicate under saturation and fluid analysis plots above the line indicate supersaturation.

The activity coefficients for solutes is calculated via the Debye-Hückel theory where the ionic strength I is calculated. This is the number of electrical charges in the solution and is given by:

$$I = 1/2 \sum (m_i / m_i^0 \cdot z_i^2) \equiv 1/2 \sum m_i \cdot z_i^2$$

Where z_i is the charge number of ion i , and m_i is the molality of i . The ionic strength of freshwater is less than 0.02 whereas the ionic strength of seawater is approximately 0.7 (Appelo, 2005). Highly saline fluids can reach much higher ionic strengths above 1. Activity coefficients at an ionic strength greater than 0.1, something that can apply to dominantly-chloride solutions, has been derived by Parkhurst (1990) as:

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + Ba_i} + b_i I$$

Where A and B are temperature dependent coefficients, a_i and b_i are ion-specific fit parameters (for example in Na^+ $a_i = 4 \times 10^{-10} m$). At 25°C $A = 0.5085$ and $B = 0.3285 \times 10^{-10} m$. The variation in A and B is quite small for most groundwater temperature ranges. It is found that solubility of minerals increases with ionic strength roughly up to 0.7 while in more saline solutions, the solubility decreases again as activity coefficients increase (Appelo, 2005).

Ions in aqueous solutions can attach to one another as ion pairs or aqueous complexes and include major cation complexes (like CaSO_4^0) as well as heavy metal/metal complexes (like PbOH^+ or CuC_2O_4). Complexation and activity coefficients lower the 'free' ion activity in the water hence increasing the mineral's solubility. In Na^+ and Cl^- the effect of complexation is small while activity coefficients makes the ultimate activity 30-40% lower than total concentration (Appelo, 2005). Once the activities of free ions in solution are calculated it becomes possible to calculate the state of saturation of a fluid with respect to certain minerals. This can be done by comparing the solubility product K with the analogue product of the activities derived from fluid analysis, also called the Ion Activity Product (IAP). The ratio between K and IAP can help determine the saturation state: $\Omega = IAP/K$. When $\Omega=1$ there is equilibrium; $\Omega>1$ there is supersaturation; $\Omega<1$ there is subsaturation. A logarithmic scale can be used if there are large deviations from equilibrium which gives the saturation index (SI) such that: $SI = \log(IAP/K)$. SI is analogous to Ω in that it can be in equilibrium (SI=1) or not.

3.2 Equilibria Thermodynamics

Calculation of the mass action constant should take temperature into account and for the general reaction $aA + bB \leftrightarrow cC + dD$ a corresponding thermodynamic equation can be given as:

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

ΔG_r is the change in Gibbs free energy of the reaction, ΔG_r^0 is the standard Gibbs free energy of the reaction (specified standard state at 25°C and 1 atm), the bracket quantities [i] is the activity of i , R is the gas constant (8.314×10^{-3} kJ/mol/deg) and T is the absolute temperature. The direction in which the reaction proceeds is dictated by ΔG_r , so if $\Delta G_r > 0$ the reaction proceeds to the left; if $\Delta G_r = 0$ the reaction is at equilibrium; and if $\Delta G_r < 0$ the reaction proceeds to the right (Appelo, 2005). So at equilibrium, the thermodynamic eq. is reduced to:

$$\Delta G_r^0 = -RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Since the activity product (last term) is equal to the mass action constant K then $\Delta G_r^0 = -RT \ln K$. Substituting this back into the original thermodynamic equation gives:

$$\Delta G_r = -RT \ln K + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Using tabulated data for standard Gibbs free energy, the mass action constants for any reaction can be calculated including for dissolved minerals and gases, although it is usually specified at conditions of 25°C and 1 atm. These standard conditions do not always apply to reservoir fluid where temperatures are higher and also prone to fluctuations. Mass action constants vary with temperature and the Van 't Hoff equation calculates this:

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

Where ΔH_r is the reaction enthalpy; heat gained or lost by the system (ΔH_r is exothermic if negative, and endothermic if positive). This equation demonstrates that K increases with temperature for positive ΔH_r^0 and K decreases with temperature for negative ΔH_r^0 , where ΔH_r^0 is at a standard state analogous to ΔG_r^0 . Integrating the Van 't Hoff equation gives an equation for two temperature ranges, which is generally applicable for groundwater environments:

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H_r^0}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

3.3 Pressure on Chemical Reactions

Pressure changes usually do not have a significant effect on the solubility of liquids and solids, however it does affect gasses; increasing pressures lead to an increase in solubility. Changes in pressure also affect chemical reactions and ultimately it has an impact on the equilibrium constant for different minerals. For example in anhydrite at a pressure of 500 atm, the solubility will increase anhydrite by 1.7 than if it was at 1 atm, i.e. it is 2.8 times higher at 500 atm than at 1 atm (Apello in 'Hydrochemistry'). The effect of pressure on solubility can be understood by first looking at the Gibbs free energy of a reaction where:

$$d\Delta G_r = -\Delta S_r dT + \Delta V_r dP$$

Where ΔS_r is the entropy change of the reaction, ΔV_r is the volume change of the reaction, T is the temperature and P is the pressure. The pressure dependence of this equation is:

$$\partial \Delta G_r / \partial P = \Delta V_r$$

In view of this, the logarithm of the equilibrium constant $\log K = -\Delta G_r / 2.3RT$ will change with pressure as follows:

$$\log K_P = \log K_{P=1} - \frac{\Delta V_r (P - 1)}{2.303RT}$$

Pressure effects on hydrogeochemical reactions are often explicitly account for in hydrothermal systems, and always depend on the molar volumes of the solute species (Apello et al., 2013).

3.4 Solid Solutions

Section 3.1 and 3.2 presumes the minerals as pure phases, however mineral analysis shows a variable composition and thus is considered as solid solutions of end-member minerals. Carbonates extensively form solid solutions and examples include elements that replace Ca^{2+} in calcite such as magnesium, magnetite, iron and cadmium. Other relevant solid solutions that form are Mn^{2+} in siderite and Sr^{2+} in aragonite. The main difference in solid solutions is the activity for a pure solid phase is not taken as one, and so is not omitted from the mass action expression. Instead the solid phase activity is related to the mole fraction such that $[Mineral] = \gamma_{min} \cdot x_{min}$, where γ is the activity coefficient that corrects for non-ideal behavior and x is the mole fraction. Furthermore, the solid solutions in equilibrium with the aqueous solution have to be defined by two mass action equations: one for each mineral.

3.5 Kinetics of Geochemical Processes

Mineral concentration in a fluid during dissolution is followed as a function of time. Initially the mineral concentration will increase sharply with time but eventually the rate of increase drops until equilibrium between mineral and water is reached. At this point (saturation) the mineral is independent of time and instead is determined by the equilibrium constraint. For the most part this explains the stable water chemistry found in reservoir water. However some minerals, such as silicates, are thermodynamically unstable at surface levels since they are strongly subsaturated in waters, yet still persist to form scales. The reaction of a mineral can be followed by looking at its concentration as a function of time. The reaction rate is expressed in terms of the change in concentration of any of the reacting components with respect to time. For a reaction $A + 2B \rightarrow 3C$ we get

$$rate = dc_C/dt = -3dc_A/dt = -\frac{3}{2}dc_B/dt$$

The reaction rate is heavily influenced by temperature and the Arrhenius equation describes how the rate constant (k) changes with temperature:

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right)$$

Where A is the pre-exponential factor and E_a is the activation energy. By taking the logarithm of the above equation, and plotting $\log k$ vs. $1/T$ the slope of the resulting straight line can be found. This can then be re-written as:

$$\frac{d \log k}{dT} = \frac{-E_a}{2.303 RT^2}$$

This final equation takes the same form as the Van 't Hoff equation that was earlier described to relate the temperature dependency of equilibrium constants to the reaction enthalpy.

3.6 Hydrolysis and Redox Reactions

A redox (oxidation-reduction) reaction is a type of chemical reaction involving the transfer of electrons between two species. This reaction occurs when the oxidation number of an ion, or molecule, changes by losing or gaining an electron. This is an important component to corrosion in geothermal systems. Redox reactions are composed of two parts, an oxidized part and a reduced part, both of which always occur simultaneously. The oxidized part loses an electron (thus increasing the oxidation number) while the reduced part gains an electron (thus reducing the oxidation number). Ions or molecules that accept electrons are known as oxidizing agents, while the species that donate electrons are known as reducing agents. Hydrolysis is a reaction that involves the breaking of bonds in a molecule through water. This reaction causes changes in pH of a fluid and occurs between an ion and water molecules. The three main types of hydrolysis: acid hydrolysis, base hydrolysis, and salt hydrolysis. The two applicable reactions in geothermal systems are acid and base hydrolysis as water can act as either a base or an acid. Sometimes salt hydrolysis plays a role, depending if the geothermal fluid is brine or not.

4. Corrosion and Scaling

Corrosion is a natural process through which metals in their manufactured or refined states return to their natural, more stable oxidation states. This natural process is known as a redox reaction where the metal becomes oxidized due to exposure to oxygen. Three things are required for corrosion to occur: metal, oxygen, an electrolyte. Scaling, or sometimes known as precipitation fouling, is the action by which there is crystallization of solid salts and (hydro)oxides from solutions, usually that of water or brines. Scaling depends on three physical conditions: temperature, pressure, and pH. These affect the minerals in solution which then lead to scaling. Though pressure does not directly influence mineral solubility, it instead affects the gas solubility, which consequently affects the pH and then the mineral solubility. Corrosion and scaling can occur in the production wells, heat exchangers, boilers, and injection wells.

Water has a large influence in the corrosion processes and in the formation of scales. The water's chemical characteristics will influence the stability of water as well as affect the extent of corrosion and scaling processes. The main factors that influence both corrosion and scaling are water hardness, alkalinity, and pH, while oxidizing agents (such as carbon dioxide and dissolved solids) influences corrosion only. The three factors (hardness, alkalinity, and pH) determine if the water produces scale, corrosion or stability. Water that has a more corrosive nature is indicated by low pH, soft (and non-carbonate) hardness and a low alkalinity. Water that is more scale forming in nature tends to have a high pH, hard (with carbonates) hardness, and a high alkalinity. Low pH, i.e. more acidic, waters have a lot of H^+ ions present which react with the electrons at the cathode, thus enhancing corrosion. Alkalinity measures how easily the pH of water can be changed (Figure 9). Hence water with a high alkalinity is more scale forming even with relatively low pH values, while low alkalinity waters are not able to buffer against acids, thus are more corrosive.

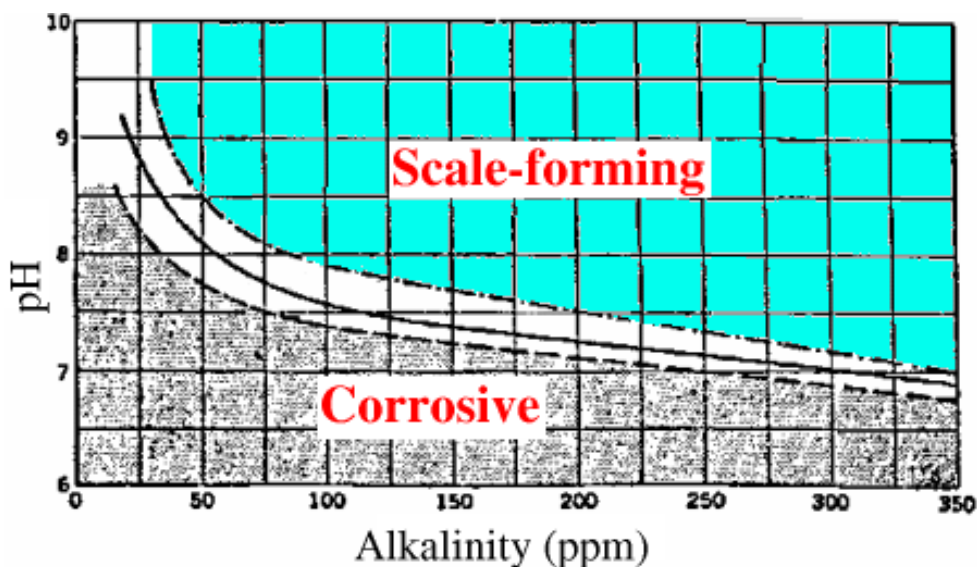


Figure 9: Known as the Baylis Curve which shows the relationship between pH, alkalinity, and water stability. The scale forming water is above the line while the corrosive water is below the line. The white area shows stable water. Source: Ocampo, 2005

Other secondary chemical factors in water can affect corrosion and scaling such as carbon dioxide and total dissolved solids (TDS). Carbon dioxide is the main gas affected by pressure change. During the production of water from the reservoir, the pressures are significantly reduced as it reaches the surface. This pressure reduction causes the solubility of gas to decline and consequently lead to degassing as the gas comes out of solution. In turn this increases the pH and lowers the solubility of many scale forming minerals. Carbon dioxide also leads to corrosion as the gas can combine with water to form carbonic acid (though this can reduce scaling) which leads to a low pH and more acidic conditions. The total dissolved solids shows what ions are in the water, and if there number of ions is great then scaling is more likely. Furthermore, the greater number of ions will increase the electrical conductivity of the water thus increasing the rate of corrosion. Other factors influencing corrosion is temperature (also affects scaling) and flow velocity. Both temperature and flow velocity have a complex effect on corrosion. Temperature has a mixed effect on scaling depending on whether it is a low or high temperature. High temperatures can slow corrosion but is more likely to cause uniform corrosion. Both high and low flow rates increase certain types of corrosion while a moderate flow is the least damaging.

It is important to understand the compositions and parameters of geothermal fluid as it can help with knowing whether scaling or corrosion is going to happen. Multiple mechanisms of corrosion and scaling is promoted by geothermal fluid (hydrogen chloride, hydrogen sulphide, iron sulphide, sulphuric acid, carbonates, silicas, and metal sulphates)

4.1 Types of Corrosion and Scale

Corrosion and scale can be classed into distinct groups to make identification of such occurrences easier. Corrosion comes in numerous forms and is usually classed by the causes of the chemical deterioration of the affected metal. The classifications of corrosion are:

- **General Attack Corrosion:** This is uniform corrosion and is by far the most common form of corrosion in geothermal systems. It is caused by a (electro)chemical reaction resulting in the deterioration of the metal's exposed surface. Eventually, the exposed metal will deteriorate to the point of failure. Though this type of corrosion accounts for the largest amount of metal destruction by corrosion as a whole, it is nevertheless easy to predict, manage and prevent.
- **Localized Corrosion:** This type of corrosion attacks specific areas in the metal structure and there are three types of localized corrosion. *Pitting:* This results when a small cavity forms in a metal due to depassivation of a small area. The small area becomes anodic while the rest of the metal becomes cathodic, thus leading to a localized galvanic reaction. As this small area deteriorates, the metal is penetrated which eventually leads to failure. This is a difficult form of corrosion to detect as it occurs on a very small area and may be covered by scales. *Crevice corrosion:* This also occurs at a specific location, but is associated with a stagnant micro-environment (SOURCE). This occurs due to acidic conditions or when there is oxygen depletion. *Fili-form corrosion:* This occurs in metals that are painted or covered with an outer layer. The water breaches the outer coating and corrosion consequently occurs beneath it. This is quite difficult to notice and eventually leads to structural weakness.

- **Galvanic Corrosion:** This occurs with the presence of two different metals in an electrolyte environment. One of the metals acts as an anode and the other as a cathode to form a galvanic couple between the two metals. The anode metal corrodes at a much faster rate than it normally would alone, and the cathode corrodes at a much slower rate than it normally would alone. Galvanic corrosion only occurs with two electrochemically dissimilar metals that are in electrical contact, and they have to be exposed to an electrolyte.
- **Environmental cracking:** This is a process of corrosion that occurs due to a combination of environmental conditions that affect the metal. These include temperature, stress-related, and chemical conditions. The types of corrosion that result from these environmental conditions are: stress corrosion cracking, hydrogen-induced cracking, corrosion fatigue, and liquid-metal embrittlement.
- **Flow Assisted Corrosion (FAC):** Also known as flow-accelerated corrosion, this occurs when an oxide layer of a metal that acts as a protective layer is removed by water which exposes the underlying metal. This exposed area is then attacked by corrosion. Three kinds of FAC exist: Impingement, erosion-assisted corrosion and cavitations.
- **Inter-granular corrosion:** This is when the grain boundaries of a metal are subject to an (electro)chemical attack. The grain boundaries tend to have higher impurities than the bulk metal and therefore the grain boundaries are more susceptible to corrosion.
- **De-alloying:** Known as selective leaching, this form of selective corrosion attacks a specific element in an alloy.
- **Fretting Corrosion:** This happens with repeated wearing and vibration on an uneven or rough surface. The corrosion leads to grooves and pits on the metal's surface. Though found in impact or rotation machinery, and in bearings, it can also be found on surfaces exposed to vibration from machinery or during the transport of fluid.
- **High-Temperature Corrosion:** Fuels, used in heat pumps or other machinery, contain sulphates or vanadium which form compounds with a low-melting point. These compounds in turn are extremely corrosive to metals that may otherwise be resistant to corrosion (such as stainless steel).

There are a number of minerals that can lead to scaling in a geothermal system, but all can be classed into a few major groups. Based on literature and information from practice a number of specific scales will be looked at; all of which will represent the most common scales found in the geothermal industry both in the Netherlands and around the world. Though pyrite occurs commonly in the industry, this will be excluded as it forms due to the aging of iron sulphide. The four main groupings of scales are:

- **Carbonates:** Includes calcite, dolomite, siderite, and strontianite
- **Silica and other siliceous materials:** Includes quartz, gibbsite, and amorphous silica
- **Sulphates:** Includes anhydrite, barite, gypsum, and celestite
- **Sulphides:** Includes all the metal sulphides such as iron sulphide and sodium sulphide

The scales that will be looked at in this paper are as follows:

- i. Calcite (CaCO_3): **Colour** - usually white but also colourless, gray, red, green, blue, yellow, brown, orange; **Streak** – white; **Lustre** - vitreous; **Diaphaneity** - transparent to translucent; **Cleavage** - perfect, rhombohedra, three directions; **Mohs Hardness** – 3;

- Specific Gravity** - 2.7; **Diagnostic Properties** - rhombohedra cleavage, powdered form fizzes weakly in dilute HCl, curved crystal faces and frequent twinning; **Crystal System** – hexagonal; **Uses** - a low hardness abrasive, acid neutralization, heated for the production of lime, soil conditioner (Anthony et al., 2003).
- ii. Dolomite [$\text{CaMg}(\text{CO}_3)_2$]: **Colour** - colourless, white, pink, green, gray, brown, black; **Streak** – white; **Lustre** - vitreous, pearly; **Diaphaneity** - transparent to translucent; **Cleavage** - perfect, rhombohedra, three directions; **Mohs Hardness** – 3.5 to 4; **Specific Gravity** - 2.8 to 2.9; **Diagnostic Properties** - rhombohedra cleavage, powdered form effervesces weakly in dilute HCl, hardness; **Crystal System** – hexagonal; **Uses** - construction aggregate, cement manufacture, natural oil and gas reservoir, agricultural soil treatments, a source of magnesia for the chemical industry (Anthony et al., 2003).
 - iii. Siderite (FeCO_3): **Colour** – yellowish, reddish, greyish, brown; **Streak** – white; **Lustre** – vitreous; **Diaphaneity** - transparent to translucent; **Cleavage** – perfect; **Mohs Hardness** – 3.5 to 4.5; **Specific Gravity** - 3.8 to 4; **Diagnostic Properties** - colour, specific gravity, dissolves in HCl; **Crystal System** – hexagonal; **Uses** - iron ore, pigments (Anthony et al., 2003).
 - iv. Strontianite (SrCO_3): **Colour** – Colourless, white, gray, light yellow, green or brown; **Streak** – white; **Lustre** – vitreous, resinous on breaks, greasy; **Diaphaneity** - transparent to translucent; **Cleavage** – nearly perfect; **Mohs Hardness** – 3.5; **Specific Gravity** - 3.74 to 3.78; **Crystal System** – Orthorhombic; **Uses** – important for the extraction of strontium (Anthony et al., 2003).
 - v. Quartz (SiO_2): **Colour** – virtually every colour. Common colours are clear, white, gray, purple, yellow, brown, black, pink, green, red; **Streak** – colourless (harder than the streak plate); **Lustre** – vitreous, resinous on breaks, greasy; **Diaphaneity** - transparent to translucent; **Cleavage** – none, typically breaks with a conchoidal fracture; **Mohs Hardness** – 7; **Specific Gravity** - 2.6 to 2.7; **Diagnostic Properties** - conchoidal fracture, glassy lustre, hardness; **Crystal System** – hexagonal; **Uses** – glass making, abrasive, hydraulic fracturing, gemstones (Anthony et al., 2003).
 - vi. Gibbsite [$\text{Al}(\text{OH})_3$]: **Colour** – Bluish, Green, Green white, Gray, Gray white; **Streak** – white; **Lustre** – vitreous, pearly; **Diaphaneity** - translucent to transparent; **Cleavage** – perfect; **Mohs Hardness** – 7; **Specific Gravity** - 2.5 to 3; **Diagnostic Properties** – tough, earthy, hardness; **Crystal System** – monoclinic prismatic; **Uses** – Important ore in aluminium (Anthony et al., 2003).
 - vii. Anhydrite (CaSO_4): **Colour** - colourless, white, and light shades of brown, red, gray, pink, blue, violet; **Streak** – white; **Lustre** – vitreous to pearly; **Diaphaneity** - transparent to translucent; **Cleavage** - Perfect cleavage in three directions to form cubic-shaped cleavage fragments; **Mohs Hardness** – 3 to 3.5; **Specific Gravity** - 2.9 to 3; **Diagnostic Properties** - cubic cleavage, harder than gypsum, higher specific gravity than calcite, no acid reaction; **Crystal System** – orthorhombic (Anthony et al., 2003).

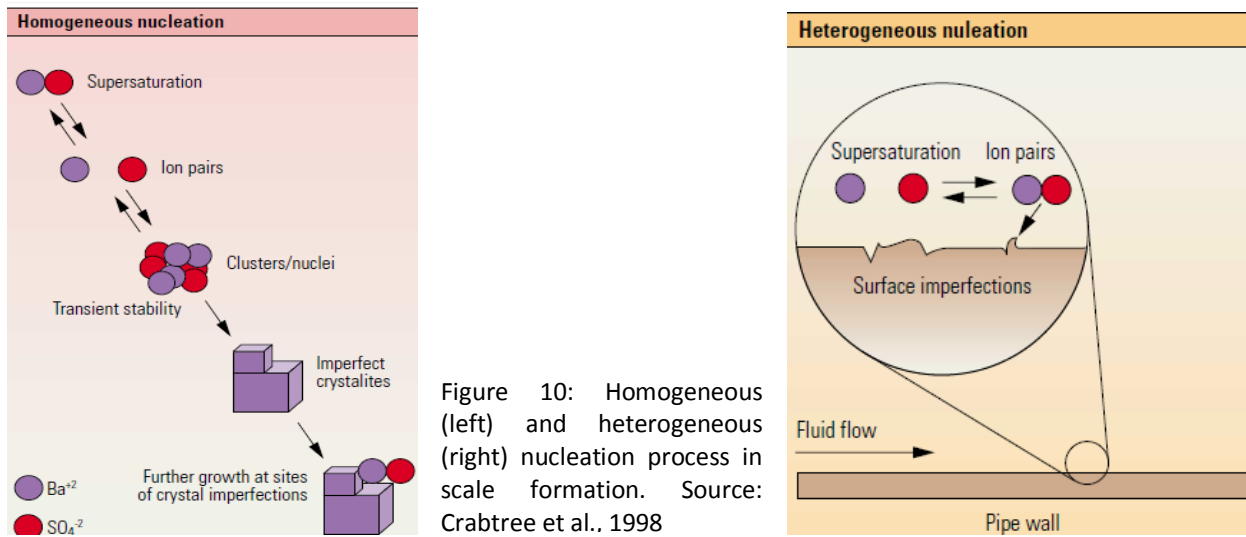
- viii. Barite (BaSO_4): **Colour** - colourless, white, light blue, light yellow, light red, light green; **Streak** – white; **Lustre** – vitreous to pearly; **Diaphaneity** - transparent to translucent; **Cleavage** - very good, basal, prismatic; **Mohs Hardness** – 2.5 to 3.5; **Specific Gravity** - 4.5; **Diagnostic Properties** - high specific gravity, three cleavage directions at right angles; **Crystal System** – orthorhombic; **Uses** - drilling mud; high density filler for paper, rubber, plastics (Anthony et al., 2003).
- ix. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): **Colour** - clear, colourless, white, gray, yellow, red, brown; **Streak** – white; **Lustre** – vitreous, silky, sugary; **Diaphaneity** - transparent to translucent; **Cleavage** - perfect; **Mohs Hardness** – 2; **Specific Gravity** - 2.3; **Diagnostic Properties** - cleavage, specific gravity, low hardness; **Crystal System** – monoclinic; **Uses** – Used in dry wall manufacturing, plaster, joint compound. An agricultural soil treatment (Anthony et al., 2003).
- x. Celestite (SrSO_4): **Colour** - Colourless, white, pale blue, pink, pale green, pale brown, black; **Streak** – white; **Lustre** – Vitreous, pearly on cleavages; **Diaphaneity** - transparent to translucent; **Cleavage** – perfect, good; **Mohs Hardness** – 3 - 3.5; **Specific Gravity** - 3.95 - 3.97; **Diagnostic Properties** – Brittle, three cleavages; **Crystal System** – orthorhombic; **Uses** – Used in fireworks and metal alloys (Anthony et al., 2003).

An important component in scaling is the possibility of radioactive scales forming; known as naturally occurring radioactive material (NORM). Barite is one scale that can be radioactive and results due to its uptake of radium. Fluids with high concentrations of barium and sulphate have the potential to form barite scales if the right conditions exist. Due to the chemical nature of barite, it can form a solid solution by substituting Ba^{2+} with alkali cations. One of the ions that barium can substitute with is radium (both have similar charge and ionic radius). The main cause for concern here is that radium can be inhaled and is linked to numerous health issues such as bone cancer and tumours.

4.2 Formation of Scale

It is known that scales tend to form by precipitation in solutions that have reached oversaturation, the driving forces of which are temperature, pressure and pH change. However, it is important to realize that waters that have reached oversaturation, and are scale prone, do not always produce scales. For a scale to actually form it must grow from solution (Crabtree et al., 1998). This means that a saturated fluid must first form unstable clusters of atoms through a process called homogenous nucleation [Figure 10]. When the chemical (ion concentration) equilibrium is disturbed, the atom clusters form tiny seed crystals in these now supersaturated solutions. Subsequently the seed crystals grow ions by adsorbing onto the crystal surface imperfections, hence enlarging the crystal size. A reduction in the surface free energy of the crystal, which rapidly decreases with increasing radius (once past the critical radius), drives the energy required for seed crystal growth. In this sense large crystals will favour continual crystal growth and small seed crystals may re-dissolve (Crabtree et al., 1998). So if there is a large enough degree of supersaturation, the formation of seed crystal, which acts like a catalyst, will help with scale-deposit growth. Crystal growth is usually initiated on a pre-existing fluid-boundary surface; a process known

as heterogeneous nucleation [Figure 10]. The sites for heterogeneous nucleation include pipe surface roughness, defects or perforations as well as joints and seams.



4.3 Rate of Scale Formation

The rate at which scales form is described as the induction time (t_{ind}); this is after a supersaturated condition exists and before the scales begin to appear (Frenier & Ziauddin, 2008). If the induction time is less than the residence time of the fluid during the supersaturated condition, then it can be assumed that no scales will form within the system. Induction time models itself are not able to predict when scale build up starts to affect operations, but they models do provide a good starting point. The induction time can be expressed in terms of the primary nucleation rate J (assuming that the nucleation time $>$ time required for growth of crystal to reach a detectable size):

$$t_{ind} = \frac{1}{J},$$

where the primary nucleation rate is given by: $J = A \exp \left[-\phi\beta \frac{\gamma^3 v^2}{(k_B T)^3 (\ln S)^2} \right]$

A is the frequency factor, ϕ is the energy barrier factor, β is the shape factor, γ is a crystal surface energy, v is the molecular volume of the crystalline phase, k_B is the Boltzmann const., T is temp., and S is the supersaturation ratio. Combining the two above equations:

$$\ln t_{ind} = \phi\beta \frac{\gamma^3 v^2}{(k_B T)^3 (\ln S)^2} + \frac{1}{A}$$

This can be applied to the nucleation mechanism. A plot of $(\ln S)^{-2}$ against $\ln(t_{ind})$ will give a slope which changes in gradient hence showing the transition from homogeneous nucleation to heterogeneous nucleation. Furthermore, the surface energy can be calculated by taking the slope values.

An equation that calculates the change in solute concentration, either due to mineral dissolution or precipitation, can also be used to further understand the rate of scaling. This

would apply after the point of oversaturation when scales are beginning to form. A change in solute concentration is given by:

$$R = k \frac{A_0}{V} \left(\frac{m}{m_0} \right)^n g(C)$$

R is the overall reaction rate (mol/L/s). k is the specific rate (mol/m²/s), V is the volume of solution (m³), A_0 is the initial surface area of the solid (m²), m is the moles of a solid at a given time, and m_0 is the initial moles of the solid. $g(C)$ is a function that conciliates the effects of the solution composition on the rate, like the pH, distance from equilibrium and effects of inhibition (Appelo and Postma, 2005). The factor $(m/m_0)^n$ as a whole accounts for the changes in reactive surface sites during precipitation.

4.4 Interrelation between Scaling and Corrosion

Composition of the geothermal fluid plus the operational parameters of the well determine the scaling and corrosion characteristics for given geothermal waters (Stáhl, 2000). In this respect scaling and corrosion as interlinked processes cannot be treated on a separate basis. Though scaling can reduce efficiency of a geothermal system, it can influence corrosion and therefore it is important to look at their interrelation. One type of scaling that occurs is a direct result of a corrosion product that forms when a metal surface is exposed to geothermal fluids. Scaling in this instance is linked to the degradation of construction materials. A specific example of this is when the action of dissolved H₂S and CO₂ leads to continuous, quasi linear corrosion of well surfaces in slightly acidic, saline environments. This leads to the formation of iron sulphide particles which are removed from the casing wall and deposited along surfaces where corrosion is not present. In geothermal brines numerous key species that contribute to corrosion have been indentified: oxygen, hydrogen sulphide, sulphate, carbon dioxide, chloride, ammonia and hydrogen ions (Mundhenk, 2013). Of these carbon dioxide and chloride are commonly found as part of the composition in geothermal fluid/brines. Carbon dioxide, a mild acid that increases corrosion rates, is a common by-product in geothermal operations that deal with water and gas. Carbon dioxide primarily affects the pH by the fact that it dissolves in aqueous solutions to form carbonic acid. Chloride is another element commonly found in geothermal brines of varying salinity as it is the main anion in such fluids. Chloride is well known for destabilizing oxide films on passivated metals as well as promoting pitting. Passive films, like metal oxides, act as a thin layer of protection for the metal against corrosion, but chloride promotes local breakdown of these films (via other corrosive agents) and therefore corrosion is concentrated in these areas (Mundhenk, 2013). This so called pitting is induced by the formation of metal chlorides on the film-metal interface which leads to expansive stresses and hence rupturing of the oxide film.

On the other hand it is possible that in CO₂ dominated environments the brine-material interaction has a beneficial effect. The newly formed corrosion products act as protective scales by depositing along surfaces where it then acts as a corrosion inhibitor. One slightly water soluble mineral that is predominantly found in geothermal pipes is siderite which is an iron carbonate. The carbon is thought to originate from the high carbon dioxide partial pressure while the iron comes from two sources: (1) it is present as ferrous iron in the formation brine/water; (2) it is released when there is corrosion of an iron-based material

(Mundhenk, 2013). In general iron carbonates that precipitate can slow down the process of corrosion by covering a portion of the steel surface (thus acting as an inhibitor), and/or by presenting a diffusion barrier for the species involved in the corrosion process (Nešić, 2007). As the steel surface corrodes under the scale (scale undermining), voids are created which are filled up by the ongoing precipitation. It is such that if the rate of precipitation at the steel surface exceeds the rate of corrosion, then thin but dense protective scales will form (Nešić, 2007). Contrastingly, if the rate of corrosion at the steel surface exceeds the rate of precipitation (when the scale is undermined faster than the voids are filled), a thick but porous and non-protective scale will form (Nešić, 2007). Figure 11 shows an example of iron carbonate scale formation as an inhibitor of corrosion.

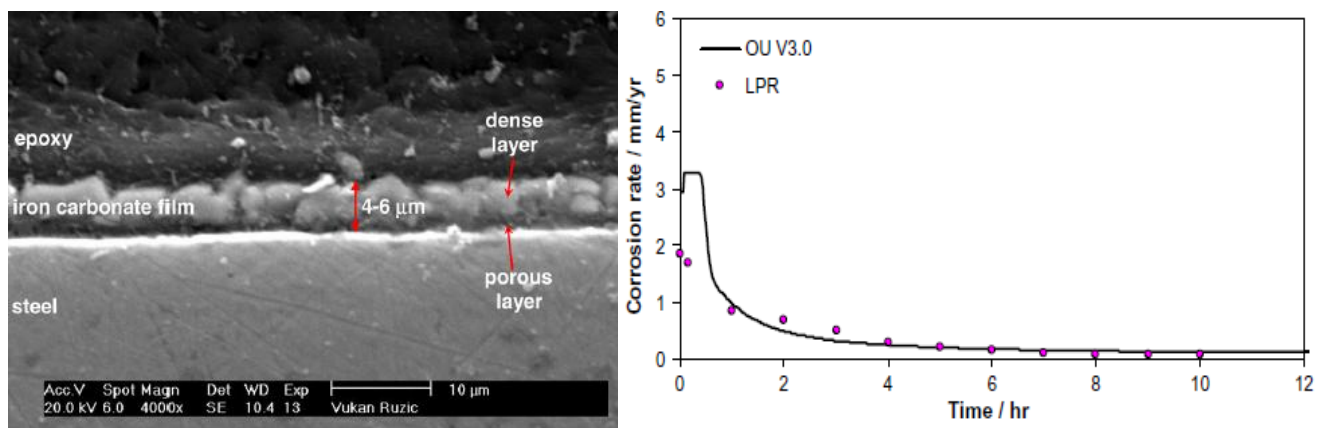


Figure 11: The left picture shows an example of protective scale on the surface of a steel specimen exposed for 10h at $T = 80^{\circ}\text{C}$, $\text{pH} = 6.6$, $P_{\text{CO}_2} = 0.54 \text{ bar}$, $c_{\text{Fe}^{2+}} = 250 \text{ ppm}$, $v = 1 \text{ m/s}$. The graph (right) shows the corrosion rate history, the lines indicates the predicted outcome while the points are experiment measurements. High supersaturation (thus high precipitation rates) reduced the corrosion rate rapidly Source: Nešić, 2007

A number of factors affect iron carbonate scale formation, the most important being water chemistry. For precipitation to occur there must be supersaturation of the iron carbonate in the solution, something that is dependent on temperature. At room temperature precipitation rates are low even if there is a high degree of supersaturation and so there is no protective scaling; at high temperatures (i.e. $>60^{\circ}\text{C}$) precipitation rates are fast enough, even with a low degree of supersaturation, for protective scales to form. Accelerated rates of precipitation make it quicker for the solution to attain thermodynamic equilibrium.

4.5 Effect of pH, CO_2 Partial Pressure & Temperature

pH strongly influences corrosion but its most important effect is an indirect one, related to how pH changes conditions for iron carbonate scale formation. High pH leads to a decreased solubility of iron carbonate and an increased precipitation rate plus a higher scaling tendency (Nešić, 2007). The higher pH also means higher supersaturation with the formation of more protective scales which is reflected by a rapid decrease of the corrosion rate with time (Nešić, 2007). One other (less important) indirect effect of pH is that it can lead to the formation of other types of scale. Generally speaking, in CO_2 -bearing environments the corrosion rate can be accelerated by increasing the CO_2 partial pressure (P_{CO_2}). The widely accepted explanation is that along with P_{CO_2} the concentration of H_2CO_3 increases which accelerates the cathodic reaction and ultimately speeds up the corrosion rate (Nešić, 2007). P_{CO_2} increase can be beneficial if other conditions are favourable for iron carbonate scale formation. For example at a high pH, a higher P_{CO_2} leads to an increase in (bi)carbonate ion

concentration and to a higher supersaturation thus accelerating precipitation and scale formation (Nešić, 2007). Temperature is one variable known to increase all the (electro)chemical processes involved with corrosion. This is true in the case of low pH where iron carbonate precipitation and protective scaling does not occur; but for high pH the solubility of iron carbonate is exceeded and therefore temperature accelerates the kinetics of precipitation and protective scaling (Nešić, 2007).

4.6 Ca^{2+} and Mg^{2+} in Scaling

Ca^{2+} and Mg^{2+} play a central role in geothermal systems that use galvanized steel pipes as a transport medium for water as a source of heat energy. However, it is not limited to galvanized steel pipe systems. Nevertheless, the effects of the Ca^{2+} and Mg^{2+} scaling ions on both the scaling and corrosion processes should be investigated. A study in 2010 by Kun-hu Wu et al., did this to learn more on how the lifetime of the galvanized steel pipes could be prolonged. These types of pipes are usually made from zinc and within a day of being exposed to geothermal fluid containing Ca^{2+} and Mg^{2+} , scales are already forming into either crystalline needles or spherical structures (Figure 12).

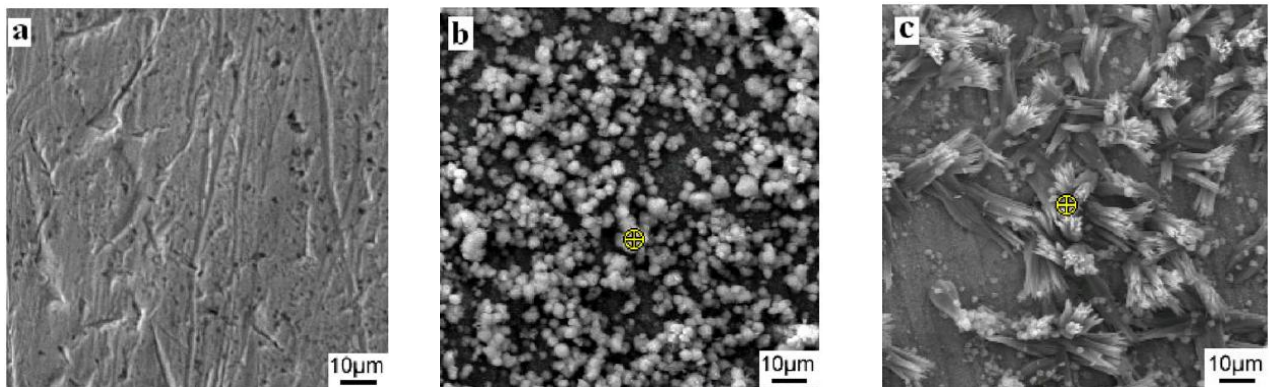


Figure 12: SEM micrographs of galvanized steel pipes before (a) and after 12h of immersion (b)(c). Needle and spherical structures can be seen on the surface in (b) and (c) after being exposed to Ca^{2+} and Mg^{2+} . Source: Wu et al.

By performing the experiment again using geothermal fluid without Ca^{2+} and Mg^{2+} ions, it becomes easier to know which structures can be attributed to each product of the processes. The study found that the needle structures were linked with corrosion products while the spherical structures were linked to scaling products. This showed that the mineralization degree of geothermal water was high; the ions Ca^{2+} , Mg^{2+} and CO_3 being to form clusters of an assortment of sizes after passing the stage of supersaturation. This cluster, or embryo, can increase in size until it reach the critical size whereby its energy state is at its maximum. If the embryo grows above the critical size it will lead to dissipation in energy so that scale nucleation can be accommodated. The nuclei will then grow and develop into either needles or spherulites. To begin with, the Zn^{2+} and OH^- generated by corrosion will dislodge the Ca^{2+} causing it to diffuse to other regions (Wu, 2010). The Zn^{2+} and OH^- then reach supersaturation causing corrosion products to form and eventually be deposited on the pipe surfaces. Meanwhile the Ca^{2+} is prevented from forming scales along the corroded surface. Instead the Ca^{2+} and CO_2^{3-} that were dislodged actually end up diffusing to the non-corroded regions thus forming scales there. Contrastingly, it is possible for the Zn^{2+} and OH^- to also diffuse to the non-corroded regions thus giving rise to corrosion products there. In turn, the corrosion products are added to the initially formed scale upon the non-corroded region leading to a combination of needle and spherical structures. It

turned out that the formation of corrosion products further inhibited the corrosion of galvanized steel pipe and so the concentration of Zn^{2+} and OH^- within the corroded region increased slowly (Wu, 2010). In some instances the scales would diffuse to back to the corroded region which gave rise to scale within corrosion products. Overall the scale that had diffused to the non-corroded regions seemed to have provided a protective layer to the steel pipe as it prevented simultaneous corrosion.

4.7 Calcite in Scaling and Corrosion

Calcite is the most stable polymorph of calcium carbonate and frequently encountered as scale in geothermal systems. Reservoir water composition is characterized by the macro-elements of the reservoir rocks to which it is exposed to, hence the presence of calcium and carbonates. These elements present in the water are influenced by several parameters: (1) Equilibrium gas-pressure of CO_2 (2) equilibrium temperature (3) activity of other ions that are present in solution and (4) residence time of the ions (Stáhl, 2000). In a research project by Stáhl et al., an experiment was carried out to investigate the solubility of calcium carbonate and how the processes of scaling and corrosion are influenced. A simplified simulated geothermal solution was used; solubility values were determined by looking at the CO_2 pressure, temperature and residence time. The least soluble component in the water is looked at from the point of view of scaling, whereby the influence of various factors (temperature, pH, flow rate, dissolved CO_2 , dissolved salt content) on the solubility, scaling and corrosion processes of $CaCO_3$ were studied. It was found that with increasing values of equilibrium CO_2 pressure, specific conductivity increases as a function of saturation (Stáhl et al., 2000). The specific conductivity is proportional to the dissolved CO_2 concentration, and at a certain pressure, the solution is saturated with respect to CO_2 . Small degree of calcite scaling was seen in all five materials tested: copper, carbon-steel, stainless steel, zinc-plated iron and PVC. An equation for the corrosion rate, or V_L , is given by:

$$V_L (s^{-1}m) = 8.76 \frac{\Delta m (kg)}{tA\rho (sm^2 \frac{kg}{m^3})}$$

The change in mass (Δm) is divided by the time for change (t) multiplied with the density (ρ) and surface area (A). The experiment concluded that equilibrium solubility depended on: quality of the calcium carbonate mineral plus replacement of the charge (since corrosion products that dissolved on the surface would influencing the dissolving process); residence times of at least 360 minutes (depending on temperature and pressure); suitable sampling conditions by preserving dissolved minerals (calcium) before analysis.

5. GEOTHERMAL SYSTEMS IN NL

5.1 A Developing Energy Resource

The Dutch geothermal industry is relatively young especially when compared to countries such as the United States, Iceland and New Zealand. One reason for this stems from the fact that the Netherlands has historically been an oil and gas producing country for decades, which most of its energy uses, as well as their exports, have utilized. It was therefore unnecessary to use renewable energy for a long time. This has begun to change due to the depleting hydrocarbon reserves and the push for a sustainable and environmentally conscious future. In fact in late June of 2015, a judicial body has ordered the Dutch government to do more for preventing climate change. The Hague District Court ruled in favour of individual Dutch citizens who had filed a suit against the Dutch government. This means that by 2020 the Dutch emissions have to be 25% lower than the emission during 1990. In the period 1975-1985 there were a number of early initiatives for implementing deep geothermal systems, i.e. great than 1500m in depth, but they were all unsuccessful and were consequently discarded (Heekeren et al., 2010). The main reason for this was the competition against fossil fuels which were at lower prices and already established within the country. At that time energy from geothermal resources would not have reached parity. However, during the late 1980's a rising demand for cold simulated geothermal applications, hot/cold storage in buildings, changed this trend (Heekeren et al., 2010). Though they were shallow geothermal systems, they nonetheless are feasible due to the suitable sedimentary geology of the Netherlands. Around this time there was also an increase in the use of GSHP for individual residential buildings. The growth in these two geothermal systems has led to an established solid base of geothermal systems that uses direct heat. Deeper geothermal systems are now starting to catch on around the Netherlands, but only provide direct heat.

Although geothermal energy is relatively new it continues to go through a learning curve as industry experience builds up. A few problems remain, some of which apply to all geothermal systems around the world. One of the main problems is that many of the implementations came during the early stages/beginning phase of the geothermal industry where experience was limited due to the gaining of familiarity in this area. However, this was necessary as early action is always required; the early stages of decision forming on energy supply steps must be made to keep the option of a sustainable alternative open (Heekeren et al., 2010). Another factor which also explains the late start in this sector, was that geothermal projects are relatively complex in the sense that a variety of disciplines are needed for successful implementation (Heekeren et al., 2010). Generally, it is easier and quicker to install fossil-energy-based systems and even other renewable energy systems such as solar and wind. The last major problem arises from geothermal energy exploitation which is the formation of corrosion and scale (discussed in the next section) in the working parts of the geothermal plant such as the wells, heat exchanger, and near-wellbore matrix.

One major advantage for developing geothermal systems in the Netherlands is the fact that there is already extensive infrastructure in place from the oil and gas industry (over 5000 in place around the country). Furthermore some of these reservoirs are suitable for exploiting geothermal energy. Since geothermal techniques, technology, and expertise are similar in nature to that of the oil and gas industry this makes implementation of geothermal systems easier at present. Lastly, costs of geothermal projects are drastically lowered (and are only 'additional costs') in places where there is already natural gas infrastructure installed. On the

other hand there has been a lack of knowledge transfer from the oil and gas industry in subsurface expertise as well as incomplete advice from contractors, and an emphasis on low costs (Degens et al., 2012). In non-geological areas there is also a lack of knowledge on the organizational and technical risks. A study on a number of geothermal projects revealed that there was well production and injection problems due to wellbore damage present in some of those operations (Degens et al., 2012). A quick solution to these problems would be to improve data gathering methods, procedures, and records so that it can be combed over and compared with country-wide operations. Moreover, complete understanding of the subsurface geological conditions (mineralogy, fluid composition, and chemical equilibrium) should be shared publicly. This recently has been supported by a government policy which states all drilling and seismic data become public information after a period of five years (Heekeren et al., 2010).

As for the total potential of (deep) geothermal energy in the Netherlands, there is an estimated 90,000 petajoules (PJ) Heat In Place (HIP) (Heekeren et al., 2010). The global annual energy consumption is 500,000 pJ. The potential for geothermal energy exploitation is huge in the Netherlands, even with current technology. Furthermore, these estimates do not take into account possible energy at deeper layers. Many of the important aquifers/reservoirs would be located in the Permian, Lower Triassic Lower Cretaceous sandstones and in two Tertiary sand units, which have already been targeted by the fossil fuel industry (Heekeren et al., 2010). Improvements in deep formation subsurface analysis is required, as this would better allow us to understand the geological risks (aquifer permeability and scale/corrosion) associated with such operations. It is also important to note that such developments depend on fossil fuel prices and government policies. Lastly, the need for uniform pressure of surface installations is great; good quality systems have pressures at 10 bars while lower standard pressures are at 5 bar.

5.2 Dutch Geothermal Platform and DAGO

The Platform Geothermal Energy is a Non-Governmental Organization (NGO), i.e. non-profit organization, which consists of approximately 80 participants who share an interest in the development of Geothermal Energy in The Netherlands. Members include government organizations (including provinces, regions and municipalities), research institutes, and a variety of private companies. In turn, the private companies consist of those who specialize in technical, financial, and organizational skills, as well as energy companies and owners of geothermal installations/plants (both licence holders and applicants). The platform serves as a springboard for the growing number of applications for geothermal operation licences. The Dutch Geothermal Platform is a member of the European Geothermal Energy Council (EGEC) and is affiliated with the International Geothermal Association (IGA). The EGEC promotes geothermal energy research and development across Europe as it understands the need/importance for Europe's energy mix both now and in the future. Furthermore they set policies related to renewable energy such as the 2020 renewable targets. The IGA provides information on geothermal energy use around the world and organizes world conferences related to geothermal activities.

The Dutch Association of Geothermal Operators (DAGO) is a newly formed group/union that consists of all people or groups operating any geothermal system or plant around the country. As a newly formed association, since the summer of 2014, it is still in the beginning phase and getting samples or data from these geothermal sites is difficult. However, there is

a very positive influence from DAGO when it comes to dealing with geothermal limitations. Operators are being urged by DAGO to provide us with relevant data and information about their projects. This will help with understanding how geothermal operations are being carried out country-wide, as well as providing relevant information on operations. If the data can be shared, then dealing with any problems becomes easier to counter or manage. Furthermore, the sharing of data is essential as studies indicate that by studying a lot of data, or by attempts for modelling this data, or by talking to experts, much is learned. Many of the operators themselves would want a report that includes results from related studies of exploitation (corrosion and scaling) and operating problems on top of the models created in this report. Hence this report, with literature studies included, will be useful for associations similar to DAGO or for anyone working in the geothermal energy sector.

5.3 Localities

There are already a number of basic heat pump systems in place in the Netherlands; however there are a number of major projects either ongoing or completed. There are about 13 major projects spread over the Netherlands, most of the localities are based in the South Holland province. A number of permits are soon to be handed out for new projects, while the number of applications for new geothermal projects has been on the rise. The initial projects are listed:

Mijnwaterproject: The Minewater project is designed to obtain renewable energy from the water of the old coal mine (Oranje Nassau III) for heating and cooling buildings. The five wells provide the energy supply needed for residential and commercial buildings. The water is extracted from the abandoned mines of the coal mine. This project was the first geothermal exploration license that was granted under the new Mining Act. Lastly, it is an innovative project in the sense that the low temperature heating and cooling is not confined to a single building, but is used in an area with various functions (housing, school, shops, offices, and healthcare centres) via a heat distribution network.

Van den Bosh 1, 2, 3, & 4: The project was to create a sustainable heat source for a greenhouse complex of 7.2 hectares for the cultivation of tomatoes. The drilling work was completed in the summer of 2007. The depth of the source is approximately 1.6 km, and the temperature is 60 degrees Celsius. The initial flow rate was 160 m³/hour, but a new pump has increased this to 200m³/hour. The numbers represent the individual wells, and a second doublet was added at a slightly deeper depth (1.8km) at 65 degrees Celsius.

Ammerlaan: The exploration license covers an area of 61 km² in the municipalities of Delft and Pijnacker-Nootdorp, and is the fourth geothermal project in the Netherlands. Interestingly, in this installation, provides heat for banks, hydroponic greenhouses, and a nearby swimming pool.. The flow rate, on the basis of borehole tests, is approximately 100m³/hour with a temperature of about 65⁰C, at a depth of 2km. Final productivity figures will be available if the pump is installed, the source is flushed and a steady state is reached in a longer run.

Duijvestijn: Drilling began in July 2010 to a depth of approximately 2km in the formation (the water is extracted from the Delft- and Rijswijk Sands) where there is a flow rate of 130 m³/hour at an expected temperature of 68⁰C. The first hole came with a few problems; due to high porosity and loss of drilling fluid at approximately 900 meters, the pit wall collapsed

during drilling and therefore there had to be a new side borehole at 450 m depth. These problems were avoided at the second borehole with the use of a drilling fluid.

Aardwarmte Den Haag: The first phase of this project will heat approximately 4,000 homes using geothermal energy. Drilling reached a depth of 2.2km with the expected flow and temperature conditions (150 m³/hour and 75⁰C) having been reached. There is also the occurrence of some natural gas (approximately 1 kg of gas per 1,000 kilos of water) processing equipment for this purpose has been invested in.

Koekoekspolder: This project is an initiative of any cooperating greenhouses, the municipality of Kampen and the province of Overijssel. The final depth was reached at the first hole at 1.95km. The test was positive with a result of 73 ⁰C and 140 m³ per hour. In late August was the 2nd well done reaching a final depth of 1924 meters but the temperature was slightly higher than expected (75 ⁰C). After operations ceased in 2013 due to some technical problems, production started again in 2014.

Greenwell Westland: The natural gas savings of this project is approximately 5.8 million m³ per year which corresponds to savings of 10,300 tons of CO² per year. The target formation is at 2.9km and is the deepest drilled project. This Pijnacker Sandstone is located under the Delft and Rijswijk sands, which are tapped by neighboring geothermal projects. The first 1km will be drilled vertically and then deviated so that the underground distance between producer and injector is approximately 1,500 to 1,600 meters. The wellheads are on the ground and the installation design at this stage to take account of possible catches of small amounts of natural gas.

Agriport A7 1 t/m 4: Construction of the rig in the greenhouse began on April 2013 with a plan for four wells. The goal is to make two doublets each rated at approximately 10MWth. In early August 2013 the test results from the first well showed the water at a temperature of 90.5 degrees Celsius. Also, the capacity looks good; there will be 200 cubic meters per hour up from the Slochteren at a depth of 2.5 km.

De Lier 1 & 2: This project is the second geothermal source in the Westland area and the project is supported by the 'Westland Agenda'. The drilling depth is approximately 2.6km. It is expected to eventually be able to produce some 250 m³ of water per hour, with a temperature of approximately 85 degrees Celsius.

Vierpolders (Brielle): This project is a geothermal project in development. The substrate in this greenhouse area is particularly suitable for the application of deep geothermal heat. At 2.2km in depth, there is a porous layer of sand with water of about 80-85 degrees. The heat source lies at this depth; the formation is highly permeable and a throughput is expected at 390 m³ per hour

Floricultura Heemskerk: This project provides energy for a horticulture area. The temperature of the water is approximately 94⁰C. Geology analysis showed more complications than was predicted during geological and seismological investigations. The second test remained well behind in capacity. The borehole is directed to the Slochteren formation at a depth of approximately 2.7 to 2.9 kilometres.

5.4 Sub-Surface Conditions in the Netherlands

Understanding the sub-surface conditions, such as the reservoir mineralogy, fluid compositions and temperature distribution, is important when planning to use or exploit geothermal energy. Figure 13 shows the onshore temperature distribution of the subsurface in the Netherlands. Table 15 shows the sand and sandstone aquifers most suitable for geothermal energy exploitation as well as their location and potential heat in place. Generally the onshore subsurface temperature varies from 60°C to 100°C at 2000m in depth all of which can be used for direct heating purposes. The majority of the onshore Netherlands subsurface shows that the prevailing temperature is between 70°C and 80°C. Generally sandstones are reservoirs with the most heat potential due to its properties.

The reservoir fluids found in the geothermal plants tend to be saturated with minerals because of the regular water-rock reactions that occur from constant contact with one another. Over time the water and rock reach chemical equilibrium as there is near stable conditions in the reservoir. The fluid can have meteoric or sea-water influences, however the latter is not common locally. Most geothermal fluids are saline with inorganic dissolved salts the most common of which is sodium chloride such as halite.

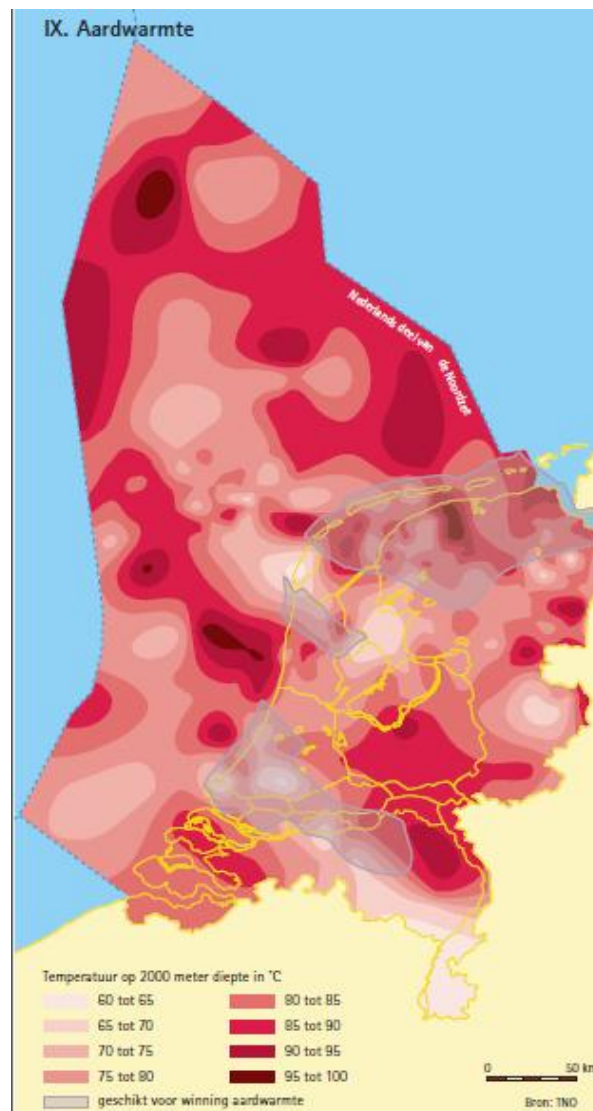


Figure 13: Subsurface temperature distribution in the Netherlands both offshore and onshore (source: TNO, 2009)

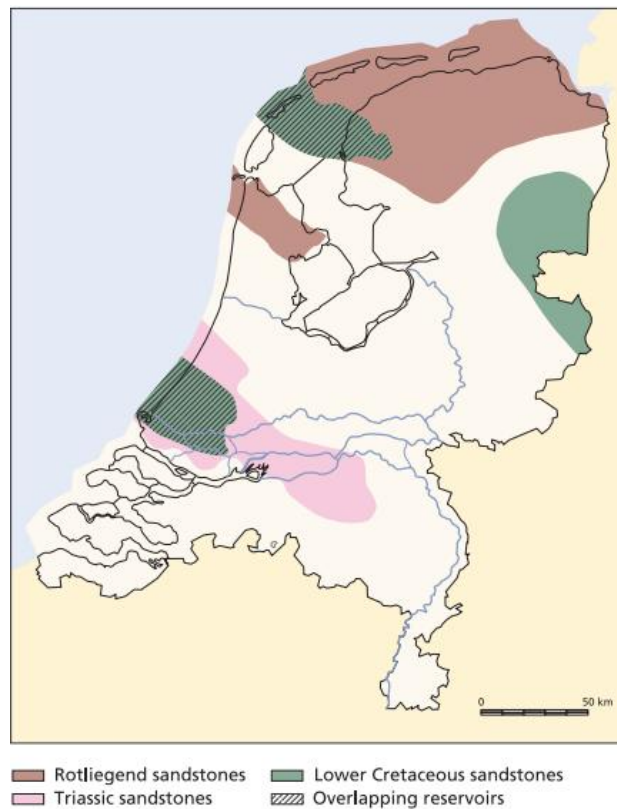


Figure 14: Distribution of deeper aquifers which are potentially most suitable for the extraction of geothermal energy. Localized potential occurrences are not indicated. Neither are Tertiary aquifers which are present under much of the Netherlands (Lokhorst & Wong, 2007).

Aquifer	Depth (m)	Gross sand thickness (m)	Porosity (%)	Perm. (mD)	Temp. (°C)	HIP (10 ¹⁸ J)
Permian, Rotliegend sandstones						
Groningen, Friesland, Drenthe & Noord-Holland	2000–4500	10–200	11–25	30–600	Max. > 100	50
Lower Triassic sandstones						
West Netherlands Basin & Roer Valley Graben (Zuid-Holland & Noord-Brabant)	2000–4000	25–300	Variable	Variable	Max. > 100	30
Lower Saxony Basin (locally)	2000–3500	Max. 80	Variable	Variable	Max. > 100	3
Other areas	300–> 5000	0–50	Variable	Variable	Max. > 100	4
Lower Cretaceous sandstones						
West Netherlands Basin (Zuid-Holland)	700–2500	Max. 250	15–30	Max. 3000	Max. 90	3
Lower Saxony Basin (especially SE Drenthe)	800–1800	3–65	15–20	220–500	40–80	0.4
NW Friesland	1800–2100	10–200	15–22	1–30	70–80	
Tertiary sands						
Brussels Sand Mbr	100–1150	0–135		Max. 600	15–45	
Breda Fm	< 835	Variable	30–35	50–> 200		
Total HIP						> 90.4

Figure 15: Reservoir parameters and Heat In Place (HIP) for aquifers in sandstone and sand in the onshore Netherlands (Lokhorst & Wong, 2007).

5.5 Lead Formation in Doublets

A number of problems affect geothermal systems in the Netherlands: corrosion (section 4), scaling (section 4), and lead formation. These are problems commonly found in the geothermal industry in general and it is important to mention the current state of lead in the Dutch geothermal industry. There are two effects of lead deposition: scaling and clogging, and NORM contamination (^{236}Pb). This type of scale is known as galena which is a metallic element caused by galvanic corrosion and exchange reactions. A study motivated by operational problems (lead deposition) led to an investigation on the electrochemical reactions between the formation water and the metal parts of geothermal installations. The study focuses on the Slochteren formation and the overlying Kupferschiefer formation. The processes studied take into account important formation water characteristics such as temperature, pH, and composition; a total of four electrochemical reactions have been pinpointed.

The first looks at corrosion of steel casings by carbon dioxide. Carbon dioxide in solution forms a weak acid which decreases the pH; therefore at the steel interface, an anodic reaction was found to take place where iron atoms are oxidized to form cations. A cathodic reaction takes place meanwhile as the protons are reduced. The carbonate and bicarbonate anions react with ferrous iron which produces an iron bicarbonate film. This carbonate film can under ideal circumstance be able to prevent the iron below for further oxidation and thus stop the corrosion process (Bressers & Wilschut, 2014). An indicator for corrosion of the steel by CO_2 is indicated by hydrogen gas evolution. The CO_2 corrosion was focused in injection well operations where there is a higher CO_2 concentration. For these types of systems it is often observed that the initial high corrosion rate decreases in time due to the formation of the passivating iron carbonate layer (Bressers & Wilschut, 2014). This iron carbonate layer is essentially a form of scale. The second electrochemical reaction looks at lead deposition due to exchange reactions. The redox potential of lead reduction is greater than the redox potential for iron in the range of 0 to 100°C . This means from a thermodynamic viewpoint that lead ions are able to oxidize metallic iron (an exchange reaction). Lead deposits have been observed with thicknesses of 10mm or more, on steel casings in Dutch natural gas systems (Bressers & Wilschut, 2014). If the lead deposits come into contact with air they can convert to secondary lead minerals.

The third reaction is galvanic element formation, where two metals are used in well casings. The two metals are in independent equilibrium with the electrolyte, and the equilibrium potential will depend on the material itself plus the interaction with the electrochemical active species in the electrolyte (Bressers & Wilschut, 2014). Both metals will polarize away from their individual equilibrium potentials which is known as galvanic element formation (one metal becomes more anodic and the other metal becomes more cathodic. This polarization will lead to electrochemical reactions where the metal/electrolyte interfaces are involved. The last electrochemical reaction is lead deposition due to the galvanic element formation. A high lead ion concentration in the Slochteren formation increases the likelihood that Pb^{2+} is reduced on the negatively polarized metal (out of the two metals). Metallic lead is then deposited on the metal while the positively polarized metal corrodes. This means that scales form on one metal when corrosion occurs on the other. After an initial deposition of lead through the exchange reaction further deposition could be taken over by the galvanic element formation (Bressers & Wilschut, 2014).

6. Economics

Generating power from geothermal energy requires no fuel except for the pumps (but that can use energy from a sustainable source), and therefore geothermal power is immune to fluctuations in fuel costs. Nevertheless, capital costs are significant with drilling accounting for over half the costs. Another factor which adds to the costs is the significant risks that are entailed from deep resource exploration. For example a typical well doublet, which includes the production and injection wells, supports 4.5 megawatts (MW) and costs approximately \$10 million. In such cases the failure rate is 20%, which adds up to be a significant cost if there is no production to make up for those initial costs (Geothermal Economics, 2009). Overall, electrical plant construction and well drilling cost about €2–5 million per MW of electrical capacity, while the break–even price is €0.04–€0.10 per kW·h (Bertani, 2007). On the other hand EGS have higher overall costs; its capital costs are over €3.6 million per MW and break–even above €0.05 per kW·h (Bertani, 2007). In the Netherlands there are many direct heating applications, as opposed to electricity generation plants, and so the use of shallow wells with lower temperatures is much more common. These smaller systems will lead to lower costs and least amount of geological risk. Geothermal heat pumps for residential areas with a capacity of 10 kilowatt (kW) are routinely installed for around €0.9–2,700 per kilowatt (Bertani, 2007). If demand is geographically dense, then district heating systems can benefit from economies of scale, but usually piping installation are the most significant capital costs. One benefit of direct heat geothermal systems is that they have lower maintenance costs per kW·h than electric generating plants. However, direct heating systems still need electricity to run compressors and pumps. Though governments may subsidize costs, it would be beneficial if this was implemented thoroughly. The costs of geothermal power varies depending on the scale it is being used, so geothermal costs in rural villages will be substantially lower than in large urban areas. It is possible for costs to be amplified in the early stages of geothermal energy development, where projects are sometimes cancelled. Projects moving forward from the exploration and exploratory drilling often trade equity for financing (Bertani, 2007).

Though most of the costs are incurred during the beginning phase the production stage still lead to additional costs but are much lower. All of the costs during the production can be broken down into two areas: maintenance and investments. Maintenance costs are usually minor and deal with things such as equipment required for renewal of mechanical or physical components, insurance, chemical consumables, contingencies, and monitoring expenses. Investment costs are much higher as they include chemical precursors (to aid in prevention of corrosion and scaling), chemical injection equipment, monitoring equipment (such as recording/measuring devices, probes and sampling ports), engineering fees, consultation fees, and well/pipe rehabilitation. Sometimes it is necessary for the plant to slow down or shut production during maintenance and rehabilitation which adds to the costs.

One important aspect during production is the occurrence of corrosion and the formation of scaling. Formation of scale has a negative impact on the efficiency of a geothermal system as a whole. As mentioned in earlier, it can be seen that a number of areas within the geothermal system including production and injection well oil/gas separator and the heat exchanger itself are affected negatively through scaling, albeit in different proportions. Performance is reduced significantly over time, and that heat exchangers become less

efficient over time. In turn significant cleaning operations are required if carried out too late, or continuous cleaning operations are necessary if carried out immediately when production begins. It is important to clean carefully so that there is no internal damage. It is possible for energy production to be hampered due to heat exchangers losing efficiency in heat transfer, caused by excessive pressure drop (due to presence of scales), until a point is reached where maintaining flow is nearly impossible. Consequently an emergency shutdown is required hence creating a lack of productivity and a decrease in heat supply, which is undesirable in the energy industry. In fact, at the onset of scaling, the pressure needed to drive the fluid through the heat exchanger has to be increased over time to keep nominal efficiency constant. Ultimately this will degrade the quality of the associated mechanical components as well as decrease life expectancy of joints.

Extra costs come from chemical injections or other preventive methods something that is vital for future production as it slows the onset of developing scales. Continuous monitoring of the situation is required hereafter to see if prevention methods are effective. It might even be beneficial to realize the problem of scaling at the design and development stage so that adequate steps are taken to ensure the problem is controlled. Ideally, the idea is to find some sort of balance between the cost of prevention methods, and how well it works or how long it will be effective. This would mean checking to see whether the maintenance & investment cost due to scaling is cheaper with the treatment methods than it is without the treatment methods. Though initial costs will be higher, in the long run spread over the operational lifetime of the geothermal plant, the correct treatment methods could reduce the maintenance/investment frequency. One of the main problems with corrosion and scaling is that losses are induced from less efficient water flow and heat production per volume of time. Even if the plant is not shut down, production is below nominal values as is heat available per unit cost. For corrosion, measures are required to be taken into account during the designing stage as the right materials have to be selected to minimize corrosion. Once corrosion has occurred it is much more costly and difficult to deal with it as it means the production wells have to be shut down. Corrosion events of geothermal equipment require occasional replacement of failed materials and components. Corrosive dissolved gases and salty brines tend to corrode steel equipment in the reservoir system.

In some cases there is a formation of radioactive scales due to the decay of uranium. This requires extra precautions, regulations and disposal thus adding to overall costs. As there are strict government regulations and environmental procedures in dealing with NORM, they must be followed closely. Workers in clean-up and disposal operations must be trained correctly, which adds to training costs that may not otherwise have been needed. One benefit of drilling into areas with slight radioactive concentrations is the steeper temperature gradient. This is because radioactive elements such as thorium and uranium (found in granite at 10ppm) release radioactive heat through decay which raises the rock temperature. This means one can drill at a shallow depth and reduce drilling costs.

7. Actions For Corrosion and Scaling

A number of precautions can be taken when dealing with corrosion and scaling. If these problems have already occurred then a diagnosis (identifying and evaluating) is required to identify the exact nature of the problem, and how best to tackle it. The easiest way of identifying problems related to production is noting a decrease in the flow rate and a drop in overall pressure relative to the initial/nominal flow and pressure rates. Periodic well testing and monitoring can usually provide such information. More expensive options are possible such as using ultrasonic or multi-finger calipers to give logging data. Following the diagnosis it is then necessary to use the best methods that can minimize or prevent the same problem from occurring in the future. This would require monitoring to make sure the methods of prevention and inhibition are effective in its task.

7.1 Removal and Disposal

A number of geothermal plants use steam or turbine washing techniques to remove scales and as a consequence extend the time periods between cleaning and maintenance. Steam washing consists of injecting water upstream of steam scrubbers as a counter-current to steam flow while turbine washing is a procedure to gently hydro-blast deposits off all the turbine blades. Washing techniques do present new challenges as the right waters and chemicals are required so that sensitive equipment is not damaged. Oxygen in solution for example can augment corrosion rates along surfaces. Technically this provides a temporary solution to scaling, but extra steps are required to first understand then prevent scale formation in the first place. Dealing with NORM is slightly more complicated as health and safety guidelines must be adhered to. There have been two methods for dealing with NORM as experienced in the oil and gas industry: brine pits and burn pits. The brine pits consist of water or brine that contains NORM-sludge while the burn pits store the non-hazardous materials which are later burned (USEPA, 2012). Another method of disposal is through recycling; where equipment containing NORM is cleaned, sent to the recycling facility, and recycled. These facilities are equipped with filters to help stop radioactive emissions into the atmosphere (USEPA, 2012). Removing corrosion is a lot more complicated as this entails to loss of material in the inner casings of wells and pipes. In most cases this means the inner casings themselves have to be removed, or the production and injection well pipes have to be renovated or changed. If the material or inner casings have been changed then this usually is disposed of by sending it to recycling facilities (assuming there is no NORM).

7.2 Prevention and Inhibition

There are many ways of preventing or inhibiting the formation of scales and the process of corrosion in geothermal systems. Though it may not prevent these problems 100%, it can slow the processes of scale and corrosion formation and therefore increase the time in between periodic cleaning of the systems. One common practice in the industry is to oversize the diameter of the water flow circuit so as to compensate for the formation of scales. Another is to install inner casings that are easily removable to deal with corrosion problems. Table 1 shows an overview of the different ways in dealing with scale formation. There are a number of methods being used in geothermal plants around the world when dealing with scale formation. These methods include chemical inhibitors, ion exchange, pH equilibration (brine acidification or acid dosing), mechanical methods, and magnetic treatment (ongoing research).

Option	Mechanism	Reported effectiveness
Ion exchange softening	Removes scale forming calcium species	100% scale control
Acid dosing	Changes calcium carbonate solubility	100% scale control, although corrosion issues
Chemical inhibitors	Block growth sites stopping crystal formation	Up to 100% achievable but dependent on chemical type, water quality and dose
Metal ions	Block growth sites or react with carbonate	80% reduction
Magnetic conditioners	None agreed	80% reduction
Electronic conditioners	Preferential formation of particles in bulk	40% reduction
Electrolytic	Release inhibitory metal ions in to solution	30% reduction
Ultrasound	Local pH changes induce precipitation	65% reduction
Surface modification	Produce lower fouling surface	90% achievable

Table 1: Summary of both chemical and non-chemical (calcium carbonate) treatment options and how effective they are. Source: MacAdam and Parsons, 2004.

Chemical Inhibitors

Chemical inhibitors are by far the most common method but must meet certain criteria to be of use. The chemicals must be activated before the scaling process begins, i.e. before the fluid is subjected to compositional or physical changes, which usually means injecting the chemical inhibitors at the bottom of the production well (just above the reservoir). This is carried out by specialized injection lines such as the auxiliary injection tubing (AIT) shown in Figure 16. Additionally, the inhibiting agent has to not only suppress crystal germination (by blocking nucleation sites); it also has to make sure it provides a protection casing against corrosion.

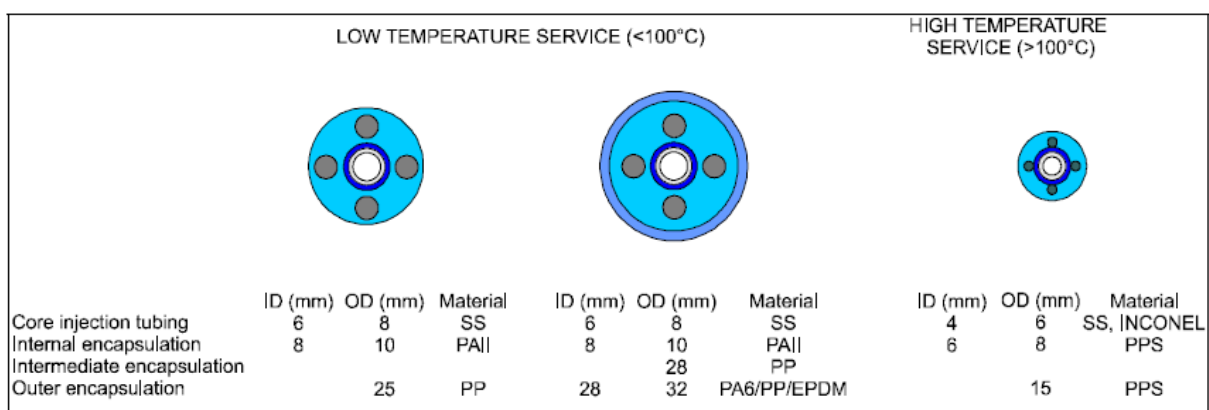


Figure 16: The typical candidate structures of Auxiliary Injection Tubing chemical inhibition lines. Source: Ungemach, 1999

Carbonate scales and calcite in particular are suppressed by using lime slurry inhibitors, phosphoric acids, polymeric carboxylic acid, phosphate with sand, and highly carboxylated polymers. Silica scales can be suppressed or slowed down by phosphonates with polymers, ethylene oxide polymers, hydroxethylcellulose, low molecular weight carboxylic acid, and amines. One major advantage of the chemical inhibitors that suppress silica is that they also help control corrosion. In geothermal systems where silica is dominant these chemicals will work best, but it still does not solve carbonate scaling or sulphate scaling. Polyacrylates are an effective chemical inhibitor used presently to prevent all scales in general, but does not address the problem of corrosion. Phosphonates with sand are one of the few chemical inhibitors that deal with barite and calcium sulphate scales.

Ion Exchange

This method is used for dealing with metal sulphate scaling including the radioactive scales. Ion exchange methods aim to suppress the uptake of radium by introducing a competing ion with a similar chemical nature (in terms of the orthorhombic isomorphous structure, the ionic charge, and the radius). One competing ion used is strontium, so while this may help with preventing radioactive scales, it may also lead to strontium sulphate scales forming. Additionally, it has no effect on corrosion rates. Investigating the performance of barite scaling inhibitors at surface installations is a useful way of determining the optimal adjustment for scale inhibition especially at the heat exchanger. Ideally, the inhibitor has to continue to be effective even as it reaches to the cooling region around the wellbore of the injection well, up until the point where the injection of the fluid is heated up so that saturation of the dissolved barite decreases. Furthermore, the inhibitor may react with the host rock which could potentially lead to secondary mineral formation and thus should be avoided. This means it is important to take into account the presence of fracture zones within the host rock, as the mineralogy between host rock and fracture fillings can differ. Testing the barite scale inhibitor interaction with both the host rock and fracture fillings beforehand will therefore avoid any problems during actual operations.

pH Equilibration

This involves lowering the pH in the brine or geothermal fluid and thus making it more acidic. One of the most common methods is using hydrochloric acid which deals with carbonate, silica and sulphide scaling, but these can increase the speed of corrosion as well as have an impact on the environment. One sustainable method of lowering the pH is using geothermal gases which can be extracted from the condenser in power plants (not applicable in the Netherlands as of yet). The gases tend to be made of carbon dioxide, hydrogen sulphide, nitrogen, and oxygen, and can be mixed with the geothermal fluid to decrease the pH.

Magnetic Treatment

Magnetic treatment of water is one method being looked at in the prevention of scaling, though is not applied on large scales presently. One advantage of this method is that the water composition is not affected by chemicals, unlike the inhibitor injections. This in turn will not aggravate the occurrence of corrosion. The main drawback is the controversy on how efficient these treatment methods are, but well documented laboratory tests have demonstrated that some magnetic devices work well by choosing good working conditions (Gabielli, 2001). All in all, it is widely agreed that magnetic treatments lead to calcium

carbonates particles to form in the bulk of the scaling water, and it cannot precipitate on the inner surfaces of any pipes and equipment. The CaCO_3 particles are carried away by the continuous flow of water as calcareous mud but can be removed after filtering this mud. There are various propositions by authors on how exactly the magnetic water suppresses scale formation. One author credits its effect on the formation of CaCO_3 particles by its suppression of nucleation and its acceleration of crystal growth (Barrett and Parsons, 1998). Another author, via turbidity measurements of the treated water, said that homogenous nucleation had increased giving resultant crystals greater in number with smaller sizes (Wang et al., 1997). Further adding to this suggestion, one author suggested that a magnetic term be involved in the activation energy, as it allows the critical radius of nucleation to be lowered (Ferreux et al., 1993). On a microscopic scale, the magnetic field was shown to have influenced the zeta potential and size distribution of the particles formed in solution (Parsons et al., 1997).

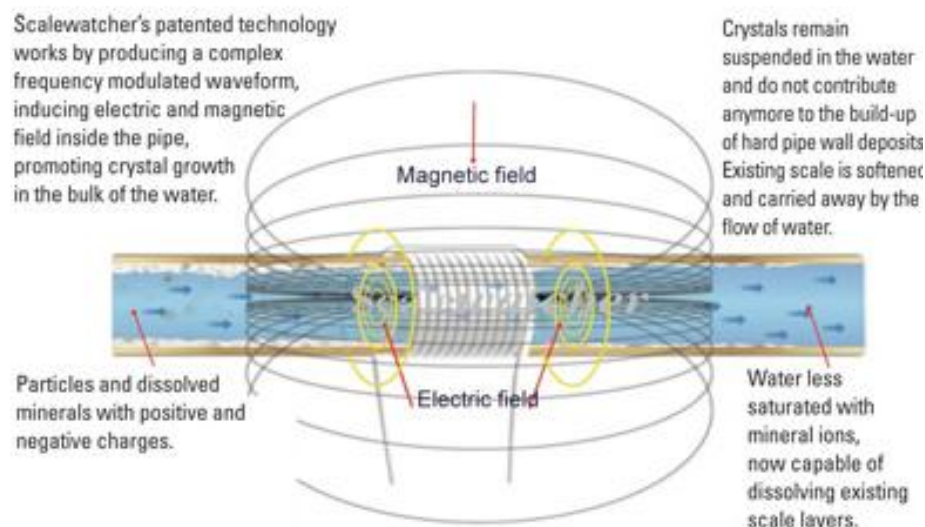


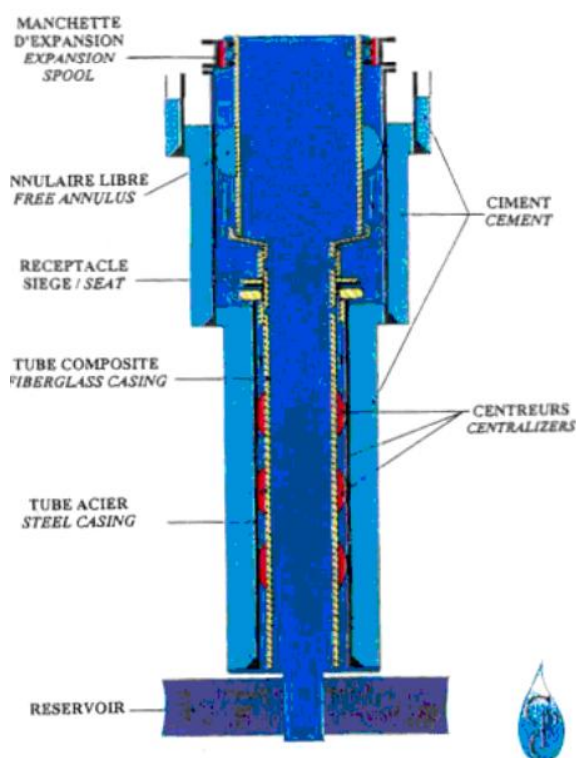
Figure 17: Concept and theory of using magnetic treatment on saline water to prevent scale formation. This specific example of a commercial-scale technology is not necessarily a representative of what is/would be used in geothermal operations. Source: Doelman, 2013

Gabrielli et al., investigated the efficiency of the magnetic water treatment in scale prevention by following both the change of ionic calcium concentration at the output of the magnetic device, and the resulting scaling power of the treated water via an electrochemical test. Scaling water made from salts and pure carbonic water was tested. It was found that in carbonic water with magnetic treatment and carbonic water without magnetic treatment showed fairly similar results, however in water that was magnetically treated, there was a 40% loss of active calcium. It was found that the scaling power of magnetically treated water and non-magnetically treated water did not differ much. The scaling time, which was the time it took for the electrode to be covered by scale, and the mass change, which was the change in mass of the electrode as scale was deposited on it, were recorded. Furthermore, the time delay for nucleation and crystal growth was recorded. In all situations, magnetically treated water did not perform that much better but there was slightly less scale and longer delays in nucleation time. The results indicated that the efficiency of magnetic treatment in independent of the water hardness. Next, the flow velocity's influence on magnetic treatment was tested. It was found that flow velocity did not change/affect the pH at the electrode output but it did reduce the ionic concentration. Though any velocity showed at

least some reduction in ionic concentration, the larger the velocity was the larger percentage of ionic concentration was removed. Inversion of the polarity in the used magnets was looked at, which showed to have a bigger impact in treating the water. For example, if standard magnetic treatment was twice as effective in inhibiting scale as non-magnetically treated water, then magnetic treatment with polarity inversion was thrice as effective in inhibition as non-magnetically treated water (Gabrielli, 2001). The polarity inversion also proved to be better when it came to delaying nucleation time. Lastly, different materials (representing real world examples) were tested to see if they had any influence during magnetic treatment. It was found that some materials did actually reduce the concentration of ion calcium. The effect was more pronounced for conducting materials than it was for insulating materials (Gabrielli, 2001). Overall, magnetic treatment of water does show benefits into reducing the ionic calcium concentration. While the actual power of the water to form scale does not vary much between magnetic treatment and non-magnetic treatment, the scaling time and scale mass is lower for water that has undergone magnetic treatment. Furthermore, the right conditions under which magnetic treatment operates are needed to have a bigger impact on reducing scaling.

Fibreglass Design

One promising technological concept is a design that utilizes a material that is able to reduce corrosion (and scaling), while at the same time is able to keep an optimal heat transfer in addition to overall nominal system efficiency. This design seeks to combine cemented steel casings with fibreglass liners while the annulus is kept free as shown in Figure 18. The outer cemented steel casing provides mechanical strength and well stability while the inner fibreglass casing provides chemical resistance (Ungemach, 2005). This chemical resistance will mean that the inner surfaces will not be affected by pH changes or chemical inhibitors and therefore will not be susceptible to corrosion. Furthermore, the inner surface will not have indentations due to the corrosion and thus remain smooth for longer periods of time. The annular space can be used for the circulation of chemical inhibitors to deal with any scales present in the geothermal system (and adjusted according to type of scale found). Additionally the annular space is used to remove or restore liners that do get damaged.



In other studies it has been shown that casings made of American Petroleum Institute's steel J-55 are dominant, because they are less sensitive to chemical attack, N-80 is considered to be more sensitive (Ocampo et al., 2005). However, the electrochemical corrosion action has damaged casings of API steels J-55, K-55 and N-80 (Ocampo et al., 2005).

Figure 18: Fibre-glass design. Source: Pierce, 2010

Mechanical Removal

A relatively straightforward way of removing scale is doing it physically through mechanical cleaning. A wider array of tools and techniques exist but the ones used depend on the scale encountered. Nevertheless, each method should ensure that the process is non-damaging to the wellbore or pipes. Mechanical approaches have shown to be an alternative and successful way for scale removal, especially if chemical inhibitors fail to prove their effectiveness. An overview of the conventional mechanical methods for removal of scale is shown in Figure 19 below.

Tool	Description	Clean hard bridges	Clean tubular jewelry	Other advantages	Other disadvantages
Mechanical cleaning					
Positive displacement motor and mill	Fluid-powered 'Moineau' motor and mill. Mill removes deposits by grinding.	Yes. Clean rate may be very slow.		Positive surface indication of cleaning Small cuttings make hole cleaning easier	Motor stator and mill are expensive expendables ~300°F [150°C] limit Not compatible with scale dissolvers Mill can damage tubulars
Impact hammer	Fluid powered percussion hammer. High shock forces shatter brittle deposits.	Yes. Clean rate may be very slow.		Positive surface indication of cleaning Simple, robust tool	Large cuttings size makes hole cleaning more difficult Not compatible with scale dissolvers
Chemical cleaning					
Fixed wash tool	Fixed tool with many large-diameter nozzles. Normally used only with chemical dissolvers.		Yes, if deposit is soluble.	Simple, robust tool	Most fluid power lost to circulating friction Low nozzle pressure—cannot remove inert deposits
Spinning-jetting tool	Rotational torque provided by nozzles offset from tool axis. No speed control.		Yes, if deposit is soluble.	Simple tool Complete wellbore coverage by rotating jets	Inefficient jetting due to high rpm (>5000)
Indexed-jetting tool	Nozzle head rotates ~90° when coiled tubing pressure is cycled. Head has many small-diameter nozzles to improve wellbore coverage.		✓		Requires multiple cleaning runs increasing job time and coiled tubing fatigue No surface indication of cleaning Small cleaning radius due to small nozzles
Turbine-powered jetting tool	Fluid turbine rotates nozzle with two nozzles. Eddy current brake controls rpm.		✓	Complete wellbore coverage with large cleaning ratios	Abrasives cannot be pumped through turbine Complex tool
Sonic tools	Used to create high-frequency pressure pulses that remove deposits by shock waves or cavitation.		Yes, if deposit is soluble.	Simple	Hydrostatic pressure suppresses cavitation Tools not effective in removing hard scales in lab tests
Jet Blaster tools					
Scale Blasting technique	Nozzle head rotated by two nozzles offset from tool axis. Viscous brake controls rpm.		✓	Complete wellbore coverage with large cleaning radius Positive surface indication of cleaning	
Bridge Blasting technique	Fluid-powered 'Moineau' motor and jet/mill head. Radial jets follow pilot mill.	✓	✓	Positive surface indication of cleaning	Motor stator is an expensive expendable ~300°F limit

Figure 19: Conventional mechanical scale removal tools and techniques including advantages and disadvantages of each method. Source: Crabtree, 1998

7.3 Predicting Corrosion and Scaling

Using predictive models gives an idea or an estimate on the type of corrosion and scales that will form and where these events are most likely to occur. Consequently it allows one to choose the optimal prevention method that works best in each of the predicted simulations, and it can give an idea on what one can expect in future exploitation operations. Generally it is the chemical make-up of the geothermal fluid that can allow us to predict the sort of problems that we are most likely to encounter. Since corrosion and scaling processes are interactive and complex, there is no single test or determining factor that is an infallible indicator for both these processes. Nevertheless, as mentioned there are various ways in slowing down these processes all of which can be tested in simulations.

Geothermal fluids that are oversaturated or saturated with calcite can lead to moderate corrosion. Overall, the pH value can be used as a basic indicator to know the fluids tendency to cause scaling or corrosion, and how intense the corrosion might be. Geothermal fluids with a pH below 6.5 are very corrosive to steel and less so to alloys. Geothermal fluids with a pH above 7.5 are mildly corrosive but scaling is more likely. Sometimes the scales can protect against corrosion which makes the corrosion rates harder to predict. For corrosion the amount of carbon dioxide, the TDS, the temperature and the flow velocity should be known to even begin any prediction on the corrosion rates. If the carbon dioxide concentration exceeds 20 mg/l, then one can already assume that there is significant localized damage, especially if the well material is made of iron or steel. Creating a redox potential vs. pH diagram (overview of the thermodynamic properties for a system) is a good way to interpreting the corrosive behaviour of geothermal fluids on various metals. These diagrams are constructed using the Nernst equation as well as the solubility data of various metals. Such measurements (redox and pH) can indicate the molecular and ionic forms most likely to be available in the specific fluid being tested. Subsequently, this will reveal whether metal protection or metal dissolution is to be expected. Generally, metals with more negative redox potentials than hydrogen tend to be corroded by acidic solutions. One disadvantage of such diagrams is that they cannot predict the rate of the reaction as these diagrams represent equilibria conditions. Knowledge of the equilibrium conditions that exist in the particular geothermal system in mind should be known before estimating reaction rates.

One way of predicting scales in the field is to use the Langelier saturation index (LSI) equation which is defined as $LSI = pH - pH_s$. The pH_s is the pH of the water if it were perfectly saturated with the mineral being examined. The $pH_s = p[ion] + pAlk + K$, where K is a constant, the $p[ion]$ in mol/L is the negative logarithm of the ion concentration, and the $pAlk$ in equivalents per litre is the negative logarithm of the total alkalinity. The pH can be measured in the field. A value can be calculated for the LSI which consequently shows the process most likely to occur (Table ?). A negative LSI value shows undersaturation of the ion and therefore precipitation into scale is unlikely, while a positive LSI values indicated oversaturation, thus making precipitation likely.

LSI (Carrier)	Indication
-2,0 < -0,5	Serious corrosion
-0,5 < 0	Slightly corrosion but non-scale forming
LSI = 0,0	Balanced but pitting corrosion possible
0,0 < 0,5	Slightly scale forming and corrosive
0,5 < 2	Scale forming but non corrosive

Figure 20: LSI calculation model from Carrier which calculates the corrosion and scaling tendency in any geothermal fluid. Source: Jones, 1988

One important consideration in scale prediction is predicting radioactive scale formation which requires knowledge of the geologic and lithologic distribution for uranium and thorium. Moreover the mechanism of radium transfer into the fluid phase must also be understood. If there are high levels of NORM, then one can assume that there are high local concentrations of thorium and uranium in the reservoir. Another safe assumption is that these NORM levels have transferred into the fluid phase via ordinary geological processes, i.e. throughout the basin's evolution. One geological program used for predicting radioactive scale is SOLMINEQ which looks at temperature and pressure conditions changes from the reservoir to the surface, and then calculates the amount of barite that will form.

Predicting Calcite Scaling

Calcite is the most common scale to appear in geothermal systems due to the large presence of carbonates in fluids. The degree of calcite saturation is very useful in corrosion and scaling studies and thus will be looked at here. The solubility of calcite increases with decreasing temperature, which means that calcite scales don't form with cooling of geothermal fluid. Calcite solubility can be described by the following equation: $CaCO_3(s) = Ca^{++}(Aq) + CO_3^{-}(Aq)$

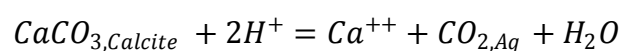
The equilibrium constant is:

$$K_{Calcite} = a_{Ca^{++}} \cdot a_{CO_3^{-}}$$

Chemical species activity and the solubility product for calcite is calculated via the chemical composition:

$$Q_{Calcite} = a_{Ca^{++}} \cdot a_{CO_3^{-}}$$

Calcite can deposit if the solubility product Q is higher than $K_{Calcite}$ for a specified temperature as there is supersaturation. To understand heating of GT water at the stage of saturation, the dissolution of calcite is needed which is given by:



The equilibrium constant for the above equation: $K_{calcite} = a_{Ca^{++}}/a_{H^{+}}^2 \cdot a_{CO_2,aq}$. K for the first dissociation constant (carbonic acid), and for the second dissociation constant are given by: $K_{H_2CO_3} = a_{H^{+}} \cdot a_{HCO_3^{-}}/a_{H_2CO_3}$ and $K_{HCO_3^{-}} = a_{H^{+}} \cdot a_{CO_3^{--}}/a_{HCO_3^{-}}$ respectively. It can be seen that the hydrogen activity H^{+} and therefore the pH affect the calcite equilibria.

7.4 Monitoring

This is an important aspect when dealing with corrosion and scaling as it allows one to check how effective the inhibition and prevention methods are. This means that any prediction theories previously made can be validated or confirmed through monitoring. Continuous monitoring is required to see which processes are causing the wellbore damage. Sometimes monitoring of the geothermal system may show that the corrosion and scaling control methods are not working as expected, thus further steps can be taken to solve this problem. A large number of variables should be assessed during monitoring of fluid flow systems including: chemical-physical data (such as pH, electric conductivity, and redox), chemical data (such as cations, anions, organic compounds, tracers and isotopes), thermo-physical data (density, enthalpy, viscosity, specific volume, entropy, thermal conductivity, and heat capacity), solid phase data (scales and filter residues), gas composition and water composition. In this regard looking at the scales can determine if certain corrosion processes are apparent in the system. The monitoring of the fluid flow dynamics is also an important aspect of monitoring as this can change over time with the formation of scales and the occurrence of corrosion, or by the addition of chemical inhibitors, or by pH equilibration. Measurements that help with monitoring the fluid flow dynamics include fluid composition (gas and water composition), redox potential, oxygen, density, volume, pH, temperature, pressure, and electrical conductivity. Measurements of the redox potential from practice do not always correlate with calculated values, but nevertheless is useful. A typical monitoring schedule, of inhibitor effectiveness for example, can be done as follows:

Week 1: Analysis check once a day

Week 2: Analysis check once every two days

Weeks 3-6: Analysis check once a week

Week 6+: Analysis check once or twice a month

8. Methods

8.1 Sampling and Procedures

Scale research is an integral part of overall geothermal system efficiency and it requires the necessary sampling techniques and analysis techniques to predict such occurrences⁴. Some geothermal operators may neglect sample collection and subsequent analysis as it is both time consuming and expensive. This can lead to underestimations of the severity of scale formation (and sometimes corrosion rates) in geothermal systems. Sample collection is taken at all sites where the scales occur, usually a few samples from each of the locations. The pressure and temperature should also be noted. A stainless steel scraper can be used to remove scale samples which are then put into plastic bottles and transported to the laboratory. Once at the lab the sample should be dried at 90°C for 24 h, after which it is ground and homogenized. The scale chemical composition can be analyzed by x-ray diffraction and/or x-ray fluorescence. To determine radium isotopes, one must make sure that the collected samples are sealed in an air-tight container and stored for four weeks. This allows for secular equilibrium to occur between ²²⁶Ra, ²²⁸Ra and ²²⁴Ra and their decay products. The smaller samples with high activity content can be mixed with PVC powder so that the mixture is homogenized to obtain an appropriate volume of sample (necessary for the counting geometry). Gamma spectrometers with high-resolution, low background HeGe detectors can be used to measure the radioactive content in the scale sample. ²²⁶Ra, ²²⁴Ra and ²²⁸Ra can be determined by measuring their gamma emitter daughters: ²¹⁴Pb, ²¹⁴Bi, ²¹²Pb, ²¹²Bi and ²²⁸Ac respectively. All elements found in the scale can then be linked with the elements found in the water composition. To get an idea of corrosion processes and rates the water chemical composition (including elements such as Cl, Na, Mg, C, Si, Al, Ba, Pb, K, Fe, and S), the gas composition, and the gas-water ratio should be measured. An ideal volume of fluid can be from 0.5 – 2 litres. The depth, TDS, pressure, and temperature from where the fluid samples were taken are also important to note as this can give an idea whether corrosion rates are aided. One method for testing corrosion rates and linking it with the measured data is using simulated geothermal water on different materials with different prevention methods. An example of wellbore activities and sampling is shown below:

Date	Activities	Sample name	Sample type abbreviation
04.2011–06.2012	Several production-tests; determination of TD	Collection of fluid (wellhead) and filter residue samples (FR1-FR114)	WH-FI, FR
26.07.2012	Drive down bailer	Three bailer samples (B115, 116, 117) from 4200 m (GrSk04)	B
7.8.–8.8. 2012	Short production tests (~7 h; 198 m ³)	–	–
8.8.2012	Drive down bailer and TD	Bailer sample of GrSk04 (B119)	B
30.11.2012–3.12.2012	Coiled tubing operation	33 samples (back flushing suspension)+ three sediment container samples	CT
10.12.–12.12.2012	Production test (332 m ³)	Well head fluid and filter residue samples	WH-FI, FR
21.12.2012	Drive down bailer and TD	Bailer sample of GrSk04 (134), 4162 m	B
27.12.2012	Multi finger caliper and TD	–	–
05.2013	Deep fluid sampling during shut-in	Fluid collected in 2313, 2900, 3500, 4120 m depth	D-FI
01.2014	Wellbore cleanout	Samples collected by reverse circulation up to 4346 m	CO
02.2014	Several production lift tests with simultaneous deep fluid sampling	Deep fluid in 4200 and 4240 m	D-FI

TD, total depth; WH-FI, wellhead fluid; D-FI, deep fluid; FR, filter residue; CT, coiled tubing; CO, cleanout; B, bailer.

Figure 21: Example of sample collection with activities; source - Regensburg, 2015

⁴ Corrosion is best understood from past experiences and previous research on the topic and does not necessarily need sampling analysis. It is more productive to predict corrosion and prevent it in the first place by understanding the materials used and conditions present. Sometimes analysis of certain scales will point to the fact that corrosion is happening in the system.

8.2 Minimizing Discrepancies

Reliability can be improved if pH and alkalinity are measured as soon as the water sample is collected, something that is not always the case. If the water sample is collected in a pressure container and taken to a lab for analysis prediction calculations would be much more accurate as it ensures that there is no loss of dissolved gases. If the water sample is measured at a later date from the moment it was taken, its pH could be higher than it would be if the water was measured in place within the system; at the point the water was at equilibrium with dissolved gas. PH changes arise when there is a loss of dissolved gas from the water and this leads to HCO_3^- ions converting to CO_3^{2-} ions, and thus increasing alkalinity. A major risk in taking samples from the surface installation of geothermal plants is the exposure the sample may have to oxygen which can lead to overestimations of O_2 . A very important component in corrosion and scale studies is looking at practice data in previous research dealing with the same problems. One other thing to bear in mind is that gas analyses of the fluid/solution carried out on the surface (i.e. surface samples) are not always reliable even when collected at a pressure above the bubble point.

A number of questions posed need to be answered: Has the risk of scaling been examined and if so, what was the result? How much material is left behind in the filter units and in the degasser? Is there evidence of increased pressure losses in the system or the need for increasing injection pressure? Is there evidence of deterioration in the heat transfer from the heat exchanger(s)? Have measures been taken to prevent scaling and if so which? Furthermore some basic data is needed to provide a risk estimate of the situation. The following questions should be kept in mind for geothermal operators collaborating with consulting firms/research institutes. Which formation water is recovered and pumped back? For how long has the system been pumping thus far (amount of water)? What is the composition of the water pumped water? How much gas is contained in the water and what is its composition? Where are the relevant samples taken? How does the pressure and temperature change as the water flows through the system? These questions will form the basis of creating a simulated theoretical geothermal model.

8.3 Understanding and Using Models

The main aims of modelling is to test chemical substances that can prevent corrosion and/or scaling, as well as identifying parameters that will indicate specific changes in the geothermal system and/or well casing alteration. Modelling beings with equilibration of pure water, a defined mineral assemblage (which represents the deep formation rock matrix), and a co-existing gas phase (with fixed-pressure). These will allow us to reproduce all hydrogeochemical compositions present with formation water. Modelling corrosion is beyond the scope of this paper but one can simulate corrosion, along with its sampling effects (mineral precipitation, degassing) on the hydrogeochemical composition, by exposing the modelled solution to Fe(0) and cement. The corrosion can be modelled as an iron release of 0.01 mol. The cement represents the well casing and can be changed to suit a specific well in mind. High temperature material phases can be used to make results more realistic.

The next section will look at actual modelling for scaling, by looking at the minerals and gas phases, as well as other minor factors. The geochemical program PHREEQC will be used and a few general points are described. Generally speaking the modelled composition of formation waters, which represents the first main step in the model, happens because of the

following hydrogeochemical processes: pure water dissociation at reservoir temperature, salt mineral dissolution which forms reservoir brine (based on the observed state of undersaturated concentrations of K^+ , Na^+ , Ca^{2+} , Cl^- , and Mg^{2+}), brine and mineral assemblage equilibration of the reservoir rocks, and irreversible reaction of carbon dioxide, methane and nitrogen (multi-component gas phase at reservoir conditions). For corrosion electrochemical investigations are very useful and can be carried out with simulated geothermal waters. For example corrosion on carbon steel in NaCl waters can be tested with and without sulphide ions as well as in the presence of additives. The latter is used to know more about the affect of corrosion inhibiting properties. Electrochemical studies require AC (measurements of impedance vs. Frequency) and DC (open circuit potential measurements vs. Time as well as the $\log(I)$ vs. Applied potential). Additives that can be used to test as inhibitors against corrosion include polymeric additives, organophosphorus compounds, commercial products (Solamine, Norust), and organic compounds. Mathematical models are usually needed for corrosion processes, and they have to be solved numerically.

9. PHREEQC Simulations

The geochemical program PHREEQC was created by the US Geological Survey and simulates chemical reactions and transport processes for fluids. The models in this section look at how three physical system changes (temperature, pressure, and pH) influences the solubility of minerals and gases in the fluid during circuit flow. The models give an idea of when oversaturation, and precipitation, is most likely to occur. The minerals modelled are those that have been frequently mentioned in literature as well as those that are most likely to form as scales based on current sub-surface fluid compositions in the Netherlands. The minerals include: calcite, dolomite, siderite, strontianite, quartz, gibbsite, anhydrite, barite, gypsum, and celestite. The gases modelled are the three most common gases found in fluids in the Netherlands: Carbon dioxide, methane, and nitrogen. One major disadvantage of using PHREEQC is that a few processes are not taken into account: corrosion (rates), redox processes related to corrosion, organics (which affects mineral reactivity), and other gases apart from CO₂ (only when modelling the individual minerals).

9.1 Databases

Two databases were used during the modelling of scale formation in PHREEQC: Gebo.dat and Geo.dat. The first database (Gebo) was used in conjunction with a database already provided by the PHREEQC program known as Pitzer. The Gebo database extends the hydrogeochemical thermodynamic dataset in Pitzer to include the following solution master species: Fe(+2), Fe(+3), S(-2), Al, Si, Pb, and Zn. All the necessary solution species and phases (both solid phases and gases) are employed. Other implementations include the temperature and pressure adaptations of the mass action law constants, Pitzer parameters for the calculation of activity coefficients in waters of high ionic strength and solubility equilibria among gaseous and aqueous species of hydrogen sulphide, CO₂, and methane (Bozau, 2013). This database extension is used together with PHREEQC for the calculation of several additional hydrogeochemical equilibrium reactions, all of which are critical for the compositional development of highly mineralized formation waters and brines. All additional data for the extension of the Pitzer database is taken from literature, the sources of which can be found in the combined database itself. As geology varies by location, a number of phases were added to the Gebo database to suit geothermal systems in the Netherlands. These phases include: hematite, goethite, magnetite, and pyrite. Additionally some values of theta and lambda were also added. The reliability of the Gebo database has been tested and the results presented in Bozau, 2013. The paper compared experimental solubility data from various literatures to that of the modelled mineral's solubility at elevating levels of temperature, pressure, and TDS. As there is a match between the model and the experimental solubility the database is reliable.

A recent study by Moog & Cannepin (2014) provided new information based on experimental solubility data which were compiled into a new database termed GeoDat. This database uses the Pitzer formalism but is not an add-on to Pitzer like Gebo. Though some of the data in GeoDat is taken from Pitzer, other data is not which does mean that GeoDat covers some systems that are not included in Pitzer. Similarly, Pitzer includes some systems that are not included in GeoDat. The Gebo database in general was considered to be largely untested and the data comes from heterogeneous sources which may make it inconsistent (Moog & Cannepin, 2014). Both databases were tested by using real data from a project in

the Netherlands. Though initially the Gebo database was used, it was later found that the GeoDat database worked better for creating the graphs for the solid (mineral) phases. On the other hand the Gebo database was found to work better when plotting the results for the gas phases. Thus both databases have been used in the next few sub-sections, and the process describing how the databases were tested is shown in the last sub-section.

9.2 Standard Model Setup

As briefly mentioned earlier there are three main physical-environmental changes that affect a fluid as it flows through the geothermal circuit system (Figure 22). These changes, which affect the solubility of various components in the water/fluid, are:

- 1) **Temperature vs. solubility:** The temperature in the reservoir is at its maximum but starts to cool due to heat extraction from the heat exchanger. Though small amounts of heat can dissipate through to the surrounding rock as it travels up the production well, this is ignored for simplicity. Sometimes mechanical work by the electrical submersible pump (ESP) can create heat and may lead to very slight increases in temperature. Sometimes there is further cooling of the injected water to improve energy efficiency.
- 2) **Pressure vs. solubility:** These changes occur due to vertical transport of the fluid as it moves from the reservoir to the surface (via the production well) and as it is injected from the surface back into the reservoir. In the production well as the pressure drops it reaches a certain point where the solubility of CO₂ in the fluid decreases such that it is expelled from solution. This is the pressure that degassing occurs.
- 3) **pH vs. solubility:** The pH changes happen naturally or manually: added inhibitors in the fluid can increase and or decrease the pH; degassing of CO₂ in the production well decreases the pH.

Figure 22 is the basic setup of the model created in PHREEQC to simulate all geochemical processes that occur during fluid flow through an entire geothermal system. The temperature and pressure parameters suit (reservoir) systems in the Netherlands. The temperature vs. solubility graph for all scaling minerals can be seen in Figure 23, while the pressure vs. solubility graph for all scaling minerals can be seen in Figure 24. The hydrogeochemical model created in PHREEQC can help with predicting scaling and degassing during geothermal energy production. Generally, we would expect scaling to occur in the heat exchanger, the production well and the injection well. We would also expect degassing to occur at low pressures. The model simulates 1-D geothermal fluid flow while making three assumptions: no dispersion or lateral flow, not accounting for reservoir cooling over the geothermal system's operational lifetime, and pressure temperature points have a linear interpolation. The model can be adjusted for the different systems found in the Netherlands by filling in the different variables (temperature, pressure, fluid composition, pH, alkalinity, density etc.) in PHREEQC. There are about 8 steps in the model: the sample taken at the separator (here the solution is defined based on what is found in practice⁵), the sample at reservoir conditions with degassing taken into account (known from reservoir analysis), equilibration with reservoir minerals (known from reservoir analysis), the fluid at the surface again (pressure decrease and degassing; same result as step one), heat loss from heat exchanger, injection into reservoir, and finally reservoir conditions after equilibration.

⁵ An example of what this data looks like is found in the appendix (last page)

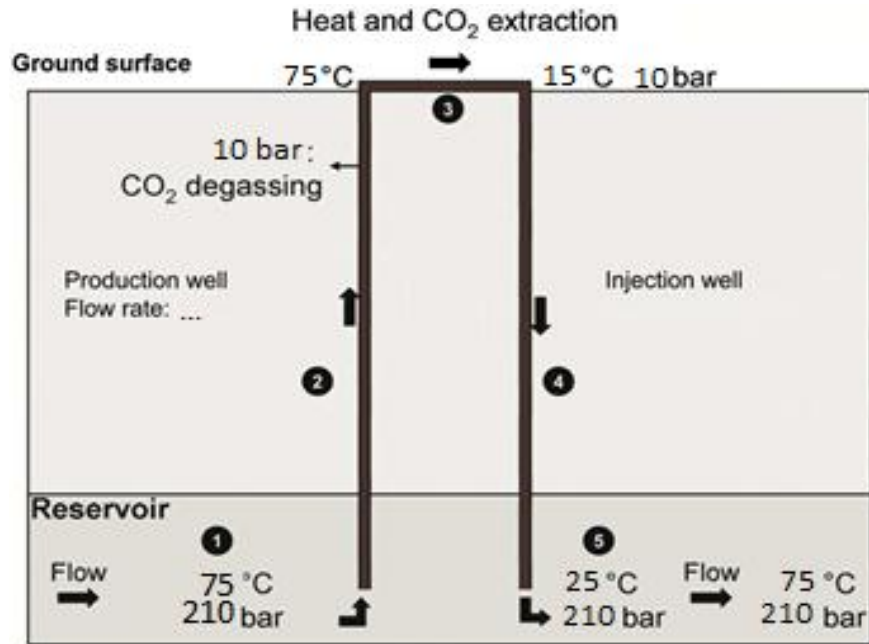


Figure 22: Schematic overview with defined *PT* regimes. The temperature and pressure are variables and can be changed to suit the system in mind. Generally, reservoir temperatures in the Netherlands will not exceed 80 degrees, correlating to pressures of roughly 200 bars. **1:** Original reservoir condition; **2:** Production well: pressure decreases and degassing eventually occurs (pressure vs. solubility and pH vs. solubility), temperature remains unchanged. **3:** Heat Exchanger: Temperature decreases due to heat exchanger (temperature vs. solubility) **4:** Fluid is injected into reservoir and pressure increases (pressure vs. solubility). **5:** Reservoir condition immediately after injection which eventually equilibrates with reservoir (temperature vs. solubility). The molar volume ideal gas is taken at 0°C; 1atm is 22.414 dm³/mol (1 dm³ of ideal gas is taken at 0°C and 1 atm is 0.044615 mol). For every 100m in depth there is an increase of 10 bars. The density of the solution is defined in mg/l.

9.3 Mineral and Gas Solubility

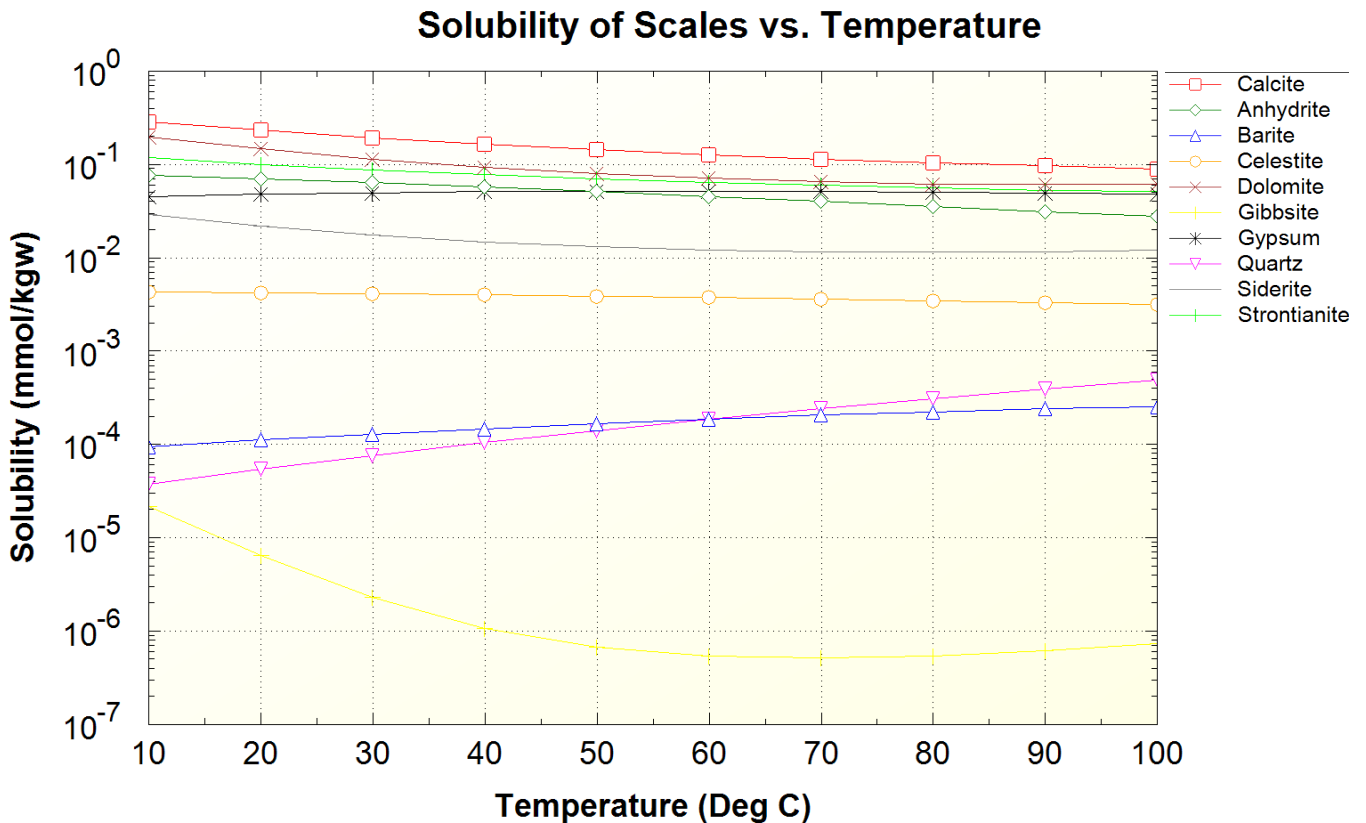


Figure 23: Log graph with the solubility of minerals that have potential to form as scales versus temperature. In Dutch systems the temperature is always below 100°C; after the heat exchanger and injection the temperature is always above 10°C. The GeoDat database is used for the minerals. The fluid/solution is pH5 at 1bar with the composition as Na 35000 and Cl 50000. Units of the solution are in mg/l.

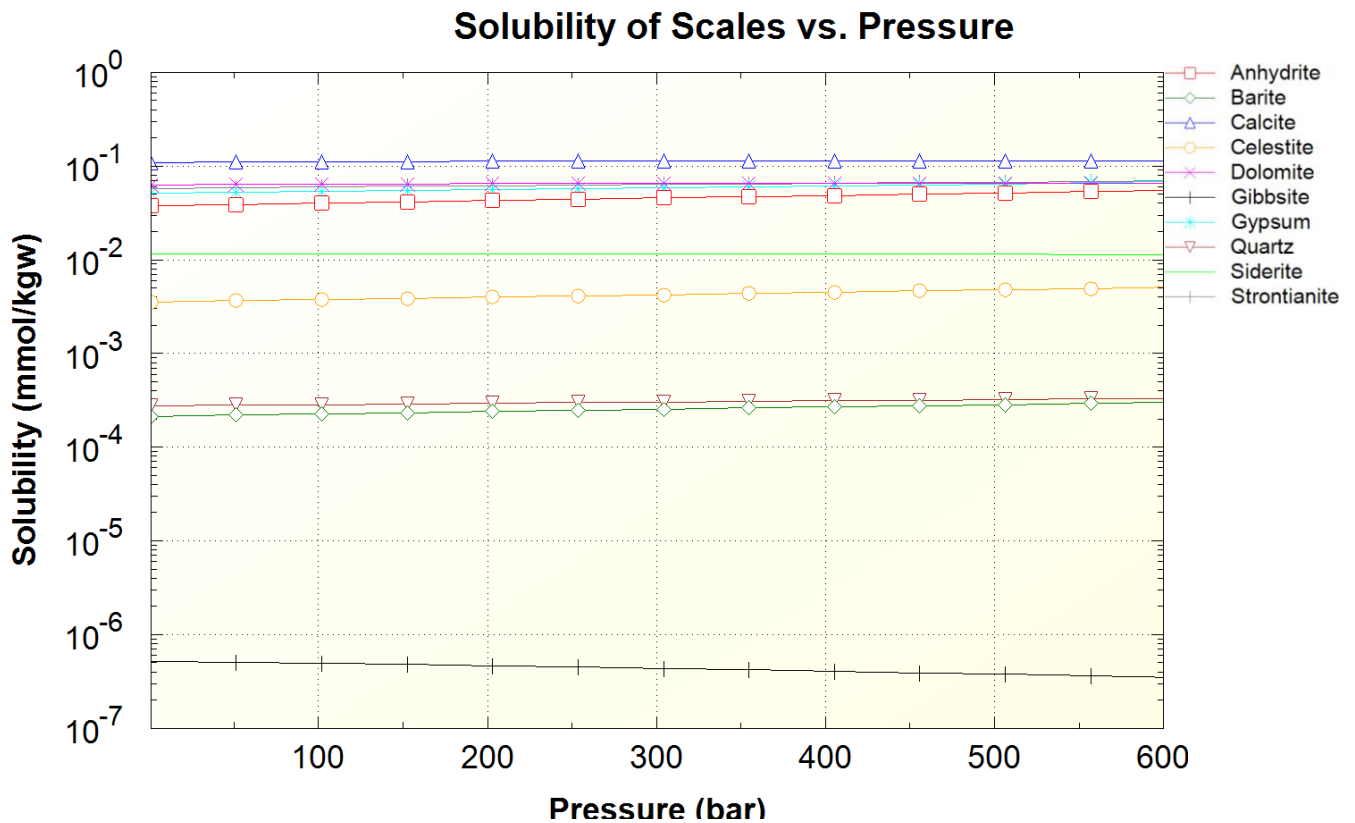


Figure 24: Log scale graph with solubility of potential scale forming minerals vs. pressure. Pressure in geothermal reservoirs in the Netherlands will never be more than 250 bar. The GeoDat database is used. Solubility for each mineral in realistic conditions shows almost no changes in solubility. The solution is pH5 with temperature of 75°C; composition of Na 35000 and Cl 50000.

It can be seen that temperature (Figure 23) has a much larger influence on the solubility of minerals than pressure (Figure 24) does. It can be seen that the minerals calcite, dolomite, celestite, anhydrite, gypsum, gibbsite strontianite, and siderite all decrease in solubility with increasing temperature. Contrastingly, with decreasing temperature these minerals become more soluble in solution. Precipitation and deposition of these minerals is therefore unlikely in both the heat exchanger or in the injection well (with additional cooling of the produced water). The fluid as it equilibrates with the reservoir temperature will increase the likelihood of these minerals to precipitate as their solubility decreases. The minerals quartz and barite however decrease in solubility with decreasing temperature thus precipitation is more likely. These two minerals are most likely to precipitate in the heat exchanger and, if any ions still left in solution, in the injection well. At higher temperatures barite and quartz are less likely to precipitate. The solubility changes are the most sensitive at temperatures between 10°C and 40°C; most heat exchangers will cool the fluid from 60°C+ until 25°C. Pressure on the other hand has a tiny influence on mineral solubility, such that its influences are usually ignored. Calcite, barite, celestite, dolomite, anhydrite, gypsum, strontianite and quartz are 'more likely' to precipitate when there is a decrease in pressure, as solubility decreases. This can occur in the production well. Gibbsite and siderite with increasing pressure will have a decreasing solubility and thus 'more likely' to precipitate. This can occur in the injection well.

As pressure has a stronger affect on the gas phase this is better to examine than pressure vs. solubility. CO₂ is the most common gas found in Dutch geothermal reservoirs, especially in those systems where oil/gas lies together with the formation water. Though methane and nitrogen are other gases commonly found in reservoirs, degassing of the CO₂ has the most

significant effect on mineral precipitation and scaling. The solubility of CO₂ as a function of pressure at different temperatures can be seen in Figure 25. The solubility of a gas is:

$$m_i = K_H \frac{\varphi_i P_i}{\gamma_i}$$

m is the molality, K_H is the equilibrium constant, φ is the activity coefficient in the gas phase (fugacity coefficient), P is the partial pressure, and γ is the activity coefficient in water. The fugacity coefficient is calculated by PHREEQC using the Peng-Robinson equation of state. This is taken from the critical pressure and temperature as well as the acentric factor of the gas in the overall gas phase. The fugacity coefficient is close to 1 when the total pressure of the gas phase is lower than 10 atm. Therefore it is neglected in the solubility calculation. The effect is much more substantial as higher pressures [Figure 25].

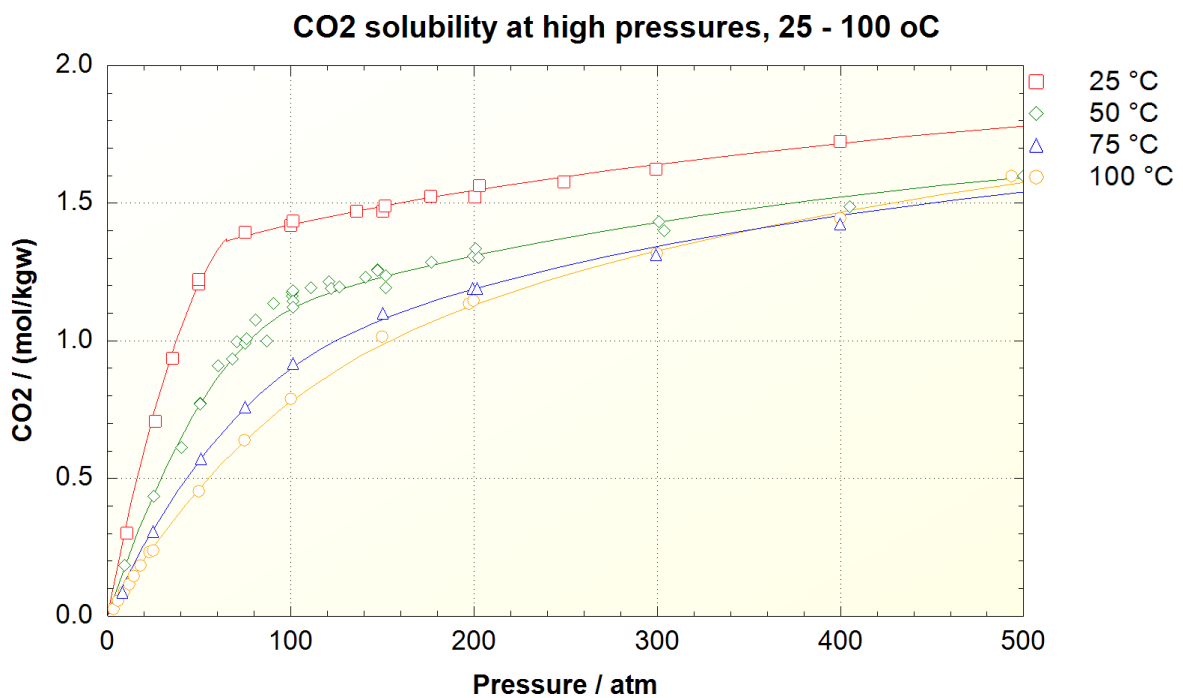


Figure 25: CO₂ solubility (as concentration in moles/kilogram water) versus pressure at temperatures of 25°C, 50°C, 75°C and 100°C. At low pressures, the concentration of CO₂ increases almost linearly with pressure. With pressures above 62 atm at 25°C the CO₂ concentration increases at more gradual rate since fugacity coefficient drops rapidly.

CO₂ Pressure vs. Calcite Saturation

Calcite is the primary mineral that forms by oversaturation directly from CO₂ degassing and therefore is important to model [Figure 26]. As degassing occurs, the CO₂ pressure decreases as does the total dissolved inorganic carbon, while the calcite saturation index increases from a negative number (undersaturation) to a positive number (oversaturation). At this point precipitation of calcite is possible. Figure 26 gives a rough idea of the evolution of calcite and CO₂ as the fluid moves through the geothermal circuit system, beginning at the reservoir and ending at the surface. The pressure of CO₂ and total dissolved C decrease at a slower rate over time, while the SI of calcite increases at a slower rate.

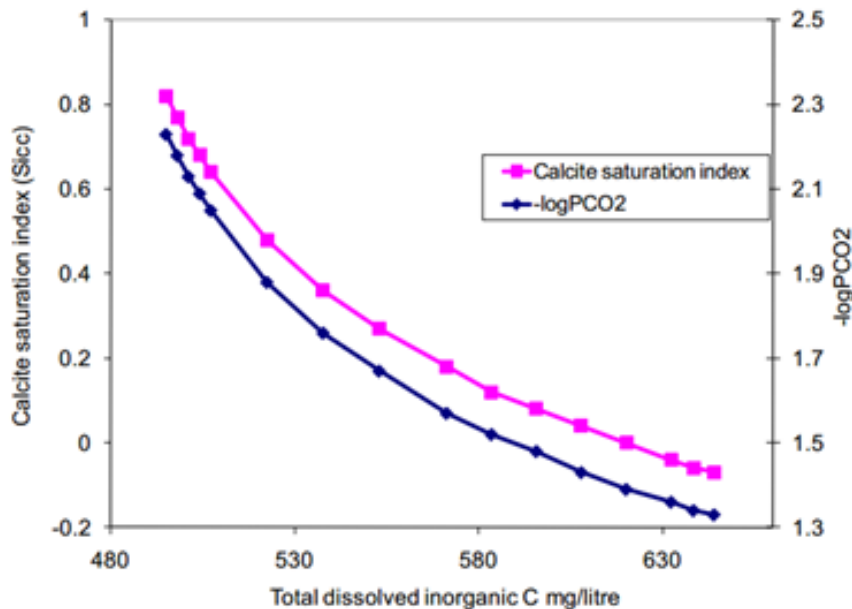


Figure 26: Saturation index (SI) of calcite and the negative logarithm of the pressure of CO₂ versus the total dissolved carbon in solution. Degassing takes place from right to left

Generally speaking pressure indirectly affects the pH because as pressure drops and CO₂ becomes less soluble, it degasses which lowers the CO₂ content in the fluid. Consequently, there is less CO₂ in the fluid and the solution becomes less acidic (since carbon dioxide in water forms carbonic acid). This causes the pH to rise and become more alkaline which has large effects on mineral solubility (Table 2). Calcite, barite, anhydrite, celestite, gibbsite, gypsum, dolomite, siderite, and strontianite increase in solubility when pH decreases (becomes more acidic) which means that precipitation is less likely. On the other hand, all minerals decrease in solubility when the pH increases (becomes more alkaline). This shows that if degassing with a pressure drop occurs, then there will be an increase in pH thus increasing the likelihood for all minerals (except quartz) to precipitate in the production well. Although it is beneficial to keep the solution pH low to prevent scaling, this may increase the rates of corrosion and the formation of quartz. Quartz is the only mineral that is more likely to precipitate, in the form of amorphous silica, with a decreasing pH since its solubility decreases. All the minerals are quite sensitive to pH changes.

Solubility Sensitivity to pH					
Mineral	Min. Solubility (mmol/kgw)	pH Value	Max. Solubility (mmol/kgw)	pH Value	Sensitivity (%)
Anhydrite	0.018	4	0.065	1	261
Barite	2.5E-05	4	2.3E-04	1	820
Calcite	0.002	6	9.4	1	8900
Celestite	0.001	4	0.005	1	400
Dolomite	0.001	6	5.1	1	5000
Gibbsite	3.1E-07	5.5	0.25	2 (& 10)	80 000 000*
Gypsum	0.023	4	0.091	1	296
Quartz	0.0005	8	0.055	11	10000*
Siderite	6E-05	6	9	1	1E+07
Strontianite	0.001	6	9	1	890000*

Table 2: The individual graphs for each mineral can be found in the appendix. Since solubility is only affected between a certain range of pH's, the minimum and maximum solubility, with the corresponding pH, is shown. Gibbsite has two maximum solubility values (pH2 and pH10); no results appeared for pH1. Max pH for quartz is taken at a pH of 11. *Rounded; actual sensitivity is higher. The fluid/solution is at a temperature of 80°C of 1 atm with Na 300 and Cl 5000.

Mineral Solubility vs. Temperature at Selected Pressures

The solubility dependence on temperature at different pressures is a useful overview to see how different operating pressures in a system can affect the mineral solubility through a range of temperatures. This is useful in the design and implementation phase where an optimal operating pressure can be chosen, one that minimizes the impact of scaling. The temperature range is taken from 10°C to 100°C at five different pressures (500, 250, 100, 50, 1 bar) for each mineral prone to precipitation (graphs shown in the appendix). Such graphs are applicable to heat exchangers where there is a temperature decrease as well as potentially different operating pressures (i.e. pressure of pipe in heat exchanger) all of which can affect mineral solubility simultaneously. Such graphs can also apply to injected water in the reservoir where there is a temperature increase in various reservoirs that have different pressures. The graphs are all modelled at 1 atm and they show a good comparison for other pressures. Anhydrite, barite, calcite, celestite, dolomite, gypsum, quartz, siderite, and strontianite have an increased higher solubility at higher pressures over the same temperature ranges. This shows that in geothermal systems operating at higher pressures than normal, there is a lower risk for scaling for the minerals mentioned. Only gibbsite has a lower solubility with increasing pressures over the same temperature range. Any part of the system that decreases in pressure where there is a temperature change will increase the likelihood of gibbsite scaling. It should be noted however that the solubility of gibbsite at the five pressures are very similar with temperature change.

Mineral Solubility vs. Pressure at Selected Temperatures

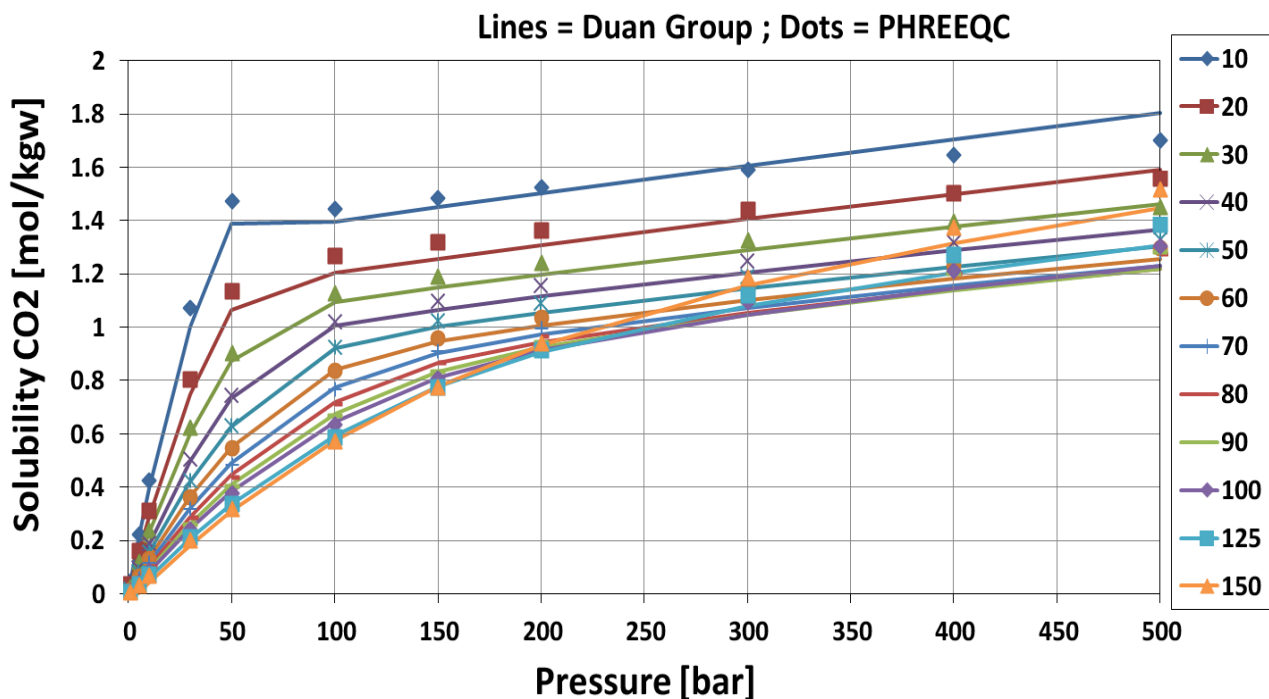
These graphs (in appendix) can apply to production and injection wells where there is a pressure change in which the temperature of the fluid can vary depending on the geothermal system in mind. Systems can operate at different temperatures depending on the reservoir properties, and some plants use additional cooling of injected water. Thus it is important to see what affect different temperatures can have on mineral solubility over a pressure range. The pressure range is taken from 1 bar to 600 bars, while there are five temperature variables at 15, 25, 50, 75, and 100 degrees Celsius. Though these high temperatures and pressures are not common in the Netherlands, it is useful for future operations looking at high temperature-pressure systems. 15 100: Anhydrite, calcite, celestite, dolomite (strong diff), gibbsite (strong), gypsum (mixing), siderite, and strontianite all have an increased solubility with lower temperatures over the same pressure range. So in shallow geothermal systems where temperatures are low, these minerals will be more soluble and less prone to scaling over changing pressures than with deep geothermal system. Most of the mentioned minerals show strong temperature dependence over the pressure range. Gypsum shows slightly strange results: the solubility overlap at the different temperatures over the same pressure range. Barite and quartz on the other hand are more soluble with higher temperatures with pressure change. This means that these minerals are less likely to precipitate in high temperature systems.

Model Validation

The two databases were validated by comparing them with the Duan website. This is an online thermodynamic model database created by the Duan Research Group (from the Chinese Academy of Sciences in the Institute of Geology and Geophysics department). The Duan models are reliable since they have been tested using experimental solubility data all of which has been published in reputable journals. The mineral phase results were very similar when using Gebo and GeoDat, but since a recent study refutes the Gebo database, the GeoDat database was used instead. The gas phases however had to be tested using both databases.

Method

The Duan website makes it possible to look at the thermodynamic properties of a single gas-NaCl-water (tertiary) system. The three relevant systems on the website were: the CH₄-NaCl-H₂O system, the CO₂-NaCl-H₂O system, and the N₂-NaCl-H₂O system. In PHREEQC the input file is modified so that only one gas in the system is tested at a time with each database. This is done by setting the mole fraction of the gas being tested to 1, while the mole fraction of the other gases are set to 0 and excluded. The pressure parameters were fixed at 500, 400, 300, 200, 150, 100, 50, 30, 10, 5, 1 bar. The temperature parameters were given at a range from 10°C to 100°C for each pressure parameter plus 125°C and 150°C as additional temperatures. The results from PHREEQC and Duan were compared by plotting the results in a single graph, with pressure vs. gas solubility at each temperature (Figure 27). For CO₂ and CH₄ there was a very good fit between PHREEQC (using the Gebo database) and the Duan Group (Figure 27). The fit for nitrogen was good, but is excluded as it is not an important gas in geothermal systems.



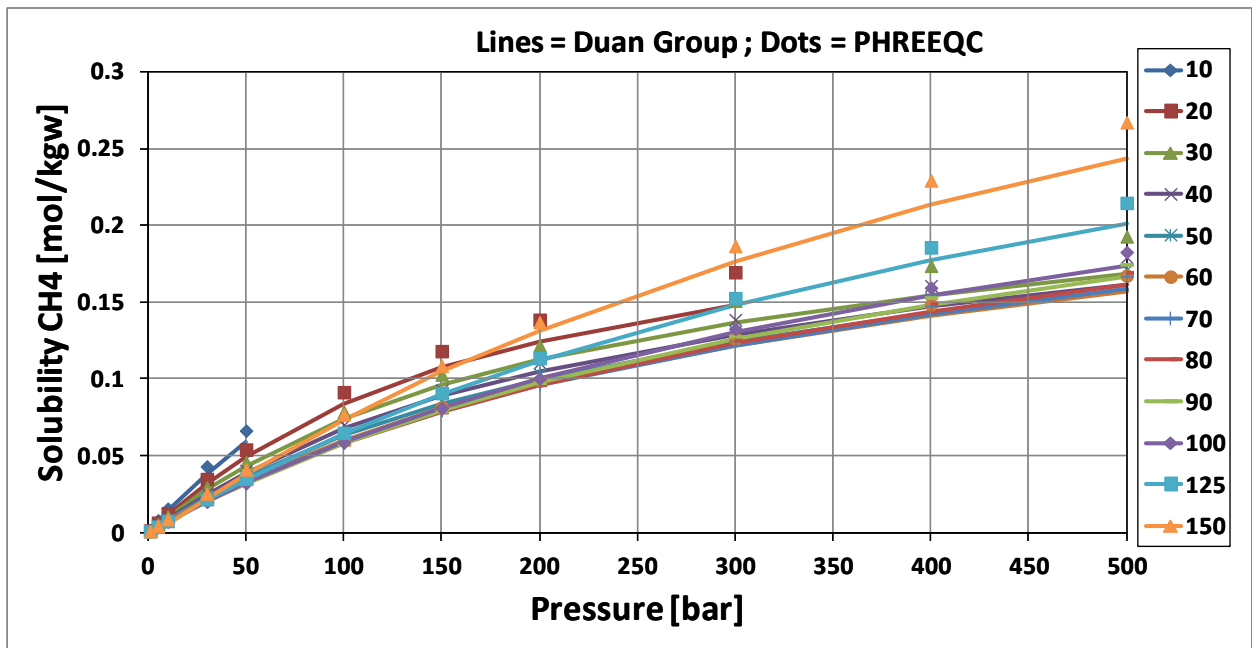


Figure 27: Gas phase validation by comparing the results between the gebo database using PHREEQC and Duan Group website for CO₂ and CH₄. Solubility against pressure for temperature parameters is shown. The lines represent the results from the Duan Group while the dots represent the results from PHREEQC (using Gebodat). For the low temperatures and high pressures, the fit is worse because in geothermal systems higher pressures correspond to higher temperatures. For example, 10°C with pressure of 500 bar is unrealistic for any geothermal

It is important to note that the input file in PHREEQC used the gas phase command: this defines the composition of a fixed-total-pressure multi-component gas phase (see model). The thermodynamic properties of each gas are defined in the database(s). Only temperature, pressure, volume, and initial partial pressure of the gas had to be specified in the gas phase. For CO₂ the critical temperature (t_c) and critical pressure (p_c) had to be re-defined in the gebo database while methane and nitrogen were blocked from the gebo database. For methane and nitrogen t_c and p_c was instead taken from the Pitzer database as it is considered more reliable. For all three gases PHREEQC uses the Peng-Robinson equation of state to calculate the pressure and molar volume relation, as well as the fugacity coefficients for each of the gases. Defining t_c and p_c for all gases is vital, otherwise the ideal gas law will be used; and PHREEQC cannot use both the Peng-Robinson and ideal gas law in one calculation.

The SI of the gases for both databases was studied and then the results were used to compare with the Duan results. The SI for all the gases were adjusted by taking the fugacity into account: $Fugacity = Press * phi / 1atm$. The SI is then the logarithm of the fugacity. Initially, the SI was calculated by assuming that the gases were ideal, in which case phi is taken as 1. The output in PHREEQC (when phi was assumed 1) contained the data for pressure and real value of phi under the SI at each step of temperature. The pressures were not that of the solution, but the gas pressures itself, thus this number varied at each step. The data for pressure and phi was used to plot a graph (pressure vs. phi) at different temperatures, i.e. the graph would make different plots depending on the temperature chosen. The line of best fit and a corresponding equation was determined to give a relation between pressure and phi. This was done at nine different temperatures for a total of nine equations. The general formula for all nine equations was $Ax^3 + Bx^2 + Cx + 1$. Three

graphs with the nine temperatures against A , B , and C were made. The consequent line of best fit and a corresponding equation gave three formulas with the temperature dependence included. Finally, the general formula was used to calculate phi by substituting x with pressure so that: $Phi = A(P)^3 + B(P)^2 + C(P) + 1$. This final equation can be used to calculate phi at a chosen pressure and temperature. The corrected SI can then be calculated. The 'uncorrected SI' for CH_4 , CO_2 , and N_2 showed a good fit between the PHREEQC output and the Duan Group results since t_c and p_c were defined. If t_c and p_c were not defined, then the 'corrected' SI gave a better fit for all three gases. Therefore the model did not need to be adjusted to accommodate for the corrected SI values for any of the gases. An example of a distance-SI-temperature; and a distance-SI-pressure graph is shown in the appendix.

When validating CH_4 , CO_2 , and N_2 by using GeoDat to compare it to the Duan Group results, it was found that the fit provided when using the gebo database was much better. Since the Duan Group results are based on experimental solubility data, the fact that the gebo database worked better overall than GeoDat meant that using gebo was more reliable. GeoDat results for CO_2 and CH_4 had a bad fit with Duan results, but for N_2 the fit was as good as the gebo results. For mineral phases, it was seen that the GeoDat research project had carried out some tests and validations on solubility data. This meant using GeoDat for the mineral phase simulations was more reliable than gebo. The final model in PHREEQC required a combination of the gebo database and the GeoDat database in two parts. The gebo database is used for the first part of the model to simulate degassing during upward transport in the production well (Figure 28) while GeoDat is used for the equilibrium phases to simulate (potential) mineral precipitation/dissolution during heat reduction in the heat exchanger. Additionally, GeoDat is also used to simulate (potential) mineral precipitation/dissolution in fluid injection and reservoir re-equilibration, but by this time there is not much of an effect on the fluid as most of its ions have been precipitated.

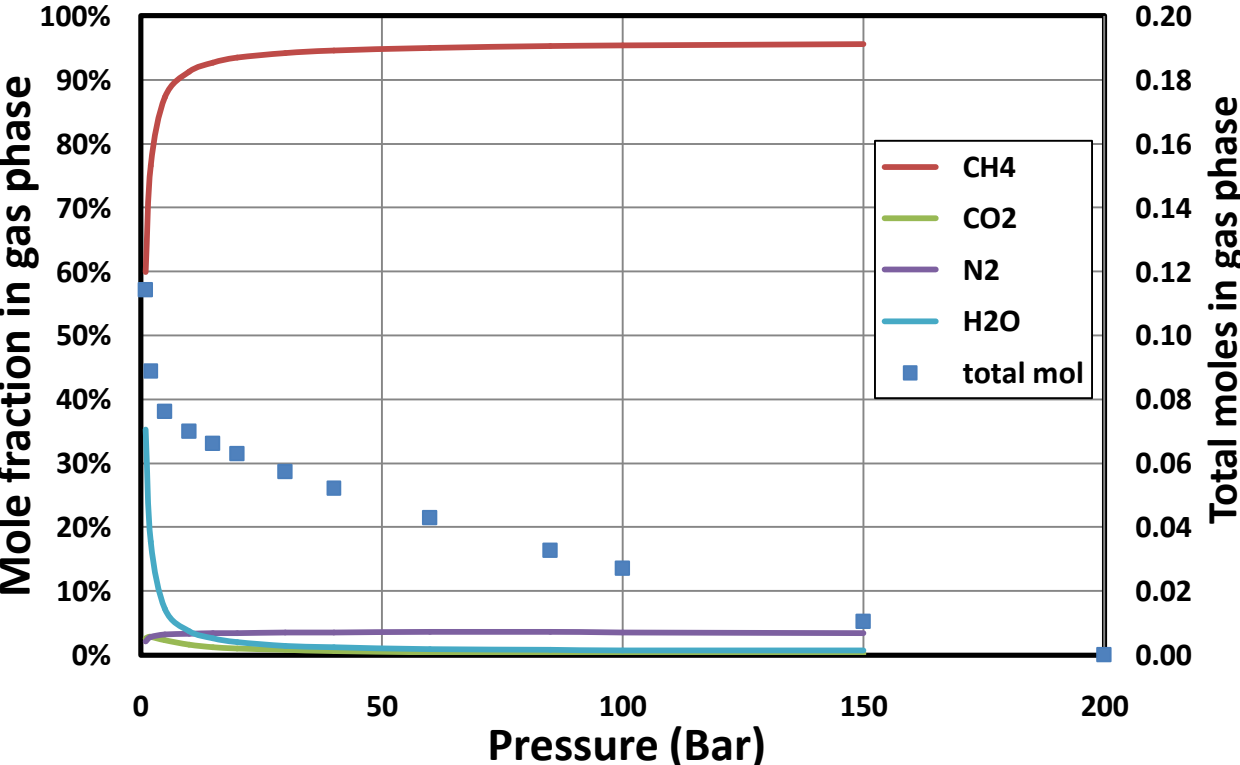


Figure 28: Mole fraction of CH_4 , CO_2 , N_2 and H_2O , and the total moles in the gas phase for a project in the Netherlands. The bubble point occurs almost immediately after pressure drop when the total moles in the gas phase starts to increase. After some time the pressure in the production well can drop below the nominal bubbling point.

The final two-part model was used to test the data gathered from a project in the Netherlands. The gas phase results (Figure 28) seems to fit expectations. Methane is the dominant gas in the reservoir with a mole fraction of 0.95, while CO₂ and nitrogen have a mole fraction of 0.015 and 0.035 respectively. Thus the largest mole fraction in the gas phase is methane. At lower pressures, close to the surface, there is an increase in the mole fraction in the gas phase of H₂O and CO₂, but a decrease for CH₄ and N₂. This means at lower pressures percentage of gas in the gas phase is higher for CO₂ and H₂O. Furthermore degassing was found to occur at around 10 bar. For the mineral phases, the Si for barite, dolomite and quartz are positive which suggest that these minerals are likely to precipitate during the degassing stage. During temperature decrease in the heat exchanger all the mineral phases are in solution and not likely to precipitate. It can also be seen during degassing that the amount of calcite increases. In the heat exchanger there are also phases found for barite and dolomite. One interesting result was from the additional modeling step which took into account transporting of the sample from the separator to the lab. A sample that does not follow a guideline on accurate sampling techniques will find that it can be affected by non-plant conditions. A surface sample taken to lab can cool down and minerals can precipitate or come out of solution which will show a lower ion concentration than reality. Additionally the pressure can decrease to atmosphere conditions which may result in additional degassing. Since this extra step was modeled, the temperature was taken at 20°C and pressure at 1 atm. Simulations showed the differing conditions led to additional degassing and precipitation of calcite and barite. This means that sampling methods have to take this potential difference into account and instead follow fixed guidelines that apply to systems around the country. The model found that the difference between water analyses from two separate firms/consultants on this project was due to inaccurate sampling procedures by one of the firms. The final step is to calculate the amount of precipitation that forms, in terms of mass and volume (build-up), by looking at the fluid flow rates.

Limitations

There are a few key points to consider with using such databases such as gebo and GeoDat. For example GeoDat is in a transient phase and is therefore subjected to further revisions. It is important to keep an eye into any future revisions as it could improve the reliability of the current model. Though some of the parameters in GeoDat have been validated via experimental data, a number of other parameters still require further testing. In general before any parameter can be used, it must be validated through simple, basic experimental data relevant to the problem. If there is no experimental data for the particular system in mind, or if no data is found from secondary sources, then all subsequent calculation will be speculative. In fact even if experimental data has been found the parameter files must represent them, otherwise it is not appropriate to the problem. In GeoDat tests have been performed for minerals such as barite and celestite, but other relevant minerals such as dolomite and calcite need further testing. A general point to note is that even though models are useful, incomplete thermodynamic data as well as limited knowledge on geochemical state of reservoir makes modelling (and prediction) complicated. Other important considerations are that scaling due to degassing not only occurs between reservoir and degasser, but also further downstream due to reaction kinetics. Additionally, since carbonates seem to be the most important scales related to degassing and the temperature decrease it can be expected that this effect does not reach further than the heat exchanger. Lastly, scaling due to the temperature decrease does not only occur in the heat exchanger, but also downstream of the heat exchanger.

10. Conclusion

Geothermal energy is considered renewable since heat extraction from the Earth is tiny compared to the Earth's heat content. It can be completely CO₂ free and numerous studies have pointed to its potential as a major energy source. Thus it has the ability to mitigate the effects of global warming. Geothermal energy is sustainable since it can sustain the Earth's intricate ecosystems and it will not endanger the future generation's capacity to use the resource to the same amount as the energy used presently. Though sustainable, local extraction must be monitored to avoid depletion. As technology has improved in this field, the heat resources that can be tapped have increased significantly. Future methods such as geo-pressured reservoirs and magma resources have opened new possibilities in geothermal energy exploration. In the Netherlands there is a large potential for geothermal energy that can be mined either for direct heating or by converting to electricity.

Geothermal systems can be classified in a number of ways usually by its reservoir temperatures (high enthalpy or low enthalpy), or by the type of geology/lithology setting it operates in. Geothermal plants that currently exist include either steam powered or liquid powered systems for either electricity or direct heat applications. Power plants that produce electricity include binary, dry steam, flash steam power plants. Geothermal heat pumps are also important aspects in the geothermal industry and are found widely around the Netherlands. New technologies have opened up two methods of heat extraction (magma resources and geopressurized reservoirs) something that looks promising for the future. Current methods such as aquifers, hot dry rock, hot wet rock, and EGS already are used to mine a great deal of heat. Existing methods can be improved upon in the future, thus reducing capital costs. Most costs result from exploration and drilling, while costs continue during production in the form of maintenance and investments.

There are a few problems that remain. Exploitation problems include corrosion and scaling which can lead to extra costs as production and energy transfer/efficiency decreases. Furthermore, it requires frequent cleaning or rehabilitation operations to restore the systems mechanical and material parts. Another problem is the occurrence of radioactive scales something that has shown up in the Netherlands as lead which poses health and safety issues. Other problems included the lack of knowledge transfer between the oil and gas industry and the geothermal industry. Since geothermal energy has not reached parity, and oil and gas is cheaper on average, development in this field has been slow. Nevertheless the potential heat in place within the Netherlands, and around the world can easily meet the majority of the world's energy requirement.

Generally there are a number of methods that can reduce, and inhibit to a certain extent, the occurrence of corrosion and scaling. Improvements are still needed in this area but the use chemical inhibitors, magnetic treatment, competing ions, and brine acidification have proved useful thus far. One development in this area has been the fibreglass well design that seeks to prevent corrosion and minimize scale formation. It is important to therefore model and be able to predict how, where, and why corrosion and scaling occur. This aids in taking pre-emptive measures to combat such problems thus reducing costs and improving heat efficiency in the system. Once again models and relevant databases need to be continuously improved. Developing corrosion models is an area that requires work and it is important to note that existing geochemical programs are not perfect.

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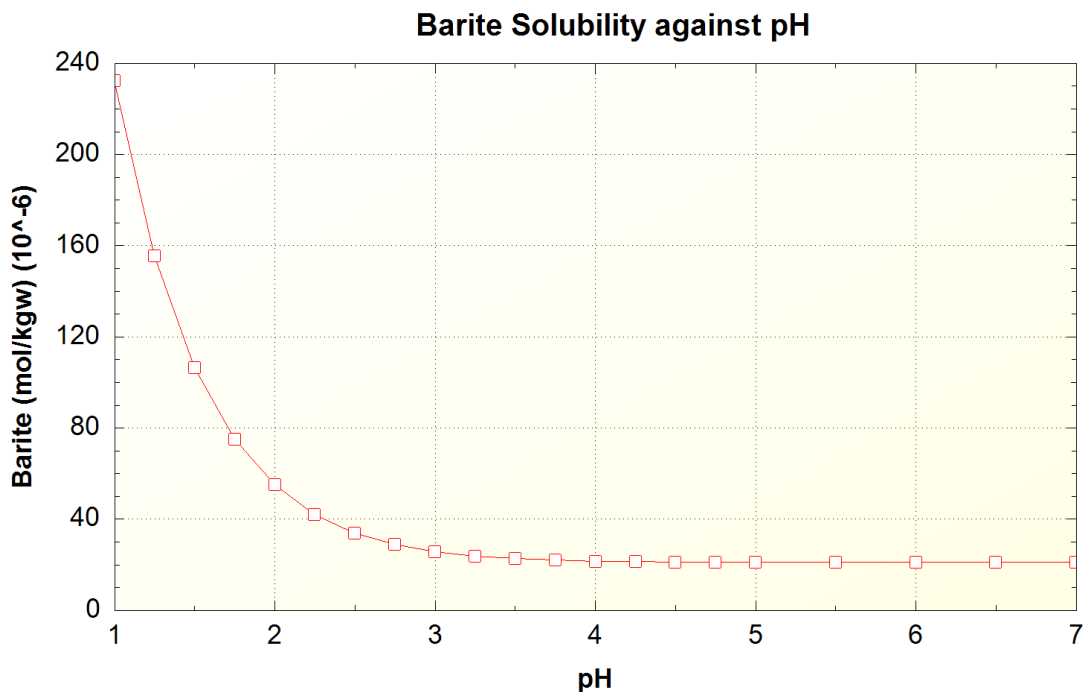
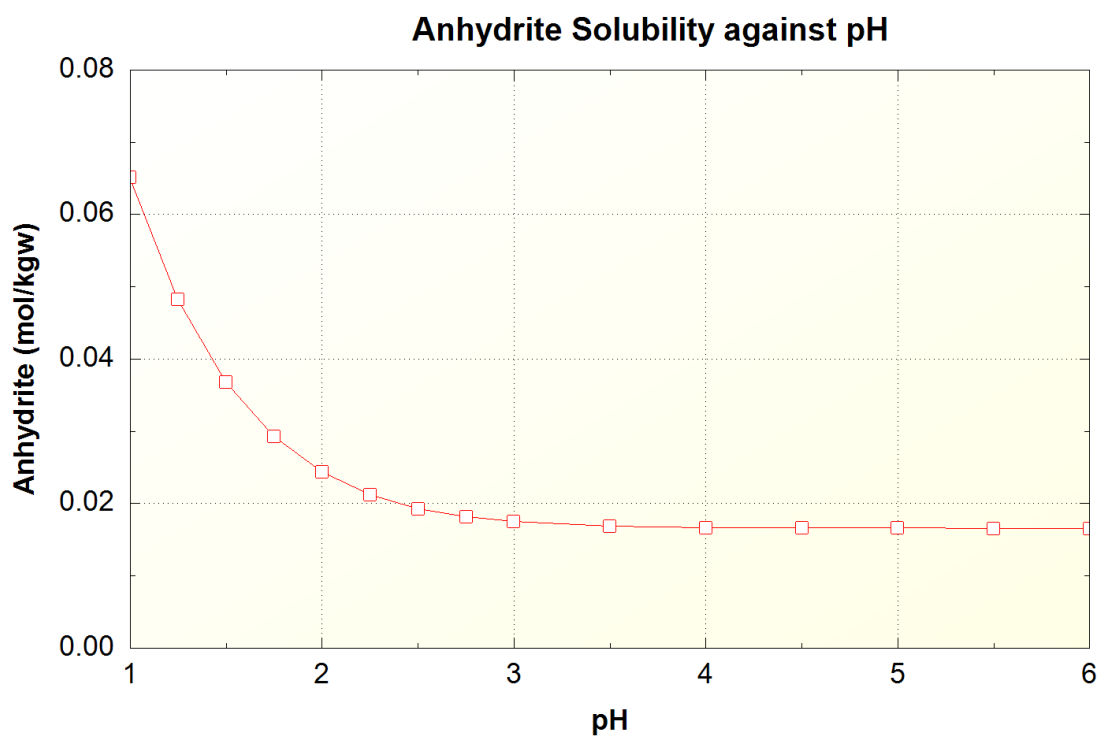
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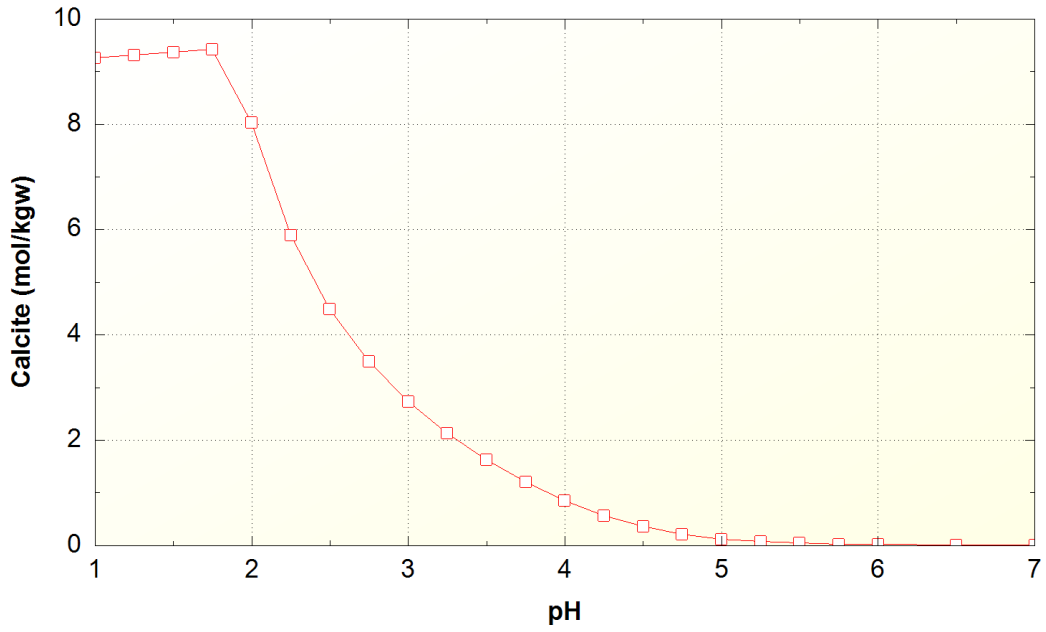
12. APPENDIX A

This section showcases every result obtained from modelling mineral solubility against temperature, pH, pressure and temperature at various pressures. Also shown are the models that provide additional insight into the secondary factors related to scaling within a geothermal system. These factors encompass: dissolution kinetics, influence of CO₂ partial pressure, transitions between two minerals, solubility against salinity and the effect of temperature on molar volumes for a select few minerals (the ones that are most significant). The graphs taken from literature are mentioned. Minerals modelled: Anhydrite (CaSO₄), barite (BaSO₄), calcite (CaCO₃), celestite (SrSO₄), dolomite [CaMg(CO₃)₂], gibbsite [Al(OH)₃], gypsum (CaSO₄.2H₂O), quartz (SiO₂), Siderite (FeCO₃) and strontianite (SrCO₃).

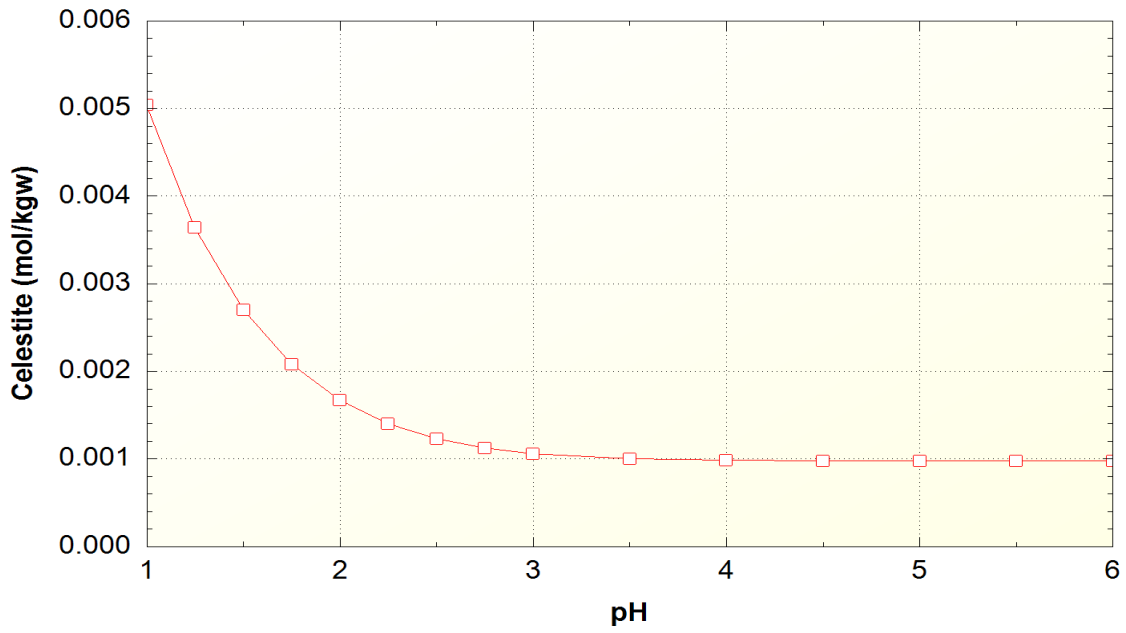
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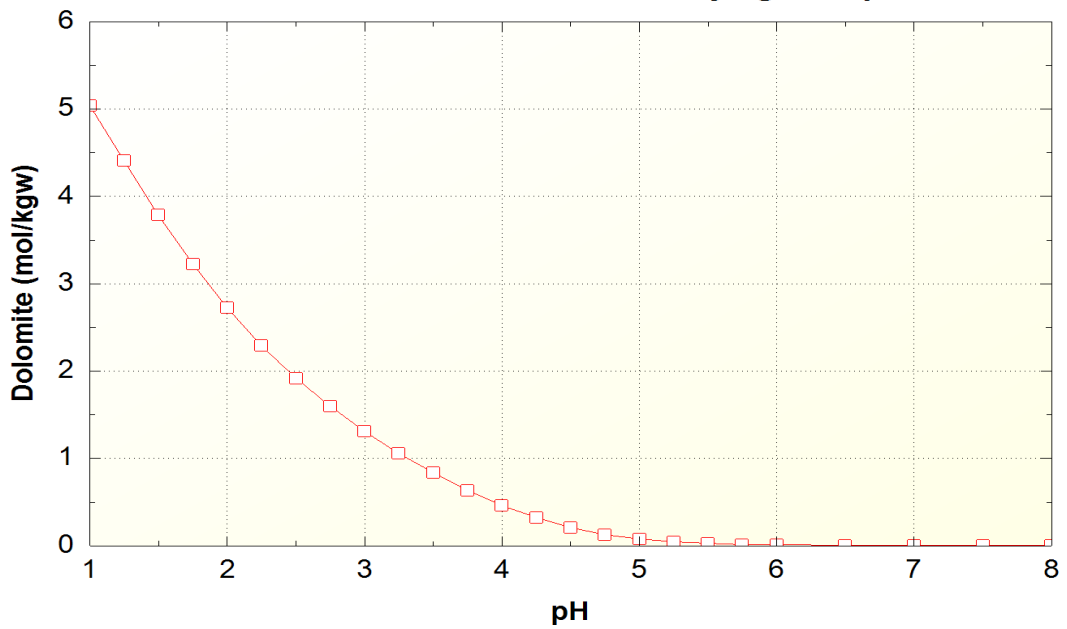
Calcite Solubility against pH



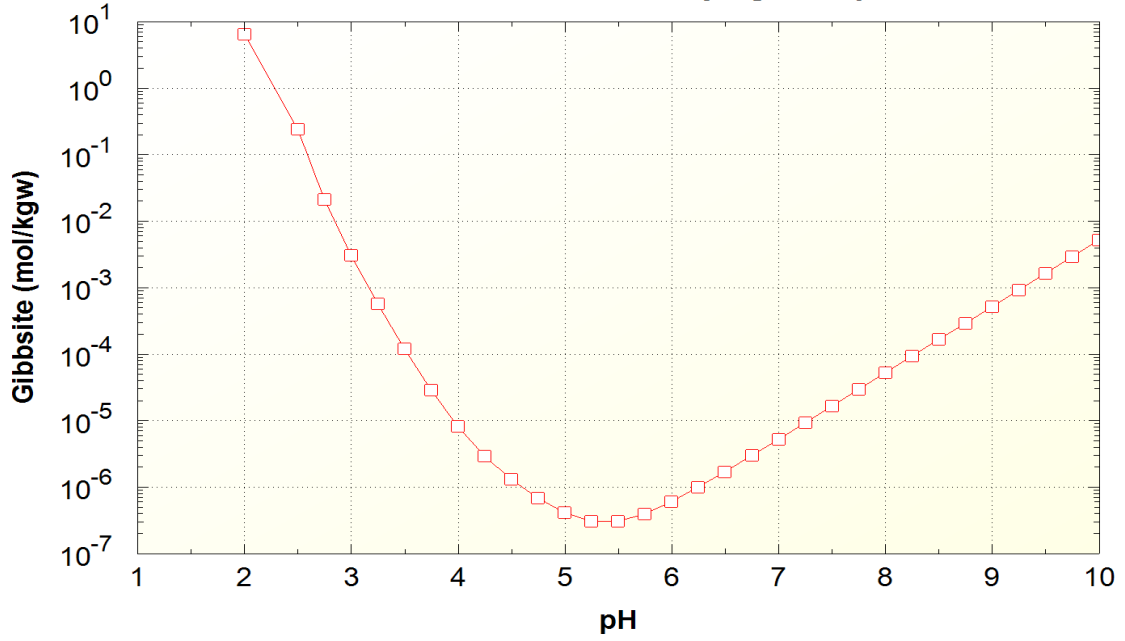
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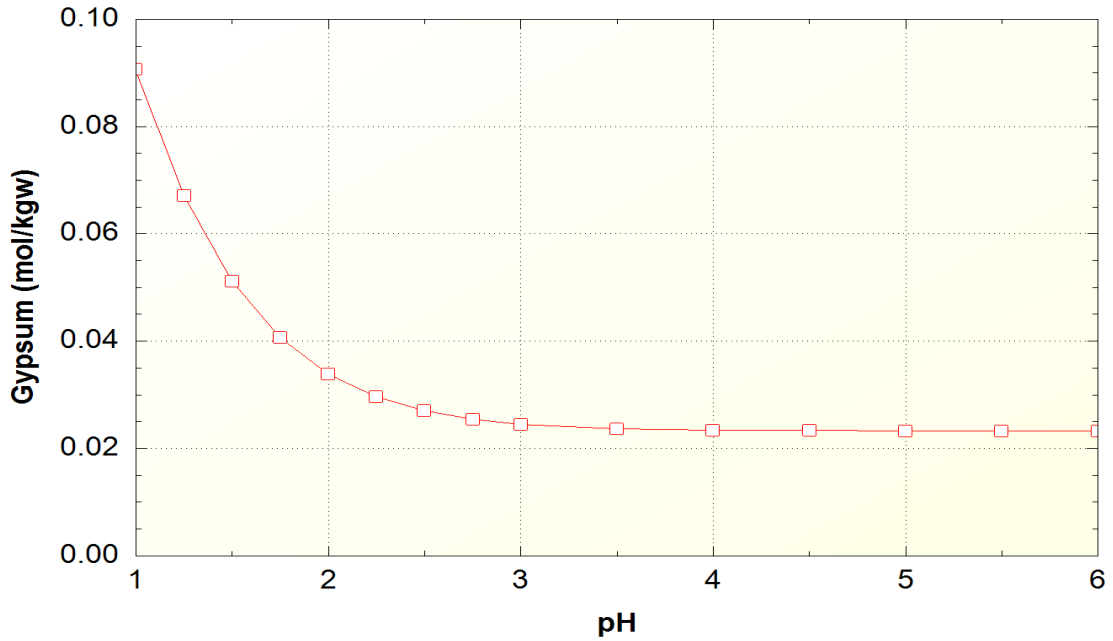
Dolomite Solubility against pH



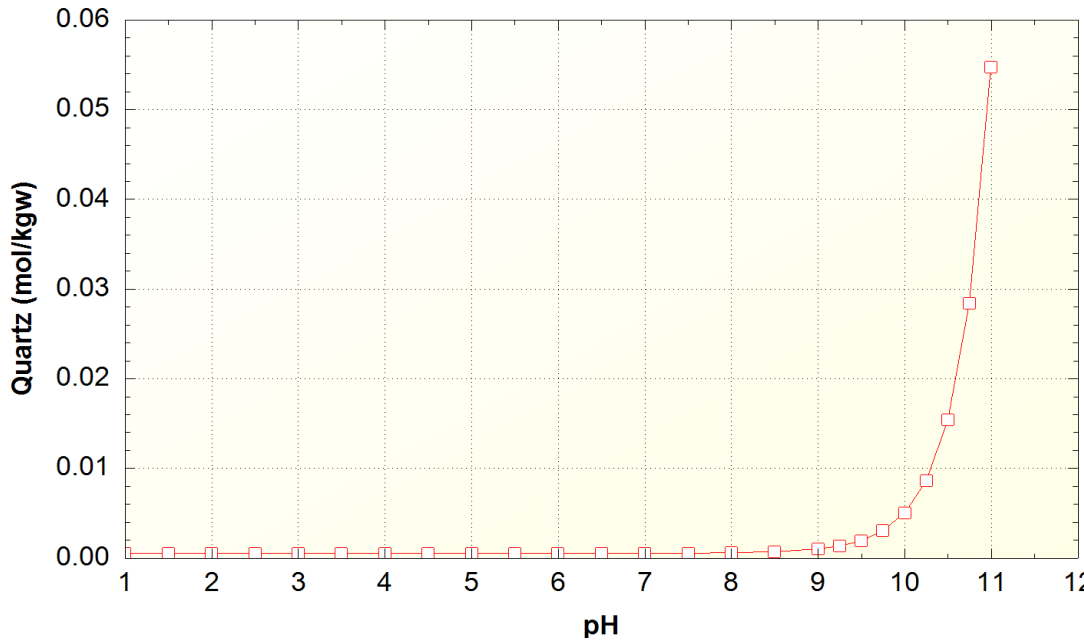
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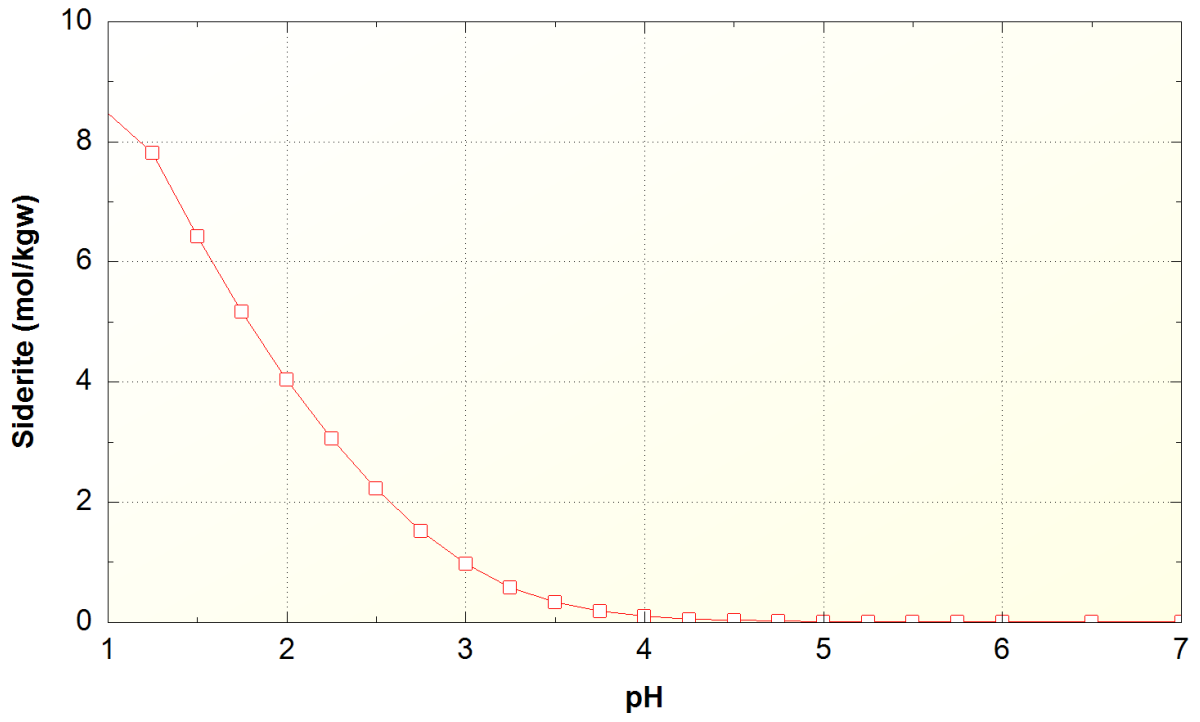
Gypsum Solubility against pH



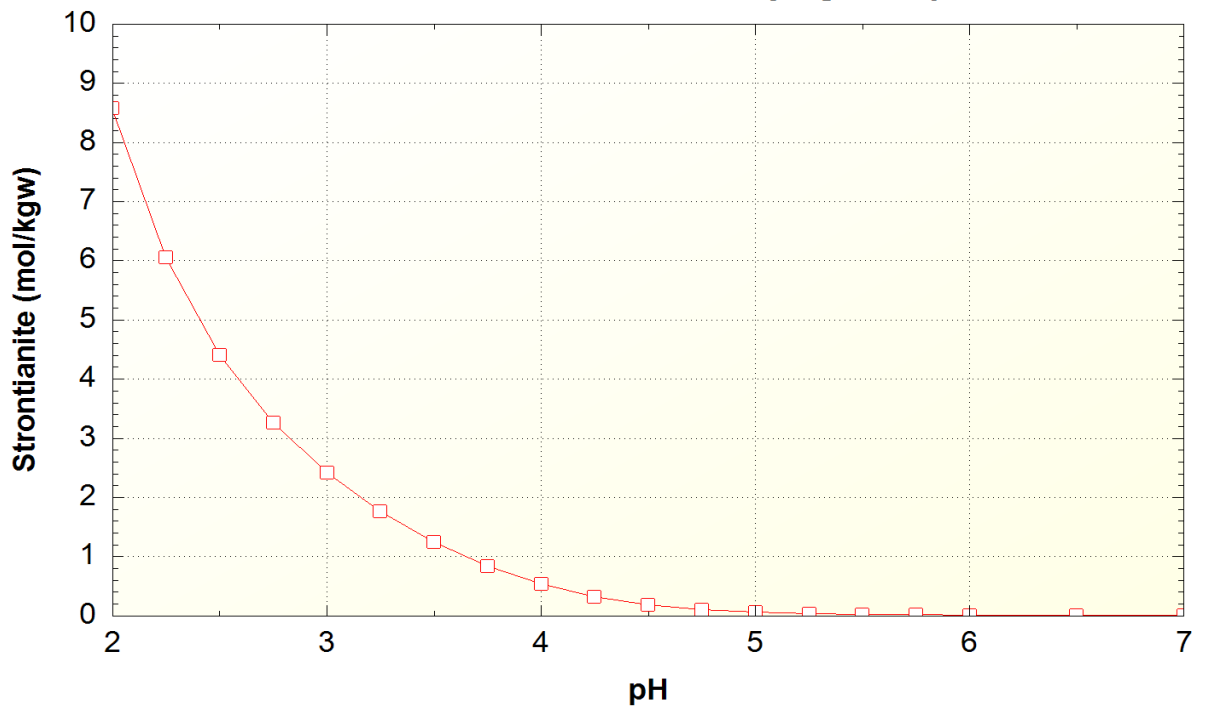
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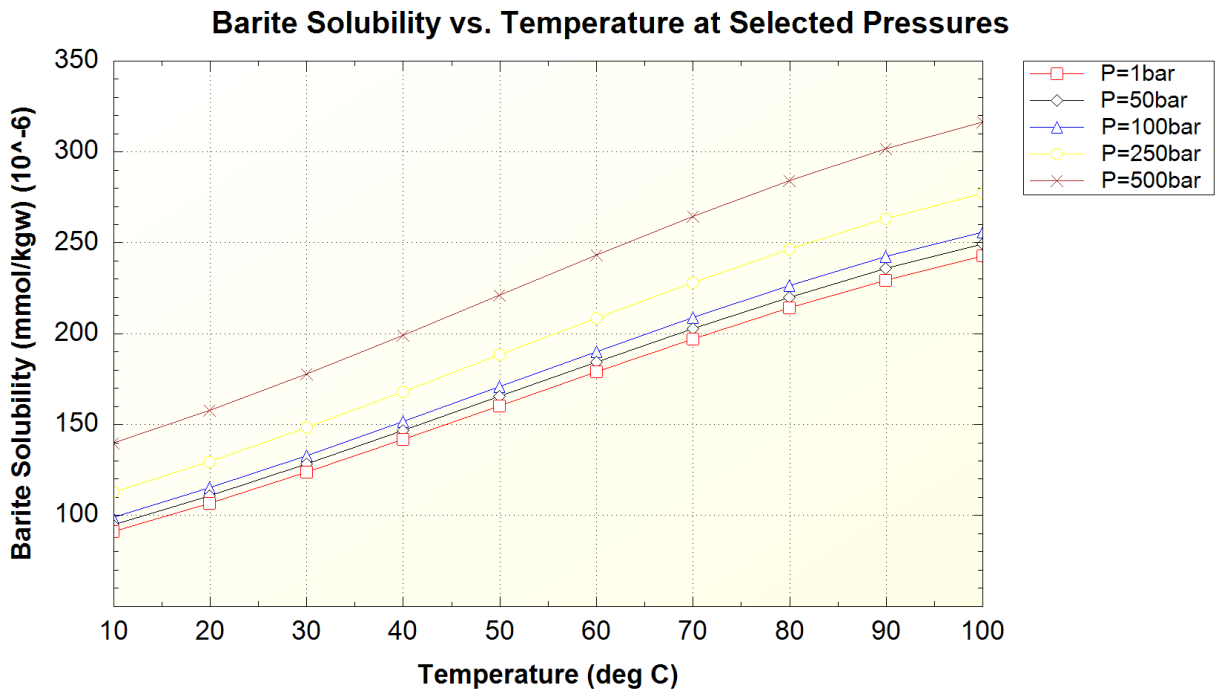
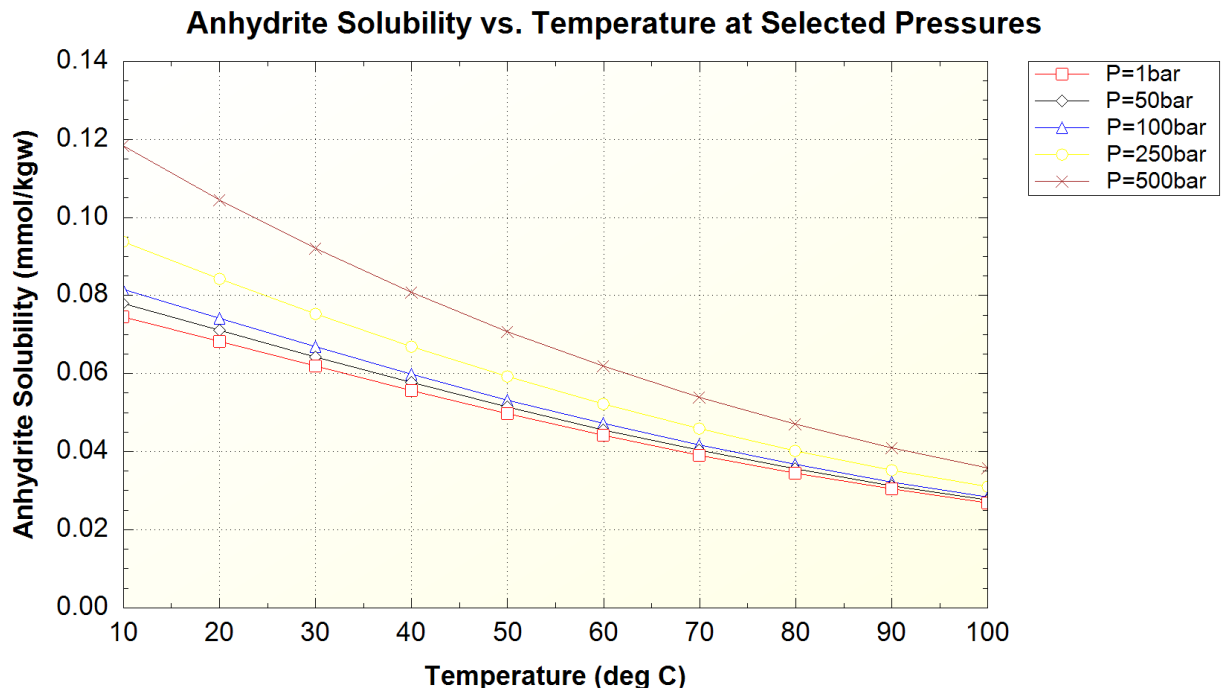
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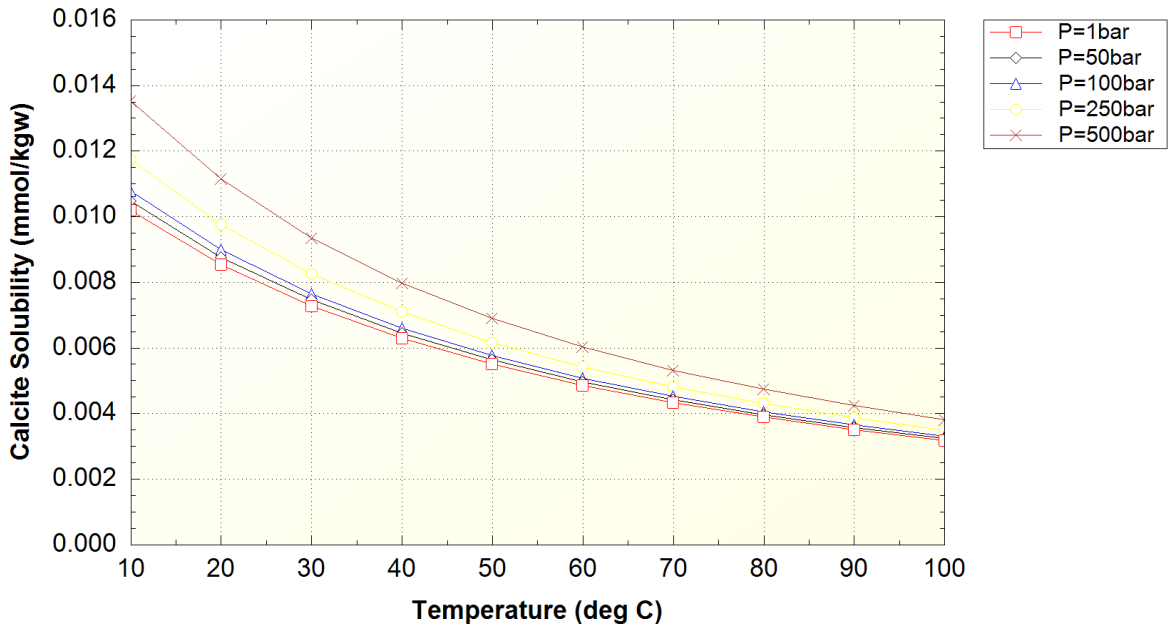
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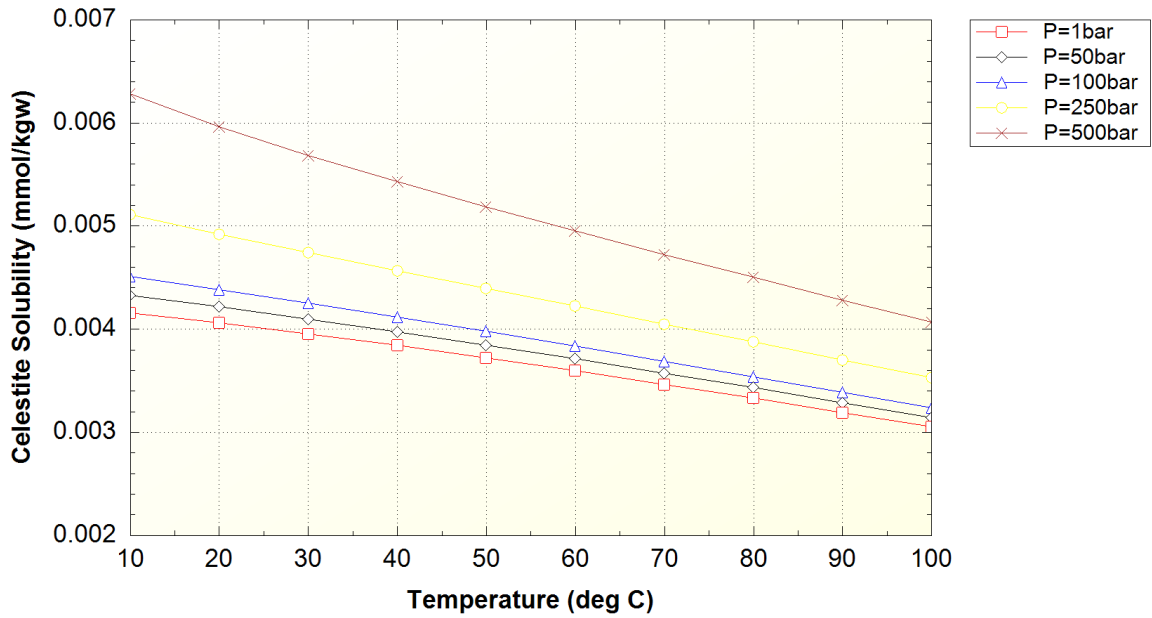
SOLUBILITY vs. TEMPERATURE at SELECTED PRESSURES



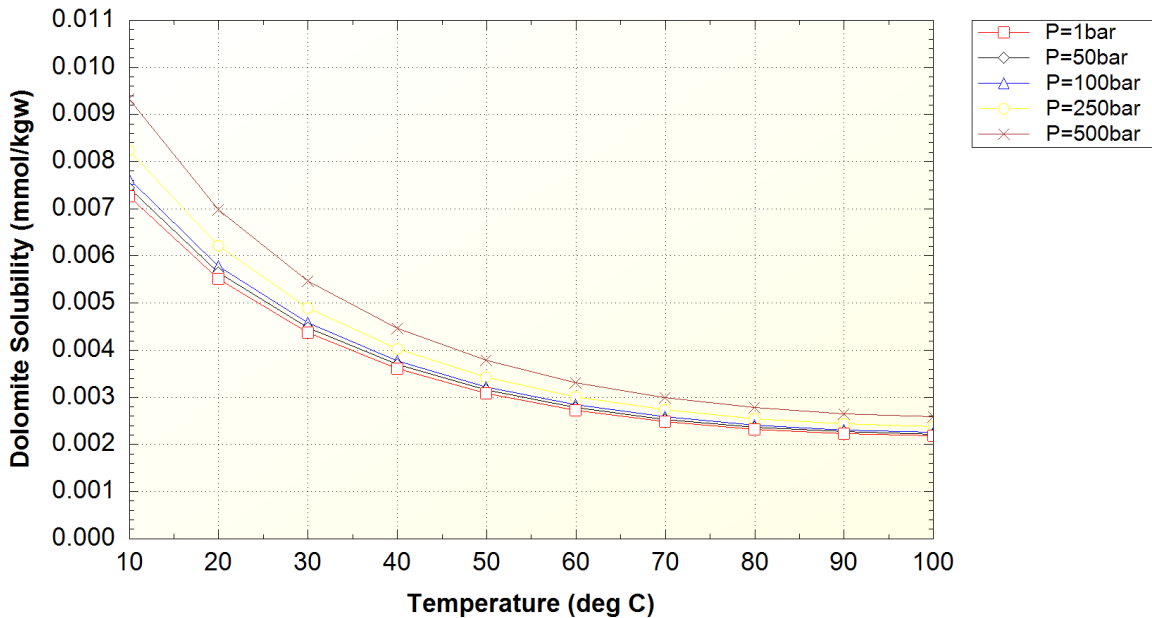
Calcite Solubility vs. Temperature at Selected Pressures



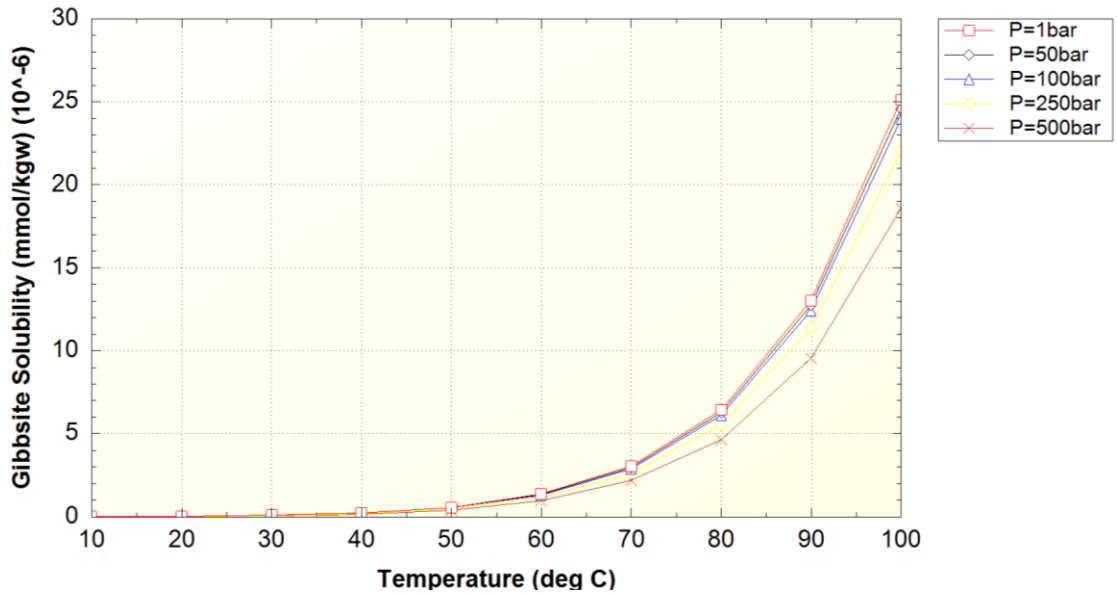
Celestite Solubility vs. Temperature at Selected Pressures



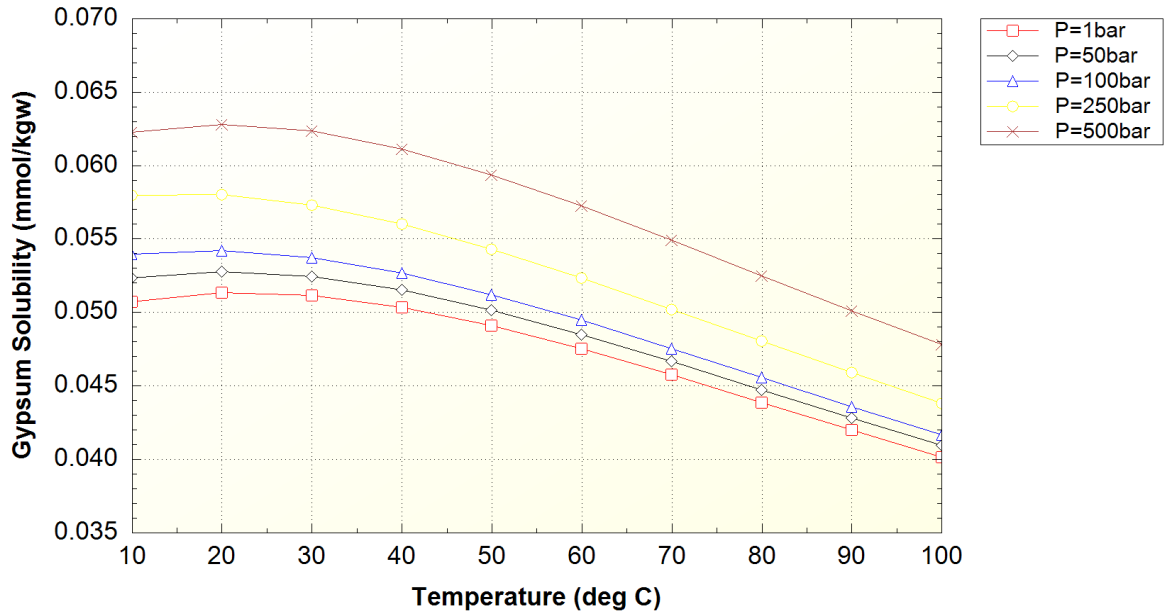
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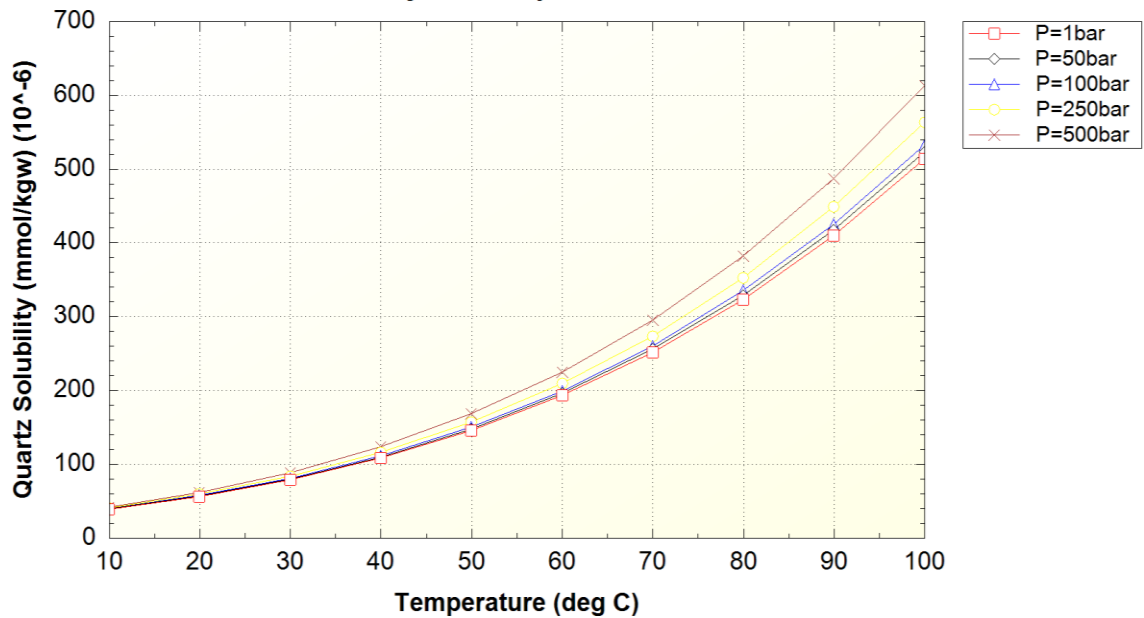
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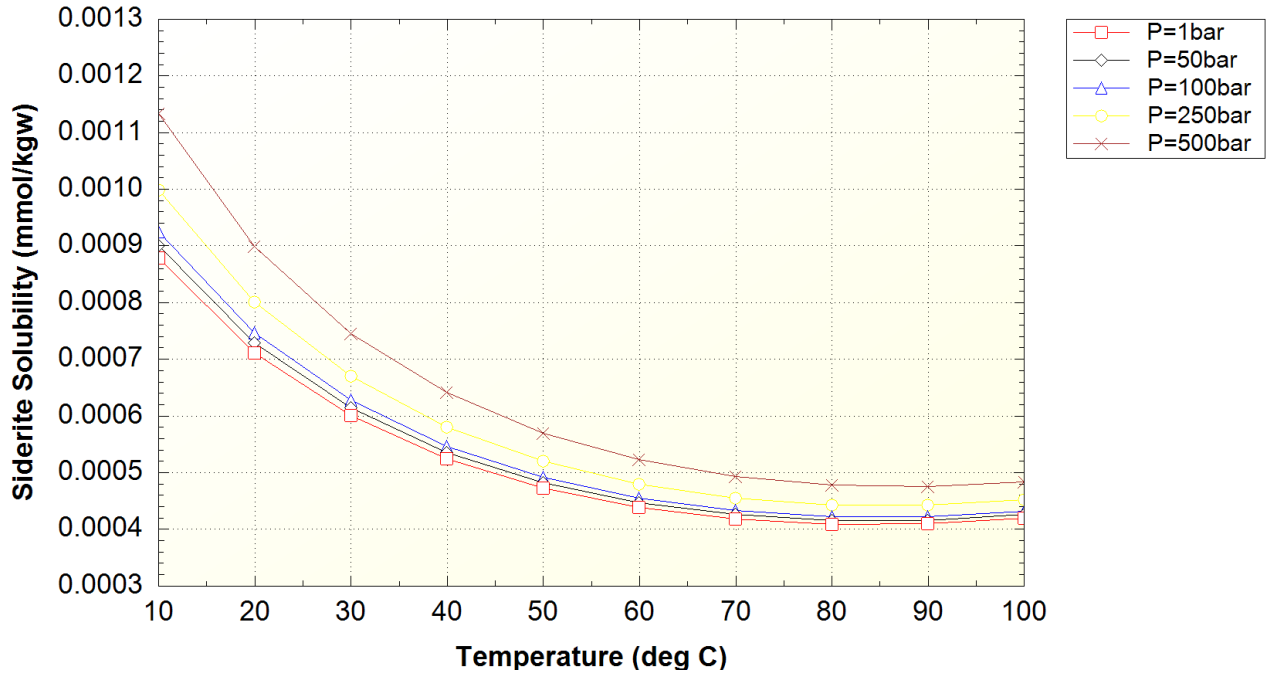
Gypsum Solubility vs. Temperature at Selected Pressures



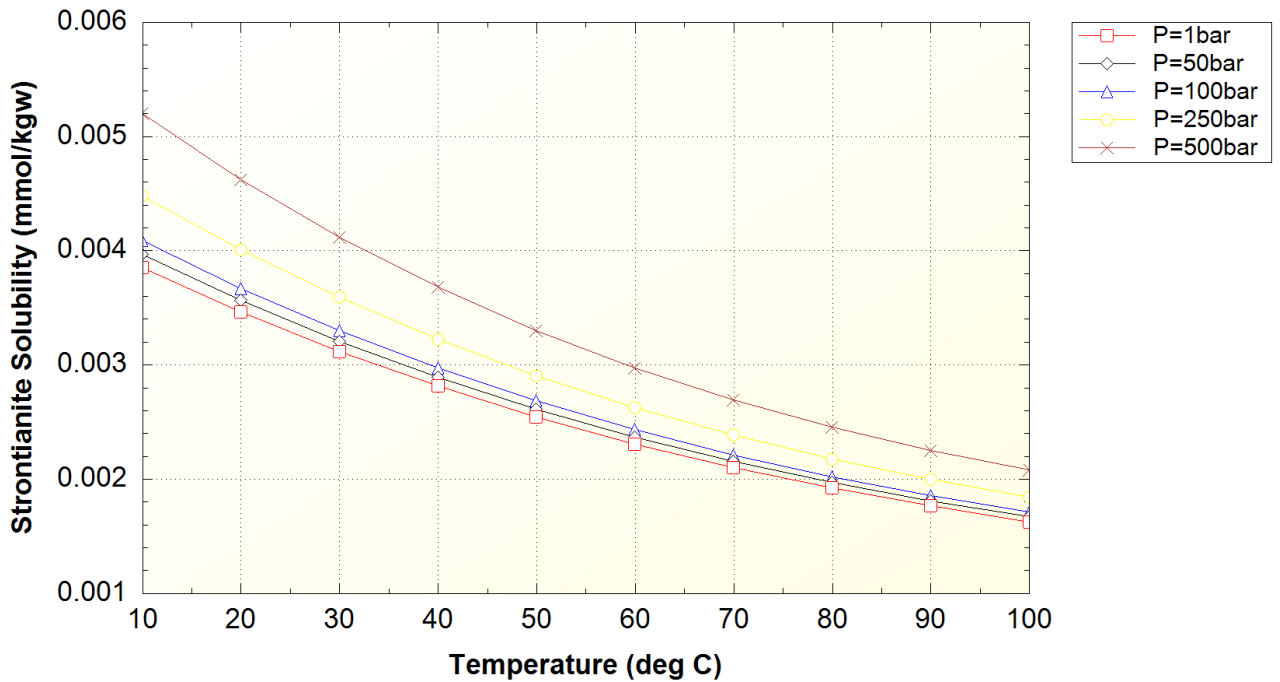
Quartz Solubility vs. Temperature at Selected Pressures



Siderite Solubility vs. Temperature at Selected Pressures

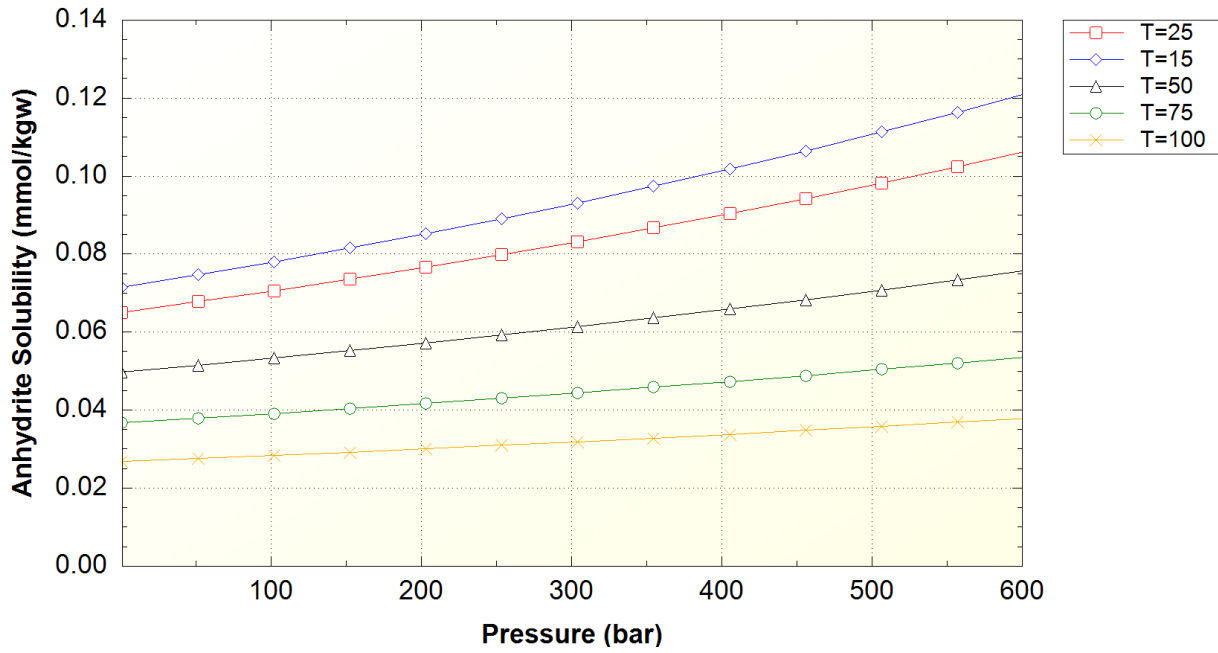


Strontianite Solubility vs. Temperature at Selected Pressures

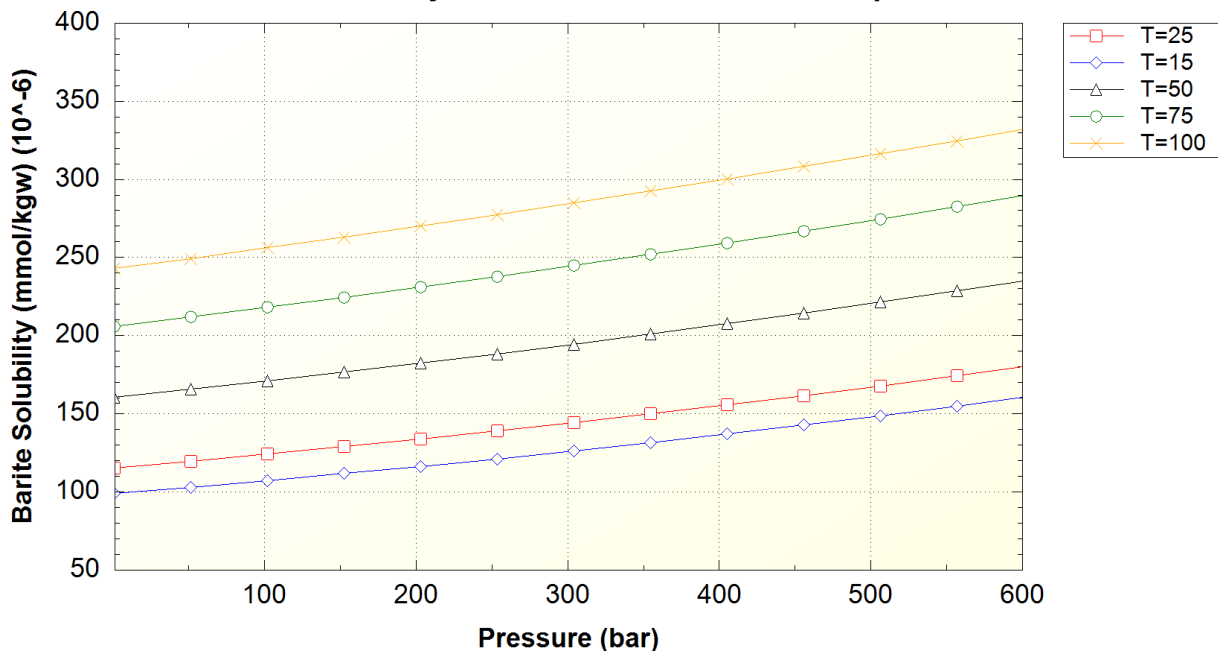


SOLUBILITY vs. PRESSURE at SELECTED TEMPERATURES

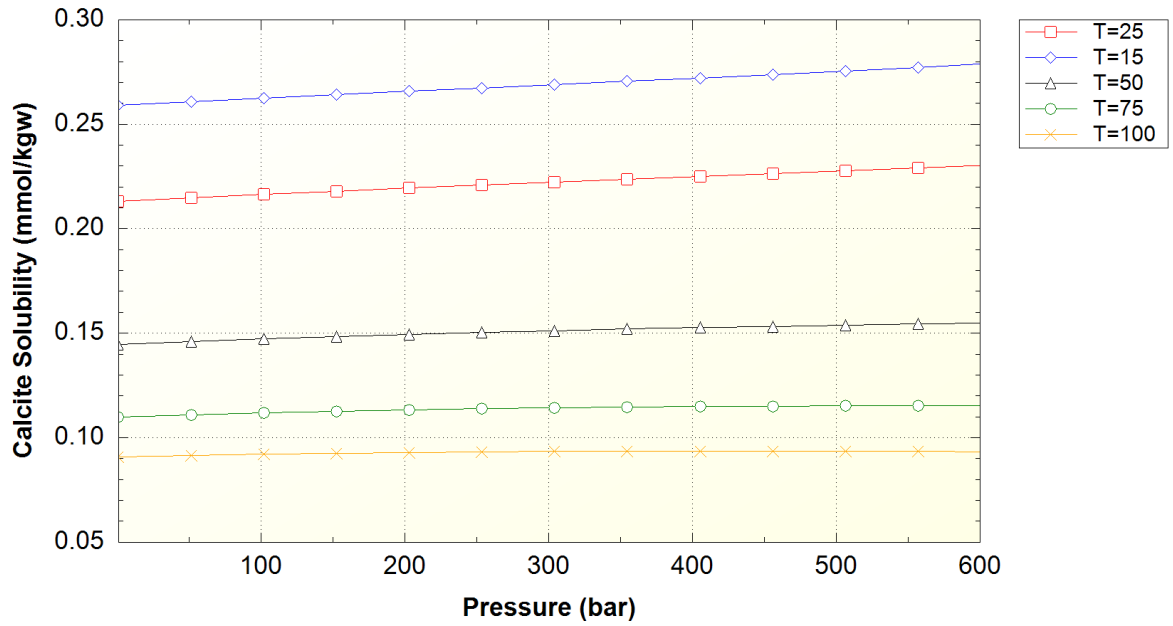
Anhydrite Solubility vs. Pressure at selected Temperatures



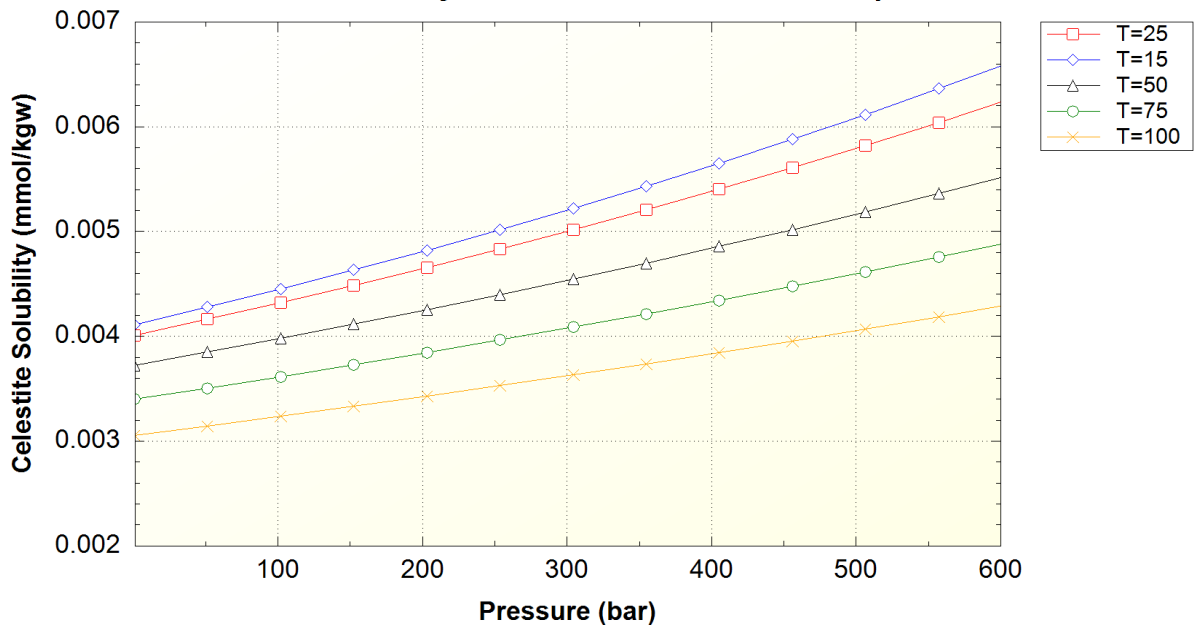
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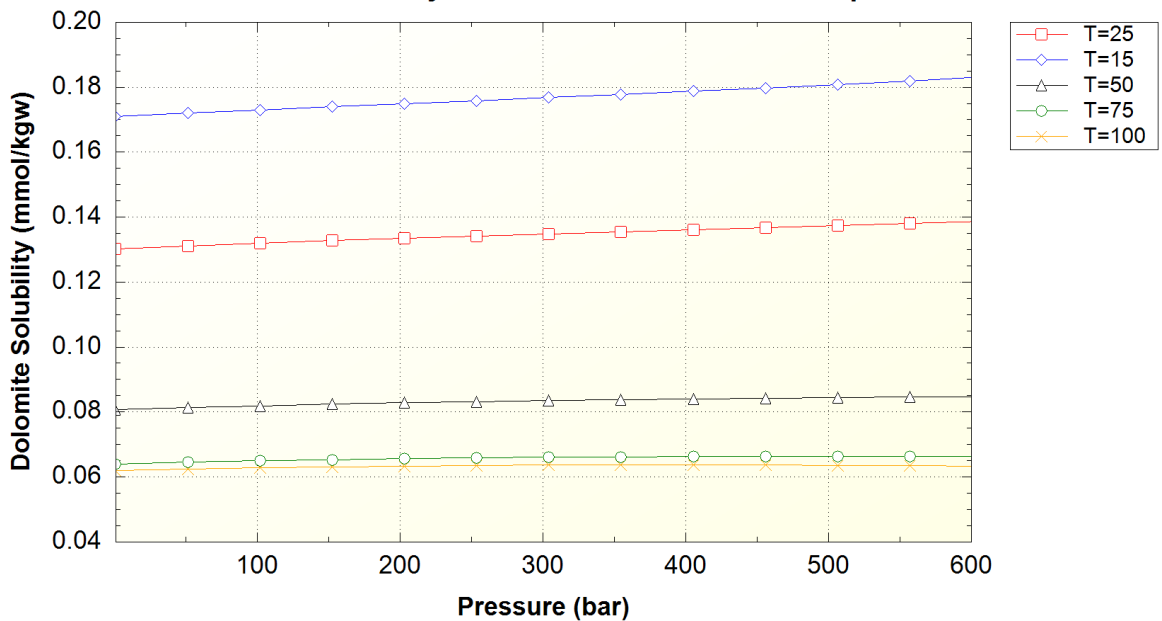
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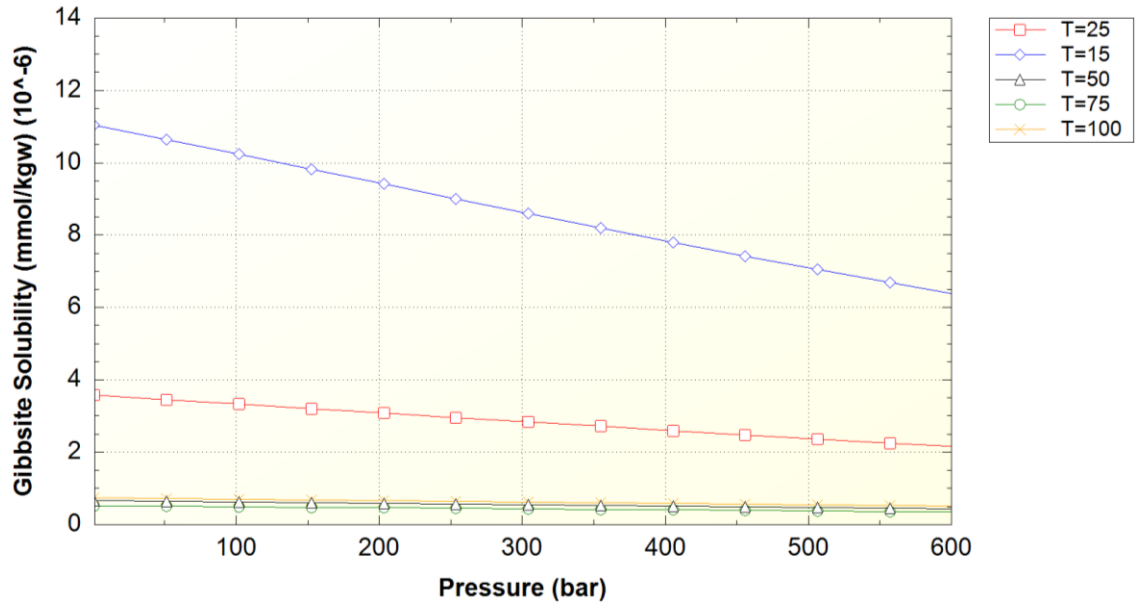
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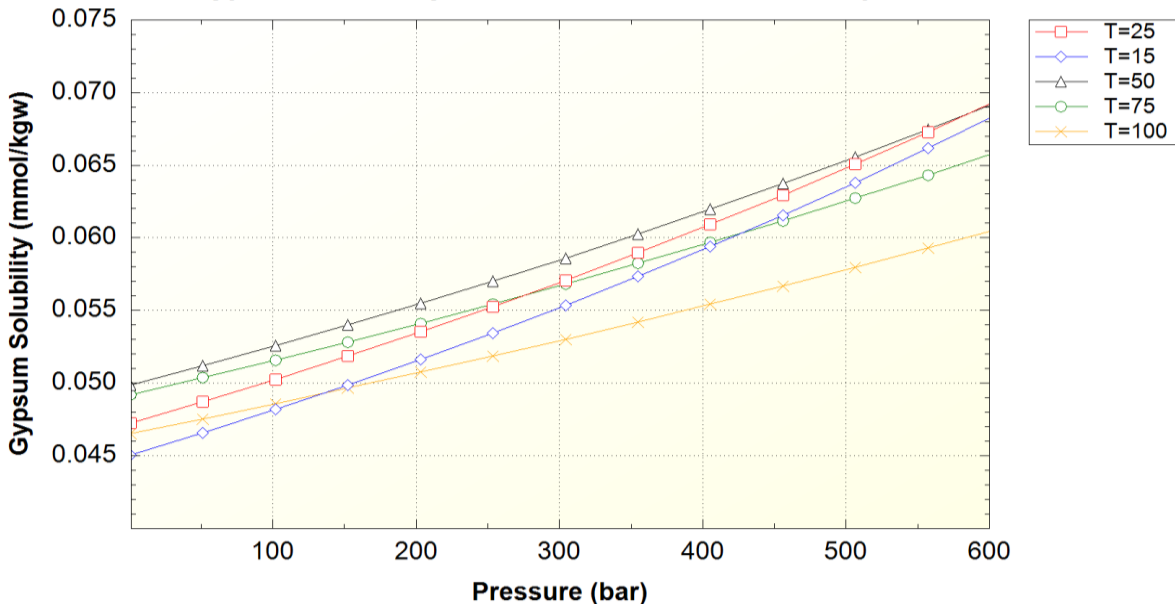
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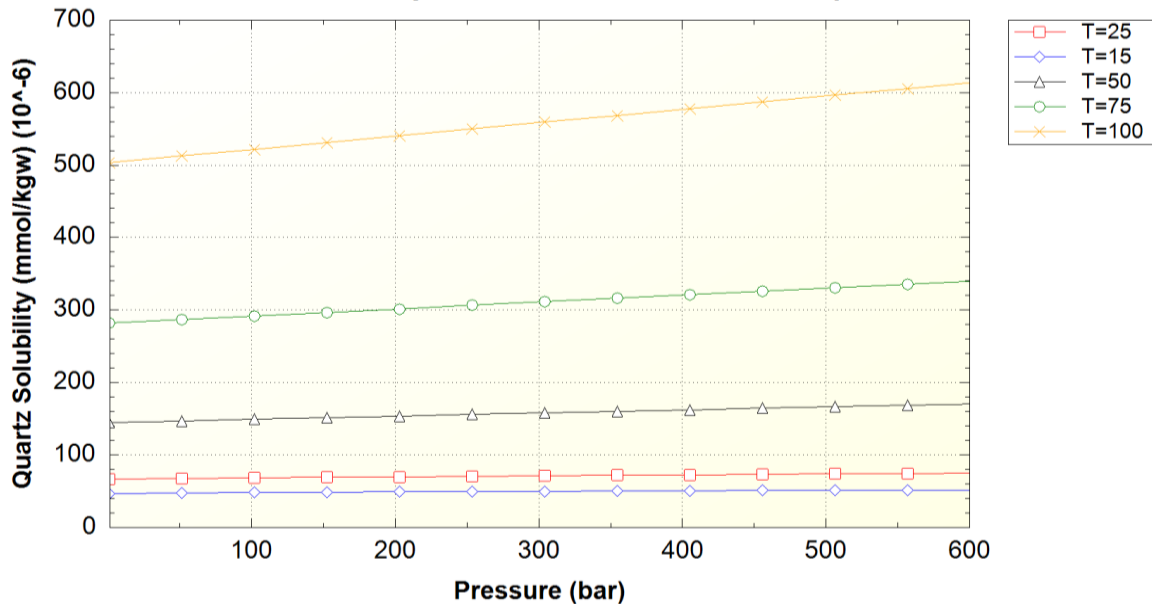
Gibbsite Solubility vs. Pressure at selected Temperatures



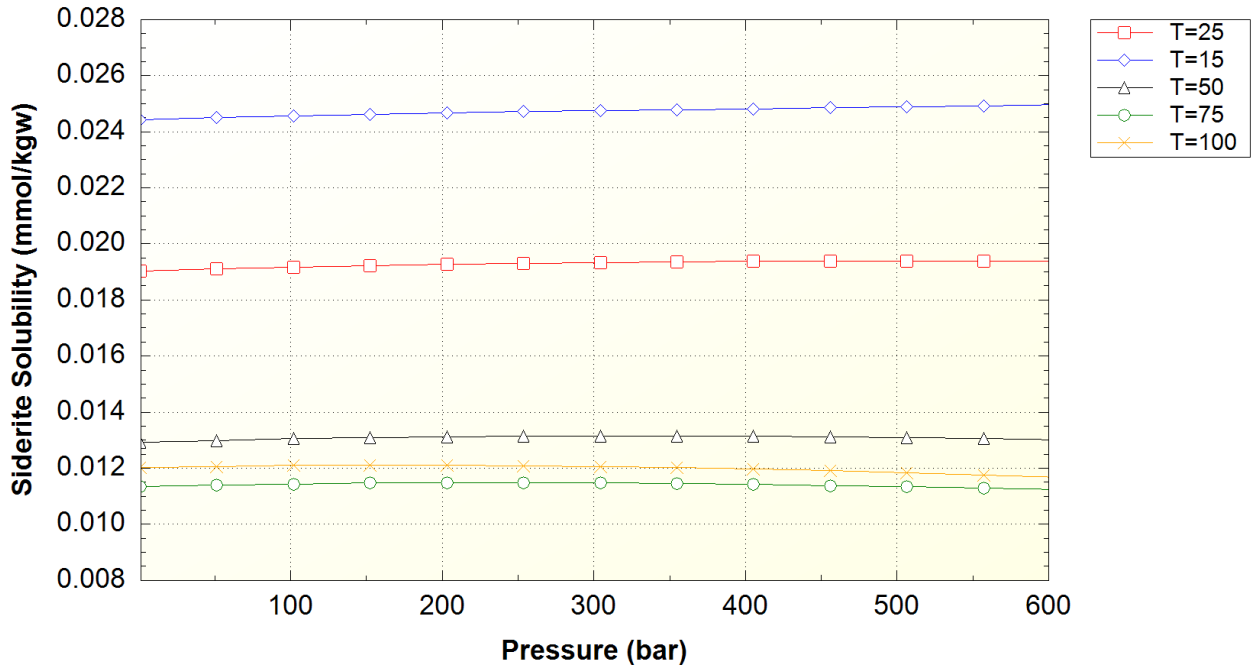
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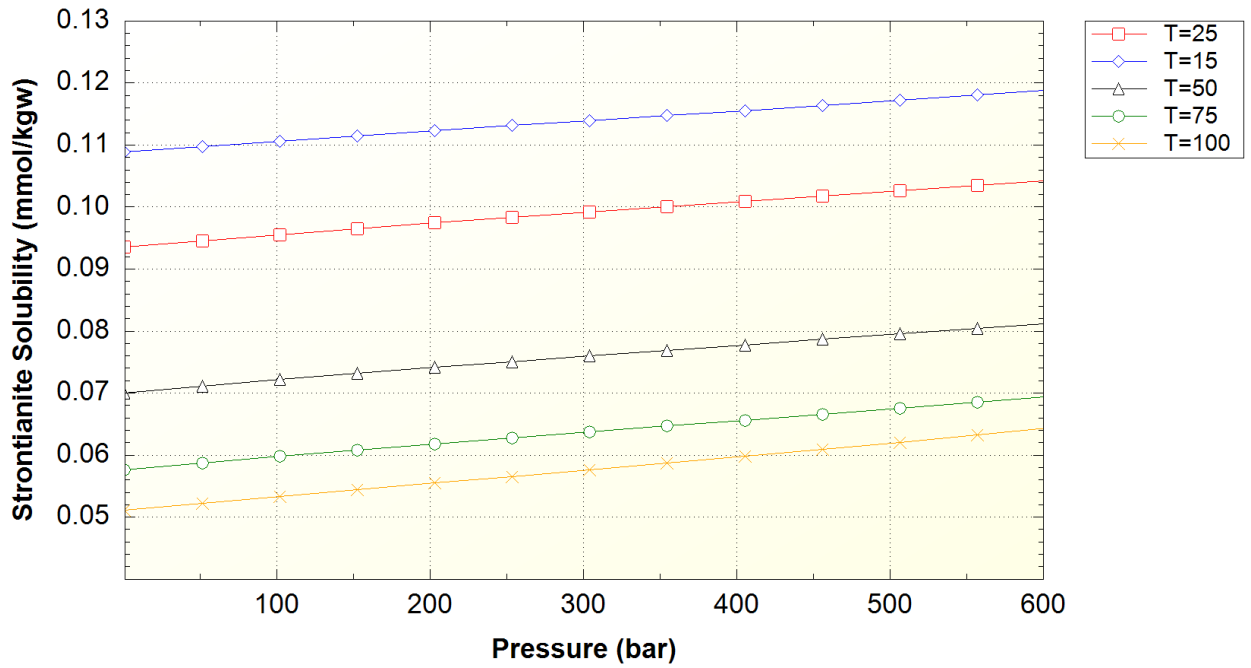
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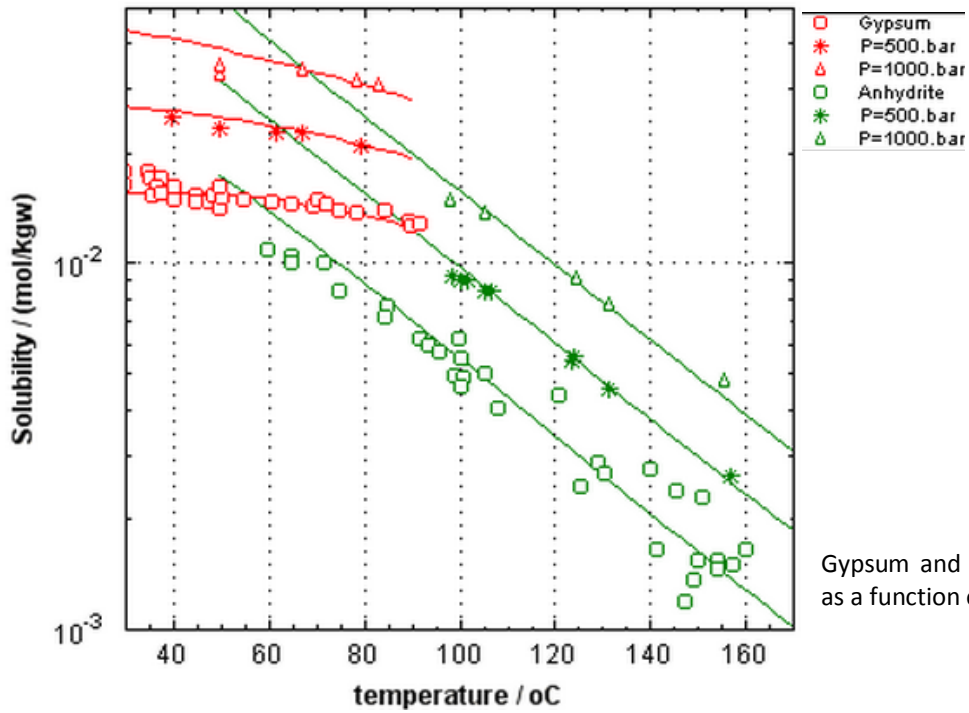
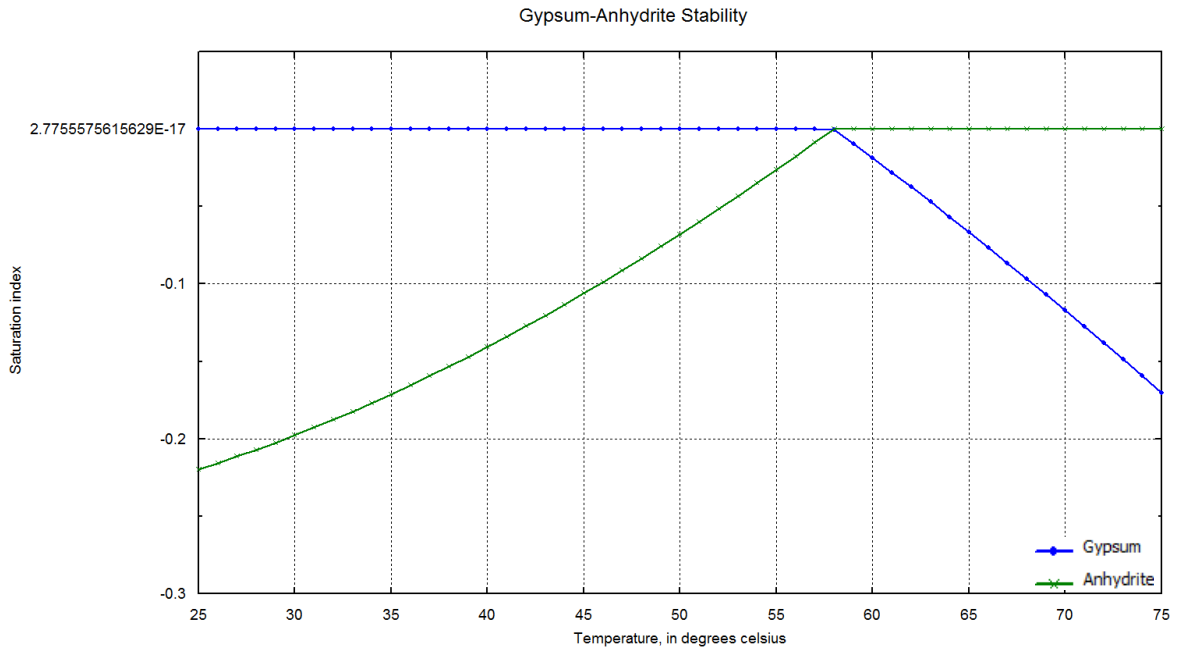
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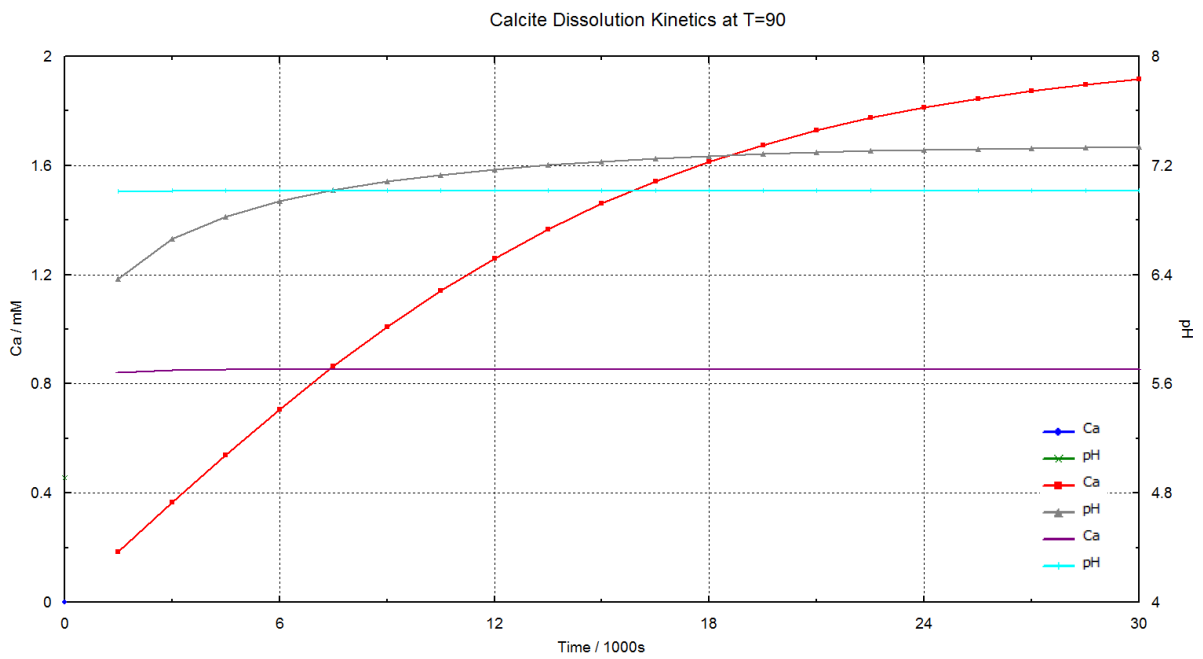
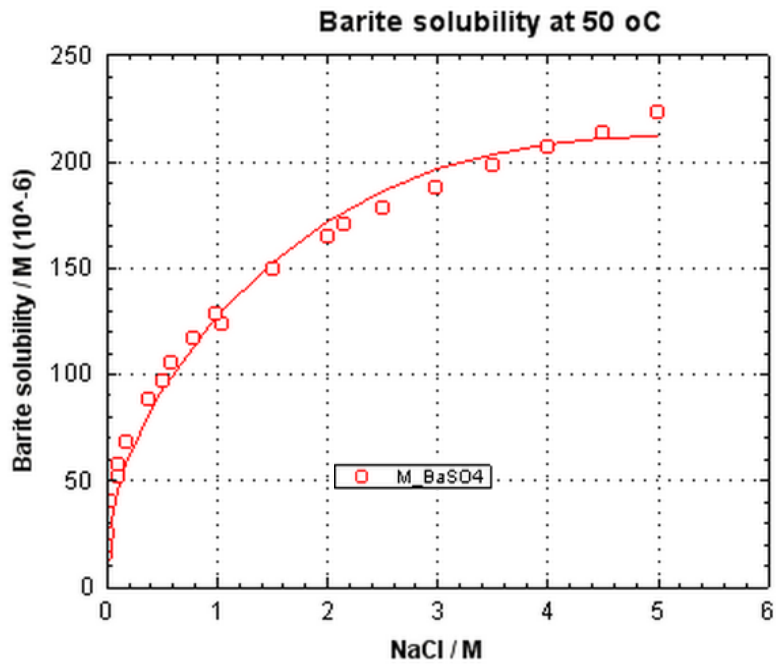
Strontianite Solubility vs. Pressure at selected Temperatures



OTHER FUNCTIONS

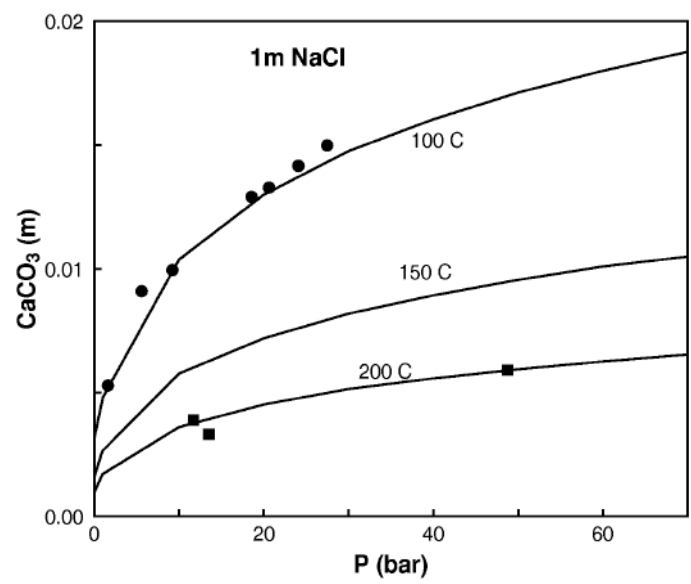
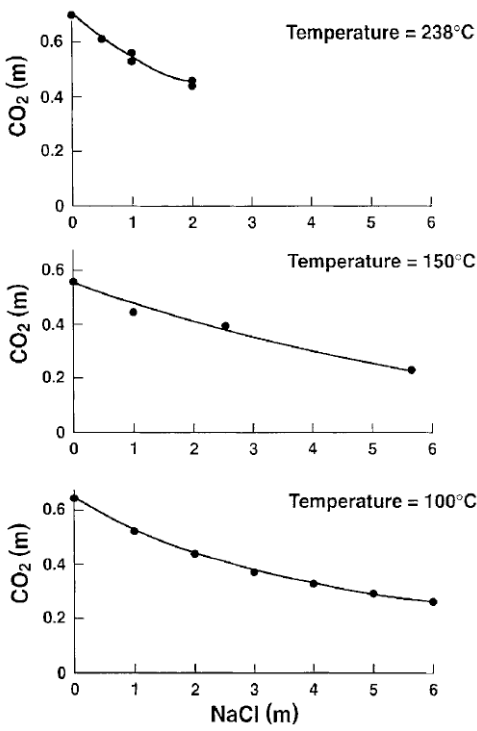
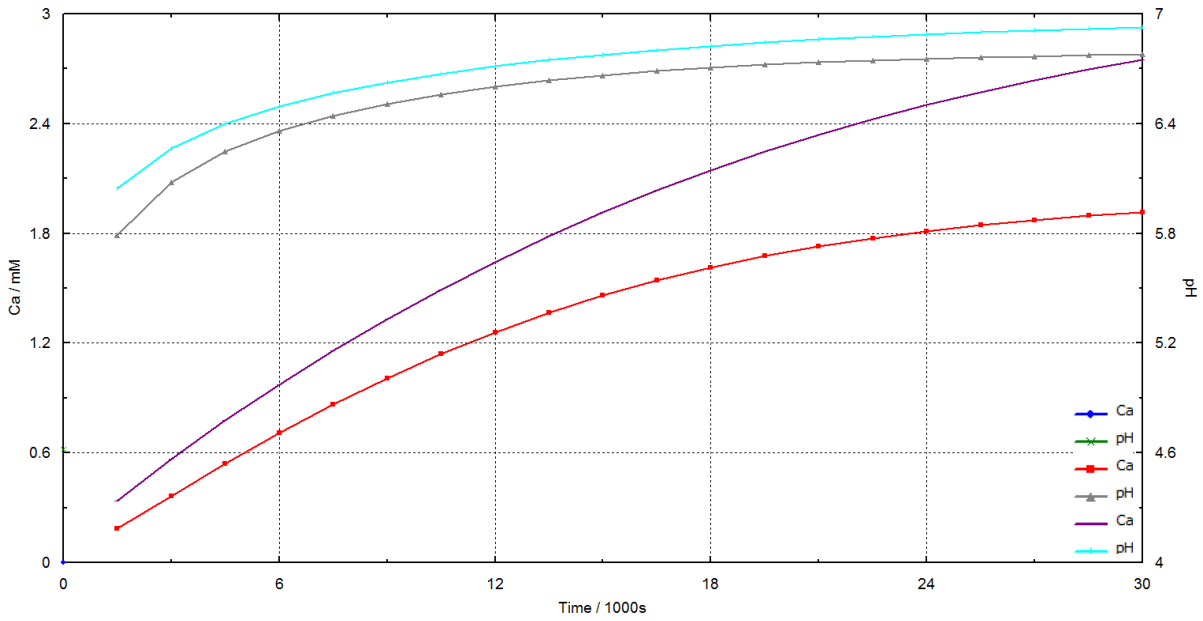


Gypsum and anhydrite solubility transitions as a function of temperature and pressures

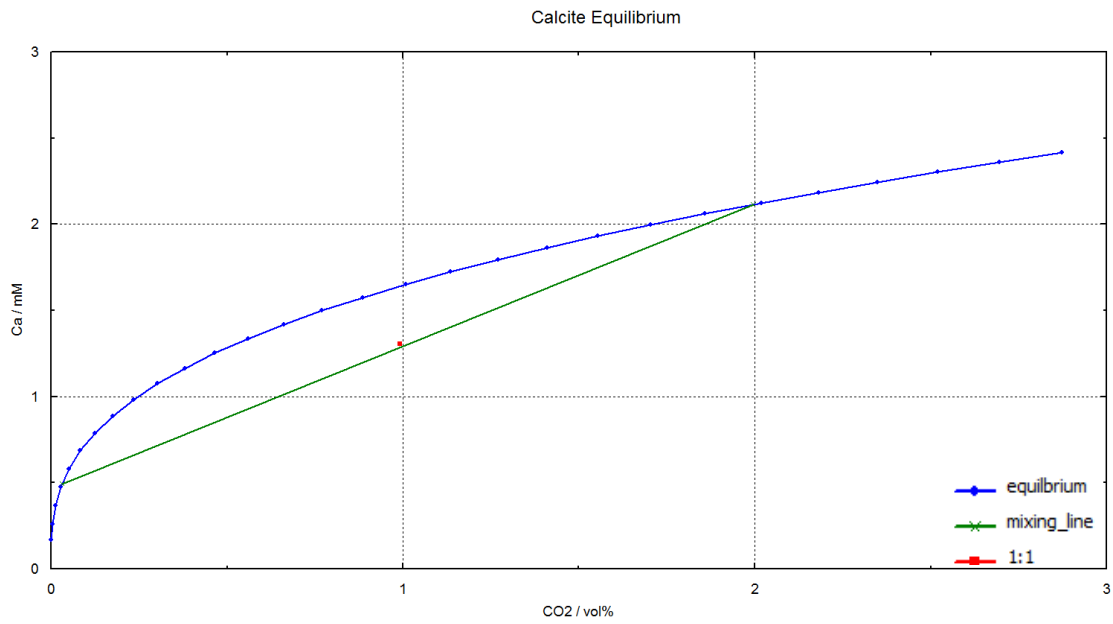


Calcite dissolution kinetics at (how calcite dissolves as a function of time) when temperature is at 90°C (above) and when temperature is at 10°C

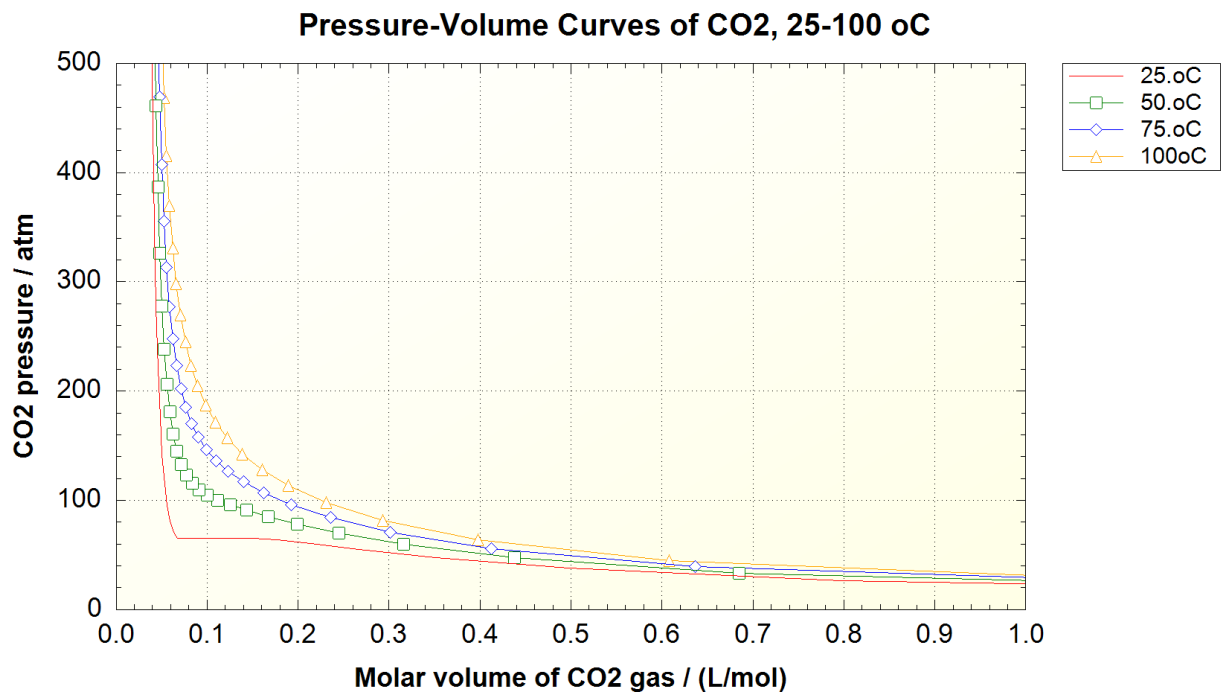
Calcite Dissolution Kinetics at T=10



Left: Solubility of CO₂ in NaCl solutions at P_{CO2} = 73.5 atm. The circular symbols show the experimental data taken from Malinin and Kurovskaya, 1975 (for both 100°C and 150°C), and from Ellis and Golding, 1963 (for 238°C). The solid black line is taken from Møller et al., 1998. Right: Calcite solubility against CO₂ partial pressure at 100°C, 150°C and 200°C in 1m of NaCl solution. The circular symbols are data taken from Holland et al., 1963 while the solid line is taken from Møller et al., 1998



Calcite dissolution as a function of CO₂ pressure



Input parameter	Value	Unit
Well depth	3165.0	m
Water flow rate	1313.4	dm ³ /min
Water temperature	171.0	°C
TDS	24855.0	mg/dm ³
Gas flow rate	6986.1.0	dm ³ /min
Gas temperature	171.0	°C
Wellhead pressure	45.0	bar
Separated GWR	1700.0	Ndm ³ /m ³
	CO ₂ 16.270 vol.%	
	CH ₄ 79.440 vol.%	
	N ₂ 4.290 vol.%	
Dissolved GWR	3400.0	Ndm ³ /m ³
	CO ₂ 32.250 vol.%	
	CH ₄ 61.910 vol.%	
	N ₂ 2.840 vol.%	
Water composition	Ca ²⁺ 1.335.10 ⁻³	mol/kg
	Mg ²⁺ 3.350310 ⁻⁴	mol/kg
	Na ²⁺ 3.453.10 ⁻¹	mol/kg
	SO ₄ ²⁻ 2.380.10 ⁻⁴	mol/kg
	Cl ⁻ 3.179.10 ⁻¹	mol/kg
	A _{TOT} 2.600.10 ⁻²	mol/kg

Left: Water and gas compositional analysis that can be used as an input for scale prediction and/or modeling. Below: distance-SI-temperature; and a distance-SI-pressure graph

