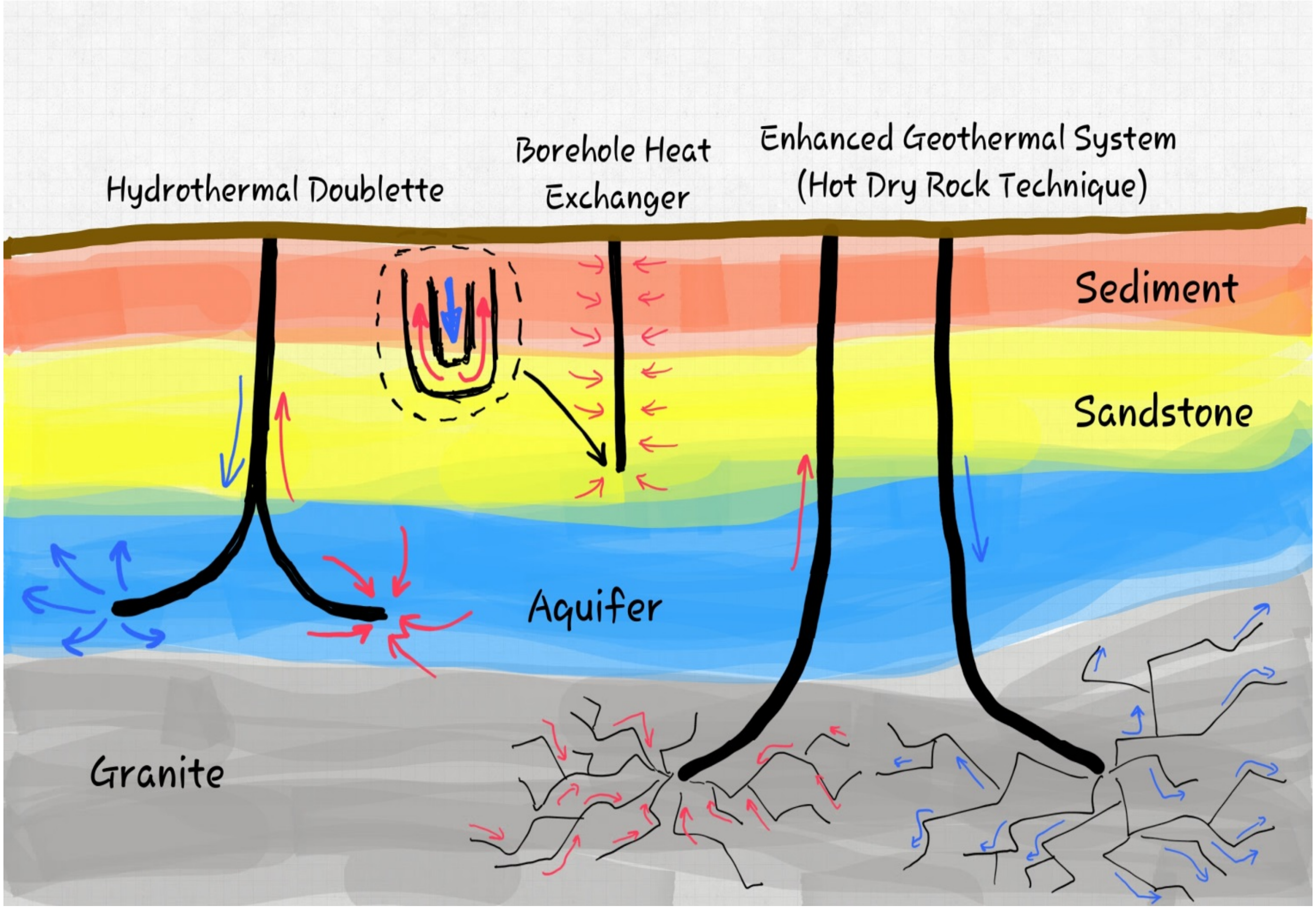
NAVEEN ILANGOVAN

Two Scale Analysis on the Effect of Calcite Dissolution in Geothermal Sandstone Reservoirs: An Experimental and Numerical Study



Two-Scale Analysis of the Effect of Calcite Dissolution in Geothermal Sandstone Reservoirs: An Experimental and Numerical Study

By
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ABSTRACT

Experimental studies and three dimensional finite element core scale and field scale models were used to study the effect of calcite dissolution on low-enthalpy sandstone geothermal reservoirs. A series of core flooding experiments were conducted, monitoring the porosity and permeability at 150 ◦C and 20 bars back pressure to see the effect of calcite dissolution by Glutamic acid Di-Acetic acid (GLDA). These experiments are supported by the critical salt concentration and critical fines migration velocity tests in order to ensure that any pressure variations in the core is due to the injected chelating agent and not due to other mechanical effects or chemically damaging reactions. This data obtained is then used in a core scale finite element model to obtain the corresponding kinetic and dissolution parameters. These parameters are then implemented on a field scale (homogeneous and heterogeneous) reservoir model to see the effect of calcite dissolution on the well productivity. Process based facies modelling is utilised to construct realistic heterogeneous reservoir models.

In an effort to understand the effect of flow direction in the reservoir, samples were tested for the critical velocity of fines migration in three directions and it was observed that the critical velocity of fines migration in the different samples were similar, showing the homogeneous nature of the samples.

From the homogeneous field scale model, for a given volume of acid injected, the effect of calcite dissolution was analysed for 5, 10, 30 and 50% calcite concentration in the reservoir. The estimated values of well productivity and equivalent permeability for 10, 30 and 50% calcite concentration were found to be in a decreasing order with 10% having the highest value. Interestingly, in the case of 5% calcite concentration the well productivity and equivalent permeability were estimated the lowest. In the case of power required by the pump the 5% calcite concentration required the highest power while the 10%, 30% and 50% were found to be in a increasing order with 10% calcite concentration requiring the least power. Although the acid penetration for the 5% calcite concentration was the furthest, the permeability improvement was too low to have a positive impact on the equivalent permeability, well productivity and power required by the pump. From the heterogeneous model, it was observed that the lifetime of the reservoir increases with increasing stimulation. This model could be used as a predictive tool for estimating the lifetime increment for a given volume of acid injected. Our simulation results show that the penetration depth (acid front) of acid is highly affected by the radial flow characteristics in field scale simulations, as the penetration depth is not linearly correlated to the volume of acid injected.

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LIST OF ABBREVIATIONS

MW_e	Megawatt Electricity
mD	Milli Darcy (10^{-15} m^2)
dP	Pressure Difference Between Two Points
WX	Wesersandstein Rock Sample Drilled In X-Direction
WY	Wesersandstein Rock Sample Drilled In Y-Direction
WZ	Wesersandstein Rock Sample Drilled In Z-Direction
NaCl	Sodium Chloride
GLDA	Glutamic acid-Diacetic Acid
H_2GLDA	Dihydrogenglutamicacid-Diacetic Acid
HCl	Hydrochloric Acid
EDTA	Ethylenediamine-Tetraacetic Acid
DTPA	Diethylenetriamine-Pentaacetic Acid
NTA	Nitrilotriacetic Acid
HEDTA	Hydroxyethylene-Diaminetetraacetic Acid
RMA	Regular Mud Acid
OCA	Organic Clay Acid
IEA	International Energy Agency
µD	Micro-Darcy (10^{-18} m^2)
CO_2	Carbon Dioxide
MB	Main Buntsandstein
L	Length of the core (m)
D	Diameter of the core(m)
r_w	Radius of the well (m)

1 INTRODUCTION

1.1 Motivation

Geothermal Energy is the heat energy stored below the earth's surface. The potential for geothermal energy is limitless and it had been used to heat up baths, water and other common purposes that can be traced back to over 10,000 years ago. The commercial harnessing of geothermal for other purposes such as electricity generation and space heating started only in the early 20th century. Currently, geothermal energy is considered as one of the best forms of renewable, clean, constant and available worldwide energy sources (K Kaygusuz et al., 2004). The utilization of geothermal energy has been constantly increasing in both electricity generation as well as direct usage. The Figures 1.1 and 1.2 show the growth of geothermal energy from 1975 to 2010.

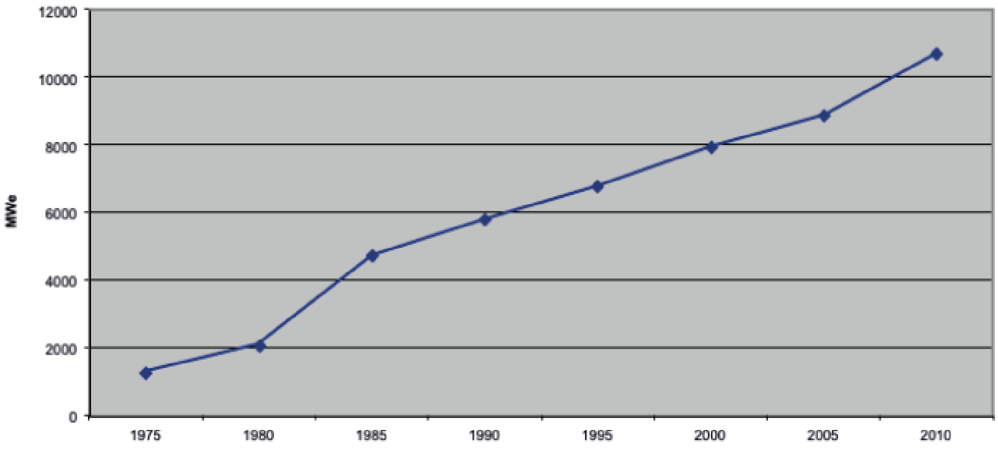

Figure 1.1: Worldwide growth of installed geothermal electricity generating capacity (IEA., 2011)

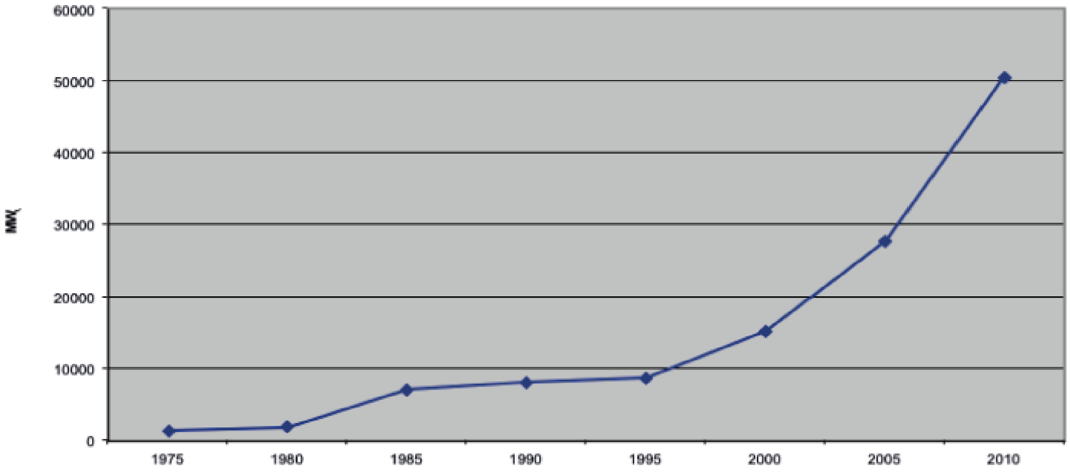

Figure 1.2: Worldwide growth of installed geothermal direct use capacity (IEA,2011)

Geothermal systems are basically divided into high enthalpy and low enthalpy geothermal systems. This work is focused on deep low enthalpy sandstone reservoirs. Sandstones are primarily composed of quartz grains, matrix and cement material such as calcite, iron oxide, silica cement or clay. The target formation for this project was the Lower Germanic Triassic group in the Netherlands. Most of such geothermal resources lack fracture permeability and hence resulting in poor fluid circulation (K Pruess., 2006).An enhanced geothermal system aims at utilizing such resources by enhancing the permeability of such regions by using techniques such as matrix/fracture stimulation. Matrix stimulation is a common procedure used in both the hydrocarbon as well as the geothermal energy production to enhance the productivity as well as remove formation damage by dissolving the cementing and/or Matrix material to create fluid pathways. Conventionally acids such as HCl, HF or both were used based on the type of material to be dissolved.

Conventional acids can be disadvantageous in geothermal fields due to a number of issues in the past like increased corrosion and acid/rock reaction rates at high temperatures, less penetration, hazardous nature and expensiveness. To avoid these problems, other alternatives such as retarded acid and foam acid systems were developed. Although these systems proved to be effective, the presence of a strong acid like HCl causes problems like excessive tubular corrosion and unwanted precipitation. Studies using Organic acids such as acetic acid and formic acid were also conducted but their main disadvantages being the cost per weight of dissolution and precipitation at concentrations greater than 9 and 13 weight % respectively. These limitations established the need for a different stimulation fluid without corrosion problems, ability to implement low injection rates or sludge precipitation.

Attention was then focused to chelating agents. Chelating agents are negatively charged organic substances their ability to form metal complexes that are reasonably stable and hence reducing the ion reactivity (A Rabie et al., 2011). Chelating agents have been used and studied in the oil industry for iron control, scale removal and matrix acidizing especially for deep reservoirs. Some common chelating agents include ethylenediaminetetraacetic acid (EDTA), Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetetraacetic acid (HEDTA) and Glutamic acid diacetic acid (GLDA). Later, studies were conducted for using chelating agents as stimulating fluids (Fred et al., 1998a). A lot of research has been conducted comparing the effect of different chelating agents, their stability, dissolution capacity, corrosiveness, kinetic parameters and other such properties. Studies conducted established that GLDA is an effective option for stimulation compared to other chelates (LePage et al., 2011 and A Rabie et al., 2011).

There is very limited to almost no literature using chelating agents to stimulate geothermal wells. A combination of regular Mud Acid (RMA), NTA and organic clay acid (OCA) was used in the EGS system at Soultz –sous-Forêts in France and proved to be successful (S Portier et al. 2009).Although studies have been conducted to determine the exact kinetic parameters and the chelating mechanism, this seems to still be quite an active research topic with quite some uncertainties. One of the most important parameters determining the rate of chelation of calcite is the available reactive surface area for the interaction of chelating fluid with calcite. The available reactive surface area is a Darcy scale parameter and varies widely. This work seeks to determine an average available reactive surface area for calcite dissolution and use this determined value to see the effect of calcite dissolution and stimulation temperature in field scale. This can be done by experimentally monitoring permeability and porosity changes during calcite dissolution and utilising this data in a finite element numerical model to match and analyse the effect of calcite dissolution.

A detailed study on the basic acid treatment technique, procedure involved, injected acid composition and problems involved is given in the appendix (section B).

1.2 Scope of the Thesis

This work investigates the effect of calcite dissolution on core level to obtain an average value for the available reactive surface area and analyse the effect of changing calcite concentration and temperature. The objectives of this study are

- To conduct the critical salt concentration and critical velocity of fines migration studies required in the lab for optimizing the chelating agent injection study for the chosen sample.
- To experimentally monitor the variation of permeability and porosity changes due to injection of a chelating agent(H_2GLDA).
- Build a core scale model to simulate the dissolution of calcite using a finite element modelling environment.
- To Model these experimental results and fit them in the core scale model and obtain the available reactive surface area for calcite dissolution.
- To build a field scale model for a homogeneous and heterogeneous system.
- To Use these best-fit relationship parameters in field-scale and analyse the effect of calcite dissolution on the injectivity in homogeneous and heterogeneous reservoir models.

2 Materials and Methods

2.1 Theoretical Background of the tests conducted

As mentioned earlier, the cementing material can be made of either calcite, iron oxide, silica cement, clays or a mixture of these minerals. Clay minerals in sandstone reservoirs can potentially create problems in both geothermal and hydrocarbon reservoirs because of their reaction to drilling, cementing, completions, stimulation or workover fluids. The most common clay minerals are kaolinite, montmorillite, illite, smectite, chlorite and mixed-layer clays. These clay minerals are mainly classified into swelling and non-swelling clays. Clay minerals can lead to formation damage by causing an undesirable loss of permeability.

Formation damage is the impairment to the reservoir (reduced production) caused during drilling, completion, production and workover operations. It is a zone of reduced permeability within the vicinity of the wellbore as a result of incompatible-fluid invasion into the reservoir rock. Formation damage due to clay swelling is important since most reservoirs contain clay minerals that were originally deposited during sedimentation or precipitated from fluids flowing through the matrix (L Kalfayan, 2008). Another important cause of formation damage is the migration of fines in the reservoir. It is one of the most common mechanisms of formation damage.

This section aims at establishing the importance of determining the formation damage due to change in salinity of the injected solution and flow velocity.

2.1.1 Formation Damage due to clay Minerals

2.1.1.1 Swelling Clays

Clay minerals usually have a sheet-like structure in which the building blocks are linked to each other by sharing oxygen ions. These sheets are bound to each other in layers that could extend up to thousands of nanometres. The interlayer surfaces are usually negatively charged in general and attract positively charged ions in the solution. Due to this attractive forces water molecules are adsorbed in these layers and cause swelling of the layers.

Mixed layer clays and smectites can swell with changing ionic concentration and eventually disperse and migrate with the flowing fluid. The swelling of the clay particles implies that the effective pore space is reduced and thus, decreasing the permeability of the rock.

Another method of formation damage due to clay swelling is when the particle swells it causes the breakage of other particles in contact with them. This phenomenon is called swelling induced migration (K K Mohan et al., 1993).

2.1.1.2 Non-Swelling clays

This process of non-swelling particles resulting in permeability reduction is similar to fines migration. The non-swelling clay particles like kaolinites and Illites tend to detach from the rock provided the colloidal conditions are conductive for release. These particles get trapped in the pore throats causing a reduction in permeability.

2.1.2 Formation Damage due to fines Migration

For a given rock of a certain permeability, there exists a certain maximum flow velocity above which mechanical particle mobilization begins to occur. This velocity is called critical flow velocity. The existence of a critical flow velocity has been established by and the damage mechanisms (G.A. Gabriel et al., 1983).

The mobilized particles in suspension can clog pore throats and cause a reduction in permeability (figure 2.1). The extent of permeability damage is a function of the permeability of the core, salinity of the solution, available flow area as well as flow direction, particle size and pore structure.

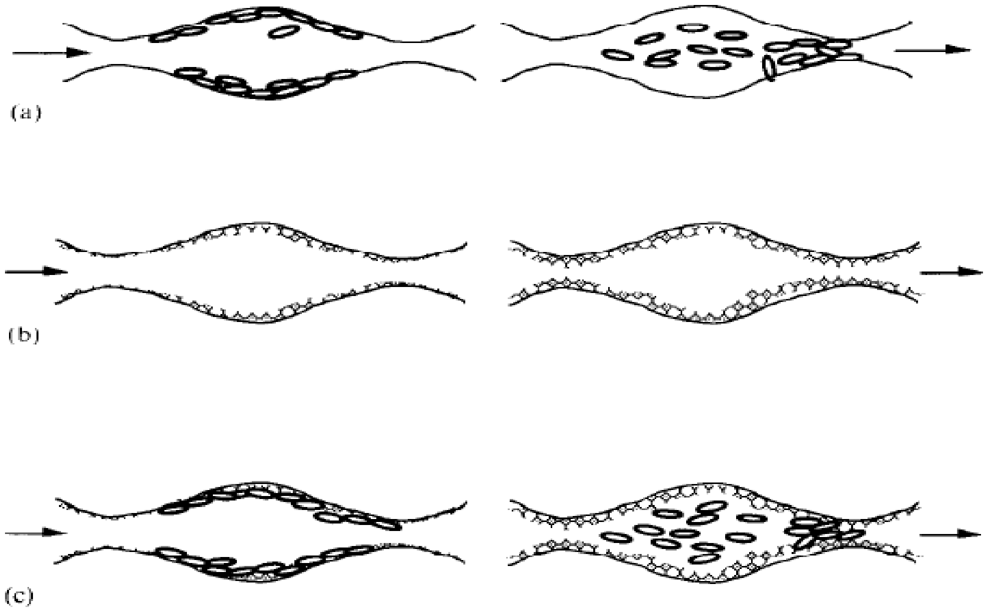

Figure 2.1: Mechanisms of permeability reduction caused by clays in porous media. (a) Migration (b) Swelling (c) Swelling-induced migration source (K K Mohan et al., 1993)

In this study, the samples were analysed for the critical flow velocity. Once the critical flow velocity is reached the flow rate is increased to a large value to see if the effect persists or the mobilized particles are flushed along with the suspension.

2.1.3 Chemistry of GLDA Chelation

It is important to understand the basic concept of chelation and the effect of pH on the chelating fluid in order to select the appropriate chelating agent and also to determine the rate controlling reactions. A number of chemical reactions occur at the surface of the calcite- GLDA interface. Three surface reactions have been reported in literature which is as follows (Plummer et al., 1978)

The hydrogen attack $H^{+} + CaCO_3 \leftrightarrow Ca^{+2} + HCO_3^{-}$

Water reaction $H_2CO_3 + CaCO_3 \leftrightarrow 2HCO_3^{-}$

Calcite reaction $H_2O + CaCO_3 \leftrightarrow Ca^{+2} + HCO_3^{-} + OH^{-}$

The hydrogen attack predominantly controls the reaction rate at low pH values and water reaction in case of high pH values (Fredd and Fogler 1998a). The following reactions given below may also occur in addition to the above-mentioned reactions depending on the pH of the solution.

$$CaCO_3 \leftrightarrow Ca^{+2} + {CO_3}^{-2}$$

$$H_2GLDA^{-2} + CaCO_3 \leftrightarrow CaH_2GLDA + {CO_3}^{-2}$$

$$HGLDA^{-3} + CaCO_3 \leftrightarrow CaH_2GLDA^{-1} + {CO_3}^{-2}$$

$$GLDA^{-4} + CaCO_3 \leftrightarrow CaH_2GLDA^{-2} + {CO_3}^{-2}$$

These reactions take place when the different ligands attack the calcium site rather than the carbonate site during the chelation reaction (A Rabie et al., 2011). In this study, as the pH of our setup was around 4 and hence H_2GLDA was used as it had the highest amount of acid dissociation at the given pH.

2.2 Samples selection and collection

Sample collection procedures are necessary mainly to ensure that used samples are representative for the planned geothermal reservoir. Additional consideration for sample collection activities is the assurance of sufficient volume of the test material to conduct all necessary studies. For the laboratory test of matrix acidizing in the geothermal wells large volume of test material is needed due to two reasons: (1) an extended investigation needed in prior to main acid injection tests; (2) To ensure the results obtained are representative of the field being analysed.

An example of outcrop and well samples selection process for the geothermal operations in the Lower Germanic Triassic Group in the Netherlands is presented below. The aquifer planned for the thermal extraction spans the whole Main Buntsandstein, thus it contains lithostratigraphic members and formations from the Solling Sandstone down to the Lower Volpriehausen (Figure.2.2).

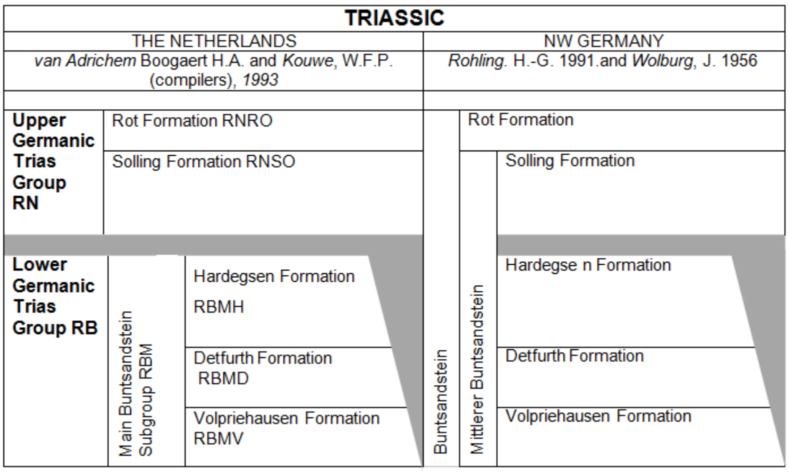

Figure 2.2: Lithostratigraphy of the Middle Triassic of the Germanic Basin

The Hardegsen formations, a subgroup of Main Buntsandstein, that are considered as potential geothermal reservoirs are characterized by poor matrix permeability and flow is mainly controlled by natural fracture and faults network. The main experimental material was collected from existing boreholes, however, additional material needed to be obtained from the outcrop locations. Due to limited availability of the Hardegsen Formation samples, the investigation of the well samples for final tests was diversified throughout the Main Buntsandstein (MB) formation (Figure 2.2) the sedimentary facies in the larger interval are exhibiting similarities. Selection of the appropriate samples has been done based on available mineralogical/petrographic composition data in the literature and the geological conditions determined from the well cores in the Westland concession. The selection of samples was directed towards low porosity sandstones, the average reservoir matrix porosity of Triassic Formation at 4 km depth may not exceed 8% and permeability may be around 4 mD (S Nelskamp et al., 2012)

In this regard, analog sandstones (both well and outcrop) with similar properties and cement types– regardless of their stratigraphic position were chosen (Table 2.1); three different outcrop samples from Germany and one offshore sample from a borehole Q16-02 from depths of 3629 – 3838 m (Figure 2.3).

Name of the rock	**Sample name**	**Location**	**Stratigraphy**
Borehole	Q16-02	Offshore	MB, Volpriehausen
Wesersandstein (Quarry)	W-1	Bad Karlshafen, North Hessen	MB, Solling-Folge, Karlshafener Schichten
Friedewalder Buntsandstein, pale, (Quarry)	F-1	Friedewald, South Hessen	MB, Solling-Folge
Kordeler Sandstein (Quarry)	K-1	Trier, Rhineland-Palatinate	Upper Buntsandstein Voltziensandstein

Table 2.1: Representative rock samples from the Lower Germanic Triassic Group that were selected

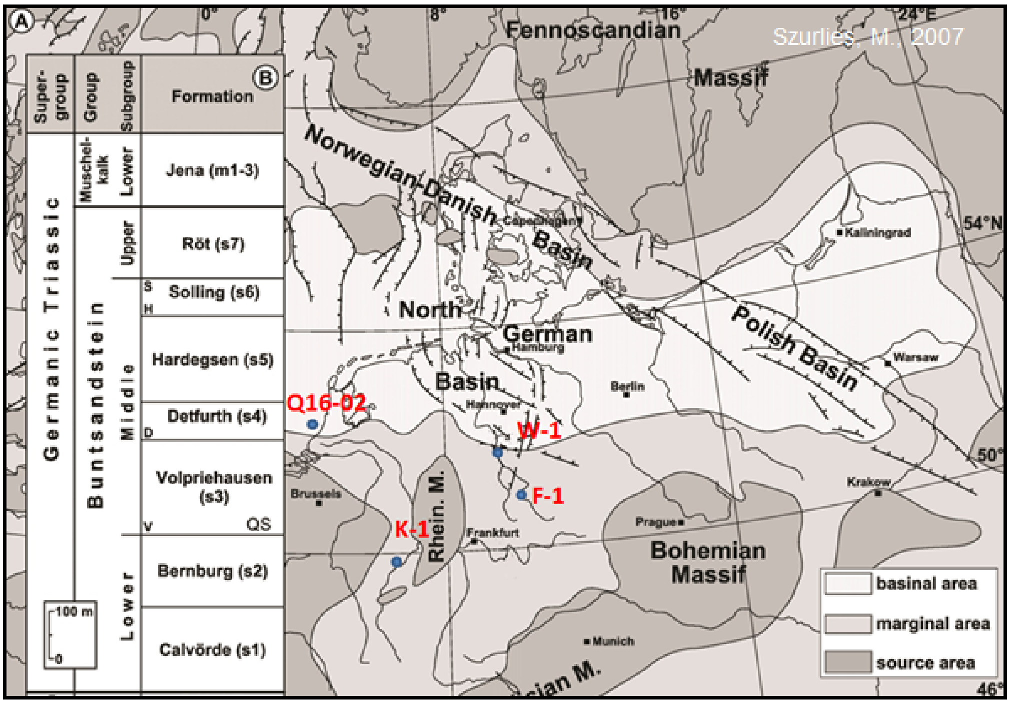

Figure 2.3: Map showing the location of the selected samples

2.3 Experimental approach

The main experiments consisted of injecting 0.1M KCl brine, before and after the injection of diluted H2GLDA solution (50%) through the core. The experiment was carried out at a temperature of 150 C using KCl of 0.1 M concentration to saturate the core to mimic the fluid in the field. Both the fluids (GLDA and brine) were injected at a constant volumetric flow rate (Q) corresponding to Q = 8.333 x 10^{-11} m^3s^{-1}. The flow rate is chosen such that it is lower than the critical flow velocity to avoid any mechanical damage due to fines migration. The concentration of the brine is chosen such that it is above the critical salt concentration required to prevent clay swelling (K.K Mohan et al). 5-7 pore volumes of the chelating agent are injected.

Two additional tests were conducted in order to obtain the critical salt concentration and the critical velocity of fines migration. A Sodium Chloride (NaCl) and Potassium Chloride (KCl) brines were used for determining the critical salt concentration and sodium chloride brine for determining the critical velocity of flow migration. These experiments are described in more detail under the secondary experiments.

2.3.1 The Apparatus

A cylindrical core of 40 mm diameter (D) and 80 mm length (L) is placed into the core holder. The core is coated with epoxy resin at the sides to avoid bypass of fluid through the sides. The Core holder was made of peek and it could withstand temperatures up to 350 ◦C and pressures up to 80 bars. The Oven can operate from 25 to 250 ◦C is maintained at 150 ◦C at all times of the experiment. The temperature of the fluid is monitored before entering the core as well as after leaving the core by using two thermocouples.

A syringe type ISCO pump is used to inject fluid into the system, equipped with microprocessor enabled controller system which enables accurate control of the flow rate. This pump system has a maximum capacity of 266.3 x 10^{-6} m^3 and is designed to obtain continuous flow rates ranging from 1.6667 x 10^{-11} to 1.7778 x 10^{-6} $m^3 s^{-1}$. The main reasons for choosing an ISCO pump were the accuracy in volume injected, injection control by pressure and flow rate, sufficient tank capacity for the complete acid injection process enabling constant and accurate pressure monitoring

The pressure is maintained above 20 bars to prevent the produced CO_2 from forming a new gas phase by using a back pressure system that imposes a constant pressure in the system. Nitrogen gas is used to maintain this backpressure and a manual control is employed in the case of this experiment. The fluctuations in this value have no impact on the permeability value of the sample. The back pressure is maintained at atmospheric level while determining the critical velocity of fines migration and the critical salt concentration.

The acid composition, density and viscosity are monitored and are analysed before and at regular intervals after injection using Inductively Coupled Plasma atomic/optical emission Spectrometry (ICP- AES), viscometer and density meter respectively. This gives an idea of the amount of calcite dissolved and the effect of acid injection can be studied by analysing this ICP results along with CT scans and permeability data.

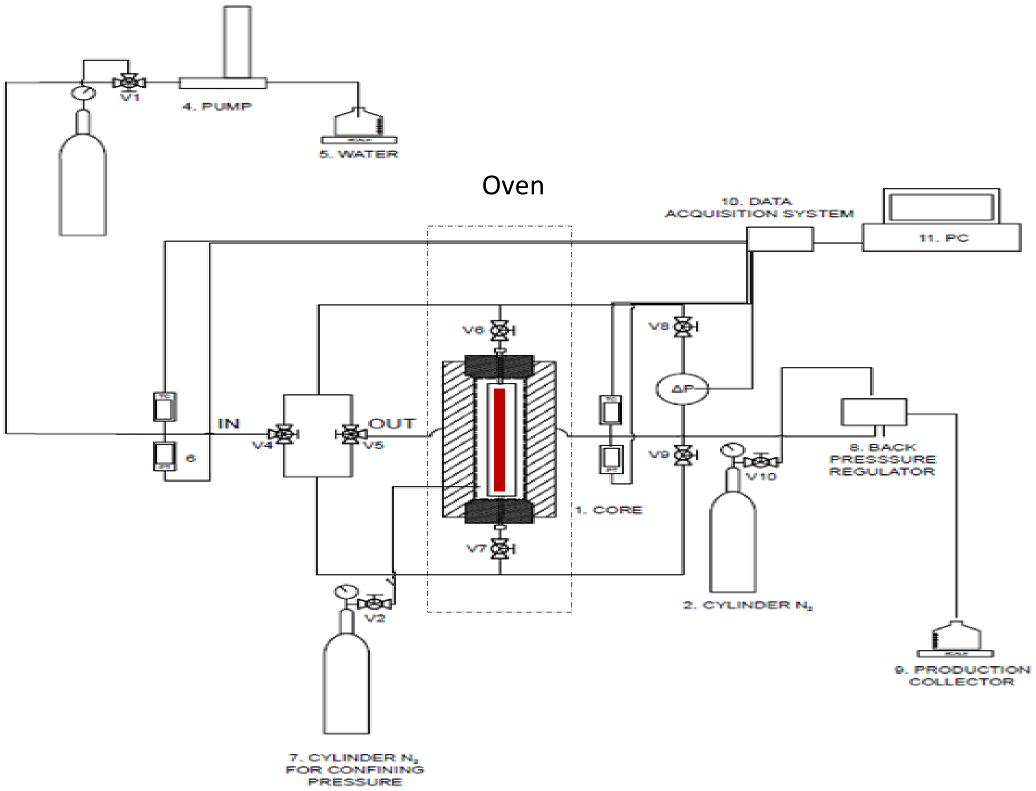

Figure 2.4: Schematic representation of the setup used in the laboratory for core flooding experiments

2.3.2 Sample Characterization

All samples are analysed by X-ray diffraction (XRD), X-ray fluorescence (XRF), Electron microprobe (EMP), and Scanning electron microscope (SEM) to get a clear idea of the mineral composition, pore structure, identification of the mineral phases present (XRD) ,whole rock chemistry(XRF), crystal chemistry (EMP) and morphology and alteration details (SEM).

Samples for X-ray diffraction and X-ray fluorescence were pulverized to a 2 mm powder and used for the determination of mineral composition and element oxide distribution. Table 4.1 shows the results obtained from XRD analysis estimating the possible phase composition of a sample.

The dry porosity of the cores was measured using a helium gas injection method in a gas expansion Ultra Pycnometer 1000 (Quantachrome Instruments™) using Boyle's gas expansion law.

Sample w1, compound	Formula
Quartz	SiO_2
Microcline	$K(Al\ Si_3)O_8$
Montmorillonite, heated	$NaO.3(Al, Mg)_2si_4O_{10}(OH)_2$ x $2H_2O$

Table 2.2: Possible phase composition of the sample (W1) from XRD analysis

2.3.3 Monitoring Changes in Porosity and Permeability

Core-scale permeability k (t) at a given time t can be calculated from the pressure difference measured between the inlet and the outlet of the core. According to Darcy's law,

$$k(t) = \frac{Q\mu L}{A\Delta P(t)}$$

Where, Q is the volumetric flow rate [m^3s^{-1}]

μ is the dynamic viscosity of the fluid [kg $m^{-1}s^{-1}$]

A is the cross sectional area of the sample [m^2]

$\Delta P(t)$ is the pressure drop across the core [Pa]

L is the length of the sample in flowing direction [m]

Initial porosity is measured using helium gas and Boyle's law that relates the pressure of a given mass of ideal gas to its volume at a constant temperature. The Core is also imaged through a micro-CT device before and after the experiment to determine initial and final porosity by using AVIZO, a 3D analysis software for image data processing and analysing. The resolution of this Micro-CT imaging is in the range of 25-32 microns.

2.3.4 CT scan

The cores were scanned by Computed Tomographic (CT) imaging technique, where a cross-sectional image of an object is created from X-ray attenuations. The image display matrix is 807 x 784 with each pixel representing a volume element of 0.02 x 0.02 x 0.08 mm in size. CT scans are first taken once the core is 100% saturated with the residual fluid (brine in this case) and later CT scans are taken again during the acidizing process for the same location and for various time steps. Thus by image subtraction, the effect of acid propagation can be visualized.

2.4 Secondary Experiments

2.4.1 Critical Salt Concentration

The effect of the salt concentration in the injection solution is studied in this section. Clay minerals in sandstone reservoirs can potentially create reservoir problems in both geothermal and hydrocarbon reservoirs because of their reaction to drilling, cementing, completions, stimulation or workover fluids. Formation damage due to clay swelling is important since most reservoirs contain clay minerals that were originally deposited during sedimentation or precipitated from fluids flowing through the matrix (L Kalfayan., 2008). The mechanism of clay particles causing formation damage is well studied (K K Mohan et al., 1993).The flow procedure is as follows:

- The Core is saturated at a very low flow rate (to avoid fines migration) with a brine having a salt concentration higher than that of the field is used (2 M NaCl/l in our case) and is left undisturbed for a long time in the same condition. A constant pressure drop indicates a constant permeability which indicates that there is no formation damage happening in the core.
- The Concentration of the brine is reduced in steps 0.25M and the same procedure is carried out until we see a variation in the pressure drop indicating a change in permeability. This concentration of brine is then fixed critical salt concentration to avoid formation damage by clay swelling.

The goal of this part of the experiments is to confirm the presence of swelling clays and to determine the critical salt concentration required to prevent clay swelling.

2.4.2 Critical Velocity of Fines Migration

Formation damage can occur due to an inflow of fluids into a reservoir, or when formation fluids are displaced at extreme velocities, causes substantial reductions in permeability and, as a result, in productivity in many reservoirs. Critical velocity tests provide insights into the reservoir structure to minimize geotechnical damage and/or to avoid fines migration by applying correct flow rate. The purpose of this test is to determine the critical interstitial velocity at which fines migration starts to occur. The setup used is the same as the one used for determining the critical salt concentration. The experimental procedure is described below:

- This test is based on the fact that permeability is an intrinsic property. The flow rate is increased from a very small value in steps of 2ml/h. As the flow rate is increased in small steps, permeability is monitored. The permeability remains constant as long as the flow rate is not high enough to move the fines.
- The flow is kept increasing until we see a sudden change in permeability indicating fines migration. This velocity is fixed as the critical flow velocity above which particle migration will take place.

The goal of this part of the experiment is to determine the critical velocity of fines migration in the given sample in order to make sure that the fines are not migrated in the primary study.

3 Model implementation in COMSOL

A core scale and field scale 3-Dimensional finite elements models were created in COMSOL for the purpose of this study.

3.1 Governing Equations

The governing equations for this study can be based on the following physical phenomena

- Transport of chelating agent and/or other fluids in the reservoir
- Fluid/rock interaction resulting in permeability and porosity alteration
- Heat transfer in the subsurface for geothermal extraction

3.1.1 Fluid Flow

The differential form of the mass conservation equation assuming a fully saturated pressure driven flow without gravity effects in the reservoir that can be obtained from the general continuity equation is

$$\frac{\partial}{\partial t}(\phi\rho) + \nabla.(\rho\, U) = Q_m$$

Where, U represents the velocity field of the fluid which is a dependent on the Permeability, dynamic viscosity of the fluid and is expressed using Darcy's law as

$$\vec{U} = \frac{k}{\mu}\nabla P$$

ϕ Is porosity (m^3/m^3)

ρ is the density of the fluid (Kg/ m^3)

Q_m is the source / sink term (the mass flux per unit volume)

$\vec{U}$ is Darcy Velocity (m^2/s)

k is rock permeability (m^2)

μ is viscosity of the fluid [Kg/ (m.s)]

3.1.2 Transport of HCl

The general convection-diffusion equation that represents the transport of a chemical species (i) in a porous medium can be derived from the continuity equation is as follows

$$\frac{\partial c_i}{\partial t} + \nabla.(D_i \nabla c_i) + U.\nabla c_i = R_i \qquad (0.1)$$

Where,

c_i is the concentration of a given species (mol/m^3)

D_i denotes the diffusion coefficient tensor in m^2/s

R_i is a reaction rate expression for the species in mol/ (m^3.s)

The $\frac{\partial c_i}{\partial t}$ term accounts for the accumulation/consumption of the species i, while $\nabla.(D_i \nabla c_i)$ represents the diffusive transport and $\overrightarrow{U}.\nabla c_i$ describes the convective transport due to the velocity field $\overrightarrow{U}$, which in this case is obtained from Darcy's law.

The rate of the reaction (R_i) is given by the Arrhenius equation and as a function of the reactive surface area available for the rock-fluid reaction and the available carbonates for dissolution.

3.1.3 Heat transport

The heat transport in a porous reservoir assuming a local thermal equilibrium hypothesis for a common temperature, T, can be described by the following heat transport equation

$$(\rho C_p)_{eff}\frac{\partial T}{\partial t} + \rho C_p u.\nabla T = \nabla.(K_{eff}\nabla T) + Q_h$$

Where,

C_p is the specific heat capacity (J/ (kg.K))

T is the absolute temperature in K

Q_h is the heat source/sink term

k_{eff} is the effective thermal conductivity tensor

The $(\rho C_p)_{eff}$ term represents the effective volumetric heat capacity at a given pressure and the $k_{eff}\nabla T$ term represents the conductive heat flux.

3.2 Physical System

3.2.1 Core Scale Model

In the case of the core scale model, the results from the experiments are used to match the model to obtain a best fit FEM model. All the conditions that were used in the experiment are accounted for in the model. Darcy's law for porous Media and Transport of diluted species in porous media were used for modelling the transport and the rock-fluid interactions respectively. The dissolution of carbonates is implemented by using a domain scale ordinary differential equation. The main uncertain parameter is the surface area available for fluid-rock interaction which is varied to match the experimental data.

3.2.2 Field Scale Model

Two studies were conducted in this model for studying the effect of calcite dissolution in the field scale. A heterogeneous reservoir with an injection and production well was built for this part of the study. For computational and ease of modelling, the fracture network is not considered but an average initial permeability is considered. As mentioned earlier, this model uses the parameters obtained from the core scale model and studies the effect of well stimulation in field scale. A 50 m maximum radius from the wellbore was used to limit the reacting zone. The same physics that were used in the core scale model are used in this model as well. The second field scale study imports the altered permeability and porosity distribution from the previous field scale model and is used to study the effect on the energy production. Darcy's law and heat transfer in porous media were the physics used to model the flow of mass and heat respectively.

In the case of a heterogeneous system, the model is populated with data from FLUMY, a process based heterogeneity modelling software (Figure 3.1). FLUMY simulates the geometry of heterogeneous reservoirs in meandering channel systems by using a combination of process based and stochastic approaches.

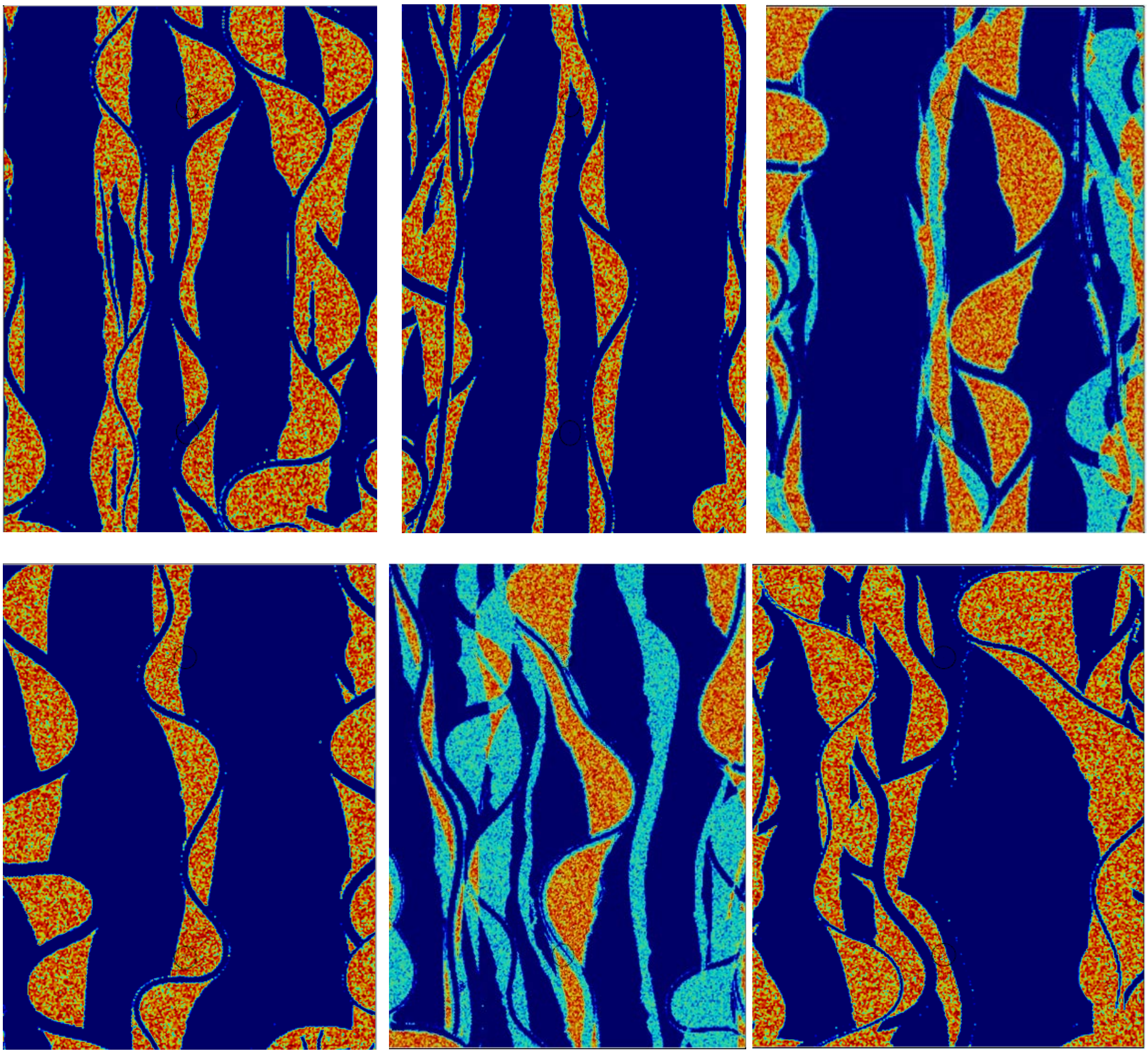

Figure 3.1: XY plane cross sections at different depths showing the heterogeneity used in the model obtained from FLUMY

A uniform amount of dissolvable material distribution is assumed in all cases.

3.3 Boundary and Initial Conditions – Field scale Model

The boundaries on the sides of the reservoir were assigned constant pressure (Dirichlet) boundary condition. The top and bottom boundaries were assumed to be a sealing layer with no heat loss. A constant initial reservoir temperature and pressure were determined based on the geothermal and hydrostatic pressure gradient which is a function of the reservoir depth. Similar to literature, the density, viscosity and thermal conductivity of water, fluid (Acid)-rock reaction rate are established as a function of temperature respectively (Crooijmans et al., 2016 and Saeid et al., 2015).

Parameters		
Name	Value	unit
Inlet Temperature	40	C
Initial Reservoir Temperature	100	C
Initial Reservoir Pressure	200	bar
Reservoir Depth	3000	m
Reservoir Thickness	50	m
Reservoir Length	2000	m
Reservoir Width	1000	m
Geothermal Gradient	0.03	°C/m
Pressure gradient	0.1017	Bar/m
Doublet Distance	800	m
Borehole Diameter	0.15	m
Production/Injection Rate	100	m^3/s
Initial Permeability	50	mD
Initial porosity	0.1	
Injected Acid concentration	13.6	wt %
Acid injection rate	0.5	m^3/min
Acid total injection time	250	hours
Effective reactive radius	15	m
Acid diffusivity	1.00E-09	m^2/s

Table 3.1: Initial parameters for the homogeneous field scale model

3.4 Finite Element Mesh

Figure 3.2 shows the mesh that was discretized in COMSOL Multiphysics to represent the field scale model. A Free triangular swept mesh with predefined block size range was used to be more efficient and also to make sure the near wellbore region is finely meshed. A swept mesh usually starts the mesh construction at the source boundary and sweeps along to a specified destination boundary. Another advantage of using a swept mesh is that the number of elements is considerably less eventually reducing the computational time and processor requirements.

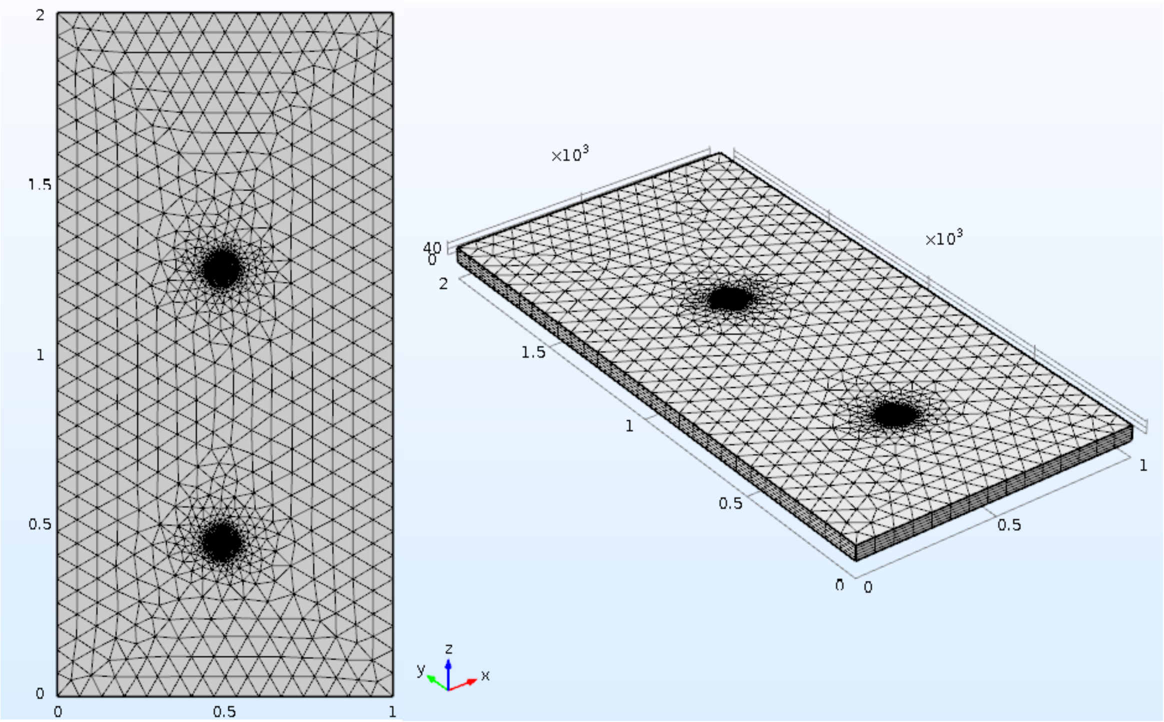

Figure 3.2: Illustration of the Finite element mesh used in the reservoir scale model

	Element Size Parameters	Value	
		Homogeneous	heterogeneous
General Mesh sizing Parameters	Maximum element size	70 m	20
	Minimum element size	30m	2
	Maximum element growth rate	1.5	1.45
	Curvature Factor	0.6	0.6
	Resolution of narrow regions	0.5	0.5
Free Triangular Mesh	Maximum element size	well radius	well radius
	Maximum element growth rate	1.15	1.15
Swept Mesh	Face Meshing Method	Quadrilateral	Quadrilateral
	Distribution (layers)	5	10

Table 3.2: Meshing parameters used in the homogeneous and heterogeneous reservoir scale model

4 Results and Discussion

4.1 Experiments

4.1.1 Critical salt concentration

To examine the effect of the salt concentration on the reservoir, experiments were performed using KCl and NaCl brine solutions. In each experiment, the salt concentration of the injected solution was reduced in steps of 0.25 mol/l until a change in the pressure difference (DP) response was observed.

Wesersandstein Sample

Figure 4.1 shows the pressure drop response for an injected brine concentration of 2 moles of NaCl/l. It is observed that the pressure drop is fairly constant. After leaving the system undisturbed at the same conditions for 2 days and observing a constant pressure response, the solution is changed to 1.75M NaCl/l solution and pressure difference response remained constant.

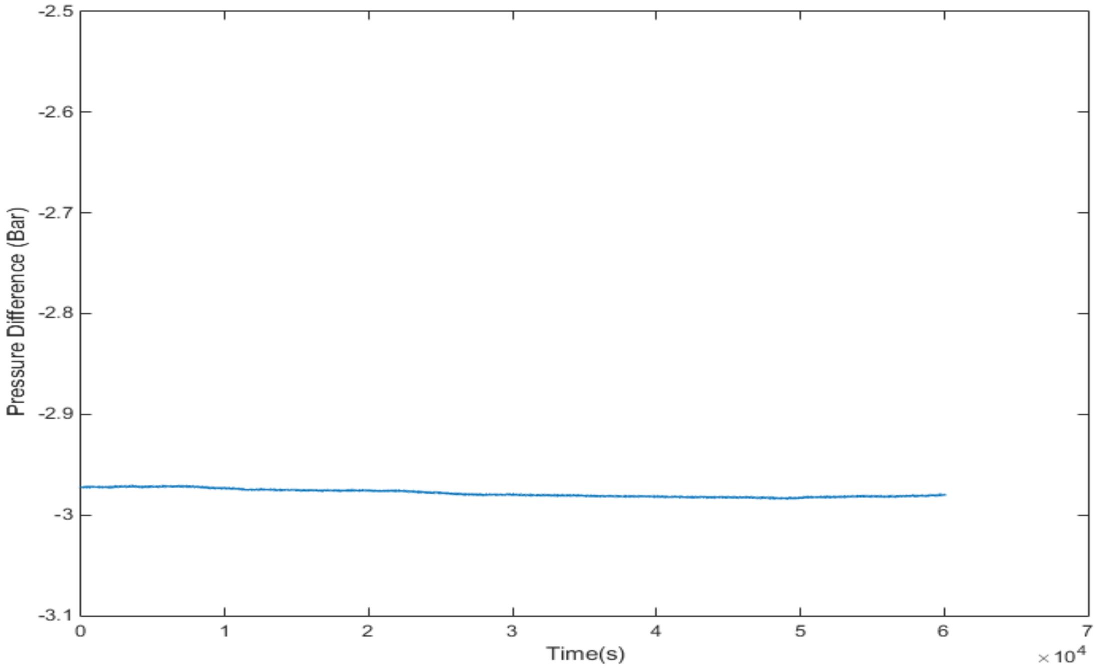

Figure 4.1: Pressure drop response for the injection of 2M NaCl

The salt concentration is further reduced until a change in the pressure drop response is observed. Figure 4.2 shows the DP response obtained for the change in brine concentration from 0.3 - 0.2 M NaCl/l. As the ionic concentration changes, the clays in the sample starts to swell and a decrease in the permeability is observed. This proves the importance of the critical salt concentration for the future tests.

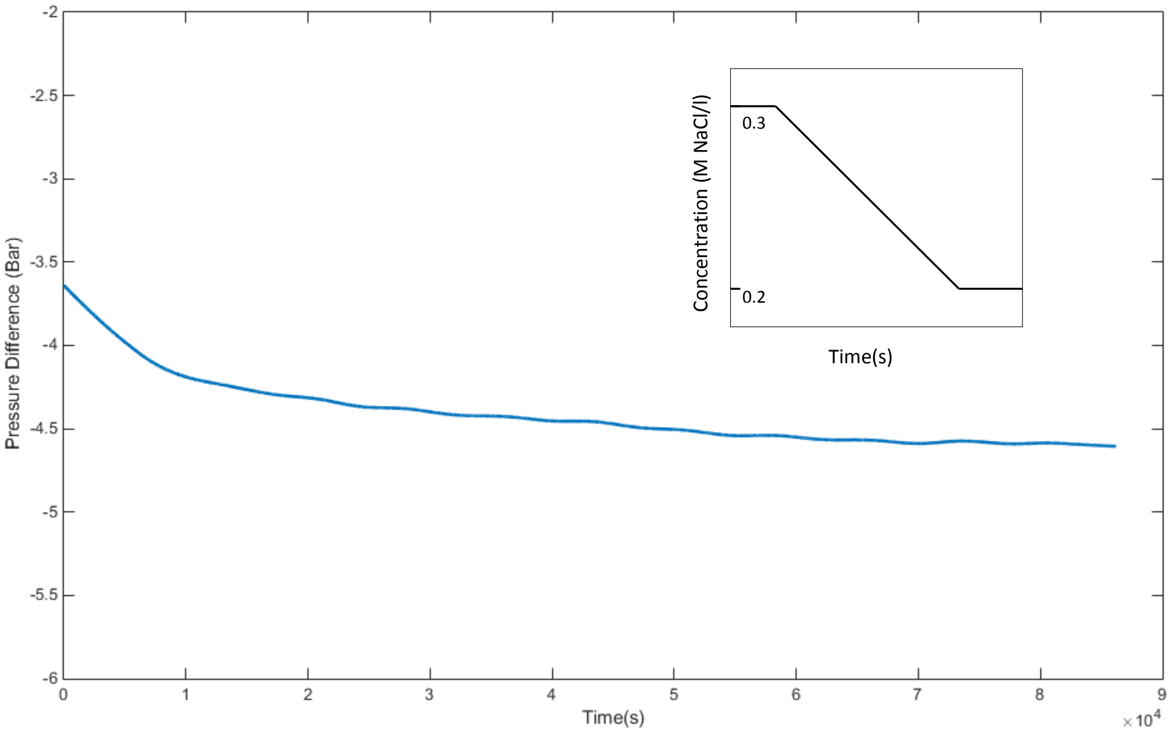

Figure 4.2: Pressure response for the change in brine concentration from 0.3M - 0.2M NaCl

Thus for the future tests, the salt concentration in the injected brine was maintained above 0.3M NaCl/l. In order to be sure that there was no chemical damage induced due to the brine injected, a factor of 1.5 was taken and the brine concentration was fixed at 0.5M NaCl/l.

4.1.2 Critical Velocity of Fines migration

In this section, the critical velocity of fines migrations is calculated. A brine of 0.5 M NaCl/l is used in this study to avoid clay swelling.

Additionally ,In an effort to understand the effect of flow direction three samples were obtained in three different directions and tested with the objective of estimating the critical velocity of fines migration and analyse the influence of permeability anisotropy.

NaCl brine is injected in this test at various flow rates to determine the critical velocity of flow migration. The following plot gives an example of the test conducted for the critical velocity of flow migration where the flow rate is increased in small steps and then decreased back in the same manner while monitoring the permeability. The response shown for flow velocities below the critical flow velocity is given in figure 4.3. Once the critical velocity of flow migration is reached, as the fines migration and clogging of the pore throats take place, the permeability of the sample goes down and it can be observed in the pressure drop response. This is shown in figure 4.4.

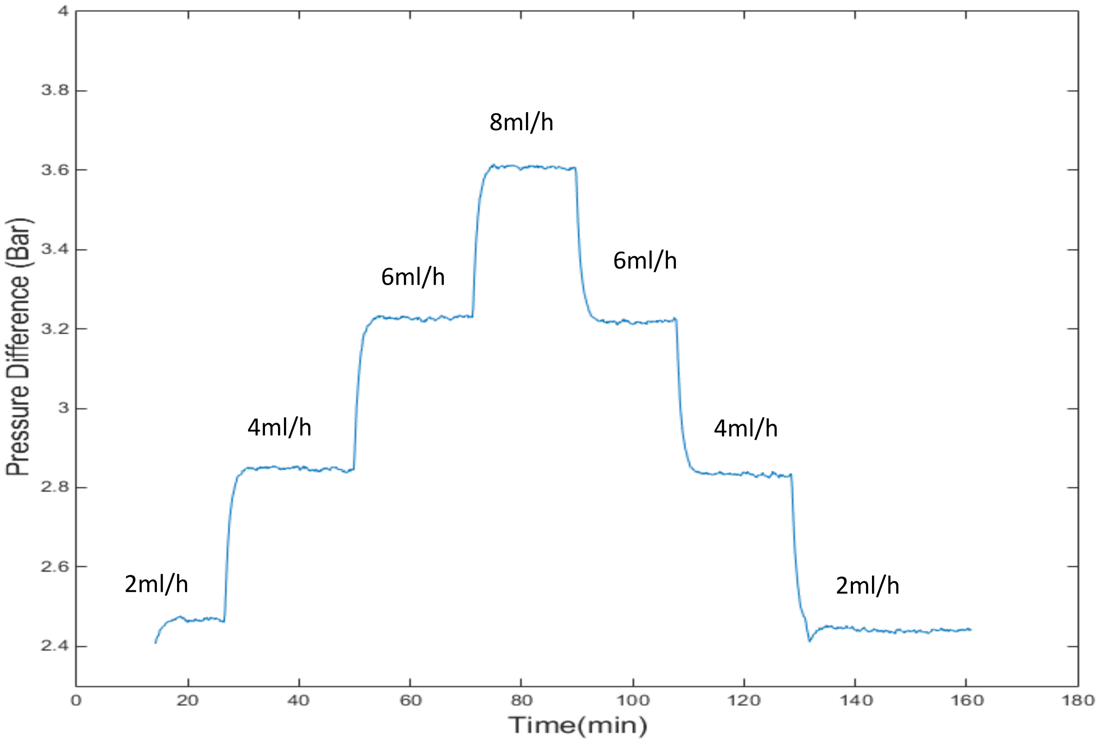

Figure 4.3: Pressure drop response for flow velocities less than the critical velocity of fines migration

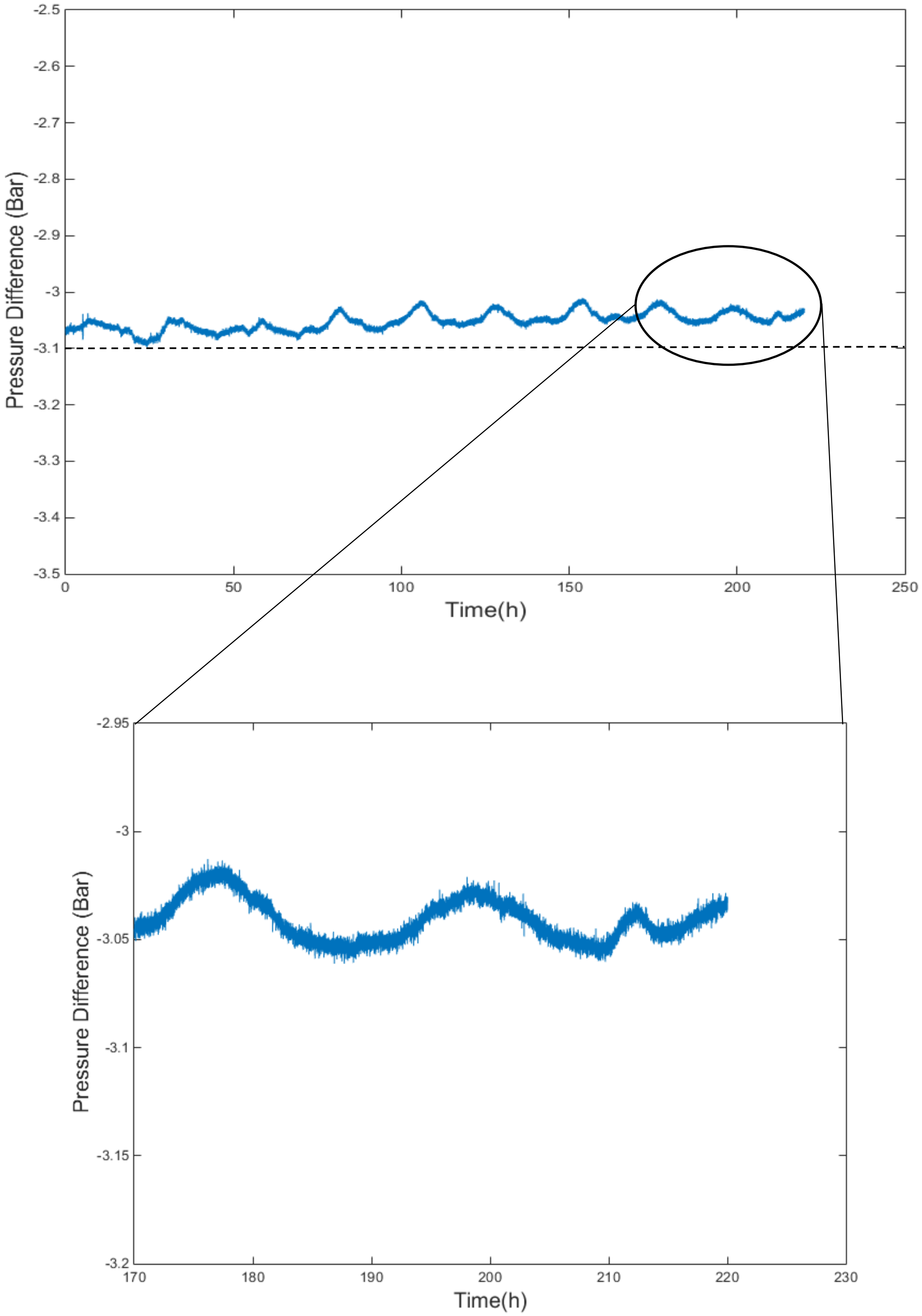

Figure 4.4: Pressure response for the point where the critical velocity is reached with an enlarged section showing the response for injection rates from 11 to 12 ml/h

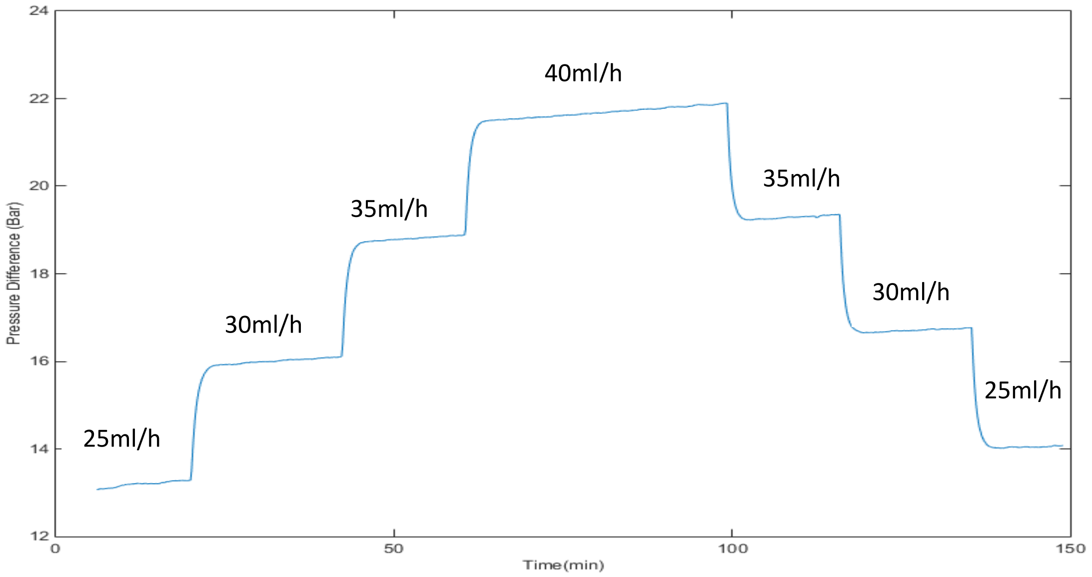

Figure 4.5: Pressure drop response for flow velocities much higher than the critical velocity of flow migration

The flow velocity was then increased to very high values to see if the migrated fines get flushed away due to the high velocity. The plot above (figure 4.5) shows the pressure drop response for the sample WY, for flow velocities up to 4 times or higher than the estimated critical velocity. It was observed that the pressure drop keeps increasing for a constant velocity and never reaches the initial value when the flow rate is decreased back to sub-critical velocities.

It was observed that the critical velocity in these samples was very close to each other and thus showing that there would be a very small effect of the direction of sample obtaining in terms of the critical flow velocity.

4.1.3 Acid Injection studies

After the core is saturated with brine, 50 volume % chelating agent is injected with a constant back pressure above 20 bar. As shown in the equations earlier, carbon dioxide (CO_2) gas is released as the calcite in the core is absorbed by the chelating agent. This released CO_2 is dissolved in the liquid phase by the back pressure maintained in the system. The permeability increase in carbonates can be by huge magnitude but in the case of sandstone, it depends on the amount of cementing material available to react with the chelating solution.

Initial permeability = 1.45 µD

Final permeability = 2.10 µD

The porosity changes were too low to be measured with the certainty of being outside the error zone.

4.2 Numerical Model

4.2.1 Core scale Model

As explained earlier the available surface area for the acid-rock interaction was varied so the experimental results from the acid injection study (permeability and porosity) were matched with the results obtained from the model. As the available reactive surface area is varied, the permeability- porosity relationship changes accordingly. Thus, the available reactive surface area value is changed within the limits from literature to obtain a match between the experimental and numerical results. The same determined value of the available reactive surface area is maintained throughout the rest of the modelling process. For the consistency of the results, all the plots in this section were obtained for injection of 13.6 wt% HCl.

4.2.1.1 Effect of calcite concentration

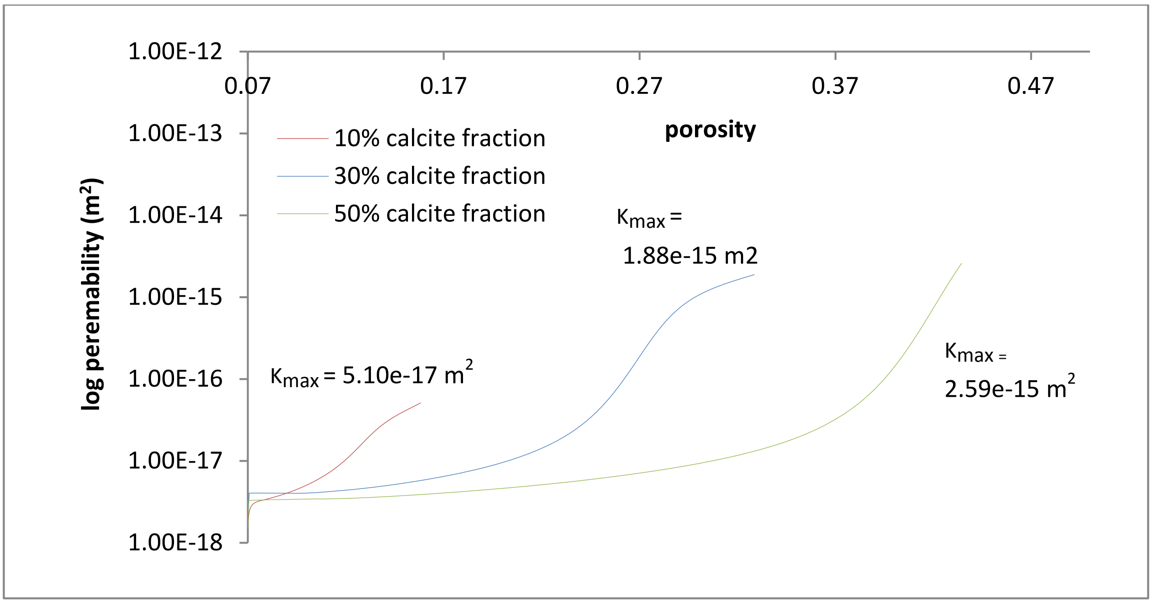

Figure 4.6: Effect of calcite concentration on the permeability - porosity plot

The plot in figure 4.6 shows the effect of increasing calcite concentration on the permeability –porosity plot in core scale. As the calcite fraction increases the dissolution increases and so does the permeability and porosity accordingly. It is also important to notice the two different slopes in figure 4.6. The initial slope represents the period when the acid front has not reached the outlet, representing phase dissolution. The second slope represents the period where the acid front has reached the outlet and uniform dissolution takes place resulting in a great increase in permeability.

Figure 4.7 shows the effect of calcite concentration on the scaled permeability relationship.

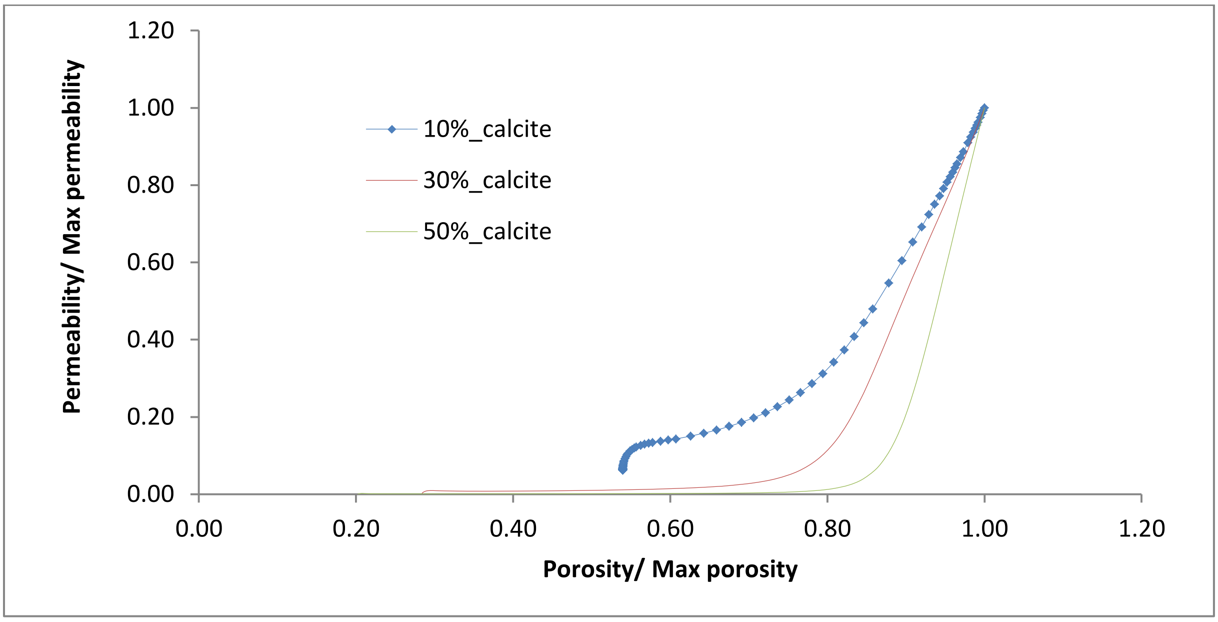

Figure 4.7: Effect of calcite concentration on a scaled permeability against scaled porosity plot

4.2.1.2 *Effect of temperature*

The effect of temperature on calcite dissolution for a core scale model is given in Figure 4.8. The plot shows the permeability-porosity development for injection of HCl for an initial calcite concentration of 10%.

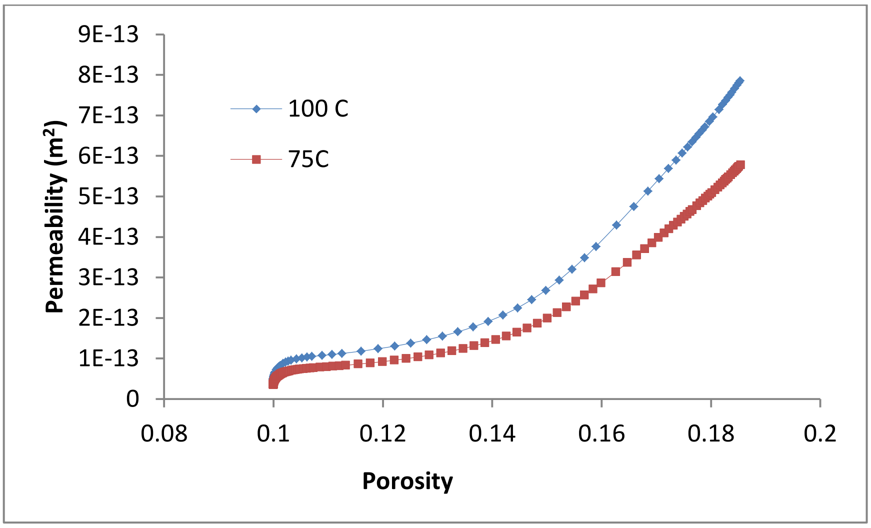

Figure 4.8: Effect of temperature on Core scale Model for 10% calcite fraction

With increasing temperature, the rate of reaction increases thus improving the permeability development across the core for the same volume of acid injected. Although we see the trend above, on injection of enough acid to dissolve all the calcite present, the final permeability reached would be the same in a homogeneous case, assuming all the calcite present is accessible to the acid.

4.2.1.3 *Effect of Injection Rate*

The effect of varying injection rates for the same volume of acid injected is analysed on the core scale model. The injection rate is an important parameter that determines the type of dissolution. The existence of an optimum injection rate a well-established phenomenon in carbonate reservoirs has been established (Fred et al., 1999). At extremely low flow rates most of the dissolution takes place close to the injection point and it might not have an effect on the overall permeability making it undesirable. This dependency of dissolution pattern on flow rate is very common in carbonates as in carbonates the whole matrix is being dissolved. In the case of sandstones, it might be important depending on the amount of calcite available and many other parameters.

An example for the dependence of carbonate dissolution patterns on the injection rate is given in figure 4.9.

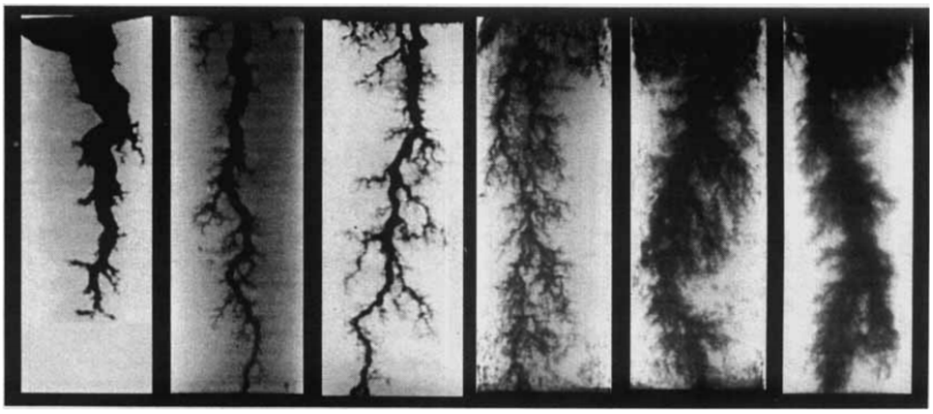

Figure 4.9: Dependence of the dissolution patterns on injection rates

The effect of different injection rates on a sandstone core scale permeability-porosity relationship is analysed. Figure 4.10 shows the permeability-porosity development for a constant volume of acid injected and temperature at two different flow rates.

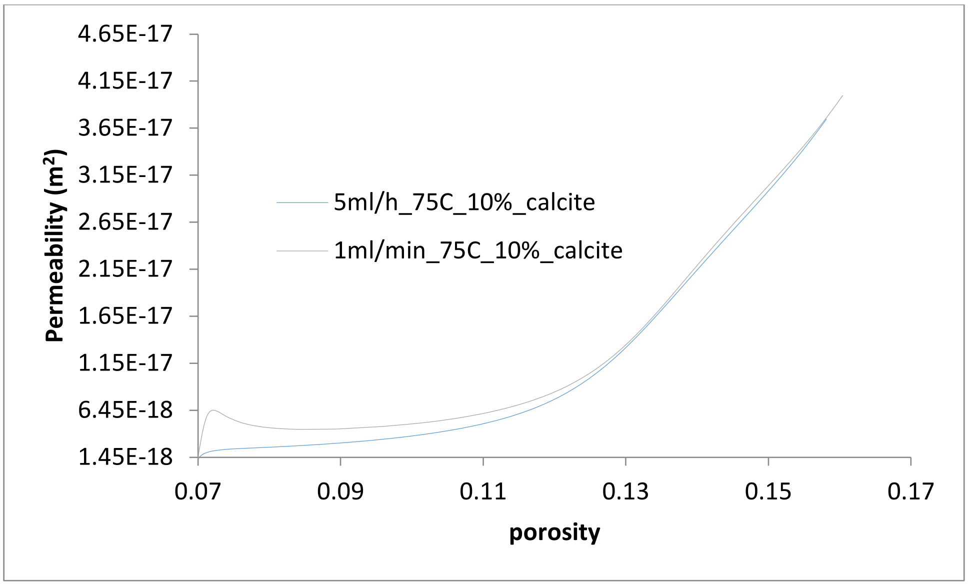

Figure 4.10: Effect of flow rate on core scale model for 10% calcite fraction

Although the effect of flow rate is a very important parameter in carbonate reservoirs, there is no significant change observed for varying flow rates in our case. It is also important to understand that modelling the creation of wormholes is a very complex process that requires detailed modelling.

4.2.2 Homogeneous system

In this section, the Average value of the available reactive surface area obtained from the core scale model has been used to analyse the effect of calcite dissolution in a homogeneous field. This part of the model is done under the assumption of a homogeneous field with constant permeability and porosity value throughout. The heat loss during geothermal production is not considered in this section and will be discussed later in the heterogeneous model. All the plots shown in this section were obtained for 13.6 wt% HCl injection.

4.2.2.1 Effect of calcite concentration

The effect of calcite concentration on the radius of influence is shown in figure 4.11. The radius of influence is defined as the radius surrounding the wellbore that has permeability improvement. In this case for a constant volume of acid inejcted, the radius of influence is defined as the radius at which the permeability falls below 30% of the maximum permeability achieved.

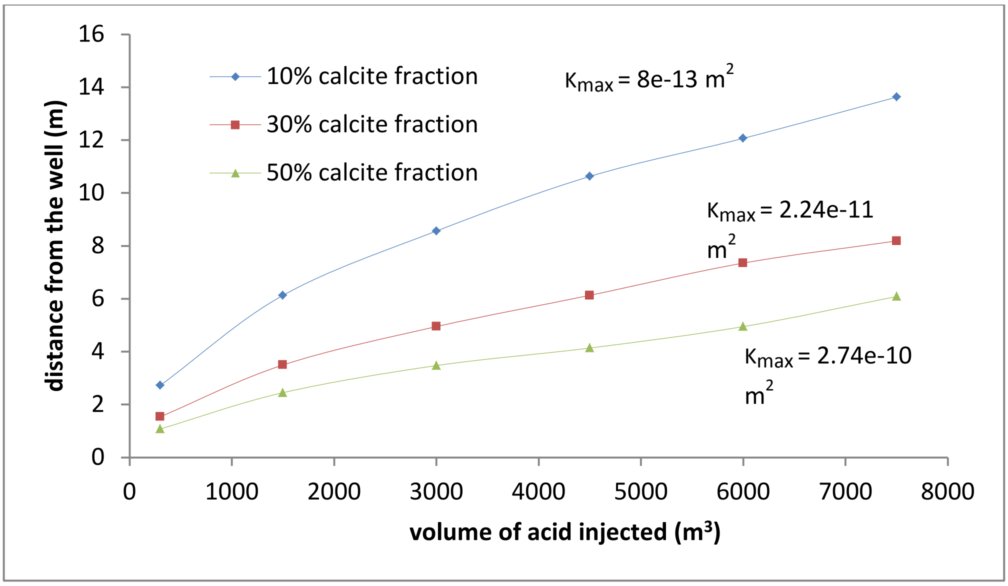

Figure 4.11: Effect of calcite concentration on the radius of influence as a function of the volume of acid injected

Volume of acid injected(m^3)	300	1500	3000	4500	6000	7500
% calcite	Distance from the well (m)					
10	2.72	6.13	8.56	10.63	12.07	13.63
30	1.54	3.49	4.94	6.13	7.35	8.19
50	1.07	2.45	3.47	4.14	4.95	5.77

Table 4.1: Effect of calcite concentration for a constant volume of acid injected as a function of the radius of influence

From the figure 4.11 and table 4.1, for a constant volume of acid injected it can be observed that as the calcite concentration increases the reactions taking place close to the well increases and therefore increasing the amount of acid spent close to the wellbore. This, in turn, implies that with the dissolution of calcite increasing close to the wellbore, the porosity and permeability increase close to the wellbore. This effect can be observed clearly in figure 4.12 and 4.13, which shows the effect of changing calcite concentration as a function of log-scale permeability close to the wellbore.

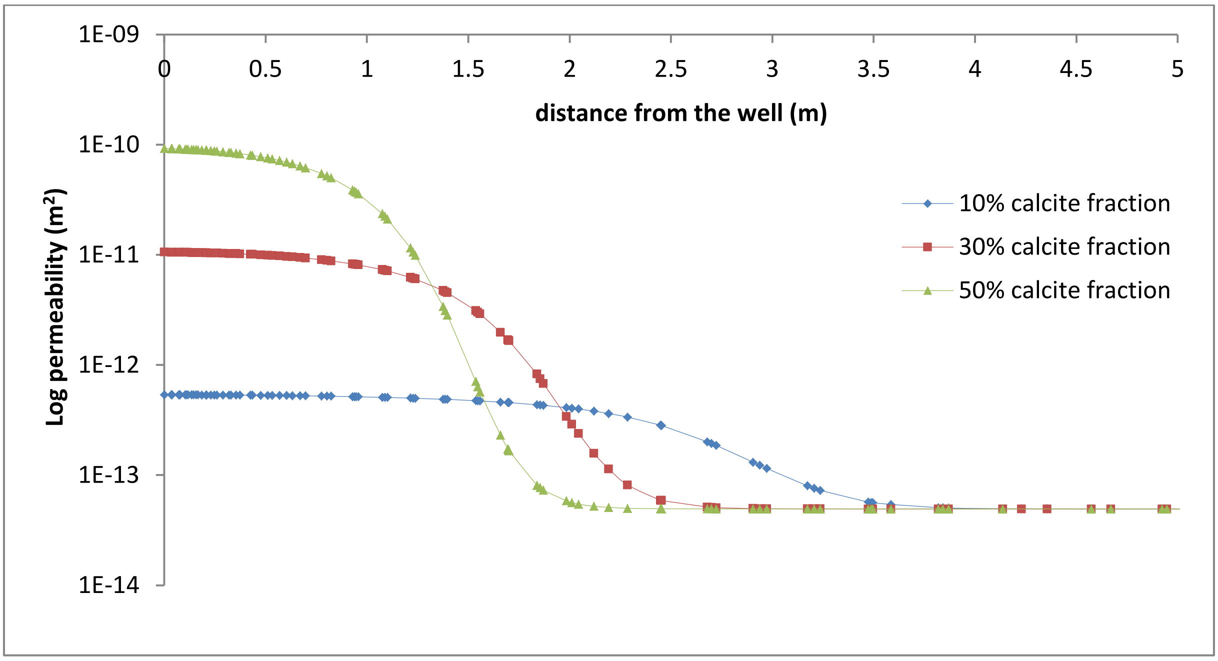

Figure 4.12: Effect of calcite concentration on the permeability as a function of the distance from the well after 10 hours of acid injection

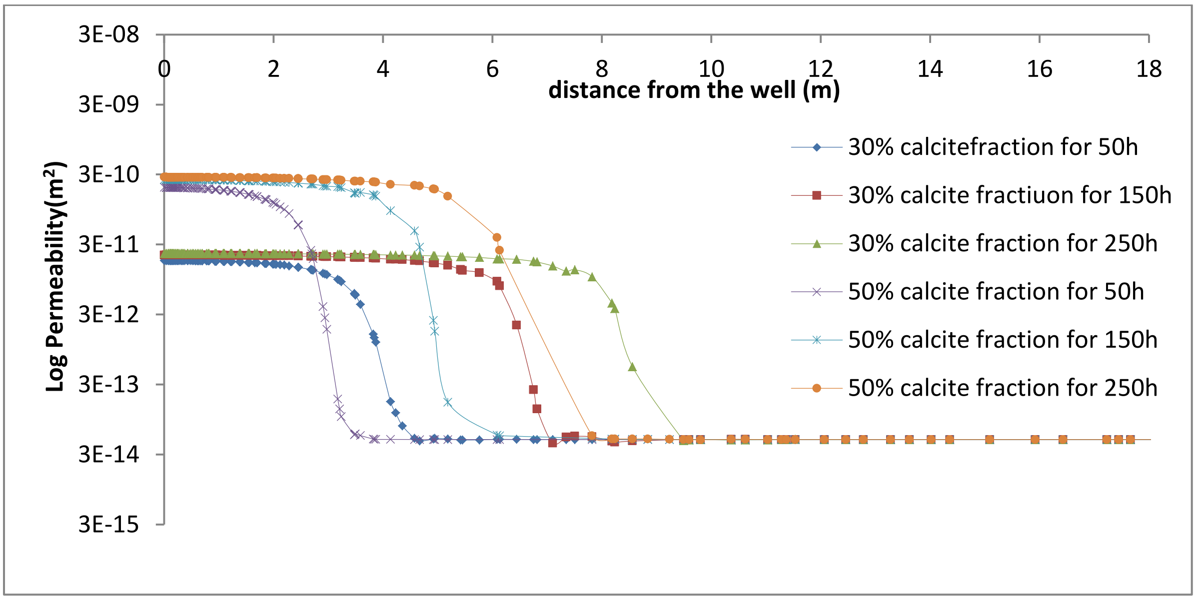

Figure 4.13: Effect of calcite concentration on the permeability as a function of the distance from the well at different volume of HCl injected

According to Figure 4.13, the penetration depth of acid (acid front) and the permeability of the region surrounding the wellbore increase as the volume of injected acid is increased. However, the increase in permeability is not linearly correlated to the volume of acid injected. For example, by increasing the acid volume from 1500 m^3 to 7500 m^3, the penetration depth increases from 4m to 9m away from the wellbore. This is attributed to the fact that at the field scale, the flow is essentially radial, whereas core flood data are obtained for the linear flow of acid in a confined porous medium. Note that this conclusion is valid for the conditions considered, i.e. the uniform distribution of dissoluble material and uniform dissolution at the acid front.

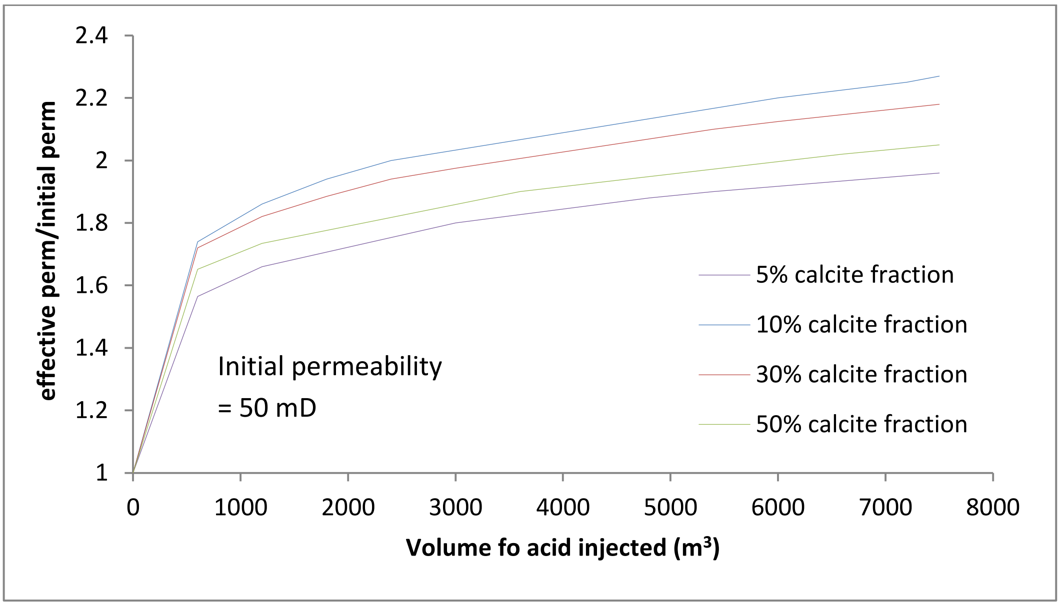

Figure 4.14: Effect of calcite concentration on scaled permeability as a function of volume of acid injected

Figure 4.14 shows the equivalent permeability for a certain volume of volume injected assuming a constant porosity value of 10%. Equivalent permeability obtained for a certain volume of acid injected can be calculated by increasing the initial permeability in a homogeneous system such that the pressure difference between the two wells is equal to the pressure difference obtained after stimulation. This could be used as an indicator of the effect of acid stimulation between the two wells.

It can be observed (figure 4.14) that the equivalent permeability for a lower calcite fraction is higher when compared to that of a greater calcite fraction except for the 5% calcite concentration case. As explained earlier, in a homogeneous system, the amount of calcite dissolved close to the wellbore increases with increasing calcite concentration and hence consuming greater amounts of acid. This implies that the radius of influence for a homogeneous system with 10% calcite concentration is greater than that obtained for a system with 30% calcite concentration. Although in the case of 5% calcite concentration the acid penetration is the highest, the amount of permeability increase is too low to have the expected impact on the Equivalent permeability .

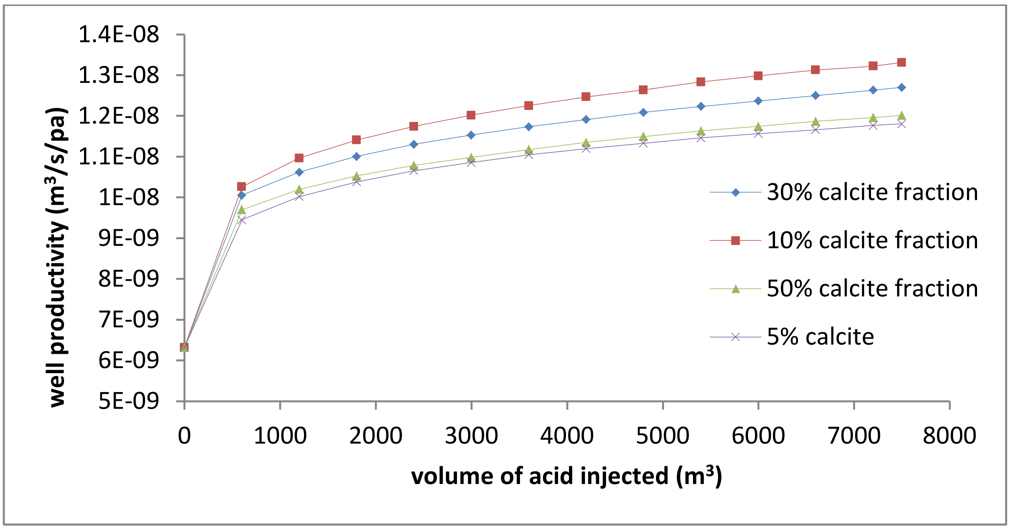

Figure 4.15: Effect of calcite concentration on the well productivity as a function of the volume of acid injected

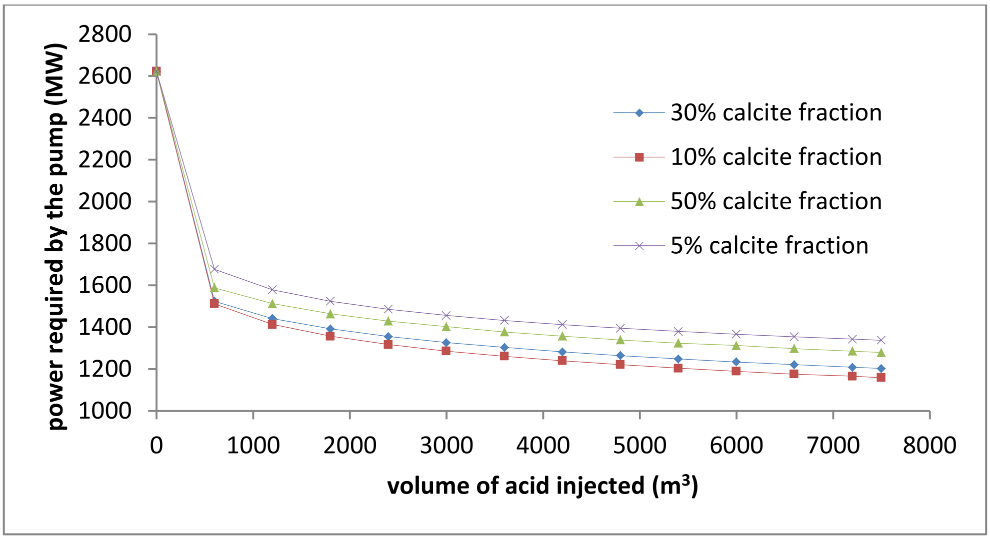

Figure 4.16: Effect of calcite concentration on power required by the pump as a function of the volume of the acid injected

Figure 4.15 shows the well productivity or productivity index versus the injected volume of stimulating fluid. The productivity index (PI) expresses the ability of a reservoir to deliver the fluid to the wellbore . The productivity index of a well can be given by

$$PI = \frac{Flow\ rate}{(Average\ reservoir\ pressure - \ Well\ pressure\ )}$$

As the productivity index increases, the total liquid flowrate to the surface increases for a given pressure drawdown. This could also be related to the economy of the process as it directly affects the pump power required. Figure 4.16 shows the effect of the change in calcite concentration on the pump power required for a long term production of a closed loop doublet system as a function of the volume of acid injected respectively. It can be seen from the figure 4.15 and 4.16 that pump power required and well productivity follow a similar trend as that of the equivalent permeability. Thus, the efficiency of the stimulation process is impacted by both the permeability improvement produced and the penetration of the acid.

4.2.2.2 Effect of temperature on radius of influence and pump power

For a homogeneous system with constant permeability and porosity, the effect of temperature at which the calcite dissolution takes place is discussed in this section. The system has been analysed for temperatures of 75 and 100 ◦C.

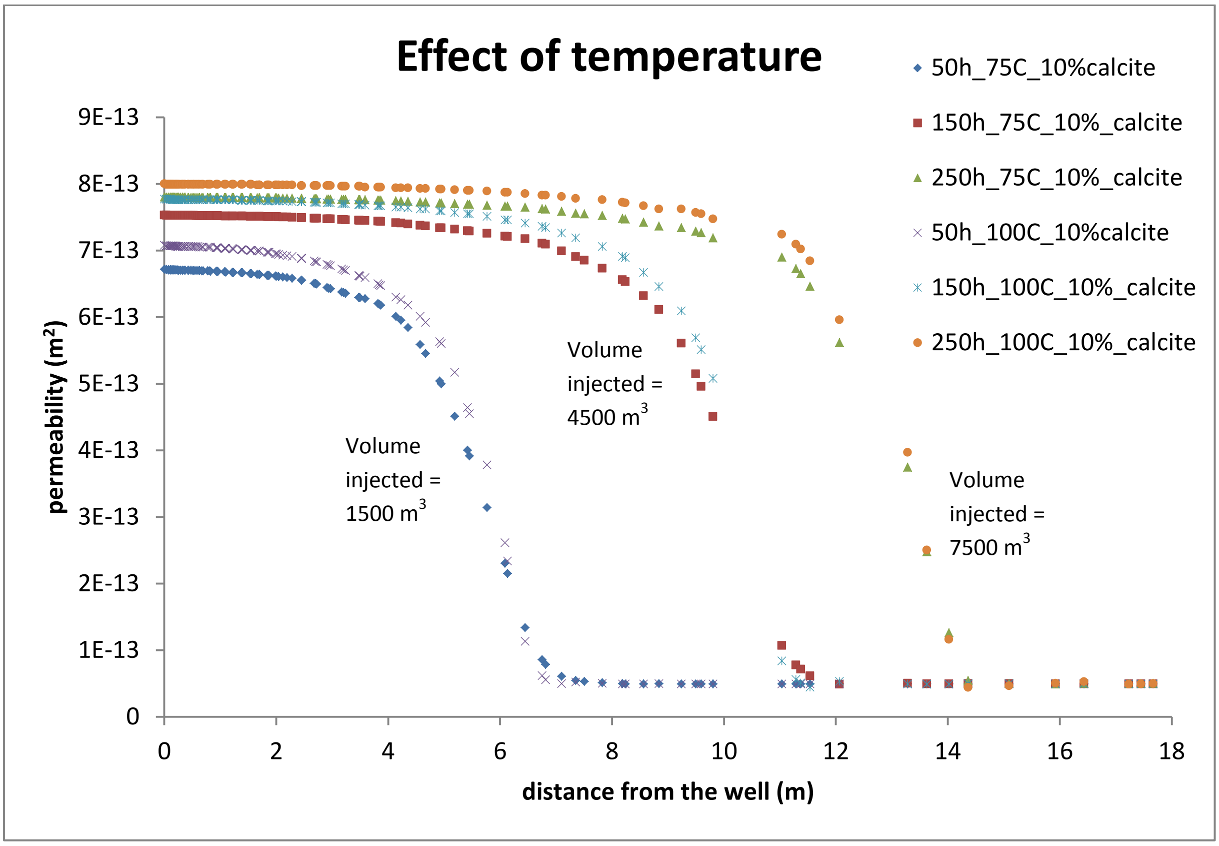

Figure 4.17: Effect of temperature on the permeability as a function of the distance from the well for different temperatures

From the figure 4.17, it can be observed that for a constant volume of acid injected the penetration depth and the permeability development increases with temperature. This can be explained by the temperature dependence of the rate of acid-calcite interaction. Thus, the amount of calcite dissolved increases and hence the permeability improvement is better. The increase in penetration depth can be explained by the decreasing viscosity with temperature. As the viscosity is lowered, the ease of flow in the reservoir increases and hence the acid penetration increases.

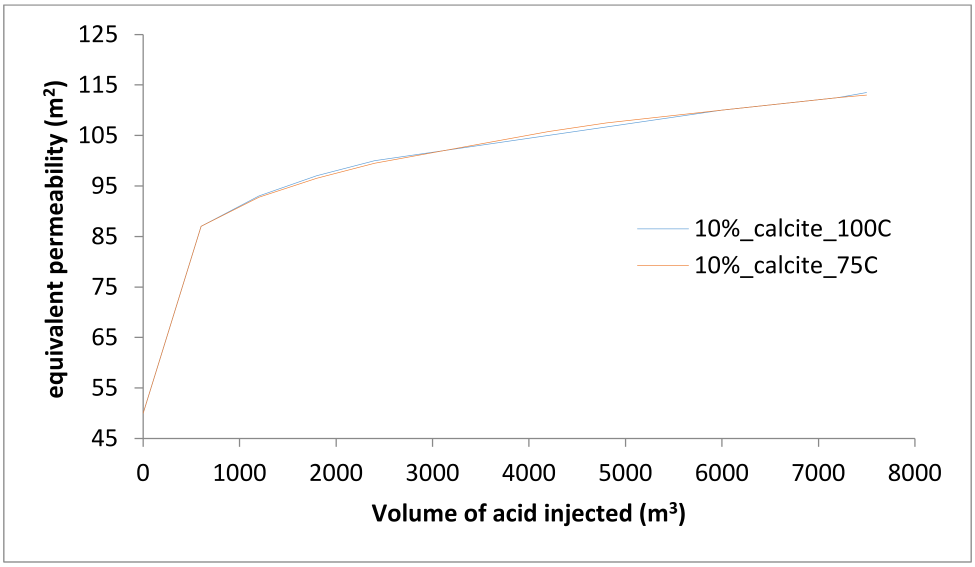

Figure 4.18: Effect of temperature on effective permeability as a function of the volume of acid injected

As the rate of reaction increases with temperature, the amount of calcite dissolved increases accordingly. The increase in equivalent permeability is quite small (Figure 4.18). On the other hand, this effect of temperature can be of great positive impact in the well productivity and the power required by the pump. Figure 4.19 and 4.20 show the effect of temperature on the well productivity and the power required by the pump for long term production.

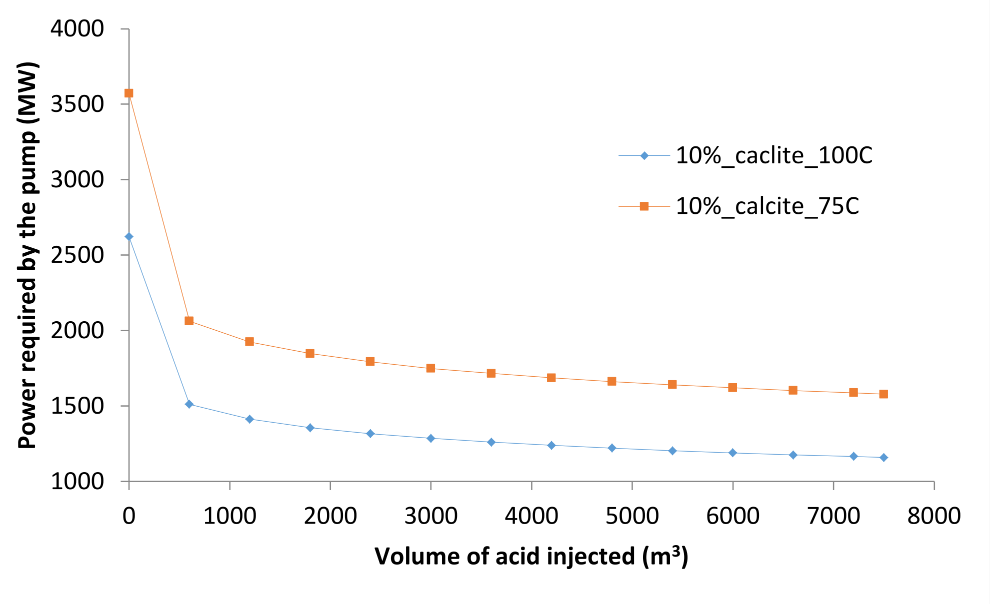

Figure 4.19: Effect of temperature on the pump power as a function of the volume of acid injected

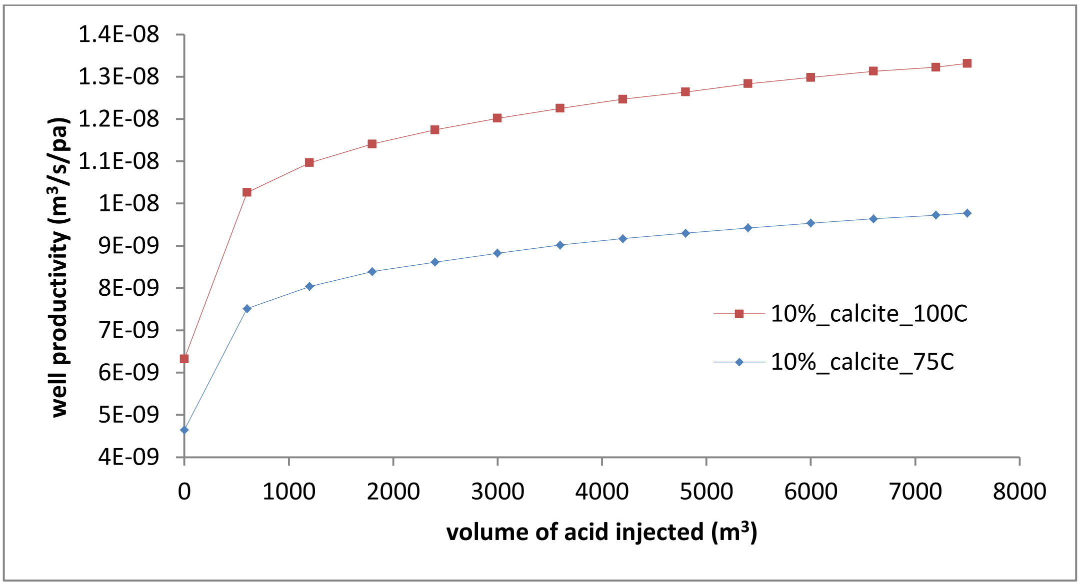

Figure 4.20: Effect of temperature on the well productivity as a function of the volume of acid injected

The well productivity and power required by the pump follows a similar trend as discussed in the earlier case. Temperature has a major effect on the well productivity as well as pump power required. This is due the fact that temperature directly influences the viscosity of the fluid. Thus, the temperature of the field is an important factor affecting the well productivity as it also influences the rate of the acid/rock reaction and thereby influencing the effective reach of the acid injected.

4.2.3 Heterogeneous Model

The effect of calcite dissolution on a heterogeneous field sclae model is analysed in this section. Further, the water viscosity, thermal conductivity, heat capacity and water denstity are also defined here as functions of temeprature in order to obtain accurate simulations.

4.2.3.1 Effect of heterogenity

As shown earlier in figure (3.1), heterogenity was implemeted using FLUMY data. This results in effects like fingering in the acid front which in turn cause an uneven porosity and peremeability development.

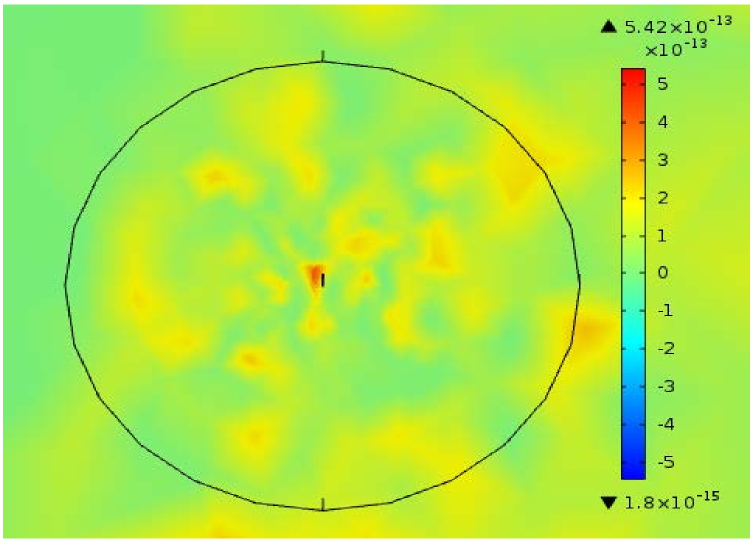

Figure 4.21: Permeability plot of the XY plane near the wellbore before stimulation

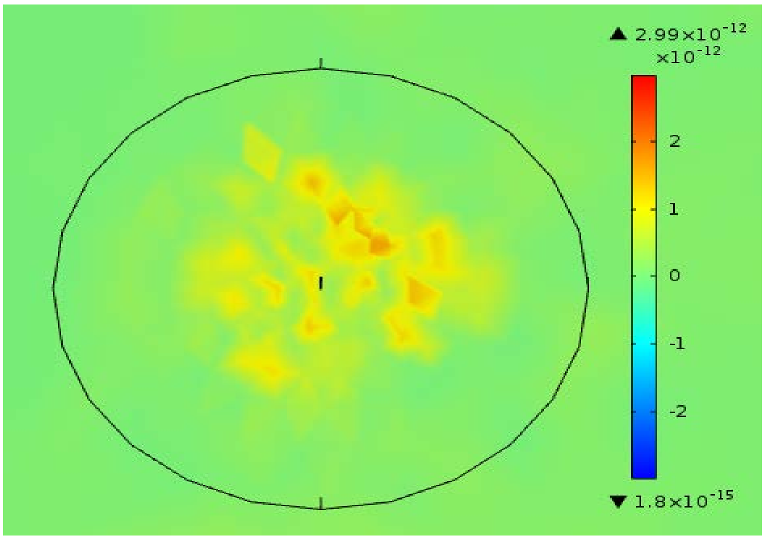

Figure 4.22: Permeability plot of XY plane near the wellbore after stimulation

The Figures (4.21) and (4.22) show the peremeability of the region around the wellbore before and after stimulation. It can be observed that the peramability increase is focused in the high peremability regions observed in the figure (4.21). It is important to notice that the scales vary between figure (4.21) and (4.22).

It can be thus confirmed that chanelling takes place causing uneven dissolution based on the ability of the acid to flow. This implies that the effective radius of influence is not uniform and varies based on the heterogenity in a given direction. The radial pattern in the permeability improvement can be observed in figure (4.22). Thus, from homogeneous and heterogeneous models it can be confirmed that the penetration depth follows a radial pattern rather than linear flow in coreflood experiments.

4.2.3.2 Effect of temperature

The effect of temperature on calcite dissolution over a heterogeneous field is discussed below. The Figure 4.23 shows the change in well productivity versus the volume of stimulating fluid injected. The Figure 4.24 shows the effect of different temperatures during calcite dissolution on the pump power required for long term closed loop doublet system production. It can be observed that the well productivity and pump power required follows a similar trend to that of a homogeneous field. Although the pump power required follows a similar trend, the magnitude of the difference seems much less than the homogeneous case.

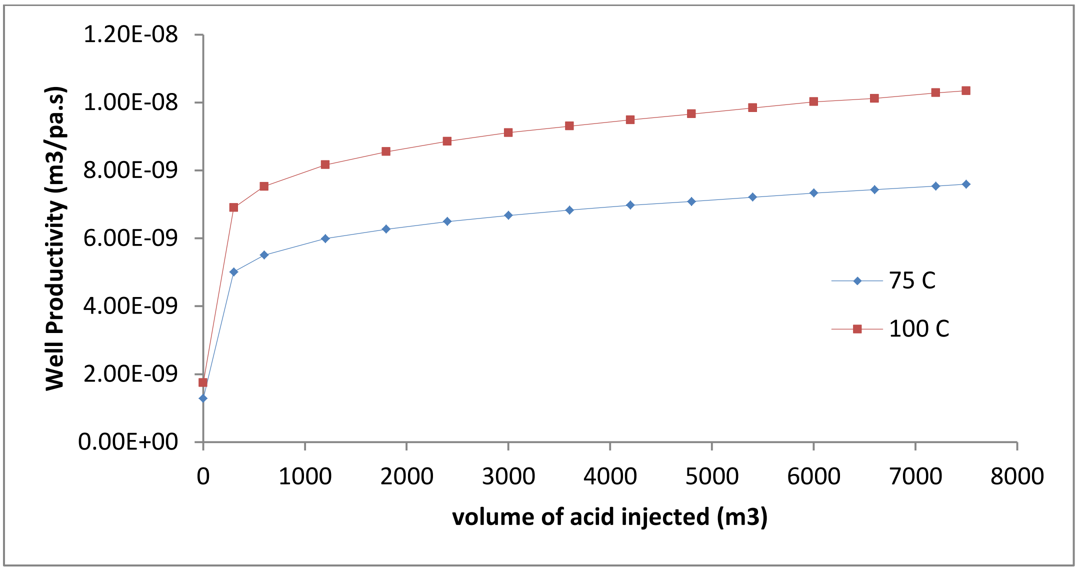

Figure 4.23: Effect of varying temperature during calcite dissolution as a function of well productivity and volume of acid injected

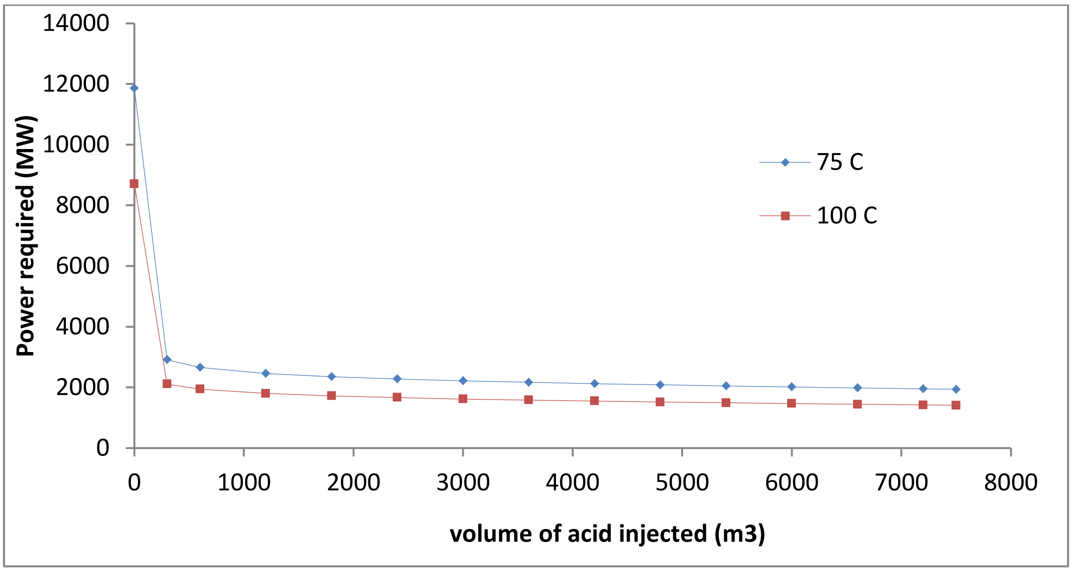

Figure 4.24: Effect of varying temperature during calcite dissolution as a function of power required by the pump and volume of acid injected

4.2.3.3 Effect of stimulation of field life

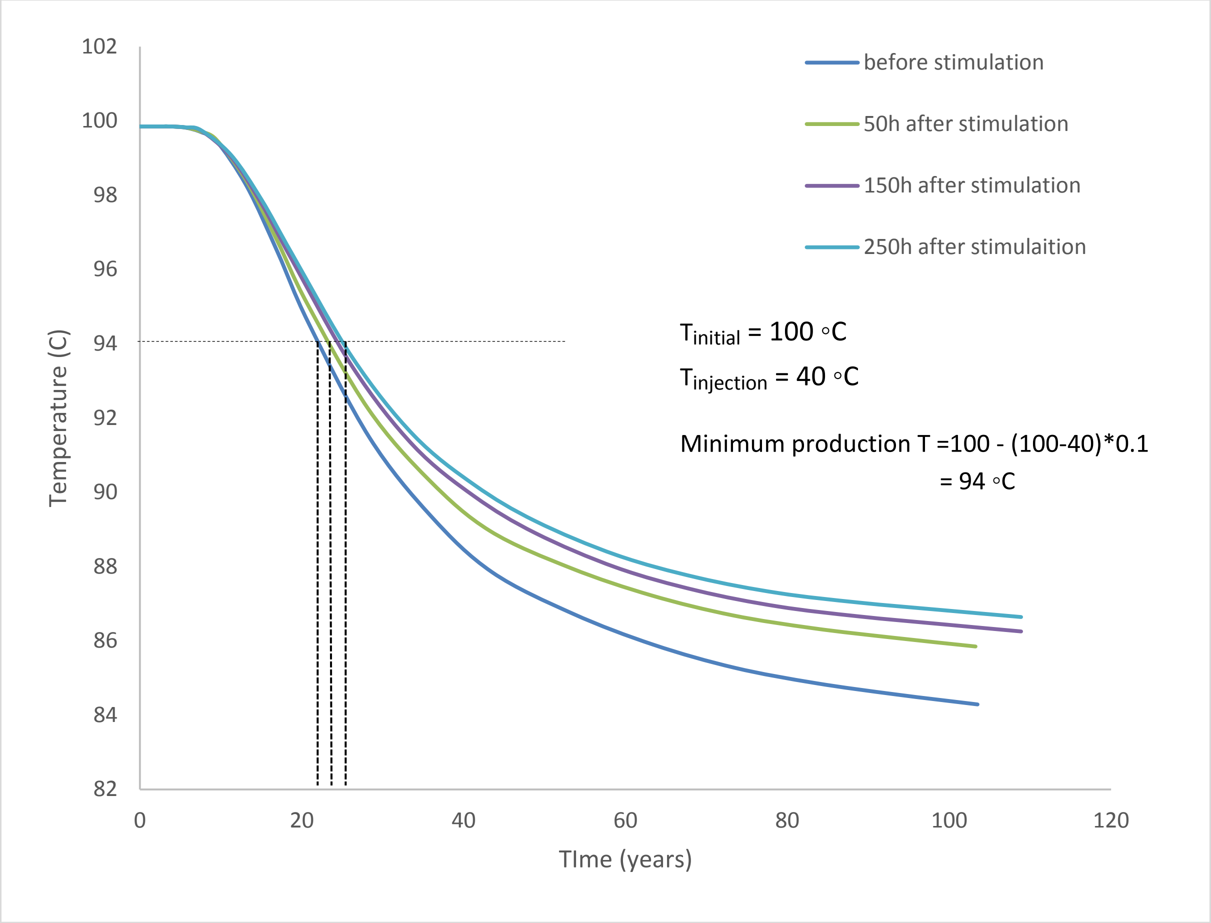

Figure 4.25: Effect of acid stimulation on field life for different volumes of acid injected

Figure 4.25 shows the effect of acid stimulation on the field life. Acid stimulation can improve the life of a geothermal field by enhancing the permeability in previously impermeable rock. This effect can be observed from the figure 4.25. For example, for a minimum production temperature of 94 ^{0}C, the lifetime of the reservoir increases as the stimulation is done. Thus, this model can be used to predict the effect of acid injection and also to calculate the amount of acid needed to extend the life for a certain amount of time.

4.3 Discussion

4.3.1 Experimental Data

In an effort to analyse the effect of calcite dissolution in sandstone reservoirs, three different experiments were conducted. The critical velocity of fines migration and the critical salt concentration were determined and later used in the acid injection studies.

Although extensive laboratory studies of formation damage due to fines migration and varying salt concentration have been conducted, it is important to realize that these parameters have to be calculated individually for each formation in order to prevent the undesirable effects. Consistent with the literature, there is a clear decrease in the permeability of the sample when the salt concentration is less than the critical value (K C Khilar et al., 1983). Similarly, a decrease in the permeability is observed when the flow rate is increased above the critical velocity of fines migration. Once the fines are released, the particles either should get retained at other locations in the porous media causing a reduction in the rock permeability or exit the porous media in the fluid stream. This is a function of the diameter of the particles released and the size of the pore throat (C Gruesbeck et al., 1982). Figure 6.5 showed that the pressure drop increases as the flow velocity is increased beyond critical velocity indicating a reduction in permeability. This highlights the importance of estimating the critical velocity of fines migration and critical salt concentration which can be crucial in designing acid jobs, minimizing geotechnical damage, and determining production and injection rates.

Another interesting observation was that the direction in which the sample was obtained did not have an effect on the critical velocity of fines migration. One possible explanation could be the homogeneity in the lower Triassic resulting in no influence of the direction of flow. Another possible explanation could be that the samples, being obtained from an outcrop, might contribute to the homogeneity of the sample used. It must also be borne in mind that the study was only conducted on a small number of samples and hence it might not be completely representative of the target formation. More samples from the wells and further work are needed to statistically show the above-discussed results.

4.3.2 Numerical Model

The model aimed at utilizing the average available reactive surface area calculated from matching the experimental results with a core scale model and analysing the effect of calcite dissolution on a field scale. It was observed that for a field of constant permeability and porosity, the effective radius of influence is more important than the amount of calcite dissolved itself. The effect of calcite dissolution on the well productivity and the power required by the pump were also analysed. The plots were found to be following a similar trend showing the importance of the effective radius of influence.

An important observation from the numerical model was the difference in the flow pattern between the core floods and the field. It is important to understand that the linear core flood data cannot be translated directly and needs to be corrected for the radial flow of acid in the formation. This effect is very important especially if the dissolution is not uniform.

Another interesting observation is the increase in the field life after stimulation due to the reduction in the rate of production temperature decline(figure 4.23). One possible explanation could be that the acid dissolving the calcite helps the fluid reach some impermeable regions that were not being utilized before. Thus, it might create new flow paths or increase the rock surface in the available flow paths for heat transfer. The production temperature starts to drop once the cold water front has reached the producing well. Once the cold front has reached the producing well the temperature beings to drop slowly based on the rate of heat transfer between the solid and the fluid. Differential heat transport due to heterogeneity also adds to the complexity of this effect.

This model can be used as a predictive tool to simulate the improvement in the lifetime for a given volume of acid injected. It can be also be used to conduct an economic analysis on the effect of acid injected in terms of pump power required, power produced by the system as well as the improvement in the lifetime of the reservoir. Similarly , this model can be used to guess the amount of acid needed to achieve a certain improvement in well productivity.

It is important to understand the limitations of the model as the above statements can be argued for various cases. The permeability porosity relationship obtained from the core scale model is an average relationship and pore scale reactive modelling is required to duplicate the dissolution. The reactive surface area is an important parameter in this study. Although this varies with the calcite dissolved, a constant value was assumed for this parameter. The calcite concentration was assumed to be uniform for the ease of modelling. This parameter varies in the pore scale, making it hard to be duplicated in a model. The availability of calcite for dissolution is an important parameter determining the permeability development and hence future work could be focussed on ways to implement the calcite distribution similar to the field.

Further work is needed to improve the accuracy of the permeability porosity relationship, changing the available reactive surface area such that it is a function of the calcite dissolution and finally implementing heterogeneity in calcite distribution. Further work could also be focused on validating the model with field data.

5 Conclusions

In this thesis the effect of calcite dissolution was analysed on two scales and the core scale model was linked to the field scale model by using an average value for the available reactive surface area. The conclusions that are drawn from this research may be split into two parts: conclusions regarding the experimental data and those from the numerical model.

Experimental data

The critical salt concentration to prevent clay swelling for the Wesersandstein sample was found to be at about 0.3-0.2 M NaCl/l.

The corresponding injection rate for the critical velocity of fines migration was calculated to be around 12 ml/h. Fluid injection at a higher rate than this would result in pore plugging and consequent reduction in permeability. In an effort to understand the effect of flow direction, three samples were obtained in the X, Y and Z direction. It was observed that the critical velocity of fines migration was close to 12 ml/h in each direction, indicating the homogeneity of the samples and possibly the Wesersandstein.

The Acid injection studies conducted showed an increase in the rock permeability indicating the dissolution of calcite.

Numerical Model

The core scale acid dissolution model was created and the model was matched with the experimental data by using an average value for the available reactive surface area.

The average available reactive surface area value obtained from the core scale model was used in the field scale model to predict the effect of calcite dissolution, thereby linking the core scale model with the field scale model.

The equivalent permeability was found to be a function of the radius of influence and the permeability improvement achieved.

The Field scale simulation results show that the acid penetration depth should be corrected for the radial flow of acid in the formation. Thus, the penetration depth (acid front) cannot be directly translated from the linear coreflood data specifically if the dissolution is not uniform.

Temperature has a considerable effect on the well productivity and pump power. Interestingly, in a heterogeneous reservoir this improvement in well productivity did not translate completely to a reduction in power required by the pump.

Results showed that the acid stimulation has a positive effect on the lifetime of the reservoir. Thus, the model can be used as a predictive tool for lifetime development given a volume of acid injected. Additionally the model can be used to predict the required volume of acid injected for a certain improvement in the well productivity.

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Nomenclature

Q	flow rate
M	Molarity
R_i	Rate of reaction of a given species i
u	Velocity vector
D_i	Diffusion coefficient of a given species i
k	Permeability
C_i	concentration of a given species i
C_p	Specific heat capacity
T	Absolute temperature
K_{eff}	Effective thermal conductivity
L	Sample Length
A	Cross sectional area
$K_{eff}\nabla T$	Conductive heat flux
Q_h	Heat source/sink term
$u.\nabla C_i$	convective transport due to velocity u

Greek

ρ	Density
μ	Viscosity of the fluid
ϕ	Porosity
$(\rho C_P)_{eff}$	Effective volumetric heat capacity
$\frac{\partial C_i}{\partial t}$	Rate of accumulation/ consumption of a given species i

Appendix - Introduction to Acid Stimulation

Acid stimulation

Acid Stimulation refers to the process of injecting acid into a formation to increase the permeability and enhance productivity. Acid stimulation is as old as oil well drilling itself. A standard oil patent for acidizing limestone with hydrochloric acid dates from 1895.[3] Acid Stimulation is of two types mainly, Matrix Acidizing and Fracture acidizing.

Matrix Acidizing

Matrix Acidizing is the process of injecting acid into reservoir formations below the formation fracturing pressure[2]. Matrix acidizing is carried out in both sandstone and carbonate formations although the primary aim and the acid used in each treatment vary according to the solubility of the minerals in the formation.

Matrix Acidizing in Sandstone Formations

In sandstone formations, matrix acidizing treatments are primarily designed to remove formation damage or plugging of perforations and also to dissolve solids and fines entrapped in pore throats and pore spaces that hamper fluid flow. In most cases acidizing in sandstone formations is used to remove formation damage.

Conventionally the most often used acid for sandstone stimulation is a mixture of HCl and HF, also famously known as mud acid. Based on the mineralogy of the sandstone, the composition of this mud acid injected is varied as shown in table 1 of Appendix.

Along with the mineralogy of the rock, the location of the target minerals, and the type and severity of formation damage play an important role in determining the type and composition of the acid being used.

Reactions Involved

The reaction of hydrofluoric acid [HF] on the pure quartz component of sandstone follows these two equations:

$$SiO_2 + 4HF \leftrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2F^- \leftrightarrow SiF_6^{2-}$$

Where SiF_4 is silicon tetrafluoride and SiF_6 is silicon hexafluoride respectively.

A number of mineral precipitation reactions can take place based on the mineral composition of the rock and might result in the formation of compounds like aluminium hydroxide[$Al(OH)_3$],aluminium fluoride [AlF_3], Ferric hydroxide [$Fe(OH)_3$], Ferrous sulphide[FeS],calcium fluoride [CaF_2].

$$Al_3 + 3F^- \leftrightarrow AlF_3$$

$$Al_3 + 3OH^- \leftrightarrow Al(OH)_3$$

$$CaCO_3 + HF \leftrightarrow CaF_2 + H_2O + CO_2$$

These precipitates can cause potential damage to the formation permanently and should be handled carefully.

Most sandstone acidizing treatments include the following three stages

- Pre-flush
- Main flush
- Overflush

Preflush is a fluid stage pumped ahead of the main treating fluid [1]. The main aim of the preflush is to displace the formation brines that usually contains Na, Ca or K ions, and these ions when in contact with HF results in the formation of alkali-fluosilicates. Another important function of the preflush is to dissolve as much of the calcareous materials as possible, prior to the injection of the HF acid to minimize calcium fluoride precipitation [1].
The main flush is the treatment stage that injects the mud acid to get rid of the formation damage or to enhance permeability in the formation.

Overflush is an important part of a sandstone acid treatment and it mainly used for displacing the non-reacted acid into the formation, displace the reaction products away from the wellbore and finally remove the oil-wet relative permeability problems caused by some corrosion inhibitors.

Proper design of the treatment, use of adequate preflush, and carefully chosen additives ad diverting agents can help prevent the formation of above such mentioned precipitates and help in achieving the desired permeability improvement.

Matrix Acidizing in Carbonate Formations

The primary purpose of matrix acidizing is to improve flow capacity through a damaged region near the wellbore. This can be achieved by dissolving rock through near-wellbore formation damage.

Conventionally HCl is the most commonly used in Carbonate acid treatments. HCl in carbonates dissolves limestone and dolomite to produce conductive channels, wormholes and enhanced permeability regions. Other commonly used acids for carbonate acidizing treatment are Acetic acid (CH_3COOH) and formic acid ($HCOOH$). Acetic and formic acid being weakly ionized slow reacting organic acids will have lower spending rates and naturally because of their higher equivalent weights will have a less dissolving power for the same percentage acid solutions[2]. On the other hand, these weak acids sequester iron, reducing iron precipitation and thus helps to inhibit corrosion.

Reactions Involved

The reaction rate of acid in carbonate formations are influenced by a number of factors like temperature, pressure, Acid type and concentration being used, flow velocity, reaction products, mineralogy of the formation and much more. Some of the possible reactions that can occur during the acid treatment in carbonate formations are as follows.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 \uparrow + H_2O$$

$$4HCl + CaMg(CO_3)_2 \rightarrow CaCl_2 + MgCl_2 + 2CO_2 \uparrow + 2H_2O$$

$$2CH_3COOH + CaCO_3 \rightarrow Ca(CH_3CO_2)_2 + CO_2 \uparrow + H_2O$$

$$4CH_3COOH + CaMg(CO_3)_2 \rightarrow Ca(CH_3CO_2)_2 + Mg(CH_3CO_2)_2 + CO_2 \uparrow + H_2O$$

$$2HCOOH + CaCO_3 \rightarrow Ca(HCO_2)_2 + CO_2 \uparrow + H_2O$$

$$4HCOOH + CaMg(CO_3)_2 \rightarrow Ca(HCO_2)_2 + Mg(HCO_2)_2 + 2CO_2 \uparrow + 2\,H_2O$$

Where $CaMg(CO_3)_2$ is dolomite, $CaCO_3$ is calcium carbonate, $Ca(HCO_2)_2$ is calcium formate, $Mg(HCO_2)_2$ is magnesium formate, $Ca(CH_3CO_2)_2$ is calcium acetate, $Mg(CH_3CO_2)_2$ is magnesium acetate respectively.

A standard carbonate acid treatment consists of the following four stages

- Pickling
- Preflush
- Acid Stage
- Overflush

Pickling is a process that is common for both sandstone and carbonate formations. Its main objective is to remove impurities such as stains, inorganic contaminants, rust or scale from ferrous metals such as the injection string, production tubing, drill pipe and coiled tubing [4]. The standard pickling acid is 7.5% HCl with added iron control agents and corrosion inhibitor [2].

Preflush is used to remove organic or inorganic scale from wellbore tubular prior to injection of acid stage [2].Based on the composition of the scaling particles solutions like xylene or terpene-based solvents can be quite effective.

Acid Stage is done to remove or bypass any formation damage. Conventionally HCl of 15% - 28% is used. Due to the different kinds of porosity present in carbonate formations, the penetration of acid is not uniform throughout. Such heterogeneities in the pore structure can cause channelling or wormholing of acid through the formation [2].

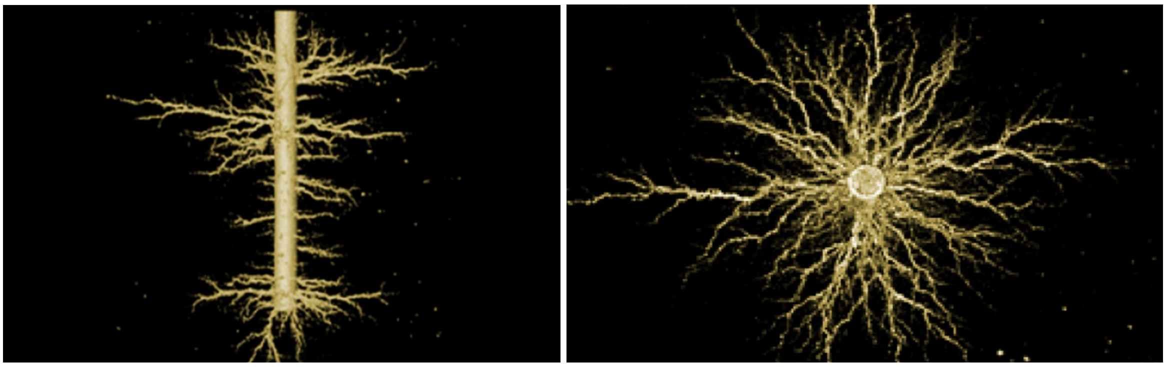

Figure 0.1: Example of Matrix Acid Stimulation (a) Side View (b) Top View [6].

Overflush is used for the same purpose as mentioned earlier in sandstone formations, which is to displace acid into the formation and increase the penetration distance.

Proper design of the treatment stage along with effective use of retardation systems, placement techniques and additives can help in achieving an effective carbonate acid treatment.

Fracture Acidizing

Fracture acidizing is the process of injecting acid into a reservoir above the fracture pressure of the formation , thus fracturing the reservoir and dissolving the permeability inhibitive sediments. Fracture Acidizing is different from hydraulic fracturing for the fact that in fracture acidizing the matrix elements are dissolved while in hydraulic fracturing the fracture created is maintained by the use of proppants.

Acid fracturing treatments can be a solution for wells with impaired production. Not only would acid fracturing increase well productivity, but also would help retain the general hydraulic conductivity for a longer period [1].

Fracture acidizing in sandstones

Fracture acidizing in sandstones has been considered on many occasions in the past and had been mostly dismissed under the generally correct notion that sandstone surfaces are not etched by acid as in the case of carbonate formations[7]. Another reason for the reduced usage of fracture acidizing in sandstones is the reactivity of sandstone formations with acids like HCl. However, certain HF acid systems utilizing low total acid concentration with flexible (and potentially high) generated HF concentration, can create substantial differential sandstone dissolution patterns [7]. The main problems with sandstone acid stimulation are discussed later.

Fracture acidizing in carbonates

As mentioned earlier acid stimulation in carbonate formations dates back to the 1890's. Since then numerous developments have been made with an emphasis on treatment design, fluid development, acid loss (leak-off) control, acid reaction retardation and influencing fracture length and conductivity. There have been two general methods of achieving an acid-etched fracture in carbonate formations that continue to remain the basis of fracture acidizing treatments [7].

- Viscous Fingering (Pad Acid)
- Viscous Acid Fracturing

Viscous fingering although applicable in all carbonate formations but is most useful in more homogeneous formations. With viscous fingering, a fracture is first created with a viscous gelled water pad. Following this a low viscous acid is injected which fingers through the viscous pad rapidly and unevenly, thereby penetrating deeply and etching the fracture face unevenly [3].

Viscous acid fracturing used viscous acid systems such as gelled, emulsified and foamed acid, or chemically retarded acids to both create and differentially etch the fracture face.

Acid Stimulation in Geothermal Wells

Geothermal reservoirs differ significantly from hydrocarbon reservoirs and so does their remedial techniques. Most of these geothermal reservoirs producing steam or hot water from naturally fractured formations are from either volcanic quartz of silicate based formations with low formation permeability [2].The low permeability could be either naturally occurring or be caused by damages occurring during drilling and /or production phases. Most geothermal wells with formation damage are damaged by the following:

- Drilling mud solids and drilled cuttings lost to the formation fractures
- Scale (Calcium Carbonate, silica, calcium sulfate and mixtures)

Very successful geothermal well acidizing has been achieved using a high-rate brute force method [8].In geothermal well acidizing, more acid often is better. The naturally fractured volcanic formations can withstand high concentrations of HF [2]. The most common conventional HF solution for geothermal well acidizing is 10% HCl and 5% HF.

For carbonate scale removal, 15% HCl is most commonly used. HF should not be used in such cases due to its reactivity. If the scale formed is mixed and layered scales, a combination of HCL and HF (or acid stages) is required in order to at least partially dissolve the scale [2]. In addition to conventional acid formulations, geothermal wells have been successfully treated with low-total acid-strength, high-HF-strength systems. The first such formulations included a 3% HCl, 5% HF solution containing an organophosphonic acid [9]. More recently, similar low concentration HCl–high-concentration HF formulations (containing as much as 9% HF), delivered through 2" coiled tubing, have been used in geothermal wells [10].Despite the high HF strength, these mixtures are less corrosive due to their low total acid strength.

The main difference being the high temperature that reduces the efficiency of corrosion inhibitors as well as increasing the acid/rock reaction rate which requires the use of a retarded acid system to ensure that the acid is not spent immediately close to the wellbore, but will penetrate deeper into the formation. The other two additives necessary in a geothermal acid job are the high temperature iron control agent and corrosion inhibitor intensifier [1]. Treatment volumes, injection rates, acid placement techniques, acid system selection and evaluation of the results when stimulating geothermal wells, all follow the same criteria as for oil wells.

Acid treatments that were developed by the oil industry for improving productivity have been partially adapted to the geothermal wells [1] in the past decade and a lot of improvements has been achieved since then. The fact that the geothermal fields are less profitable compared to hydrocarbon wells calls for more efficiency and accuracy to maintain the economy of the project. The next challenge in the line of processes would be to increase productivity and maintain it over a longer period of time. New and innovative stimulation technologies are emerging that will modify or help improve the efficiency of the process of stimulation. It seems likely that well stimulation will remain a dynamic part of the petroleum and the geothermal industry.

Problems in Acid Stimulation

Even though the process of acid stimulation has been in practice since the early 1920’s, a lot of challenges still exist in the successful application of an acid job. There are a number of possible reasons based on the type of formation to explain the reason for the failure of an acid job. It is important to also think about what is defined as success in the case of an acid stimulation job, in most cases, this is very much site-specific and largely influenced by the practices involved. In many cases, acid stimulation is considered a hit or miss type of prospect. This could be true if it’s based on single well results alone, rather the field-wide results, the factors leading up to it and during the job should also be considered.

Problems in sandstone acidizing

As clearly explained by Portier et al., [1] Some of the major challenges that exist in acid stimulation of sandstone acidizing include multiple types of co-existing formation damage; uncertain rock mineralogy; multiple fluids and pumping stages; complex chemical reactions between fluids and formation minerals; inadequate zonal coverage; limited active acid penetration; rock deconsolidation due to acid-rock interactions; acid emulsion and sludge tendencies. A number of controllable causes can be avoided with proper planning and candidate selection. We have to bear in mind that there exist some uncontrollable causes that can be unforeseen. The most common causes for acidizing treatment as identified by industry experts could be either one or a combination of the following reasons[2]

- Using the wrong type of acid
- Using improper acid volumes and/or acid concentrations for the formation mineralogy
- Over/misusing additives
- Inadequately perforated wells
- Inadequate contacting the damage
- Shutting in the acid treatment too long before producing back
- Wrong identification of the cause of formation damage

There are a great number of other non-trivial reasons that could result in the failure of the acid treatment in sandstone formations. Avoiding the controllable factors and proper design of the stimulation treatment using well-analyzed data can contribute to the success of the treatment.

Problems in carbonate acidizing

Carbonate acidizing differs from sandstone acidizing in terms of both the chemistry and the physics. The chemistry of carbonate acidizing is relatively much straight forward when compared to the complex reactions possible in the case of sandstone acidizing. In the case of matrix acidizing, the wormholing phenomenon has been modelled and studied extensively starting in the early 1970's. Provided the complexity of wormholes, there is a wide range of possible channeling or dissolution patterns. Determining the optimum combination of injection rate and fluid type is still a challenge when it comes to field scale. This is mainly because leak-off of reactive fluids to the surrounding formation cannot be determined accurately. Some other major factors like reservoir heterogeneities and different pore types also contribute to the challenges in carbonate acid stimulation.

Carbonate stimulation is increasingly performed in horizontal wells. The most important challenge involved in acid treatment in horizontal wells is the low drawdown making the treatment placement a very important factor in the design of carbonate acidizing treatments in horizontal wells.

. With proper design and careful placement successful matrix acidizing and fracture acidizing can be achieved in horizontal well carbonate formations. Though there exists an unpredictability in carbonate formations, the chances of a successful treatment are quite high due to the constant advancements being made such as foam diverting, pumping acid in stages and increased usage of coiled tubing placement technique have resulted in increased success rate of acidizing treatments in carbonate formations.

Problems in Geothermal Acid stimulation

In geothermal reservoirs with increased downhole temperatures, the acid/rock interaction rate increases, the rate of corrosion increases while the efficiency of the corrosion inhibitor decreases, resulting in the usage of retarded acid systems and corrosion inhibition intensifier respectively. Retarded systems ensure that the acid is not spent close to the wellbore itself. The designing of an acid treatment process is very similar to its hydrocarbon counterparts with the careful determination of the effect of elevated temperatures on the various steps involved. Other challenges include changing fluid properties with temperature, producing from multiple layers with long open hole systems contribute to the increased complexity of the acid treatment of geothermal reservoir. Recent developments with better design of retarded acid systems, placement techniques, use of organophosphonic acid along with proper treatment design and additive selection can result in improved success rate in the acid treatment of geothermal reservoirs.

Conclusion

A lot of challenges has been presented in acid treatment of reservoirs and developments in technology has resulted in solving most of these challenges. It is worth understanding that sometimes acid treatments are performed even though there is not enough data to fully evaluate a well which is crucial in designing an effective acid treatment. New innovative stimulation techniques/modifications of the existing techniques seem to continually emerge that improve the design and performance of stimulation technologies.

Conventional Sandstone Mud Acid Use Guidelines [2]		
	Recommended Acid for	
Formation Characteristics	Preflush	Main Acid Stage
Solubility In HCl > 15%-20%	Avoid use of HF, if possible	
calcite or dolomite	5% NH4Cl	15% HCl only*
High Iron Carbonate	5% NH4Cl + 3% acetic acid	15% Hcl** + iron Control*
high permeability (>100 mD)		
High Quartz (>80%), low Clay (<5%)	15% HCl	12% HCl - 3% HF
Moderate Clay (<5%-8%), low feldspar (<10%)	10% HCl	7.5% HCl - 1.5% HF
High Clay (>10%)	5-10% HCl	6.5% HCl - 1%HF
High Feldspar (>15%)	5%-10% HCl	6.5%HCl - 1.5% HF
High Feldspar (>15%) and clay (>10%)	10% HCl	9% HCl - 1% HF
High Iron chlorite clay (>8%)	5% HCl	3% HCl - 0.5% HF
	10% Acetic acid + 5% NH_4Cl	10% Acetic Acid - 0.5% HF
Medium Permeability (10-100 mD)		
Higher clay (>5% - 7%)	10%HCl	6% HCl - 1.5 % HF
Lower clay (<5%-7%)	10%HCl	9% HCl - 1% HF
High feldspar (>10%- 15%)	10%-15% HCl	12% HCl -1.5% HF
High feldspar (>10%- 15%) and Clay (>10%)	10% HCl	9% HCl - 1% HF
High iron carbonate clay (>~ 8%)	5% HCl	3% HCl - 0.5% HF
	10% Acetic acid + 5% NH4Cl	10% Acetic Acid - 0.5% HF
High iron Carbonate (>5% - 7%)	10% HCl	9% HCl - 1% HF
	10% HCl	5% HCl - 0.5% HF[#]
Low Permeability (1 -10 mD)[$]		
Low clay (<5%)**, and HCl Solubility (<10%)	5% HCl	6% HCl - 1.5 % HF
High Clay (>8% - 10%)	5% HCl	3% HCl - 0.5% HF
High iron chlorite clay (>5%)	10% Acetic acid + 5% NH4Cl	10% Aceitc Acid - 0.5% HF
High Feldspar (>10%)	10% HCl	9% HCl - 1% HF

- * the location of the carbonates in the matrix is important; it may be possible to include HF in naturally fractured formations with high carbonate content.
- ** Although fracturing may be preferable , low permeability ,low clay sands may respond favorably to acidizing with HF
- # k <25 mD
- $ if zeolites are present (>3%) consider replacing HCl with proprietary organic acids. For higher temperatures (>225-250 F)consider replacing HCl with acetic acid or formic acid.

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