Chair of Petroleum and Geothermal Energy Recovery

Master Thesis

Screening of organic acids suitable for stimulation treatments

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Kurzfassung

Karbonatgestein wird seit Jahrzehnten mittels einer Säuerungsrezeptur, deren Hauptbestandteil Salzsäure (HCl) ist, stimuliert. Die Gründe der häufigen Verwendung von Salzsäure sind einerseits die hohe Auflösungskapazität und andererseits die niedrigen Kosten der verwendeten Chemikalien. Da jedoch Salzsäure bei hohen Temperaturen ausgesprochen schnell abreagiert, ist die Eindringtiefe in etwaige Gesteinsformation limitiert. Zudem ist es als negativ zu betrachten, dass Salzsäure sehr korrosiv ist. Daraus ergibt sich ein Potential für die Verwendung von schwächeren Säuren.

Diese Studie untersucht nun das Reaktionsverhalten verschiedener schwacher Säuren mit Karbonatgestein sowie das Korrosionsverhalten derselbigen. Des Weiteren wird überprüft, ob die Säuren als Hauptbestandteil für eine Säuerungsrezeptur geeignet sind. Im Rahmen dieser Arbeit wurde eine Entscheidungsmatrix für die OMV Exploration & Production GmbH geschaffen, welche potentielle Säuren für Stimulationen identifiziert. Diese für die Studie entwickelte Matrix wurde hauptsächlich für organischen Säuren aber auch für potentiell verwendbare andere Säuren angewandt. Die ausgewählten Säuren wurden äquimolar einer 10%igen Salzsäure hergestellt und deren Verhalten bei unterschiedlichen Temperaturen untersucht. Für die Auflösungsversuche wurden Dolomit- und Kalksteinproben verwendet. Die Proben der reagierenden Säure wurden während der Auflösungsstudie in gleichbleibenden temporalen Abständen entnommen, um die Calciumkonzentration und Magnesiumkonzentration mittels Ionenchromatographie zu bestimmen. Die Ionenkonzentration gibt Aufschluss über das Reaktionsverhalten der Säure mit den Karbonatproben. Weiters wurde anhand des Massenverlustes von niedrig legierten Stahlproben die Korrosivität ermittelt.

Die Auflösungsstudie zeigt, dass die schwächeren organischen Säuren nicht vollständig dissoziieren und somit weniger Karbonatgestein auflösen können als Salzsäure. Des Weiteren konnte gezeigt werden, dass bei höherer Temperatur die Reaktion beschleunigt abläuft. In der Korrosionsstudie konnte demonstriert werden, dass der Gewichtsverlust und somit die Korrosionsrate der schwachen organischen Säuren weitaus geringer ist als jene der Salzsäure. Im Gegensatz hierzu weisen die stärkeren organischen Säuren jedoch einen höheren Massenverlust und eine höhere Korrosionsrate verglichen zu Salzsäure auf.

Abstract

Carbonate formations are stimulated since decades with the use of hydrochloric acid (HCl) based fluids due to its cost advantage and its high dissolving power. This stimulation design is associated with two distinctive drawbacks in high temperature formations. First, HCl has a high reaction rate with carbonate rocks that limits its penetration into the formation and second, its high corrosion rate. As a result, weaker acids becomes a viable alternative to mitigate these drawbacks.

The purpose of this study is to gain an understanding of the reaction behavior of weaker acids with carbonate rocks, to evaluate their corrosion behavior and prove their applicability. Possible candidates were identified by screening selected acid parameters. The screening process mainly concentrated on organic acids, but other promising acid opportunities were also investigated. The dissolution and corrosion behavior of selected acids were compared equimolar to a 10% HCl solution at different temperatures. Dolomite and limestone samples were used for the dissolving study and samples of the spent acid were periodically collected to measure calcium and magnesium concentrations using ion chromatography. The ion concentration was used to determine and study the acid-mineral reaction behavior. The corrosion study was performed using low carbon steel samples and the corrosivity was determined via mass loss.

The results of the dissolution experiment show that weak organic acids do not fully dissociate and therefore cannot dissolve the same amount of carbonate which HCl can dissolve. It also shows that a higher temperature leads to a higher reaction rate. In the corrosion experiment, the weak organic acid showed a lower mass loss and corrosion rate than HCl. The strong organic acids showed a higher mass loss and a higher corrosion rate compared to HCl.

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1 Introduction

Most wells are stimulated during their production life to add value to the field by accelerating production rates and/or by increasing the wells ultimate recovery.

The cornerstone of today’s stimulation technology are hydraulic fracturing and matrix acidizing. Stimulation treatments are designed to remedy or even improve the originally existing conductive network of flow paths between reservoir and wellbore. Hydraulic fracturing is a treatment where new conductive pathways are created in the reservoir formation as result of applying pressure at surface. Matrix acidizing however, utilizes the dissolving ability of solvents to dissolve and remove any resistance concentrated around the wellbore and is injected below fracturing pressure to avoid any creation of fractures during the treatment. The type of stimulation treatment chosen depends on various parameters such as lithology, production rate, operational limitations and other considerations. Carbonate rock formations can be stimulated using acid fracturing, propped fracturing and matrix acidizing, but the preferred choice for OMV Exploration & Production GmbH in Austria is matrix acidizing.

For decades’ carbonate formations are stimulated using hydrochloric (HCl) based acids mixtures. The advantages using concentrated hydrochloric based acids mixtures are that they are relatively inexpensive and have a high dissolving ability, but they have two characteristic drawbacks in deep and high temperature wells. The high temperature causes high reaction rates between the acid and the carbonates which limits its penetration depth. Furthermore, hydrochloric acid is corrosive to the downhole equipment and can cause downhole failures. As a result of the drawbacks, weaker acids become a viable alternative to mitigate the drawbacks. One part of this study aims to identify possible acid candidates by screening selected acid parameters. The general screening procedure is presented as a flowchart and each screening parameter is separately discussed. Furthermore, the identified acids are presented with their properties and are compared to each other.

The experimental setup of the dissolution, the fluid compatibility and the corrosion study are presented as well as experimental requirements. In the performed experiments the acid candidates were compared equimolar to a 10% HCl solution.

The dissolution study aims to gain an understanding of the reaction behavior of weaker acids with dolomite and limestone samples at different temperatures. In order to study the carbonate reaction behavior, samples of the reacting acids were periodically collected and their respective calcium and magnesium concentration was determined using ion chromatography. The ion concentration determines the amount of rock that was dissolved and gives information about the acid mineral reaction. The compatibility study aimed to ascertain the behavior of the fluid system when in contact with formation oil. This compatibility study proves the general applicability of the fluid system. The aim of the corrosion study is to evaluate and compare the corrosivity of the selected acids at 50°C. The mass reduction of low carbon steel coupons was determined to measure the corrosivity of the acids.

2 Reservoir Stimulation in Petroleum Production

This chapter describes the principles of a petroleum production system and the fluid inflow into the well. Furthermore, it contains a description of the parameters controlling the production rate and gives an overview on near wellbore damaging mechanism.

Petroleum production comprises two separate but connected systems: (I) the reservoir and (II) the artificial structure. Figure 1 illustrates the connected petroleum production system. The reservoir is a subsurface rock body with sufficient porosity and permeability. The porosity describes a property of the rock that measures the storage capacity that the formation is capable to hold. The permeability of a rock is a measure of the capacity and ability of the rock body to transmit fluids. An artificial structure transports the reservoir fluid from the reservoir to the surface. It includes the well, subsurface tools, wellhead, surface gathering lines, separation systems and storage facilities. [1]

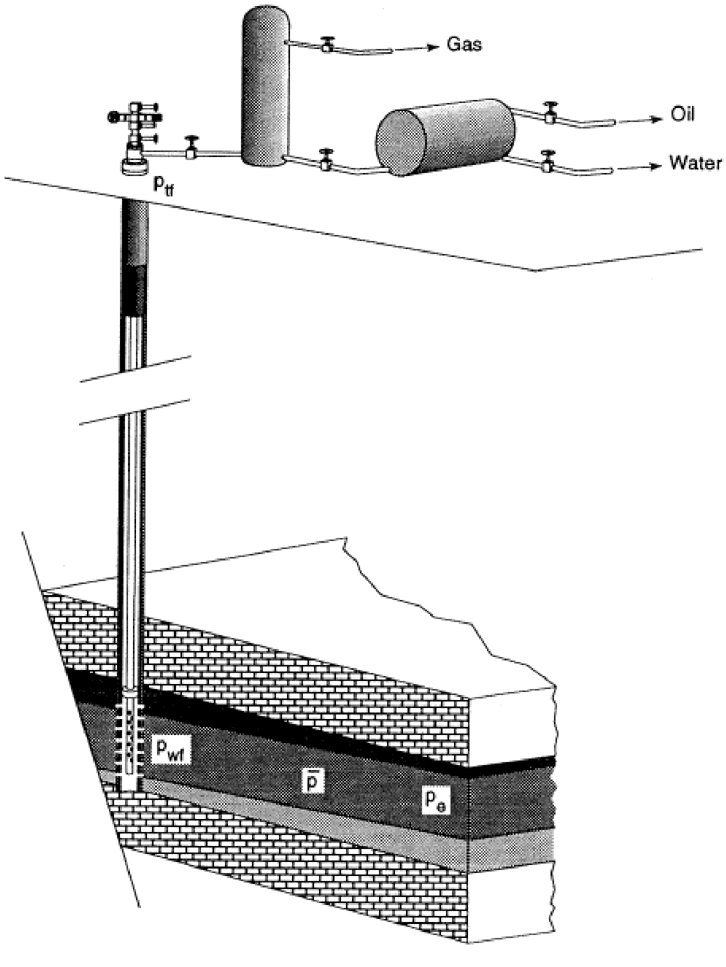


Figure 1: A typical petroleum production system involving a reservoir and an artificial structure; from [2]

Reservoir stimulation and artificial lift operations are the two main measures taken to enhance production in a cost effective way. The main objective of reservoir stimulation is to accelerate recovery of oil and gas and/or add reserves which increases the ultimate economic recovery of the well. The existing stimulation techniques include hydraulic fracturing, matrix acidizing, acid fracturing and explosive fracturing. However, the cornerstone of the stimulation technology is matrix acidizing and hydraulic fracturing. The two technologies have been intended to increase the flow conductivity from the reservoir to the well. This measure could delay the need for artificial lift operations. The objective of artificial lift operations is to bring the reservoir fluids to the wellhead at sufficient surface pressure while keeping the bottomhole pressure at a minimum to ensure high drainage from the reservoir. [1]

2.1 Well Inflow

The fundamentals of petroleum engineering can be explained by the inflow of fluids into a well. It quantifies the production through a well from the reservoir body and therefore describes its potential. The equation is referred to as diffusivity equation and can be derived by combining the conservation of mass equation with the equation of motion for a single phase fluid (Darcy's Law) and with an equation of state (isothermal compressibility) for a fluid. It characterizes the pressure profile of an infinite acting porous reservoir that is drained by a single phase slightly compressible fluid having constant viscosity. Equation (1) shows the radial diffusivity equation, where ϕ is the *porosity*, t is the *time*, k is the *permeability*, μ is the viscosity of the flowing fluid, p is the *pressure*, c_t is the total compressibility and r is the *radial position*. [3]

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial p}{\partial r}\right)=\frac{\phi\mu c_t}{k}\left(\frac{\partial p}{\partial t}\right) \tag{1}$$

The diffusivity equation can be used to solve for different radial pressure-rate behaviors of the reservoir. Describing the diffusivity equation at different initial and boundary conditions yields to various reservoir conditions. The three reservoir conditions are known as steady state, pseudo steady state and transient pressure rate behavior.

The parameters controlling the production rate are described based on the steady state reservoir condition. The steady state flow regime describes a condition where the pressure remains constant at every location in the reservoir with respect to time. This condition implies that the outer boundary pressure is maintained with time and that there is a natural (water drive) or forced (water injection) fluid inflow. Considering steady state initial and boundary conditions the pressure-rate relationship will result in equation (2), where q is *flow rate* and h is the *reservoir height*: [3]

$$p(r)-p_{wf}=\frac{q\mu}{2\pi kh}\ln\frac{r}{r_w} \tag{2}$$

2.2 Well Productivity

The parameter that describes the productivity of a well best, is the *well productivity index J*. It relates all downhole parameters of the petroleum system. The productivity index is the relationship between *gross volume of liquid produced per day q* and the *pressure differential between reservoir and the wellbore p-*p_{wf}. The understanding of each parameter controlling the well productivity becomes imperative to optimize the wells efficiency. The well productivity can be mathematically expressed as equation (3). [1]

$$J = \frac{q}{p - p_{wf}} = \frac{2\pi kh}{\mu\left[\ln\frac{r_e}{r_w} + s\right]} \tag{3}$$

The product of the *formation permeability* and the *reservoir thickness kh* shows a parameter set that has an enormous influence on productivity and cannot substantially altered by a petroleum engineer. This parameter set was of enormous importance for the exploration of current mature field. [1]

Another important parameter set, especially for mature fields, is the pressure depletion described by the *reservoir pressure p* and the *well flowing pressure* p_{wf}. Assuming a constant right-hand side, the production rate *q* will ultimately reduce as the reservoir gets depleted. The effect of reservoir depletion *p-*p_{wf} comes from the reduction of reservoir pressure while the well flowing pressure is kept constant. [1]

In order to maximize productivity dealing with an unalterable parameter set *kh* and a given *reservoir pressure p*, the *skin s* or the *bottomhole flowing pressure* p_{wf} are parameters that can be modified. The productivity index can be maximized by either reducing the skin factor or the bottomhole flowing pressure which may result in an insufficient pressure to lift the fluid to surface and expresses the need of an artificial lift system. [1]

The central purpose of this study is to maximize the productivity of the well by reducing the skin factor.

2.3 Skin Factor

The porous rock consists of irregularly, randomly shaped and distributed mineral grains that form irregular distributed and shaped flow paths. This irregular pattern is usually idealized by a collection of pore bodies interconnected by pore throats having varying sizes. The parameter that describes the ability of a porous media transmitting fluids is called permeability. It controls the fluid flow through the formation to the well and limits its production rate. [1]

During the various well operations such as drilling and workover operations, the near wellbore zone may get invaded by mud, cement, clay or other particles which damage the formation and reduce the permeability. This altered near wellbore zone is referred to as *wellbore skin s* and causes an additional pressure drop. Apart from mechanical reasons that cause a pressure drop, other effects can cause an additional skin such as partial completion (perforated height is smaller than the reservoir inflow height), phase change (effective permeability changes) and turbulences. [2]

The additional pressure drop in the near wellbore zone can be mathematically described by Hawkins skin effect as shown in equation (4). The concept is based on a reservoir that instead of having one homogeneous permeability, consists of a reservoir having two different permeabilities or even more permeabilites as shown in equation (5). Skin is a dimensionless parameter that can be determined from pressure built up tests. [4]

$$\Delta p_{skin} = \frac{q\mu}{2\pi kh} s \tag{4}$$

$$s = \left[\frac{k}{k_{skin}} - 1 \right] \ln\left(\frac{r_{skin}}{r_w} \right) \tag{5}$$

The skin and the pressure drawdown in the vicinity of the wellbore can only result in three possible outcomes; positive skin effect, negative skin effect and zero skin effect. The dashed line in the following figures indicate the undisturbed and original pressure drawdown and the solid line indicate either the damaged or stimulated pressure drawdown. [2]

- **Positive Skin Effect:** $s>0; \Delta p_{skin}>0$

  Positive skin occurs when the permeability of the damaged near wellbore zone k_{skin} is smaller than the permeability k of the undisturbed reservoir. As the damaging of the zone proceeds the magnitude of the skin factor increases which results in a higher pressure drop. Figure 2 illustrated the additional pressure drop in the near wellbore zone. [5]

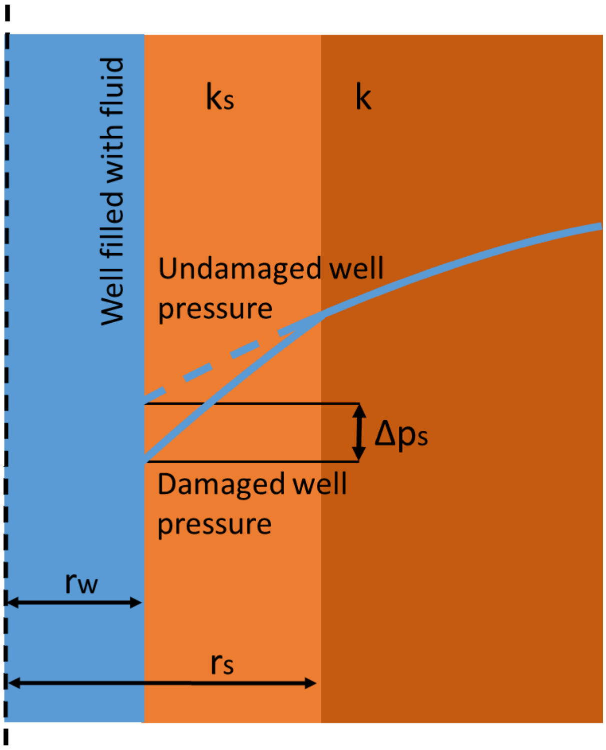


Figure 2: Positive skin effect showing additional pressure drop; modified from [2]

- **Negative Skin Effect:** $s<0; \Delta p_{skin}<0$
  Negative skin occurs when the permeability of the damaged near wellbore zone k_{skin} is higher than the permeability k of the undisturbed reservoir. This indicates a negative pressure drop and a better conductivity compared to the reservoir. Figure 3 illustrated typically stimulated well, where negative skin effect results in a smaller pressure drop. [5]

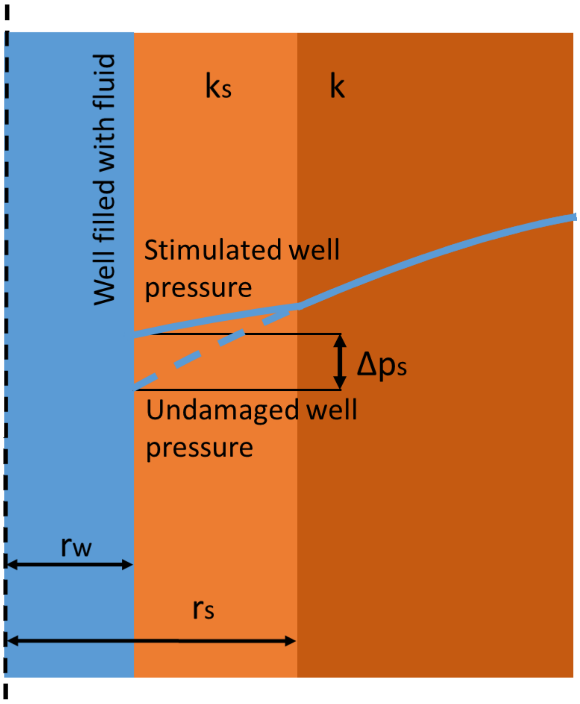


Figure 3: Negative skin effect showing diminished pressure drop; modified from [2]

- **Zero Skin Effect:** $s=0; \Delta p_{skin}=0$
  A skin factor of zero indicates equivalent near wellbore and reservoir permeability and the near wellbore zone is not altered. $k = k_{skin}$ [5]

Another expression that describes skin is the *effective wellbore radius* $r_w^{'}$. A negative skin increases the effective wellbore radius and positive skin reduces the effective wellbore radius. [2]

$$r_w^{'} = r_w e^{-s} \qquad (6)$$

The interesting finding about the effective wellbore radius can be shown when a damaged wellbore is compared with a stimulated or fractured wellbore. A damaged well has a skin for instance of $s = 5$ thus, the effective wellbore radius draining the reservoir becomes $6.7 \times 10^{-3} r_w$. Contrary to the positive skin, a stimulated well has a negative skin for instance of $s = -1$ or even $s = -5$. This negative skin effect would increase the effective wellbore radii to *2.7rw* and *148rw*, respectively. [2]

2.4 Formation Damage Mechanisms

Formation damage in the near wellbore region is the reason for the permeability reduction and the generation of skin. The next few subchapters describe the various plugging mechanisms of pore space by solid particles. Pore plugging sources include injection of solids in the reservoir formation, clay or fine migration and precipitation. [2] Other formation damaging mechanisms such as biological growth and fluid effects play a minor part in this study.

Biological damage is prone to occur in water injection wells, because the injected water is not sufficiently treated and bacteria are introduced in the near wellbore zone. It can be prevented by treating injection water with bactericides. Fluid damaging effects can be the creation of an emulsion, the alteration of the relative permeability or changing the wettability. The damage caused by fluids can be described as temporary, because fluids are moveable and can be removed. [2]

2.4.1 Particle Plugging of Pore Spaces

When small particles move through the pore throats of the porous medium, they will often deposit at different areas in the rocks void space. Any deposition occurring in pore throats will lead to a reduction of permeability. An example of fluid carrying large particles and flowing towards the surface of a porous medium is shown in Figure 4. The particle size is too big to enter the pore throat, thus they will accumulate at the surface, bridge it and form a filter cake. The formation of a filter cake on the near wellbore wall is absolutely desirable during drilling operations to prevent fluid loss, but is a drawback during production. [2]

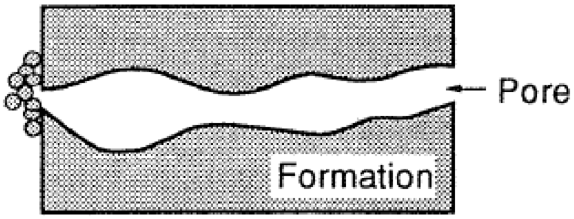
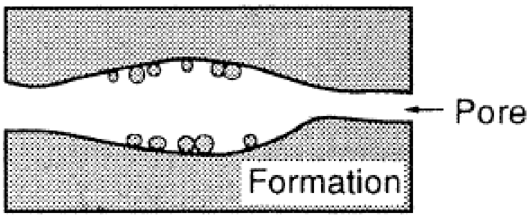


Figure 4: Generation of filter cake; from [2]

The adherence of particles in the pore throat is illustrated in Figure 5. This results in a permeability reduction or may result in bridging the pore throat shown in Figure 6. The particle size gives information if pore throat bridging can occur. Formation damage due to pore throat bridging may occur if particles have a size larger or in the range of one-third to one-seventh of the pore throat. [2]



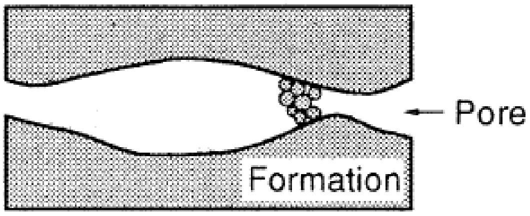


Figure 5: Adherence in the pore throats; from [2]

Figure 6: Pore throat plugging; from [2]

2.4.2 Fines Migration

The source of the pore plugging particles described above can either come from the porous rock medium itself as fines or can be brought to the system by external sources. Fines may be produced in the porous medium by changing the chemical composition of the water or when moving fluid or particles shear the mineral grains. Clays are very prone damaging the formation, because their surface area and their susceptibility to changes in salinity or ionic composition in the water. [6]

A sudden salinity reduction of the brine flowing through the sandstone formation leads to clay dispersion. Dispersion depends on the amount of cations dissolved in brine, the pH and the change of salinity. Generally, monovalent cations (Na^+, K^+, NH_4^+) are more prone to damage the formation than multivalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}). Hence, any fluid that will be used in the downhole producing formations should have low concentrations on monovalent cations or an adequate concentration of divalent cations. [2]

2.4.3 Chemical Precipitation

Precipitation is a chemical process that creates solid material from a saturated solution. The precipitates formed in the pore space can either be inorganic nature from the brine or organic nature from the oil. Solids formed in the pore space reduce the available flow path and therefore reduce the potential available flow paths. [2]

Inorganic precipitates are usually formed by a combination of divalent cations such as calcium or barium and carbonate or sulfate ions. Initially, the reservoir brine is saturated with ions and a chemical equilibrium between the brine and the formation minerals exist. Altering the composition of the reservoir brine by introducing a fluid with a different composition can cause precipitation. A typical example for an equilibrium reaction between calcium (Ca^{2+}) and bicarbonate (HCO_3^-) can be as shown in equation (7). [2]

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + CO_2 + H_2O \tag{7}$$

The formation brine is initially saturated with calcium and bicarbonates. Precipitation of the solid calcium carbonate ($CaCO_3$) can be triggered by increasing the concentration of any species on the left side of by decreasing the concentration of any species on the right side. This precipitation problem is common for reservoirs having high bicarbonate concentrations and using completion fluids with high calcium concentrations ($CaCl_2$). Precipitation is also triggered by the production of the reservoir itself, where the pressure decreases in the near wellbore region and CO_2 liberates from the brine. [2]

Organic precipitations are paraffins and asphaltenes. Paraffins are heavy, long unbranched chains consisting of carbon and hydrogen atoms only. Typically, paraffin solids have carbon chain lengths higher than 18 atoms per molecule up to 70 and even more. Sometimes they are also referred to as waxes. Paraffin will start precipitate out of solution as soon as equilibrium temperature and pressure is reached. As the pressure decreases in the near wellbore, gas liberates out of solution and leads to paraffin precipitation. [7]

Asphaltenes consist of high molecular weight aromatic and polycyclic ring compounds that are substituted with nitrogen, sulfur and oxygen. They are defined as fraction of the crude oil that is insoluble in a straight chain solvent such as heptane or pentane. Its fine distribution is stabilized by the presence of resins which causes flocculation of asphaltenes when the resin concentration is changed. Large particles created by flocculation, can cause formation damage. [2]

2.5 Inflow Performance

The effect of the skin on the production can be shown in the inflow performance relationship (IPR). The IPR is an important parameter to relate the production rate to the bottomhole flowing pressure. Plotting the bottomhole flowing pressure versus the production rate gives a straight line for steady state reservoir conditions. The vertical intersection shows the value of the average reservoir pressure and the horizontal intersection shows the absolute open flow potential (AOF). A single phase flowing well has a constant slope which is exactly the reciprocal of the productivity index. Figure 7 shows the effect of various skin values on the production of a steady state oil well. [1]

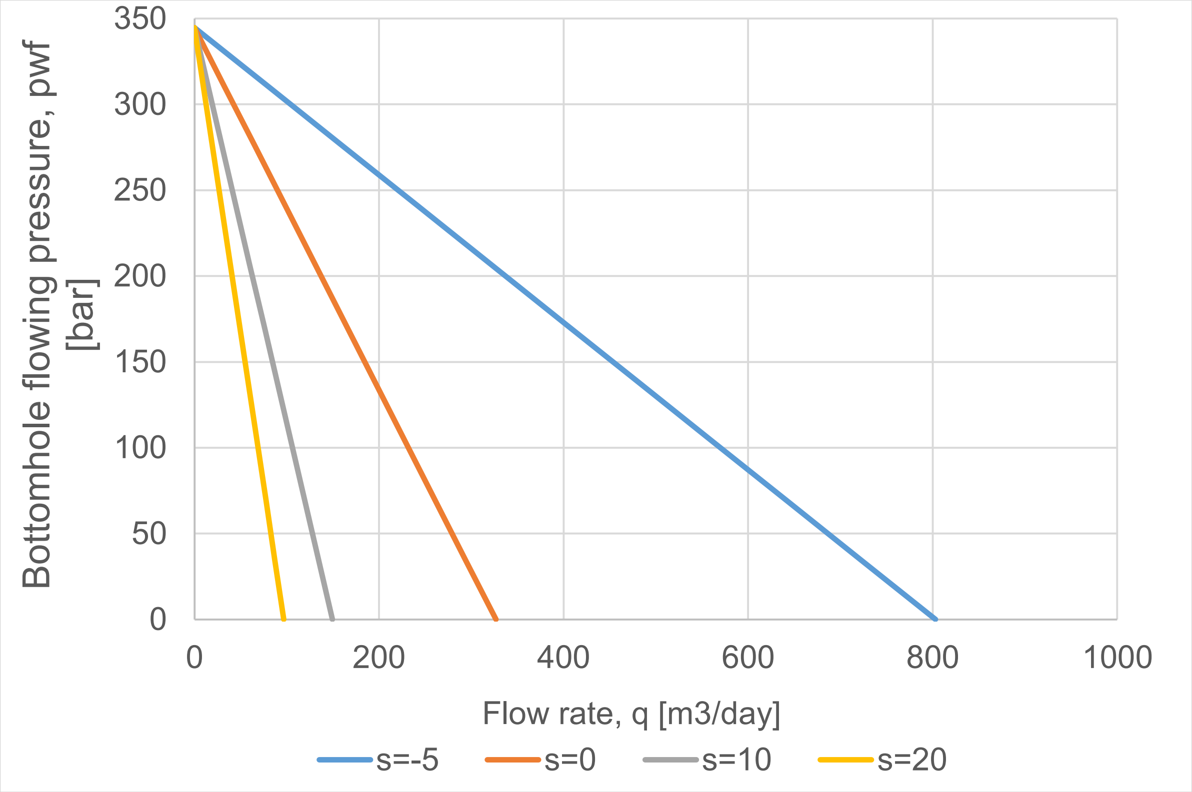


Figure 7: Skin effect on the steady-state IPR of an oil well; modified from [1]

Assuming a reasonable p_{wf} = 100bar, the production at s = 20, 0 and -5 are roughly 70, 230 and 560 m^3/day, respectively. The impact of skin on the production is extraordinary, especially the negative skin effect.

Usually reservoirs are saturated and consist of more than one phase. Therefore, several approximations which account for more phases are available such as Vogel correlation, Multirate Fetkovich correlation and Multirate Jones correlation [1].

3 Stimulation Technologies

Most wells in the oil and gas industry are either stimulated in the very beginning of the production life or in later phases of the wells life. The main objective of stimulation is to increase the production and/or increase the ultimate recovery. Stimulation of the reservoir can be achieved by removing or bypassing the formation damage in the near wellbore region. [1]

It can be distinguished between fractured and non-fractured treatments to stimulate the reservoirs. Fractured treatments can be classified by propped fracture and acid fracture. Non-fractured treatments can be classified by wellbore cleanup and matrix stimulation. [8]

3.1 Hydraulic Fracturing

Hydraulic fracturing is a stimulation operation in which fluid is pumped into a well at a rate that the reservoir cannot accommodate, thus the pressure in wellbore rises. As the pressure exceeds the initial splitting or breakdown pressure, the rock will split open and fracture. The fracturing process opens new conductive flow channels and thus the fluid leaking rate due to the increased draining area will increase. As long as the pumping rate is higher than the fluid leaking rate, the fracture will continue to propagate and new formation area will be exposed. Once pumping stops and all the fluid leaks off into the formation, the newly created fractures and flow paths will close due to the overburden pressure. Different measures have been taken to prevent the closure of the newly created fractures including propping material and acids. [1]

- **Propping the fractures:**
  Propping material is mixed at surface with a viscous media and pumped down as a slurry to the fracturing interval. During pumping operation, the propping material will distribute into the newly created conductive fractures to keep them open for production. The propping material is either a sand or an artificially generated substitute with equal or higher strengths. Figure 8 illustrates a hydraulic fracturing treatment using propping material. [1]

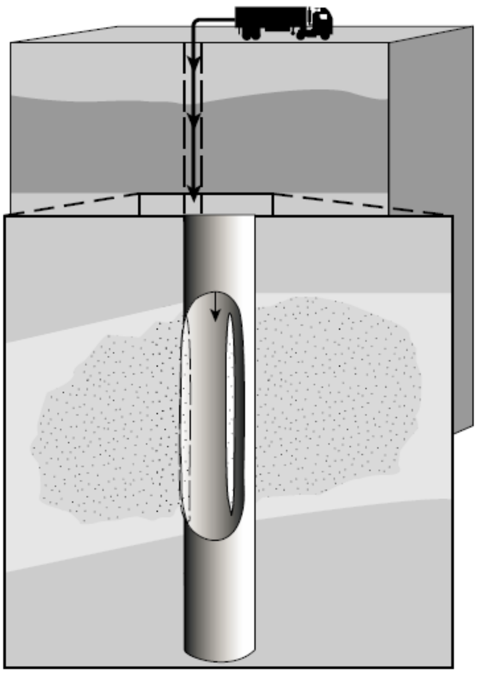


Figure 8: Hydraulic fracture filled with propping material; from [1]

- **Acid etching the fracture channels:**
  An acid is injected under high pressure to fracture the formation and etch the fracture walls. Thus, creating irregularly shaped fracture surfaces that remain partially open and provide conductive flow paths after injections stops. This measure is only applicable to dolomite and limestone reservoirs, because they are acid soluble. The reaction stoichiometry of acid etching will be described in acid-mineral interactions (Chapter 3.3.1). [1]

Contrary to matrix stimulation, hydraulic fracturing operations create new conductive channels deep into the reservoir and can actually increase the productivity beyond the original value. [1]

3.2 Wellbore Cleanup

Wellbore cleanup treatments are used to remove bacteria, paraffin, scale and other materials that are attached to tubing, casing or gravel pack. The idea is to place an acid or a solvent in the wellbore area to soak. The parameter controlling the effectiveness of the treatment are the dissolving capacity of the chemical solvent for a certain damage and the soak time. In wellbore cleanup operations the amount of treatment fluid can be minimized by properly placing the fluid using packers, bridge plugs and coiled tubing. [1]

3.3 Matrix Stimulation

Matrix stimulation is a technique utilizing the dissolving ability of a solvent to dissolve materials that are present in the flow paths. The main objectives are to dissolve the restricting materials in the flow path and to dissolve the matrix itself, thus recovering or even enhancing the permeability. The highest pressure drop in the reservoir occurs in the near wellbore region, thus matrix acidizing is the preferred stimulation treatment for wells having a high skin effect.

Stimulation treatments using pressures below the parting pressure of the formation are called “matrix” stimulation because the aim of the treatment is the rock matrix. [2]

Matrix acidizing is the most common matrix stimulation technique in which an acidic solution is injected into the wellbore. Other stimulation techniques utilize organic solvents to dissolve organic damaging materials (asphaltenes, paraffins, waxes and others), oxidizers to remove polymer damage, scale removers to dissolve sulfates or oxides and break polymer debris. [1]

Hydrochloric acid (HCl) is the most common acid used to dissolve carbonate minerals. Mixtures of hydrochloric acid and hydrofluoric acid (HF) referred to as mud acid, are mostly used to attack the clay and feldspar minerals in sandstone formations. [1]

A basic acidizing treatment consists of a preflush, a main stage and an overflush.

1. The preflush stage is a nonreacting and a nondamaging fluid to displace the crude oil and the formation water and to establish conductivity.
2. The main stage accommodates the acidic solution. The acid type depends on the stimulating formation and reacts with the rock matrix and the plugging material.
3. The last stage is the overflush which is needed to clear and dilute the reactive acid from the tubing and the near wellbore region. It also makes sure that secondary reactions do not impact the productivity of the well. The components of the overflush depend on the acid treatment, but usually consists of water containing ammonium chloride (NH_4Cl), a weak acid, diesel oil or a mutual solvent. [1]

Once the treatment is pumped, the well is cleaned up by producing the reacted and spent acid solution including undissolved damage (i.e. drilling mud, scale, asphaltenes and paraffin) back to surface [1]

3.3.1 Acid-Mineral Interaction

An acid is defined according to the Brønsted and Lowry theory as a substance that can ionize. The dissociation process is shown in equation (8) where the acid loses a proton (H^+) and creates the conjugate base. Strong acids are defined as acids that totally ionizes at ordinary concentrations, whereas weak acids only partially ionize at ordinary concentration. [9]

$$\text{Acid} \leftrightarrow \text{Conjugate Base} + H^{+} \tag{8}$$

In the reaction between calcium carbonate ($CaCO_3$) and acid, the protons from the acid attack the insoluble calcium carbonate and dissolve it. The chemical reaction between acid and mineral provides quantitative information on the molar ratio of the reactant and the product. It describes the amount of acid moles required to dissolve a certain amount of the mineral expressed in moles and provides a measure of the acid efficiency. The relationship between the moles of each species is referred to as stoichiometry and is shown in equation (9). It presents the dissolving reaction of hydrochloric acid and calcite ($CaCO_3$). The protons from the acid react with the calcite and produce calcium chloride (CaCl), carbon dioxide (CO_2) and water (H_2O). The stoichiometry of the dissolution reaction shows that 2 moles of acid are consumed in order to dissolve 1 mole of $CaCO_3$. [1]

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O \tag{9}$$

For reactions between HCl and dolomite ($CaMg(CO_3)_2$) the reaction stoichiometry anticipates that 4 moles of HCl will consume only one mole of dolomite as illustrated in equation (10). Thus, more HCl will be needed to dissolve the same weight of dolomite compared to calcite. [1]

$$4HCl + MgCa(CO_3)_2 \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O \tag{10}$$

3.3.2 Precipitation Products

Secondary reactions and their reaction products are another main acid selection criterion. Precipitates formed as reaction product will damage flow paths and induce damage. Reaction products from the dissolving reaction must form soluble products to prevent any induced damage. When precipitation occurs, the location and the amount of the precipitation in the wellbore directly affects the well productivity. In the near wellbore region, a certain amount of precipitation will have a higher damaging impact on well productivity than precipitation occurring deeper in the reservoir. [1]

In limestone and dolomite stimulation operations, one of the reasons for using HCl are its highly soluble reaction products, calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$). [1]

Stimulation of sandstone reservoirs requires a specific sequence of acid injection in order to prevent precipitation of insoluble calcium fluoride (CaF_2). Calcium fluoride is typically formed as a reaction product from the reaction of HF with calcite. Thus, HCl is injected prior to HF to dissolve the calcite and mitigate the risk of calcium fluoride formation. [1]

Additionally, if the acid gets in contact with the crude oil, it can form asphaltenic sludges. Thus, fluid-fluid compatibility has to be verified prior injecting the treatment fluid by emulsion breaker tests where the acid is mixed with a sampling crude oil. When the formation of sludge and the precipitation of asphaltene is an issue, surface active additives or aromatic solvents can be used. [1]

3.3.3 Weak Acids

Hydrochloric acid is the most commonly used acid to dissolve carbonate minerals due to its cost advantage and its high dissolving capacity. However, concentrated hydrochloric acid solution is accompanied by two major drawbacks in deep wells: (I) acid penetration limitation and (II) high corrosion rate. [10]

The high reaction rate of between HCl and carbonates limits its penetration depth especially at high temperature. Retarding agents such as gels, emulsifiers or viscoelastic surfactants can be added to the acid solution to reduce the acid spending rate. At high temperatures, HCl is very corrosive to downhole well tubulars. The corrosivity can be mitigated by using corrosion inhibitors. Most retarding agents and corrosion inhibitors are expensive and thus organic acids such as formic acid and acetic acid are attractive and common as alternatives. [10]

Stimulation operations using weaker organic acids benefit from the retarded reaction with the rock minerals and the low corrosivity with the well tubulars. Recent research concentrated on organic acids as an alternative to HCl. However, organic acids have certain limitations that reduce their applicability. [10].

The concentration of the organic acid is typically limited by the solubility of their reaction products. Commonly used organic acids for stimulation treatments are formic and acetic acids. Formic and acetic acids are typically utilized at concentrations less than 9% and 13%, respectively. The acid concentration is restricted to avoid any precipitation of calcium formate or calcium acetate. However, acetic acid could be used up to a concentration of 20% to 25% without encountering any precipitation problem. [1]

In calcite dissolution reactions, the protons attack the insoluble carbonates. The more protons the acid supplies, the more calcite can be dissolved. The proton supply can be described by the strength of the acids which is either expressed by the acidity constant K_a or the pK_a. The pK_a is the negative decadic logarithm of the acidity constant. Typically, organic acids have lower strengths and this is reflected in the acidity constant. The higher the acidity constant or the smaller the pK_a, the stronger the acid and their degree of dissociation. Strong acids such as HCl dissociates totally, whereas weak acids do not fully dissociate and therefore cannot dissolve the same amount of mass. [10]

During the reaction, the protons are consumed which drives the reaction to the right and results in an increase in pH. The final equilibrium state of the acid/mineral reaction depends on the amount CO_2 in the system. The produced CO_2 can either stay in aqueous phase or in gaseous phase. At reservoir conditions it is likely to stay in solution and parts form carbonic acid (H_2CO_3). Carbonic acid acts as buffering agent and the final acid/mineral equilibrium state will be in the pH range of 4.0 to 6.0. At this pH range, weak acids are not yet fully dissociated at downhole conditions. Therefore, the cost of dissolving a certain mass of rock using weak acid is significantly higher than when the strong hydrochloric acid is used. [11]

A stimulation operation can benefit from mixing of a strong acid with an organic acid. The combination of the acids can enhance the acid penetration. This is because the organic acid does not dissociate until the strong acid is almost spent due to its low dissociation constant. [10]

3.4 Treatment Design Considerations

Generally, a basic stimulation operation consists of the following design considerations.

- **Fluid selection:**
  Specifies the acid type used for the stimulation operation, the concentration and the volume. [1]
- **Injection schedule:**
  Lists the planned sequence of the fluids, their injection rates and the maximum allowable pressures. [1]
- **Acid distribution:**
  Characterizes diverters to evenly distribute the acid along the wellbore which improves the overall efficiency. [1]
- **Real-time monitoring:**
  Determines injection rates and pressures during the stimulation job. [1]
- **Additives:**
  Additional chemicals are included to the various stages to enhance injection, protect the downhole equipment or retard the acid reaction and increase the penetration length. [1]

3.4.1 Physical and Chemical Interactions

An ideal stimulation treatment remedies the permeability at least to its initial undamaged permeability and covers the whole producing interval. In order to stimulate the well at low costs, physical and chemical reactions that take place between injected fluids, reservoir minerals and the existing downhole fluids must be considered: [1]

- **Mass transfer:**
  The acid molecules must be transported to the reservoir minerals either by convection or by diffusion before the reaction can take place. The reaction takes place at the phase boundary between the solid minerals and the liquid. The reaction rate of the acid is either limited by the rate of mass transfer to the mineral or by the surface reaction rate of the acid. Typically, one process is the limiting parameter and controls the overall reaction rate. [1]

- **Pore structure changes:**
  The composition of the rock formation is important, because the minerals in sandstone and carbonates dissolve in a different manner, thus creating different pore structures. This becomes important when modelling the dissolution behaviour of the solution. [1]
- **Secondary reactions:**
  Reaction products and other ions in solution can trigger secondary reactions that result in precipitation and reduce the available pore space. This would counteract the main goal of the stimulation treatment. [1]
- **Acid fluid – reservoir fluid or rock incompatibility:**
  Reservoir fluids or rock matrix can interact with the injected acid physically or chemically. Any incompatibility can result in wettability changes, changes of the reservoir saturation and may cause precipitation or emulsification. [1]
- **Damage and permeability distribution:**
  Typically, wellbores consist of layers with various permeabilities due to geologic development or induced damages. Layers having higher permeability will receive a higher amount of acid solution than layers having lower permeability. Thus, evenly distribution of the acid is an important factor. Acid diverters can help reduce the varying injectivity along the wellbore. [1]

3.4.2 Additives in Stimulation Fluids

The main treating fluid is designed to remove and bypass the damages in the near wellbore region, whereas additives are generally used to prevent high corrosion rates, prevent the formation of sludge and emulsions, prevent iron precipitation, prevent precipitation of reaction products and improve wellbore cleanup and acid diversion. Additives can also be used in preflush and overflush stages to stabilize clay, paraffins and asphaltenes. [1]

- **Corrosion inhibitors:**
  A corrosion inhibitor is a chemical substance that slows down the acid corrosion on any metal when in contact with the acid. [1]
- **Surfactants:**
  Surfactants are used in stimulation treatments to break emulsions from acid-oil interaction. It reduces the surface tension and/or interfacial tension which reduces the capillary pressure and makes fluid recovery easier. Furthermore, it adjusts wettability, improves wellbore cleanup, disperses additives, prevents formation of sludges and keeps them in stimulation fluid. Typically, small concentrations of 0.2% up to 1% are sufficient. [1]
- **Mutual solvents**
  Mutual solvents are chemicals that are mutually soluble in water and in hydrocarbons. The most commonly used and efficient mutual solvents are based on glycol ethers since they are relatively safe and easy to handle. They are used in the main stage and in the overflush stage and are designed to reduce the surface tension of water and prevent water blocking. Furthermore, they are designed to solubilize small parts of water into the hydrocarbon phase which alters the saturation. They provide and

maintain a water-wet environment which is necessary to achieve high relative oil permeability, prevents indissoluble fines from turning oil wet and from creation of emulsions. Moreover, they are designed to reduce adsorption of surfactants and inhibitors which helps maintaining the required concentrations. They also de-emulsify and improve the cleanup of the spent acid treatment. [1]

- **Iron control additives**

  When acid oxidizes metallic iron in sufficient quantities to Fe^{3+} (ferric ions) rather than Fe^{2+} (ferrous iron), iron precipitation and permeability reduction can occur after the acid is spent. Generally, precipitation from ferric ions starts at a pH of around 2 and precipitation from ferrous ions start at a pH around 7. When acid solution reacts with the minerals, the hydrogen ions consume the mineral and thus the pH of the solution increases. This increase of the pH will trigger precipitation of ferric ion and will cause formation damage.

  The iron in the well can come from corrosion products of tubulars and mill scales or from iron containing formations. Different methods have been used to keep the iron in solution such as pH control, sequestering agents and reducing agents. Controlling the pH-value prevents the precipitation of iron and can be accomplished by adding a weak acid as a pH buffer to the treating fluid. A sequestering agent is used to bind iron and keep it in solution. Common sequestering agents are citric acid ($C_6H_8O_7$), Ethylendiaminetetraacetic acid ($C_{10}H_{16}N_2O_8$) and nitrilotriacetic acid ($C_6H_9NO_6$). Reducing agents reduce the ferric ions (Fe^{3+}) to ferrous irons (Fe^{2+}). Thus the secondary reaction that forms iron precipitation is delayed until the solution reaches a pH of 7. [1]

- **Diversion**

  When there are layers with different permeabilites, the injected treating fluid will enter the most permeable layer rather than the damaged lower permeable layer where the treatment is needed the most. Diverting agents equalize the flow into the formation and allow treating of damaged zones. An ideal diverter should be insoluble in the treating fluid, create an impermeable layer on the most permeable zones and should be easily removable. [1]

4 Candidate Selection

This chapter describes the selection process of possible candidates, describes the criteria for the acid selection and presents the potential candidates. The properties of the selected acids will be discussed in detail and compared to each other. The potential acid candidates are compared to hydrochloric acid and acetic acid. Both acids were chosen to allow technical comparisons between the current technology and the identified acids.

4.1 General Screening Procedure

This screening focuses mainly on organic acids and other promising acids. An organic acid is a chemical compound that contains one or more carboxyl group.

In order to reduce the amount of potential organic acids for the screening procedure, it was concentrated on the functional group aliphatic carboxylic acids. A functional group is substitute within the compound that is the reason for their characteristic reaction and their specific chemical and physical properties. Aliphatic carboxylic acids contain a carboxyl group (–COOH) and can be subdivided in their degree of saturation. For this study the focus has been put on saturated aliphatic carboxylic acids. The general structure of an aliphatic carboxylic acid is shown in Figure 9. The R in the structure refers to the rest substituent which can be an atom or another group of atoms. [12]

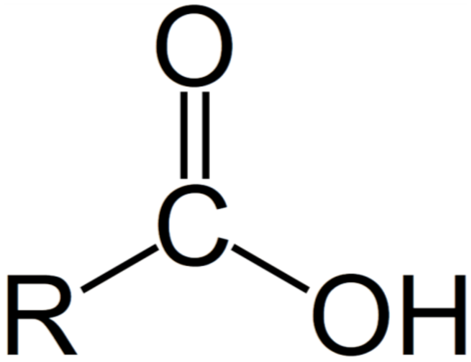


Figure 9: Structure of a carboxylic acid, from [13]

Acids having up to five carbon atoms have been screened including substitution with the elements fluorine (F^-), chlorine (Cl^-), bromine (B^-), iodine (I^-), and the hydroxyl group (OH^-). In order to start the screening process, all the possible acids had to be identified.

The general screening procedure can be illustrated by the example of acetic acid in Table 1. In this example each hydrogen atom existing in acetic acid was substituted with chlorine and the properties of the new molecule were screened. Additionally, this example shows that the molecule properties change during the substitution process. The molecular weight during the substitution increases because each substituent has a higher molecular weight than hydrogen. Furthermore, the acidity constant decreases with substitution due to the higher electronegativity of the substituent compared to hydrogen. Decreasing the electronegativity of the substitutes results in increasing *pKa* values. Multiple substitution has an additive impact on the *pK_a* and is illustrated in the following table. The table also shows that the acid solubility values change. It is a measure of how much of the acid either in liquid or solid form can dissolve in water at a specific temperature. Miscible indicates the acids can be dissolved in water in any concentration.

Table 1: Illustration of identification process [14] [15] [16]

Condensed Formula	**Systematic Name**	**Molecular Weight [g/mol]**	**Acid Solubility [g/l]**	pK_a
CH_3-COOH	Acetic acid	60.05	miscible	4.76
CH_2Cl-COOH	Chloroacetic acid	94.50	3,170 @ 10°C	2.81
$CHCl_2$-COOH	Dichloroacetic acid	128.94	miscible	1.3
CCl_3-COOH	Trichloroacetic acid	163.39	1,300 @ 20°C	0.65

In a further screening process, dicarboxylic acids and tricarboxylic acids have been investigated. The advantage of having more carboxyl groups is that the reaction stoichiometry changes as shown in equation (11) and equation (12). The dissolving reaction of a dicarboxylic anticipates that 1 mole of any dicarboxylic acid will consume 1 mole of calcite. This means that less moles of acid will be needed to dissolve the same amount calcite compared to HCl. [14]

$$\mathrm{R(COOH)_2} + CaCO_3 \leftrightarrow C\mathrm{aR(COO)_2} + CO_2 + H_2O \tag{11}$$

The dissolving reaction of calcite and any tricarboxylic acid is shown in equation (12). This reaction shows that 2 moles of tricarboxylic acid will dissolve 3 moles of calcite. [14]

$$2\mathrm{R(COOH)_3} + 3CaCO_3 \leftrightarrow C\mathrm{a_3 2R(COO)_3} + 3CO_2 + 3H_2O \tag{12}$$

After the screening area was formulated, the screening procedure was specified. The screening procedure can be described by the flowchart in Figure 10. The following parameters were defined as knock out criteria: dissolving power, acid solubility, the solubility of the calcium salts and health, safety, security and environmental aspects. [1]

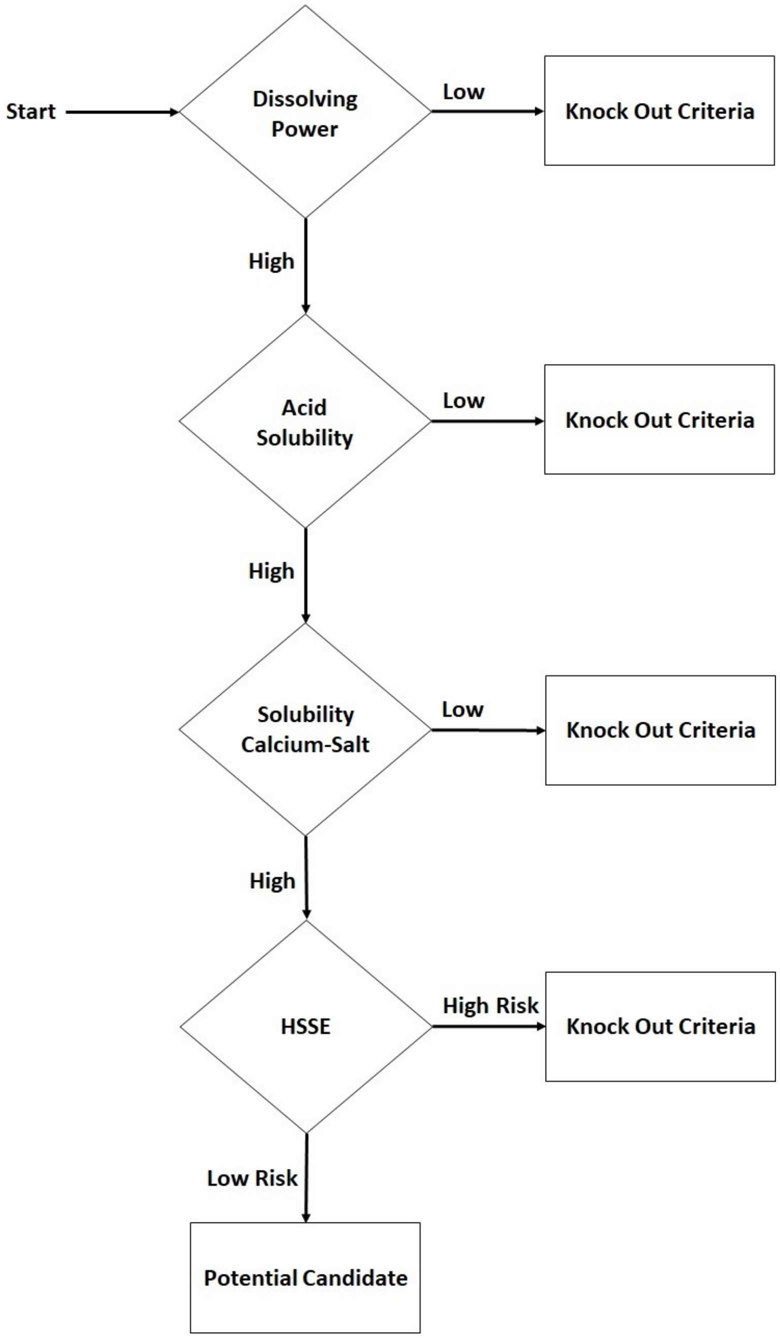


Figure 10: Decision criteria flowchart for the weak organic acids; modified from [1]

4.1.1 Dissolving Power

The calcite dissolving reaction (Chapter 3.3.1) shows that the amount of acid required to dissolve a certain amount of mineral is a good start to find potential acid candidates. A more convenient way to express the reaction stoichiometry is the dissolving power of the acid described by equation (13). It represents the amount of mineral theoretically consumed by a given amount of acid. [1]

$$\beta_x = \frac{\nu_{mineral} * M_{mineral}}{\nu_{acid} * M_{acid}} \tag{13}$$

The dissolving power is calculated using the stoichiometric coefficients ($v_{mineral}$ and v_{acid}) and the molecular weights ($M_{mineral}$ and M_{acid}) of the mineral and the acid. The subscript x denotes concentration of the acid. Equation (14) shows an example dissolving calculation between a 100% HCl solution and calcite. [1]

$$\beta_{100} = \frac{1*100{,}1}{2*36{,}5} = 1.37\,\frac{kg\ CaCO_3}{kg\ HCl} \tag{14}$$

It shows that one kilogram of a 100% HCl solution can dissolve theoretically 1.37 kilogram of calcite. Typically, HCl concentration range from 10% to 28% in matrix acidizing operations. Any lower concentrated acid solution can be calculated by multiplying β_{100} with the weight fraction of the acid. The commonly used HCl solution of 15% HCl can theoretically dissolve 0,21 kilogram $CaCO_3$ per kilogram 15% HCl. [1]

Table 2 shows the dissolving power of the selected acids at various weight fractions. The table underlines the importance of hydrochloric acid in the stimulation operations. Comparing it to the other acids, it has the highest dissolving power. The commonly used weak organic acids formic and acetic acid show high dissolving power values which underlines their importance in stimulation operations. The acids in the table are descending arranged, where darker colors indicate a higher dissolving power. [1]

Table 2: Dissolving power of selected acids; modified from [1]

Systematic Name	$\beta_x = \frac{kg\ CaCO_3}{t\ acid}$						
	β_{100}	**β_5**	**β_{10}**	**β_{15}**	**β_{20}**	**β_{25}**	**β_{30}**
Hydrochloric acid (HCl)	1,373	69	137	206	275	343	412
Formic acid	1,087	54	109	163	217	272	326
Maleic acid	862	43	86	129	172	216	259
Acetic acid	833	42	83	125	167	208	250
Lactic acid	556	28	56	83	111	139	167
Methanesulfonic acid (MSA) [17]	521	26	52	78	104	130	156
Sulfamic acid	515	26	52	77	103	129	155
Glycolic acid	342	17	34	51	68	86	103
Ethylenediaminetetraacetic acid (EDTA)	171	9	17	26	34	43	51

4.1.2 Acid Solubility in Water

The second screening criteria has been the solubility of the acid in water. It is a measure of how much of the acid either in liquid or solid form can dissolve in water at a specific temperature. Thus it is a measure of the maximum possible acid concentration. It is expressed in grams per liter and high values are around 1000 g/l. The theoretical solubility of the acid dictates the theoretical dissolving capacity of the calcite. This can be calculated using the acid solubility, the reaction stoichiometry and the molecular weight as shown in equation (15).

$$Acid\ Dissolving\ Capacity = Solubility_{acid} * \frac{v_{mineral}}{v_{acid}} * \frac{M_{mineral}}{M_{acid}} \tag{15}$$

Equation (16) examines the acid dissolving strength for a HCl solution.

$$Acid\ Dissolving\ Capacity = 740 * \frac{1}{2} * \frac{100.1}{36.5} = 1015.7 \frac{g\ CaCO_3}{l\ H_2O} \tag{16}$$

A HCl saturated solution would theoretically dissolve 1016 grams of calcite. A further limitation or cut for the screening of organic acids was set at 10% of the dissolving capacity of hydrochloric acid. Therefore, all acids that can theoretically dissolve more than 102 grams of calcite per liter solution were further investigated. This is a reasonable approach because it is still the theoretical dissolving capacity. Since weak acids do not fully dissociate, their actual dissolving capacity is anticipated to be even smaller. The solubility of the acids and their dissolving capacities are shown in Table 4.

4.1.3 Solubility of the Calcium Salt

The third screening criteria is the solubility of the calcium salt. The acid mineral reaction produces a reaction product that can either stay in solution or precipitate. The solubility of the salt describes the concentration when precipitation will occur and determines the maximum acid concentration depending on the solubility of the salt. Usually the solubility of the salt increases with increasing temperature and thus the solubility values were compared at similar temperatures.

Equation (17) shows the relationship of the solubility of the salt and the maximum possible acid concentration. Furthermore, equation (15) can be used to solve how much calcite can be dissolved by the determined acid concentration. The solubility values of the salts, their maximum acid concentration and their dissolving capacity are shown in Table 4.

$$Maximum\ Acid\ Concentration = Solubility_{salt} * \frac{v_{acid}}{v_{salt}} * \frac{M_{acid}}{M_{salt}} \tag{17}$$

Equation (18) examines the maximum acid concentration for the hydrochloric acid.

$$Maximum\,Acid\ Concentration = 740 * \frac{2}{1} * \frac{36.5}{111} = 486.2 \frac{g\,HCl}{l\,H_2O} \tag{18}$$

This results determines the maximum HCl concentration that can be used without forming precipitation products. Although this result indicates a maximum theoretical HCl concentration of 49%, the HCl concentrations typically range from 10% to 28%. However, HCl is typically purchased at maximum concentrations ranging from 33% to 34% and has to be diluted to the required concentration. [1]

4.1.4 Health, Safety, Security and Environmental Aspects

The last screening criteria was health, safety, security and environmental aspects. Physical and mental health of the employees as well as minimizing the environmental impact are essential factors for all successful stimulation operations and therefore the acid hazardousness has been investigated.

The Institute for Occupational Safety and Health of the German Social Accident Insurance offers a substance database that provides research and investigations on substances and products, toxic effects, routes of exposure, first aid measurements, safe handling procedures and regulations. It has been used to investigate each organic acid for their harmfulness and hazardousness. [16]

The hazardousness of each acid was classified according to the globally harmonized system of classification and labelling of chemicals. Typically, acids are labelled by standardized pictograms that convey information on the type of hazard and signal words. Signal words are standardized as well and emphasize the relative severity of a hazard. Signal words used in this context are “Danger” describing a higher degree hazard and “Warning” describing a lower degree hazard. [18]

An acid can have more than one pictogram if it is dangerous in different ways. The selected acids can be classified by the following pictograms. A substance classified by the pictogram acute toxicity shown in Figure 11 means that even small quantities are life threatening when in contact with skin, when inhaled or swallowed. The exclamation mark shown in Figure 12 shows the pictogram health hazard which warns about various health risks. Substances classified by this pictogram can cause skin or eye irritation and can lead to an allergic reaction.

Figure 11: Acute toxicity; from [19]

Figure 12: Health hazard; from [19]

Figure 13 illustrates the pictogram of a substance being hazardous to the whole environment. Substances classified by this pictogram can result in long lasting environmental damages and should be properly disposed. Figure 14 shows the hazard corrosiveness. It indicates a substance that can cause severe skin burns or eye damage for humans and that is corrosive to metals.

Figure 13: Hazardous to the environment; from [19]

Figure 14: Corrosive; from [19]

Figure 15 is an indication of a substance that is highly flammable. It must be protected from heat, fire and potential heat sources since incorrect storage could cause self-ignition. [19]

Figure 15: Flammable; from [19]

The routes of exposure are similar for the all the selected acids. Exposure is possible during all acid handling operations when in contact with the skin or when vapour is inhaled. Avoiding any possible routes of exposure is of utmost importance and therefore technical measures and organisational measures are required. Technical measures include ventilation of the working area, washing facilities and emergency showers, the usage of closed loop cycles if possible, special storage containers, fire and explosion protection equipment and personal protection. Organisational measures include training and instruction on the operation in case of hazard. If the limiting values for the workplace are exceeded, additional protection is necessary to fulfil the regulations.

In order to fulfil the regulations and safe handling procedures of the Institute for Occupational Safety and Health of the German Social Accident Insurance, all acids require personal protective equipment (PPE) during handling operations. PPE includes body protection illustrated in Figure 16, eye protection shown in Figure 18 and hand protection as illustrated in Figure 19. The body protection should cover the whole body and should be antistatic and acid resistant indicated by Figure 16. Respiratory protection is mandatory in exceptional situations when the substance is released in concentration exceeding the occupational working limits. Eye protection needs side protection to avoid acid splash from the side. Hand protection equipment must be sufficiently resistant to the substance and impermeable to avoid any skin contact. The gloves should be cleaned prior to removing them and exchanged in case of damage to the material. Furthermore, the workplace must be labelled by following percept labels. [16]

Figure 16: Protective clothing; from [16]

Figure 17: Safety gloves; from [16]

Figure 18: Safety goggles; from [16]

Figure 19: Safety gloves; from [16]

Table 3 gives information about the hazardousness of the selected acids, allows comparisons and dictates the safety precaution. The table shows that almost all acids are classified as health endangering substances which can lead to irritation of the skin or the eyes. Some of the acids are corrosive and can cause severe skin burns or eye damage when in contact with humans. However, formic acid is classified by toxicity which indicates that small quantities can be life-threatening and special precautions are necessary. Thus, formic acid will not be further investigated in this study.

Table 3: Health, safety and environmental aspects of the various acids [16]

Systematic Name	**Acute toxicity**	**Health hazard**	**Corrosive**	**Flammable**
HCl		🟩	🟧	
Formic acid	🟥		🟧	🟨
Maleic acid		🟩		
Acetic acid			🟧	🟨
EDTA		🟩		
Lactic acid			🟧	
MSA		🟩	🟧	
Sulfamic acid		🟩		
Glycolic acid		🟩	🟧	

The most dangerous situation occurs at the workshop when the acid, available either in solid or liquid form is admixed with water in a container of the pumping unit. During acid preparation internal regulations of OMV Exploration & Production GmbH dictate to use a particle filter additionally to the PPE. Once the acid blend is mixed, the particle filter is no longer needed because the blend is in the closed cycle of the pumping unit.

4.2 Acid Comparison

Each acid has unique properties and thus the reaction and its intensity with the mineral differs. This chapter compares the differences in the dissolving ability and the differences in acid strength.

4.2.1 Acid Dissolving Capacity

Table 4 shows the physical properties of the selected acids. The phase of the acid is important in order to plan acid handling procedures. If the acid is provided as powder, briquettes or as liquid it is easy to process. If it is provided as bar, handling operations becomes more challenging because the bar needs to be crushed prior the mixing. The functional group describes how many protons the acid can supply and the molecular weight describes the weight of one acid molecule. Furthermore, the solubility values of the acid, the solubility of the calcium salt and their dissolving capacity are provided in the table. The solubility of the acid and the calcium salt have been investigated at values around room temperature, because preparation of the acid blend is usually performed at room temperature.

A limiting parameter can be found when the dissolving capacities, calculated from the acid solubility and the calcium salt solubility, are compared to each other. The lower value restricts the reaction and defines the maximum possible amount of calcite that can be dissolved. Exceeding the limiting factor would cause precipitation; either the acid cannot dissolve anymore or the acid reaction products start to precipitate.

Ethylenediaminetetraacetic acid (EDTA) is insoluble in water and thus it cannot be used. However, its EDTA-tetrasodium salt (Na_4-EDTA) has a higher solubility and thus it was further investigated. The salt generates EDTA when dissolved in water.

Literature defines the solubility of the calcium glycolate as slightly to highly soluble. According to the European Pharmacopoea and the Austrian Pharmacopoea the terms slightly to highly soluble range from 10 g/l to 1000 g/l. Due to the large solubility range, glycolic acid was kept for further investigation. [20]

The darker green colored rows in Table 4 indicate a higher dissolving capacity and the yellow cells indicate their limiting factor. The white row indicates that the limiting factor is not exactly defined and the red row indicates a very low limiting factor. The table shows that the limiting factor for all the acids but sulfamic acid and EDTA is the solubility of the calcium salt.

Table 4: Physical properties of selected organic acids [13] [16]

Systematic Name	**Phase**	**Func. Group**	**Molecular weight [g/mol]**	**Acid Solubility [g/l]**	**Temp. [°C]**	**Acid Concentration [g/l]**	**Acid Dissolving Capacity [g/l]**	**Calcium Salt Solubility [g/l]**	**Temp. [°C]**	**Acid Concentration [g/l]**	**Acid Dissolving Capacity [g/l]**
HCl	l	1	36.5	740	20	740	1016	740	20	486	667
Formic acid	l	1	46.0	692	25	692	752	160 [21]	20	113	123
Maleic acid	s	2	116.1	788	20	788	679	128 [21]	19	96	83
Acetic acid	l	1	60.1	miscible	25	*	833	373 [21]	0	283	236
Lactic acid	s or l	1	90.1	miscible	25	*	556	56 [22]	25	46	26
MSA [17]	s	1	96.1	miscible	25	*	521	657	23	548	286
Sulfamic acid	s	1	97.1	213	25	213	110	790 [21]	25	661	340
Glycolic acid	s	1	76.1	1000 [23]	25	1000	658	**	**	**	**
Na_4-EDTA	s	1	380.2	500 [24]	20	500	66	freely soluble	20	***	161
EDTA	s	1	292.2	0.5	20	0.5	0.1	freely soluble	20	***	125

* miscible indicates completely solubility and an acid solubility of 1000 g/l was assumed

** indicates slightly to highly soluble values [25]

** indicates freely soluble values and a calcium-EDTA solubility of 1000 g/l was assumed

Figure 20 is a graphical representation of the acid dissolving capacity calculated for calcium carbonates.

The low solubility of the EDTA of 0.5 g/l does only dissolve 0.1 gram of calcium carbonate and cannot be seen in the figure. Thus, its salt will be investigated which shows higher solubility values.

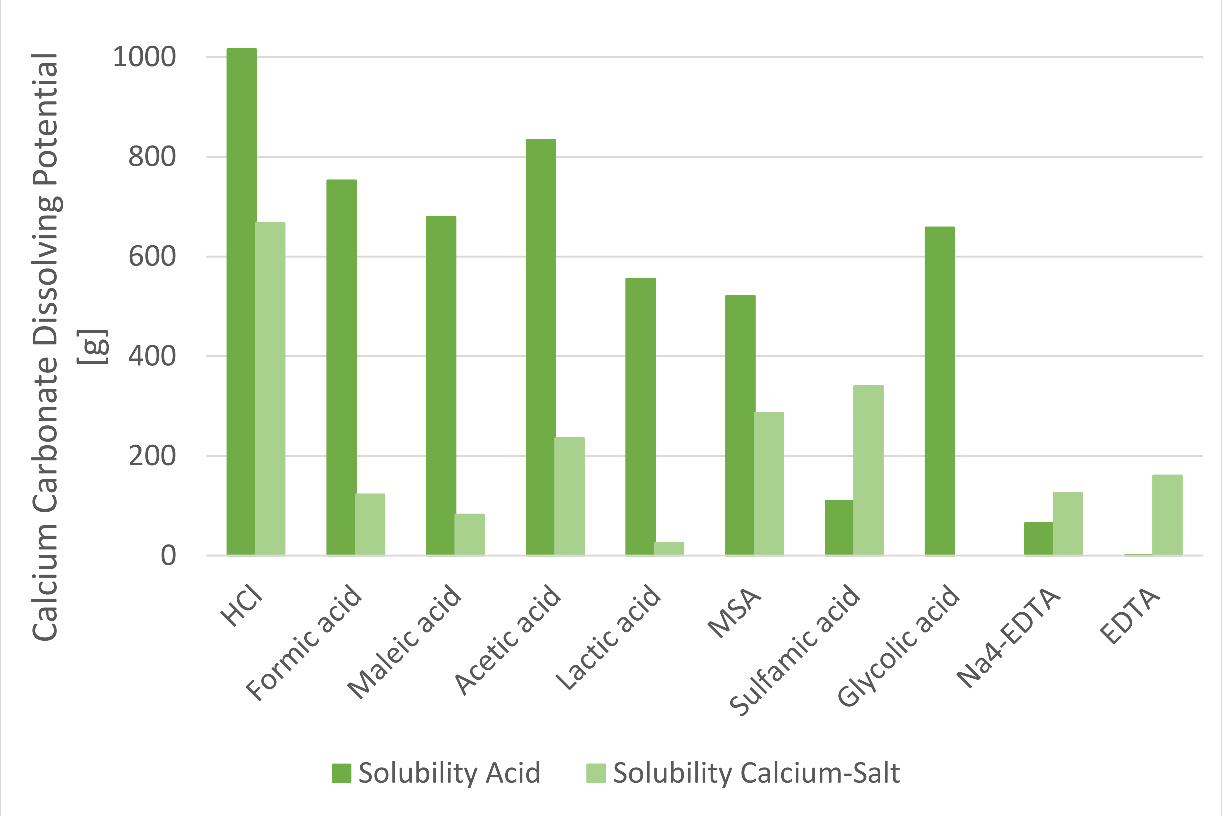


Figure 20: Dissolving potential comparison

4.2.2 Acid Strength

The strength of the acid (Chapter 3.7) influences the degree of dissociation and is described either by the acid dissociation constant or the pK_a value. The smaller the pK_a, the stronger the acid and the higher the degree of dissociation. Figure 21 shows the strength of the acids expressed in pK_a. The working principle of EDTA is fundamentally different since it works as a sequestering agent and forms metal complexes and thus any acid strength comparison is not possible. [10]

If the acid dissociation constant is varying by a magnitude of one or two, the pK_a varies only by one or two. The pK_a for sulfamic acid is around 1 and the pK_{a1} for maleic acid is around 1.9 which means that sulfamic acid is approximately ten times stronger than the maleic acid. Maleic acid is a dicarboxylic acid and could theoretically provide two protons (pK_{a1} = 1.9 and pK_{a2} = 6.2). The second pK_a is higher because it is harder for the positive proton to dissociate from the negative charged molecule.

This figure implies that HCl followed by methanesulfonic acid (MSA) will have the highest degree of dissociation and that the two acids will dissociate to a higher degree compared to the others. Sulfamic acids should show a higher degree of dissociation than maleic acid. The very weak acids such as glycolic acid, formic acid and lactic acids have similar strength and thus similar low dissociation and dissolving rate is expected. Acetic acid has the highest pK_a and should have the lowest degree of dissociation.

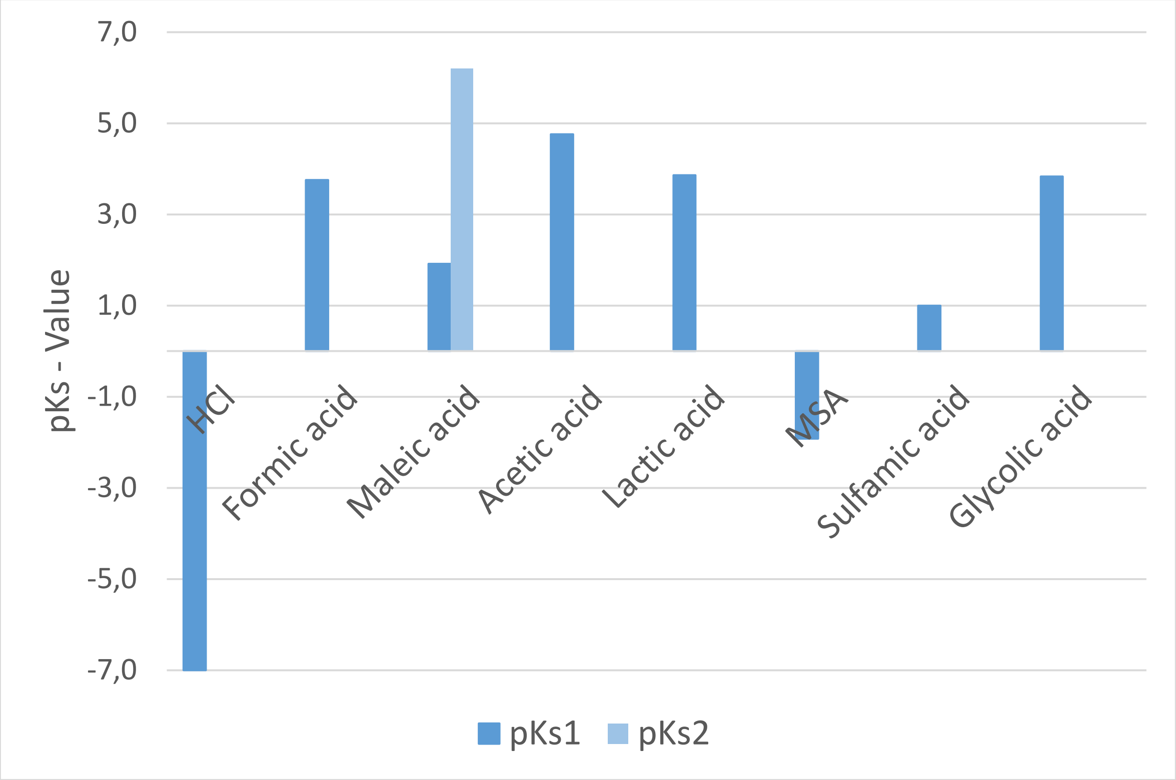


Figure 21: Acid strength comparison; from [13] [15] [16] [26]

In order to compare the different acids, an equimolar solution has been investigated. The calculation of equimolar solutions is described in chapter acid preparation (Chapter 5.1). The number of protons that can be generated for any concentration can be calculated using the molecular weight and the acid dissociation constant.

Figure 22 shows the proton concentration in equimolar solutions. An equimolar 10% HCl solution was used for this comparison, because this concentration was used for further studies. Maleic acid is a weak acid that could theoretically provide two protons. Since it does not dissociate fully during the first dissociation, the assumption for this comparison was made that the second dissociation will not support the reaction due to its even high second *pK_a*.

The diagram shows that only the strong hydrochloric acid dissociates fully and generates the required protons (2.88 H^+ moles/l). All other acids do not dissociate to completion. However, MSA can provide almost the same amount of protons. The weak acids such as maleic acid, glycolic acid, formic acid, lactic acid and acetic acid provide far less protons at an equimolar concentration.

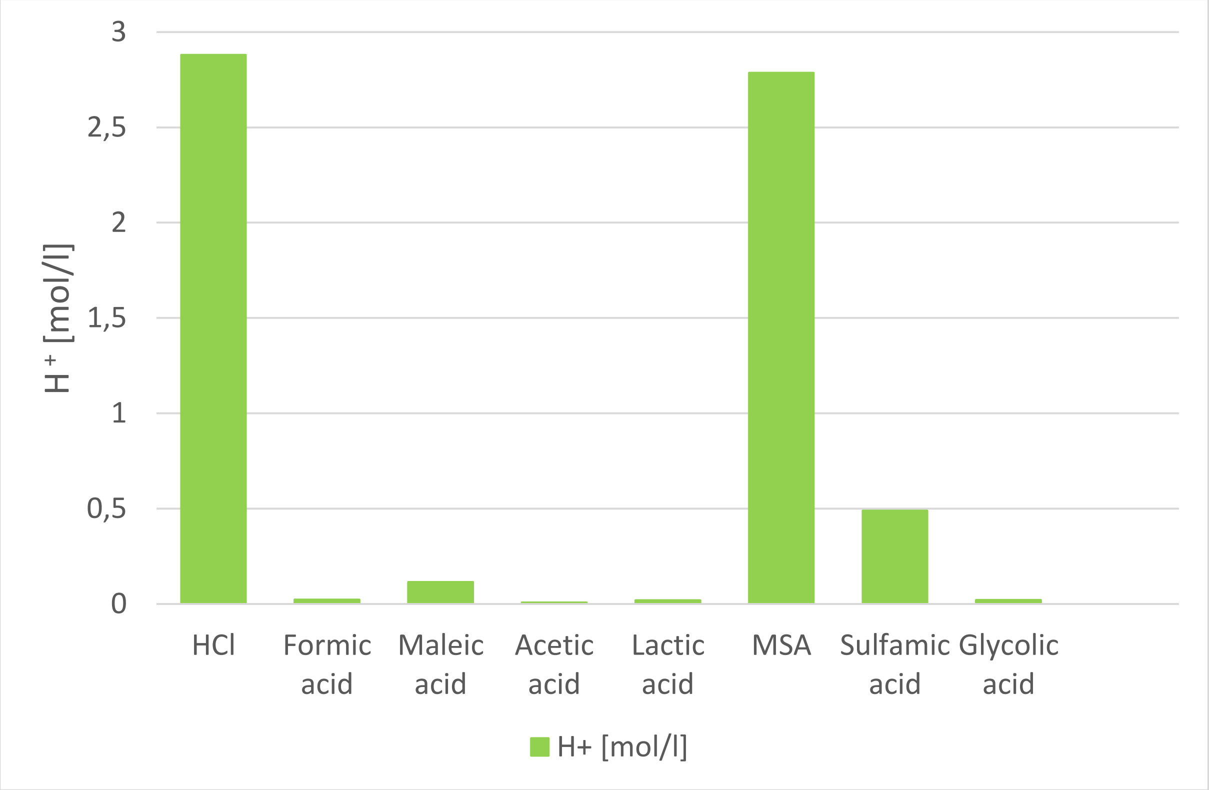


Figure 22: Proton supply of equimolar acid solutions, modified from [17]

5 Experimental Setup

This chapter describes the experimental setup and requirements of the dissolution study, the fluid compatibility study and corrosion study. It describes the preparation of equimolar acid solutions, the preparation of the rock samples and the carbon steel samples.

5.1 Acid Preparation

The main requirement for the dissolving experiment was that the mineral is available in excess during the reaction to observe the acid spending during the reaction. The acid-mineral reactions described by equations (9) for limestone and by equation (10) for dolomite define the stoichiometry of the dissolution reaction. The minimum weight of the rock sample is calculated using equation (19).

$$Acid\ Dissolving\ Capacity = wt\%_{acid} * \frac{\rho_{acid}}{M_{acid}} * \frac{v_{mineral}}{v_{acid}} * M_{mineral} \tag{19}$$

Equation (20) shows the calculation of the minimum sampling weight of the limestone sample for a 10% HCl solution.

$$Acid\ \ Dissolving\ Capacity_{10wt\%\,HCl} = \frac{10}{100} * \frac{1050}{36.5} * \frac{1}{2} * 100.1 = 144\,\frac{g\,CaCO_3}{l\,solution} \tag{20}$$

The stoichiometric relationship defines that one liter of a 10% HCl solution can dissolve 144 gram of limestone. For the experiment 100 milliliter solutions were used which can dissolve 14.4 gram of limestone. The same concentrated HCl solution can dissolve 13.3 gram of dolomite and was calculated using equation (19) and equation (10). The calculated weights indicate the minimum weight of the samples to achieve mineral excess.

In order to allow comparison between the acid solutions, the dissolving capacity of a 10% HCl solution has been used to calculate equimolar concentrations as described by equation (21).

$$Equimolar\ Concentration_{acid} = wt\%_{HCl} * \frac{\rho_{HCl}}{M_{HCl}} * M_{acid} \tag{21}$$

Equation (22) describes the equimolar relationship between HCl and MSA.

$$Equimolar\ Concentration_{acid} = \frac{10}{100} * \frac{1050}{36.5} * 96.1 = 276.5 \frac{g\ MSA}{l\ solution} \qquad (22)$$

276.5 gram of pure MSA need to be diluted using deionized water to a liter to get the required equimolar solution. One liter of this equimolar solution is theoretically able to dissolve 144 gram of limestone as required. The equimolar concentrations provided in Table 5 were used for the acid preparation, but in some cases they had to be adjusted due to limiting effects. Table 5 shows the required equimolar concentrations, the limiting concentrations and the adjusted concentrations of the acids.

The red cells in Table 5 show that the required equimolar concentration exceeds the limiting concentration. Thus, either the acid cannot fully dissolve or the reaction products can start to precipitate. Figure 23 is a graphically illustration of the concentrations.

Table 5: Equimolar and limiting concentration

Systematic Name	**Equimolar Concentration [g/l]**	**Limiting Concentration [g/l]**	**Adjusted Concentration [g/l]**
HCl	10wt%	486**	10wt%
Maleic acid	167	96**	167
Acetic acid	173	283**	173
Lactic acid	259	47**	259
MSA	277	548**	277
Sulfamic acid	280	213*	195
Glycolic acid	219	***	219
Na_4-EDTA	1095	500*	547

* limiting concentration is solubility of acid

** limiting concentration is solubility of Ca-salt

*** limiting concentration is narrowed to a range: slightly to highly soluble

Literature describes acetic acid, lactic acid and MSA as completely miscible acids and glycolic acid as a highly soluble salt, hence high acid concentrated solutions can be prepared as shown in Figure 23.

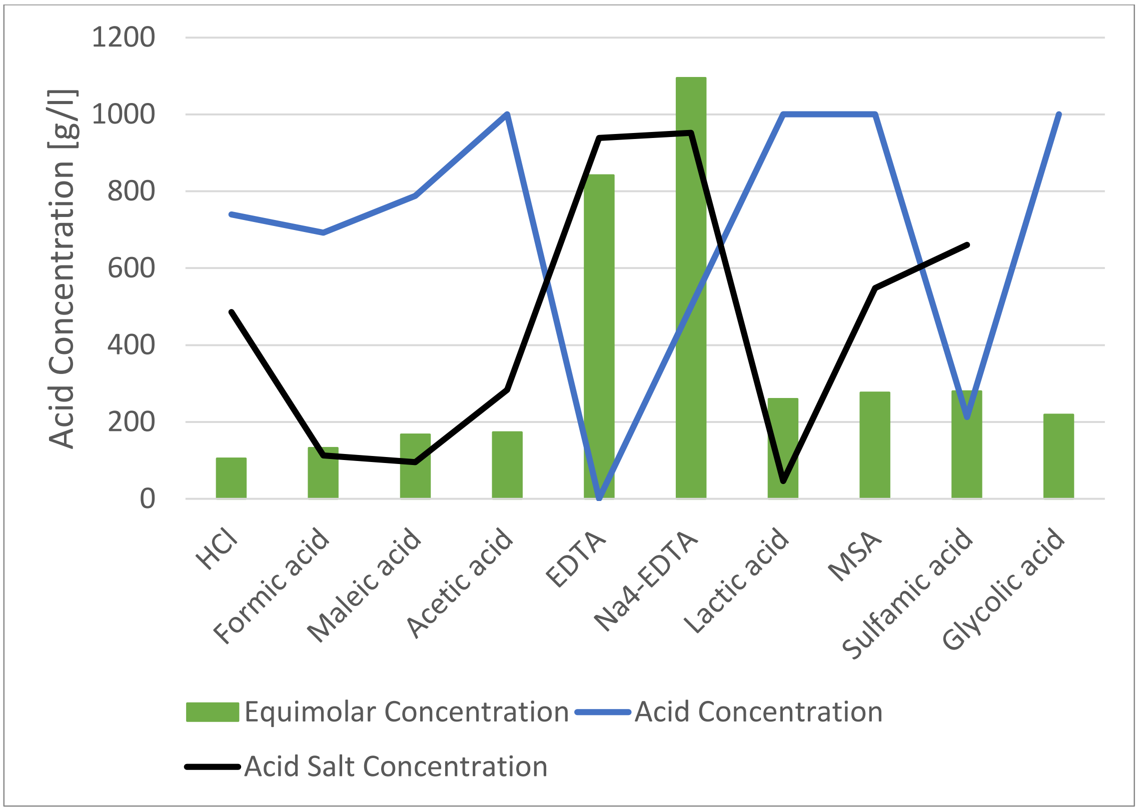


Figure 23: Impact of limitations on equimolar concentration

shows that the solubility of the calcium maleate and calcium lactate increases with temperature. The solubility values at room temperature are colored blue and solubility values at elevated temperatures are colored orange. Thus, the risk of precipitation diminishes at higher temperature. The equimolar concentrations for maleic acid and lactic acid are 167 g/l and 259 g/l, respectively. The increased calcium-maleate solubility would not cause any precipitation during the experiment. Thus, maleic acid was prepared using 167.1 grams of its salt (maleic anhydride). The salt generates maleic acid when dissolved in water. The rise of the calcium-lactate solubility is not sufficient to completely avoid precipitation. Nevertheless, it was studied at equimolar concentration.

Table 6: Calcium-salt solubility dependence on temperature

Systematic Name	**Solubility of Salt [g/l]**	**Temp. [°C]**	**Acid Concentration [g/l]**	**Solubility of Salt [g/l]**	**Temp. [°C]**	**Acid Concentration [g/l]**
Calcium-Maleate [21]	128	19	96	335	60	251
Calcium-Lactate [22]	57	20	47	203	53	203

Table 7 shows that acid solubility values defined from literature are different to the practically determined acid solubility values. It shows that the acid concentrations for Na_4-EDTA and sulfamic acid was restricted to 547 g/l and 195 g/l, respectively. Furthermore, sulfamic acid is recommended for applications where the formation temperature is lower than 70°C, because decomposition starts around 80°C. [27]

Table 7: Practically determined acid solubility properties

Systematic Name	**Theoretical Acid Solubility [g/l]**	**Temperature [°C]**	**Acid Dissolved [g/l]**	**Temperature [°C]**
Na_4-EDTA [24]	500	RT	547	RT
Sulfamic acid [16]	213	RT	195	RT

Since the exact calcium-glycolate solubility data was not found, it was kept for further studies. Evidence was found that glycolic acid is chemically stable to a temperature of 50°C. Above this temperature polymerization begins. [28]

5.2 Mineral Sample Classification

The dissolution experiments were performed with dolomite and limestone plugs from outcrop rock material. The cored rocks have been cut into cylinders having a minimum weight of the previous mentioned 14.4 gram for limestone and the 13.3 gram for dolomite in order to achieve an excess of mineral.

Dolomite Plugs were prepared from the “Hauptdolomit Formation” which is a lithostratigraphic unit in the Northern Calcareous Alps. As the name indicates, the main fraction of the formation is dolomite with minor fractions of calcite, quartz and clay. The Hauptdolomit was originally formed in a shallow lagoon intertidal zone. This characterization comes from bird eyes which are small layers of calcite cement that have been formed during decomposition of the organic matter. Bird eyes can be found in the prepared plugs as calcite veins and can be seen in Figure 24. [29]

Since this formation is a producing reservoir rock unit it was characterized by OMV Exploration & Production GmbH. The formation composition data for sample wells is shown in Table 9 in the appendix and shows that the formation mainly consists of dolomite having fractions of calcite, clay and quartz.

Figure 24: Hauptdolomit Formation rock sample

Limestone samples were prepared from “Untersberg Formation” which is a detrial carbonate. Petrographical investigation of this limestone shows that it is a tight carbonate having calcium carbonate content of approximately 98% and a low porosity of 0.5 %. In order to compare the acid properties properly, the calcite has been used due to its homogeneity. The limestone sample is shown in Figure 25. [30] [31]

Figure 25: Untersberg Formation rock sample

5.3 Dissolution Procedures

The acid solution was heated to desired temperature using a heating plate. A stir bar was used in the beaker to continuously stir and mix the acid solution to ensure acid dispersion. Once temperature was reached and rock sample was prepared, the experiment started in a simple beaker. The beaker was either open for the low temperature experiment or covered with a parafilm for the high temperature experiment. The setup is shown in Figure 26. Since the dissolving behaviour of the selected acids was unknown, every 15 minutes a 2 milliliter sample was taken and filtered using syringe filter. The study duration was chosen to be 2 hours, because acidizing pumping operation in Lower Austria usually takes less than 2 hours, depending on the pumping depth and pumping volume.

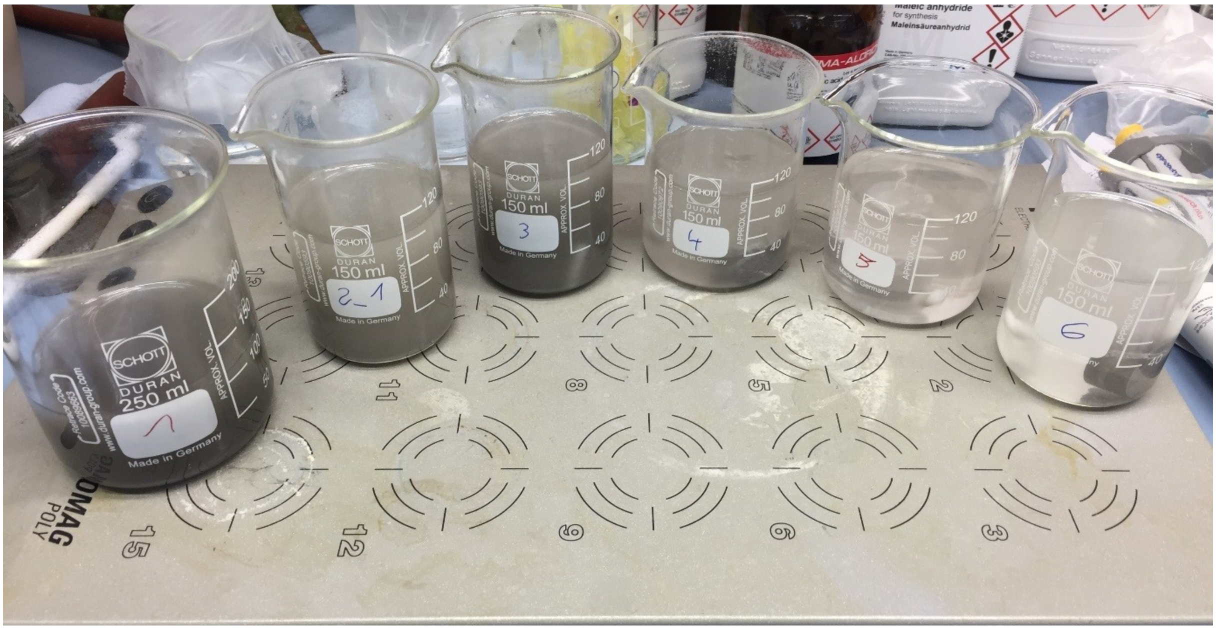


Figure 26: Illustration of the experimental setup

At the beginning and at the end of the experiment, various acid and rock properties were investigated such as the net weight of the acid, the solubility of the acid in water, pH values, temperatures and the difference of rock mass of the sample. The pH-values and the temperatures have been measured with a pH-Meter (Metrohm's *827 pH lab)*. The rock mass was determined at the beginning and at the end of the study using a *Sartorius Analytical* weighting device. Since the rock samples were wet after the experiment, they were heated and dehydrated in a desiccator to obtain the dry weight difference. Since rock fractions were dissolved and kept in solution, the suspension was filtered using 2 µm filters.

Once a run was finished, the collected samples were diluted and analysed using an ion chromatograph. An ion chromatograph measures the electrolytic conductivity from predefined ions having the opposite charge. Dilution was necessary to stay within the conductivity range of the ion chromatograph. The calcium and magnesium concentration of the samples is directly related to the dissolution behaviour and can be used to calculated the amount of rock that was dissolved over time. [32]

5.4 Fluid Compatibility Procedures

The fluid compatibility study is to ascertain the behaviour of the treating fluid system when in contact with formation oil. A fluid system composes of a base or main acid solution and its additives. The different additives that are available for stimulation operations are described in treatment design considerations (Chapter 3.4.2). This study investigates the compatibility of the stimulation fluid system and formation crude oil. It ensures that the mixture is compatible and additive separation or precipitation does not occur. An incompatible fluid mixture can form emulsion and sludge that can introduce damage to the formation and make fluid pumping difficult due to higher fluid viscosity. [33]

This experiment was performed by using an actual stimulation recipe. An assumption has been made that only HCl needs an inhibitor to protect downhole equipment from corrosion, whereas the other selected acids do not need inhibition.

- HCl treatment
  10% HCl + 2% Citric Acid + 10% Ethylene Glycol Monobutyl Ether (EGMBE) + 1% GreenDEM 2 + 0,5% Cronox 242 ES
- Selected acid treatment
  Equimolar acid solution + 2% Citric Acid + 10% Ethylene Glycol Monobutyl Ether (EGMBE) + 1% GreenDEM 2

Citric acid is generally used as sequestering agent to control and bind the iron in solution. EGMBE is used as mutual solvent to ensure that the reservoir remains water wet after the acidizing operation. [1]

GreenDEM 2 is a surfactant that is used as non-emulsifing agent in water based stimulation treatments. It has great demulsifying properties in a wide temperature range and is compatible with different oils and other fluids such as lean and spent acids, Newtonian and power law fluids. [34]

Cronox is the corrosion inhibitor developed and produced from Baker Hughes. The assumption for this scenario was that the corrosion inhibitor is only needed for HCl stimulation treatments, because of its high corrosion rate. [35]

Once the acid solution was prepared a clear treating mixture was obtained. The treating fluid was then mixed with oil from the sampling unit. The oil is internally described as A-oil and is classified as oil having high content of higher carbon molecules. The composition of the crude oil is shown in Figure 64 in the appendix. Mixture rations were 1:1 and 2:1. After pouring the oil to the acid solution, the mixture was agitated and left to stand at room temperature and at 50°C for the emulsion break test. The same procedure was performed with live and spent acid solutions.

5.5 Corrosion Procedures

In this experiment an oversupply of acid is required to evaluate the dissolving capacity of the acid. The maximum amount of iron that can be dissolved by a 10% HCl solution was calculated using equation (19) and the stoichiometric relationship of the iron dissolving reaction. The amount of iron that is dissolved is calculated in equation (23).

$$Acid\ \ Dissolving\ Capacity_{10wt\%\,HCl} = \frac{10}{100} * \frac{1050}{36.5} * \frac{1}{2} * 55.9 = 80.4 \frac{g\,Fe}{l\ solution} \tag{23}$$

It describes that one liter of 10% HCl solution can dissolve 80.4 gram of iron. In the experiment only 200ml of 10% HCl solution has been used and this translates to a dissolving capacity of 16.1 gram of iron. In order to fulfill the requirement for the experiment the mass of the iron coupon had to be smaller than 16.1 gram.

The coupon used for the corrosion study is a low carbon steel that allows accurate monitoring of corrosion rates in any acidic environment. The composition of the metal coupon is given in Table 8. This steel composition was used because it is used in most tubulars from OMV Austria Exploration & Production GmbH.

Table 8: Composition of the low carbon steel used for the corrosion study

Grade	**C**	**Mn**	**P**	**S**
AISI 1010	0.08-0.13	0.3 - 0.6	0.04 max	0.05 max

The coupons were cut into equally sized pieces having a smaller weight than the calculated 16.1 gram. They were cleaned using hot water and an abrasive cleaning powder to remove any inhibitors that might be present on the coupons. When the coupons were cleaned, they were dried using acetone and compressed air, were weighted and stored in a desiccator to maintain dehydration.

Once the sampling coupons were prepared, the water quench (Lauda Eco Gold) was heated to the desired temperature of 50°C and the desired volume of the acid solution was filled in Florence flasks. A Florance flasks is a glass flask which has a round body and a long neck is designed for uniform heating and boiling. The experimental setup describes a worst case corrosion scenario, because the flasks were not pressurized and hydrogen was able to escape the solution which drives the reaction towards the right. However, this setup was constructed and tested to verify that only minor parts of acid solution is lost due to evaporation. Eight flasks were arranged in the water quench to test the corrosion behaviour of the acids. In order to allow comparison of the various acids, one flask was always filled with HCl as reference to investigate the mass reduction.

Figure 27: Illustration of the corrosion experimental setup

Samples were taken after 1h, 2h, 4h and after 24 hours to investigate the corrosion of the acid via mass reduction. The time steps were chosen to cover the duration period of typical matrix acidizing treatments. After the experiment, the samples were mechanically cleaned using an abrasive powder, dried using acetone and compressed air and were weighted.

6 Results

This chapter presents the results from the dissolution study using limestone and dolomite, the fluid compatibility study and the corrosion study. Each experiment was performed twice in order to validate the results.

6.1 Limestone Dissolving Study

The mass reduction from the Untersberg dissolving study shows that the mass dissolved in the both same temperature experiments is similar and varies less than one gram.

6.1.1 Treatment using HCl

Figure 28 shows the reaction profile when HCl is used for acidizing limestone samples. It is clearly visible that at higher temperature the reaction reached an equilibrium state after 30 minutes, whereas the reaction takes longer (60 minutes) to reach equilibrium at room temperature.

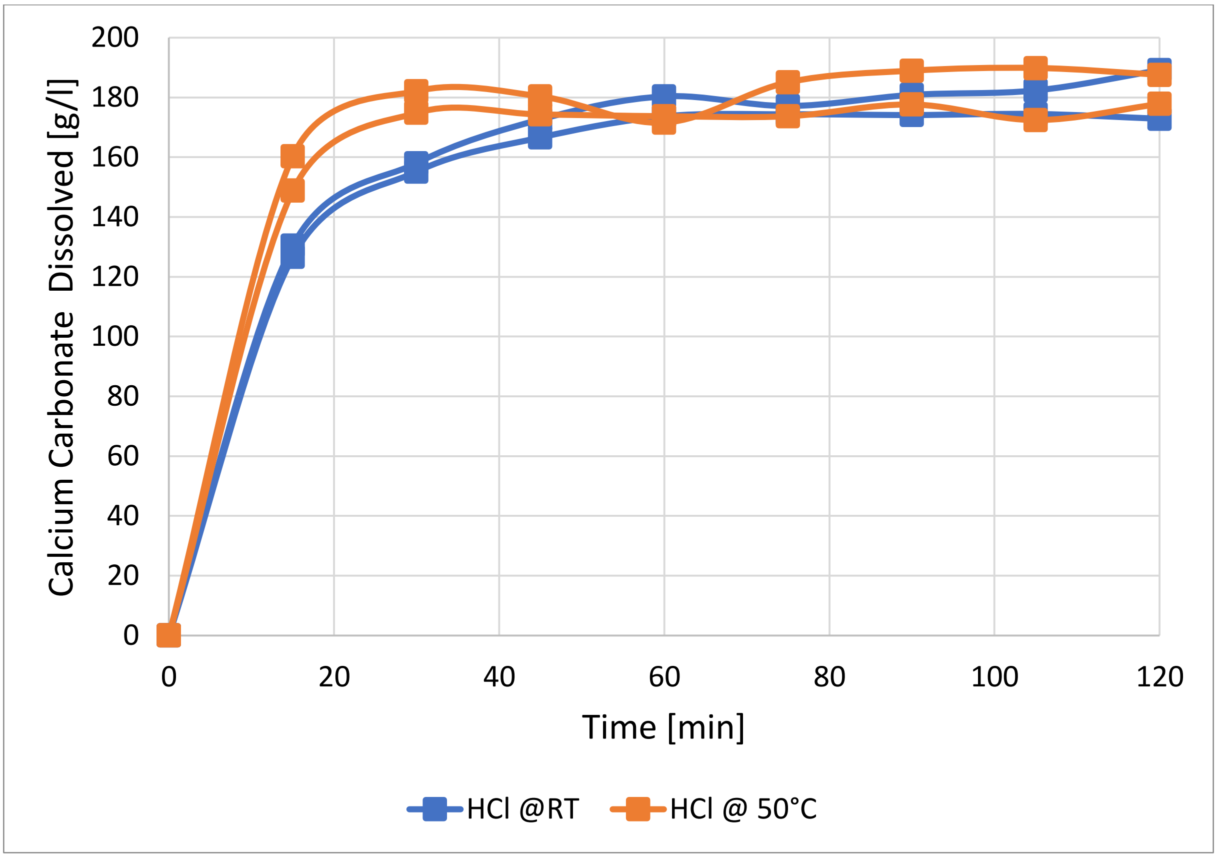


Figure 28: Amount of limestone dissolved by HCl indicating

6.1.2 Treatment using Maleic Acid

Figure 29 illustrates the maleic acid limestone dissolving reaction. It can be seen that at room temperature the acid is able to dissolve around 50 grams of limestone and reaches an equilibrium state after 90 minutes. The graph derived from the 50°C experiment does not show any equilibrium state, thus the instabilities were verified by repeating the experiment. Additionally, precipitation was noticed after the sample was dried. The precipitation is shown in the red circles in Figure 30.

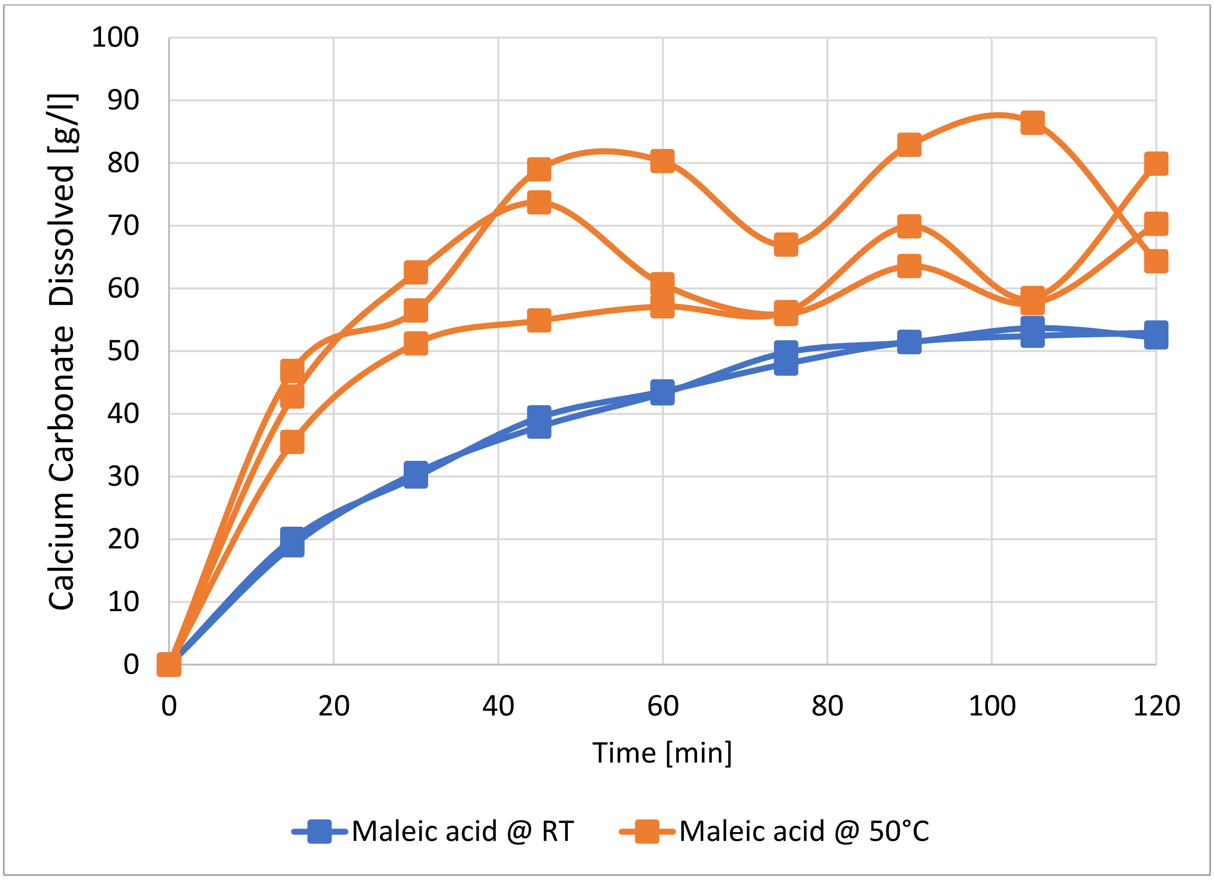


Figure 29: Amount of limestone dissolved by maleic acid

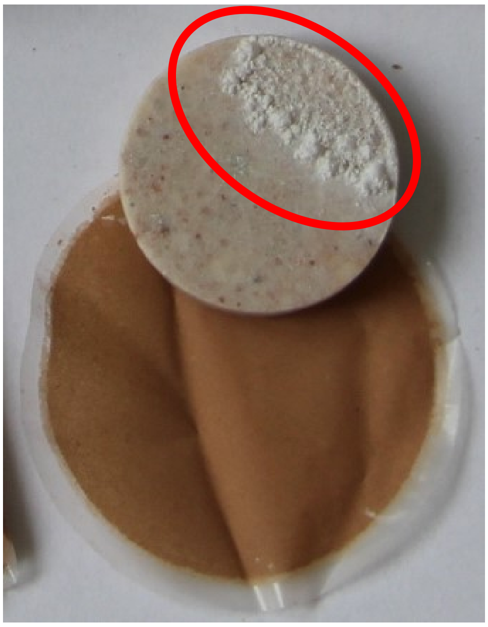


Figure 30: Reaction product formed during the limestone dissolving study using maleic acid

6.1.3 Treatment using Acetic Acid

The reaction behavior of acetic acid and limestone is shown in Figure 31. It shows that more limestone is dissolved at the 50°C temperature study. After the predefined reaction duration, the reaction rate indicated by the slope did not reduce and equilibrium was not reached. Since both temperature experiments did not reach equilibrium, an additional experiment was performed where the reaction duration was doubled.

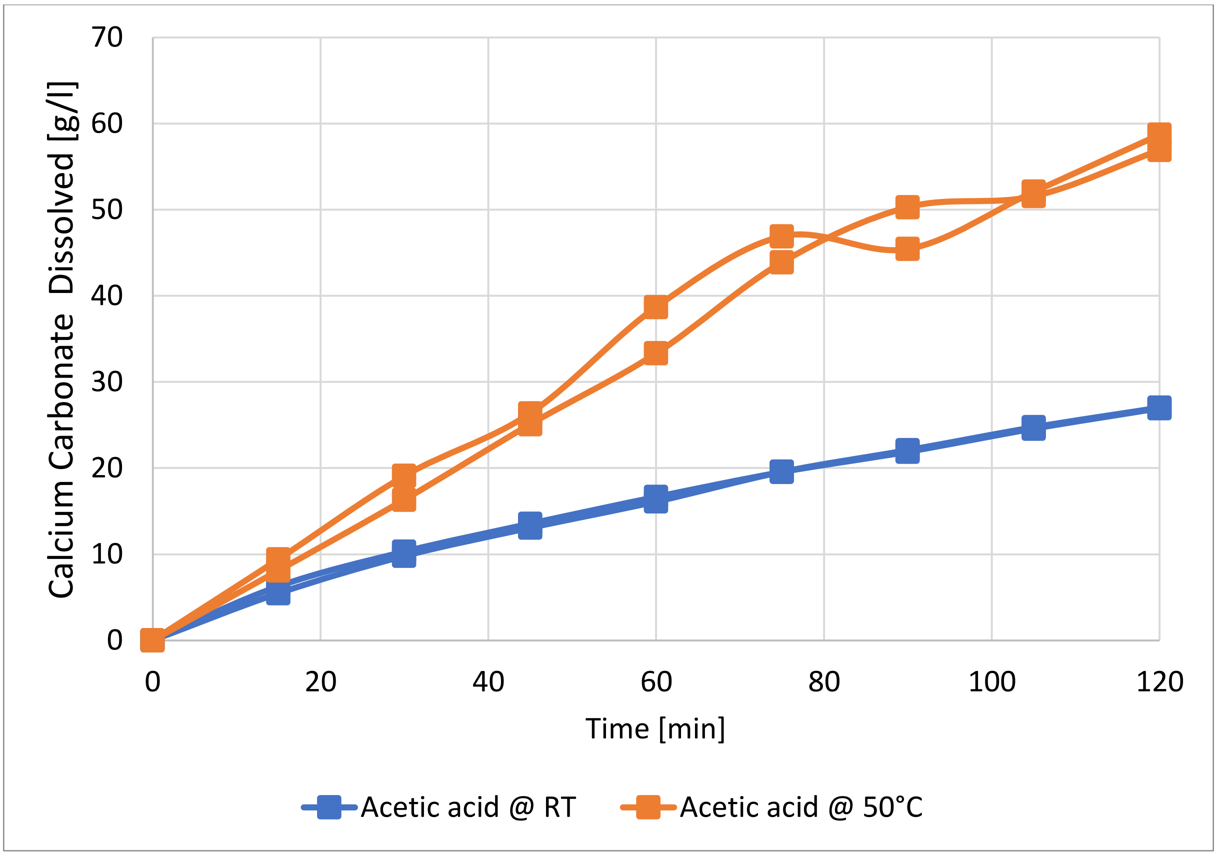


Figure 31: Amount of limestone dissolved by acetic acid

The results of the extended acetic acid dissolution study are shown in Figure 32 and Figure 33. The mass limestone dissolved after 4 hours increased by around 30% to 5.9 gram instead of the 4.6 grams that were dissolved after 2 hours. Investigation on Figure 33 showed that the dissolving ability slowed down which is indicated by a reduced slope for the extended 2 hours. In the first two hours of the study around 55 gram of limestone was dissolved. During the extended two hours 15 gram of limestone was additionally dissolved which verifies the mass comparison. However, equilibrium was not reached after the investigated 4-hour study.

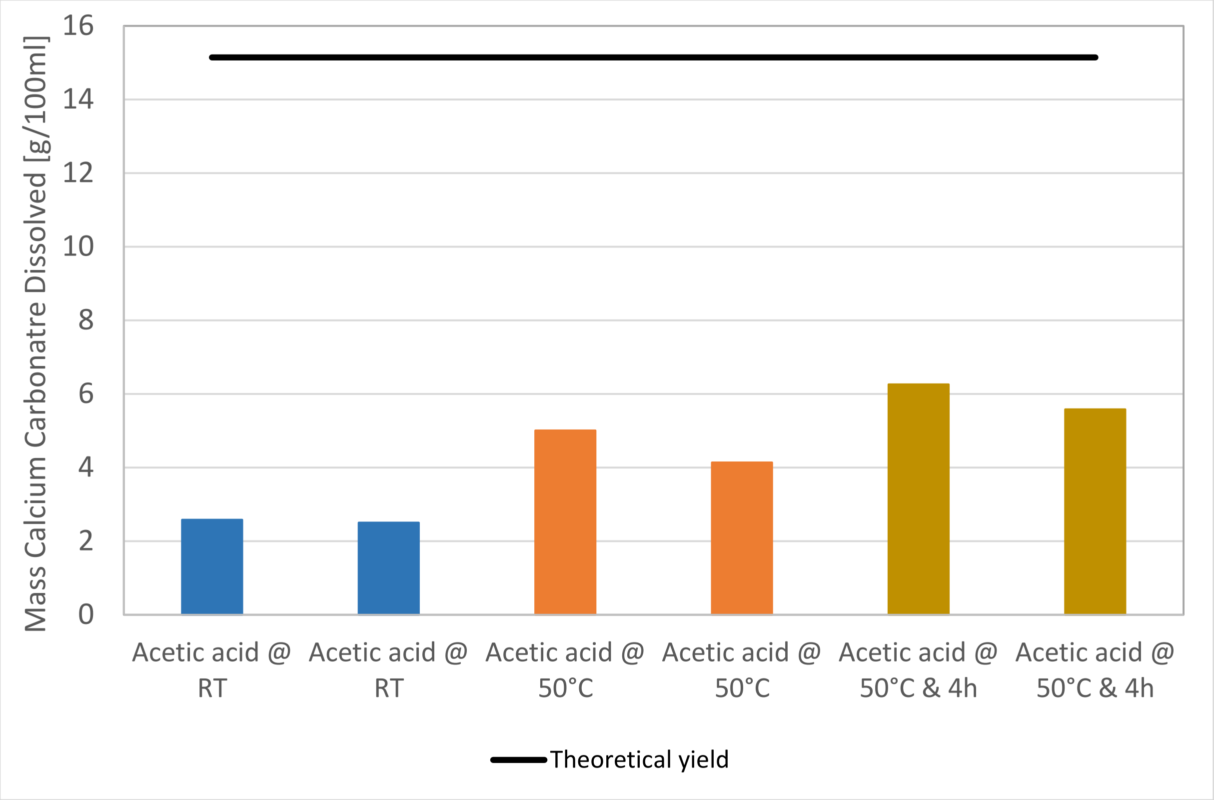


Figure 32: Amount of limestone dissolved by acetic acid in different scenarios

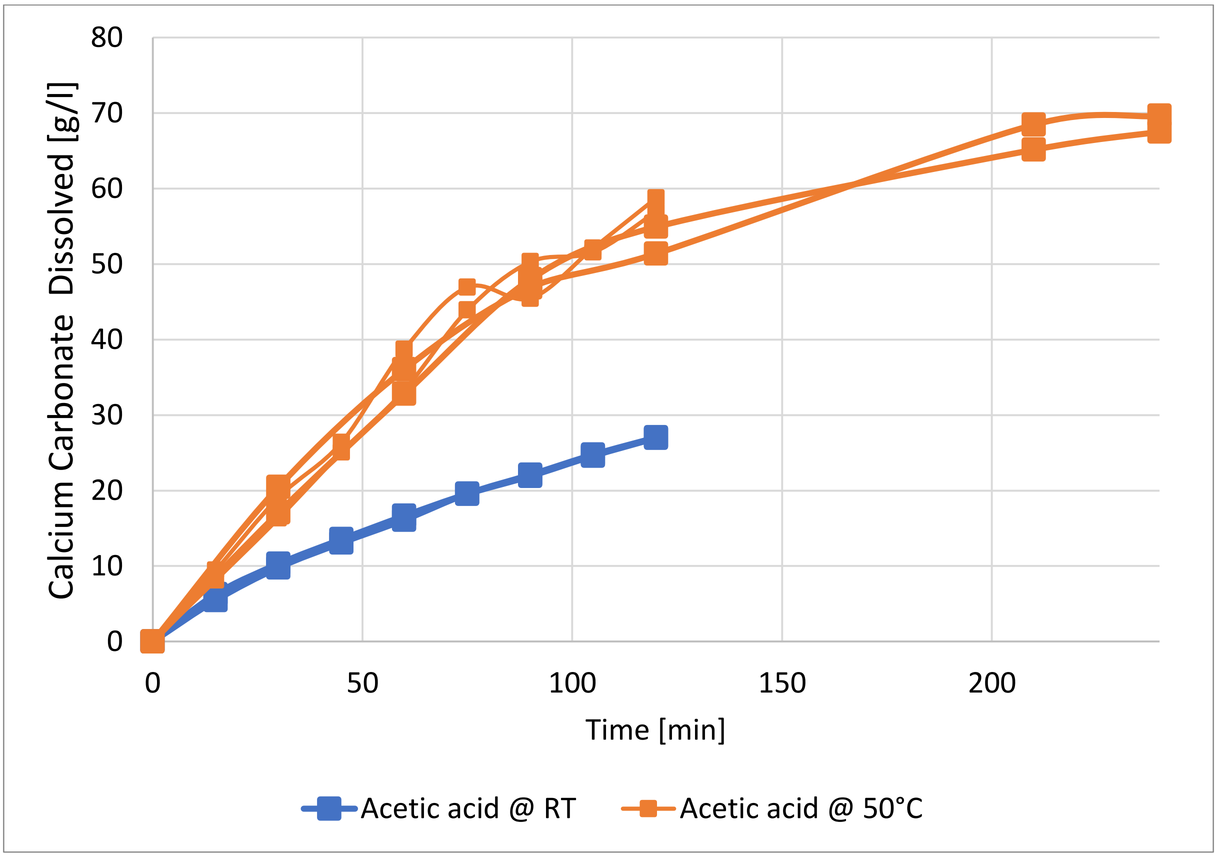


Figure 33: Extended study of the limestone dissolving capacity using acetic acid

6.1.4 Treatment using Lactic Acid

Figure 34 shows the limestone reaction profile using lactic acid. It shows that at room temperature after 105 minutes the concentrations of both experiments drop and no equilibrium state could be established. Similar to room temperature experiment, the 50°C study showed that no concentration equilibrium could be reached. An additional experiment was performed to verify the instabilities. Precipitation was encountered in both experiments after drying the sample as shown in Figure 35.

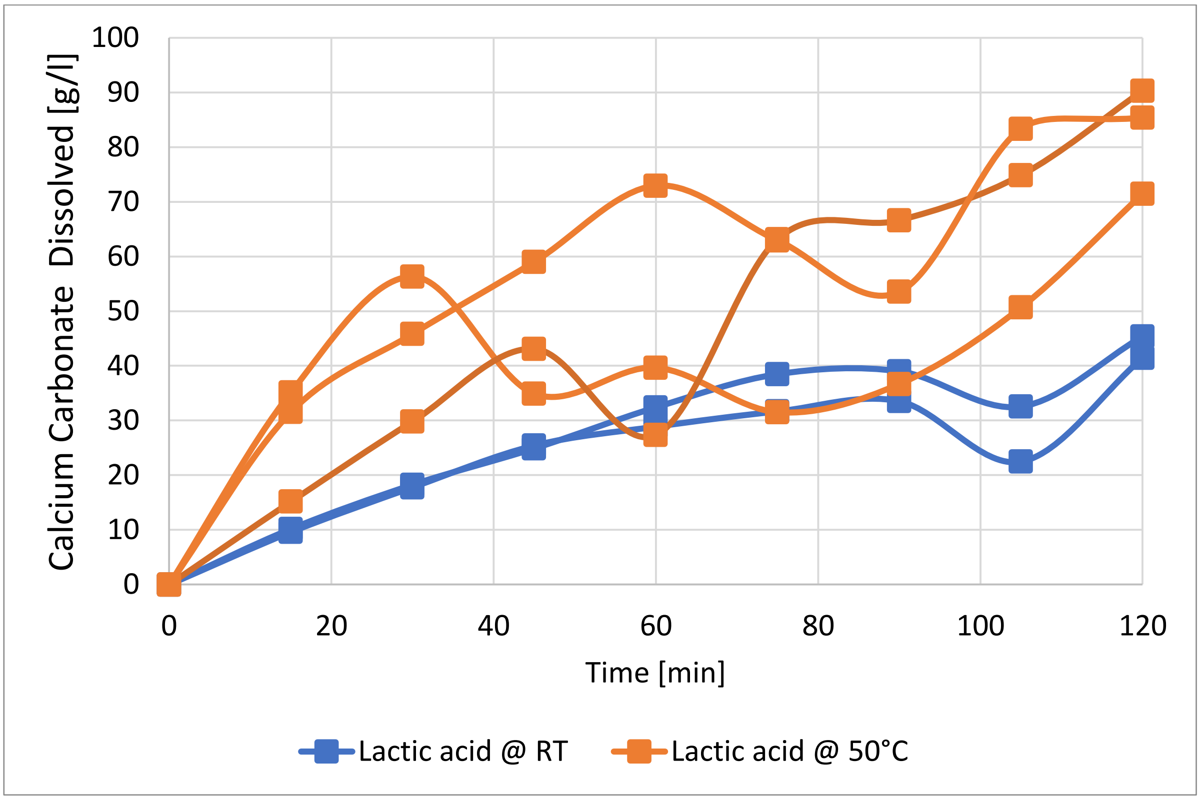


Figure 34: Amount of limestone dissolved by lactic acid

Figure 35: Reaction product formed during the limestone dissolving study using lactic acid

6.1.5 Treatment using Methanesulfonic Acid

Figure 36 shows the limestone dissolving study when MSA is used. It illustrates that the acid reaches equilibrium regardless the temperature. The higher temperature study reaches equilibrium after 30 minutes, whereas the study performed at room temperature takes longer to reach equilibrium (60 minutes).

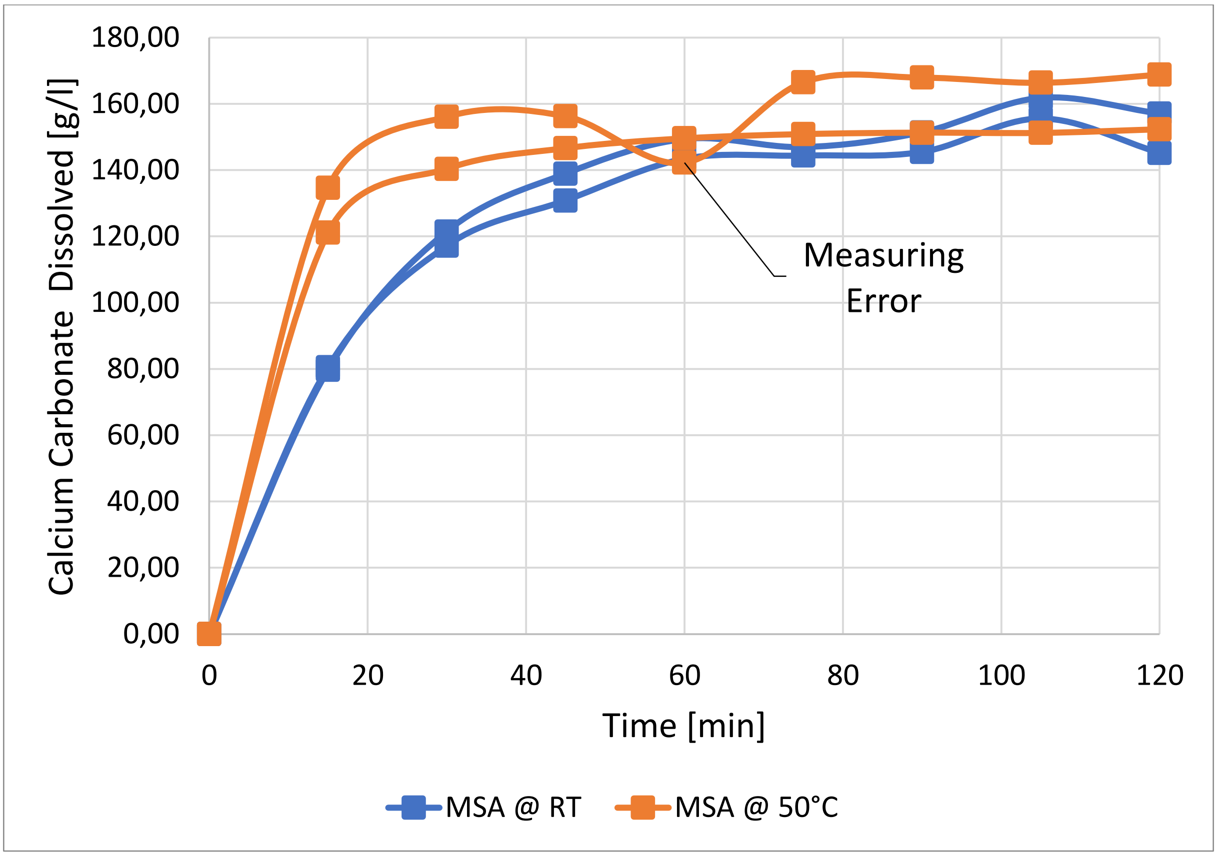


Figure 36: Amount of limestone dissolved by MSA

6.1.6 Treatment using Sulfamic Acid

Figure 37 illustrates the acid - limestone reaction behavior when sulfamic acid is used. It can be seen that the acid is spent after around 60 minutes in the 50°C experiment. The acid at room temperature is not yet spent after the two hours of testing and an equilibrium state was not reached.

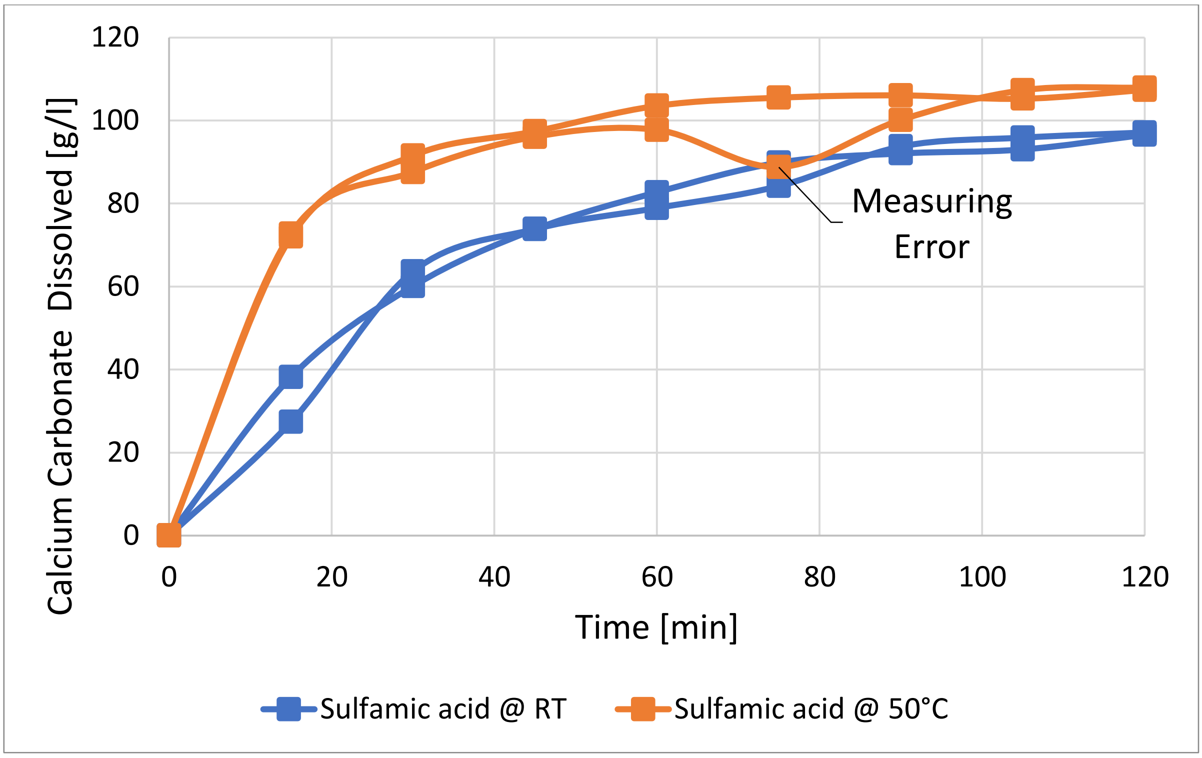


Figure 37: Amount of limestone dissolved by sulfamic acid

6.1.7 Treatment using EDTA

The limestone dissolving study performed with EDTA at 50°C shows that EDTA is a very low acting chelating agent as shown in Figure 38. The temperature helped increasing the dissolving capacity as can be seen in Figure 51. After the study duration of 2 hours only around 8 gram of limestone were dissolved.

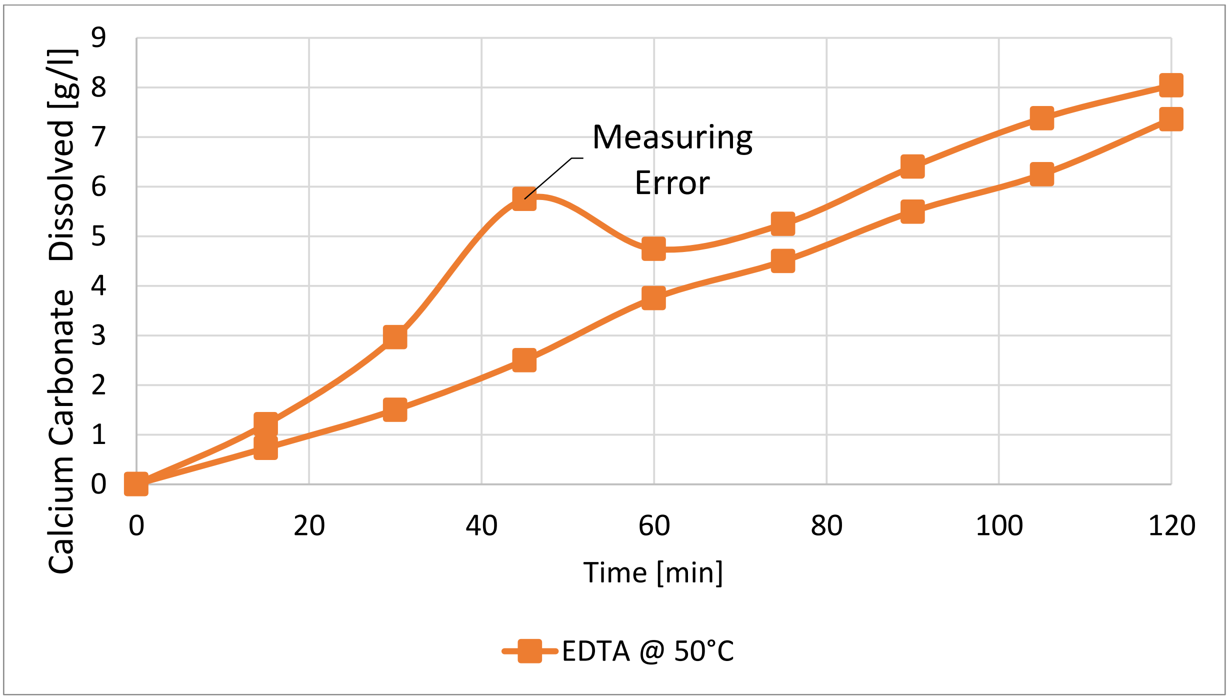


Figure 38: Amount of limestone dissolved by EDTA

6.2 Dolomite Dissolving Study

The mass reduction from the “Hauptdolomit Formation” dissolving study shows that the mass dissolved in the both same temperature experiments varies. The dissolving capacity measured by the ion concentration was therefore only measured at 50°C.

6.2.1 Treatment using HCl

Figure 39 shows the reaction profile when HCl dissolves dolomite samples. It shows that the acid is spent after 45 minutes and concentration equilibrium was established after approximately 45 min.

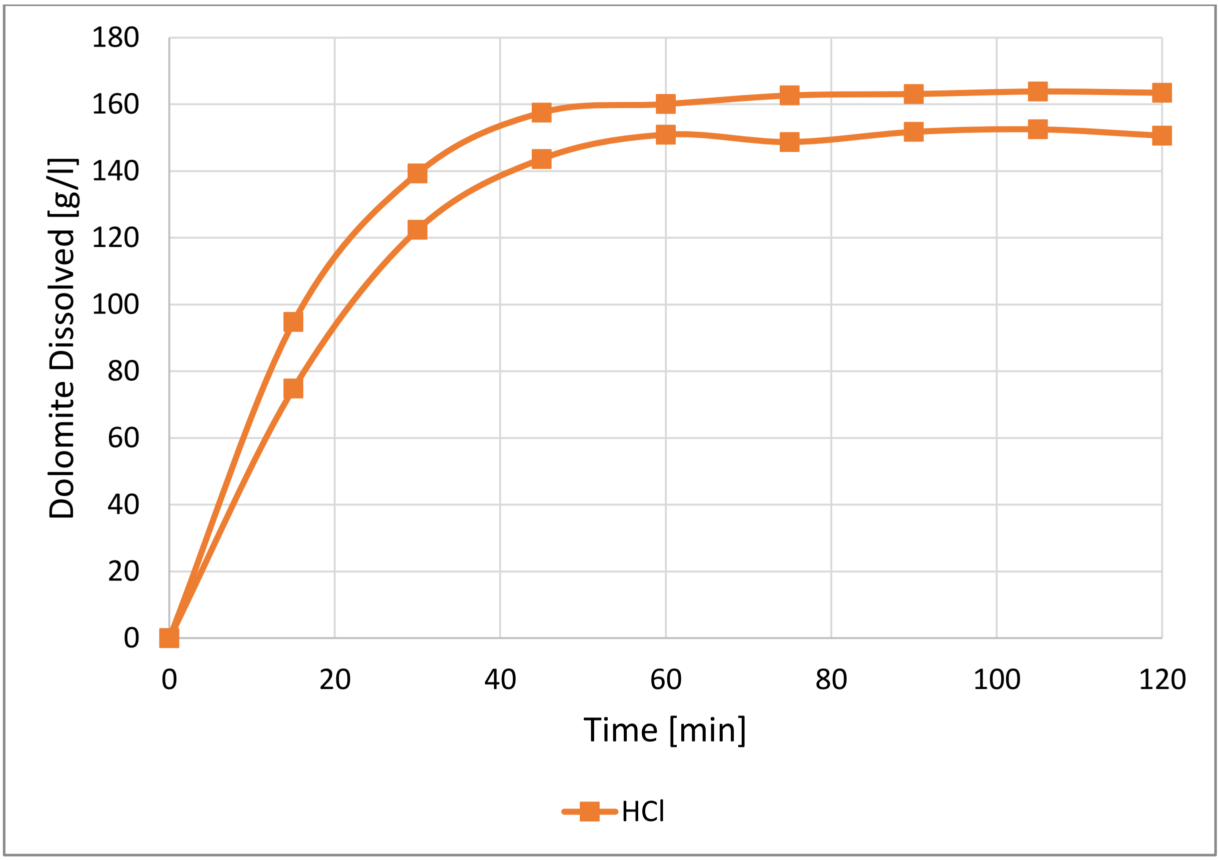


Figure 39: Amount of dolomite dissolved by HCl

6.2.2 Treatment using Maleic Acid

Figure 40 shows the reaction profile when maleic acid is reacting with dolomite. It shows that an equilibrium state was not achieved during the study. Precipitation was found after the sample was dried as shown in Figure 41. As shown in the figure, the precipitation was water soluble.

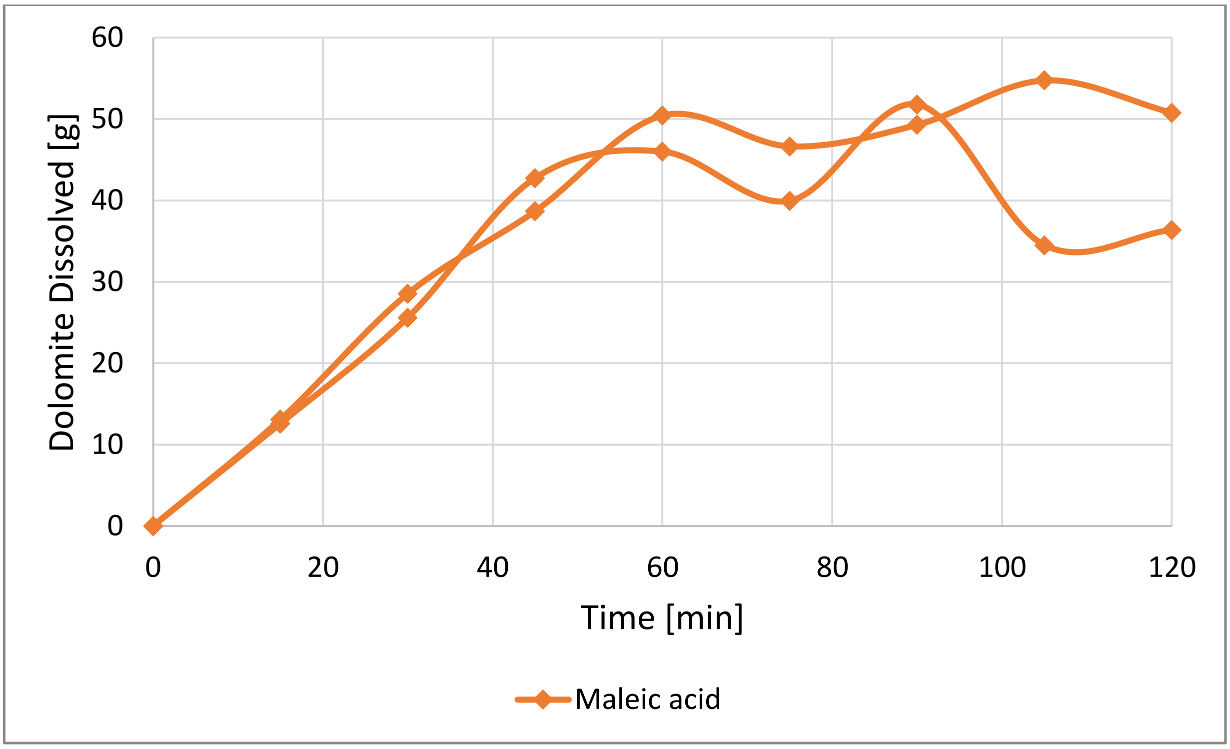


Figure 40: Amount of dolomite dissolved by maleic acid

Figure 41: Reaction product formed during the dolomite dissolving study using maleic acid

6.2.3 Treatment using Acetic Acid

The reaction profile of acetic acid and dolomite is shown in Figure 42. It clearly indicates that the acid is still reactive after the examined 2-hour study, because the concentration has not yet stabilized.

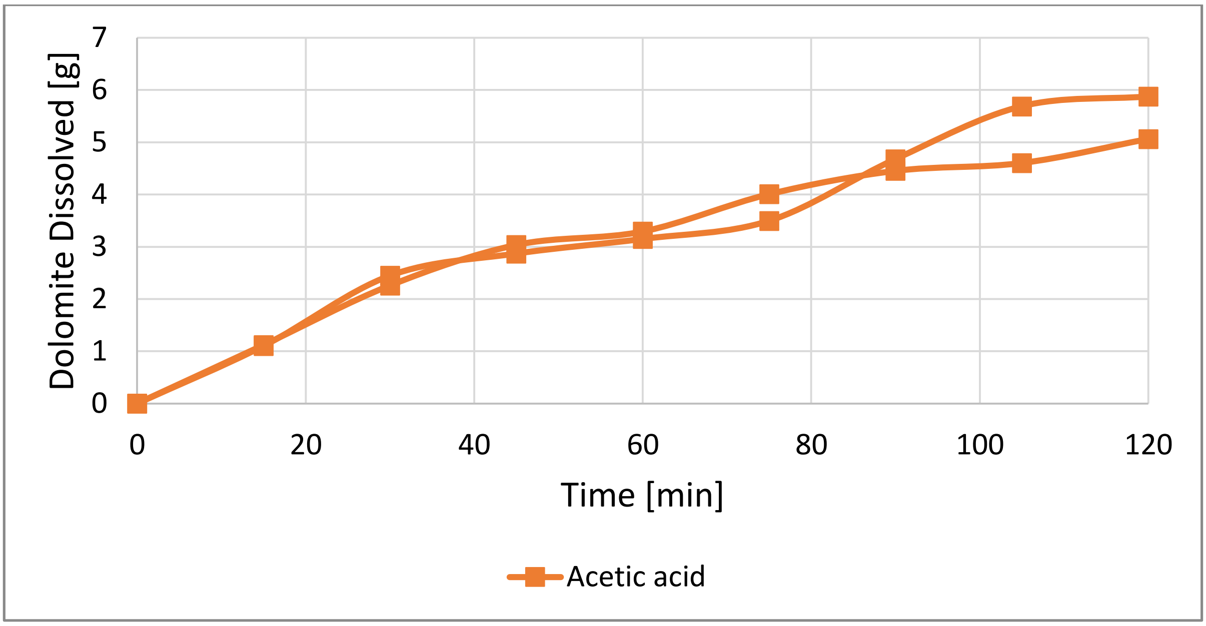


Figure 42: Amount of dolomite dissolved by acetic acid

6.2.4 Treatment using Lactic Acid

Figure 43 shows the dolomite dissolving reaction profile when using lactic acid. It shows that no equilibrium state was established and different amounts of dolomite were dissolved.

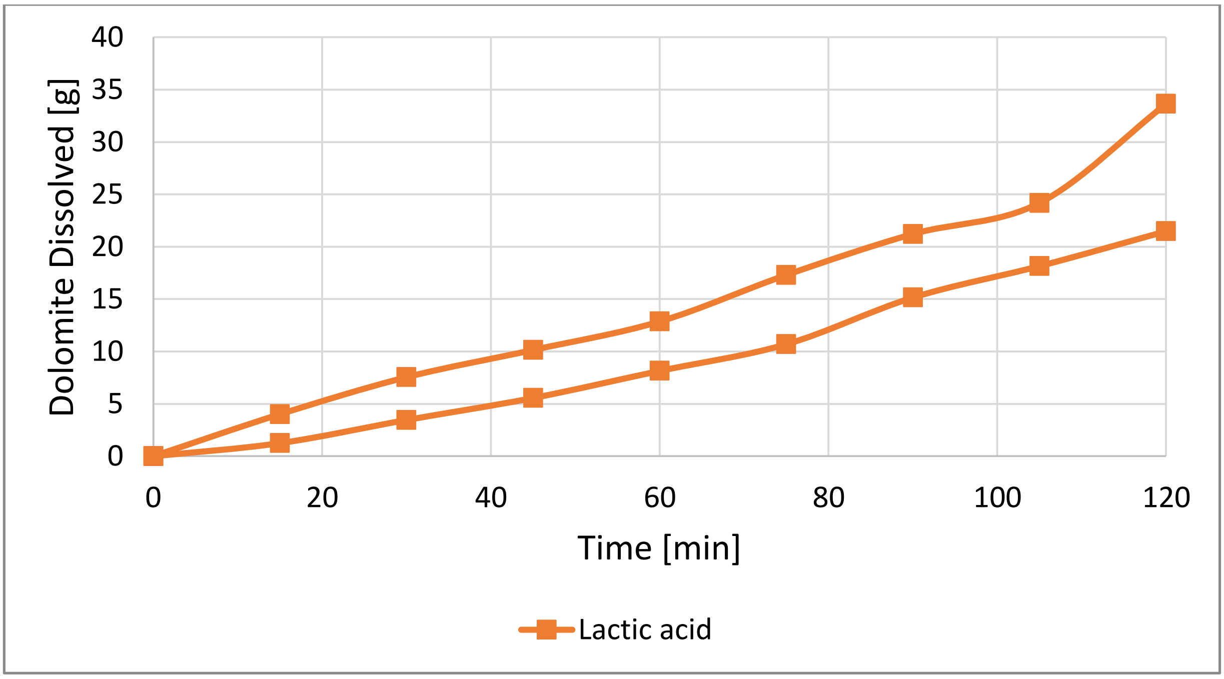


Figure 43: Amount of dolomite dissolved by lactic acid

6.2.5 Treatment using Methanesulfonic Acid

Figure 44 illustrates the dolomite dissolving study when MSA is used. It shows that the reaction has reached equilibrium after 90 minutes.

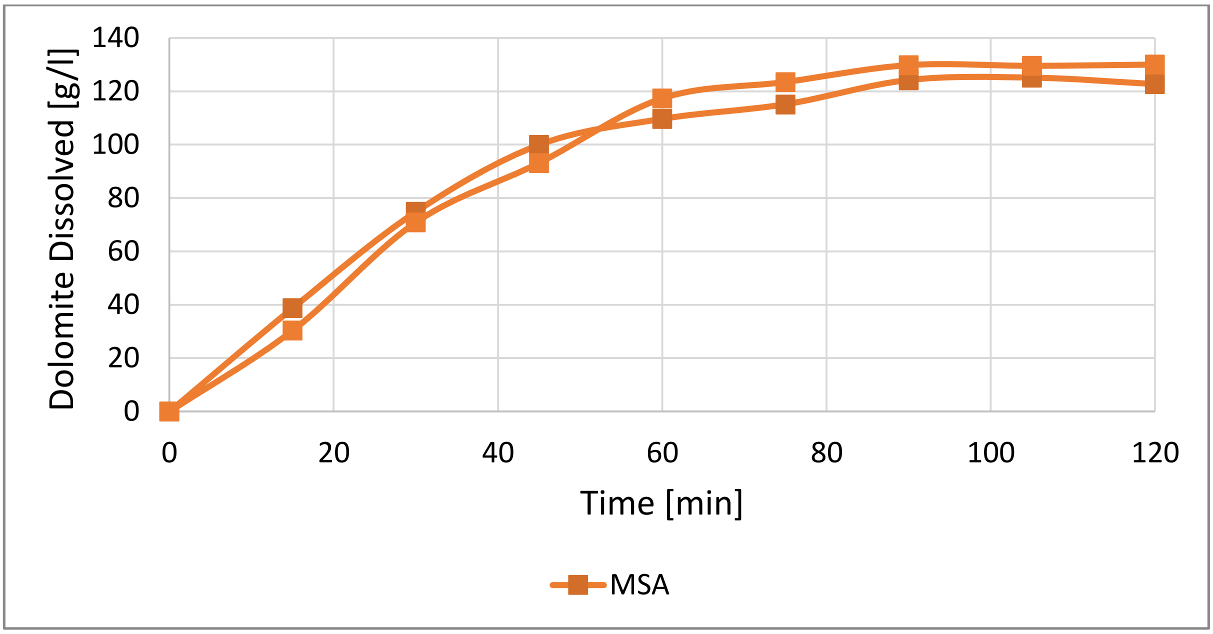


Figure 44: Amount of dolomite dissolved by MSA

6.2.6 Treatment using Sulfamic Acid

Figure 45 shows the sulfamic reaction behavior when dissolving dolomite. It illustrates that although the reaction rate differs between the two experiments the acid was spent after 90 minutes and that the same equilibrium concentration was established.

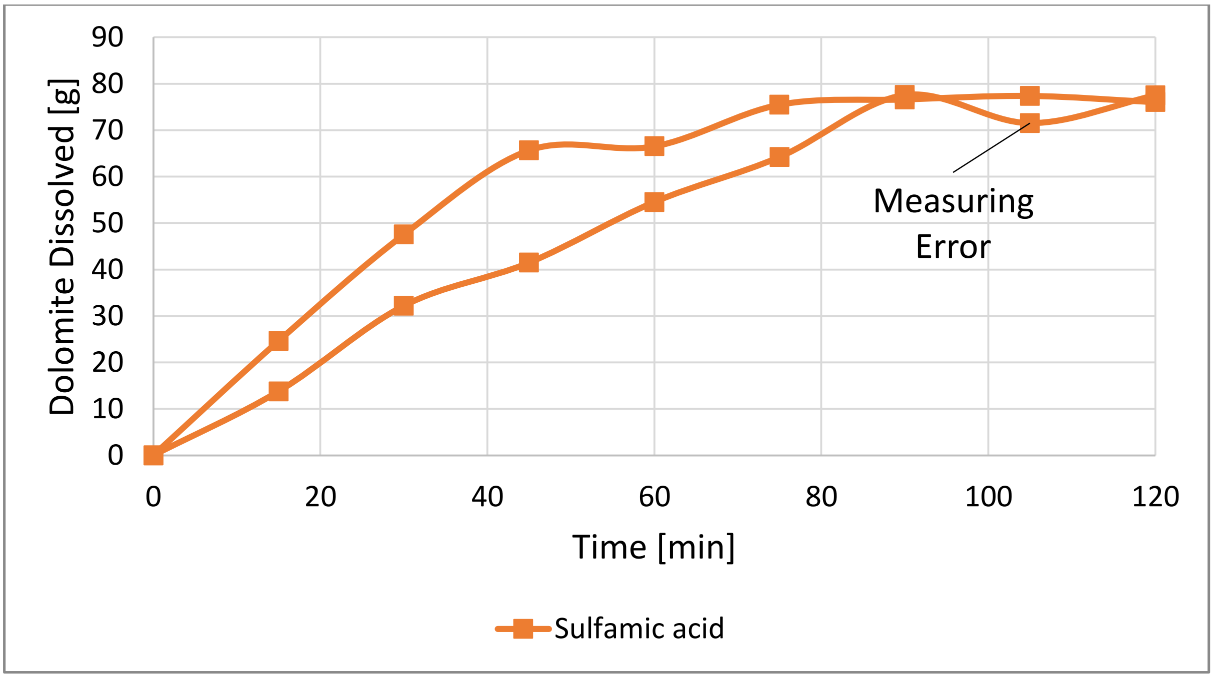


Figure 45: Amount of dolomite dissolved by sulfamic acid

6.2.7 Treatment using EDTA

The reaction behavior study performed with dolomite and EDTA is shown in Figure 46. It illustrates that EDTA is a very low acting chelating agent. After the study duration of 2 hours only around 0.3 gram of dolomite were dissolved.

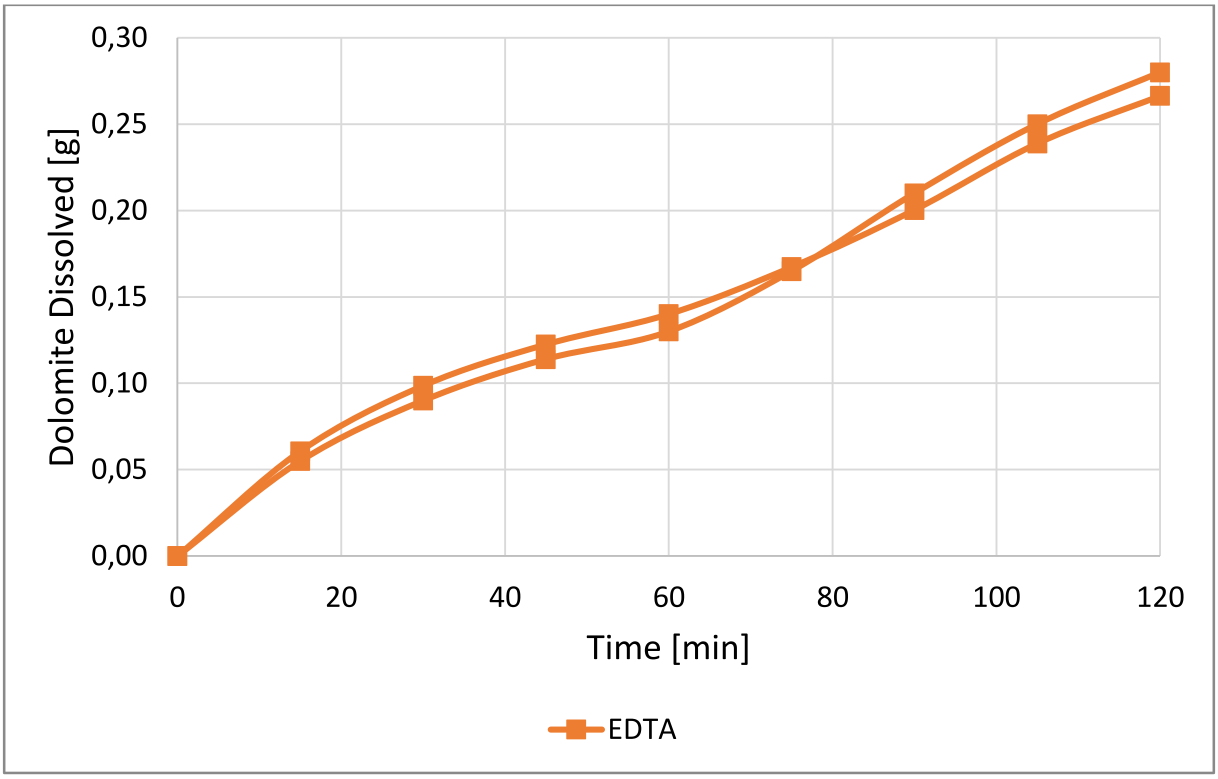


Figure 46: Amount of dolomite dissolved by EDTA

6.3 Fluid Compatibility Study

A small fraction of the sulfamic acid briquettes could not be fully dissolved and thus 32.5 gram of water was added to the treatment fluid to allow acid dissolution.

The life acid study showed that all mixtures achieved a 100% separation having a clean break within ten minutes. At 50°C the separation process was increased. The spent acids study showed that complete separation was achieved within ten minutes and that at 50°C the separation duration was reduced. The only difference between the spent and the life acid study was that the acids had different colors ranging from bright brown to darker brown, because limestone was dissolved in the solution. No formation of sediments or other precipitation was observed for both studies. Figure 47 and Figure 48 are examples of the spent acid study and shows a clean break and a different colored treatment fluid.

Figure 47: Emulsion breaker test using HCl in a 2:1 ratio

Figure 48: Emulsion breaker test using sulfamic acid in a 1:1 ratio

6.4 Corrosion Study

The corrosion experiment shows that all acids corrode the low carbon steel coupons at 50°C and that the differences in the mass change in both experiments are minor. EDTA was not investigated due to its very poor performance in the rock dissolving studies at 50°C. Figure 49 shows the corrosion reaction profile. It shows that MSA is the most corrosive acid after 24 hours and dissolves around 10 grams of the low carbon steel coupon, whereas sulfamic acid dissolves around 5.7 grams and HCl dissolves around 5.3 grams of the steel coupon. Lactic acid dissolves around 1.2 grams, maleic acid around 0.9 grams and acetic acid dissolved only around 0.4 grams of the corrosion coupon.

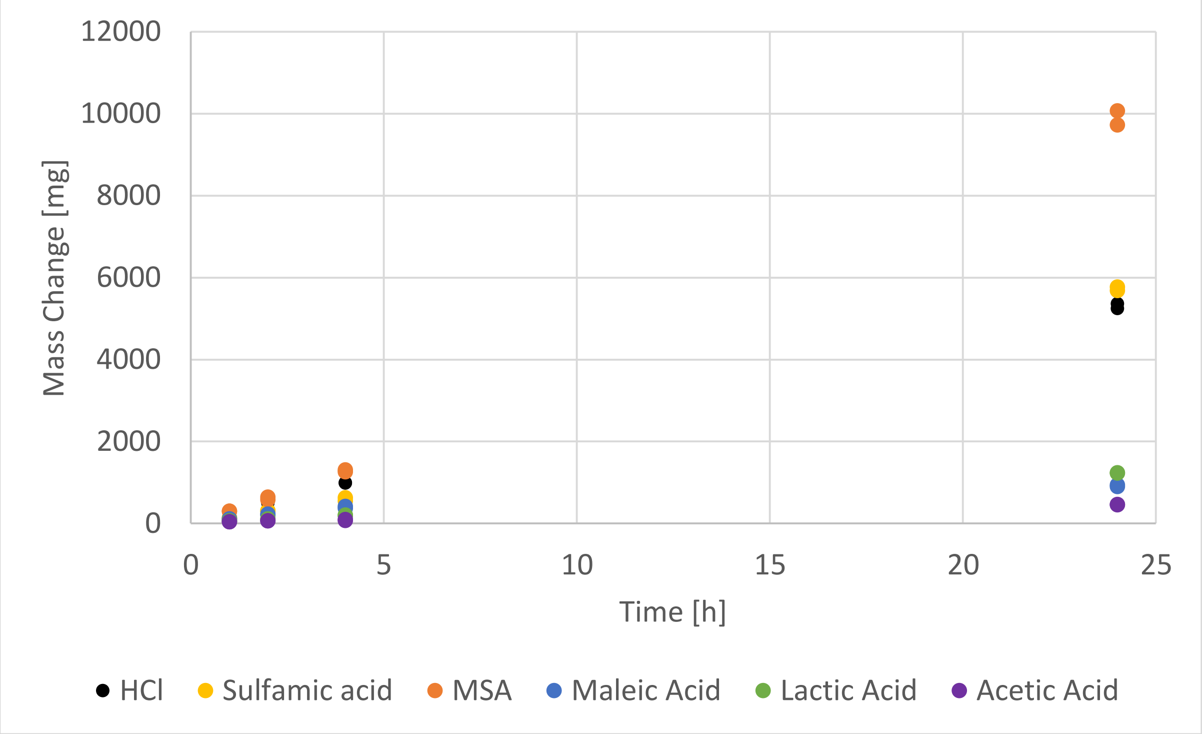


Figure 49: Amount of iron corroded by different acids

7 Discussion

This chapter summarizes the obtained results and illustrates parameters that influence the results. Furthermore, the results are compared to each other and qualitative evidence are formulated.

The acids that showed precipitation are not included in the concentration comparison, because the dissolving reaction cannot establish equilibrium concentration. However, the precipitation formed during the dissolving reaction was water soluble.

7.1 Comparison of Acidizing Limestones

In general, the limestone dissolution study using the samples from the “Untersberg Formation” showed a uniform mass reduction. An example of this uniformly dissolving is illustrated in Figure 50.

Figure 50: Untersberg formation tested with HCl @ 50°C

The minor differences in the dissolved amount of limestone underlies the homogeneity of this rock samples and thus it was used to compare the acids. The amount of mass dissolved by the acids is shown in Figure 51. It shows that the stronger acids (HCl, sulfamic acid and MSA) dissolved the same amounts of calcite regardless of the temperature and that they could dissolve the theoretical yield indicated as black line. The calcite mass reduction at room temperature using EDTA was again within the measuring tolerance and thus no mass reduction was assumed. At higher temperatures the mass dissolved by EDTA was around 1 gram of limestone.

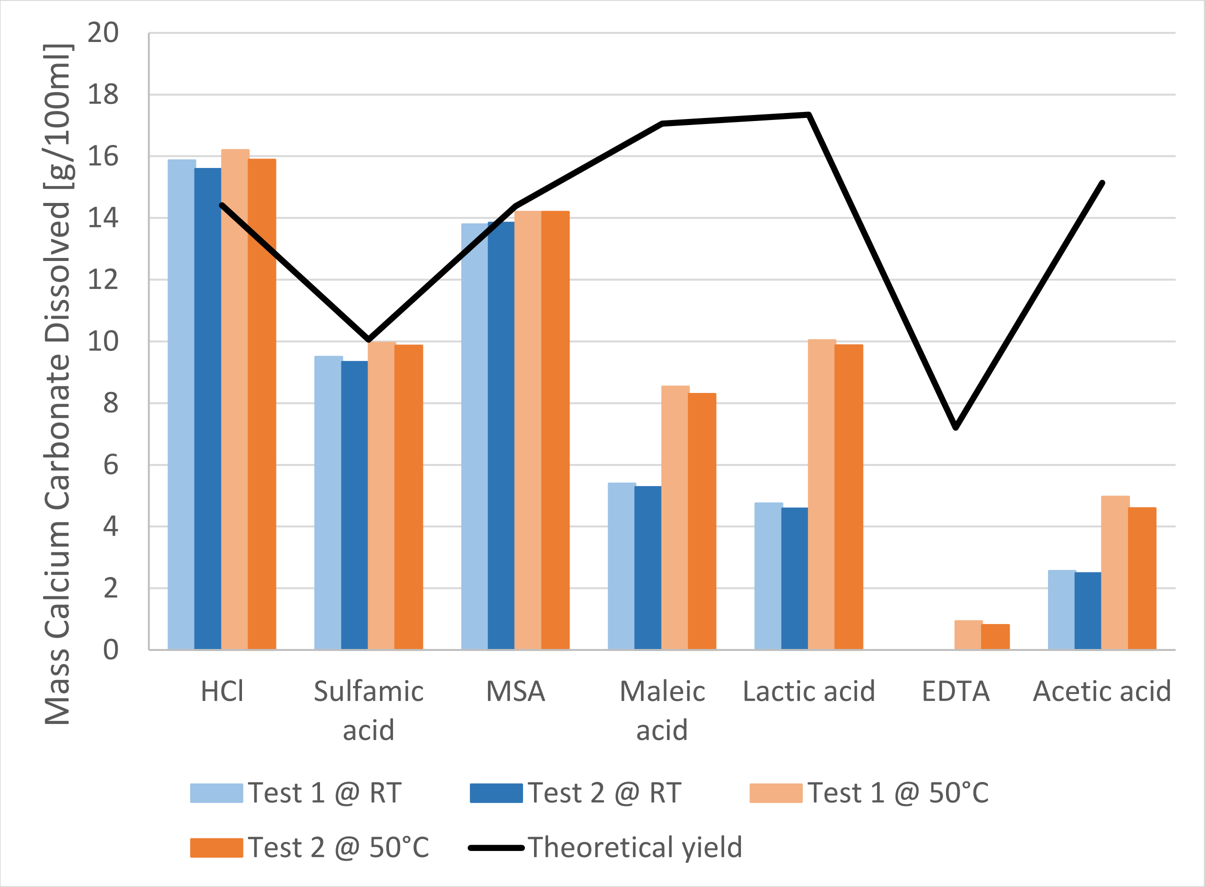


Figure 51: Acid dissolving capacity for limestone samples

The acid spending behavior can be seen in Figure 52 and illustrates the proton consumption. The lower value indicates the proton concentration at the beginning of the experiment, whereas the higher *pH* value at the end of the study indicates that protons were consumed. The higher the *pH* at the end of the experiment, the smaller the proton concentration and the more protons were consumed during the reaction. The *pH* at the beginning is similar to the calculated values in Figure 22 which is a first validation of the acid concentration.

The *pH* measured at the end of the experiment differs slightly which means the acids were not exact equally spent. However, differences in a high *pH* solutions result in a negligible small difference of the proton concentration and negligible mass difference. [9]

Since EDTA has a different reaction behavior, a *pH* change does not give any information on the acid spending and its behavior is not included in this figure.

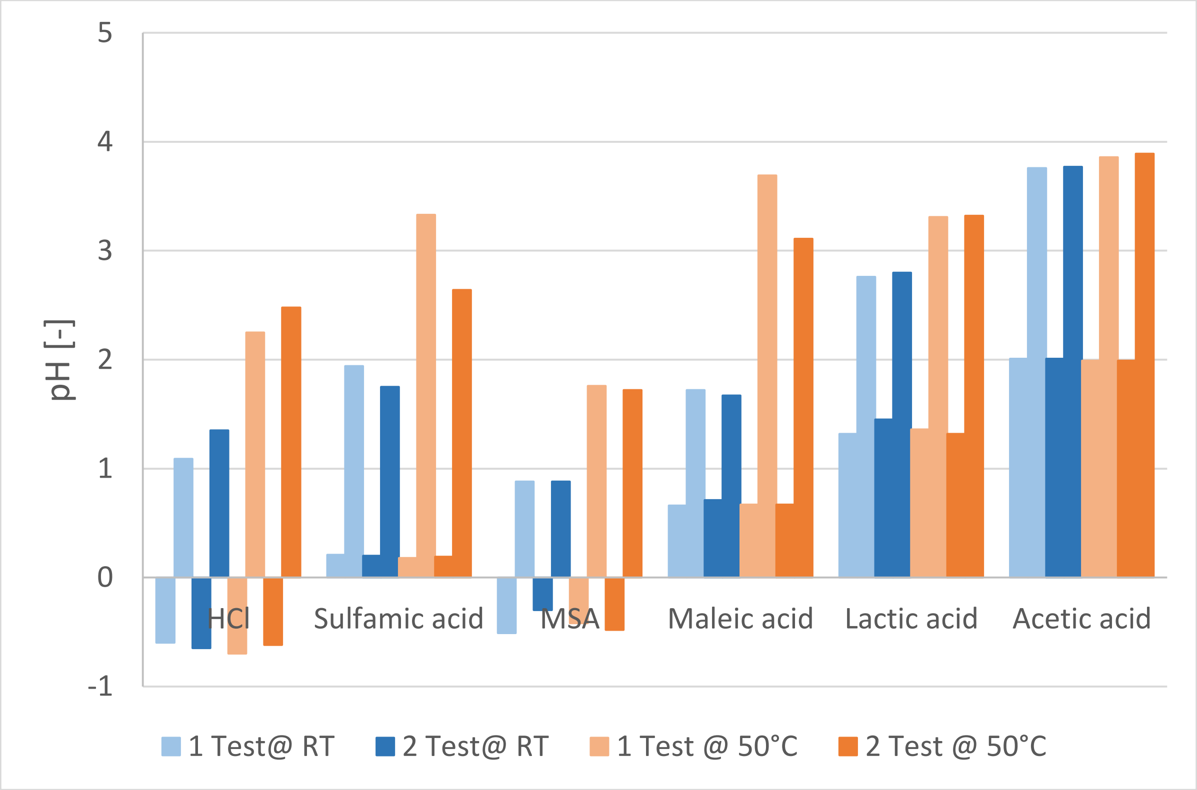


Figure 52: Acid spending behavior for limestone samples

The acid comparison between the selected acids at room temperature is shown in Figure 53, where the individual graphs were averaged. Many acid samples required a dilution of 1:1000 to stay within in the conductivity range of the ion chromatograph, thus the error in the graphs can be in the order of around 5%.

The final comparison shows that MSA has the highest potential to replace HCl as main treatment fluid. It has a marginally lower dissolving capacity but compared to the others has the highest efficiency. Sulfamic acid dissolved around the half that HCl has dissolved. Comparing the reactivity at room temperature, HCl and MSA show similar acid spending, whereas sulfamic acid shows a longer reactivity. The weak acetic acid shows that it can dissolve only a small fraction of what HCl dissolves, but it is still reactive after 2 hours.

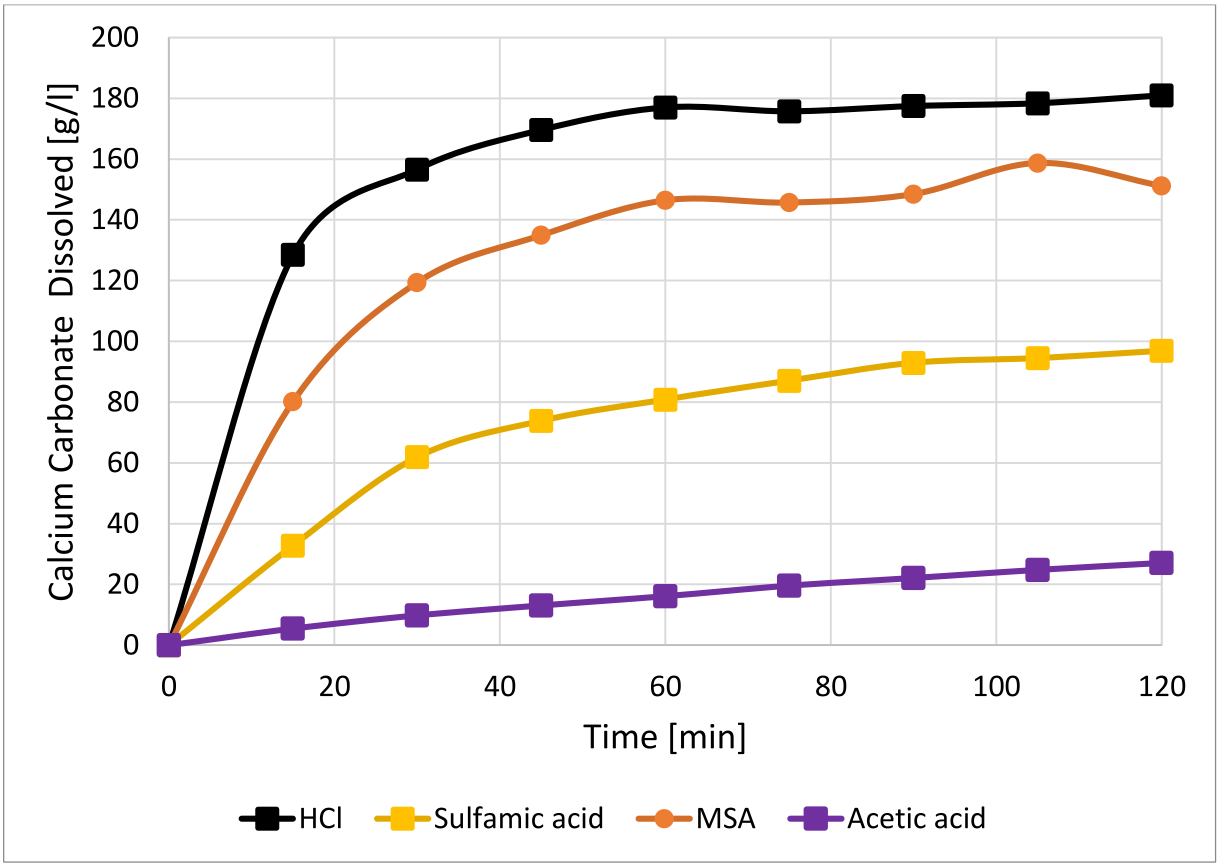


Figure 53: Limestone dissolving comparison investigated at room temperature

The acid reactivity behavior at 50°C is shown in Figure 54. When comparing the acids, MSA has the highest efficiency and to keep up with HCl (180 g/l) dissolving around 160 g/l. Sulfamic acids shows because of its acid solubility limitation that it can dissolve around 108 g/l and has exhibits longer reactivity compared to HCl and MSA. Acetic acid shows the longest reactivity, but its dissolving capacity is only a third after two hours (60 g/l), but increases to 70 g/l after reacting four hours with limestone. EDTA shows a very low dissolving capacity of around 8 g/l after the studied two hours.

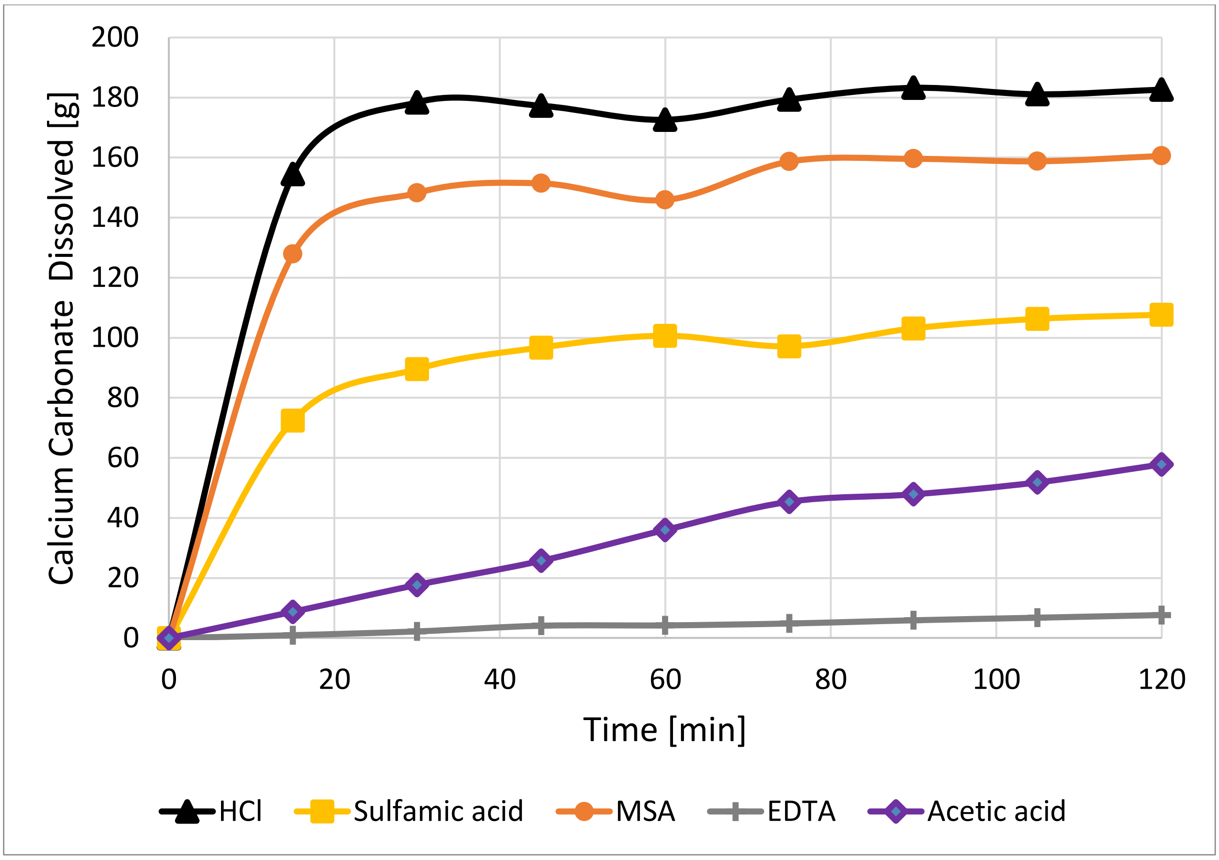


Figure 54: Limestone dissolving comparison investigated at 50°C

7.2 Comparison of Acidizing Dolomites

The heterogeneity of the dolomite samples can be seen in the variation of the mass dissolved shown in Figure 58. The different amounts of mass of dolomite dissolved is because the rock samples have varying amount of calcite within in the rock. Since calcite is preferably attacked, the mass reduction is influenced by the amount of calcite present in the sample.

Figure 55 and Figure 56 are samples of the dissolution reaction of the strong hydrochloric acid and the weak lactic acid. It shows that the strong acid has already dissolved most of the calcite and simultaneously dissolved the dolomite minerals, whereas the weak acid has only attacked and dissolved the calcite veins and minor parts of the dolomite.

Figure 55: Hauptdolomit tested with HCl @ 50°C

Figure 56: Hauptdolomit tested with lactic acid @ 50°C

The amount of dolomite mass dissolved by the acids is shown in Figure 58 and shows that the acids tested at a higher temperature dissolve higher amounts of dolomite. HCl is the strongest acid and only acid that was totally spent at room temperature and at 50°C. It dissolved similar amount of dolomite. The figure also shows that the strong acids (HCl, sulfamic acid, MSA) could dissolve the theoretical yield at 50°C temperature, whereas the weaker acids such as maleic acid, lactic acid and acetic acid did not react to completion. EDTA showed for the experiments at room temperature that the mass reduction was within the measuring tolerance and thus no mass reduction was assumed. At higher temperatures EDTA could form complexes that lead to the mass reduction around 0.1 gram.

The mass comparison of the 2 hours' experiment and the 20-hour experiment at room temperature showed that all acids but HCl were still reactive after the 2 hours. It also showed that the reaction between glycolic acid and dolomite created a not soluble sludge on the dolomite sample as shown in Figure 57.

Figure 57: Polymerization of glycolic acid

Comparing the 20-hours room temperature study with the 50°C study, it can be seen that HCl, sulfamic acid, MSA, lactic acid and acetic acid could finally dissolve similar amounts of dolomite as was dissolved in the 50°C experiment. It also shows that maleic acid could not dissolve similar amounts.

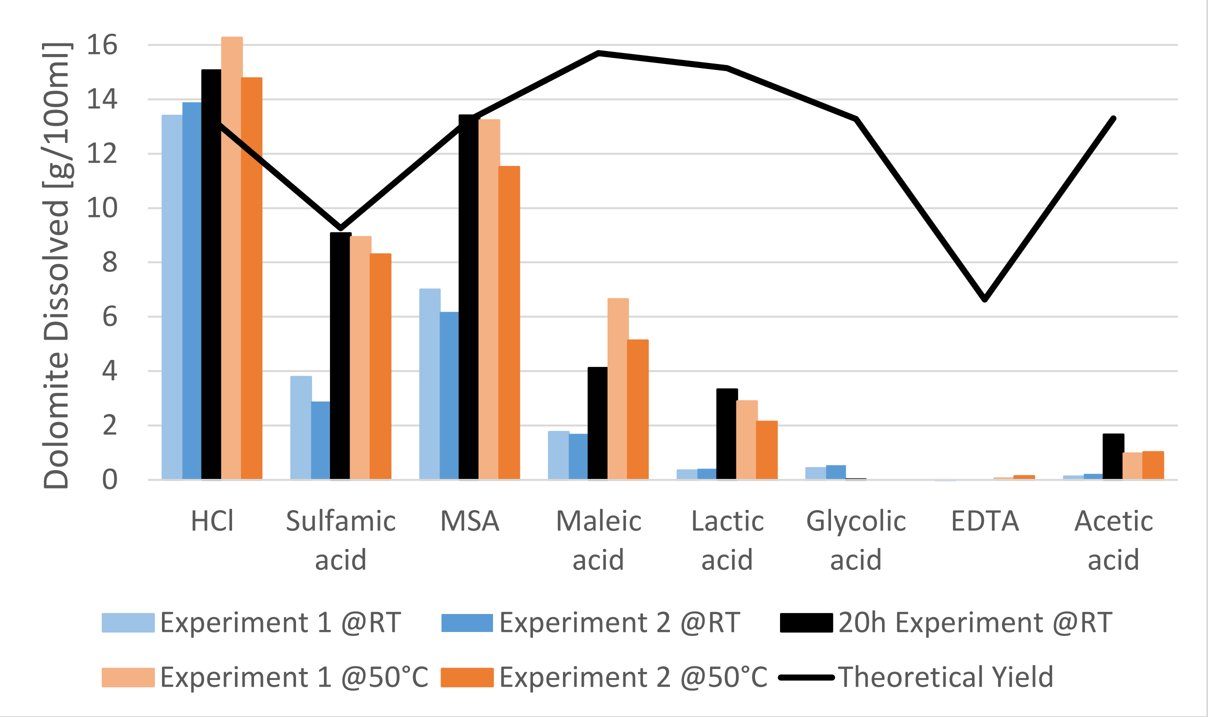


Figure 58: Acid dissolving capacity for dolomite samples

The acid spending behavior can be seen in Figure 59 and illustrates the proton consumption.

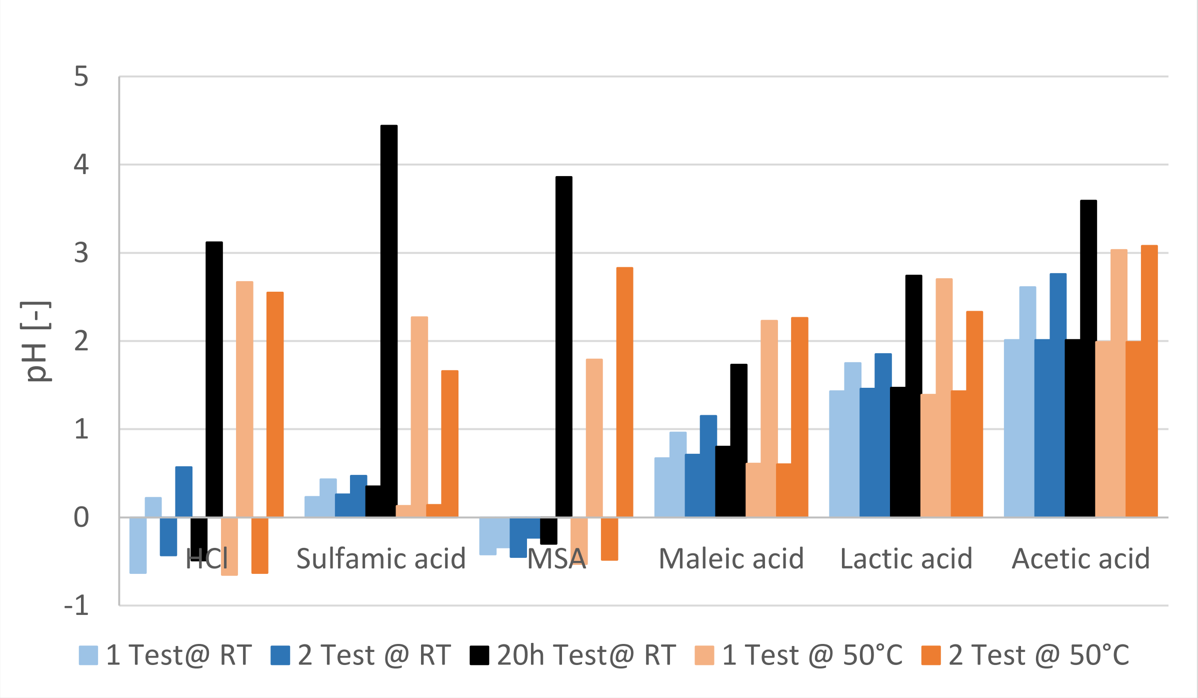


Figure 59: Acid spending behavior illustrated with dolomite samples

The acid dissolving behaviors are compared in Figure 60. It shows that HCl (160 g/l) has the highest dissolving capacity followed by MSA (130 g/l). Sulfamic acid dissolved around 80 g/l due to its acid solubility limitation. HCl has the highest reactivity and is spent after 60 minutes, whereas MSA and sulfamic acid are spent after 90 minutes. The weak lactic and acetic acid dissolved only 25 g/l and 6 g/l, respectively. However, both were not totally spent after two hours. EDTA is not plotted on the figure, because it shows a very low dissolving capacity of around 0.3 g/l.

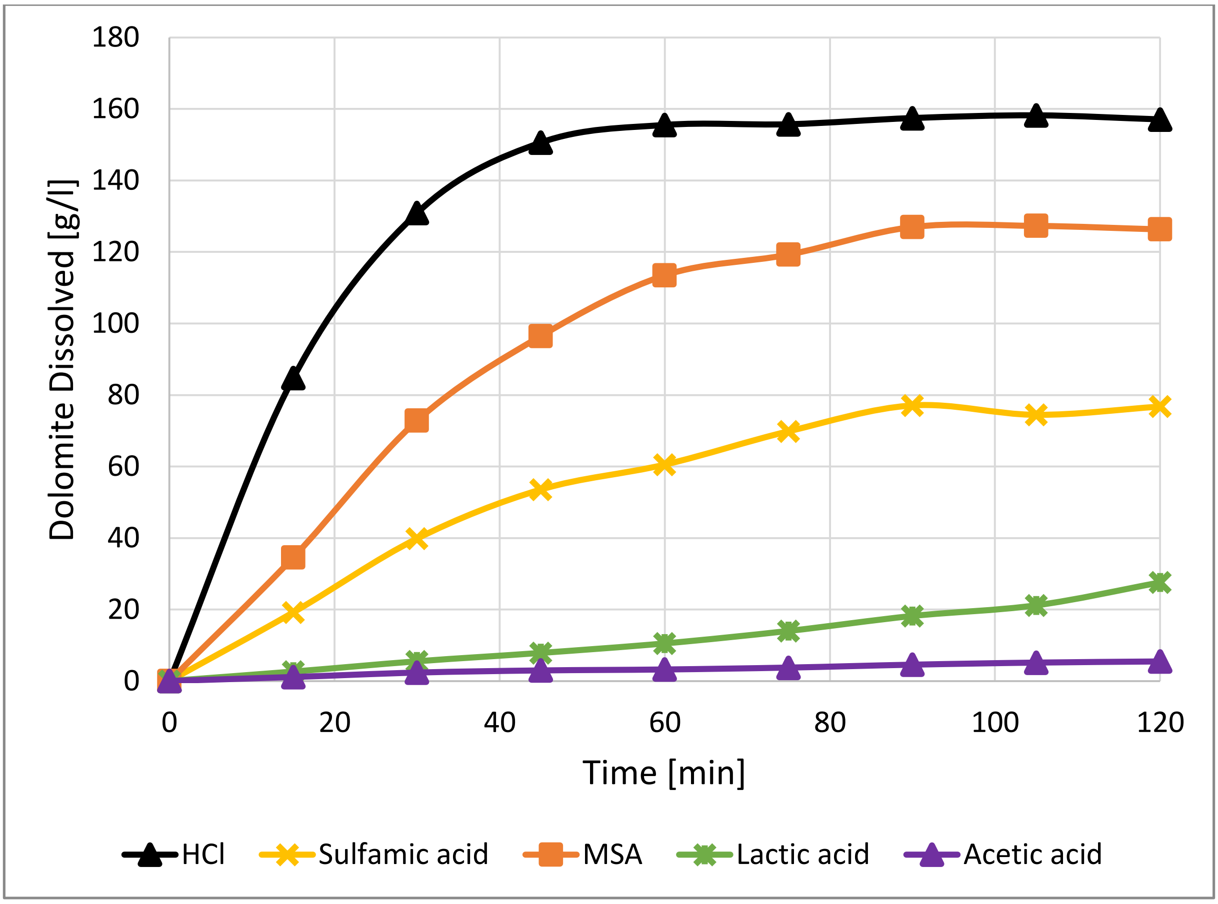


Figure 60: Dolomite dissolving comparison investigated at 50°C

7.3 Fluid Compatibility Study

The applicability of the acids as main treatment fluids was examined during this study. The solubility of the sulfamic acid had been exceeded and this verifies that it is restricted in the acid solubility.

This experiment shows that the acid mixture and the crude oil exhibited a clean break and a sharp interface. The study shows that at higher temperature the separation process was accelerated. Any kind of precipitation was not observed during the experiment and thus validates that all acids are compatible with the crude oil.

7.4 Corrosion Study

The rock mineral dissolving study showed that MSA and sulfamic acids are the most applicable acids to replace HCl. Since HCl is known to be very corrosive in high temperature applications, the corrosivity of the selected acid was studied. An example of a corroded coupon is shown in Figure 61.

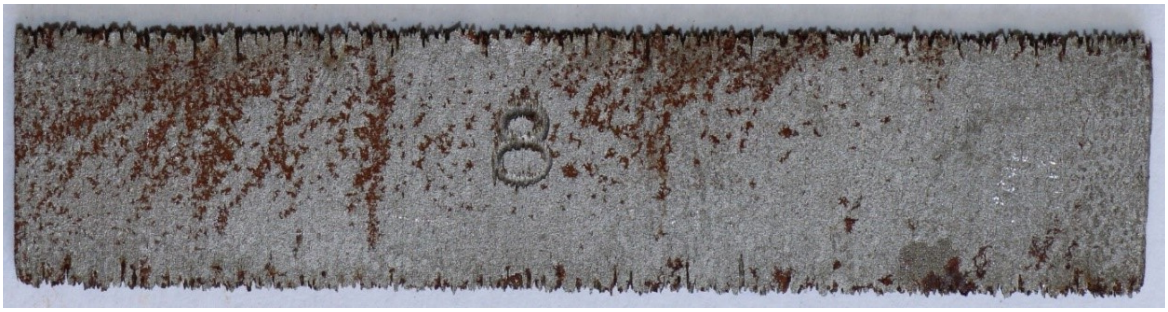


Figure 61: Visible alteration of the corrosion coupon tested with HCl after 24 hours

As studied during the limestone dissolving experiment, the stronger acids were able to dissolve the highest amount of rock. HCl and MSA were the most effective acids during the carbonate dissolving study and show that they are most effective acids to dissolve steel within the first four hours. In the first hours of the experiment, the corrosion of the sulfamic acids and the weaker acids has similar magnitude, but it starts to differ in the ongoing experiment.

The results were fitted into curves to illustrate the corrosion behavior over time as shown in Figure 62. MSA and sulfamic acids show a progressive corrosion rates, whereas HCl shows a linear corrosion behavior. The corrosion behavior of maleic acid shows a declining corrosion behavior as known from the corrosion behavior of stainless steels where the passivation of steel mitigates corrosion. Lactic and acetic acid show linearly corrosion relationship having a small slope. [36]

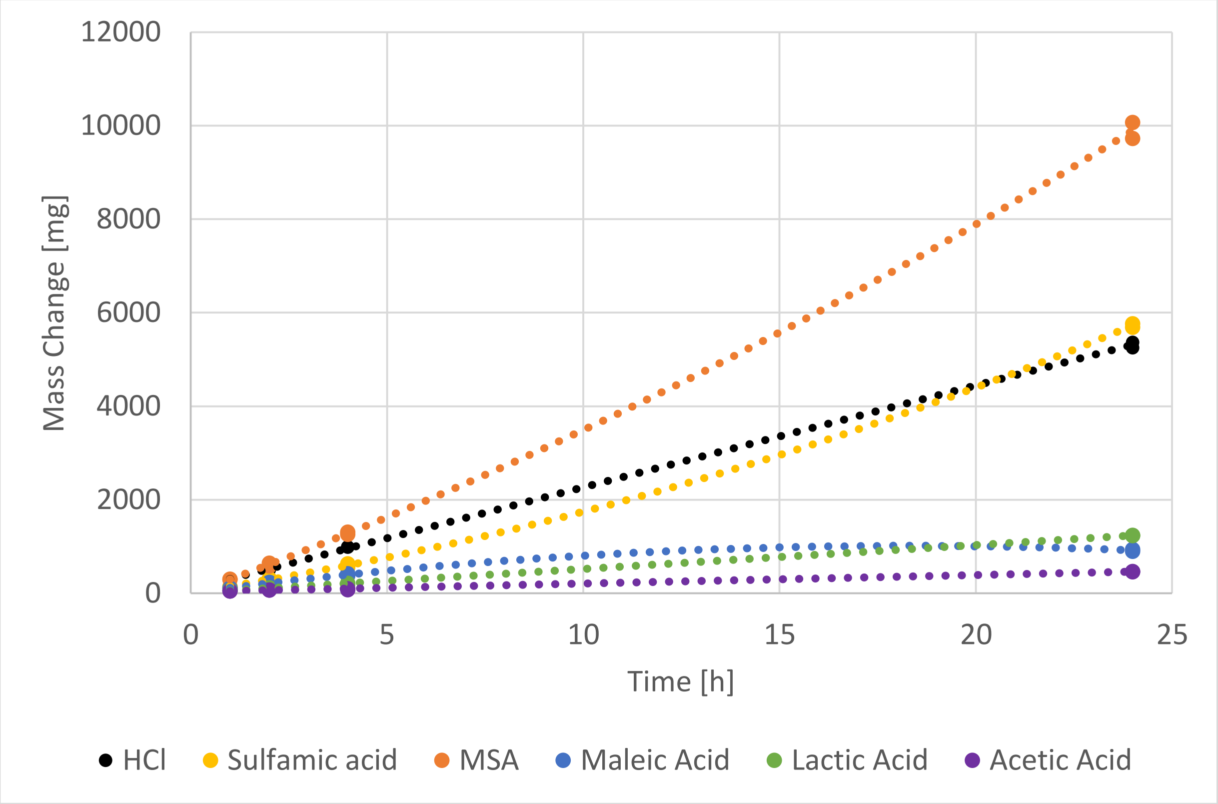


Figure 62: Corrosion behavior of the investigated acids

Typically, corrosion rates are expressed in g/m^{3}h and thus the results were normalized and this is shown in Figure 63. It reflects the previously described corrosion behavior. If the corrosion rate is not changing over time a linear corrosion is anticipated, whereas changing corrosion rates result either in an increasing or decreasing corrosion rate. HCl has corrosion rates ranging around 90 g/m^{3}h to 120 g/m^{3}h, whereas the highly corrosive acid MSA has ranges around 120 g/m^{3}h to 180 g/m^{3}h. Sulfamic acid shows corrosion rates ranging around 50 g/m^{3}h to 100 g/m^{3}h. The weaker acids such as maleic acid shows corrosion rates ranging around 20 g/m^{3}h to 45 g/m^{3}h. The corrosion rate of lactic acid ranges from 20 g/m^{3}h to 28 g/m^{3}h and the corrosion rate of acetic acid is low compared to the others and ranges from 8 g/m^{3}h to 20 g/m^{3}h.

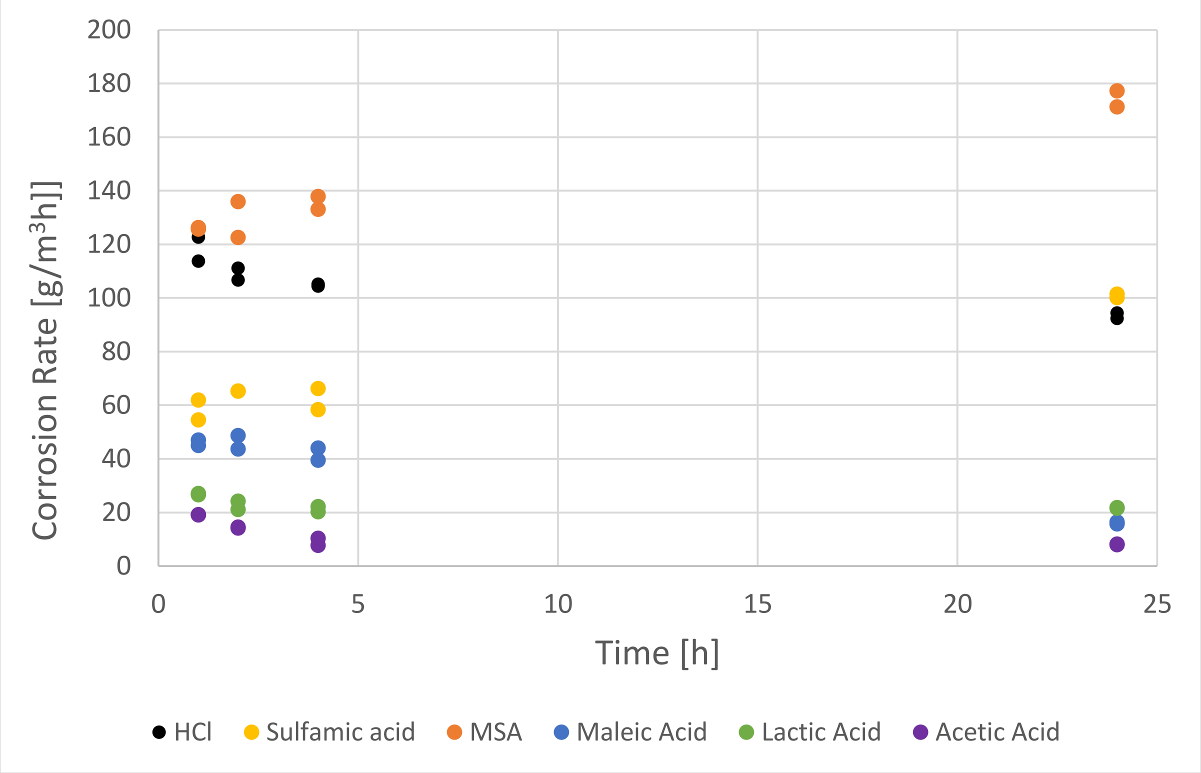


Figure 63: Normalized corrosion rates of the investigated acids

8 Conclusion

The major challenge in matrix stimulation is to design an economical fluid system that improves the oil recovery without forming any sludge or precipitation due to fluid incompatibilities. This study examined the applicability of currently uncommon or not economically utilized organic acids to stimulate carbonate reservoirs.

Based on the results from the dissolving study, methanesulfonic acid (MSA) and acetic acid can be used to prepare solutions that are equimolar to a 10% hydrochloric acid (HCl) solution. Sulfamic acid and EDTA can be used at reduced concentration due to their limitation of acid solubility. Maleic acid and lactic acid showed precipitation products from secondary reactions when prepared equimolar to a 10% HCl solution and thus may be a viable replacement at lower concentrations. The dissolving reaction using EDTA showed that at temperatures of 50°C the sequestering reaction is too low to consider it in any form as replacement.

Comparing the results from the room temperature dissolving study to the 50°C dissolving study it can be seen that the acid reactivity is decreased. The 50°C limestone study shows that MSA was the only acid that dissolved roughly as much as HCl. The dissolving capacity of sulfamic acid was limited by the solubility of the acid and it dissolved around the half of what HCl dissolved. The reaction spending of HCl and MSA is similar and both acids were completely spent during experiment. Sulfamic acid exhibits a longer reactivity compared to HCl and also completely spent during the experiment. Acetic acid could dissolve only a third of what HCl could dissolve in the same testing interval, but was still reactive at the end of the experiment.

The fluid compatibility study showed no incompatibilities between the treating fluid, its additives and the oil. It showed that at higher temperature the time needed to separate the fluids is reduced and that a clean break between the fluids was observed.

Based on the results of the corrosion study, MSA and sulfamic acids show a higher corrosivity compared to HCl after the examined 24 hours. The weaker organic acids such as maleic acid, lactic acid and acetic acid exhibit smaller corrosivity. MSA and sulfamic acid show a progressive corrosion rate, whereas HCl, lactic and acetic acid show a linear corrosion rate. Maleic acid shows a declining corrosion behavior.

Although MSA and sulfamic acid need corrosion inhibition, they are the best alternatives for the stimulation treatment. Additional experiments with MSA and sulfamic acid at different concentrations are suggested to validate their applicability. Eventually, core flood experiments are suggested to study the applicability on core samples and to study wormholing effects.

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Abbreviations

p	*Pressure [Pa]*
r	*Radius [m]*
k	*Permeability* [m^2]
v	*Velocity [m/s]*
μ	*Viscosity [Pa*s]*
g	*Gravitational acceleration* [m^2/s]
ρ	*Density* [kg/m^3]
ϕ	*Porosity [-]*
t	*Time [s]*
c	*Isothermal compressibility [1/Pa]*
IPR	*Inflow Performance Relationship*

A Appendices

A.1 Hauptdolomit Composition

The following table provides composition data for the Hauptdolomit formation from two wells drilled into the Upper Austrian Vienna Basin. It gives an overview that this formation mainly consists of dolomite having fractions higher than 90%.

Table 9: Chemical composition of the Hauptdolomit formation determined from cores

Well	**Depth [m]**	**Quartz [%]**	**Calcite [%]**	**Dolomite [%]**	**Clay$_{total}$ + Mica [%]**
ST 91	3011.4	0.4	0.3	98.3	1.0
Prottes S1	2802.3	0	3.0	93.0	4.0

A.2 Fluid Compatibility Study

The composition of the crude oil is shown in Figure 64 shows the composition of the crude oil that was used for the fluid compatibility study. The oil was retrieved from the sampling unit TL-AU.

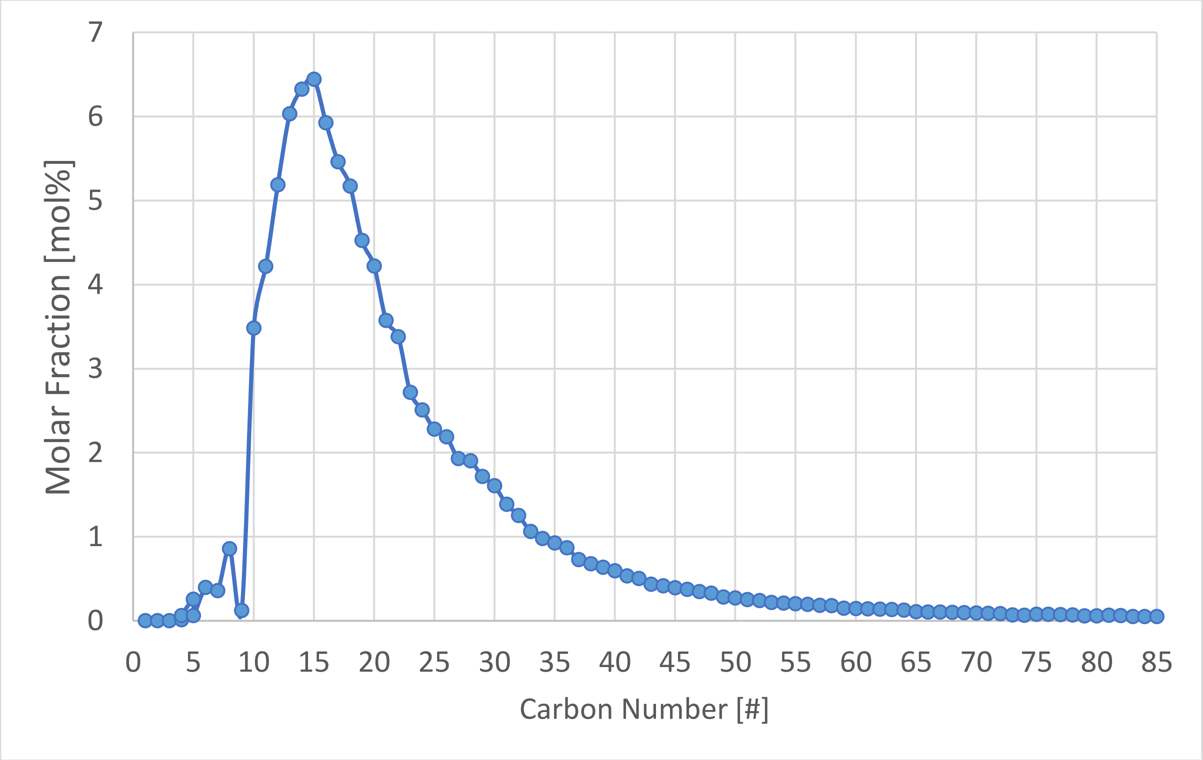

Figure 64: Composition of crude oil from Lower Austria