*The Case for Chelants Versus Acids**

HDC Mk II and Pyrosol ES
vs.
HCL and HF

Stated in the next few pages are definitions, basic descriptions, and information from sources found in the web. There are many excerpts from technical papers listing the advantages and disadvantages of chelants and acids for stimulation and descaling.

The first acid job was performed in 1895. The improvements in the technology have been mainly with the corrosion inhibitors allowing a higher concentration of acid. Other attempts to improve the performance has been to mix it in different states, emulsified acid, delayed acid, inhibited acid, varying combinations of acids, and even using chelating agents.

Historically they have shown a documented 32% failure rate.

Corrosion inhibitors, clay inhibitors, de-emulsifiers, $CaSO_4$ scale inhibitors, iron control agents. All of these chemicals are added in a typical acid job to counteract the damage acid does to the well. **None are included to HELP your well.**

With Feldspars, Carbonates, and clays, the concern is **Fluorosilicate precipitates**.

HCL causes carbonate liquefaction (softening)

HCL causes rapid corrosion of tubulars and requires corrosion inhibitors and buffers

HCL can cause CO_2 and H_2S release

HCL requires poses a significant HSE hazard and specialist equipment and personnel it

HCL changes wettability thus causing emulsion blockage.

HCL can cause clay hydration and particle migration

*When referring to acids in this context we mean inorganic acids such as HCL and HF. There are organic acids that are capable of chelating metal ions, but not with the capacity or variety of metal ions as many Chelants used in oilfield applications. The organic acids are typically weak acids and do not completely disassociate in water. The chemistry of HCL and HF is completely different. When dissolved in water produce hydrogen ions (H^+) which makes them corrosive. They also produce precipitates and gaseous by-products. Thus, even though Pyrosol, a chelant mentioned in this document, is technically an acid at a pH of 5.5, it is a chelant with chelation chemistry. To further complicate the discussion, sometimes such Chelants are described as acids. Many chelants are acidic. To maintain the distinction, we only refer to the inorganic acids, HCL, and HF in this document as acids. In general, the technical literature does the same with some exceptions.

Chelating agents cause NONE of the above problems

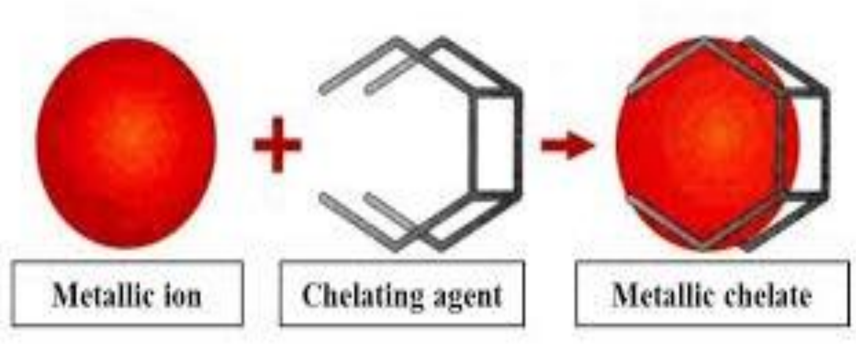
No precipitates or gaseous byproducts

Simply put, acids are old, outdated, and flawed technology.

Chelating agents are organic compounds capable of linking together metal ions to form complex ring-like structures called **chelates**.

Chelation is the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. Usually, these ligands are organic compounds and are called chelants, chelators, chelating agents, or sequestering agents; the resulting complexes are called chelate compounds.

A chelating compound is formed when a metal cation combines with an anionic chelating agent. The chelating agent surrounds the metal with a ring-type structure which resembles a claw. Once chelated, the metal is bound to the chelating agent and will resist reactions with other compounds. Chelating agents will react with most metal cations. Unlike acids, no gaseous or precipitate by-products are produced.

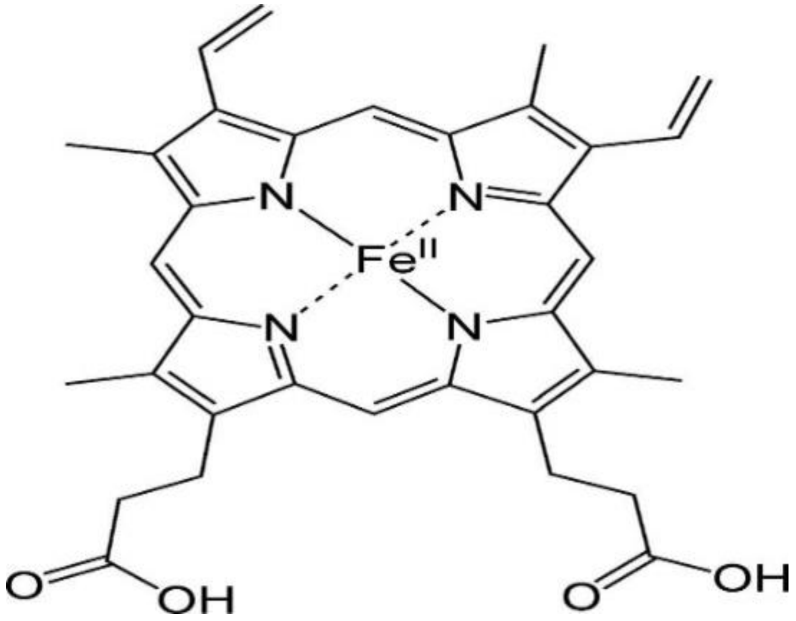


This picture shows the ring structure and the double bonded “claw-like” structure.

This excerpt is from Schlumberger's online Oilfield Glossary. Interesting comments on acid given it is a core product line.

A chemical used to bind metal ions to form a ring structure. Chelating agents stabilize or prevent the precipitation of damaging compounds. In the oil field, chelating agents are used in stimulation treatments and for cleaning surface facilities. They are also used to treat or remove scale or weighting agents in reservoir drilling fluids. During acid or scale-removal treatments, various compounds may be dissolved in the treatment fluid. As the acid reacts and the pH increases, reaction products may precipitate as a gelatinous, insoluble mass. Should this occur within the formation matrix, it is almost impossible to remove and permanent permeability damage may occur. Chelating agents prevent precipitation by keeping ions in a soluble form until the treatment fluid can be flowed back from the formation during cleanup.

Chelating agents are used in many industries. In the medical industry to take out heavy metals in the blood such as mercury, lead, copper, calcium, and more. In the food industry to prevent food spoilage. In water treatment to take out heavy metals and in consumer products for the same reason. Very versatile and obviously benign.

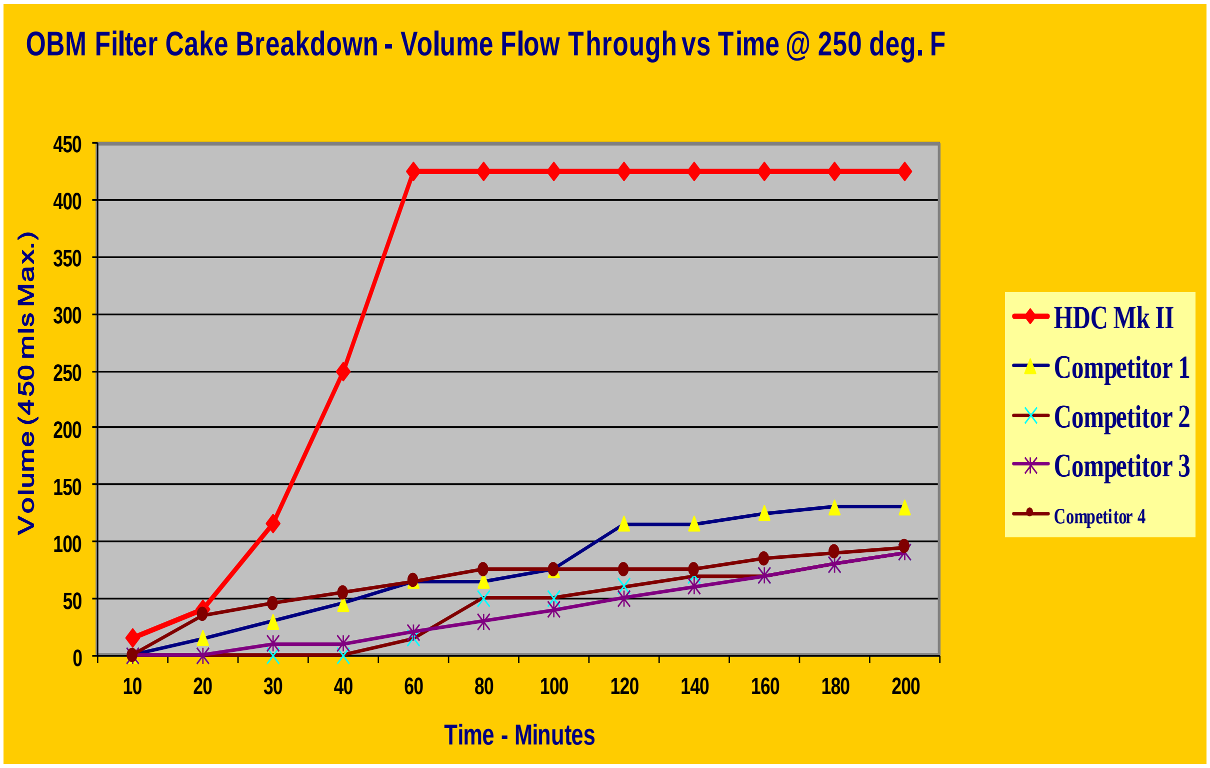


Not All Chelating Agents Are Created Equal

There are many hundreds of chelating agents and even products called multichelates. Used in the O&G industry are malic acid, tartaric acid, citric acid, NTA, HEIDA, HEDTA, EDTA, CyDTA, GLDA, and DTPA amongst others. New ones are being evaluated for oilfield usage regularly.

Typically, these compounds exhibit a low capacity and dissolution rates too slow for the industry, but nevertheless are marketed for use. HDC Mk II is the result of a 10 year development project with the sponsorship of Amerada Hess and BP. Note the performance below. The other compounds would be the off-the-shelf chelating agents available in the market. They are not the same as HDC Mk II which is a complex blend of chelating agents and catalyst to both speed up the reaction time and increase the dissolve capacity.

BP Sunbury Results



Well Engineering & Technology (WellTech) market two chelating agents, or mixtures of chelating agents and catalysts. ***HDC Mk II***$^{\text{TM}}$ *is used in stimulation, de-scaling, and to free differentially stuck pipe.* ***Pyrosol ES*** *is primarily an iron compound dissolver, i.e., iron sulphide, iron sulfate, iron carbonate, and other iron based compounds.*

HDC Mk II™

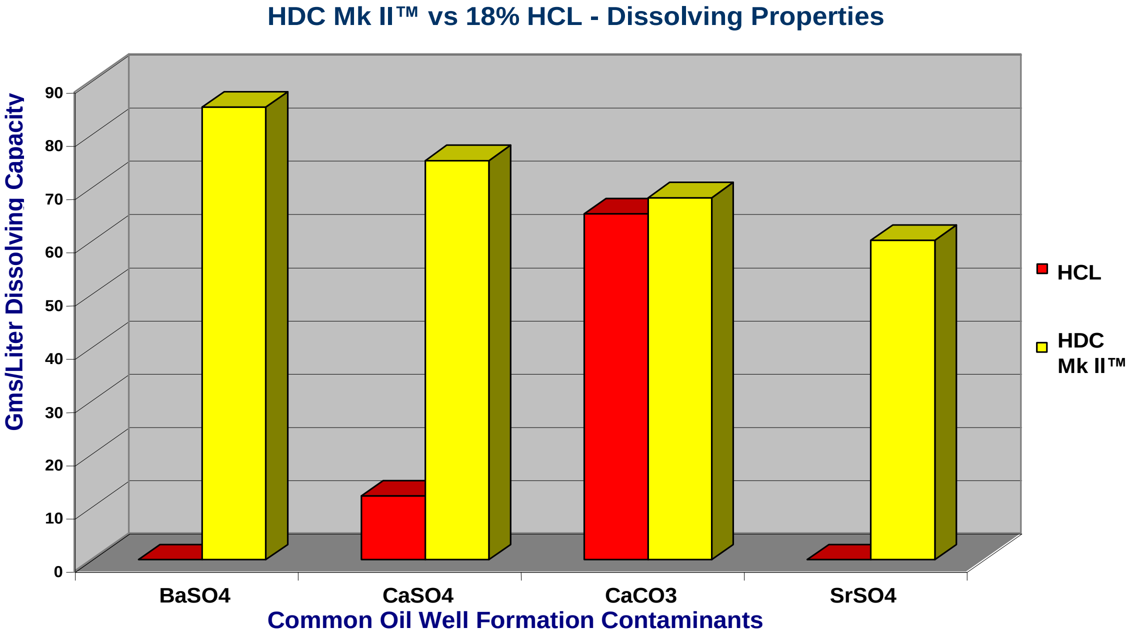
HDC Mk II™ is a non-damaging stimulation fluid (as opposed to acid which can be damaging). **HDC Mk II™** is a chelating compound that is the result of a 10 years development project by OCA in the UK and funded and technically supported by Amerada Hess and BP. It is used for stimulation (the anti-acid), descaling, and as a pipe release agent for differentially stuck pipe. It dissolves barite, $CaCO_3$, $CaSO_4$, some drilling fluid additives, and other sulfate scales. **HDC Mk II™** will also dissolve up to 50% of cellulosic LCM material over a 24 hr period.

HDC Mk II™ is a single phase, alkaline (pH +/-12) chemical that is non-corrosive, environmentally benign, and produces no precipitate or gas by-products. **HDC Mk II™** is inhibitive to clays. Also it is inorganic, so has no known temperature limits. **HDC Mk II™** is also unique in that it works significantly faster at a higher capacity than any competitive products. Due to all these attributes **HDC Mk II™** is effective, safe, and easy to use with significant advantages over acid.

HDC Mk II™ is Gold Banded in the OCNS CEFAS system in the UK, the best environmental rating possible.

HDC Mk II

- *Dissolves Barite, barium sulphate scale and other sulphate compounds*
- *Dissolves $CaCO_3$, other carbonate compounds, amorphous silica*
- *Inhibitive to clays and dissolves clays at 2-4%*
- *Tends to de-emulsify any emulsion blockages*
- *Inhibitive to clays and will shrink and dehydrate clays*
- *Non-corrosive and environmentally friendly*
- *Temperature stable to over 300°C (570°F)*
- *No precipitate or gas by-products*
- *As a mixture, faster acting and higher capacity compared to other chelants*
- *Strong water wetting action*



After 6 hours soaking at 90°C, filtercake is 96% dissolved. Works equally well on WBM filtercakes

One of the properties of **HDC Mk II™** is that it has a high excess of potassium hydroxide in solution. KOH is one of the best alkalis for dissolving silica (it is used to etch glass.) However, the dissolved silicate can then reprecipitate by reaction with ions such as Ca, Fe, which happens with acids. That is where the chelating nature comes in, to prevent that reaction and reprecipitation so to continue to dissolve the silica. Depends on the exact nature of the silica deposits (crystallinity) just how much will be dissolved.

Pyrosol ES

Pyrosol ES is a formation scale and powerful tubing scale removal product. It dissolves iron sulphide, a common scale that is often difficult to remove. **Pyrosol ES** also dissolves CaCO3 and other sulfate scales with the exception of barium sulphate.

Pyrosol ES dissolves Calcium, Strontium, Magnesium, and Iron Sulphide scales an order of magnitude faster than commercial de-scalers with four to six times the dissolving capacity of the same products.

Pyrosol ES is **non-corrosive**, non-damaging to formations, and safe to handle. **Pyrosol ES** has a SG of 1.145 and a pH of 5.5. **Pyrosol ES** is Gold Banded in the OCNS CEFAS environmental rating system, which means it is environmentally benign and approved for unlimited discharge.

Pyrosol ES

- *Dissolves Iron Sulphide and other sulphate compounds*
- *Dissolves CaCO3, other carbonate compounds, amorphous silica*
- *Tends to de-emulsify any emulsion blockages*
- *Non-corrosive and environmentally friendly*
- *Temperature stable to over 300°C (570°F)*
- *No precipitate or gas by-products*
- *As a mixture, faster acting and higher capacity compared to other chelants*
- *Strong water wetting action*

HCL dissolves about 120 g/l of CaCO3. Pyrosol ES dissolves 60 g/l. Also 45 g/l of FeS or iron sulphide, a common scale. Temperature will not affect dissolving capacity but will speed up the rate. As Pyrosol ES is non-corrosive (single digit mpy), it can be left in the well as long as desired to continue dissolving further back in the well.

Removal of Pyrite and Different Types of Iron Sulfide Scales in Oil and Gas Wells without H2S Generation

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Abstract

Iron Sulfide scale is a significant problem in oil and gas industry where the iron sulfide depositions have adverse impact to the production operations. Typically, iron sulfide scale formed as result of the reaction between the hydrogen sulfide and iron. Iron sulfide scale has several forms; pyrrhotite (Fe_7S_8), troilite (FeS), pyrite (FeS_2), greigite (Fe_2S_4), and mackninawite (Fe_9S_8). Pyrite, which has good thermal stability, tends to deposit at shallower places downhole and is inert to acid. Other iron sulfides react with acids. Thermal stable species are much harder to be removed by acids. Thus the iron sulfide downhole are mainly pyrrhotite, pyrite, marcasite and mackinawite, in which pyrite cannot be removed by acid treatment. Both pyrite and marcasite have very low solubility in HCl, and the only available method of removal in the oil industry is to mill these types of scale. In this paper we introduced new formulations that can be effectively used to remove the pyrite and marcasite scales with removal efficiency reaches 85%. The new formulation will not release H_2S during the removal of pyrite scale or any other iron sulfide scale as HCl, therefore, no need for H_2S scavenger and also no HSE consideration are required during the removal because the new formulation can be considered as environmentally friendly. No need for additives such as corrosion inhibitors because these fluids pH is above 11 and they are not corrosive. The new formulation consists of high pH chelating agents such as DTPA (di ethylene tri amine penta acetic acid) at pH range from 11 to 14 and catalytic or converting agent such as potassium carbonate (K_2CO_3), (Cesium Carbonate) Cs_2CO_3, or (Cesium formate) CsCOOH. The optimum concentration of the chelating agents is 20 wt % DTPA and 7 wt% for the catalyst/converter. In the oilfield treatment water wetting surfactant or solvent should be injected first to remove the organic scale that covers the iron sulfide scale and then DTPA/Converting agents can be injected. No gases will be released during the scale removal process and this will not increase the pressure of the well during the treatment process. Currently the removal efficiency of the pyrite scale type is maximum 20 % by HCl. using the new formulations the solubility of actual field samples of pyrite reached 85%. The new formulation can be used effectively to remove all types of iron sulfide scales especially those cannot be removed by HCl. One more advantage of the new formulation is that the H_2S will not evolve during the treatment and that will cut the cost of safety considerations bedside the cost of H_2S scavengers.

Molecular Design of Novel Chemicals for Iron Sulfide Scale Removal

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Abstract

Scale deposition is a pertinent challenge in the oil and gas industry. Scales formed from iron sulfide are one of the troublous scales, particularly pyrite. Moreover, the use of biodegradable environmentally friendly chemicals reduces the cost compared to the conventional removal process. In this work, the chelating abilities of four novel chemicals, designed using the *in silico* technique of density functional theory (DFT), are studied as potential iron sulfide scale removers. Only one of the chemicals containing a hydroxamate functional group had a good chelating ability with Fe^{2+}. The chelating strength and ecotoxicological properties of this chemical were compared to diethylenetriaminepentaacetic acid (DTPA), an already established iron sulfide scale remover. The new promising chemical surpassed DTPA in being a safer chemical and having a greater binding affinity to Fe^{2+} upon optimization, hence, a better choice. The presence of oxime (-NHOH) and carbonyl (C=O) moieties in the new chemical showed that the bidentate form of chelation is favored. Moreover, the presence of an intramolecular hydrogen bond enhanced its chelating ability.

Introduction

Scale deposition is a cogent problem facing oil and gas production. Scales formed from iron sulfide are one of the troublous scales, particularly pyrite [1, 2]. Other types of scales include calcium carbonates and sulfates, barium sulfate, and strontium sulfate. The costs related to scale deposition were estimated to be about 800 million $US in the United Kingdom, 9 billion $US in the USA, and 3 billion $US in Japan while the global cost amounted to about 2.5 trillion $US [3, 4]. The reaction of iron and hydrogen sulfide forms the iron sulfide scale. The former occurs in the oil and gas production system including pipes, reservoirs, and wellbore tubular. Hydrogen sulfide, on the other hand, is found in sour gas wells as free gas and sometimes it evolves during the degradation of organic sulfur-containing chemicals due to the presence of sulfate-reducing bacteria [5, 6].

Conventional treatments used in iron sulfide scale removal include chemical and mechanical treatments [7]. Nevertheless, the former is preferred over the latter as mechanical treatment frequently exacerbates the situation by leading to more corrosion. On the other hand, chemical treatments involving the use of hydrochloric acid increase the corrosion rate and also produce toxic hydrogen sulfide as a by-product. Chelators have been suggested as a better chemical solution for scale removal [8–12]. Diethylenetriaminepentaacetic acid (DTPA) is one of the effective chelators used for iron sulfide scale removal [1, 2]. However, there is a need to develop novel biodegradable chelators. Hence, in this work, we design novel chemicals based on the hydroxamate functional group and also the carboxylic functional group present in DTPA.

ACIDS

> *"Carbonate acidizing is a more difficult process to predict than sandstone acidizing, Because despite the chemistry of the process being much simpler than that of sandstone acidizing, the physic is decidedly more complex."*
>
> *M. J Economides*

Herman Frasch, chemistry chief at Solar Refinery is credited with the first patent in acidizing in 1896, and the Frasch's patent "increasing the flow of oil well" is the baseline of modern matrix stimulation (Tambini 2003).

Recent years have seen a marked increase in well stimulation activity (acid and frac jobs) with the number of treatments performed more than doubling through the 1990s. In 1994, 79% of the jobs were acid jobs, but since they are lower cost than hydraulic fracturing treatments, they only consumed 20% of the money spent for well stimulation. **For acid jobs, the observed failure rate was 32%.** Failure rate for the less frequent but more expensive hydraulic fracturing treatments was much lower, only 5%. In analyzing the reasons for job failure, **one-third were due to incorrect field procedures, while two-thirds were attributed to incorrect design or improperly identifying well damage.** (by Sandrine Portier, Laurent André & François-D. Vuataz, 2007)

Hydrochloric acid was discovered around 800 AD by alchemist Jabir ibn Hayyan (Geber). Acidizing predates all other stimulation techniques according to an API briefing paper I read. **The first acidizing job was done in 1895**. A year later in 1896, Standard Oil got a patent for acidizing limestone with HCL. Acidizing was hard on wellbore tubulars, so it did not come into its own until the 1930's. In 1931 Dow Chemical discovered that arsenic inhibited the action of HCL on metal - corrosion inhibition was born. Thru much research by many great minds, the problems of emulsions were solved with surfactants and iron control was designed to prevent dissolved iron from being left in the formation. Acid Washing as it is called by some is what many refer to as "pickling" the wellbore tubulars, this removes rust and varnish. Matrix Acidizing is simply injecting acid under the fracture pressure of the formation. Fracture Acidizing is injecting acid at or above the formation frac pressure. Diversion has long been needed to create successful stimulation of the formation. Different diversion techniques have been invented like emulsified acid, chemically retarded acid, spacer between acid stages and foam acidizing.

Most of the advances in the application of acid have to do with the improvement of corrosion inhibitors allowing higher concentrations of acid.

Schlumberger’s Oilfield Glossary: The treatment of a reservoir formation with a stimulation fluid containing a reactive acid. In sandstone formations, the acid reacts with the soluble substances in the formation matrix to enlarge the pore spaces. In carbonate formations, the acid dissolves the entire formation matrix. In each case, the matrix acidizing treatment improves the formation permeability to enable enhanced production of reservoir fluids. Matrix acidizing operations are ideally performed at high rate, but at treatment pressures below the fracture pressure of the formation. This enables the acid to penetrate the formation and extend the depth of treatment while avoiding damage to the reservoir formation.

Back in 21 Apr 2003, SLB applied for a patent to use chelants with their acid jobs. It is a public document. In it, they state the following as quoted below.

SLB Patent Application US7,192,908 B2
Composition and Method for Treating a Subterranean Formation

- With HCL and HF…dissolution is so rapid…is spent in…a few inches.
- These reactions produce solids…which can damage the formation…
- Chelating…based on EDTA have been used to control iron precipitation and dissolve scale.
- In scale removal, high decline rates followed HCL treatments, but wells treated with EDTA maintained production.
- Sandstone matrix “stimulation” is often ineffective and…damaging.
- There is a need for fluids….that will not damage sandstone formations.
- A serious problem with mud acid is that when it contacts calcium ions, CaF_2 is precipitated.
- Re-precipitation…is responsible for much of the damage observed in sandstone matrix stimulation. Furthermore…will slow or stop the dissolution.

Hydrochloric acid is not a good solvent for $CaSO_4$. The maximum solubility of calcium sulfate in HCl is only 1.8 wt% at 25 °C and atmospheric pressure.

Scales are frequently coated with hydrocarbons, thus making it difficult for acid to contact and dissolve the scales.

More recently, some authors have called for the necessity of using **non** HF-based systems because of the nature of damaging potential inherent in the reactions between sandstone minerals and HF. They insist in the capability of these new systems to stimulate effectively, especially those formations with high content of HCl soluble minerals.

The main acid stage requires the greatest emphasis because of the damage mechanisms, directly associated to precipitation of products from the HF reactions. Secondary reactions may occur between fluorosilicic acid H2SiF6, a byproduct of primary reaction, and aluminum-silicates, clays and feldspars. These reactions are considered to have adverse effects since silicon can be precipitated as hydrated silica, which contributes to damage if mobile even though the presence of HCl to reduce the pH to prevent silica and flourosilicate precipitation.

Additionally, HF dissolves native clays and feldspars, and when reacting with quartz may also cause **formation deconsolidation** by weakening the matrix.

Precipitation will always take place, associated with HF concentration among other things; however, it tends to be more severe if HF acid treatments are not properly displaced. Acid stimulation techniques have to account for both chemistry and treatment execution to accurately predict the effectiveness since the effect of these precipitates could be minimized if they are deposited far from the wellbore. Careful selection of mixtures, additives, acids formulations, and treatment volumes must be accounted to minimize these secondary adverse effects. Reservoir geology and mineralogy are the relevant issues for successfully removing the acid-soluble particles present in reservoirs; removal mechanisms are strongly related to dissolution pattern of the matrix. Recent studies have shown that one of the most important factors that determines the etching pattern is the heterogeneity of the rock. In sandstones, the variations in permeability, porosity, and mineralogy may drive the acid to follow certain paths, the highly permeable channels called wormholes. There is experimental evidence that wormhole dissolution patterns can be achieved particularly using high HF concentrations and elevated temperatures; however, the risk of precipitation and rock deconsolidation might significantly be increased.

Sandstone matrix acidizing cannot be considered as an exact and predictable set of rules; thus, the appropriate design of treatments almost never has only one right answer. That is an inherent problem of the complex and heterogeneous nature of most sandstone matrices. The interactions between different minerals and the injected acid depend on the chemistry, as well as temperature, pressure, pore-size distribution, surface morphology, and pore- fluid composition. (Gomez)

Note in the additives below, none of them are to improve well production, but to keep the acid from damaging the well.

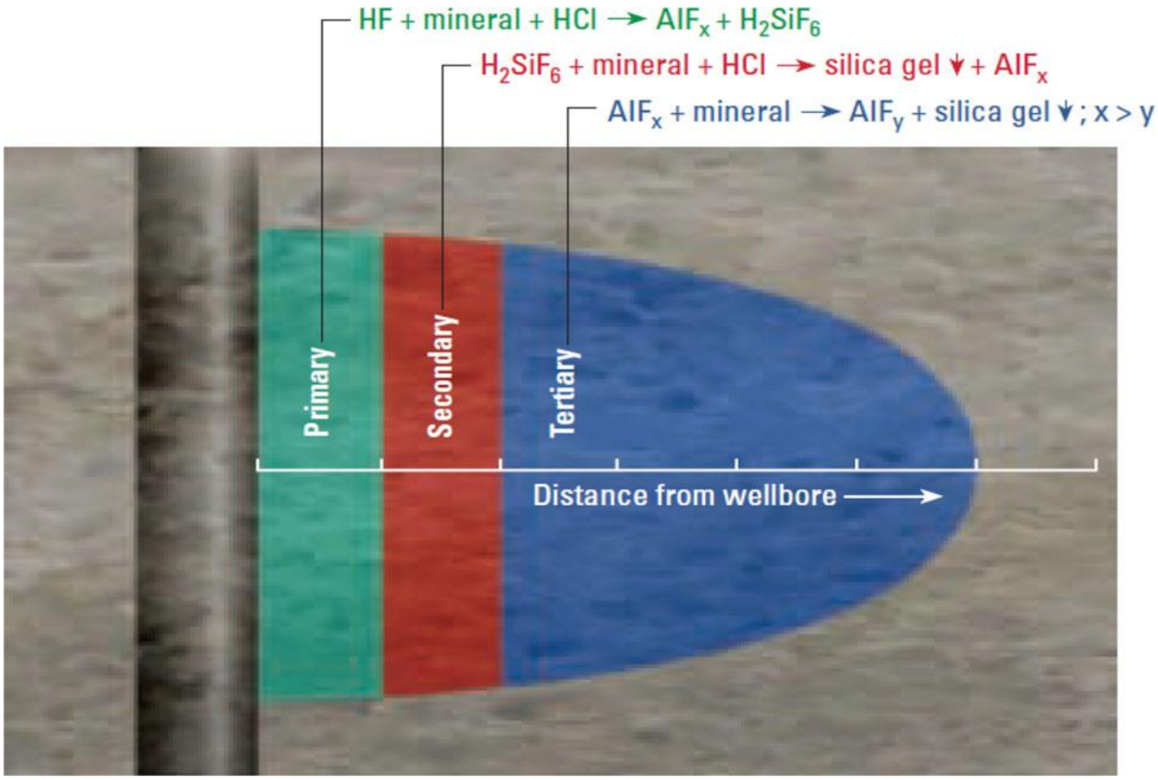
- **Corrosion inhibitor** is always necessary. It must be added to all acid stages (acid preflush, main acid, and acid overflushes)

- **Iron control** is required in any acidizing treatment. Therefore, an iron-control agent is almost always needed. Products exist in two general categories: iron-complexing or iron-sequestering agents, and iron reducing agents. One or more of these can be used in an acid mixture. Combinations can be effective, especially at higher temperatures, where dissolved iron contents may be high.

- A **clay stabilizer is often recommended** but not necessary for the purpose of preventing migration and/or swelling of clays following an acid treatment.

- An **emulsion blocker** (surfactant) to prevent formation of oil-water emulsions.

- It may be advisable to include a **calcium sulphate (CaSO4) scale inhibitor** in the acid stages or the overflush if treating a well containing high sulphate concentration (>1000 ppm) in the formation water. CaSO4 scale inhibitors are typically phosphoric acid or polyacrylate polymers.
  (Sandrine Portier, Laurent André & François-D. Vuataz; 2007)



When the sandstone formation is treated with the mud acid, usually three groups of reactions take place which are explained by Al-Harthy (2008/2009). The primary reaction occurs close to the wellbore, which results in the formation of aluminum and silica fluorides. In these reactions, minerals are usually dissolved rapidly and without any precipitation. Away from the wellbore, the secondary reaction takes place in which these primary products further reacted to form silica gel (slow reaction), which is a precipitate. At a greater distance from the injection zone, additional silica gel precipitates due to tertiary reactions. The sandstone acidizing treatment may fail due to the rapid kinetics of the secondary and tertiary reactions at a higher temperature.

HF acid is the main reactant with formation rocks, while HCl acid is intentionally added into the mixture to reduce HF consumption and to maintain an acidic environment, which prevents precipitations of HF reaction by-products (Al-Harthy 2008/2009).

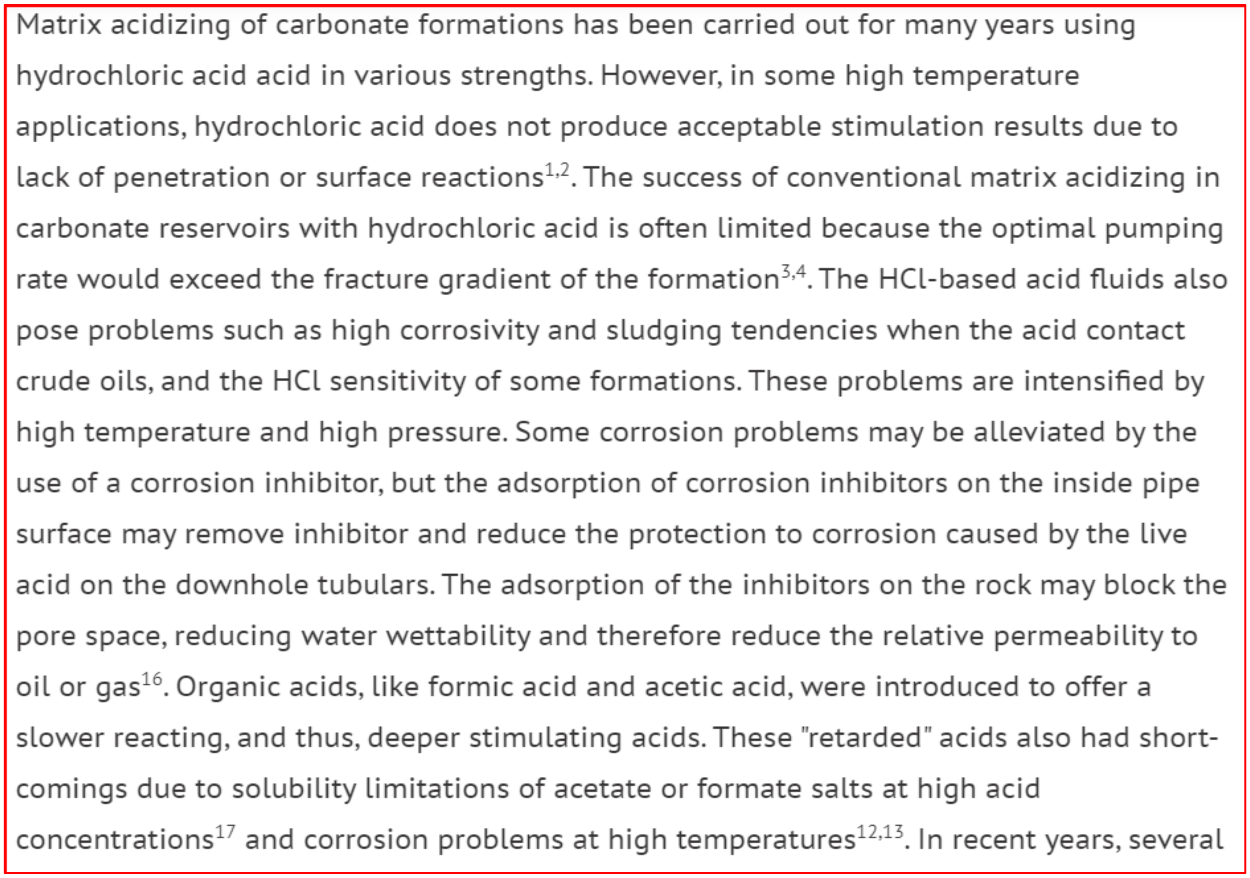
Problems associated with mud acid

Despite the reasonable success of mud acid application on sandstone formation in recent years, still some critical problems are associated with its use, which limit its effectiveness. Shuchart and Gdanski (1996), (Thomas et al. 2001, 2002) and Al-Dahlan et al. (2001) discovered that the most likely limitations of mud acid are rapid spending due to fast reaction, which results in consequent precipitations of reaction products followed by secondary and tertiary reactions (Li 2004). This limits the acid penetration in the formation especially at elevated temperatures. A combination of problems such as precipitations, matrix unconsolidation, high corrosion rate and incompatibility of hydrochloric (HCl) acid with sensitive clays (illite) resulted in the inconstant success rate or failure of stimulation treatments with mud acid reported by Shuchart and Gdanski (1996), Thomas et al. (2002).

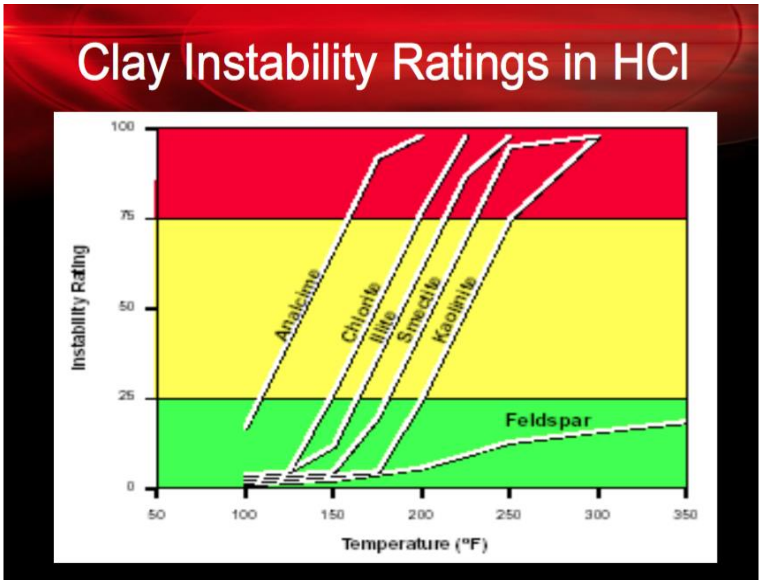
Retarded mud acids

Gdanski (1985), Thomas et al. (2001) and Gomaa et al. (2013) applied retarded mud acids during the main acid stage, which are supposed to decrease the reaction rate between acids and minerals. Three retarded hydrofluoric acids (RHF acids) based on boric acid (H3BO3), aluminum chloride (AlCl3) and phosphonic acid were tested. However, these methods also posed similar problems at high temperatures. For example, when RHF acid was applied: some minerals form precipitates that were not formed when normal mud acid was used. For example, Thomas et al. (2001) investigated the formation of potassium tetrafluoroboron (KBF4) precipitate when the fluoroboric acid reacted with feldspar. Fluoroboric acid has been produced when boric acid reacts with HF acid, presented in Eq. 4 and 5, respectively.

- HCL causes carbonate liquefaction (softening)
- HCL causes rapid corrosion of tubulars and requires corrosion inhibitors and buffers
- HCL can cause CO2 and H2S release
- HCL requires poses a significant HSE hazard and specialist pumping equipment and personnel to deploy it
- HCL changes wettability thus causing emulsion blockage.
- HCL can cause clay hydration and particle migration


Matrix acidizing of carbonate formations has been carried out for many years using hydrochloric acid acid in various strengths. However, in some high temperature applications, hydrochloric acid does not produce acceptable stimulation results due to lack of penetration or surface reactions[1,2]. The success of conventional matrix acidizing in carbonate reservoirs with hydrochloric acid is often limited because the optimal pumping rate would exceed the fracture gradient of the formation[3,4]. The HCl-based acid fluids also pose problems such as high corrosivity and sludging tendencies when the acid contact crude oils, and the HCl sensitivity of some formations. These problems are intensified by high temperature and high pressure. Some corrosion problems may be alleviated by the use of a corrosion inhibitor, but the adsorption of corrosion inhibitors on the inside pipe surface may remove inhibitor and reduce the protection to corrosion caused by the live acid on the downhole tubulars. The adsorption of the inhibitors on the rock may block the pore space, reducing water wettability and therefore reduce the relative permeability to oil or gas[16]. Organic acids, like formic acid and acetic acid, were introduced to offer a slower reacting, and thus, deeper stimulating acids. These "retarded" acids also had short-comings due to solubility limitations of acetate or formate salts at high acid concentrations[17] and corrosion problems at high temperatures[12,13]. In recent years, several

- **Feldspar** – contain sodium and potassium. The major concern is **fluorosilicate precipitate**. K-Spars cause the most precipitation problems.
- **Carbonate** – consumes HCl and can **cause precipitation of fluorosilicates and aluminum** from spent acid.
- **Illite** – causes **fines migration problems** and is ion-exchanging. It contains potassium which can cause **fluorosilicate precipitation** from spent acid.
- **Kaolinite** – causes **fines migration problems**. It disperses in fresh water and and **causes plugging**.
- **Smectite** – is an ion-exchanging mineral that **swells** in fresh water.
- **Chlorite** – is ion-exchanging and **unstable** in HCl.
- **Mica** – is ion-exchanging and **unstable** in HCl. It contains potassium which can cause **fluorosilicate precipitation** from spent acid.
- **Zeolite** – is ion-exchanging and **unstable** in HCl. It often contains sodium which can cause **fluorosilicate precipitation** from spent acid.



The graph is extracted out of a major service company’s Stimulation Manual.

Acid causes damage to many wells in several different ways. Acid produce emulsion blockage, carbonate liquefaction, Co2 and H2S production, hydration of clays, migration of clays, and of course severe corrosion. A wide range of precipitates are also produced. The HSE aspects are also of significant concern.

HF Precipitates (not the only damage mechanism)

Table 5: Possible precipitates in sandstone acidizing (Schlumberger, 2003)

Precipitate	Origin
Calcium fluoride (CaF_2)	Carbonate-HF reaction CaF_2 can be caused by an inadequate HCl preflush to remove calcium ions from calcite cementing materials or to flush calcium chloride completion fluids away from the near wellbore.
Amorphous silica	Clay and silicate dissolution in HF. Amorphous silica results from both secondary and tertiary HF acidizing reactions.
Sodium and potassium fluosilicates	Feldspar and illite clay dissolution in HF produce these primary reaction products. They can also form if seawater or sodium or potassium brines are mixed with spent HF.
Sodium and potassium fluoaluminates	Silico-aluminate dissolution in HF. Fluoaluminates, like fluosilicates, occur when spent mud acid (H_2SiF_6) reacts with the formation. They can also form if seawater or sodium or potassium brines are mixed with spent HF.
Aluminium hydroxides and fluorides	Clay and feldspar dissolution in HF can cause these precipitates.
Iron compounds	Iron minerals or iron oxides (rust) can react with HCl-HF to produce these compounds.

The iron released from tubing due to acid corrosion during acidizing treatment is another major source of iron sulfide deposition in the near wellbore region, downhole tubing and surface facilities. Large amount of iron sulfide could form during acid treatment.

Review of Iron Sulfide Scale Removal and Inhibition in Oil and Gas Wells: Current Status and Perspectives

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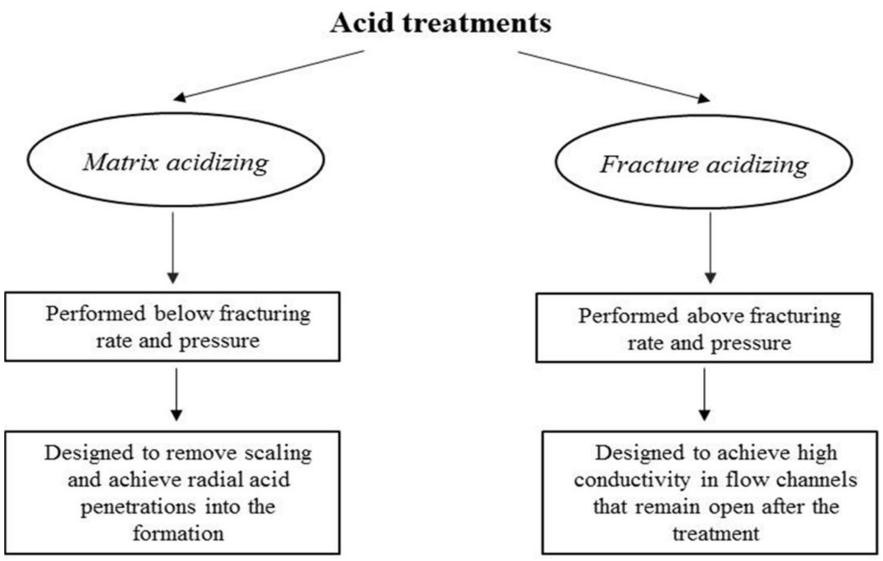
Abstract

Iron sulfide scale is one of the main types of inorganic scales that block oil and gas wells. Iron sulfide has polymorph crystallinity structures, which complicate its dissolving and inhibition. Hydrochloric acid (HCl) is used conventionally to remove iron sulfide scale; however, toxic hydrogen sulfide (H_2S) is released. Consequently, tubular corrosion and formation damage are accelerated.

Stimulation – Chelants vs Acid

Frenier et al. (2004, 2000) showed that a chelant removed the calcium, magnesium, and iron carbonate minerals without inducing damage through clay degradation and precipitated byproducts. Chelating agents were able to stimulate high temperature sandstone formations in the field; they removed the scale and stimulate the high-temperature wells.

HCl-based fluids have been used in the oil industry for a long time. Using HCl in stimulation is not favorable in the following cases: high temperature reservoirs, illitic sandstone reservoirs, wells completed with Cr-13 tubing, sandstone with high percentage of calcite, and acid-sensitive crudes bearing formations. HCl can cause damage to sandstone reservoirs if its illite content is high.



Applications of Chelating Agents in the Upstream Oil and Gas Industry:

A Review by Amjed Hassan, Mohamed Mahmoud, Badr S. Bageri, Murtada Saleh Aljawad, Muhammad Shahzad Kamal, Assad A. Barri, and Ibnelwaleed A. Hussein. *(Energy Fuels* 2020)

Chelating agents show very effective performance in different applications in the upstream oil and gas industry. This study presents a critical review of the application of chelating agents in acidizing, scale removal, filter cake removal, wettability alteration, enhanced oil recovery (EOR), and hydraulic fracturing treatments. The advantages and disadvantages of using several types of chelating agents for improving the well/reservoir productivity and enhancing the oil recovery from sandstone and carbonate reservoirs are discussed. Also, detailed comparisons between different chelating agents and their applications in many oil and gas areas are presented. Moreover, the combination of chelating agents with different chemicals to achieve better performance is addressed. Hydroxy amino carboxylic acids [such as ethylenediaminetetraacetic acid (EDTA) and glutamic acid diacetic acid (GLDA)] have replaced conventional acids, such as hydrochloric acid (HCl), hydrofluoric acid (HF), and organic acids, at high temperature and salinity conditions to stimulate carbonate and sandstone reservoirs without any side effects on the formation integrity. Furthermore, diethylenetriaminepentaacetic acid (DTPA) and GLDA **are effective in removing different types of scales, such as carbonate, sulfate, and sulfides, without releasing hydrogen sulfide (H_2S) and using corrosion inhibitors.** Also, DTPA, EDTA, and GLDA are very active in dissolving filter cake layers formed by different drilling fluids**. Aminopolycarboxylic groups can be injected into sandstone and carbonate reservoirs to adjust the wettability conditions and enhance oil recovery.** Chelating agents, such as GLDA, EDTA, and DTPA, optimize the fracture conductivity and, meanwhile, minimize the number of additives in hydraulic fracturing, which significantly cut the cost of the operation. Overall, chelating agents are economically attractive chemicals for various upstream operations since produced, and seawater can be used without further treatment.

Chelating agents

Chelating agents may be used to stimulate sandstone formations entirely using without using any HF-containing chemical. Different chelating agents have been used at high-temperature conditions. Ethylenediaminetetraacetic acid (EDTA) and hydroxyethylenediaminetetraacetic acid (HEDTA) used at a high temperature resulted in the increase in gas production without the use of HF-containing fluids. Wormholes can be formed by EDTA and HEDTA at temperatures up to 400˚F. Frenier and Hill (2002) and Mahmoud et al. (2011) used chelating agent Na3HEDTA and found it more effective in sandstone acidizing as compared to mud acid. Using trisodium HEDTA (Na3HEDTA) has given better results in stimulating sandstone as compared to HCl. Various stimulating studies on sandstone formation using HEDTA chelating agent have been conducted by Frenier et al. (2004), Ali et al. (2008) and Mahmoud et al. (2011) and showed that it gave better results in increasing permeability compared to mud acid especially at high temperatures. Hydroxethylaminocarboxylic acid (HACA) group of chelating agents can be used as an alternative to the mud acid.

The Composition Of Acid/Oil Interface In Acid Oil Emulsions

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In well stimulation treatments using hydrochloric acid, undesirable water-in-oil emulsion and acid sludge may result and then cause operational problems in oil field development. The processes intensify in the presence of Fe(III), which are from the corroded surfaces of field equipment and/or iron-bearing minerals of the oil reservoir.

During well operations, reservoir porosity and permeability of bottomhole rock deteriorate as a result of clay swelling, mineral scaling, asphaltene and wax deposition, formation of high viscosity water-in-oil emulsions, etc. To improve well-to-reservoir connectivity and restore rock permeability in the bottomhole formation zone, well stimulation treatments with various acids are used. However, the use of acid is accompanied by a number of negative consequences (Fredd and Fogler 1998).

During acid treatment there is an interaction of acid with the rock, in which significant quantities of soluble and insoluble inorganic products capable of precipitating and clogging the reservoir pores can form, thereby reducing the rate of production wells and the intake capacity of injection wells. In addition, a serious danger is also posed by the products of the direct interaction of acidic formulations with petroleum fluid. The interaction of the acid with crude oil is accompanied by the formation of stable water-in-oil emulsions and/or asphaltic sludge. The formation of water-in-oil emulsion and asphaltic sludge may cause operational problems in field development such as permeability reduction, increase in fluid viscosity and formation wettability alteration from water wet to oil wet (Shirazi et al. 2019).

As mentioned before, it is generally assumed that sludge is asphaltenic in nature. However, crude oils that contain little or no asphaltenes can produce sludge too (Shirazi et al. 2019; Rietjens 1997). This type of sludge is referred to as non-asphaltenic sludge. Rietjens (1997) showed that all Bronsted acids (HCl, acetic, etc.) have a similar effect on sludge formation.

Besides, the variety of acid additives (anti-sludging agents, corrosion inhibitors, and iron reducing agents) is used to prevent the sludging and emulsion forming problem. However, their effectiveness is limited by the need to obtain a compatible combination of additives and a lack of understanding of the complex chemistries involved in the precipitation reactions (Fredd and Fogler 1998).

Removing of Formation Damage and Enhancement of Formation Productivity Using Environmentally Friendly Chemicals. (May 2011)

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Matrix acidizing is used in carbonate formations to create wormholes that connect the formation to the wellbore. Hydrochloric acid, organic acids, or mixtures of these acids are typically used in matrix acidizing treatments of carbonate reservoirs. However, the use of these acids in deep wells has some major drawbacks including high and uncontrolled reaction rate and corrosion to well tubulars, especially those made of chrome-based tubulars (Cr-13 and duplex steel), and these problems become severe at high temperatures. Hydrochloric acid (HCl) and its based fluids have a major drawback in stimulating shallow (low fracture gradient) formations as they may cause face dissolution (formation surface washout) if injected at low rates. The objective of stimulation of sandstone reservoirs is to remove the damage caused to the production zone during drilling or completion operations.

Many problems may occur during sandstone acidizing with Hydrochloric/Hydrofluoric acids (HCl/HF) mud acid. Among those problems: decomposition of clays in HCl acids, precipitation of fluosilicates, the presence of carbonate can cause the precipitation of calcium fluorides, silica-gel filming, colloidal silica-gel precipitation, and mixing between various stages of the treatment. To overcome problems associated with strong acids, chelating agents were introduced and used in the field. However, major concerns with most of these chemicals are their limited dissolving power and negative environmental impact.

Carbonate Matrix Acidizing

Formation damage may be defined as any impairment of well productivity or injectivity due to plugging within the wellbore, in perforation, in formation pores adjacent to the wellbore or fractures communicating with the wellbore. Almost all wells are damaged, the problem is to determine the degree of damage, location, probable causes of damage and approaches to alleviate any serious damage. Formation damage may be indicated by well tests, pressure build up and draw down tests, comparison with offset well, careful analysis of production history. If multiple zones are open in a single completion, PLT (Production logging Techniques) runs in a flowing well will often show some permeable zones to be contributing little or nothing to the production.

A reservoir study may be required to differentiate between: Production decline due to gradual formation damage decline due to loss in reservoir pressure, comparison with offset well may not be sufficient to detect gradual damage because all of wells may be subjected to the same damaging mechanisms. In a relatively high permeability well with skin damage, reservoir pressure may be measured in the well, and it may stabilize within few hours. If reservoir the permeability is low, days or weeks may be required to stabilize the reservoir pressure. Under these conditions, it may be difficult to determine skin damage. Skin damage calculation using pressure build up and draw down analysis are carried out in many areas prior to planning well stimulation. Once mechanical pseudo skin effects are identified, positive skin effects can be attributed to formation damage. Formation damage is typically categorized by the mechanism of its creation as either natural or induced. Natural damages are those that occur primarily as a result of producing the reservoir fluid. Induced damages are the result of an external operation that was performed on the well such as a drilling, well completion, workover, stimulation treatment or injection operation. In addition, some completion operations, induced damages or design problems may trigger the natural damaging mechanisms.

Natural damages include:

- Fines migration
- Swelling clays
- Water-formed scales
- Organic deposits such as paraffins or asphaltenes
- Mixed organic/inorganic deposits
- Emulsions

Induced Damages Include:

Plugging by entrained particles such as solids or polymers in injected fluids
Wettability changes caused by the injected fluids.

Carbonate Matrix Acidizing has been carried out for several years using hydrochloric acid based stimulation fluids in various concentrations. At high temperatures HCl does not produce acceptable stimulation results because of its fast reaction in the near wellbore area, low acid penetration, and surface dissolution (Huang et al. 2003). Williams et al. (1979) recommended that carbonate acidizing treatments should be carried out at the highest possible injection rate without fracturing the reservoir rock (qi,max). Wang et al. (1993) discovered an optimum acid injection rate to obtain breakthrough during acid treatments for carbonate cores in linear coreflood using a minimum acid volume. The optimum acid injection rate was found to be a function of the rock composition and reaction temperature as well as the pore size distribution of the reservoir rock.

A problem occurs if the required optimum injection rate is greater than the maximum acid injection rate. In this case HCl cannot be used because it will cause face dissolution if used at low injection rates, or will fracture the formation if used at high injection rates. Therefore stimulation fluids other than HCl-based fluids such as chelating agents need to be used to achieve deep and uniform penetration and eliminate face dissolution problems. Another problem encountered during stimulation using HCl-based fluids is the high corrosion rate of these fluids to the well tubulars. Well tubulars are often made of low-carbon steel and may contain rust. HCl will dissolve the rust and produce a significant amount of iron, which in turn will precipitate and cause formation damage.

Corrosion becomes more severe at high temperatures, and special additives are needed to compensate for the loss in corrosion inhibition at higher temperatures. The cost of these additives exceeds 5% of the treatment cost (Fredd 1998). **Also the excessive use of corrosion inhibitors may cause other problems, as the corrosion inhibitor may adsorb on the reservoir rock and change its wettability, especially in low permeability reservoirs (Schechter 1992).**

Major challenges associated with conventional stimulation fluids include the corrosive nature of these fluids on well tubulars particularly at high temperatures (Wang et al. 2009) and their inability to treat heterogeneous formations without employing diversion techniques. Additionally, highly reactive conventional acids tend to preferentially flow to the higher permeable zones in heterogeneous formations. The diversion and reaction of injected acid into areas of highly permeable zones created increased flow and reaction in these zones. This occurs at the expense of bypassing the low permeable zones leading to inefficient stimulation of the target low permeability or damaged intervals. **This is also true for matrix acidizing of long open-hole horizontal wells and extended reach wells. The success of conventional matrix acidizing in a carbonate reservoir with HCl is often limited because of the optimal injection rate would exceed the fracture gradient of the formation (Haung et al. 2000).** Different acid systems have been used to reduce the problems associated with HCl such as rapid acid spending and face dissolution at low injection rates. Acid systems based on weak acids, like formic and acetic have a low concentration of H+ in comparison to HCl and will react with calcium carbonate at a slower rate than HCl (Abrams et al. 1983). Retarded acid systems can also be employed to reduce the reaction rate of HCl with carbonate formations. One such system employed HCl emulsified in an oil phase that reduces acid diffusion to the carbonate surface and allows for deeper penetration of the live acid (Hoefiner and Fogler 1985). Foamed acids have also been employed in a retarded acid system during stimulation of carbonate formation, as the foam will lower the liquid saturation and thus increase the convection rate for the same injection rate. The foam also will lower the liquid permeability and decreases the amount of live acid that leaks-off from the primary channel (Bernadiner et al. 1992). Acetic and formic acids suffer from having a low solubility of calcium salts formed and cannot be used at high acid concentrations (Economides and Kenneth 2000) in addition to corrosion problems at high temperatures (Huang et al. 2002).

Chelating agents have been used as stand-alone stimulation fluids to stimulate calcite formations. Fredd and Fogler (1998a) tested the use of different chelating agents‘ formulas reaction with calcium carbonate cores and the ability of these chemicals to form wormholes. **The efficiency of the chelating agents at low injection rates is consistent with the dependence of wormhole structure on the Damköhler number and relatively low diffusion coefficients of DTPA and EDTA compared to of HCl.** The kinetics of dissolution of dolomite by HCl is completely different than that of HCl with calcite.

Hill et al. (1993) stated that the wormhole penetration formed during matrix acidizing by HCl was much less in dolomite formations than calcite formations at the same conditions (Hill et al. 1993).

Stimulation of Sandstone Reservoirs

The objective of stimulation of sandstone reservoirs is to remove the damage caused to the production zone during drilling or completion processes. Sandstone acidizing consists of three main stages of sandstone acidizing: a preflush, normally of hydrochloric acid, a mud-acid stage of hydrochloric and hydrofluoric, and an after flush that may be hydrochloric acid The amount of mud acid required to remove the damage can be determined through the experience within a given area. Oil and gas wells respond differently to the amount of mud used in the treatment. They recommended displacing the oil zone with CO2 to reduce the interaction between spent acid and oil during the acid treatment process. This process reduces the need to treat spent acid returns and allows the use of large mud-acid treatment for deeper acid penetration (Gidley et al. 1996).

Many problems may occur during sandstone acidizing with HCl/HF mud acid. Among those problems:

- Decomposition of clays in HCl acids,
- Precipitation of fluosilicates,
- The presence of carbonate can cause the precipitation of calcium fluorides (CaF2), silica-gel filming, colloidal silica-gel precipitation,
- Mixing between various stages of the treatment (Gdanski and Shuchart 1998).

Bryant and Buller (1990) noticed during using HCl acid in sandstone acidizing that the migration of amorphous silica (hydrated silica) and mineral fragments occurred. Their study indicates damage normally occurs during the HCl treatment. Aluminum is preferentially leached during the dissolution of kaolinite in HCl. The structure of kaolinite is layered (made up of sheets) in which acid attacks preferentially at the edge. In turn this may cause fines migration and formation damage (Hartman et al. 2006). Magnesium and Aluminum could have been leached from the crystalline lattice during dissolution in 15 wt% HCl (Kline and Fogler 1981). Quartz reacts relatively slowly with HF, whereas aluminosilicates (clay minerals, feldspar, and mica) reacts relatively rapidly (Li et al 1998).

Secondary reaction: HF with aluminosilicates is the reaction of fluoroslilic acid derived from the primary reaction with an aluminosilicates to form hydrated silica gel.

Dissolving the silicon in aluminosilicates results in an amorphous silica gel film. In addition, the silica in SiF62- also precipitates as silica gel. Tertiary reaction: The tertiary reaction of HF with aluminosilicates involves the further reduction of the F/Al ratio in dissolved aluminum fluoride species. The reaction extracts aluminum out of aluminosilicates and leaves silica gel in the matrix.

The reaction will continue reducing Al/F ratio in the spent HF until the remaining HCl is consumed. Mud acid cannot be used in sandstone with high calcite concentration. Calcite reacts very quickly and completely with HCl acid, but in the presence of HF, the reaction proceeds (Martin 2004).

CaF2 has very low solubility. Preflushing the near-wellbore with HCl minimized this problem.

The reaction products of fluorosilicic acid and fluoroaluminic acid are readily soluble in water, but their potassium, sodium, and calcium salts are partially insoluble.

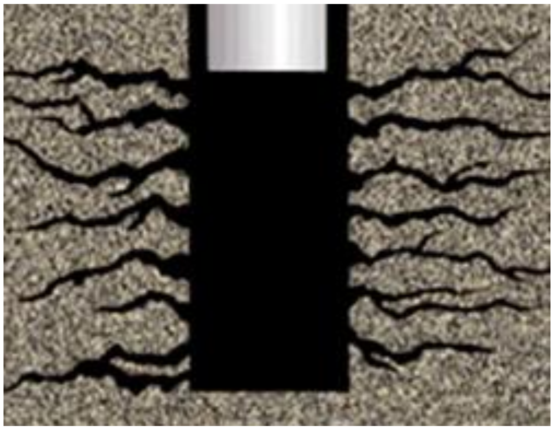
Calcium, potassium, and sodium ions should not be mixed with either spent or unspent HF. Formation water, which contains calcium chloride, potassium chloride, and sodium chloride should be avoided. The only compatible salt solution with HF is ammonium chloride. Ferric hydroxide forms when acid spends and pH rises. Sources of ferric iron include some minerals, such as chlorite, siderite, and hematite, and tubing rust. Problems of stimulating high temperature sandstone reservoirs with HCl are: sand deconsolidation, clay destabilization, tubular corrosion

There are several minerals that may precipitate during an acidizing treatment such as:

Fluorides: **Calcium fluoride (fluorite)**, CaF2, has a very low solubility and, consequently, a high potential for precipitation. However, calcium fluoride precipitation can be virtually eliminated if an adequate HCl pre-flush is used to remove carbonates from the near-wellbore region prior to injecting HF. **Aluminum fluoride** (fluellite), AlF3, is another potentially damaging precipitate. Precipitation of AlF3 occurs at high HF/HCl ratios or when the HF concentration exceeds 4 wt%. ii. **Fluorosilicate and Fluoroaluminate Salts**: K2SiF6, Na2SiF6, N3AlF6, and K3AlF6 salts are all contingent precipitates. They contended that high HF concentrations favor the precipitation of these minerals, thus, they are more likely to occur during the initial phases of dissolution. iii. Colloidal

Silica: Colloidal silica, Si(OH)4, is perhaps the most important precipitating mineral in sandstone acidizing. Several core flood experiments have produced evidence of the precipitation of Si(OH)4. In addition, several acidizing models have demonstrated significant colloidal silica precipitation. As reservoir minerals are dissolved, aluminum and silica compete for the available fluorine. Aluminum has the greater affinity for fluorine; thus when the level of free fluorine is reduced, silica precipitates in the form of Si(OH)4.

Iron Compounds: Sandstone reservoirs commonly contain iron bearing minerals such as siderite, ankerite, pyrite, and chlorite. In the presence of HCl, however, iron compounds are unlikely to precipitate**. Iron compounds can become a real possibility in carbonates, where there is enough carbonate material present to cause the HCl acid to spend itself completely.** This condition is rarely found in sandstones, and, therefore, does not pose much of a problem in sandstone acidization (Quinn et al 2000). HF can dissolve carbonates, clays, feldspar, micas, and quartz. The primary reason to use HF acid is to remove clays. If carbonates are encountered in sandstone, these should be removed with a preflush of HCl to avoid CaF2 precipitation. Table 3 shows the solubility of the different mineral types in mud acid (Allen and Roberts 1993).



Smectite and Smectite mixtures swells by taking water into its structure. It can increase its volume up to 600%, significantly reducing permeability, creating impermeable barrier to flow. The removal of these clays can be accomplished during HF treatment if the depth of penetration was small. If it the depth of penetration was large, the best treatment is to fracture the well to bypass the damage. iii. Illites are interlayered. Therefore, illites combine the worst characteristics of the dispersible and the swellable clays. **The illites are most difficult to stabilize.** Also, this type of clay can swell, because it adsorbs water. Osmotic swelling results from concentration imbalances between the ions held at the exchange sites on the clays and the solute content of the contacting fluid, Fig. 3.

Amaefule et al. (1988) stated that rock-fluid interactions in sedimentary formations can be classified in two groups: (1) chemical reactions resulting from the contact of rock minerals with incompatible fluids, and (2) physical processes caused by excessive flow rates and pressure gradients. Illites are interlayered, Fig. 4. Therefore, illites combine the worst characteristics of the dispersible and the swellable clays. The illites are most difficult to stabilize.

Flowing HCl in cores containing illite and chlorite (high surface area, Table 4, Ezzat 1990 and Welton 1984) caused the pressure drop to increase due to the clay reaction product migration, formation of reaction product and/or increase in the viscosity**. Illite and chlorite are attacked by HCl to produce an amorphous silica gel residue** i.e. the aluminum layer extracted. The alumina layer if attacked, it will weaken the clay structure and make it more sensitive to fluid flow (Thomas et al. 2001). Thomas et al. (2001) showed that HCl has degraded Illite and chlorite in the tested cores from actual producing sandstone reservoirs. Degradation of Illite and chlorite led to potential core damage. Treating the actual reservoir cores by mud acid caused fines migration during the overflush.

Chelating Agents in Sandstone Stimulation

Parkinson et al. (2010) studied the use of chelating agents to stimulate sandstone formations with high calcite content. Pinda formation in West Africa has a wide range of carbonate content (varying from 2% to nearly 100%) and formation temperature is 300°F. This field was treated using 7.5 wt% HCl with foam, a sequence of job failures was noticed, with constant problems of tubular corrosion. Na3HEDTA at pH 4 was tested using Berea sandstone cores and was compared with mud acid (9 wt% HCl + 1 wt% HF). The results showed that Na3HEDTA was more effective in stimulating Berea core than mud acid and HCl.

After the core flood experiments they performed Na3HEDTA was decided to be used alone in the field treatment. The old stimulation fluid was 7.5 wt% HCl with corrosion inhibitors, surfactants, iron-control agent, and mutual solvent. The use of this system caused several corrosion-related coiled-tubing failures. HEDTA with 0.2 wt% corrosion inhibitor was used instead of 5 wt% with the 7.5 wt% HCl and HEDTA showed less corrosion rate than HCl. After treating 6 wells in this filed the production rate from the six wells was increased from 2,881 BOPD (Pre-job production) to 4,531 BOPD (One-year post-job production). Ali et al. (2008) showed that low pH solutions of HEDTA (pH = 4) were capable of stimulating carbonate and sandstone formations at high temperatures. Because of reduced reaction rates and corrosion rates, these fluids effectively stimulated high temperature reservoirs without the damage to the well tubulars and formation integrity that is commonly caused by strong mineral acids.

High temperature sandstone acidizing is challenging due to the very fast reaction rates and instability of clays at these temperatures. **Gdanski and Scuchart (1998) have shown that essentially all clays are unstable in HCl above 300ºF.** The ideal stimulation fluid would remove the near-wellbore damage without depositing precipitates in the formation, and preventing well production declines due to solids movements.

Ali et al (2002) stimulated Berea sandstone cores Na3HEDTA and it gave results better than HCl. **EDTA performed better than HCl in actual formations, because the formation is sensitive to HCl because of some silt and fines will react with low pH solution to form precipitates and reduce the final permeability. Wells treated with EDTA fluid produced an average of 1.84 MMscf/d more gas after the treatments. This benefit was approximately twice that observed in wells in the area treated with conventional sandstone stimulation fluids.** EDTA was used to remove the calcium carbonate scale from the sandstone reservoirs caused by the drilling fluid and removed the damage caused during the drilling operations (Tyler et al. 1985). HCl leached the metal aluminum from the clay or feldspar. EDTA or HEDTA removed only calcium from the core. HEDTA removed essentially calcium containing minerals (Calcite, dolomite, Ca-feldspar, etc.) and small amount of aluminosilicates. Removing aluminum may cause fines migration for the clay minerals. **Damage was noticed after treatment of wells using HCl but not after Chelant treatments (Shaughnessy and Kline 1982). If the reservoir pressure was not high, the damage may be permanent, as the precipitates may never be produced back.**

Descaling – Chelants vs Acid

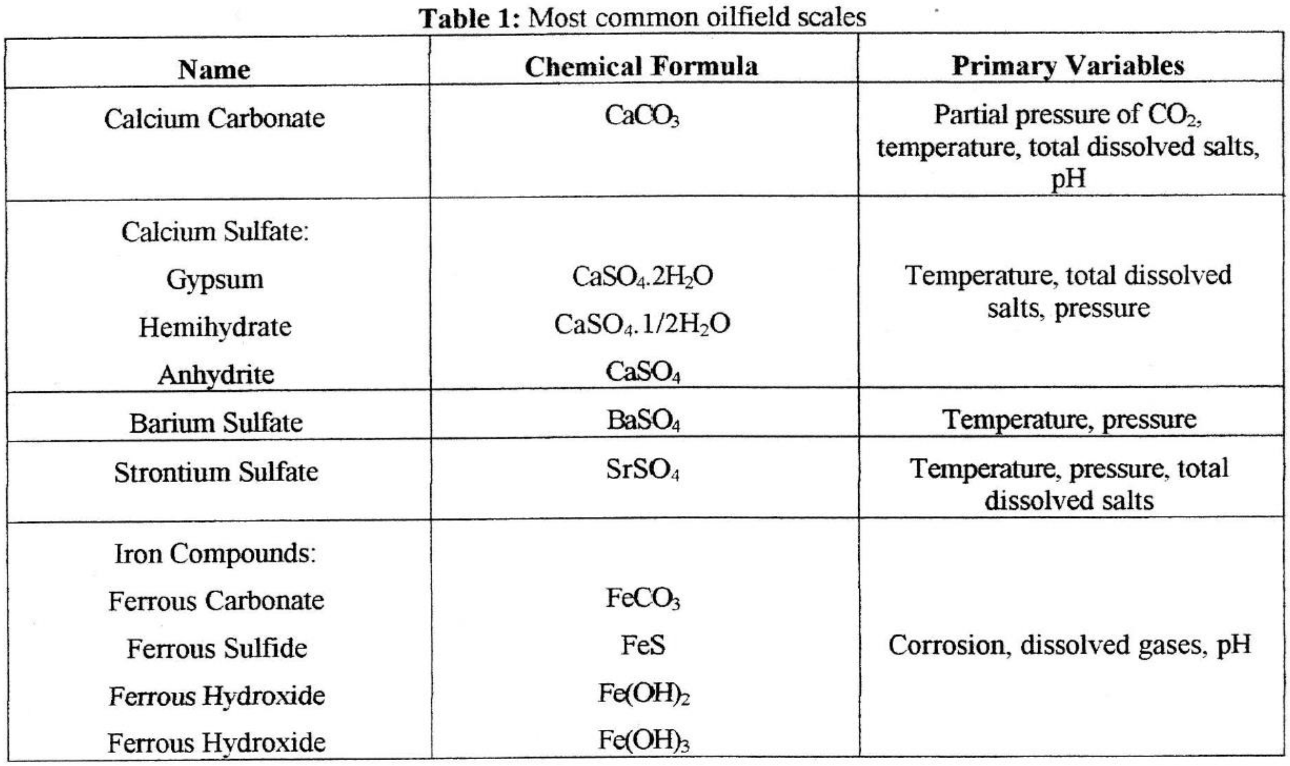


Table 1: Most common oilfield scales

Name	Chemical Formula	Primary Variables
Calcium Carbonate	$CaCO_3$	Partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate:		Temperature, total dissolved salts, pressure
Gypsum	$CaSO_4.2H_2O$	
Hemihydrate	$CaSO_4.1/2H_2O$	
Anhydrite	$CaSO_4$	
Barium Sulfate	$BaSO_4$	Temperature, pressure
Strontium Sulfate	$SrSO_4$	Temperature, pressure, total dissolved salts
Iron Compounds:		Corrosion, dissolved gases, pH
Ferrous Carbonate	$FeCO_3$	
Ferrous Sulfide	FeS	
Ferrous Hydroxide	$Fe(OH)_2$	
Ferrous Hydroxide	$Fe(OH)_3$	

In the table above, chelants can dissolve ALL of those compounds. Acids can dissolve the calcium carbonate and iron compounds, but is a poor dissolver, or cannot at all, dissolve the sulphate compounds in the middle of the table.

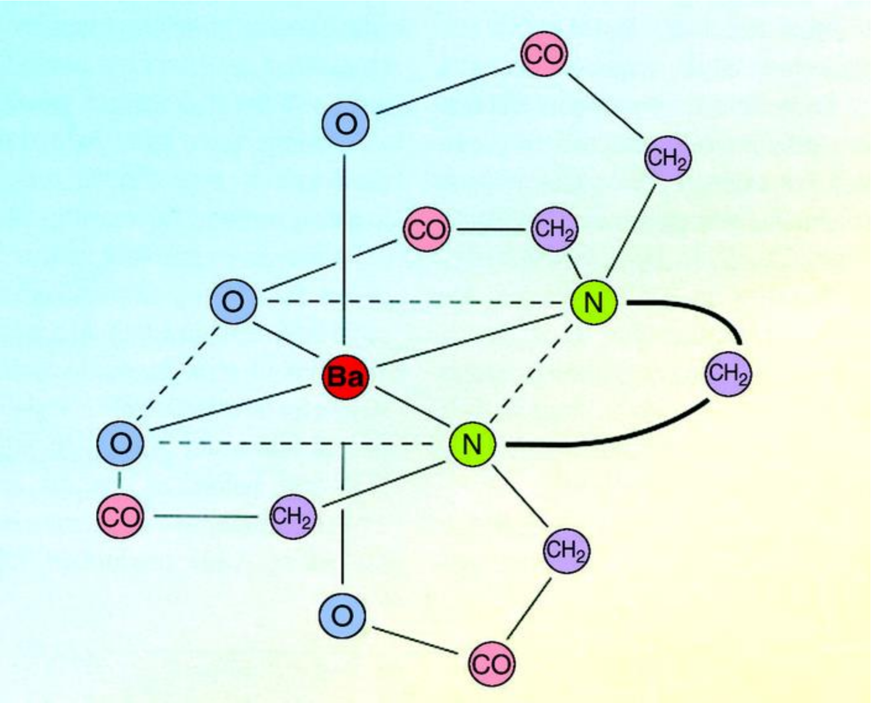
Bicarbonate

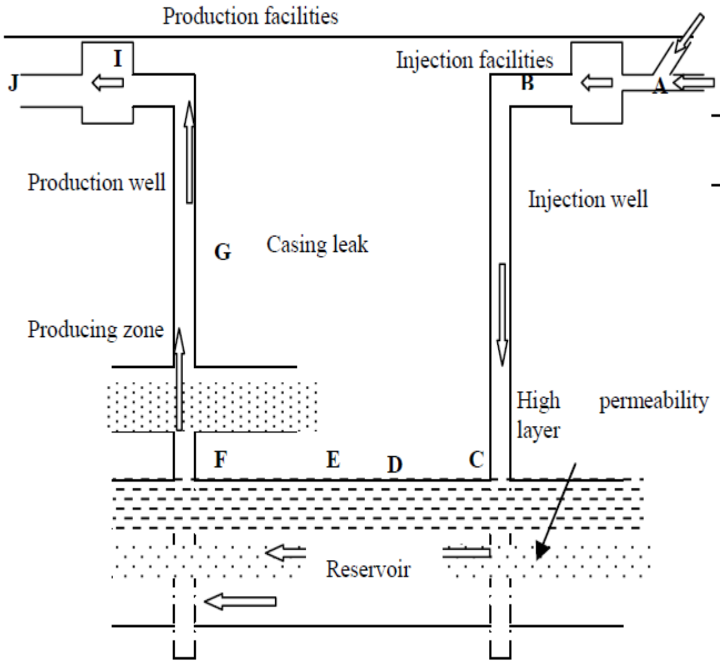
HCO_3^- presence in a formation water is critical to calcium carbonate or other carbonate scaling. However, there is less certainty with regard to the bicarbonate concentration as *analysed* from water samples. As its presence in aqueous phase is dependent on CO_2 pressure and pH as well as temperature, it should be aware that the $[HCO_3^-]$ obtained from lab analysis may be far from that actually present in the reservoir water.

The chief source of oil field scale is mixing of incompatible waters. Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. A typical example of incompatible waters are sea water with high concentration of SO_4^{-2} and low concentrations of Ca^{+2}, Ba^{+2}/Sr^{+2}, and formation waters with very low concentrations of SO_4^{-2} but high concentrations of Ca^{+2}, Ba^{+2} and Sr^{+2}. Mixing of these waters, therefore, causes precipitation of $CaSO_4$, $BaSO_4$, and/or $SrSO_4$. Field produced water (disposal water) can also be incompatible with seawater. In cases where disposal water is mixed with seawater for re-injection, scale deposition is possible (Bayona, 1993; Andersen *et al*, 2000; Bedrikovistsky *et al.*, 2001; Stalker *et al.*, 2003; Paulo *et al*, 2001).

During the production, the water is drained to the surface and suffers from significant pressure drop and temperature variations. The successive pressure drops lead to release of the carbon dioxide with an increase in pH value of the produced water and precipitation of calcium carbonate (Mackay, 2003).

A representation of a chelant/scale dissolver molecule, ethylenediaminetetraacetic acid (after Crabtree *et al.*).





Location	Change which could produce scale formation
A to B	Mixing of brines for injection
B to C	Pressure and temperature increase
C to D	Pressure decline and continued temperature increase
C to F	Solution composition may be adjusted by cation exchange, mineral dissolution or other reactions with the rock
D to F	Mixing of brines in the reservoir
E to J	Pressure and temperature decline. Release of carbon dioxide and evaporation of water due to the pressure decline if a gas phase is present or forms between these locations.
F	Mixing of formation water and injection water which has “broken through” at the base of the production well
G	Mixing of brines produced from different zones.
H	Mixing of produced brine with brine from casing leak

Fig. 1 Operational changes which may lead to scale formation at different locations

Table 1 Most Common Oilfield Scales

{PRIVATE}Name	Chemical Formula	Primary Variables
Calcium Carbonate	$CaCO_3$	partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate:		
Gypsum	$CaSO_4 \cdot 2H_2O$	temperature, total dissolved salts, pressure
Hemihydrate	$CaSO_4 \cdot \frac{1}{2}H_2O$	
Anhydrite	$CaSO_4$	
Barium Sulfate	$BaSO_4$	temperature, pressure
Strontium Sulfate	$SrSO_4$	temperature, pressure, total dissolved salts

Although the exact chemical compositions change from well to well and also vary with depth in a given well, the scale deposits are usually mixtures of many compounds and often dominated with iron sulfide minerals. These iron sulfides include pyrrhotite, troilite, mackinawite, greigite, pyrite and marcasite. Other iron containing compounds, such as iron oxide and iron carbonate, are also found in significant amounts in most cases. Additionally, mineral scales, such as calcium carbonate and barium, strontium and calcium sulfate, are often present.

Research Article

Molecular Design of Novel Chemicals for Iron Sulfide Scale Removal

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Introduction

Scale deposition is a cogent problem facing oil and gas production. Scales formed from iron sulfide are one of the troublous scales, particularly pyrite [1, 2]. Other types of scales include calcium carbonates and sulfates, barium sulfate, and strontium sulfate. The costs related to scale deposition were estimated to be about 800 million $US in the United Kingdom, 9 billion $US in the USA, and 3 billion $US in Japan while the global cost amounted to about 2.5 trillion $US [3, 4].

The reaction of iron and hydrogen sulfide forms the iron sulfide scale. The former occurs in the oil and gas production system including pipes, reservoirs, and wellbore tubular. Hydrogen sulfide, on the other hand, is found in sour gas wells as free gas and sometimes it evolves during the degradation of organic sulfur-containing chemicals due to the presence of sulfate-reducing bacteria [5, 6]. Conventional treatments used in iron sulfide scale removal include chemical and mechanical treatments [7]. Nevertheless, the former is preferred over the latter as mechanical treatment frequently exacerbates the situation by leading to more corrosion. On the other hand, chemical treatments involving the use of hydrochloric acid increase the corrosion rate and also produce toxic hydrogen sulfide as a by-product. Chelators have been suggested as a better chemical solution for scale removal [8–12]. Diethylenetriaminepentaacetic acid (DTPA) is one of the effective chelators used for iron sulfide scale removal [1, 2]. However, there is a need to develop novel biodegradable chelators. Hence, in this work, we design novel chemicals based on the hydroxamate functional group and also the carboxylic functional group present in DTPA.

This gives rise to free Fe2+ ions which can now be removed with chelating agents. The chelating agents can capture or bind to these free Fe2+ ions and aid in their removal. Hence, the binding affinities, ecotoxicological properties of these novel chemicals, are studied. Moreover, the calculation of the binding affinities of chelating agents to a central metal ion such as Fe2+ using DFT (Density Functional Theory) has been found to correlate with their corresponding experimental stability constant [11, 29]. The electronic-structure properties, such as the electrostatic potential map and frontier molecular orbitals of the most promising chemical, are calculated and overall activity is compared to DTPA, which is a well-known iron sulfide scale remover.

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Acid Stimulation of Geothermal Wells In Mexico, El Salvador And The Philippines

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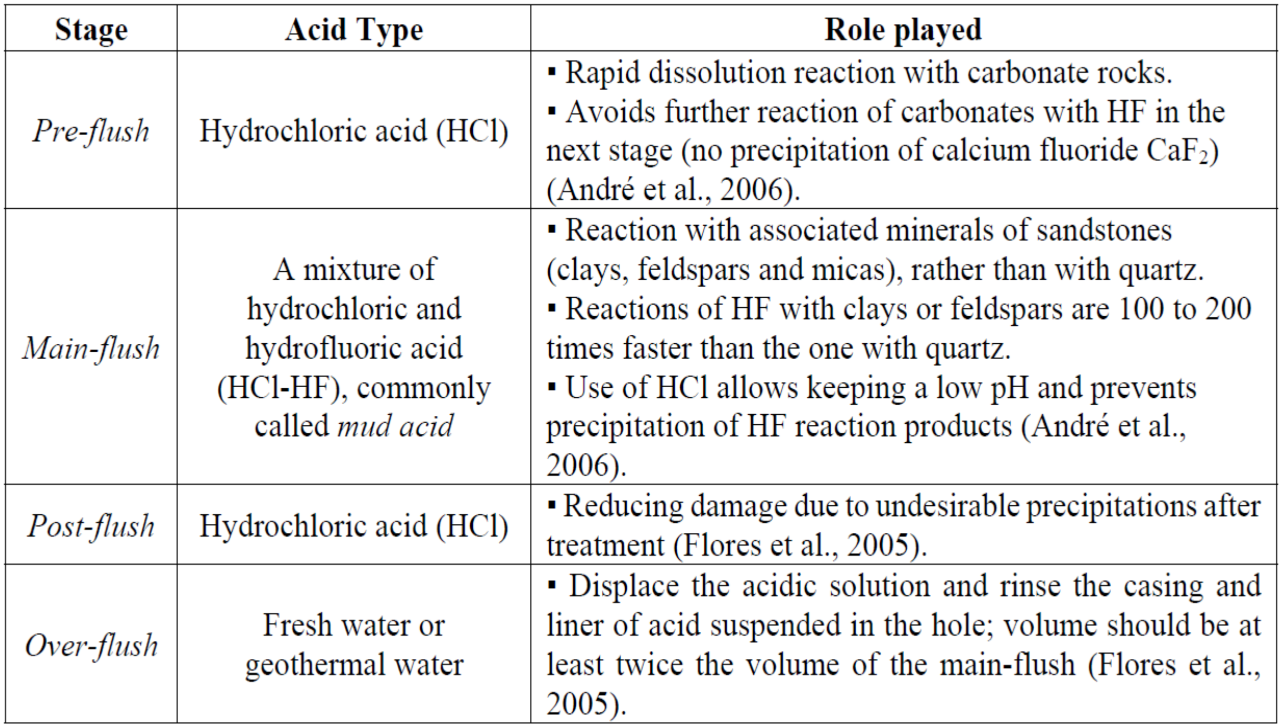
TABLE 1: Acid treatment design



Stage	Acid Type	Role played
Pre-flush	Hydrochloric acid (HCl)	▪ Rapid dissolution reaction with carbonate rocks. ▪ Avoids further reaction of carbonates with HF in the next stage (no precipitation of calcium fluoride CaF_2) (André et al., 2006).
Main-flush	A mixture of hydrochloric and hydrofluoric acid (HCl-HF), commonly called *mud acid*	▪ Reaction with associated minerals of sandstones (clays, feldspars and micas), rather than with quartz. ▪ Reactions of HF with clays or feldspars are 100 to 200 times faster than the one with quartz. ▪ Use of HCl allows keeping a low pH and prevents precipitation of HF reaction products (André et al., 2006).
Post-flush	Hydrochloric acid (HCl)	▪ Reducing damage due to undesirable precipitations after treatment (Flores et al., 2005).
Over-flush	Fresh water or geothermal water	▪ Displace the acidic solution and rinse the casing and liner of acid suspended in the hole; volume should be at least twice the volume of the main-flush (Flores et al., 2005).

HCl is selected to treat limestone, dolomite and calcareous zones, whereas HF is used to dissolve clay minerals and silica. Acid concentrations vary from 6 to 12% for HCl and from 0.5 to 3% for HF. These two acids are the most effective ones. The concentration of each acid depends on the reservoir characteristics and the specific purpose for the treatment. Corrosion inhibitors and intensifiers are also added to the acid mixtures (pre-flush, main-flush and post-flush) to reduce the corrosion rate of the casing and equipment by the acid.

Factors controlling the reaction rate of acid are (Portier et al., 2007):

Area of contact per unit volume of acid**:** Reaction time of a given acid is indirectly proportional to the surface area of carbonates in contact with a given volume of acid. Extremely high area volume ratios are the general rule in matrix acidizing.

Formation temperature*:* As temperature increases, acid is consumed faster by carbonates. It is often necessary to increase the pumping rate during acid fracturing to place acid effectively in the damage zone before it is consumed. Pre-cooling the formation or alternating stages of acid and water is another approach.

Pressure: An increase in pressure of up to 34 bar will increase the reaction time for HCl. Above this pressure, only a very small increase in the reaction rate time can be expected with increased pressure.

Acid concentration and type: As the concentration of HCl increases, acid reaction time increases because acid of higher strength dissolves a greater volume of carbonate rocks. This reaction releases greater volumes of CaCl2 and CO2, which further retards HCl.

Physical and chemical properties of formation rocks are a major factor in determining the reaction time. Generally, the reaction rate of limestone is more than twice that of dolomite; however, at high temperatures reaction rates tend to be nearly equal.

Flow velocity of acid**:** HCl and HF are two acids that react quickly with carbonates and silicates. Rapid reaction means that the acid does not penetrate very far into the formation before it is spent.

Technical report

Review On Chemical Stimulation Techniques In Oil Industry And Applications To Geothermal Systems

by Sandrine Portier, Laurent André & François-D. Vuataz
CREGE – Centre for Geothermal Research, Neuchâtel, Switzerland, May 2007

Recent years have seen a marked increase in well stimulation activity (acid and frac jobs) with the number of treatments performed more than doubling through the 1990s. In 1994, 79% of the jobs were acid jobs, but since they are lower cost than hydraulic fracturing treatments, they only consumed 20% of the money spent for well stimulation. **For acid jobs, the observed failure rate was 32%.** Failure rate for the less frequent but more expensive hydraulic fracturing treatments was much lower, only 5%. In analyzing the reasons for job failure, one-third were due to incorrect field procedures, while two-thirds were attributed to incorrect design or improperly identifying well damage. The acidification of geothermal wells is not frequently used but the operations were borrowed from the treatments performed on oil or gas wells.

A number of different acids are used in conventional acidizing treatments. The most common are:

- Hydrochloric, HCl
- Hydrofluoric, HF
- Acetic, CH3COOH
- Formic, HCOOH
- Sulfamic, H2NSO3H
- Chloroacetic, ClCH2COOH.

These acids differ in their characteristics. Choice of the acid and any additives for a given situation depends on the underground reservoir characteristics and the specific intention of the treatment, for example near well bore damage removal, dissolution of scale in fractures, etc. Factors controlling the reaction rate of acid are: area of contact per unit volume of acid; formation temperature; pressure; acid concentration; acid type; physical and chemical properties of formation rock and flow velocity of acid. These factors are strongly interrelated.

Reaction time of a given acid is indirectly proportional to the surface area of carbonates in contact with a given volume of acid. Extremely high area-volume ratios are the general rule in matrix acidizing. Therefore it is very difficult to obtain a significant acid penetration before spending during matrix treatments.

As temperature increases, acid spends faster on carbonates. It is often necessary to increase pumping rate during acid fracturing to place acid effectively before it is spent. Pre-cooling the formation, or alternating stages of acid and water is another approach. An increase in pressure up to 500 psi will increase spending time for HCl. Above this pressure, only a very small increase in spending time can be expected with increases in pressure. As concentration of HCl increases, acid spending time increases because the higher strength acid dissolves a greater volume of carbonate rocks. This reaction releases greater volumes of CaCl2 and CO2, which further retards HCl. Physical and chemical composition of the formation rock is a major factor in determining spending time. Generally, the reaction rate of limestone is more than twice that of dolomite; however, at high temperatures reaction rates tend to be nearly equal.

Velocity has a large effect on reaction rate. Retarded acids should be evaluated under flowing conditions since static tests often yield misleading results. In fracture acidizing, an increase in pumping rate increases fracture width. This decreases area-volume ratio, thereby increasing acid reaction time.

The majority of acidizing treatments carried out utilize hydrochloric acid (HCl). However, the very fast reaction rate of hydrochloric acid, and other acids listed above, can limit their effectiveness in a number of applications. All conventional acids including HCl and organic acids react very rapidly on contact with acid sensitive material in the wellbore or formation. Wormholing is a common phenomenon. **The rapid reaction means the acid does not penetrate very far into the formation before it is spent.** Conventional acid systems are therefore of limited effectiveness in treatments where deep acid penetration is needed. There was an early recognition that it was desirable to delay the rate of reaction of the acid and a variety of techniques have been developed to achieve this. Patents relating to several of these techniques have been issued. Further information on these retarded acid systems is given below.

Besides acids, the chelatants are solutions used as formation cleanup and for stimulating wells especially in formations that may be damaged by strong acids (Frenier et al., 2001). If these compounds are applied in gas and oil wells, this is not yet the case in a routine mode for the development of geothermal reservoirs. They act as a solvent, increasing the water-wetting operations and dissolving (entirely or partially) some minerals containing Fe, Ca, Mg and Al. The chelatants are mainly used in oil and gas wells and they present as advantage to have very low corrosion rates, much lower than the one observed with HCl solutions, in the same conditions. Among the chelatants, the most used are compounds of the EDTA family (EDTA: Ethylenediaminetetraacetic acid; HEDTA: Hydroxyethylenediaminetriacetic acid; HEIDA: Hydroxyethyliminodiacetic acid; NTA: Nitrilotriacetic acid). The disadvantages of using chelatants are their high cost compared to acids and for some of them, their impact on the environment.

Sandstones can be sensitive to acid depending on temperature and mineralogy. Ions of silicon, aluminum, potassium, sodium, magnesium and calcium react with acid and can form precipitates at downhole temperatures, once their solubility product is exceeded. If these precipitates occur in the near wellbore area, they can damage the formation. Sensitivity depends on the overall reactivity of the formation minerals with the acid. Reactivity depends on the structure of the rock and the distribution of minerals within the rock, i.e., the probability of the acid reaching the soluble minerals. The sensitivity of sandstone will also depend on the permeability of the formation. Low permeability sandstones are more sensitive than high-permeability sandstones for a given mineralogy. Acid formulations should be optimized on the basis of a detailed formation evaluation (Davies *et al.*, 1992, Nitters and Hagelaars, 1990).

All sandstone acid treatments are variations of the following maximum step procedure:

1. formation water displacement;
2. acetic acid stage;
3. HCl preflush stage;
4. main acid (HF) stage;
5. overflush stage;
6. diverter stage;
7. repeat steps 2-7 (as necessary);
8. final displacement stage.

Corrosion inhibitor is always necessary. It must be added to all acid stages (acid preflush, main acid, and acid overflushes). It is the “dilute” acid mixtures, like 15% HCl, that have a lot of water present that are corrosive. If concentrated HCl (37% solution) is pumped, corrosion inhibitor is not necessary. That is water present (more than 63% by weight) in acid mixture that causes corrosion. Iron control is required in any acidizing treatment. Therefore, an iron-control agent is almost always needed. Products exist in two general categories: iron-complexing or iron-sequestering agents, and iron reducing agents. One or more of these can be used in an acid mixture. Combinations can be effective, especially at higher temperatures, where dissolved iron contents may be high. Iron-control agents react with dissolved iron and other dissolved metal ions to inhibit solids precipitation by maintaining iron cations in solution, as acid spends and pH increases. A clay stabilizer is often recommended but not necessary for the purpose of preventing migration and/or swelling of clays following an acid treatment. Common clay stabilizers are either polyquaternary amines (PQA) or polyamines (PA), at 0.1-0.4%.

Clay stabilizer seems to be most effective when added to the overflush only. It may be advisable to include a calcium sulphate ($CaSO_4$) scale inhibitor in the acid stages or the overflush if treating a well containing high sulphate concentration (>1000 ppm) in the formation water. $CaSO_4$ scale inhibitors are typically phosphoric acid or polyacrylate polymers.

Acidizing damage mechanisms include:

- Inadvertent injection of solids.
- Use of incompatible additives or improper mixing procedures.
- Reprecipitation of acid reaction products.
- Loss of near-wellbore formation compressive strength.
- Formation of emulsions.
- Formation of sludge.
- Water blocking.
- Wettability alteration.
- Post-treatment fines migration.

The reprecipitation of reaction products is a serious concern in sandstone acidizing containing aluminosilicates. Many reactions take place in the formation as HF injection proceeds.

Table 5: Possible precipitates in sandstone acidizing (Schlumberger, 2003)

Precipitate	Origin
Calcium fluoride (CaF_2)	Carbonate-HF reaction CaF_2 can be caused by an inadequate HCl preflush to remove calcium ions from calcite cementing materials or to flush calcium chloride completion fluids away from the near wellbore.
Amorphous silica	Clay and silicate dissolution in HF. Amorphous silica results from both secondary and tertiary HF acidizing reactions.
Sodium and potassium fluosilicates	Feldspar and illite clay dissolution in HF produce these primary reaction products. They can also form if seawater or sodium or potassium brines are mixed with spent HF.
Sodium and potassium fluoaluminates	Silico-aluminate dissolution in HF. Fluoaluminates, like fluosilicates, occur when spent mud acid (H_2SiF_6) reacts with the formation. They can also form if seawater or sodium or potassium brines are mixed with spent HF.
Aluminium hydroxides and fluorides	Clay and feldspar dissolution in HF can cause these precipitates.
Iron compounds	Iron minerals or iron oxides (rust) can react with HCl-HF to produce these compounds.

Geothermal wells acidizing procedures

Acidizing geothermal wells is related to sandstone acidizing in that most geothermal reservoirs produce from volcanic rocks (andesite). Formation conditions are often conducive to large-volume, high-rate acid treatments. In geothermal wells, the strongest indication of acid-removable formation damage is a sharp drop in production rate. Nearly all geothermal wells that are acidizing candidates have been damaged by:

- Drilling mud solids and drill cuttings lost to the formation fractures.
- Scale (calcium carbonate, silica, calcium sulphate, and mixtures).

Various methods have been tried to prevent scaling in geothermal wells, including varying pressure, temperature or pH changes and scale inhibitors. If scale inhibitors have solved many problems, one promising alternative method is the acidizing. One thing geothermal wells have in their favour is that complete damage removal is not necessary. Partial removal of damage with acid treatment may eventually result in complete damage removal when the treated well produces back. The high-rate and high-energy backflow from geothermal wells can blow out damage that was not dissolved by acid. Damage that was softened, broken up, or detached from downhole tubulars and fracture channels can be produced back through a large diameter casing completion.

Erosion of production lines may occur if drill cuttings are produced back during blow down of a well after stimulation. Care must be taken in this regard. A temporary flow line may be required until solids production has stopped. A very successful method of acidizing geothermal wells has been a basic, high-rate, brute-force method. High acid concentrations have been shown to be effective in geothermal wells producing from natural fractures not containing separate, large carbonate zones. Hydrochloric acid (HCl), hydrofluoric acid (HF) or both have been used since the 1980’s in hydrothermal wells. Strawn (1980) listed yet these two acids as the most effective ones. HCl was selected to treat limestone, dolomite and calcareous zones whereas HF was used to dissolve clay minerals and silica.

The only acid additives necessary in a geothermal acid job are:

- Corrosion inhibitor and inhibitor intensifier (often required).
- High-temperature iron-control (reducing) agent.

Water-wetting surfactants, necessary in oil well stimulation, are not needed in geothermal wells because of the absence of hydrocarbons. Suspending agents (nonemulsifier surfactants) are also not needed, although they seem to be included often in geothermal well stimulation job proposals. Clay stabilizer is not needed. Conventional acid placement techniques are less effective for the long, open-hole or liner-completed intervals typically encountered in geothermal wells. High-temperature foam systems may improve zone coverage. Gelling agents for thickening acid have been shown to be ineffective in geothermal liner completions. **The best way to maximize acid coverage in geothermal wells is by pumping at maximum injection rates.** During the 1990's, the acidification technique has been used more often, principally for the reservoir development or to treat formation damage caused by drilling mud and scaling (mineral deposits) in geothermal wells (Buning et al, 1995; Buning et al, 1997; Malate et al., 1997; Yglopaz et al., 1998; Malate et al., 1999, Barrios et al., 2002, Jaime-Maldonado and Sánchez-Velasco, 2003). This protocol has not really evolved since these years. In each of the experiments proposed by the authors, the same technique is used.

The acidification occurred in three main steps:

1. A preflush, usually with hydrochloric acid (10%). The objective of this preflush is to displace the formation brine and to remove calcium and carbonate materials in the formation. The preflush acid minimizes the possibility of insoluble precipitates.

2. A main flush with hydrochloric – hydrofluoric acid mixture. A mixture of 10% HCl – 5% HF (called Mud acid) is generally prepared by dissolving ammonium bifluoride (NH4HF2) in HCl. A mixture of 1% of HCl and 56 kilos of NH4HF2 will generate 1% HF solution. Regular mud acid (12% HC l- 3% HF) is made from 15% HCl, where 3% HCl is used to hydrolyse the fluoride salts.

3. A postflush/overflush usually by either HCl, KCl, NH4Cl or freshwater. Concerning the injected amounts for the cleaning out of the geothermal wells, the mainflush volume was based on a dosing rate of 900 litres per metre of target payzone. The preflush volume was based on a dosing rate of 600 litres per metre of target zone (Malate et al., 1997; Barrios et al., 2002).

Chemical stimulation with chelating agents

An alternative to acid treatment is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA). Such chelating agents have the ability to chelate, or bind, metals such as calcium. Through the process of chelation, a calcium ion would be solvated by the chelating agent, allowing the calcite to be transported either to the surface by flowing the well or further into the formation by injecting into the well. The rate of calcite dissolution using chelating agents is not as fast as is the rate of calcite dissolution using strong mineral acids. The lower dissolution rate means that the chelating agent will be able to take a more balanced path and more evenly dissolve calcite along the wellbore and in all available fractures, rather than following the first fluid entry zone and leaving the rest of the wellbore relatively untouched.

The current state-of-the-art method for chemically removing wellbore silica scale is through HF treatments, which are expensive and hazardous. Laboratory data indicate, however, that aqueous solutions at high pH can dissolve wellbore silica and near-wellbore formation silica and quartz reasonably well and at much lower cost than HF treatments. What has prevented geothermal operators from using caustic solutions in the past is the fear of calcite deposition, which is strongly favored at high pH. Laboratory studies have indicated that calcite is dissolved rather than precipitated at high pH in the presence of chelating agents. This suggests that thermally stable chelating agents at high pH can provide the basis for an affordable and effective mineral dissolution approach.

Although thermal stability studies have not been completed, the literature suggested that NTA could be used at temperatures as high as 290°C, whereas the other two chelating agents, EDTA and HEDTA, were significantly less thermally stable with maximum use temperatures in the range of 200°C. The calcite dissolution experiments in the high temperature flow reactor confirmed the superior performance of NTA above 200oC. Therefore, a field experiment was designed for dissolving calcite and other minerals with a high pH solution of NTA in GPK4 well.

Challenges in sandstone acidizing still exist, although great improvements have been made in the last decade. Factors that contribute to these challenges include: multiple types of co-existing formation damage; uncertain rock mineralogy; multiple fluids and pumping stages; complex chemical reactions between fluids and formation minerals; and fast reaction kinetics at elevated temperatures. Others are: inadequate zonal coverage; limited active acid penetration; rock deconsolidation due to acid-rock interactions; acid emulsion and sludge tendencies; corrosion; and health, safety and environmental (HSE) concerns. These factors contribute to the low success rate of sandstone acidizing treatments especially in acid-sensitive, and clay- and carbonate-rich sandstone formations at high temperatures.

New Environmentally Friendly Acid System for Iron Sulfide Scale Removal

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Iron sulfide scale exists in several forms with troilite (FeS) and pyrite (FeS2) as the most common types based on how rich the scales are in sulfur and ferric ions [5,9]. Iron sulfide scale type depends on the range of temperatures and the scale age. The scale materializes in a crystalline form having different ratios of sulfur to iron. The different forms of iron sulfide scale are: pyrrhotite (Fe7S8), troilite (FeS), marcasite (FeS2), pyrite (FeS2), greigite (Fe2S4), and mackinawite (Fe9S8) [5,9]. Several types of iron sulfide scale might exist in the same well. Usually hard or insoluble scales exist at shallower depths compared to the soft or soluble scales [10]. **Using HCl cannot remove all the existing forms of iron sulfide in the same well because it can remove FeS, but it cannot remove the FeS2 [11]**. Therefore, both chemical and mechanical treatments are used in such cases.

The other component of iron sulfide scale is the iron that is produced either from the formation brine or by the corrosion of the tubing which is controlled by using ineffective corrosion inhibitors [6]. Iron can be introduced into the formation during acidizing with iron from the corroded tank surfaces or from the corroded well tubular. This will cause iron scale deposits in the formation or in the wellbore. Well stimulation acids can dissolve rust of storage tanks which contains a mixture of iron (II) and iron (III) [13]. Iron-containing minerals in the formation represent other iron sources such as chlorite clay mineral, iron carbonate compounds, etc. **Iron compounds that precipitate during well stimulation can badly decrease the permeability of the reservoir** [9].

Iron Sulfide Scale Removal

There are several chemicals that are being used to remove iron sulfide scales. Such chemicals include hydrochloric and organic acids, acrolein, tetrakis (hydroxymethyl) phosphonium salts (THPS), and chelating agents (sequestrants). Generally, the iron sulfide scale is soluble in hydrochloric acid and organic acids as formic acid (HCOOH) [6]. When the iron scale depositions contain low sulfur content, it would have a higher degree of solubility in HCl acid [17]. Leal et al. [18] reported that pyrite and marcasite iron sulfides are acid-insoluble, pyrrhotite showed a slow pace solubility, while mackinawite and trolite are highly soluble in low pH DPTA with 5 wt.% HCl. Lawson [19] showed that maleic acid was supposed to be one of the ferrous sulfide dissolvers with minimal production of H2S. Wang et al. [10] concluded that HCl can be used to remove the soft type of iron sulfide scale (FeS). The major problem of using HCl to remove soft scale is the high corrosion rate, especially at high temperatures. In addition, acid dissolution reaction generates a large amount of H2S gas which can be a serious issue for well integrity and can increase the operational risk at surface facilities [3]. HCl also has a corrosion e_ect and, therefore, the removal formulation should include a corrosion inhibitor.

On the other hand, using corrosion inhibitors resulted in decreasing the dissolution rate of iron sulfide while using the surfactants increasing the dissolution rate [20]. Mutual solvents such as monobutyl glycol ether were useful as it removed the hydrocarbons exist on the surface of the iron sulfide scale [21]. The reaction of hydrochloric acid HCl with iron sulfide produces the toxic H2S gas as indicated by Equation (1), therefore, H2S scavenger has to be added to the removal formulation to remove the H2S [22]: FeS + 2HCl ! Fe+2 + 2Cl□1 +H2S.

Using other chelates such as ethylenediaminetetraacetic acid (EDTA) will possibly have the same reduction for the iron sulfide dissolution rate. Mahmoud et al. [24,25] introduced a new formulation that can be used to remove pyrite iron sulfide scale from oil and gas wells. The tested scale contained more than 80% pyrite and they used 20 wt.% diethylenetriamine pentaacetic acid (DTPA) chelating agent at pH 11 with 9 wt.% potassium carbonate as a catalyst. The DTPA formulation dissolved 85% of the scale at 70°C for 48 h. Using THPS with EDTA as a chelating agent for removal of iron sulfide scale from a real field sample resulted in 70% solubility. The THPS and EDTA solution made had a neutral pH that would reduce the corrosion rate and consequently reduce the adding of corrosion inhibitors [35].

Scale Deposits in Porous Media And Their Removal By EDTA Injection

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Abstract

Formation damage has been observed in several oil reservoirs and production equipment in Iranian oil fields. Laboratory and field testing confirmed that the primary cause of damage was the build-up of calcium carbonate, calcium sulfate and strontium sulfate scale either in the perforation tunnels or in the formation sandstone nears the wellbore. Conventional acid treatments could dissolve this scale, but scale precipitation from the spent acid caused rapid productivity decline. A scale removal treatment with EDTA has been developed that can effectively dissolve scale and chelate the dissolved metal ions. Chelation of the dissolved scale prevents scale reprecipitation.