Technical report

Review on chemical stimulation techniques in oil industry and applications to geothermal systems

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1   Introduction

The Enhanced Geothermal Systems (EGS) are dedicated to the exploitation of the heat present in deep hot rocks of limited permeability. But this extraction is only feasible if the reservoir permeability is sufficient to ensure a fluid circulation between injection and production wells. Economic exploitation of enhanced geothermal systems is dependant on natural or induced mineral precipitation and associated decrease in permeability of the system. This may inhibit fluid flow in well casings or in rock fractures and therefore decrease the heat extraction from the system. One solution to this problem consists in injecting a reacting fluid into the wells, in order to dissolve the secondary minerals scaled on the casing or partially sealing the fractures, to increase the permeability and hence to develop the reservoir.

A study of the literature on acidification of geothermal reservoirs has been attempted mainly based on the Proceedings of the annual Stanford Workshop on Geothermal Reservoir Engineering, the annual Transactions of the Geothermal Resources Council and the last three World Geothermal Congress. Surprisingly, the number of references is very limited, with few recent papers and most of the studies were carried out by a team from the Philippines. Apparently, experiments in geothermal fields are not all published. On the other hand, a wealth of research and publications is mainly available on these topics in the oil industry literature.

Chemical stimulation techniques were originally developed to increase or to recover oil and gas wells production rates to commercial levels. This technology, developed for more than one century by oil industry for the stimulation of oil and gas wells, has also been used in geothermal wells for the last 20 years.

Acid stimulation jobs intend to clean (pre-existing) fractures by dissolving filling materials (secondary minerals or drilling mud) and mobilizing them for an efficient removal by flow transport. Acid treatments have been applied to wells in oil and gas bearing rock formations for many years. Acidizing is probably the most widely used work-over and stimulation practice in the oil industry. By dissolving acid soluble components within underground rock formations, or removing material at the wellbore face, the rate of flow of oil or gas out of production wells or the rate of flow of oil-displacing fluids into injection wells may be increased.

The role and the impact of the different reactants used for the chemical treatments (hydrochloric acid (HCl), hydrofluoric acid (HF), chelatants and mixed compounds) will be explained and some examples of acidizing treatments in geothermal wells will be described. First, various methods used to prevent scaling in oil, gas and geothermal wells or to improve the reservoir fracturation will be presented in this note. The second part of this note will be focused on the chemical stimulation of sandstone reservoirs. Acidizing geothermal wells can be related to sandstone acidizing techniques, because most geothermal reservoirs produce from silicated magmatic or volcanic rocks. Finally, the third part of this technical note is more focused on the cleaning of geothermal wells.

2 Brief history and experience acquired with acidizing

The main objective of a stimulation treatment is to increase the rate at which the formation delivers hydrocarbons naturally. Acid treatments have been applied to wells in oil and gas bearing rock formations for many years. Acidizing is a widely used work-over and stimulation practice in the oil industry. By dissolving acid soluble components within underground rock formations or removing material at the wellbore face, the flow rate of oil or gas out of production wells or the flow rate of oil-displacing fluids into injection wells may be increased.

Acidizing predates just about all well stimulation techniques. Other techniques, such as hydraulic fracturing, were developed much more recently. Acidizing may, in fact, be the oldest stimulation technique still in modern use. The earliest acid treatments of oil wells are believed to have occurred as far back as 1895. The Standard Oil Company used concentrated hydrochloric acid (HCl) to stimulate oil wells producing from carbonate formations in Lima, Ohio, at their Solar Refinery. The acidizing process was applied with great success in the Lima, Ohio wells. Many wells were acidized with remarkable results in the short term. However, the first acid treatment in 1895 was probably considered a novel idea that would not last very long, and acidizing was used very infrequently during the next 30 years probably due to the lack of an effective method for limiting acid corrosion. However, throughout its history, acidizing has a repeating record of quickly and inexplicably losing popularity, seemingly independent of results at times.

Because of the growing interest surrounding acid treatments of limestone formations, new treatments for sandstone formations began to appear. In 1933, Halliburton conducted the first sandstone acidizing treatment using a mixture of hydrochloric and hydrofluoric acid (HF), in a test well belonging to the King Royalty Co., near Archer City, Texas. Unfortunately, the results of first attempt were very discouraging. Dowell did introduce a mixture of 12% HCl – 3% HF, called "Mud acid", in 1939. Successful wellbore treatments were pumped in the Gulf Coast area. This acid mixture is still quite common and is now known as "regular strength" mud acid.

In 1947, the first hydraulic fracturing treatment was completed in the Hugoton Field (Kansas) and fraccing has also become a standard treatment to improve production. Since that time, hydraulic fracturing has increased recoverable reserves more than any other technique. Historically, carbonate fracture acidizing has experienced limited success in geologic reservoirs characterized by high-closure stress or temperatures above 120° C. Although many formations in North America are sandstone and require the use of granular propping agents, acid fracturing is more commonly used in Europe and the Middle East, especially in Bahrain and Saudi Arabia.

Numerous matrix acidizing treatments of sandstone formations have been conducted since the mid-1960s. In the 1970s and early 1980s there was a proliferation of "novel" sandstone acidizing systems, in order to provide certain benefits such as retarding HF spending, stabilizing fine particles, preventing precipitation of HF-rock reaction products. In the 1980s and into the 1990s, developments in sandstone acidizing addressed treatment execution more than fluid chemistry. More recently, fluid chemistry has again stepped to the forefront (twists on old systems are developed).

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.

3 Technology overview

Advances in oil and gas well stimulation—matrix acidizing, fracture acidizing, hydraulic fracturing, extreme overbalance operations—enable operators to optimally increase well/reservoir productive capacity. Two basic types of acidizing operations can be conducted:

(1) **Matrix acidizing** is performed below fracturing rate and pressure. Acid flows through the matrix with reactions taking place in existing pores and natural fractures.

(2) **Fracture acidizing** is performed above fracturing rates and pressures. Etching of the created fractures provides well stimulation, not just damage removal.

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

The design of any acid-stimulation treatment should begin with a thorough evaluation of the characteristics of the targeted formation. The composition, structure, permeability, porosity, and strength of the rock must be determined, along with formation temperature and pressure and the properties of reservoir fluids.

Furthermore, understanding reservoir mineralogy is essential to designing truly effective acidizing treatments. For most of the 20th century, acidizing oil and gas wells to optimize production gave unacceptably erratic results in primary and remedial applications. The reliability and effectiveness of acid-stimulation technology began to change for the better in the mid-1990s, driven by improved understanding of the complex chemical and physical reactions of minerals with acidizing fluids. Both fundamental and applied research, and results of field work all have confirmed that—whether in a sandstone or carbonate reservoir, a mature field, deepwater environment, or high-temperature reservoir—reliably achieving long-term production increases from acidizing requires a thorough understanding of the formation mineralogy.

Essentially, the productivity of a given well may be impaired either by the natural characteristics of the reservoir rock and fluids or by damage resulting from drilling, completion or production operations. Fracture acidizing treatments can be designed that penetrate deep into lower permeability rock.

3.1 Matrix acidizing

This process is performed below fracturing flow rate and pressure and is normally used for the removal of skin damage associated with work-over, well killing or injection fluids and to increase formation permeability in undamaged wells.

3.1.1 Protocol

It is in the removal of near-wellbore formation damage that acidizing find its primary application. With respect to acidizing, especially sandstone acidizing, assessment of formation damage is perhaps the single most important factor in treatment design. To assess formation damage, it is first necessary to know the skin term in the Darcy's law equation defining well production rate, and its effect on production rate. The production rate is directly proportional to permeability and inversely proportional to skin. Skin damage is a mathematical representation of the degree of damage present. Permeability and skin can be measured with a pressure transient well test. Formation damage can occur during any well operation, including:

- drilling;
- cementing;
- perforating;
- production;
- workover;
- stimulation.

Therefore, in assessing formation damage, all aspects of a well and its history should be investigated, including:

- reservoir geology and mineralogy;
- reservoir fluids;
- offset well production;
- production history;
- drilling history (including fluids used);
- cementing program (including cement bond logs);
- completion and perforation reports (including fluids used);
- workover history;
- stimulation history.

In order to make the most of acidizing, acid treatment design must be approached as a process. The general approach is as follows:

1- select an appropriate stimulation candidate well;
2- design an effective treatment;
3- monitor the treatment for subsequent improvement.

Treatment volumes for matrix acidizing range from 120 to 6,000 liters per meter (L/m) of targeted interval, pumped at the highest rate possible without fracturing the formation.

3.1.2 Conventional acid systems

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

- Hydrochloric, HCl
- Hydrofluoric, HF
- Acetic, CH_3COOH
- Formic, HCOOH
- Sulfamic, H_2NSO_3H
- Chloroacetic, $ClCH_2COOH$.

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 $CaCl_2$ and CO_2, 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.

3.1.3 Retarded Acid Systems

HCl and HF are two acids reacting quickly with carbonates and silicates. However, the objectives of acid treatment are to increase porosity and permeability of the medium, deeply in the formation. Methods, which have been developed to slow the acidizing process, include:

- Emulsifying the aqueous acid solutions in oil (or solvents such as kerosene or diesel fuel) to produce an emulsion, which is reacting slower.

- Dissolving the acids in a non-aqueous solvent (alcohol, gel,...).

- The use of non-aqueous solutions of organic chemicals which release acids only on contact with water.

- The injection of solutions of methyl acetate, which hydrolyses slowly at very high temperatures to produce acetic acid.

In addition to these methods, of which emulsifying the acid is probably the most important, some retardation of the reaction rate can be achieved by gelling the acid or oil wetting the formation solids. Gelled acids are used to retard acid reaction rate in treatments such as acid fracturing. Retardation results from the increased fluid viscosity reducing the rate of acid transfer to the fracture wall. However, use of the gelling agents (normally water soluble polymers) is limited to lower temperature formations as most gelling agents degrade rapidly in acid solution at temperatures above 55°C.

Some retardants can be added to the mud acid (HCl-HF mixture) to slow the reaction rate of acid with the minerals. A key is to inject a solution not containing HF explicitly but a compound able to generate HF at greater depth of penetration and longer reaction time for maximum dissolution of fines (Crowe et al., 1992). This retardant hydrolyzes in water when it enters in the reservoir to form HF according to the reaction:

$HBF_4 + H_2O \rightarrow HBF_3OH + HF$
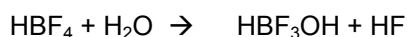
Other retardant systems can be used as the emulsifying of the aqueous acid solutions in oil, the dissolving of the acids in a solvent (alcohol, gel…) or the injection of solutions of methyl acetate, which hydrolyses slowly at very high temperatures to produce acetic acid.

Malate et al. (1998) also proposed an acid system applicable for moderate to deep penetrations. They used a phosphonic acid complex (HEDP) to hydrolyse NH_4HF_2 instead of HCl. HEDP has 5 hydrogens available that dissociate at different stochiometric conditions. Mixture of HEDP acid with NH_4HF_2 produces an ammonium phosphonate salt and HF.

3.1.4 Other compounds: Chelatants

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. As a consequence, the use of chelatants needs small amounts of inhibitor to protect the casings.

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.

3.2 Fracture acidizing

Fracturing treatments are defined as treatments in which the injection rate of the fluid is larger than the fluid leakoff into the matrix of the formation. Pressure in the wellbore will therefore buildup and eventually lead to tensile failure of the rock, creating a conductive channel. Because of the reactive nature of the fluid, the addition of acid in treatments can dissolve and remove primary and secondary minerals (scales) sealing the fractures. The aim is to change the future flow pattern of the reservoir from radial to linear to effectively stimulate the reservoir and increase production.

In fracture acidizing, the ideal, but rarely achieved outcome is a fracture plane that is continuously conductive from the wellbore all the way to the tip to provide maximum production enhancement from the

surrounding rock. To be effective, etched fracture surfaces must retain sufficient conductivity for production enhancement after fracture closure.

Although a large mass of rock may be dissolved, if the resultant fracture face dissolution does not render the surfaces with sufficient differential relief, the fracture conductivity under closure stress will be low at least for sedimentary rocks. If the acid spends too quickly, excessive spending and acid leakoff near the wellbore will result in little or no conductivity toward the fracture tip. Lack of active acid penetration deep along the fracture plane will result in very short conductive fractures.

Sometimes, acid fracturing was preferred to hydraulic fracturing because proppant cleanout in a well with coiled tubing required operational and safety resources. Additionally, the high conductivity of an acid-etched fracture made acid fracturing a more attractive technique if comparable fracture lengths could be achieved. After several acid fracturing treatments were experienced, it became clear that a normal response of the treated wells was a sharp production increase followed by a slight gain in average production.

Also called acid fraccing, this technique is widely used for stimulating limestone, dolomite formations or formations presenting above 85 % acid solubility. It consists to inject first a viscous fluid at a rate higher than the reservoir matrix could accept leading to the cracking of the rock. Continued fluid injection increases the fracture's length and width and injected HCl acid reacts all along the fracture to create a flow channel that extends deep into the formation. The key to success is the penetration of reactive acid along the fracture. However, the treatment volumes for fracture acidizing are much larger than the matrix acidizing treatment, being as high as 12 000 - 25 000 L/m of open hole.

Three geometric quantities are needed for proper treatment design:

- Acid penetration: distance travelled by acid at end of pumping.

- Live acid penetration: farthest point reached by live acid at end of given pumping stage (live HCl strength > 0.10%).

- Etching distance: maximum distance that etching has occurred. For a one acid stage treatment this is the same as live acid penetration.

3.2.1 Techniques

Acid fracturing is a stimulation technique where acid, usually HCl, is injected into the reservoir at fracturing pressures. Fracture acidizing is also called acid fracturing, acid-fraccing or acid-fracture treatment.

Acid (normally 15% HCl) is then injected into the fracture to react with the formation and create a flow channel (by etching of the fracture surface) that extends deep into the formation. This allows more reservoir fluid to be drained into the wellbore along the new fractures once the well is put back to production.

As the acid flows along the fracture, the fracture face is dissolved in a nonuniform manner, creating conductive or etched channels that remain open when the fracture closes. The effective fracture length is a function of the type of acid used, the acid reaction rate, and the fluid loss from the fracture into the formation. The length of the etched fracture limits the effectiveness of an acid-fracture treatment. The fracture length depends on acid leakoff and acid spending. If acid fluid-loss characteristics are poor, excessive leakoff will terminate fracture extension. Similarly, if the acid spends too rapidly, the etched portion of the fracture will be too short. The major problem in fracture acidizing is the development of wormholes in the fracture face; these wormholes increase the reactive surface area and cause excessive leakoff and rapid spending of the acid. To some extent, this problem can be overcome by using inert fluid-loss additives to bridge wormholes or by using viscosified acids.

The effective length of an acidized fracture is limited by the distance that acid travels along the fracture before it is spent. This is controlled by the acid fluid loss, the reaction rate and the fracture flow rate. This problem is more difficult to solve when the acid reaction rate is high, owing to high formation temperature.

The acid fluid-loss mechanism is more complex than that of non-reactive fluids. In addition to diffusive leak off into the formation, flowing acid leaks off dynamically by dissolving the rock and producing wormholes. Wormholes are very detrimental in fracture acidizing. They greatly increase the effective surface area from which leak off occurs and are believed to affect acid fluid loss adversely. Acid leaks off predominantly from wormhole tips rather than the fracture face. As wormholing and excessive leak-off occur, the leak-off rate exceeds the pump rate, and a positive net fracturing pressure cannot be

maintained to keep the fracture open. At this point in the treatment, this may be as soon as 6 minutes after starting to pump acid, the fracture extension slows or stops.

Acid fluid loss control has long been a problem in fracture acidizing. The most common techniques involve use of viscous pads. The principle behind these is to lay an impermeable filter cake on the fracture face and minimize wormholing. In practice these filter cakes are relatively ineffective in controlling acid fluid loss because of the quick penetration in wormholes and the constant erosion of fracture faces during treatment.

The key to success is penetration of reactive acid along the fracture. This is more difficult to achieve in acid fraccing than in propped fractures (the other main form of frac treatment). Acid penetration is particularly important in low permeability formations which are frequently subject to scaling where small fractures meet larger fractures. Acid fracturing methods, which can achieve deep acid penetration, offer large potential to solve scaling problems.

3.2.2 Fluids used

To achieve deeper penetration in fracture acidizing, it is often desirable to retard acid reaction rate. This can be done by gelling (polymers and surfactants), emulsifying, or chemically-retarding the acid, in effect, making it more difficult for the H^+ ions to contact a reactive surface. Also HCl can be retarded by adding $CaCl_2$ or CO_2. Another approach is to use naturally retarded acetic or formic acid.

An ideal fracture acidizing fluid is able to penetrate long distances, etch fracture faces, increase the permeability of the matrix where the fluid enters the formation by diffusion, and remove any existing formation damage (Table 1). In addition the low viscosity of the fluid means that maximum production rate should be attained quickly following the treatment. The pad fluid used in conventional treatments would probably be needed.

Table 1: Fluid properties required from an acid fracturing fluid are shown in Table below.

Acid fracturing fluid properties required	Low viscosity
	Etches fracture face by dissolution
	Leaks off into formation mainly by diffusion
	Causes minimal formation damage
	No wormholing

Fluids used in the fracture acidizing process (pad fluid, acid or additives) can be detrimental to well performance following the job. This can be due to clean up problems or a reduction in the formation permeability adjacent to the fracture.

A particular problem is the removal of high viscosity fluids. The time required to achieve cleanup increases significantly as fluid viscosity increases. Similar increases in cleanup time are seen as fracture length increases.

Ideally the best acid system for fracturing is one that only etches the fracture face by dissolution and leaks off into the formation mainly by diffusion. It is also very desirable to be able to obtain deep penetration along fractures without resorting to the use of high viscosity components.

3.2.3 Typical treatment modes

Acid solubility of the formation is a key factor influencing whether fracture acidizing or proppant treatments should be employed. If the formation is less than 75% acid soluble, proppant treatments should be used. For acid solubilities between 75 and 85%, special lab work can help define which approach should be used. Above 85% acid solubility, fracture acidizing would be the most effective approach.

There are four primary fracture acidizing processes:

   - Fluid-loss control strives to contain the acid in natural/ created fractures.
   - Conductivity enhancement pumps a viscous fluid padpumped ahead of the acid to generate a fracture geometry. Subsequent acid injection then fingers through the viscous pad. The process

results in longer acid penetration distances and more effective conductivity at a greater distance along the induced fracture.

- Etched height control uses fluid density differences to control fluid placements, such as avoiding water-producing zones or gas caps.

- Tailored treatments may include foamed acids, heated acids, zonal coverage acid, and closed-fracturing acid.

Fluid-loss control is critical for achieving a good fracture acidizing treatment. Acid leakoff can be controlled by viscosifying the acid, adding solid particulates or using alternate stages of acid and nonacid fluids. Methods for thickening acid include emulsified acid, foamed acid, polymer gelled acid, and surfactant gelled acid. Silica flour and 100-mesh sand are common solid particulates.

In larger open hole, acid diversion is important, otherwise only the interval, which breaks down or fractures first will be treated. Diversion can be achieved with packers.

The following techniques have been developed:

- Viscous preflush in fracture acidizing.
- Chemically retarded acid for selective etching.
- Combination of density and viscosity controlled fracture acidizing.

Various acid combinations are employed. However, a frequent mixture is 15% HCl and 10% acetic acid.

A typical treatment consists of pumping the acid mixture at pressures of 0.1 to 0.3 bar per metre. When acid is pumped at high rates, over 1000 liters per minute, it is called fracture acidizing. Several services companies offer some or the whole series of chemical treatments for oil, gas or geothermal wells as shown on figure 1.
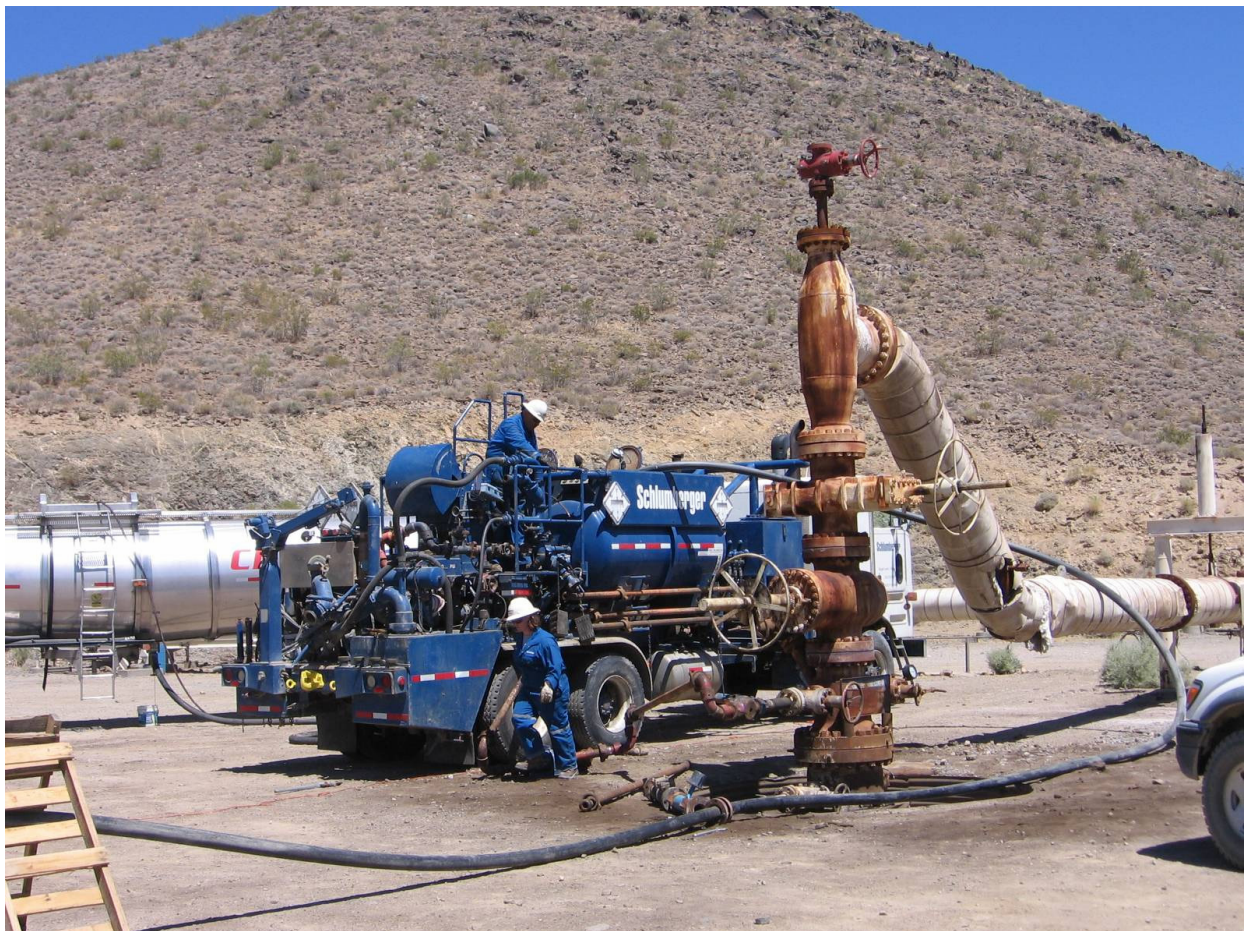
Figure 1: Installation of a pumping unit for injection of chemical compounds at Coso geothermal field (photo P. Rose, EGI, Univ. of Utah)

4   Chemical stimulation in sandstone reservoirs

The objective of acidizing sandstone wells is to increase permeability by dissolving clays and other pore plugging materials near the wellbore. Clays may be naturally occurring formation clays or those introduced from drilling, completion or workover fluids.

Treatment fluid selection in sandstone formations is highly dependent on the mineralogy of the rock as well as the damage mechanism. Hydrofluoric (HF) acid is typically used to dissolve the damaging silicate particles. Nonacid systems are sometimes used to disperse whole mud and allow it to be produced with the treating fluid. The criteria for selecting the treating fluid are mineralogy, formation damage mechanism, petrophysics and well conditions.

The treating fluid, therefore, must remove existing damage without creating additional damage through interactions with the formation rock or fluids. A formation is sensitive if the reaction between the rock minerals and a given fluid induces damage to the formation. The sensitivity of a formation to a given fluid includes all the detrimental reactions that can take place when this fluid contacts the rock. These detrimental reactions include the deconsolidation and collapse of the matrix, the release of fines or the formation of precipitates. The precipitation of some damaging compounds cannot be avoided. Treating and overflush fluid stages are sized; so, there is sufficient volume to push potential precipitates deep enough into the reservoir to minimize their effects because of the logarithmic relationships between pressure drop and distance from the wellbore.

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).

4.1   Sandstone acidizing process (treatment design)

There are a limited number of reasons why sandstone acidizing treatments do not succeed.

The six-step process to successful sandstone acidizing is as follows:
1. determine the presence of acid-removal skin damage;
2. determine appropriate fluids, acid types, concentrations, and treatment volumes;
3. determine proper treatment additive program;
4. determine treatment placement method;
5. ensure proper treatment execution and quality control;
6. evaluate the treatment.

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.

Sandstone acidizing reactions occur where the fluids meet minerals. As fluid is injected, the position of the zone where reactions take place moves radially outward from the wellbore. As the acid moves through the near wellbore region where all acid soluble minerals have been dissolved, it retains its full strength. Acid spending takes place in the reaction front. The radial width of this zone depends on the

minerals present and the temperature of the reservoir at the point of contact, which is affected by any residual cool down effects due to difference between fluid and rock temperature. When the injected fluid is totally spent, it moves through the unreacted minerals.

The primary reactions occur when fresh acid contacts fresh reservoir. This typically happens in the near wellbore region. As spent acid moves through this same matrix, the secondary and tertiary reactions occur with the reaction products precipitating further away from the wellbore. It is important to keep the injected fluid moving to carry reaction products past the critical matrix region of the well.

Proper treatment design can be very effective in decreasing the negative effects of pumping acids into sandstone through the use of multiple injection stages and correct fluid selection. A typical matrix treatment in a sandstone will include a preflush, a main fluid and an overflush. When long intervals are treated, diversion stages are pumped after the overflush and before the next stage of preflush.

4.1.1 Preflush

The sequence of fluids used in a sandstone treatment is largely dependent on the damage type(s) being addressed.

A preflush is a fluid stage pumped ahead of the main treating fluid. Multiple preflush stages are sometimes used to address multiple damage mechanisms and prepare the surface for the main treatment fluids. In sandstone reservoirs, the acid preflush, performed most often with a HCl solution, serves two purposes:

- To displace the formation brines, usually containing K, Na, or Ca ions, away from the wellbore so there will be no mixing with HF acids. This decreases the probability of forming alkali-fluosilicates such as potassium hexafluorosilicate.

- To dissolve as much of the calcareous material as possible, prior to injection of the HF acid to minimize calcium fluoride precipitation.

Due to reservoir heterogenities, it is unlikely that the acid preflush will remove all of the calcite. However, it has been shown that reducing calcite below 6% is sufficient to avoid precipitation (Figure 2). This has been investigated and confirmed by fieldwork done by McLeod (1984) and others. Strength and volume guidelines are based on this criterium (Economides and Nolte, 1987).
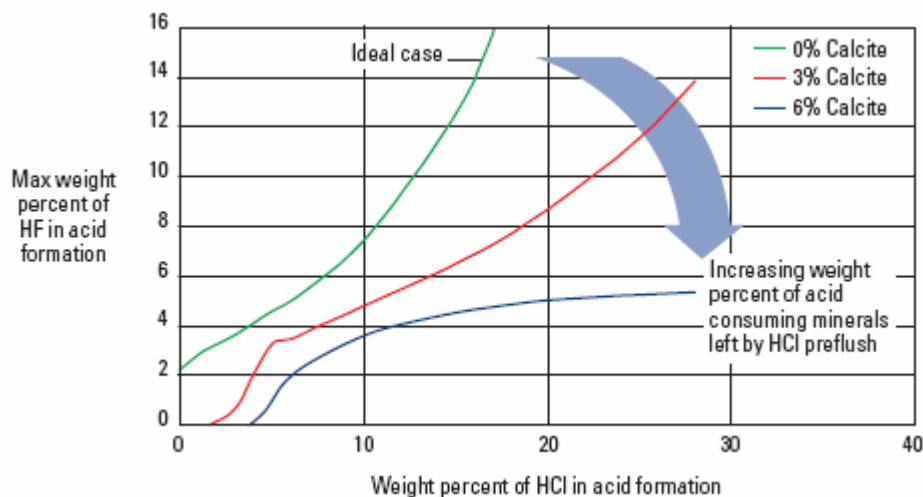
Figure 2: HCl/HF ratio to avoid precipitation, based on AlF$_3$ and CaF$_2$ precipitation (Schlumberger, 2003)

HCl can shrink hydrated clays, however, most clays have very little solubility in HCl. One possible exception is chlorite, an iron-rich, three-layer clay. Strong HCl can leach Fe^{2+} iron (and possibly aluminium and magnesium) from chlorite, leaving an amorphous silica residue. HCl does not dissolve sand. However, HCl can dissolve carbonates present in sandstone formations.

Using an additional ammonium chloride (NH4Cl) brine preflush for sandstone acid treatments is an emerging practice. This preflush conditions the formation clays as it moves formation water away from

the near wellbore area. The NH4$^+$ ions in the brine exchange with the alkali (Na, K, or Ca) ions on the clay particles; so, they will be displaced from contact with the mud acid. The effectiveness of this procedure appears to be controlled by the brine concentration at a radial distance of 0.75 m from the wellbore. This preflush is pumped at the start of the job to establish injectivity before the regular mud acid treatment is pumped. It is only pumped once and is not a part of the regular treating sequence.

4.1.2 Main flush

The main fluid in a sandstone acid treatment is the fluid used to remove the damage. It is typically a mixture of hydrofluoric (HF) and hydrochloric (HCl) or organic acids. HF acid is used because it is the only common, inexpensive mineral acid able to dissolve siliceous minerals. It is mixed with HCl or organic acid to keep the pH low when it spends to aid in prevention of detrimental precipitates. These mixtures are called mud acids because they were originally developed to treat siliceous drilling mud damage. HF acid should not be used in sandstone formations with high carbonate content. The risk of forming calcium fluoride precipitates is too great, since it is unlikely that a sufficient amount of HCl acid preflush can be pumped. The accepted cutoff point for the use of hydrofluoric acid is 20% calcite + dolomite based on the guidelines developed by McLeod in 1984.

Hydrofluoric acid (HF) can dissolve carbonates, clays felspars, micas, chert and quartz. However, the primary reason to use HF acid is to remove clay. If any carbonates are present in a sandstone, these should be removed with a preflush of HCl. If a sandstone formation contains more than 20% carbonate, the well should be acidizied with HCl only. Table 2 shows the chemical composition of minerals that are typically present in sandstones and generalizes the solubility of these minerals in HCl and HCl-HF.

Table 2: Solubility of sandstone minerals

Minerals	Solubility	
	HCl	HCl-HF
Quartz	No	Very low
Felspars	No	Low to moderate
Micas	No	Low to moderate
Kaolinite	No	High
Illite	No	High
Smectite	No	High
Chlorite	Low to moderate	High
Calcite	High	High, but CaF$_2$ precipitation
Dolomite	High	High
Ankerite	High	High
Siderite	High	High

During the mainflush, the HF acid reacts mainly with the associated minerals of sandstones (clays, feldspars and micas), rather than with quartz. The reaction rates of HF with clays or feldspars are 100 to 200 times faster than the one with quartz. It results from these reactions an enlargement and interconnections of the pores in the matrix, facilitating fluid flow. The risk of using HF acid is the strong affinity of Si and Al with F, which can cause the precipitation of silicium or aluminum complexes (SiF_6^{2-}, AlF^{2+}, AlF_2^+, AlF_3, AlF_4^-), then damaging the formation by plugging. This is why HCl is added to HF: hydrochloric acid keeps a low pH and prevents the formation of fluorosilicates, fluoroaluminates, and fluoride salts.

The trend in HF acid concentration is away from the previous standard 3% HF + 12% HCl.

1.5% HF + 13.5% HCl is becoming the normal choice and Table 3 shows general recommandations for specific well conditions.

Table 3: Alternate sandstone acid procedures for specific formation conditions

Well and formation conditions	Treatment fluid recommandation
Bottomhole treating temperatures > 100°C	1.5% HF + 13.5% HCl
Permeability < 5 md	1.5% HF + 13.5% HCl
Quartz content: Over 90% 50 to 90%	 3% HF + 12% HCl 3% HF + 12% HCl or retarded HF
Feldspar, 15 to 30%	1.5% HF + 13.5% HCl
Chlorite clay: 1 to 5% > 5%	 3% HF + 10% Acetic 1.5% HF + 10% Acetic or Formic

4.1.3 Overflush

The overflush is an important part of a successful sandstone acid treatment. It performs the following functions:

- Displacement of the nonreacted mud acid into the formation.
- Displacement of the mud acid reaction products away from the wellbore.
- Removal of potential oil-wet relative permeability problems caused by some corrosion inhibitors.

The overflush fluid must be miscible with the acid in order to displace it. Therefore, aqueous base liquids should be considered as the first displacing and flushing fluid. This may be followed by other fluid systems depending on the concerns and well conditions. Studies of displacement fronts indicate that the reactivity and fluid character of the overflush have a major influence on the volume required to displace the spent mud acid. Recent experience indicates the advantage of including HCl or acetic acid in the first part of the overflush to maintain a low-pH environment for the displaced spent mud acid stage. The minimum total overflush volume should provide at least 0.9 m of radial penetration into the formation to move potential problems past the critical matrix where the greatest pressure drop occurs. Damage effects are minimized beyond the critical matrix because of the logarithmic relationship between pressure drop and distance from the wellbore. Volumes that are less than twice the mud acid stage volume should be considered inappropriate. Formation permeability anisotropy may require doubling or even tripling this volume, if the reservoir pressure is sufficient to unload the injected fluid.

Large overflushes help prevent the near wellbore precipitation of amorphous silica. At formation temperatures of 93°C or greater, amorphous silica precipitation occurs while the mud acid is being pumped into the formation. The precipitate is somewhat mobile at first, but it can set up as a gel after flow stops. If this potentially damaging material is kept moving by the overflush fluid, it will be diluted and moved beyond the critical matrix.

4.2 *Acid strength versus composition of the formation*

The acid used as a preflush or an overflush to a main treatment containing hydrofluoric acid depends on the silt and clay content of the formation, its permeability and the presence of HCl sensitive minerals, like chlorite, glauconite and zeolites. For operational simplicity, the same acid is used for both pre- and overflush. Organic acids are recommended for use in conjunction with, or instead of, HCl in sensitive formations. Although they will dissolve the carbonate, they work more slowly. When pumping organic acids as stand-alone fluids, they should be mixed in ammonium chloride rather than fresh water. Organic acids also act as a low-pH buffer and complexing agent that helps minimize the tendency of iron compounds to precipitate as the acid spends. However, they do not dissolve iron scale or prevent clay swelling.

Determining the proper blend of HCl and HF to use in a mud acid mixture, and whether HCl or organic acid is used, is a complex process. The selection depends on the silt and clay content of the formation, its permeability and the presence of HCl sensitive clays. The criteria are similar to those for choosing the acid preflush or overflush concentration.

For the preflush operation in acidizing treatments, a solution of hydrochloric acid at a concentration of 10 to 15 % is most often used. For the mainflush, the mud acids generally range from 10 % HCl – 5 % HF to 12 % HCl – 3 % HF. Some examples of mud acids are given in Table 4 for the treatment of sandstones.

Table 4: Acid guidelines for the chemical treatment of sandstones according to the composition of the formation (after Crowe et al., 1992)

Temp. (°C)	Rock mineralogy (%)	Rock permeability (milliDarcy [md])					
		> 100 md		20 to 100 md		< 20 md	
		HCl (%)	HF (%)	HCl (%)	HF (%)	HCl (%)	HF (%)
< 100	High quartz (> 80), low clay (< 10)	12	3	10	2	6	1.5
	High clay (> 10), low silt (< 10)	7.5	3	6	1	4	0.5
	High clay (> 10), high silt (> 10)	10	1.5	8	1	6	0.5
	Low clay (< 10), high silt (> 10)	12	1.5	10	1	8	0.5
> 100	High quartz (> 80), low clay (< 10)	10	2	6	1.5	6	1
	High clay (> 10), low silt (< 10)	6	1	4	0.5	4	0.5
	High clay (> 10), high silt (> 10)	8	1	6	0.5	6	0.5
	Low clay (< 10), high silt (> 10)	10	1	8	0.5	8	0.5

The cleaner the sandstone (lower silt and clay content) and the higher the permeability, the lower the HCl/HF ratio, and the more aggressive the treatment can be. Typically, the HCl/HF ratio is either 4/1, 6/1, or 9/1. A higher volume of weak acid must be pumped to attain the same results as a smaller volume of a stronger acid. This is an important consideration when designing treatments for environmentally sensitive areas, where disposing spent acids can create problems. The ratio of HCl/HF should be increased if the formation contains clay rather than calcite cementing materials. If the HCl/HF ratio is less than 9/1, change the recommendation to the 9/1 ratio that contains a lower HF content. For example, if a 6% HCl + 1% HF fluid is normally used, change to a 4.5% HCl + 0.5% HF mixture. Mud acids should only be used in formations with less than 20% carbonate (calcite + dolomite) because of the increased risk of forming damaging calcium fluoride precipitates at higher carbonate content. HCl or acetic acids are used for these formations. The specific acid used is dependent upon reservoir temperature and the presence of HCl sensitive clays as shown in Table 4.

4.3   Review of current practices to successful sandstone acidizing

The rate of acid injection is dictated by allowable injection pressure. Selection of acid concentrations must be based on the formation characteristics. Knowledge of permeability, porosity and mineralogy is imperative. Amounts and types of clays and felspars are especially important to ascertain. This information can be obtained trough X-ray diffraction analysis. However, the location of minerals is of greatest importance. SEM (scanning electron microscopy) and thin-section analysis are additionally useful in identifying locations of quartz, clays, feldspars, carbonates, and other minerals.

For HCl-HF mixtures, a small amount of acetic acid (e.g., 3%) may be added to reduce precipitation of aluminium fluoride compounds, as the pH of the HCl-HF mixture rises with acid spending, by buffering the acid mixture and by complexing with aluminium, chelating effect.

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.

Coiled tubing (CT) is a very useful tool for improving acid placement. Coiled tubing utility is versatile. However, when applied properly, it is an excellent tool. Coiled tubing is of less use in fracturing acidizing because of rate limitations. It is still best to pump fracturing treatments through larger strings, such as production tubing. Coiled tubing is most useful in matrix and wellbore treatment. It offers some major advantages in acidizing, including:

- Ease with which an acid injection can be terminated, if it appears that continuing injection is not doing any further good, and switch to flush.

- Ease with which treatment displacement with nitrogen can be achieved quickly to push reactive fluids away from the wellbore, energizing the near-wellbore fluid zone, thereby enhancing flowback.

Disadvantages include:

- Pump rate limitations.

- Depth limitations in openhole sections of very deep deviated wells. But some experiments report coil tubing applications up to a depth of 4000 m.

- If solids are needed (perhaps for diversion), there may be problems pumping them through smaller diameter CT strings.

- Acid mixtures must be very thoroughly mixed and must remain that way prior to and during injection. Corrosion in a CT string is especially disastrous.

Overall, coiled tubing is very effective in placing acid, especially in smaller treatments, and treatments for damage very near the wellbore. Treatment evaluation involves the following:

- Pressure monitoring during injection will indicate diverter effectiveness and possibly evolution of skin removal. These methods for evaluating pressure responses are based on interpreting recorded wellhead pressure values and corresponding injection rates as treatment progresses.

- Flowback sample analysis is important for observation of sludge, emulsion, solids production, and related problems.

- Production rate comparison and analysis (before and after) is the most obvious and simple measure of success. Rate comparison should only be made seriously after all spent acid has been returned and well production has returned to formation fluids only.

- Well test analysis (skin removal). Post-stimulation well testing is the truest indicator of success or failure.

- Payout and ROI (return on investment) are among the bottom-line factors to the operator. Relative low-cost formation damage removal treatments, such as acidizing, are unrivaled in their potential financial significance.

Recently, there have been advancements with unconventional methods introduced to the industry by creative, reasonable risk-taking, stimulation design engineers. Some examples of such interesting methods are:

- Maximum rate/maximum pressure HF acidizing.

- High-concentration HF acidizing.

- CO_2-enhanced HF acidizing.

- On-the-fly minimum volume HF acidizing.

4.4 Acidizing damage

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 alumino-silicates. Many reactions take place in the formation as HF injection proceeds.

The chemical reactions between sandstone minerals and HF acids have been extensively described in the literature. There are three classes of HF reactions: primary, secondary and tertiary.

Primary reactions describe the action of the unspent acid with the various minerals. The presence of calcium (Ca^{2+}) will cause calcium fluoride (CaF_2^+) to precipitate. Sodium (Na^+) and potassium (K^+) can create alkali-fluosilicates and alkali-fluoaluminates when formation minerals, or sodium or potassium brines, react with the hexafluorosilicic acid produced by this reaction. The fluosilicate and fluoaluminate compounds are more likely to form during the initial phases of the dissolution, since a high concentration of HF relative to the clay enhances the reaction. Precipitation of these compounds will occur when the amount present increases above the solubility limit.

Secondary reactions result from the action of the hexafluorosilicic acid with remaining acid and the rock. The driving force for this reaction is the greater affinity of fluorine for aluminum than for silicon. Silica gel precipitation is well documented. This precipitation occurs when the initial HF is nearly consumed. An exchange reaction occurs on the surface of the clays and fines to generate fluoaluminates and silica gel. The silica is deposited on the surface of the mineral particles, and the fluoaluminates remain in solution. This precipitate is more like to occur when fast-reacting aluminosilicates, such as clays, are present. The damaging effect of silica gel precipitates is still a point of debate; however, it does appear that they are more damaging at higher than lower temperatures.

Tertiary reactions are the reactions of the aluminum fluorides and aluminosilicates. The reaction is insignificant at temperatures below 90°C. At higher temperature, the reaction can be considerable depending on the stability of the formation clays with HCl. As the reaction drives on, and HF is spent, complex aluminofluorides may be precipitated out deep in the matrix. Kalfayan (2001) recommendations of 9% HCl + 1% HF are based on these observations.

Post-treatment fines migration is quite common in sandstone acidizing. It may be difficult to avoid in many cases. The reaction of HF with clays and other aluminosilicates minerals, and quartz, can release undissolved fines. Also, new fines may be generated as a result of partial reaction with high-surface-area minerals, particularly the clays. Postacidizing fines migration problems can be reduced by bringing a well on slowly after acidizing, and increasing rate step-wise over time (e.g., one to two weeks), rather than maximizing return production right away.

Besides that, dissolved iron precipitate as iron compounds when acid spends. Iron is another potential source of precipitation during sandstone acidizing. Precipitation is due to the formation of colloidal ferric hydroxide as the acid spends (pH > 2). Sources of ferric iron (Fe^{3+}) include some minerals (chlorite and glauconite clays) and tubing rust (iron oxide). These reactions begin to precipitate gelatinous ferric hydroxide at a pH of 2.2. The nature of the precipitate (crystalline or amorphous) varies as a function of the anions present (Smith *et al.*, 1969). Precipitation of ferric hydroxide during acid injection is normally not a problem, if an adequate HCl tubing wash was used to remove most of the soluble FeO_2. All acids used for matrix treatments should also contain iron control additives, either sequestering or reducing agents or both. Ferrous iron (Fe^{2+}) is typically not problematic, since ferrous hydroxide precipitates at a pH between 7.7 and 9.

The main sources and causes of precipitates formed during sandstone matrix acidizing are summarized in Table 5. The formation of these potentially damaging precipitates is affected by the complex mineralogy of many sandstones.

Damage can be caused during hydraulic fracturing operations too.

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.

4.5 Completions versus composition

To help improve completions for reservoirs rich in one or more of the minerals listed in Table 6 special consideration should be given to drilling procedures and to treatments/stimulants with the aim of minimizing damage or considering remedial treatments.

Table 6: Mineral – related procedures for completions

Mineral	Potential Effect	Maximizes Damage	Minimizes Damage	Remedy
Smectite	swelling	fresh water, HF	air, KCl, oil-based mud drilling	HCl; re-perforate. & fracturing
Mixed Layer Clay	swelling; mobile fines	fresh water, HF	air, KCl, oil-based mud drilling	HCl; re-perforate. & fracturing
Kaolinite	mobile fines	HF	air, foam drilling	clay stabilized; low flow rates
Chlorite	iron gel precipitate	high pH muds; O_2 rich	air, foam; HCl sequestered	HCl sequestered, low strength
Carbonate minerals	complex CaF precipitates	HF	salt muds; oil-based mud	HCl
Quartz, Feldspar Glass (silt)	mobile fines; gel precipitate	high pH muds	air, foam; bland fluids	clay stabilized; foam fracturing

5   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 (NH_4HF_2) in HCl. A mixture of 1% of HCl and 56 kilos of NH_4HF_2 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, NH_4Cl 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).

In geothermal well acidizing, more acid often is better. Naturally fractured volcanic formations can withstand high HF concentration. The HCl-HF stage can be 10% HCl - 5% HF, or 10% HCl - 7% HF, for example. These acid mixtures have been used successfully in stimulating geothermal wells in Southeast Asia (the Philippines), where a large number of acid treatments have taken place. Acid volumes can vary quite a bit. These acidizing treatments have also employed an acid formulation containing 3% HCl - 5% HF and an organophosphonic acid. The mixture is less corrosive and may help slow scale reprecipitation, as the phosphonic acid complexes with certain cations in spent acid.

HCl-HF mixture dissolves clays originating from drilling mud and reacts with most constituents of the sandstone formation. It results from these reactions an enlargement and interconnections of the pores in the matrix, facilitating the fluid flow. But, it seems that rapid acid consumption with clays and silicates, matrix disintegration in near wellbore and subsequent precipitation of various reaction byproducts (i.e. complex fluosilicates, fluoaluminates, and fluoride salts) have somewhat restricted the usefulness of mud acid for matrix stimulation treatment. A new acid treatment system (called sandstone acid) is used in treating sandstone formations at some geothermal wells in the Philippines. The new HF acid compared with the usual mud acid systems has a lower reaction rate and a limited solubility action on clays but higher reaction rate and dissolving power with quartz (Malate et al., 1998).

Some retarded or slow reacting HF acid such as fluoroboric, fluoroaluminic and hexa-fluoro-phosphonic were developed to improve rock permeability. Most of these acid systems rely on the use of weak organic acids and their secondary reactions to slowly generate HF acid. Malate et al. (1998) proposed a new acid system applicable for moderate to deep penetrations. They used a phosphonic acid complex (HEDP) to hydrolyse NH_4HF_2 instead of HCl. HEDP has 5 hydrogens available that dissociate at different stochiometric conditions. Mixture of HEDP acid with NH_4HF_2 produces an ammonium phosphonate salt and HF. 76 liters of HEDP acid per 3785 liters of water are required to react with approximately 56 kilos of NH_4HF_2 to produce a 1% HF solution.

The advantages of sandstones acid are:

- Limiting clays dissolution and preventing disintegration of pore matrix by coating them with a film blocking reactions.

- Sandstone acid has better dispersing properties and is an excellent antiscalant inhibiting precipitates formation in the vicinity of the well.

- Excess HCl are not needed to avoid the fluoride salt precipitates. As a consequence, sandstone acid aids in reduction of corrosion.

All these protocols are listed in Schlumberger (2003). However, these properties of acid mixtures should be investigated if one wishes to influence the fractures properties beyond a radius of 5 meters around the wells.

Treatment volumes, injection rates, acid placement techniques, acid system selection and evaluation of the results when stimulating geothermal wells, all follow the same criteria as for oil wells. The important difference is the formation temperature. High temperature reduces the efficiency of corrosion inhibitors (and increase their cost) as well as increasing the acid/rock reaction rate. The high acid rock reaction rate requires the use of a retarded acid system to ensure acid will not all be spent immediately next to the wellbore, but will penetrate deeper into the formation. Protecting the tubulars against corrosion is another serious challenge. This requires careful selection of acid fluids and inhibitors (Buijse et al., 2000), while cooling the well by injecting a large volume of water preflush may reduce the severity of the problem.

6 Review of the chemical treatments in geothermal reservoirs

A study of the literature on acidification of geothermal reservoirs has been attempted. The majority of the papers concern the cleaning out of geothermal wells.

The cleaning out of geothermal wells to increase their productivity after scaling deposits constitutes the main application of the acid treatments. This technique has been used extensively in some geothermal fields in the Philippines (Buning et al, 1995; Buning et al, 1997; Malate et al., 1997; Yglopaz et al., 1998; Malate et al., 1999, Jaime-Maldonado and Sánchez-Velasco, 2003, Amistoso et al., 2005), in El Salvador (Barrios et al., 2002) and in USA (Morris et al., 1984; Entingh, 1999). It presents interesting results, such as the well injectivity increasing by 2 to 10-folds according to the studied reservoirs.

At the Larderello geothermal field (Italy), several stimulation methodologies have been used successfully by ENEL (Capetti, 2006). Among them, chemical stimulation operations were carried out by injection of acid mixtures. First, various laboratory tests were realised on reservoir rock samples to optimize the HCl/HF ratios and the effect on mineral dissolution. Field tests have shown impressive results on five deep wells for reservoir rocks composed of phyllites, hornfels and granites: the improvement of injectivity, respectively productivity ranged from a factor 4 to 10.

In the field of EGS, few chemical treatments have been applied to stimulate fractured reservoirs. Since 1976, some experiments have been tried with more or less of success at Fenton Hill (USA) and Fjällbacka (Sweden). At Coso geothermal field however, 24 wells were successfully treated.

A summary of the chemical stimulation experiments carried out on geothermal fields and EGS reservoirs are presented in Table 7.

Table 7: Results of HCl-HF treatments for scaling removal and connectivity development

Geothermal Field	Number of treated wells	Variation of the injectivity index before and after acid treatment (kg/s/bar)	Improvement factor
Bacman (Philippines)	2	0.68 → 3.01	4.4
		0.99 → 1.4	1.4
Leyte (Philippines)	3	3.01 → 5.84	1.9
		0.68 → 1.77	2.6
		1.52 → 10.8	7.1
Tiwi (Philippines)	1	2.52 → 11.34	2.6
Mindanao (Philippines)	1		2.8
Salak (Indonesia)	1	4.7 → 12.1	2.6
Berlín (El Salvador)	5	1.6 → 7.6	4.8
		1.4 → 8.6	6.1
		0.2 → 1.98	9.9
		0.9 → 3.4	3.8
		1.65 → 4.67	2.8
Las Tres Virgenes (Mexico)	2	0.8 → 2.0	2.5
		1.2 → 3.7	3.1
Los Azufres (Mexico)	1	3.3 → 9.1	2.8
Beowawe (USA)	1	-	2.2
Coso (USA)	30	24 wells	sucessful
Larderello (Italy)	5	11 → 54	4.9
		4 → 25	6.3
		1.5 → 18	12
		-	4
		11 → 54	4.9

6.1 Salak geothermal field (Indonesia)

An acid treatment was carried out to improve the production characteristics of a geothermal well in the Salak geothermal field following an accurate analysis of the possible causes for the initial poor performance of the well. Despite promising indications, the initial steam flow rate from the Awi 8-7 well, drilled during 2004, was below expectations (Pasikki, R. G. and Gilmore, T. G., 2006). An acid stimulation treatment was designed and carried out to improve well performance. The treatment used a hydrofluoric acid system known as Sandstone Acid. The acid was placed to the target interval zone with a two-inch coiled tubing unit to maximize control over the treatment. Well test results before and after stimulation demonstrate that the acid stimulation has successfully produced improvements in overall well

characteristics such as reduction of skin, increase of injectivity and permeability-thickness product, and production output. Based on the positive results obtained in this case, further application of this method is envisaged for other poor-performing wells with similar characteristics.

6.2   Las Tres Virgenes and Los Azufres geothermal fields (Mexico)

In Las Tres Virgenes geothermal field, the steam is supplied by four wells located near the power plants, but LV-11 and LV-13 recorded low wellhead pressure and marginal steam production. LV-11 is a deviated well and was drilled in September 2000 to a total depth of 2081 m. LV-13 was drilled to a total depth of 2200 m. An acidizing job was performed in order to improve the production characteristics of these wells. Acid treatment included a pre, post and over flush using chloride acid (HCl) and a chloride acid-fluoride acid (10% HCl- 5% HF). The acid was injected using a coiled tubing unit. Matrix acid stimulation job for production well LV-11 and LV-13 was successfully conducted without major problems. Post-acid completion tests results indicated major improvements in the injectivity index where a considerable drop in wellbore pressures of the two wells (~30 bars) were recorded that indicated a reduction in the pressure resistance inside the wellbore. The post-acid pressure falloff data also confirmed the improvement in the well where a negative skin (-5.8) was obtained in LV-13 and similar for LV-11. The post-acidizing discharge tests also showed substantial improvement compared with the previous well production characteristics to the acid job. As a result, within less than a month the field steam production increased from 3.2 MW_e to 7.3 MW_e.

The Los Azufres geothermal field is located in the northern portion of the transmexican volcanic belt, 250 km of Mexico city. Currently, 78 wells have been drilled at depths ranging between 700 and 3500 meters. Well Az-9AD is located in the northern zone of Los Azufres geothermal field and it was drilled from January 7 to April 22 on 2003, to a total depth of 1500 m. Early testing and survey analysis indicated that the low output of Az-9AD was caused by considerable drilling induced wellbore damage in its open hole section, where 1326 m^3 of mud were lost. Skin factor of 16 was causing additional pressure drop equivalent to 41 bars, reducing its optimal flow rate. The success of earlier acid treatment jobs in Mexico and the analysis of the available information encouraged the company to apply the same technique for this well during 2005. Acid treatment of well Az-9AD introduced very significant improvement in the wellbore showing 174% increase in production capacity. The results of this job have been used for encouraging new stimulation programs, such as those in wells Az-56R and Az-9A located in the north zone of Los Azufres geothermal field.

6.3   Beowawe geothermal field (Nevada, USA)

The Beowawe geothermal field is composed of a production zone within a volcanic and sedimentary rocks sequence. The geothermal fluid contained in the formation is of $NaHCO_3$ type with a very low salinity (1000-1200 ppm of total dissolved solids).

A first acid stimulation was performed in November 1982 on the Batz well (Epperson, 1983). The acid amounts consisted of about 18.9 m^3 of 15 % HCl acid for the preflush followed by a mainflush composed of 37.8 m^3 of 12% HCl - 3% HF. Then, a Beowawe fluid injection of 35 m^3 was performed to displace the acid farther in the formation. As a consequence, the acidification impact modified the acid displacement pressure from 27.5 bars to about 13.8 bars.

In August 1983, a second acidification test was performed on another well, Rossi 21-19 (Morris et al., 1984). Firstly, 79.5 m^3 of a 14.5% HCl solution was pumped at rates of 40-42 $L.s^{-1}$ and was displaced deeper in the formation by injecting 389 m^3 of water. A water injection test followed this first acidification but no significant change was noted in the injectivity of the well. Secondly, a new reservoir acidification was performed, using 156 m^3 of a 12% HCl - 3% HF acid solution. A total of 480 m^3 of water were injected to displace the acid solution in the formation. The following water injection test then showed a 2.2 fold increase of the injectivity.

6.4   The Geysers geothermal field (California, USA)

An acid stimulation was performed in January 1981 on the OS-22 well (Entingh, 1999). An amount of 75.7 m^3 of 5 % HCl and 10% HF were pumped and 70 m^3 of fresh water were injected to displace the acid mixture deeper into the formation. But, no effect on the well productivity was recorded.

6.5 Coso geothermal field (California, USA)

The Coso Geothermal Field, located in east central California, hosts a world-class power-generating project that has been in continuous operation for the past 15 years. A field experiment was designed for dissolving calcite in a wellbore at the Coso field. The most promising mineral dissolution agent to emerge from the laboratory studies was the chelating agent nitrilotriacetate (NTA) (Rose et al., 2007). The well that was selected was producer 32A-20, which had recently failed due to calcite deposition. A total of 57 m^3 of a 10 wt% solution of NTA was injected into the well in a series of three injections. The solutions were each injected at 13.5-16 $L.s^{-1}$. The total volume of fluid injected (57 m^3) was calculated to be approximately the volume of the open-hole section of the well. Upon completion of the injection of the NTA solution, the well was shut in for approximately four hours, giving the chelating agent time to dissolve the calcite scale.

Once the well was opened, at first the brine was clear, but soon turned to milky white, indicating the presence of the calcium-NTA complex. The concentration of the unreacted NTA dropped from about 34'000 ppm to approximately 2'000 ppm during the experiment. The final value of 2'000 ppm indicated that the milky white NTA solution being produced was nearly completely complexed with calcium. These experiments indicate that NTA can be an effective dissolution agent for the dissolution of wellbore calcite. The production of unreacted NTA early in the production cycle indicated that a longer shut-in period may have resulted in a more complete reaction of the NTA solution and more wellbore calcite dissolution.

A total of 30 wells were treated with HCl and 24 gave successful results (Evanoff et al., 1995).

6.6 Baca geothermal field (New Mexico, USA)

For the development of the fracture network in the Baca Union Project, different methods of reservoir stimulation were compared. Acid stimulation had not been selected because of the filling of the natural fractures. Composed of authigenic material such as quartz, feldspar and pyrite (Pye and Allen, 1982). Therefore the acid stimulation should require substancial amounts of hydrochloric acid with uncertain results. A hydraulic fracturation was selected and performed on Baca-20 well in October 1981 utilizing a cooling water followed by a high viscosity frac fluid (Morris and Bunyak, 1981). Different compounds were used to do this hydraulic stimulation as proppant (sintered bauxite), hydroxypropyl polymer gel (stable at high temperature) and calcium carbonate added to act as a fluid-loss additive.

Nevertheless, all these treatments have not allowed a significant increase of the injectivity. It was also thought that the calcium carbonate has plugged the natural fractures and flow paths in the formation. As a consequence, an acid treatment was performed. A volume of 166 m^3 of hydrochloric acid at a concentration of 11.9% was used but this acidizing treatment has not allowed the development of the well productivity (Entingh, 1999).

6.7 Fenton Hill HDR project (New Mexico, USA)

This HDR reservoir, located in north-central New Mexico, is composed at a depth of 3-4 km of a highly jointed Precambrian plutonic and metamorphic complex, basically of granitic composition. This HDR project was operated by Los Alamos National Laboratory. Many experiments, in the laboratory and on the field, were performed to study the impact of a chemical treatment on this rock.

Different works were performed on cuttings and granite cores at the laboratory scale to study the impact of chemical treatments on permeability increases. Aqueous solutions of Na_2CO_3, NaOH and HCl were investigated on well-known crystalline rocks. Sarda (1977) reported the results (Table 8).

Table 8: Impact of three chemical treatment at 100 °C and 100 bars during 144 h (Sarda, 1977)

Chemical Treatment	Weight Loss	Permeability increase
Na_2CO_3	-0.3 %	2-fold
HCl	- 6 %	negligible
NaOH	- 6 %	20-fold

Those laboratory experiments have demonstrated that Na_2CO_3 dissolves SiO_2 primarily by attacking the quartz component of the granite. Holley et al. (1977) showed that the amount of dissolved silica increased with increasing sodium carbonate concentration and with increasing time.

Field experiments were attempted in November 1976 to reduce the impedance of the deep enhanced reservoir by a chemical leaching treatment. Na_2CO_3 was used to dissolve quartz from the formation. A total of 190 m^3 of 1 N Na_2CO_3 solution was injected. About 1000 kg of quartz were dissolved and removed from the reservoir but no impedance reduction resulted.

6.8 Fjällbacka HDR project (Sweden)

The experimental HDR reservoir of Fjällbacka is made of a granite composed of two main facies, the predominant variety being a greyish-red, biotite monzogranite. This granite contains abundant fractures and minor fractures zones, which showed an evidence of being hydraulically conductive and which were filled with calcite, chlorite and clay minerals (Sundquist et al., 1988; Wallroth et al., 1999). Most of the stimulation experiments were hydraulic fracturing but an acid treatment was performed in 1988. An amount of 2 m^3 of HCl-HF acid was injected in Fjb3 to leach fracture filling. The results have shown the efficiency of acid injection in returning rock particles.

6.9 Experiments at EGS reservoir of Soultz-sous-Forêts (Alsace, France)

The Soultz-sous-Forêts Enhanced Geothermal System (EGS), established in the Rhine Graben, North of Strasbourg (France), has been investigated since the mid 1980's. The final goal of this project is to extract energy for power production from a regional randomly permeable natural geothermal reservoir with the complementary resource coming from a forced fluid circulation between injection and production boreholes within a granitic basement.

Recently chemical treatments were performed at Soultz-sous-Forêts (France). This deep granitic reservoir contains fractures partially filled with a mixture of secondary carbonates (calcite and dolomite), various kinds of clay minerals (Illite, chlorite….) and silica. In order to dissolve these carbonates and to enhance productivity around the wells, each of the three 5-Km deep boreholes (GPK2, 3 and 4) were treated with different amounts of hydrochloric acid. If GPK3 has shown weak variations of its injectivity, GPK4 presented a real increase of its injectivity and productivity after the treatments and GPK2 presented also a very sensible improvement despite the fact that the treatment was only a very little test.

6.9.1 Preliminary tests on cores

In order to define the most effective acid mixture to be used in the stimulation of the deep reservoir, laboratory test were performed both in batch and in the continuous flowing conditions (Erga, 2000). The batch experiments consisted to test the reactivity of acid mixtures (HCl/HF) on core samples of granite formed by micas, phylites, hydrothermal veins, quartz and feldspars at 50°C and 150°C. Batch results indicated the mixtures 12/3 and 12/6 (in weight %) as the best one to attack these rocks and minerals. These 12/3 (wt%) and 12/6 (wt%) mixtures were then used in a series of tests in flowing conditions at 30, 50, 70 and 90°C. The evolution of the weight losses were followed by electronic scanning microscope analyses to determine the mineralogical phases influenced by acidification treatment. On a core coming from a depth of 1996 m in EPS1, weight losses of about 80-100 $mg.cm^{-2}$ were measured and the most effective acid mixture was the ratio 12/3 percent by weight.

6.9.2 GPK2 well

The first injection tests performed on GPK2 on January 23 and February 12, 2003, with water injection volumes of 9214 m3 and 5814 m3 respectively, showed an injectivity in GPK2 estimated to about 0.3 $L.s^{-1}.bar^{-1}$. It was then decided to improve the well injectivity by a soft acidizing. During this test, only 1.5 tons of HCl were injected. First, 500 kg of HCl were injected at a concentration of 1.8 $g.L^{-1}$ and with a flow of 30 $L.s^{-1}$.

It showed an immediate and strong impact (see "A" on Figure 3), demonstrating that part of the injection pressure required to inject the total flow was due to very near well bore scaling. The second part of the test, performed at concentrations of 1.8 $g.L^{-1}$ and 0.9 $g.L^{-1}$ for flows of about 15 and 30 $L.s^{-1}$ respectively, showed less immediate impacts but nevertheless the global result was impressive (see differences between "D" and "E" on Figure 3) for such a little quantity of acid injected, the injectivity has increased up to approximately 0.5 $L.s^{-1}.bar^{-1}$.
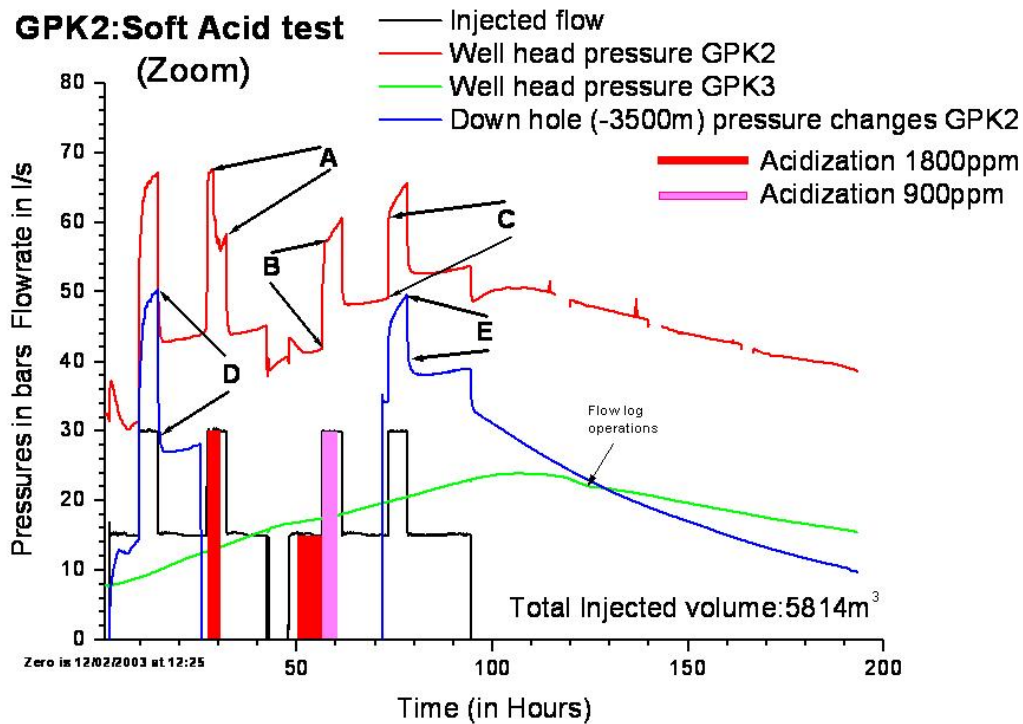
Figure 3: Impact of soft acidification test on GPK2 (Gérard et al, 2005).

6.9.3 GPK3 well

The second acidification test was run in GPK3 in June 2003 during a circulation test between GPK3, the injection well, and GPK2, the producer. A total of 950 m^3 of an acid solution, with a concentration of about 3.2 $g.L^{-1}$, were injected at a flow of 21.3 $L.s^{-1}$. Up to 3 tons of HCl were used in GPK3. The results are shown on Figure 4. Figure 4 shows a sudden drop of the wellhead pressure of GPK3 (slope break at 240 h) after the injection of about 4000 m^3 of acid and fresh water. This break could be caused by acidic water and its action in the reservoir, in particular in the large fault identified at 4750 m and able to absorb more than 75 % of the injected fluid (Gérard et al, 2005). Nevertheless, it is difficult to estimate the real improvement of the GPK3 injectivity due to acid treatment, because no water injection test was performed in the same conditions before and after acid injection, unlike for GPK4 well.
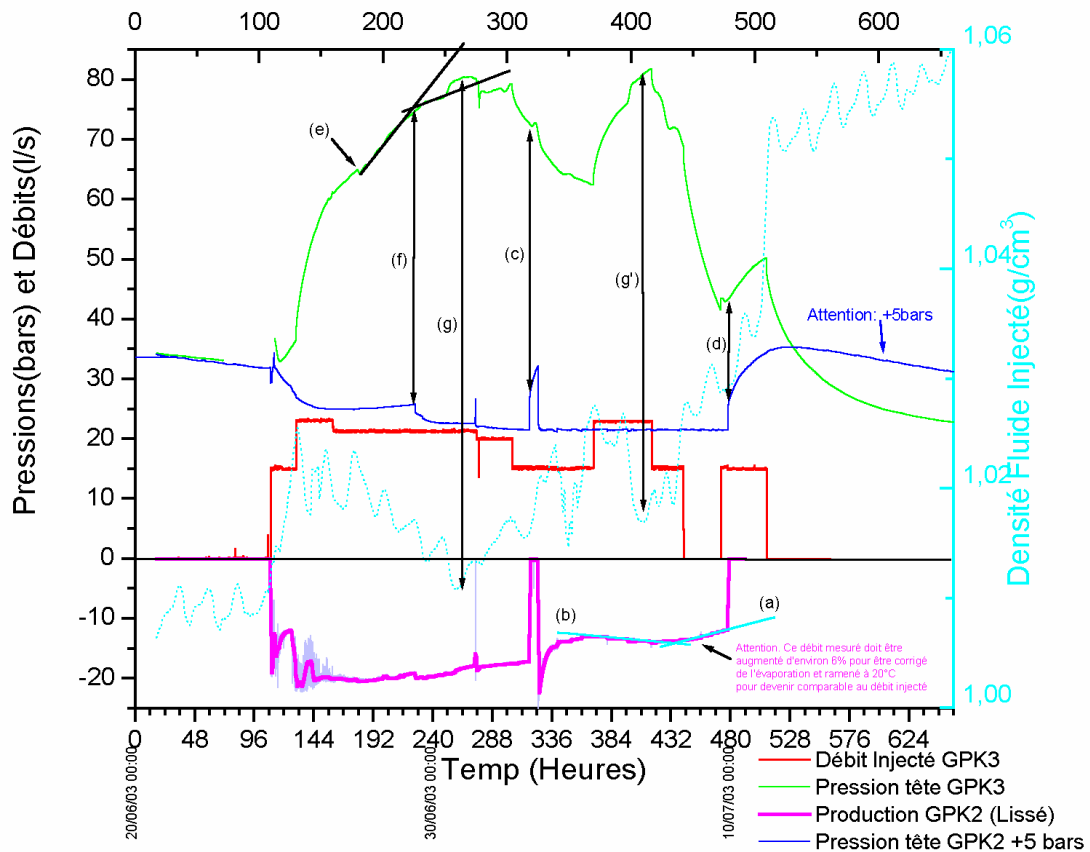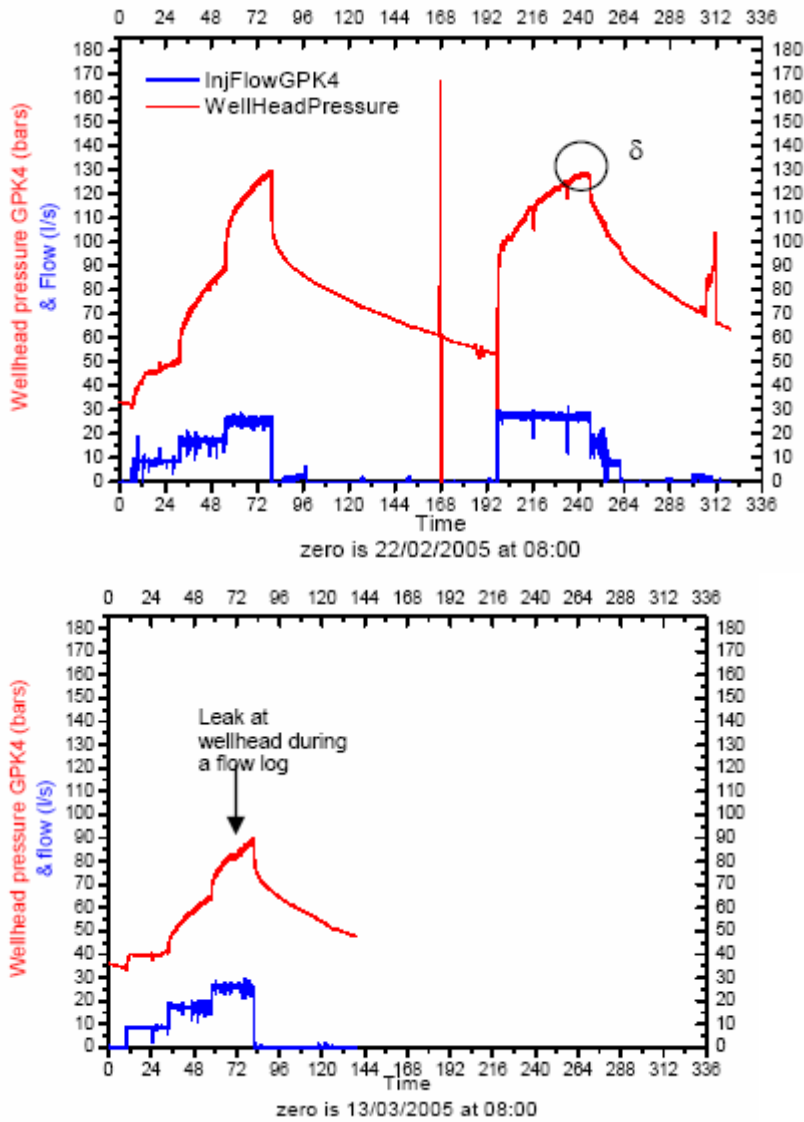
Figure 4: Impact of acidification test on GPK3 (Gérard et al, 2005).

6.9.4 GPK4 well

In February 2005, an acidified (HCl) water injection was tested to improve the injectivity around GPK4 well. The experiment began on 22 February 2005 with an injectivity test of the well before soft acidification. It consisted of the injection of 4'500 m^3 of water at increasing flow rates (9 L.s^{-1}, 18 L.s^{-1}, 25 L.s^{-1}) in 24-hour steps. The injection of water acidified by the addition of approximately 2 g.L^{-1} of hydrochloric acid started on 2 March 2005 at a flow rate of 27 L.s^{-1}. It lasted 2 days, followed by one day of injecting fresh water at much lower rates in decreasing steps. A total volume of 5'200 m^3 was injected; with a total weight of acid (HCl) of 11 tons. When the wellhead pressure was back to the value observed during the previous injectivity test, an identical test was repeated on 13 March 2005, that is injection of 4'500 m^3 of water in flow rate steps of 24 hours at 9 L.s^{-1}, 18 L.s^{-1} and 25 L.s^{-1}.

The impact of the acidified water on the wellhead pressure during the first acid injection in GPK4 well is shown on Figure 5. Despite the fact that the injection was performed in an over-pressurised reservoir, the injection pressure was decreasing during the last hours of the acidification test. Moreover, it is interesting to compare the data from two tests of water injection performed in the same conditions before (February 22, 2005) and after (March 13, 2005) the acid injection. Results (Gérard et al., 2005) show that after some 72 hours of water injection in the second test (24 hours at 9 L.s^{-1}, 24 hours at 18 L.s^{-1} and 24 hours at 26 L.s^{-1}), the GPK4 wellhead pressure was about 40 bars below the value observed in the same conditions before acidification. This represents a decrease of the apparent reservoir impedance seen from the wellhead by a factor ~1.5 (0.20 to 0.30 L.s^{-1}.bar^{-1}).
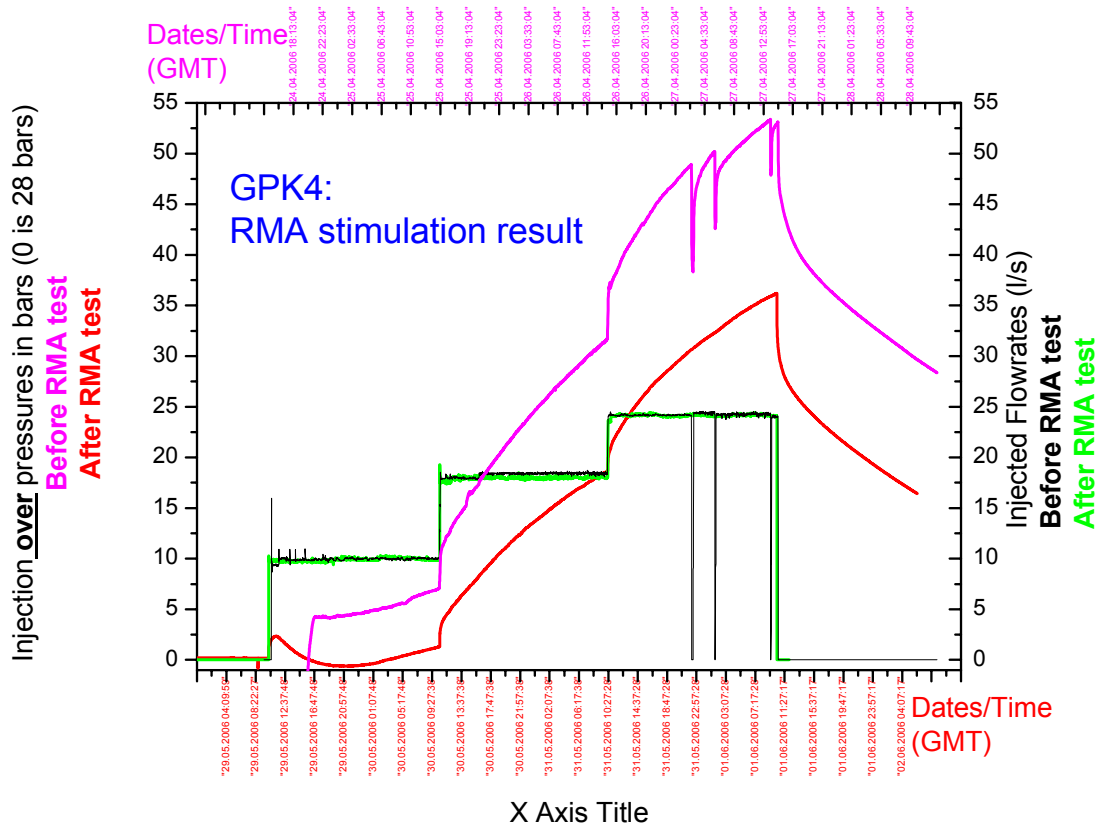
Figure 5: Impact of acidification test on GPK4; above, before and during acidification injection, below, after acidification (Gérard et al, 2005).

In May 2006, new tests began with a test of the well injectivity before acidification. The acid treatment was performed in four stages:

- Injection of 2000 m^3 of cold water deoxygenized at 12 $L.s^{-1}$, 22 $L.s^{-1}$ then finally at 28 $L.s^{-1}$.

- A preflush of 25 m^3 HCl diluted at 15% (3 tons) (with deoxygenized water) was pumped ahead of the HCl-HF acid mixture during 15 minutes at 22 $L.s^{-1}$.

- A main flush consisted of the injection of 200 m^3 of Regular Mud Acid (RMA), (12% hydrochloric (HCl) - 3% Hydrofluoric (HF) acid mixture treatment), with addition of a corrosion inhibitor, at a flow rate of 22 $L.s^{-1}$ during 2,5 hours.

- A postflush by injection of 2'000 m^3 cold water deoxygenized without inhibitor at a flow rate of 22 $L.s^{-1}$ then 28 $L.s^{-1}$ during 1 day.

When the wellhead pressure was back to a value identical to that observed in the previous injectivity test, a 3-day test identical to that of March 13, 2005 was repeated. Figure 6 shows the impact of RMA acid job on the wellhead pressure by comparison before and after the second acid injection in GPK4 well. The repetition of the injectivity test showed that the difference in the over pressure values at the wellhead between the beginning of the test and the end were 16 bars. This represents a 35% reduction of the wellhead pressure due to the acidification treatment. After some preliminary evaluation of downhole pressure changes, performed by GEOWATT, this leads to a provisional estimate of GPK4 injectivity after chemical treatment slightly lower than 0.40 $L.s^{-1}.bar^{-1}$.

Figure 6: Impact of the RMA acidification test on the wellhead measured by comparison before and after the acidification test on GPK4 well (May 2006) (GEIE, 2006).

6.9.5 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 200°C. Therefore, a field experiment was designed for dissolving calcite and other minerals with a high pH solution of NTA in GPK4 well.

In October 2006, the chelatants stimulation was performed (Figure 7). About 38 tons of NTA were injected with 200 m³ of cold water at a flow rate of 35 L.s⁻¹. A total of 850 m³ of water were injected to displace the chelating agent in the formation. Figures 7 and 8 show the impact of the chelatants stimulation after the production test on the wellhead pressure and flow rate.
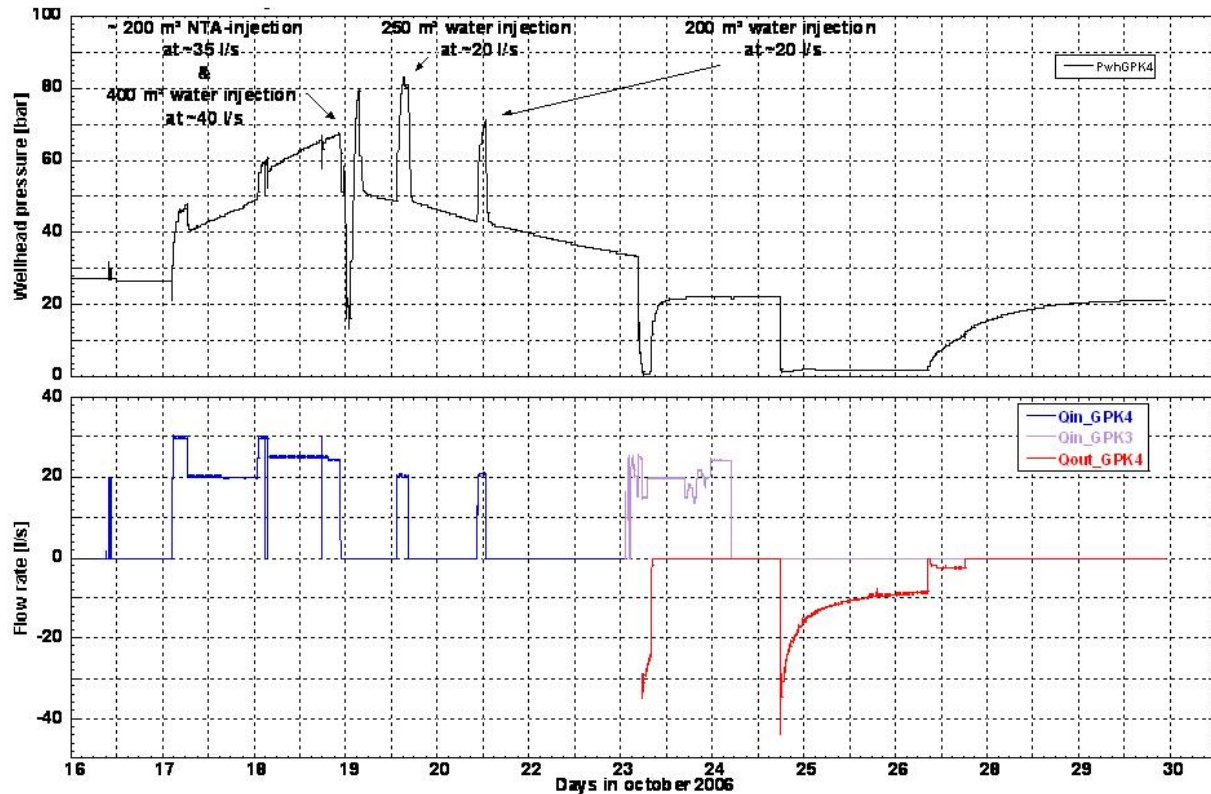
Figure 7: History plot of the chelatants stimulation 06OCT16 and production test 06OCT23 in GPK4 well (GEIE, 2006).

6.9.6 Chemical stimulation of the farfield of the wells GPK4 and GPK3

Although conventional stimulation fluids, such as hydrochloric (HCl) or mud acid, can clean up the wellbore and stimulate the matrix, they do not penetrate deep into the formation nor stabilize fines. Conventional acids can also have adverse effects in formations with certain types of clays, or alumino-silicates like zeolite and chlorite, that are unstable in HCl acid. Consequently it was decided to develop the expected result of the NTA treatment in GPK4 by using Organic Clay Acid for High Temperature (OCA-HT). This stimulation fluid penetrates deep into the sensitive formation and stabilizes clays and fines without the adverse effects of conventional acid systems. OCA fluid is a high-performance acid system designed for sensitive sandstone matrix formations that can present the biggest challenge to conventional acidizing treatments. Because of the damaging precipitation of secondary and tertiary reaction products, conventional mud acid has the highest chance of failure in formations with very high temperature or a high clay content that is sensitive to HCl. OCA fluid combines a retardation effect and advanced chelation technology for stimulation deep into the reservoir with minimal precipitation. It reduces the risk of diminished production as well as secondary and tertiary mineral precipitation that can block pores. Its retarded properties allow a reduced corrosivity. OCA fluid also combats sludging problems that plague conventional acid systems and stabilizes formation fines while maintaining the integrity of the sandstone structures to promote long-term production.

New tests were run in February 2007. The operation consisted in cooling the GPK4 well and only stimulating it with 200 m³ of "Organic Clay Acid HT". The operation was also performed on well GPK3. Organic Clay Acid is a delayed acid proposed in its high temperature version (OCA HT). Its maximum

temperature of use is slightly higher than 200°C, while the inhibition of corrosion can be efficiently ensured until 177°C. In fact, it was considered as being safe enough to use a corrosion inhibitor to guarantee a protection during 4 hours with 80°C for steels.

Figure 8 illustrates the impact of the successive chemical treatments on the productivity of GPK4 well. One can remark that now (March 2007) the productivity of GPK4 after few days only reached a stable value of 5l/s/MPa despite the fact that the produced fluid was stored in a lined lagoon and not reinjected in the well GPK3 during that test. One can also observe on figure 8 that during that production test of March 2007 the pressure in the reservoir at the impact of GPK3 dropped at a rate of around 1 bar/day. That implies a possible higher productivity of GPK4 when some reinjection in GPK3 will be performed.
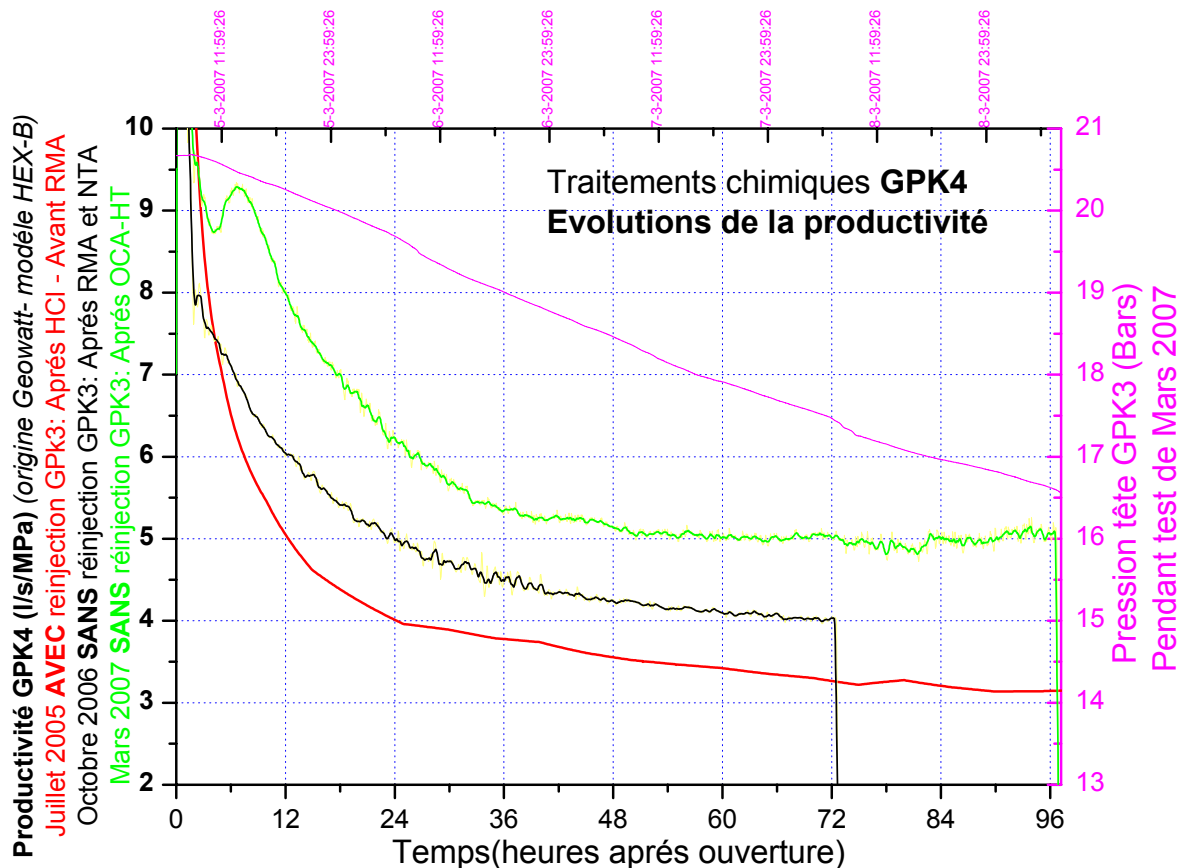

Figure 8: GPK4 productivity evolution with time during chemical treatments (GEIE, 2007).

7 Conclusions

Current economic conditions dictate that oil field operators maximize well/reservoir productivity or injectivity. Achieving the goal of long-term, low-cost sources of hydrocarbons will require significant technology advances in the area of well stimulation. From this papers review, it is apparent that these technological advances will affect many different portions of this industry, from old, mature fields, where significant reserves have previously been economically unattractive, to the new, major ultradeepwater projects that are being evaluated today. The challenge will be to increase productivity, and then to maintain that increased productivity throughout the life of the field to provide improved ultimate recovery.

New and innovative stimulation technologies are emerging that will modify some of previous tried and more or less proven methods. Still, in other cases, we see enhancements to improve the performance of existing technologies. It appears that the future challenge will be for the petroleum industry to find more-cost-effective ways to improve well productivity. It appears that well stimulation will remain a dynamic part of the petroleum industry.

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.

Deleterious side-effects of acidizing in sandstone formations—such as clay swelling, fines migration, gel formation or particle precipitation—may be minimized or avoided altogether by designing hydrofluoric acid (HF) stimulation treatments with compatible chemical and physical properties. Smectite and mixed illite-smectite clays are among the most water-sensitive clays, while illites and chlorites are less prone to ion exchange. Also of concern when acidizing sandstone in the presence of illite, potassium feldspars, sodium feldspars, and zeolites, because these compounds can contribute to the formation of matrix-blocking precipitates.

Clay swelling can occur when acidizing fluids exchange ions with formation minerals, choking off production by obstructing the matrix, unless care is taken to sustain the salinity of the injected fluid after ion exchange. Many water-sensitive clays contain potassium chloride (KCl) and sodium chloride (NaCl) ions that can be exchanged with ions in injected fluids to lower the salinity of the fluid. For example, when a 3% ammonium chloride (NH_4Cl) acidizing fluid flows across a typical ion-exchanging clay, the fluid becomes 3.3% NaCl, a brine too weak to prevent clay swelling, thus requiring a 5% NH_4Cl or equivalent solution.

The acid treatments were developed by oil industry for improving the productivity of oil and gas wells. This technology was partially adapted to the geothermal wells, most often to remove the mineral scaling deposited in the wells after several years of exploitation. Nevertheless, acid treatments also allow the enhancement of the fractures network. They have been successfully performed in geothermal granitic reservoirs like Fjällbacka or Beowawe. In recent years, the reliability of acidizing sandstone intervals has been significantly improved. In the USA, about 90 percent of wells treated have responded with two- to four-fold production increases.

Recently, this technology has been applied to the Soultz reservoir. The three 5-Km deep wells (GPK2, GPK3 and GPK4) were treated with different amounts of chemicals and the injectivity of each well was differently affected. If encouraging results were obtained with GPK2 and GPK4, the injectivity improvement of GPK3 well is apparently less marked but the diagnostic for this well was not really performed[1].

Nevertheless, the high reactivity and a weak flow prevent the penetration of acid in the far field between the wells. This high reactivity also involves the risk of creating wormholes, able to increase the porosity but not always the permeability of the medium.

The increase of acid concentration augments the reactivity in the vicinity of the injection well and creates a new porosity. But the high acidity of the solution has also the disadvantage to decrease the solution pH and to augment the risk of damaging the casing.

The answer could be an increase of the flow to force the acid transport farther in the formation or the use of another acid (e.g. HF), which will dissolve silicates minerals. The result will be an enhancement of the fractures network and of the fractures connectivity.

Finally, simulators have been developed to track the propagation of reaction fronts and to gain insight into the effectiveness of acid injection as a well stimulation techniques. Reactive transport modelling was used to simulate injectivity recovery by acid injection (Xu et al., 2004; André et al., 2006). The predicted amount of scaling minerals dissolved by acid was consistent with the estimal amount.

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[1] *It can be also noted that the likely origins of the very limited efficiency of all the methods (including hydraulic stimulation) used for trying to improve the injectivity of GPK3 well seem rather specific and are still a subject of discussion.*

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Selected websites

Guides to acid stimulation for improving productivity in oil, gas, injection, and disposal wells: outlines the purposes and benefits of acidizing, and shows how to design and execute successful acid treatments.

http://www.bjservices.com/

http://www.cleansorb.com/

http://www.corelab.com/

http://www.halliburton.com/

http://www.slb.com/content/services/stimulation/

NB: This list is not exhaustive and does not represent any recommendation for specific services companies.