

Chemical stimulation techniques for geothermal wells: experiments on the three-well EGS system at Soultz-sous-Forêts, France

Sandrine Portier^{a,*}, François-David Vuataz^a, Patrick Nami^b, Bernard Sanjuan^c, André Gérard^d

^a CREGE c/o CHYN, University of Neuchâtel, Emile-Argand 11, CP 158, CH-2009 Neuchâtel, Switzerland

^b Leibniz Institute for Applied Geosciences (GGA-Institute), Stilleweg 2, D-30655 Hannover, Germany

^c Bureau de Recherches Géologiques et Minières, 3 Av. Claude Guillemin, 45065 Orléans Cedex 02, France

^d ESGéothermie, 3a Chemin du Gaz, 67500 Haguenau, France

ABSTRACT

Rock matrix stimulation is a method of enhancing well production or injection within a broad range of challenging environments, varying from naturally fractured limestones to sandstones with complex mineralogy. A common and often successful stimulation option, matrix acidizing, utilizes acids that react and remove mineral phases restricting fluid flow. Reviewed is the technology of chemical treatments available for oil, gas and geothermal wells and the key elements and results of the chemical reservoir stimulation program at the Soultz-sous-Forêts, France, Enhanced Geothermal System Project.

Keywords

Enhanced Geothermal Systems, Scaling, Chemical stimulation, Acid injection, Chelating agent, Well cleaning, Fractured granite, Soultz-sous-Forêts, France

1. Introduction

The goal of Enhanced Geothermal System (EGS) projects is to harness the heat stored in deep, hot and very low permeability rocks. The economic success of the operation depends largely in opening existing fractures or creating new ones, and keeping the fracture network open to allow fluid circulation. EGS projects are at risk from natural or induced mineral precipitation in the fractures and the associated decrease in permeability. This may inhibit flow in the fractures (and in some extreme situations within the well itself), thereby lowering the rate at which heat can be extracted from the system.

A problem frequently observed in the exploration of geothermal reservoirs is the poor hydraulic connection between the production/injection wells and the fractured reservoir restricting considerably the possibility of extracting the thermal energy from the subsurface. The main reservoir lithologies currently being targeted in EGS projects tend to be crystalline igneous rocks with inherently very low natural porosity and permeability. In a given

reservoir, some wells can be productive, and others not, or less so, due to a strong heterogeneity of the fracture networks. In such cases it is necessary to improve or create around the wells a permeable fracture network with a fluid-rock surface area large enough to be efficiently connected to the most permeable fractures draining the reservoir in the vicinity. Hydraulic and/or chemical stimulation methods can be used to increase the hydraulic connection between the wells and the reservoir fracture networks. Stimulation by thermal cracking is rarely used (Combs et al., 2004) but can be efficient in some high-temperature geothermal wells (Correia et al., 2000).

Chemical stimulation techniques consist mainly of acid injection into the formation at below fracturing pressures with the aim of removing near-wellbore permeability damage and material deposited in fractures through transport and precipitation processes. The oil industry has been developing these operations for more than a century in order to improve the productivity of oil and gas wells (Smith and Hendrickson, 1965; Economides and Nolte, 1989; Schechter, 1992). Acidizing may, in fact, be the oldest stimulation technique still in use. The earliest acid treatments of oil wells are believed to have been done as far back as 1895.

By dissolving acid soluble components within underground rock formations, or by removing material at the wellbore face, the rate of oil or gas production or the rate of oil-displacing fluids injection may be increased (Williams, 1979). Because of successes with acid

* Corresponding author. Tel.: +41 32 718 26 95; fax: +41 32 718 26 03.
E-mail address: sandrine.portier@unine.ch (S. Portier).

treatments in limestone formations, new treatments for sandstone reservoirs were developed. In 1933, Halliburton conducted the first sandstone acidizing treatment using a mixture of hydrochloric (HCl) and hydrofluoric (HF) acids. 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 methods to retard HF consumption, stabilize fine particles, and prevent precipitation of HF-rock reaction products such as fluorite (Allen and Roberts, 1989; Kalfayan, 2001).

Despite all the differences between hydrocarbon and geothermal systems, fluid extraction and injection techniques, and reservoir management methods are similar. In both cases formation damage should be minimized to optimize well performance. The acidification of geothermal wells is not as common, but the techniques have been borrowed from the oil and gas industry (Entingh, 1999).

This paper first discusses the various methods used to prevent scaling in oil and gas wells and improve reservoir fracture connectivity and permeability, as well as describe chemical stimulation techniques for sandstone formations. Then, the paper focuses on the chemical treatments performed on geothermal reservoirs, particularly in Soultz-sous-Forêts EGS wells.

2. Chemical stimulation methods developed by the oil and gas industry

Two basic types of stimulation or acidizing operations can be conducted: matrix acidizing and fracture acidizing. Matrix stimulation is accomplished, in sandstones, by injecting a fluid (e.g. acid or solvent) to dissolve and/or disperse materials that impair or reduce well productivity/injectivity.

In carbonate formations, the goal of matrix stimulation is to create new, unimpaired flow channels between the formation and the wellbore. Matrix stimulation, typically called matrix acidizing when the stimulation fluid is an acid, is used generally to treat only the near-wellbore region. In a matrix acidizing treatment, the acid used is injected at a pressure low enough to prevent formation fracturing (Economides and Nolte, 1989). Very often carbonates show low matrix permeability and just creating wormholes around the wellbore may not be sufficient to produce fluids in commercial amounts.

Fracture acidizing is the technique that is used to provide conductive paths deeper into the formation (Burgos et al., 2005). This treatment consists of injecting an acid fluid into the formation at a rate higher than the reservoir matrix will accept. This rapid injection produces a wellbore pressure build-up leading to a fracturing of the rock. Continued fluid injection increases the fracture's length and width.

For years, mixtures of HF and HCl have been the standard in sandstone acidizing operations. HCl is selected to treat limestone, dolomite and calcareous zones, whereas HF is used to dissolve clay minerals and silica. In contrast to carbonate reservoirs, the acidification of a sandstone reservoir requires a specific procedure, which is carried out in three main steps: preflush, main flush and overflush. The preflush is performed most often with an HCl solution (10%). The objective of this first step is to displace the formation brine away from the wellbore, and to dissolve as much of the calcareous material in the formation as possible prior to the injection of the HF solution. The preflush acid minimizes the possibility of forming insoluble precipitates.

The main flush is used to remove the damage; most often, a mixture of 12% HCl–3% HF (called regular mud acid–RMA) is pumped into the well. This mixture is generally prepared by dissolving ammonium bifluoride (NH_4HF_2) in HCl. Finally, the overflush,

which usually consists of injecting HCl, KCl, NH_4Cl , or freshwater, is an important part of a successful sandstone acid treatment. It displaces the non-reacted mud acid and the mud acid reaction products into the formation away from the wellbore (Paccaloni and Tambini, 1993).

Variations of this approach to sandstone acidizing include changes in the concentration and ratio of HCl and HF acids, as well as in the volumes pumped into the formation during the different phases; these variations depend mainly on formation mineralogy (McLeod, 1984; Perthuis et al., 1989; Davies et al., 1994). Corrosion inhibition is always necessary to protect well casings, and inhibitors must be added to all acid stages (preflush, main flush, and overflush) (Buijse et al., 2000).

A problem that can limit the effectiveness of matrix acidizing relates to the proper placement of the acid, i.e. ensuring that the acid is delivered to the desired zones. This problem is exacerbated by the intrinsic heterogeneity of the permeability (common in many formations), especially the presence of natural fractures and high-permeability zones. Numerous techniques have been developed to direct the treatment fluid toward selected reservoir zones. Coiled tubing is a very useful tool for improving acid placement (Economides and Frick, 1994). In longer open-hole sections, such placement is important, otherwise treatment will be confined to the interval that breaks down or fractures first. Proper placement of the injected acid can be achieved by installing packers, or by the use of polymers.

The re-precipitation of reaction products is a serious concern in acidizing sandstones containing aluminosilicates; as HF is injected it reacts with sandstone minerals (Walsh et al., 1982; Pournik, 2004). Because of the precipitation of secondary and tertiary reaction products, conventional mud acid has a great chance of failure in formations of high ($>120^\circ\text{C}$) temperature or rich in clays sensitive to HCl (Crowe, 1986; Gdansk, 1997). Clay swelling can be caused by ion exchange between acidizing fluids and formation minerals or changes in salinity, choking off production by obstructing pores and/or fractures.

Although conventional stimulation fluids such as HCl or mud acid can clean the wellbore and stimulate the matrix, they do not penetrate deep into the formation or stabilize fines. Methods have been developed to slow the acidizing process (Templeton et al., 1975; Thomas and Crowe, 1981). A key issue is not to inject a HF solution at the wellhead, but to use a compound able to generate HF at greater depth of penetration and of longer reaction time for maximum dissolution of fines (Crowe et al., 1992). Most of these chemically retarded acid systems rely on the use of weak organic acids, such as fluoroboric, fluoroaluminic and hexa-fluoro-phosphonic acids, and their secondary reactions to improve rock permeability (Malate et al., 1998). Other types of acid systems can be used, such as gelling agents (polymers and surfactants), emulsified solutions of aqueous acid in oil, acids dissolved in a solvent (e.g. alcohol and gel) or the injection of solutions of methyl acetate, which hydrolyses slowly at high temperatures to produce acetic acid, making it more difficult for the H^+ ions to contact a reactive surface.

An alternative to acid treatment is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilo-triacetic acid (NTA) (Fredd and Fogler, 1998). Chelant solutions are used in formation cleanup and for stimulating wells, especially in formations that may be damaged by strong acids (Frenier et al., 2001). They act as a solvent, increasing the water-wetting process and dissolving (entirely or partially) some minerals containing Fe, Ca, Mg and Al. 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 discharging 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

Table 1
Results of chemical treatments in selected geothermal fields.

Geothermal field	Chemical agents used	Number of treated wells	Variation of the injectivity index before and after chemical treatment ($\text{kg s}^{-1} \text{bar}^{-1}$)	Ref.
Bacman (Philippines)	HCl–HF	2	0.68–3.01 0.99–1.40	Buning et al. (1995)
Leyte (Philippines)	HCl–HF	3	3.01–5.84 0.68–1.77 1.52–10.80	Malate et al. (1997); Yglopaz et al. (1998)
Tiwi (Philippines)	HCl–HF	1	2.52–11.34	Buning et al. (1995)
Mindanao (Philippines)	HCl–HF	1	Successful	Buning et al. (1997)
Salak (Indonesia)	HCl–HF	1	4.70–12.10	Pasikki and Gilmore (2006)
Berlín (El Salvador)	HCl–HF	5	1.60–7.60 1.40–8.60 0.20–1.98 0.90–3.40 1.65–4.67	Barrios et al. (2002)
Las Tres Vírgenes (Mexico)	HCl–HF	2	0.8–2.0 1.2–3.7	Jaimes-Maldonado and Sánchez-Velasco (2003)
Los Azufres (Mexico)	HCl–HF	1	3.3–9.1	Flores et al. (2006)
Beowawe (USA)	HCl–HF	1	Successful	Epperson (1983)
The Geysers (USA)	HCl–HF	1	No effect	Entingh (1999)
Coso (USA)	HCl and NTA ^a	30	24 wells successful	Evanoff et al. (1995); Rose et al. (2007)
Larderello (Italy)	HCl–HF	5	11–54 4–25 1.5–18 Successful 11–54	Cappetti (2006)
Fenton Hill (USA)	Na_2CO_3	1	About 1000 kg of quartz were dissolved and removed from the reservoir but no impedance reduction resulted.	LANL (1977)
Fjällbacka (Sweden)	HCl–HF	1	Efficiency of acid injection in returning rock particles.	Sundquist et al. (1988); Wallroth et al. (1999)

^a NTA: nitrilotriacetic acid ($\text{C}_6\text{H}_9\text{NO}_6$).

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. Laboratory data also indicate that aqueous solutions at high pH can dissolve wellbore silica and near-wellbore formation silicates and that dissolution capacity increases with temperature (Sarda, 1977; Rose et al., 2007).

3. Present use of chemical stimulation in geothermal wells

Various acidizing treatments have been performed in geothermal wells over the last 30 years (Strawn, 1980; Epperson, 1983; Barelli et al., 1985; Barrios et al., 2002; Serpen and Türeyen, 2000). A summary of the main chemical stimulation experiments carried out in geothermal fields is given in Table 1, showing variable results. To date, only a few chemical stimulation experiments and laboratory tests have been attempted in EGS wells and reservoirs. Only limited amount of data were found on the projects at Fenton Hill, USA (Sarda, 1977) and Fjällbacka, Sweden (Sundquist et al., 1988; Wallroth et al., 1999).

In geothermal wells the strongest indication of formation damage is a sharp drop in production rate. Nearly all geothermal wells that are acidizing candidates have been damaged by either drilling mud solids and drill cuttings lost to the formation or by scaling (Buning et al., 1997; Malate et al., 1998, 1999; Yglopaz et al., 1998; Jaimes-Maldonado and Sánchez-Velasco, 2003; Axelsson et al., 2006).

Production and injection of geothermal brines strongly modifies the natural flow taking place within the fractured reservoir. Consequently, chemical and thermodynamic rock–fluid equilibria are

disturbed in the formation. One of the major problems affecting reservoir permeability is scaling (most often, calcium carbonate, amorphous silica, calcium sulfate, and mixtures of them), which leads to a decrease in well injectivity/productivity (Flores et al., 2005). This phenomenon has been observed in many geothermal fields, such as Bacman, Leyte and Tiwi, Philippines (Buning et al., 1995, 1997; Malate et al., 1997; Molina et al., 1998; Amistoso et al., 2005), Berlín, El Salvador (Barrios et al., 2002), Coso and Beowawe, USA (Morris et al., 1984; Evanoff et al., 1995) and Latera and Larderello, Italy (Barelli et al., 1985; Cappetti, 2006). Different methods have been tried to prevent scaling in geothermal wells, including varying pressure, temperature and/or fluid pH, and changing scale inhibitors. Although these inhibitors have solved many problems, one promising alternative is acidizing. Increasingly, geochemical modelling studies help geothermal field operators to anticipate scaling problems and to propose solutions in order to maintain well productivity/injectivity (Xie, 2004; Xu et al., 2004; André et al., 2006).

A very successful method of acidizing geothermal wells has been through high-rate injection of strong mineral acids. Elevated acid concentrations have been shown to be effective in geothermal wells producing from natural fractures and from formations that do not have large carbonate zones. In almost all documented cases, acidification is done following the three usual main steps—preflush (HCl), main flush (HCl–HF mixture) and overflush (HCl, KCl, NH_4Cl solutions or freshwater).

Naturally fractured volcanic formations can withstand high HF concentrations. The HCl–HF stage can be, for example, a 10% HCl–5% HF solution, or an organophosphonic acid added to a 3% HCl–5% HF solution. These acid mixtures have been used successfully in stimulating geothermal wells in Indonesia (Pasikki and Gilmore,

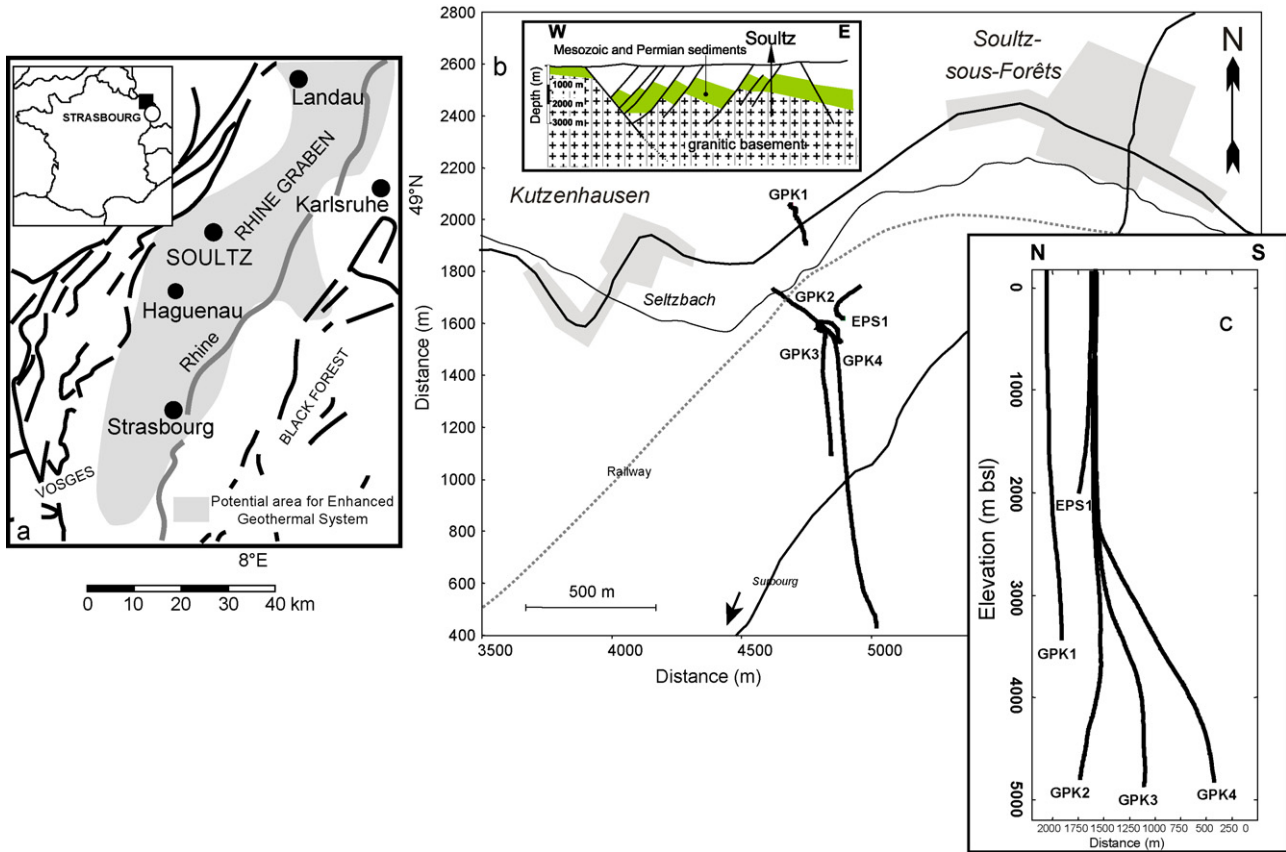


Fig. 1. Schematic geological map of the Rhine Graben and location of the Soultz-sous-Forêts EGS site (a and b). Map view and N-S cross-section of the Soultz deep geothermal wells (b and c); solid lines correspond to well traces (b and c) (after Sausse et al., 2006).

2006), as well as in Mexico (Flores et al., 2006). The only additives needed in a geothermal acid job are the corrosion inhibitor and the inhibitor intensifier that may be used to extend the performance range of the selected corrosion inhibitor at elevated temperatures, as well as a high-temperature iron-control agent. 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.

4. The case of the EGS reservoir at Soultz-sous-Forêts

The Soultz-sous-Forêts Enhanced Geothermal System, located 40 km north of Strasbourg, France, in the Upper Rhine Graben, has been investigated since 1986 (Fig. 1). The final goal of the project is to extract heat for power production from a regional, randomly permeable, natural geothermal reservoir by forced fluid circulation between production and injection boreholes drilled into the granitic basement. This site was chosen because of the large thermal anomaly in the area and because the shallow geology was well known, due to former oil exploitation in this part of the Tertiary Graben.

The shallow geology (0–1400 m depth) consists of sedimentary layers, overlying the crystalline basement of late-Palaeozoic granites that presents hydrothermally altered and fractured zones related to the normal faults of the Rhine Graben (Genter, 1990; Traineau et al., 1991). It has been observed that deep fluid circulation is supported by a network of permeable fractures. Extensive research has been done to characterize the properties of the fractures. Geophysical borehole measurements including image logs and core and cuttings analyses showed nearly vertical, low-permeability fractures that are oriented in an almost North–South direction (Dezayes et al., 1995; Genter et al., 1995). Moreover, it

appears that most of the fractures are sealed by hydrothermal deposits, mainly calcite, silica and clays, giving a random character to the overall permeability of the system.

After the successful connection to a 3.6-km deep fractured reservoir in 1997, it was decided to develop a new, deeper and hotter reservoir and to build a pilot geothermal plant. For this purpose, three wells (GPK3 as a central injection well and GPK2 and GPK4 as production wells) were drilled to 5000 m depth in the crystalline basement (Fig. 1). These wells have been stimulated hydraulically and chemically to create the underground reservoir (Gérard et al., 2006). The first implementation phase of the project is the construction of a 1.5 MWe geothermal power plant.

Low-pressure pre-stimulation hydraulic tests were conducted in the wells to characterize the natural permeability of the granite, indicating initial productivity indices of $0.01 \text{ L s}^{-1} \text{ bar}^{-1}$ in GPK4, $0.1 \text{ L s}^{-1} \text{ bar}^{-1}$ in GPK3 and $0.02 \text{ L s}^{-1} \text{ bar}^{-1}$ in GPK2.

The first hydraulic stimulations of the three wells were carried out between 2000 and 2005, and resulted in an improvement of the productivity indices of wells GPK2 and GPK4 by a factor of approximately 20 and of GPK3 by a factor of approximately 1.5 (Nami et al., 2007). The limited performance of the hydraulic stimulation operations, with high costs and public concern about induced seismicity, provided an important set of reasons to carry out chemical treatments as additional or even alternative methods to hydraulic stimulation. The main argument for chemical stimulation based on drill cuttings and cores analyses, as well as on geophysical logs, was that the carbonate and other soluble minerals deposits were filling the fractures.

The results obtained both from tracer (Sanjuan et al., 2006) and pressure interference tests (Dezayes et al., 2005) clearly identified the main pathways the fluid follows during stimulation and showed that some hydraulic connections exist between the boreholes via

Table 2

Summary of the chemical stimulations performed in the three 5-km deep Soultz-sous-Forêts EGS wells.

Well	Date	Concentration of chemical agents	Stimulation results
GPk2 (production well)	February 2003	One test in two steps: HCl 0.09% and HCl 0.18%	Wellhead pressure drop and productivity increase ($0.5 \text{ L s}^{-1} \text{ bar}^{-1}$)
GPk3 (injection well)	June 2003 February 2007	HCl 0.45% OCA HT	Injectivity: $0.35 \text{ L s}^{-1} \text{ bar}^{-1}$ Weak impact: $0.4 \text{ L s}^{-1} \text{ bar}^{-1}$
GPk4 (production well)	February 2005 May 2006 October 2006 March 2007	HCl 0.2% Preflush: HCl 15% RMA (HCl 12%–HF 3%) NTA 19% OCA HT	Productivity: $0.2\text{--}0.3 \text{ L s}^{-1} \text{ bar}^{-1}$ Maximum enhancement of injectivity: 35% The formation of a plug increased wellhead pressure—Productivity: $0.3\text{--}0.4 \text{ L s}^{-1} \text{ bar}^{-1}$ (after RMA and NTA treatments) Productivity: $0.4\text{--}0.5 \text{ L s}^{-1} \text{ bar}^{-1}$

RMA: regular mud acid; OCA HT: organic clay acid HT; NTA: nitrilotriacetic acid.

the natural fractures in the granite. The most important fracture zone striking N160°E and dipping 52° toward the W appears as a “direct” connection between GPk2 and GPk3 (Dezayes et al., 2005). However, in GPk2, this fracture zone is thinner and less permeable than in GPk3.

Due to the low productivities of GPk2 and GPk4 and the poor injectivity of GPk3 after successive hydraulic stimulations, it was decided to carry out a chemical stimulation program on all three wells. Chemical treatments with low-concentrations of HCl were performed in the three wells after the hydraulic stimulations (Table 2). Between May 2006 and February 2007, three chemical stimulations were done in GPk4 and one in GPk3. During these operations, solutions of RMA, NTA and organic clay acid (OCA) were successively injected with fresh water into GPk4, but only the OCA treatment was used in GPk3.

Chemical stimulations were performed by injecting acid from the wellhead through the casing string. Therefore, the entire (500–650 m long) open-hole sections of the wells were treated. Corrosion inhibitors were used to protect the inner casing string. The operations were conducted by specialized service companies. Table 2 shows the various chemical treatments conducted in the deep Soultz wells.

Hydraulic tests were performed before and after the chemical stimulations in order to evaluate changes in well productivity or injectivity; the values given in Table 2 are those measured after 3 days of injection or production. The results show that there is no significant difference between injectivity and productivity indices at moderate flows and pressure changes (Nami et al., 2008). In this case, therefore, for the Soultz wells the terms ‘injectivity’ and ‘productivity’ can be considered as interchangeable.

Geochemical monitoring was conducted during most of the chemical stimulations. Sanjuan et al. (2007) report on the fluids and deposits collected from GPk4 and GPk3 during the 2006 and 2007 production tests, after the chemical stimulation operations. This work was done in the framework of the research activities accompanying the construction of the European EGS Pilot Plant Project (Baumgärtner et al., 1998; Hettkamp et al., 2004; Baria et al., 2006; Gérard et al., 2006; Genter et al., 2009).

4.1. Soft acidizing: stimulation of the three deep wells using hydrochloric acid

The three deep wells were subjected to chemical stimulation by injection of a low HCl concentration solution. The objective of this dilute but extended stimulation was to dissolve secondary carbonates (calcite and dolomite) deposited in the formation fractures.

4.1.1. GPk2 well

Tests carried out in 2000 on the first deep well (GPk2) after hydraulic stimulation showed an improvement of its injectivity

from 0.02 to $0.3 \text{ L s}^{-1} \text{ bar}^{-1}$. A decision was then made to seek further improvement through soft acidizing. In February 2003, GPk2 was stimulated by injecting 1.5 tons of HCl in two stages. First, 500 kg were injected at a concentration of 1.8 g L^{-1} at a rate of 30 L s^{-1} . The treatment had an immediate and strong impact, showing a significant reduction of near-wellbore friction losses immediately after the acid front reached the open-hole section. The second part of the stimulation, performed at concentrations of 1.8 and 0.9 g L^{-1} and flow rates of about 15 and 30 L s^{-1} , respectively, showed less immediate effects.

Nevertheless, the overall result was impressive for such a small quantity of acid injected. No injectivity test was performed in this well after this chemical stimulation with HCl. However, the increase in injectivity was evident from the circulation tests done in 2003 (between GPk2 and GPk3) and in 2005 (between GPk3 and the two production wells GPk2 and GPk4) (Gérard et al., 2005). The injectivity index of GPk2 increased to approximately $0.5 \text{ L s}^{-1} \text{ bar}^{-1}$ after this HCl treatment.

4.1.2. GPk3 well

During a circulation test between GPk2 and GPk3 in June 2003, up to 3 tons of HCl were injected into GPk3 over a period of 12 h. A total of 865 m^3 of an acid solution with a concentration of about 4.5 g L^{-1} of HCl was injected at a rate of 20 L s^{-1} .

An injection test was carried out in August 2004 after the hydraulic and a HCl chemical stimulation of the well. A total of 7000 m^3 of fresh water was injected at flow rates of 12 , 18 and 24 L s^{-1} for a period of 6 days. The injectivity index for this test was about $0.35 \text{ L s}^{-1} \text{ bar}^{-1}$ (Gérard et al., 2005). Nevertheless, it is difficult to estimate the impact of the acid treatment on GPk3 injectivity because, unlike GPk4, no injection test was performed under the same conditions before and after the chemical stimulation.

4.1.3. GPk4 well

In February 2005, an acidified water injection experiment was conducted with the objective of improving the injectivity around GPk4. A total of 4700 m^3 of an about 2 g L^{-1} HCl solution was injected at a flow rate of 27 L s^{-1} ; in this test 11 tons of HCl were used. Despite the fact that the injection was performed in an over-pressurized reservoir, the injection pressure was decreasing during the last hours of the acidification test.

The impact of the GPk4 stimulation was evaluated before and after each phase of the operation by performing a step-rate injection test. About 4500 m^3 of fresh water were injected at increasing flow rates (9 , 18 and 24 L s^{-1}) in 1-day steps. The first step-rate injection test was carried out in GPk4 after its second hydraulic stimulation in 2005. The analysis of this test gave a productivity index, after 3 days of injection, of $\sim 0.20 \text{ L s}^{-1} \text{ bar}^{-1}$.

After injecting acid into GPk4 on 13 March 2005, a second step-rate injection test was performed. Results show that the well-

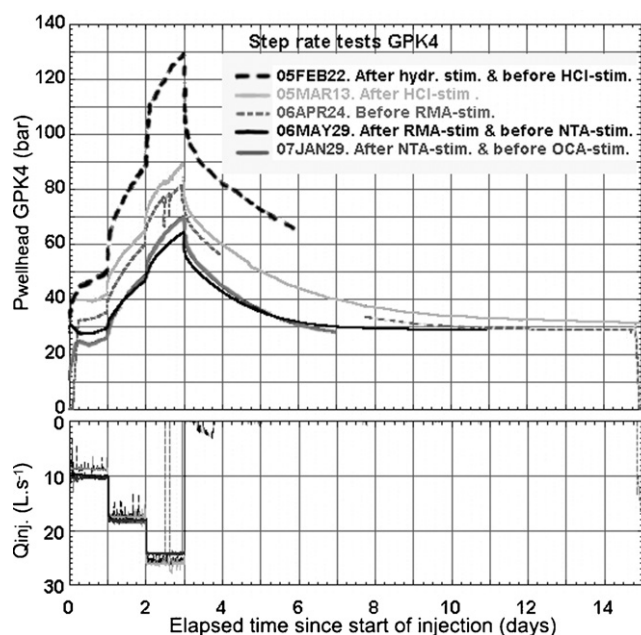


Fig. 2. Comparison of wellhead pressures and injection rates during the GPK4 step-rate tests (modified after Nami et al., 2007).

head pressure was about 40 bars below the value observed under the same conditions before acidification (Fig. 2). This represents a decrease in the apparent reservoir impedance, as inferred from the wellhead pressure, by a factor of about 1.5 (Gérard et al., 2005). The productivity index of GPK4 reached $0.30 \text{ L s}^{-1} \text{ bar}^{-1}$ after acid injection.

4.2. Stimulation of GPK4 with regular mud acid

Regular mud acid a mixture of HCl and HF, widely used in oil and gas wells, was only injected into GPK4. The purpose of the RMA treatment was to dissolve the hydrothermal minerals (e.g. carbonates, clay, feldspars and micas) deposited in the fractures and pores of the granite, and thus improve its permeability.

To determine the most effective acid mixture to use in the stimulation of the deep reservoir, laboratory tests were performed both in batch and under continuous flowing conditions (Erga, 2000). The batch experiments consisted in testing the reactivity of acid mixtures (HCl/HF) at 50 and 150°C on core samples of granite composed mainly of feldspars, quartz, micas, phyllosilicates and that presented hydrothermal veins. Batch results indicated that the mixtures 12/3 and 12/6 (by wt%) were the best to attack these rocks and minerals. These two HCl/HF mixtures were then used in a series of tests under flowing conditions and temperatures of up to 90°C .

The flowing test apparatus can be used on a circular plane sample (0.02 m in diameter) by applying an acid mixture under variable flow rate and temperature conditions. The samples were carefully weighted before and after each test using a precision balance and thus measure the weight loss per unit surface. Scanning electron microscope and quantitative X-ray microanalyses were used in order to determine the minerals affected by the acidification treatment. The most effective acid mixture was found to be 12/3 (wt%) HCl/HF mixture.

In May 2006, the RMA treatment was carried out in four steps and adding a corrosion inhibitor when needed. Before the injection of RMA, 2000 m^3 of cold deoxygenated water were introduced into the well at rates of 12, 22, and, finally, 28 L s^{-1} . Then, to avoid calcium fluoride (CaF_2) precipitation that can lead to well damage,

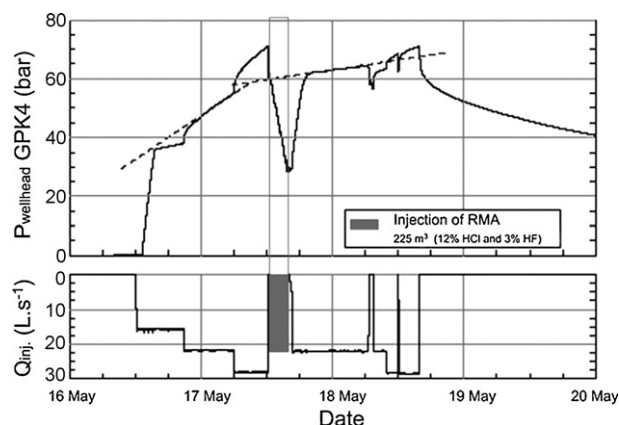


Fig. 3. Impact of the regular mud acid (RMA) acidification test performed on GPK4 in May 2006 (after Nami et al., 2007). The slope change in the pressure (dashed line) for the same flow rate before and after the RMA injection (preflush of 25 m^3 of 15% HCl solution and main flush of 200 m^3 of RMA at 22 L s^{-1} during about 3 h) indicates a gain in well injectivity (productivity).

a preflush of 25 m^3 of a 15% HCl solution in deoxygenated water (3.75 tons of HCl) was pumped ahead of the HCl-HF mixture for 15 min at a rate of 22 L s^{-1} . A main flush consisting of a total of 200 m^3 of 12/3 (wt%) RMA was then injected for 2.5 h at a rate of 22 L s^{-1} . Finally, a postflush of 2000 m^3 of cold deoxygenated water was injected after the RMA treatment during 1 day, at flow rates of 22 and 28 L s^{-1} .

After the RMA stimulation, the wellhead pressure versus time curve for GPK4 was smooth, indicating an efficient clean-up of the fractures and/or pores around the open hole (GEIE, 2006) (Fig. 3). The step-rate test performed later in May 2006 (Fig. 2), following the RMA stimulation, shows that after 3 days of injection the wellhead pressure is about 65 bars, which is about 16 bars lower than before the chemical treatment (i.e. when the April 2006 step-rate test was performed). This represents a 35% reduction in wellhead pressure due to the acidification treatment (GEIE, 2006). Before the RMA treatment, the wellhead pressure increased rapidly with flow rate indicating restricted storage capacity in the vicinity of the well.

It is estimated that the RMA stimulation of GPK4 has resulted in the enhancement of the well's injectivity index by up to 35%. However, no production test was performed after these operations to measure the productivity index.

4.3. Stimulation of GPK4 using chelating agents

After the RMA stimulation, GPK4 was chemically treated with NTA, a chelating agent, in October 2006. While the RMA treatment was used to clean the fractured and porous zones of hydrothermal mineral deposits in the near field around the borehole, the goal of the NTA stimulation was to drive the chelating agent as far as possible into these zones to improve the hydraulic connections in the reservoir.

NTA ($\text{C}_6\text{H}_9\text{NO}_6$) is a weak tri-acid that forms complexes with cations like Fe, Ca, Mg, and Al, and thereby reduces the activity of these cations, leading to an enhanced dissolution of the corresponding minerals (e.g. calcite). Chelants are much less corrosive to steel tubulars than acids.

What prevented geothermal operators from using caustic solutions in the past was the fear of calcite deposition, which is strongly favored at high pH. However, laboratory experiment results have demonstrated the potential for calcite dissolution at high pH in the presence of chelating agents (Mella et al., 2006; Rose et al., 2007). This suggests that thermally stable chelating agents at high

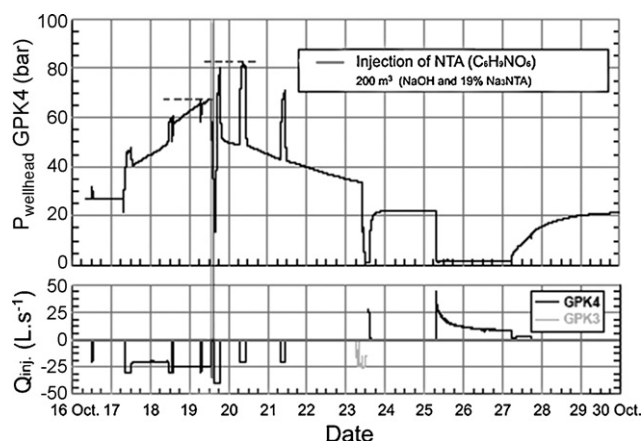


Fig. 4. Impact of the nitrilo-triacetic acid (NTA) treatment performed on GPK4 in October 2006 (after Nami et al., 2007). The wellhead pressure (dashed line) following short water injections is higher than shortly before the injection of 200 m³ of NTA at 35 L s⁻¹, followed by a postflush injection of 400 m³ of water at 40 L s⁻¹, and indicates probable plugging of the well. A production test was done on 25 October to remove NTA solution residuals.

pH can provide the basis for an affordable and effective mineral dissolution approach. Although thermal stability studies have not been completed yet, the literature suggests that NTA could be used at temperatures as high as 290 °C, whereas the other two chelating agents, EDTA and hydroxyethylethylenediaminetriacetic acid (HEDTA), are significantly less thermally stable, i.e. up to about 200 °C. Calcite dissolution experiments in a high-temperature flow reactor confirmed the superior performance of NTA above 200 °C (Peter Rose, pers. comm., April, 2008).

Before GPK4 was treated with NTA, the well was cooled by injecting 4150 m³ of fresh water at an average flow rate of about 24 L s⁻¹ for a period of 53 h. After well cooling, 200 m³ of a basic solution (pH 12) consisting of caustic soda (NaOH) and 19% Na₃NTA (about 38 tons of NTA) were injected at a flow rate of 35 L s⁻¹ during 1.6 h period. After the NTA injection, 850 m³ of fresh water were injected at 20–40 L s⁻¹.

Surprisingly, after these injections the wellhead pressure increased radically (Fig. 4). To prevent any well plugging, a production test was carried out in GPK4 (October 2006) to remove residuals of the NTA solution. During this test about 2600 m³ of fluid were discharged. At the beginning of the production test, large quantities of magnetite-rich grey sands and drilling grease deposits were produced, followed by a yellow-coloured fluid containing chelant precipitate (GEIE, 2007). At the end of the test, geochemical analysis of the produced water samples showed a neutral pH (7.1–7.4), and thus the almost complete removal of the chelating agents from the borehole and neighbouring fractures and pores (Sanjuan et al., 2007). The mobilization and accumulation of these deposits in the fractured and porous zones were probably due to the significant cleaning of the well itself and of the near-wellbore formation by the basic NTA solution, especially because of the use of NaOH. It is likely that, during the injection of chelating agents – which are also used as cleaning agents – scale deposits were detached from the casing and transported into the surrounding formation. These deposits and the drilling wastes (grease, cuttings) probably blocked some of the flow pathways in the vicinity of the well and resulted in an increase in wellhead pressures.

In January 2007, in the same manner as for the previous RMA stimulation of GPK4, a step-rate test was carried out to assess the effects of the NTA stimulation. The wellhead pressure after the NTA injection was about 7 bars higher than before the chemical treatment (Fig. 2), indicating loss in productivity; i.e. the index dropped to about 0.35 L s⁻¹ bar⁻¹.

4.4. Stimulation with chemically retarded acid systems: chemical stimulation of the GPK4 and GPK3 far fields

To complete a series of hydraulic and chemical stimulations to enhance the productivity of the three deep Soultz wells that started in 2000, GPK3 and GPK4 were treated with chemically retarded acid systems (organic clay acid for high temperature; OCA-HT). The main objectives of this operation were to dissolve the remaining solid deposits and to increase as much as possible the hydraulic connectivity between wells and the fractured and porous formation.

The OCA fluid was a mixture of citric, hydrofluoric and borofluoric acids and ammonium chloride. The solution consisted of 5–10% C₆H₈O₇, 0.1–1% HF, 0.5–1.5% HBF₄, and 1–5% NH₄Cl (Sanjuan et al., 2007). Its use is especially recommended at temperatures above 180 °C for sandstones or formations with zeolite or chlorite contents greater than 5%, which react with conventional stimulation fluids (i.e. HCl). This solution was at first tested in the laboratory by Schlumberger on GPK3 cutting samples. After 5 h of reaction, the OCA solution dissolved 24% of the cuttings samples at 80 °C and 41% at 180 °C. Other laboratory tests were carried out at BRGM showing that the solution could also dissolve metal–NTA complexes (Sanjuan et al., 2007).

The OCA solution can penetrate deep into the formation and stabilize clays and fines without the adverse effects of conventional acid systems. It attacks mainly calcite, but also silicates, aluminosilicates, iron oxy-hydroxide minerals and Ca–Fe–NTA compounds. This solution is a high-performance acid system designed for sandstone matrix formations that can present the biggest challenge to conventional acidizing treatments. The fluid combines a retardation effect and advanced chelation technology to give a deep stimulation of the reservoir with a minimal precipitation potential. It reduces the risk of diminished production as well as secondary and tertiary mineral precipitation that can block pores, and it also diminishes corrosion. The OCA solution also combats sludging problems that plague conventional acid systems and promotes long-term production by stabilizing formation fines while maintaining the integrity of the sandstone structures.

Chemical OCA stimulations were conducted in GPK3 (on 15 February, 2007) and GPK4 (on 21 February, 2007). In GPK3, 1250 m³ of fresh water were injected at 35–55 L s⁻¹ ahead of the injection of 200 m³ of OCA at 55 L s⁻¹. The amount of fresh water was reduced to 685 m³ in GPK4, whereas the amount of injected OCA was identical (200 m³ at 50 L s⁻¹; density of 1.04 g cm⁻³). After the OCA injection, about 1400 and 750 m³ of fresh water were injected into GPK3 and GPK4, respectively, at 30–45 L s⁻¹.

Wells GPK3 and GPK4 present different storage configurations and capacities around their wellbores. GPK3 is intersected by a large fracture zone (i.e. a sizable near wellbore volume of more than 1000 m³) that must be filled with the injected fluids before reaching the narrowest flowpaths. On the other hand, GPK4 shows some narrow blocked zones close to the well (i.e. a smaller volume of fluids is needed to saturate its near-well storage capacity).

A nearly similar wellhead pressure trend for the same flow rate was observed in GPK3 before and after the OCA injection (Fig. 5). The impact of the OCA stimulation on this well was evaluated by a step-rate injection test on March 2007. It consisted of a short step of 10 L s⁻¹ to slowly cool the well, followed by injection at 24 L s⁻¹ for more than 3 days. No significant pressure reduction, compared to previous tests, was observed in GPK3 after the OCA stimulation, indicating that its injectivity had not significantly improved (Fig. 6). The injectivity index after 3 days was about 0.40 L s⁻¹ bar⁻¹, very close to that measured before this chemical treatment (i.e. 0.35 L s⁻¹ bar⁻¹).

There was a fast increase in GPK4 wellhead pressure during the preflush phase (Fig. 7). The pressure reached about 120 bars just

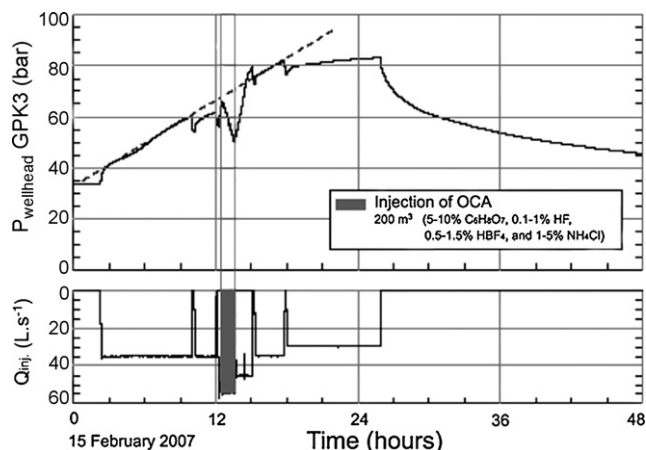


Fig. 5. Impact of the organic clay acid HT (OCA HT) acidification done on GPK3 in February 2007 (after Nami et al., 2007). A nearly similar pressure trend for the same flow rate (dashed line) is observed before and after the injection of 200 m³ of OCA at 55 L s⁻¹, and indicates that there was no gain in well productivity.

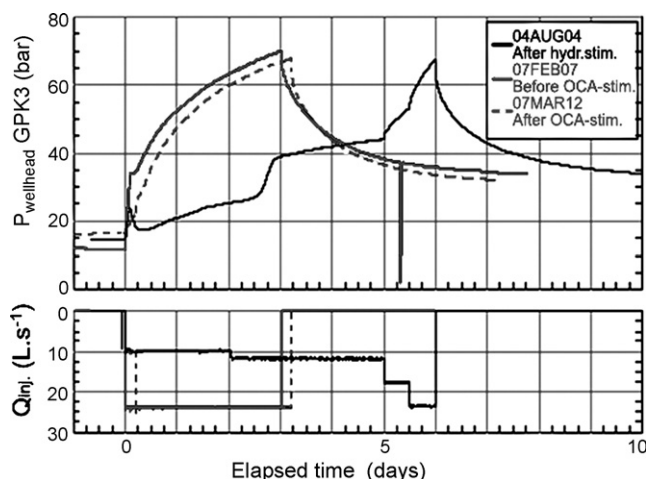


Fig. 6. Injection tests performed in GPK3 (after Nami et al., 2007). The maximum wellhead pressure measured during the injection test done after the OCA stimulation is almost the same as during the injection test performed after the 2004 hydraulic stimulation.

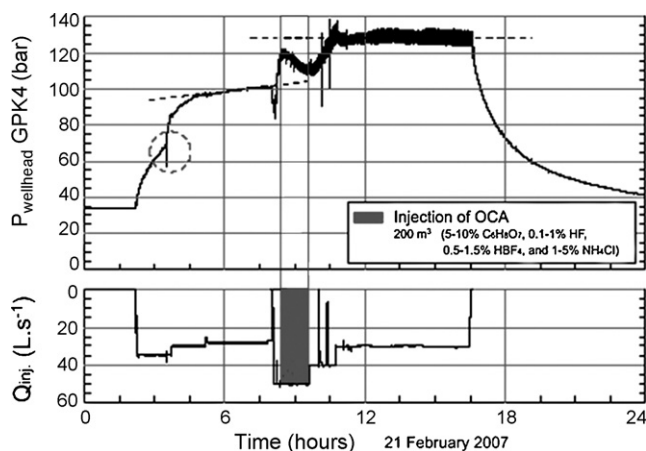


Fig. 7. Impact of the organic clay acid HT (OCA HT) acidification test performed on GPK4 in February 2007 (after Nami et al., 2007). After the injection of 200 m³ of OCA at 50 L s⁻¹, a constant pressure (dashed line) is observed during the postflush injection of fresh-water at 35 L s⁻¹.

before the injection of OCA, and rose to a maximum of 130 bars during the postflush phase until shut-in. The abrupt pressure increase suggests some plugging of the well.

After the displacement of the OCA fluid into the formation, and only 7 h after GPK4 shut-in, the wellhead pressure drastically decreased from 126 to 40 bars (Fig. 7). Part of the increase in injectivity could perhaps be attributed to shear failure, and part to chemical effects. If some feed zones in the well were plugged during injection, as indicated by the pressure versus time curve, the fracturing pressure might have been exceeded, even at the low flow rate of 30 L s⁻¹ (Nami et al., 2008).

No injection test was performed after the OCA stimulation. However, an assessment of GPK4 was possible, by analyzing the production tests carried out before and after this stimulation. The productivity index increased from 0.4 L s⁻¹ bar⁻¹ before the OCA treatment to 0.5 L s⁻¹ bar⁻¹ after it. Maybe the most important point is the fact that this index looks stable at 0.5 L s⁻¹ bar⁻¹ indicating a good connection to a large reservoir (GEIE, 2007).

4.5. Discussion

The combination of the RMA, NTA and OCA treatments could possibly explain the significant increase in GPK4 productivity. The integration of seismic monitoring, temperature and flow logging results helps in detecting the productive zones in the wells and their changes in response to chemical stimulations (Nami et al., 2008). Minor micro-seismic activity (hundreds of events with magnitudes up to 1.5) was observed around 4100 m true vertical depth (TVD) during the OCA test in GPK4 well (Nami et al., 2008). Flow logs were run and revealed two leak zones in the well casing at 4110 (15–25%) and 4440 m TVD (50 m above the casing shoe 9–15%), respectively. These leaks do not correspond to the joints of the casing, and their origin is not clearly explained, but fracture shearing may be involved. Except for these two fluid loss zones in GPK4, the flow remains constant until a last fluid loss at 4800 m TVD that corresponds to a fracture zone with abundant hydrothermal minerals.

In contrast to the previous production tests, the temperature curve for the production test performed after the OCA stimulation showed a decreasing trend despite the highest fluid production rate (Nami et al., 2008). Apparently, this gain of productivity does not originate only from the open-hole section of the well. The chemical stimulations with RMA, NTA dissolved in caustic soda solution and OCA improved the productivity of the GPK4 well by 30 and 25%, respectively, but part of this gain could be attributed to the hydraulic stimulation of two loss zones in the cemented part of the casing, assuming that they were not generated during or after the initial hydraulic stimulation had ended.

Starting with the step-rate test performed in GPK4, the pressure in GPK3 and GPK2 was monitored throughout the stimulation operations to study the connection between the wells. A clear pressure response was observed in these two wells after the stimulation with RMA. The pressure change in GPK3 is higher than in GPK2 because of its proximity to GPK4. For the same reason, the response time is shorter in GPK3. The propagation of pressures to GPK2 might be explained by the improved hydraulic interconnection between GPK3 and GPK4 and between GPK2 and GPK3. The large fracture zone connecting GPK2 and GPK3 (see Section 4) could form a short circuit and reduce fluid residence times in the reservoir, thereby affecting fluid production temperatures.

Geochemical monitoring of the fluids discharged by GPK3 and GPK4 also indicates that the percent of traced fresh water (injected in large amounts into GPK2, GPK3 and GPK4 in 2000, 2003 and 2005) is always low (<10%) in the produced geothermal brine (Sanjuan et al., 2007). The existence of at least three fluid flow pathways between the wells GPK2 and GPK3 with different effective

fluid velocities, which contrasts with a poor hydraulic connection between GPK3 and GPK4, was detected during the July–December 2005 fluid circulation loop and the associated fluorescein tracer test (Sanjuan et al., 2006).

4.6. Summary

The chemical stimulation program performed at Soultz improved well injectivities/productivities by factors ranging between 1.12 and 2.5 (Nami et al., 2008). Well GPK2 was the easiest to stimulate, but the largest gain in injectivity was obtained in GPK4 (GEIE, 2007).

Although the chemical well stimulations were not executed with the same comparable protocol, variable but encouraging results were obtained in the Soultz EGS wells. While GPK3 showed small variations in injectivity whatever technique was used (hydraulic or chemical), GPK4 presented a real increase of injectivity and productivity after the treatments, while GPK2 showed significant improvements despite the fact that the acid treatments were limited in terms of time, volume and concentration.

Table 2 summarizes the chemical stimulation methods used in the three deep boreholes of the Soultz EGS Project, as well as the results obtained so far. These results show that the acids have actively reacted with the minerals present in the fractures and pores of the Soultz granite. The injection of NTA into GPK4 dissolved in a caustic soda solution (pH 12) cleaned the borehole and part of the fractures in the granite by eliminating and extracting significant amounts of drilling wastes (grease, cuttings), rock fragments and hydrothermal deposits. In addition, dissolved and solid Ca–Fe–NTA compounds were also formed.

The maximum volumes of calcite dissolved by the RMA and NTA treatments were estimated at about 19.2 and 5.5 m³, respectively (Sanjuan et al., 2007). The use of a caustic soda solution to clean GPK4 before injecting NTA would have probably allowed NTA to reach deeper into the fractures and, consequently, to be more efficient. The OCA treatment improved GPK4's productivity index from 0.4 to 0.5 L s⁻¹ bar⁻¹, but seems not to have made much difference to the injectivity of GPK3.

No major improvement in GPK3 injectivity was observed after successive stimulation operations with HCl and OCA. Even though the distribution and sizes of the fractured areas around GPK3 and GPK4 are probably different, the failure to use a caustic soda solution to clean GPK3 and the neighbouring fractured areas (where the accumulated debris likely blocked the hydraulic connection between the wellbore and the main fracture zones) could partially explain the limited results obtained in this well. It seems that a single chemical stimulation method may not be appropriate for the Soultz wells, but that a combination of treatments might have to be considered.

5. Conclusions

Acid treatments were originally developed by the oil industry to improve the productivity of oil and gas wells. This technology was partially adapted to geothermal wells, most often to remove mineral scales deposited in the wells after several years of exploitation. Nevertheless, these acid treatments also allow the enhancement of fracture networks in the near-wellbore region. They have been successfully performed in granitic geothermal reservoirs like Fjällbacka (Sweden) and Beowawe (USA). In recent years, the reliability of acidizing sandstone intervals has been significantly improved. In the USA, about 90% of treated geothermal wells have responded with a 2- to 4-fold increase in fluid production.

More recently, this technology has been applied to the Soultz-sous-Forêts (France) EGS reservoir after massive hydraulic

stimulation operations, which, however, induced several micro-seismic events of concern to the public. The three 5-km deep Soultz wells (GPK2, GPK3 and GPK4) were treated with different amounts of chemicals in order to dissolve the maximum amount of hydrothermal minerals precipitated in fractures and pores of the granitic reservoir, and to reach as deep as possible into the formation.

The injectivity and productivity of each well was affected differently. While encouraging results were obtained in GPK2 and GPK4, the injectivity improvement in GPK3 was minimal whatever stimulation technique (hydraulic or chemical) was used. At present, GPK2 has a productivity index of about 0.50 L s⁻¹ bar⁻¹ in single-well tests.

The injectivity index of GPK3 is about 0.40 L s⁻¹ bar⁻¹, which remained almost unchanged after successive stimulation operations with hydrochloric acid (HCl) and OCA. A highly conductive fracture with a large area crosses the open-hole section of the well and prevents further improvements by chemical stimulation. The productivity index of GPK4 reached 0.20 L s⁻¹ bar⁻¹ after hydraulic stimulation and has increased to about 0.50 L s⁻¹ bar⁻¹ after chemical stimulation. The chemical stimulation with RMA and chelating agents (NTA) further improved the hydraulic communication between GPK3 and GPK4.

Despite the small number of chemical stimulation operations completed at Soultz-sous-Forêts and their limitation in terms of time, volume and concentration, the results suggest that this type of stimulation must be developed further. Combined with moderate hydraulic stimulation, it might reduce the need of carrying out high fluid pressure stimulation operations that may induce micro-seismic events that could raise public concern and negatively impact future geothermal activities.

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