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Solubility of Hydrothermally Altered Volcanic Rocks in Acid Solutions

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ABSTRACT

Rock matrix stimulation has been a methodology used to enhance well productivity in oil systems. Recently, this methodology began to be applied in geothermal systems. In order to investigate the solubility of altered volcanic rocks in acid solution used in rock matrix stimulation, experiments were carried out on samples of igneous hydrothermal altered rocks from the Los Humeros geothermal reservoir. The common acid solutions, used in three stages during acid well stimulation, are HCl 10% and a mixture of HCl 10% and HF 5%. Experiments were conducted using the referred acid solutions at atmospheric pressure and temperature of 110 ± 5°C.

The chemistry, mineralogy and permeability of selected rocks from Los Humeros geothermal field were determined before and after reactions with each acid solution. Mineral dissolution is selective, and depends on the type and intensity of hydrothermal alteration to rocks and the processes that have affected the rocks.

As it is expected, Calcite readily reacts with acids, leaving empty veins and micro fractures (worm holes). Calc-silicates are resistant to acid solutions; dissolution of minerals is observed in the external surfaces of the specimen in contact with the acid solution turning the surface with a rough texture and leaving the rock matrix unreacted.

1. INTRODUCTION

Rock matrix stimulation has been a methodology used for years to enhance well productivity in oil systems. Some years ago this methodology began to be applied in some geothermal systems in Philippines, Indonesia and the United States. This has not always been successful, especially in volcanic reservoir rocks.

As originally designed, matrix acidizing has been applied successfully in both carbonate and sandstone formations; the main purpose in carbonate formations is to form conductive channels, called wormholes, through the formation rock (Kalfayan L., 2008). The acid solution penetrates beyond the near wellbore region, extending and forming smaller channels, branching off the main wormhole. In sandstone formation, matrix acidizing treatments are usually designed to dissolve acid soluble material deposited in pore network near the wellbore.

In carbonate rocks, the acids commonly used are: Hydrochloric, Acetic and Formic. In sandstone formations, the acids commonly used are: Hydrochloric, Acetic, Formic and Hydrofluoric. Where a siliceous carbonate formation is treated, HF is used in combination with HCl.

To minimize or to eliminate the effects of scale deposition as well as restore or improve permeability, several methodologies have been used in geothermal fields. A few examples: matrix acidizing, hydraulic fracturing, thermal fracturing and chemical stimulation.

Hydraulic fracturing is commonly used, although not many successful cases are known; it is considered as an option in geothermal fields to improve wells with poor reservoir connectivity (Flores et al. 2005).

Thermal fracturing produces thermal shock by injection of cool water. It is a well-documented method but it is not suitable to eliminate scales.

As it was mentioned, matrix stimulation is an old methodology used to enhance well productivity in oil systems. Nowadays it has been extended to the geothermal industry in wells that have shown reduced productivity, either by clogged pores and fractures or scale formation. Hydrochloric acid is used widely; it is known to dissolve scales such as calcium carbonate, and is used extensively in oil field operations throughout the world.

HCl and mixtures of HF and HCl have been used in acidizing operations. HCl is selected to treat limestone and calcite in veins, pores and scales. A mixture of HF and HCl is used to dissolve silicates and silica. A mixture of 12% HCl–3% HF (called regular mud acid) is used (Malate et al., 1998).

Chemical stimulation using chelating agents such as ethylenediaminetetracetic acid (EDTA) or nitrilotriacetic acid (NTA) have been proposed as an alternative treatment. Such agents have the ability to chelate, or bond, metals such as calcium. This procedure has been studied in the laboratory as a method to dissolve calcite in geothermal reservoirs (Mella et al., 2006). They found that the rate of calcite dissolution is not as fast as using strong mineral acids.

Before an acid treatment will be designed, some important features have to be taken into account, such as the type of formation damage, reservoir geology, mineralogy, reservoir fluids and scale deposition in production wells and in the formation. An understanding of the formation type and other properties such as porosity, permeability, intensity and type of hydrothermal alteration are also critical. In geothermal systems, rock matrix stimulation must be designed especially for each system.

Mineralogy is the result of water-rock interaction in hydrothermal systems, and depends environmental conditions such as temperature, pressure, liquid and rock composition, fluid pH, ratio of steam-water, etc. Mineral deposition in pores and fractures may reduce porosity and productivity. A common mineral assemblage in geothermal systems of high temperature, where the rocks interact with neutral to basic pH fluids, is represented by chlorites, quartz, epidote and other minerals such as calcite, chain and ring silicates, etc. Calcite will readily react with HCl solutions; chlorite also will react with HCl and HF.

Another common problem in geothermal wells is scale formation; which in many cases also contributes to reduce productivity and permeability. Deposition of inorganic scale may occur during well production. Depending on the well conditions, formation and the nature of the fluids, different scale types may form. Common scales include calcite, calcium sulfate, silica and iron sulfides.

Acid stimulation techniques have been successfully used in many geothermal systems. During the past decade it has been applied in geothermal fields such as Salton Sea, in the Philippines and Indonesia. In Mexican geothermal fields, acid stimulation of wells has been carried out in Los Azufres, Mich. and Cerro Prieto B. C.

In this work, a selection of reservoir rocks of the Los Humeros geothermal field (LHGF) was used to perform solubility experiments using the common acid solutions used in acid stimulation of wells. Sets of rocks were provided by the Comision Federal de Electricidad in order to carry out laboratory experimentation.

The best results were obtained in samples where calcite was present in pores, fine or wide veins.

Mineralogical changes are not noticeable, except in samples containing calcite. The bulk mineralogy remains the same.

The objective of the experimental work was to evaluate changes in the igneous rocks mainly on the mineralogical composition and on the petrophysical and mechanical properties of rocks.

2. THE LOS HUMEROS GEOTHERMAL FIELD

The Los Humeros is one of the four geothermal fields currently operating in Mexico; it has an installed capacity of 40 MW. The field is inside the Los Humeros volcanic caldera, which lies at the eastern end of the Mexican Volcanic Belt, Figure 1.

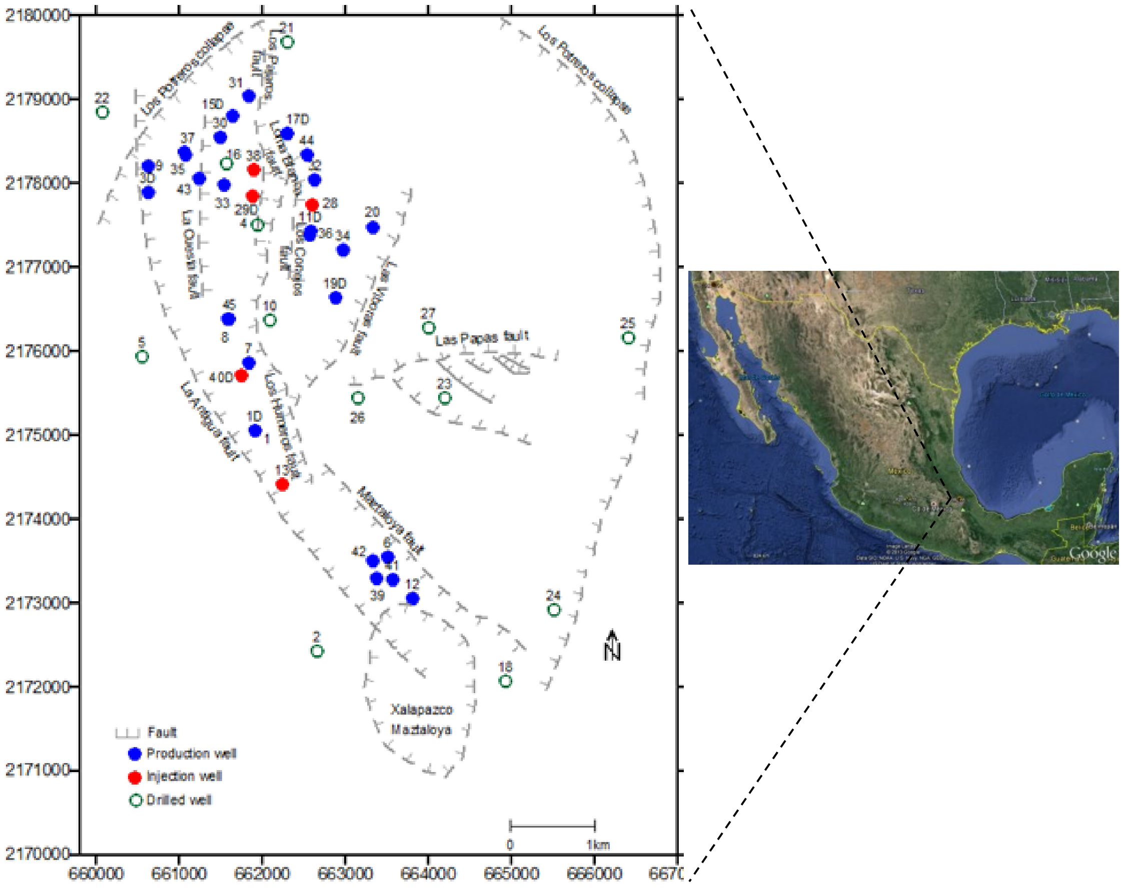

Figure 1: Map of the Los Humeros geothermal field, wells location and main geological structures.

After more than 20 years of production, as with most geothermal fields, the field has undergone several processes affecting production. Among others are the normal production decline, self-sealing by scale deposition in the formation and tubing, and other processes like silicification of reservoir rocks, etc.

In LHGF, two important features must be taken into account: the complex lithology caused by geological events that formed the large caldera, and the occurrence of aggressive fluids before and after production started.

Recently, Izquierdo et al., (2014), presented mineralogical evidences on the effects of fluid acids on the reservoir rocks of the LHGF. The aggressive fluids made changes like partial dissolution, total or partial sealing, increasing and decreasing permeability, etc. Due to the complexity of processes in the rocks of the LHGF, in case of acid stimulation work, each well must be considered individually and a specific acid treatment must be designed.

In relation to the Los Humeros caldera, a series of geologic events have occurred (Gutiérrez-Negrín, 1982b; Viggiano and Robles, 1988). The complex geology has been summarized in four Units:

Unit 1. Post-caldera volcanism. It is composed of andesites, basalts, dacites, rhyolites, flow and ash tuffs, pumices, ashes and materials from phreatic eruptions. The unit contains shallow aquifers.

Unit 2. Caldera volcanism. This unit is mainly composed of lithic and vitreous ignimbrites from the two collapses (Los Humeros and Los Potreros). It also includes rhyolites, pumices, tuffs and some andesitic lava flows, as well as the peripheral rhyolitic domes. This unit acts as an aquitard (Cedillo, 2000).

Unit 3. Pre-caldera volcanism. It is composed of thick andesitic lava flows, with some intercalations of horizons of tuffs. The characteristic accessory mineral of the upper andesites is augite, and the lower andesites is hornblende. Both packages include minor and local flows of basalts, dacites and eventually rhyolites. This unit contains the geothermal fluids.

Unit 4. Basement. This basement unit is composed of limestone and subordinated shales and flint. This unit also includes intrusive rocks (granite, granodiorite and tonalite) and metamorphic (marble, skarn, hornfels), and eventually some more recent diabasic to andesitic dikes.

3. RESULTS

3.1 Materials and methods

Cores of a suitable size, coming mainly from Unit 3, were selected to carry out the matrix acidicing experimental work. As mentioned, Unit 3 is where the geothermal fluids are contained and where the highest hydrothermal alteration of rocks is found.

The mineralogy of several cores from different wells was determined by x-ray diffraction and petrography.

Core A, from a well located south of the LHGF at a depth of 1200-1203 m, has a gray color with greenish shades. It is classified as andesite, its characteristic accessory mineral is augite; it shows medium intensity of hydrothermal alteration. Minerals identified are: Plagioclase, quartz, augite altered to chlorite, calcite, epidote and traces of hematite.

Core B, from a well almost at the central part of the LHG at a depth of 1500-1503 m, has a gray color with greenish shades. It is classified as andesite, compact, fine grain, with aphanitic to porphyric texture. It shows small irregular fractures sealed by hematite.

Core C, from a well near the central part of the LHGF at a depth of 1300 - 1303 m, has a light gray color. It is classified as andesite, whose dominant accessory mineral is hornblende. It shows high intensity of hydrothermal alteration, represented by epidote, chlorite, quartz, calcite and mica (illite).

Core D, from a well located at the central part of the LHGF, at a depth of 2000 and 2004 m. This core is rather different from the others. This core possibly was an altered andesite; which apparently was affected by aggressive fluids leaving only a frame of micro crystalline quartz, well preserved plagioclases and traces of chlorite and pyrite.

Experiments were carried out in acid and temperature resistant vessels. Pre-weigh core fragments were placed consecutively in each acid solution (HCl 10%; HCl 10% + HF 5%; HCl 10%).

Experiments were conducted at atmospheric pressure in a controlled temperature oil bath at 110 °C for 1 hour using the same specimen for each solution. After each treatment, samples were recovered from the acid solution, immersed in distilled water and were left to dry at room temperature. The weight of dry specimens was always registered. Weight loss is relative, because samples lose particles during the reaction and during handling.

At the end of the third reaction, small chips of the cores were finely powdered for mineral identification by X-ray diffraction. An Ital Structure diffractometer with filtered CuKά radiation was used; chemical analysis of reacted rocks was carried out by ICP OS (Thermo scientific, iCAP 6300).

Klinkerberg permeability was determined in the same briquette before and after the acid treatment by measuring the absolute permeability, using the stable state technique at room temperature and constant pressure, and nitrogen as the working fluid (Contreras & García, pers. comm.).

3.2 Results

In core A, calcite is present filling holes and fine veins; after the reaction with HCl, empty holes and veins were observed indicating complete calcite dissolution. It was also noted that acid penetrates the rock matrix. A fragment of the same core without calcite, after acid treatments show only discoloration of the external surface of the specimen; also after the binary solution, the external surface of the specimens turns rough. Figure 2 at the left shows a fragment of core A before any treatments, below it a cylinder after the first stage of reaction. At the right, the same fragment after the third treatment.

Chemical analyses of treated samples show lower concentrations of major elements, compared to the original/untreated specimen. Chemical, physical and mineralogical changes are related to the original rock composition, time of reaction and the type of acid solution. In core A, calcium concentration decreases due to calcite dissolution. Calc-silicates react with the mixture of HCl-HF decreasing in Si. Most of the major elements show slight decrease in their concentration. The major weight loss is observed in Core A, due to the important dissolution of calcite.

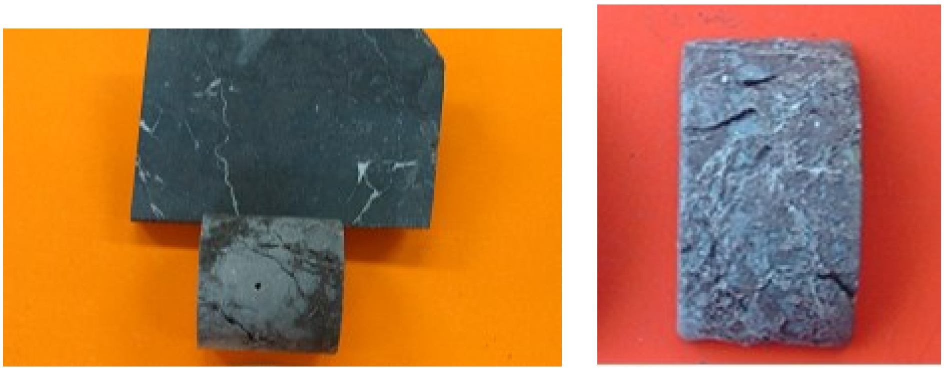

Figure 2: Core A. At the left, on top, the original fragment of the core A, below it after HCl treatment; at the right the same fragment after reaction in HCl+ HF solution. Open conduits and rough surface are observed. Dimension of specimens are 3.5 cm in diameter and 3- 4 cm high.

The fragment of core B used in the experiments is a fine grain andesite, with no apparent alteration; except the presence of hematite, which appears disperse in fine veins and fractures. After the treatments, no important weight loss was registered; also changes in permeability were small. Again the surface of the core fragment shows roughness, resembling etched glass with superimposed hematite veins (Figure 3). This means that acid solution reacted on the surface rock, forming minerals without entering in to the matrix of the core. At the conditions of our experimentation, hematite was insoluble in acids.

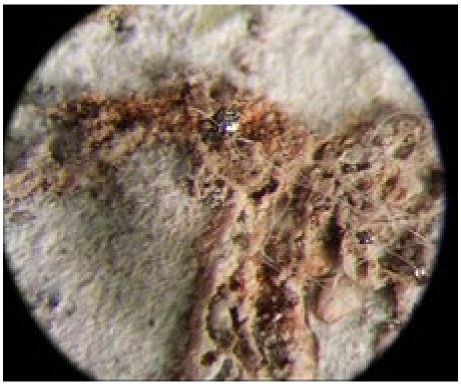

Figure 3: Image of a fragment of core B after reaction with the binary acid mixture, (16X).

Core C is an andesite with a high intensity of hydrothermal alteration represented by epidote, chlorite, quartz, calcite and small amounts of mica. The specimen selected for the experiment has a fracture filled by quartz and epidote.

As the sample lacks in calcite, the reaction with acids is at the contact surfaces. Figure 4 shows a slice of the core C before any treatment, showing a vein sealed with quartz and epidote. At the end of the acid treatments, the specimen is bleached and no apparent dissolution of quartz or epidote is observed. Small broken chips of the sample show that fluids do not penetrate to the rock matrix. As expected, when calcite is absent, small differences in loss weight and in permeability data are recorded. That means that the mixture of HCl + HF is not able to dissolve quartz and epidote.

Figure 4: A fragment of core C, before acid treatment, with a vein sealed by quartz and epidote. After reaction in acid solutions the cylinder shows a bleached surface and no dissolution of quartz and epidote. The size of the cylinder is 3.5 cm of diameter and 4 cm height.

Core D. Independent to the objective of this work, this core is a unique one; it has been studied extensively to understand other processes that locally affected the deep reservoir rocks (Izquierdo et al., 2014). In Figure 5, two specimens from different wells are compared. At the left, a fragment of core B after acid treatments, the specimen is bleached by the action of acids and patches of hematite are noted. At the right is core D before acid treatment. Their physical appearance is similar. Chemical, mineralogical, petrophysical and mechanical data of core D suggest that the rock from 2000 m deep was exposed naturally to the action of an acid fluid.

Figure 5: At the left a fragment of core B after acid treatments in the laboratory; at the right a fragment of core D as it is, without any acid treatment in the laboratory.

As the mineralogy determined previously to the experimentation is limited to quartz, plagioclase, and traces of chlorite and pyrite, there is not much to dissolve. In fact, the first treatment with HCl did not produce any change in its chemical, physical and mineralogical data determined before the laboratory experimentation.

Table 1 shows the chemical composition of major oxides in weight % for a fragment of core D before any treatment. Also included is the chemical data for fragments of core D after acid treatments. As can be seen, after the interaction with HCl the sample shows only a slight change in concentration of major oxides. After the interaction with the binary solution, the chemistry changed particularly in SiO2.

Table 1: Chemical composition of a fragment of core D before and after acid treatments.

Sample	SiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Core D- before treatment	65.940	1.019	0.644	1.951	4.111	8.980
After HCl 10 %	65.475	0.919	0.643	1.876	4.046	7.284
After HCl 10%:HF 5%	59.511	0.752	0.879	2.578	2.991	6.772

As part of the characterization of core D, tensile strength was determined before exposure to acids in the laboratory; this value is compared to the value obtained for core samples from other wells of the same field before acid treatment. Table 2 includes data for core D compared to core B; also core E is included, even though it was not part of this work. Core E comes from a well located in the Colapso Central area. It can be seen that tensile strength for core D is almost half the value for the other two cores, even though they are hydrothermally altered. This can be taken as an evidence of the acid leaching processes that occurred in deep rocks of well D (Izquierdo et al., 2014). As tensile strength is a destructive test, it was not possible to determine in reacted specimens; it is surely affected by the reaction with acids.

Table 2: Tensile strength data of core D, which has been altered by acids fluid in the natural system and data for cores hydrothermally altered.

Sample	Length (cm)	Diameter (cm)	Tensile strength (MPa – Bar)
Core D	2.53	5.14	2.21 – 22.1
Core B	2.53	5.14	4.89 -48.9
Core E	2.53	5.14	4.53 -45.3

In regards to the permeability of core D, the initial value is the same as measured after the reaction with HCl. That means that there were no minerals to dissolve so the difference in weight lost is negligible. When core D was reacted in the binary solution, the permeability increases and the weight loss was considerable.

Results indicate that when working with igneous rocks, before any attempt is made for acid stimulation, it is compulsory to know the nature of the affected rocks and the processes that have been occurred in the reservoir. This of course includes the type and intensity of hydrothermal alteration of the rocks.

Table 3 is a summary of Klinkenberg permeability data before and after acid treatments. The permeability increased in samples where calcite was present, because of the light leaching of the contact surface between the sample and the solution. The permeability increased even more after the reaction with the binary mixture of acids.

Data for core D supports the assumption that the original rock was depleted in primary and secondary minerals. After the reaction with HCl 10%, the permeability was the same. With the binary mixture, the permeability increases considerably, since bonds of the micro crystalline quartz are easily broken down as for silicates and calc-silicates.

All solutions where the rocks reacted were preserved for two weeks at room conditions, in order to have evidence of the potential formation of new phases. No new phases were formed from these acid solutions. Solid material at the bottom of vessels was separated, dried and analyzed by XRD, the identified phases are the rock forming minerals.

Table 3: Permeability values before and after acid treatments

Sample	Klinkenberg permeability Before (milidarcys)	Klinkenberg permeability After (milidarcys)
Core D HCl 10%	2.18	2.18
Core D HCl 10% + HF 5%	2.18	57.6
Core B HCl 10%	0.096	0.11
Core B HCl 10% + HF 5%	0.11	5.92
Core E HCl 10%	0.073	0.284
Core E HCl 10% + HF 5%	0.284	1.47

When metallic sulfide scales (formed by galena, chalcopyrite and other phases) react with the acid solutions, upon cooling, needle shape crystals start to form as soon as the solution reaches 94 °C. These needle shape minerals were identified as Cotunnite ($PbCl_2$). When sulfide scales react with the binary mixture, Hieratite (K_2SiF_6) and Matlockite (PbClF) are formed (Izquierdo et al., 2013).

Figure 6: Cottunite crystals formed after reaction in an HCl 10% solution at 100 °C.

4. CONCLUSIONS

Even though the results were obtained at micro scale in the laboratory, compared to the size of a geothermal reservoir, they give an idea of what may be expected in an industrial acid stimulation work.

The results showed that the effectiveness of matrix stimulation of igneous rocks will depend on the type and on the intensity of the hydrothermal alteration.

Calcite reacts rapidly with both acid solutions, leaving open pores and veins (wormholes); while calc silicates react only superficially, leaving much of the rock matrix unreacted.

Other minerals, like chlorites in veins or cavities, will be partially dissolved. Ring and chain silicates are hard to dissolve; as well as quartz, hematite and epidote. The binary mixture will penetrate empty veins and cavities, or simply act on the surface of the rock, leaving a rough surface sufficient to promote fluid circulation.

X-ray diffraction of the chemically treated samples shows the same mineralogy as the original rock samples. This means acids react by first dissolving contact minerals, leaving much of the rock matrix unaffected, except when calcite is present.

When calcite is absent, the third treatment after the binary acid mixture does not show any difference in the physical and chemical characteristics of rocks.

No new phases are formed by the interaction between the rocks and acid solutions.

The Klinkenberg permeability increases in samples where calcite was present. Values are relative to the distribution and the amount of calcite in each specimen.

In the case of sulfide, metallic scales (galena, chalcopyrite, pyrite, bornite) will react with acids forming metallic chlorides or fluorides that may provoke adverse results.

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