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Reaction of Hydrothermally Altered Volcanic Rocks in Acid Solutions

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Abstract

Rock matrix stimulation has been used to clean, to recover and to enhance well productivity in oil systems. Recently, for the same purposes 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. Industrially, the common acid solutions used during acid well stimulation are HCl 10% and a mixture of HCl 10% and HF 5%. In this work, experiments were conducted in the laboratory using the referred acid solutions at atmospheric pressure and temperature of 110 ± 5°C.

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

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

Keywords: Acid stimulation; Matrix acidizing; Acid dissolution of rocks; Productivity enhancement; Permeability enhancement

Introduction

Rock matrix stimulation has been a methodology used for years to clean, to recover and 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. Not always being 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 [1]. 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 usually are designed primarily 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. Among others: 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 [2,3].

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 and recover well productivity in oil systems. Nowadays has been extended to the geothermal industry in wells that have shown reduced productivity either by clogged pores and fractures or scale formation. Diluted Hydrochloric acid is used widely; it is known that easily dissolves scales such as calcium carbonate and is used extensively in oil field operations throughout the world. On the other hand, is extremely reactive with sulfur scales formed by pyrite, chalcopyrite, galena, among others forming secondary products.

At low concentrations, 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 commonly used [4].

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 [5]. 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

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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 and for each well.

In hydrothermal systems secondary mineralogy is the result of water-rock interaction and depends on the physical and chemical conditions in the reservoir: temperature, pressure, liquid and rock composition, fluid pH, steam-water ratio etc. Mineral deposition in pores and fractures in the reservoir rocks may reduce porosity and in consequence productivity may decrease. A common mineral assemblage in volcanic high temperature geothermal systems, 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. From these minerals calcite readily reacts in diluted HCl solutions; chlorites partly react in diluted HCl-HF solutions.

Another common problem in geothermal wells is the scale formation inside the well casing and on the wall rocks; which also contributes to reduce productivity. Deposition of inorganic scale may occur during well production. Depending on the well conditions, on the reservoir rocks and on 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 some geothermal systems. During the past decade has been applied in fields such as Salton Sea, in 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) were used to perform solubility experiments using the common acid solutions used in acid stimulation of wells. Sets of rocks were provided by the Comisión Federal de Electricidad in order to carry out laboratory experimentation.

The best results were obtained in samples where calcite was present in pores or in 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.

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 93 MW. The field is inside the Los Humeros volcanic caldera, which lies at the eastern end of the Mexican Volcanic Belt, Figure 1.

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

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

Recently [6], mineralogical evidences on the effects of fluid acids on the reservoir rocks of the LHGF have been presented. The low pH fluids react with the rock changing its chemical and physical properties.

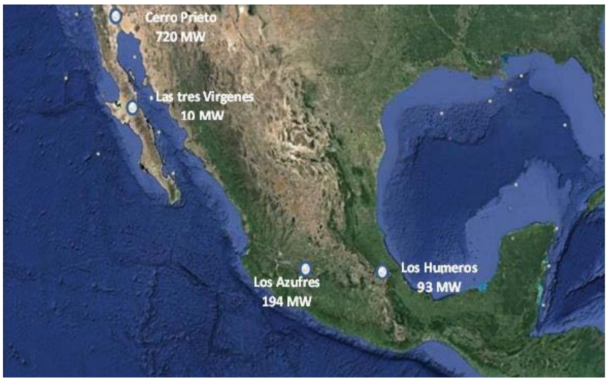

Figure 1: Location of the Los Humeros geothermal field within the Mexican Republic.

If calcite was present, dissolution occurs, total or partial sealing of vugs and fracture increasing and decreasing permeability. Due to the complexity of the processes that have affected the reservoir rocks, an acid stimulation work must be considered individually for each well and a specific acid treatment must be designed.

In relation to the Los Humeros caldera, a series of geologic events have occurred [7]. The complex geology has been summarized in four Units [8]:

Unit 1. Post-caldera volcanism. 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.

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 limestones and subordinated shales and flint. This unit includes also intrusive rocks (granite, granodiorite and tonalite) and metamorphic (marble, skarn, hornfels), and eventually some more recent diabasic to andesitic dikes.

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 at the south of the LHGF, from 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

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of hematite.

Core B, from a well located almost at the central part of the LHG, from 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 located near the central part of the LHGF, from a depth of 1300 - 1303 m has a light gray color, 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, from 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 ± 5°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 leaved to dry at room temperature. Always the weight of dry specimens was registered. Weight lost is relative, because samples loose particles during the reaction and during the 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 by the stable state technique at room temperature and constant pressure using nitrogen as work fluid (Contreras and García, pers. comm.).

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; also it was noted that acid penetrates the rock matrix. A fragment of the same core without calcite, after acid treatments show only bleaching of the external surface of the specimen; also after the reaction with the binary solution the external surface of the specimens turned bleached and rough. Figure 2, at the left shows a fragment of core A before any treatments, below of it a cylinder after the reaction with HCl 10%. At the right the same fragment after the third treatment in HCl 10% solution.

Chemical analyses of treated samples show lower concentration of major elements compared to the original and 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, the concentration of most of the major elements show slight decrease. The major weight loss is observed in Core A due to the important dissolution of calcite.

The fragment of core B used in the experiments is a fine grain andesite, with no apparent alteration; except by 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 are small. Again the surface of the core fragment shows roughness resembling an etched glass with superimposed hematite veins (Figure 3). That means that acid solution react on the surface rock forming minerals without entering in to the matrix of the core. At the conditions of our experimentation hematite is insoluble in acids.

Next example is core C. It corresponds to an andesite with 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 and 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, negligible 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.

Core D, this core is a particular one; it has been studied extensively to understand other processes that locally affected the deep reservoir rocks [6]. In Figure 5 two specimens from different well are compared. At the left, a fragment of core B which is an andesite; after the three acid treatments, the specimen looks bleached by the action of acids showing small patches of hematite. At the right, core D before acid treatments.

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.

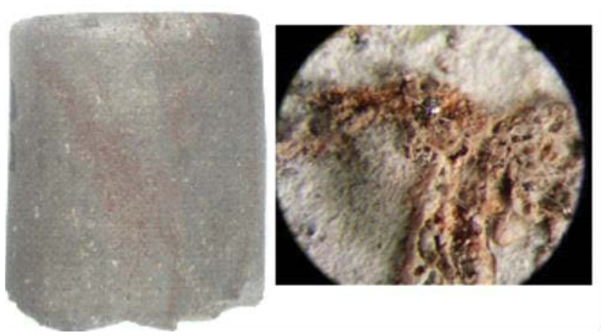

Figure 3: At the left a piece of the untreated core B (15 cm x 8 cm). At the right an image of a fragment of core B after reaction with the binary acid mixture, (16X).

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.

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.

It is remarkable that their physical appearance is similar; both look bleached. The chemical, mineralogical, petrophysical and mechanical data of core D, suggest that the rock from 2000 m deep wazs exposed naturally to the action of an acid fluid.

Assuming that the rock from core D was in contact with a low pH fluid in the reservoir, the action of such fluid was to bleach and to leach components leaving a bleached silicified mass. Probably the residence time of the fluid in contact with the original rock was not enough to form new minerals typical from acid environments; instead, the fluid reacted in the same way as we observe in the laboratory. The product in the natural system was a bleached, leached and silicified mass. The petrographic and X-ray diffraction analysis of core D indicate that quartz is the main component, plagioclase, and traces of chlorite and pyrite also are present. In our laboratory experiments using core D showed no changes when reacting with HCl 10%, mineralogy, chemical composition and permeability were exactly the same after interaction of the rock with the hot acid solution. That is because in HCl the main components of this core are insoluble. However, after the reaction with the binary acid mixture important changes were observed in the chemistry and in the permeability of the rock sample. The mineralogical composition was the same.

Table 1 presents chemical composition data, for major oxides in weight %, of a fragment of core D before any treatment. Also includes chemical data of fragments of core D after acid treatments. Samples were analyzed in a Thermo ICP-OS by the author Izquierdo G. As can be noted, after the interaction with HCl the sample shows slight change in concentration of major oxides. After the interaction with the binary solution, the chemistry changed particularly in SiO_2.

As part of the characterization of core D, tensile strength was determined before reaction in acid solutions. This value was 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 it was not part of this work. From data can be seen that tensile strength for core D is almost half of the value for the other two cores, even they are hydrothermally altered. This result has been considered as an evidence of the interaction of deep rocks of the reservoir with acid fluids [6]. As tensile strength is a destructive test it was not possible to determine in reacted specimens; for sure will be affected by the reaction with acids.

As far as permeability of core D is concerned, the initial value is the same as the 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 lost was considerable.

Table 3 is a summary of Klinkenberg permeability data before and after acid treatments. The permeability increased in samples where calcite was present and because of the light leaching of the contact surface between the sample and the solution. The permeability increases 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 and was a silica rich mass (microcrystalline quartz). After the reaction with HCl 10% as mentioned the permeability has the same value. With the binary mixture the permeability increases considerably because bonds of the micro crystalline quartz are easily to break 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 formation of new

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

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

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

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	Klinkenberg permeability Before(mD)	Klinkenberg permeability After (mD)
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

Table 3: Permeability values before and after acid treatments.

phases from them. Under this condition no new phases were formed from these acid solutions. Solid material at the bottom of vessels were separated, dried and analyzed by XRD, the identified phases are the rock forming minerals.

Results indicate that working with igneous rocks, before any attempt to acid stimulation of wells; it is very important to known the type and intensity of hydrothermal alteration, the nature of the rocks we are dealing with and the processes that have been occurred in the reservoir.

Conclusions

Even the results were obtained at micro scale in the laboratory, compared to the size of a geothermal reservoir; give an approach 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 in empty veins and cavities or just will act on the surface of the rock leaving a rough surface enough to promote fluid circulation.

X-ray diffraction of the chemically treated samples shows the same mineralogy as the original rock samples. That means that acid react by dissolving first 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 Klinkerberg permeability increases in samples where calcite was present. Values are relative to the distribution and the amount of calcite in each specimen.

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