Customized Biodegradable Fluid Systems: Premium Treatment Solutions for Versatile Challenges in Demanding Wells

By N. R. LUMMER and S. GERDES*

Abstract

Challenges encountered in the geothermal, as well as in the oil & gas sector are versatile, continuously changing and increasingly demanding. Therefore, a customized approach for production enhancing treatments is recommendable. According to actual project demands, each treatment fluid system should especially be designed. At the same time, the ever-growing claim for products with the lowest possible environmental impact dramatically influences possible recipe compositions.

This article focuses on the development of fluid systems based upon biodegradable acids with extremely low toxicity values. Furthermore, it highlights the corresponding field trials related to the following topics: Targeting Clay Minerals in Sandstone/Granite Formations, Dissolving Lead-Scale, Acidizing Carbonate Formations under H_2S-Conditions, and Cleaning of Geothermal Plants.

Environmental and Safety Issues

Because of their environmentally-friendly and non-hazardous nature, all acids presented here meet strict regulations, as well as environmental guidelines set by regulatory bodies and operators. Additionally, these systems have very low vapor pressures and high boiling points, thus they are odor-free and evolve no dangerous volatiles. Moreover, these acidic fluids show low toxicity to aquatic life and are readily biodegradable within 28 days.

Lab Experiments

Solubility tests were performed with actual cutting and scale samples from the respective project. After an exposure time of two to four hours in the biodegradable fluid system, the weight loss of the material was gravimetrically determined.

To simulate natural fractures in the formation and ensure an easy pathway for fluids, granite cores were cut in half employing a core saw. Subsequent flooding experiments were conducted with a permeability tester at 140°C. Initial and final permeability was established by pumping a solution of 20 kg/m³ Ammonium Chloride at 4 mL/min. While applying a confining pressure of 2000 psi (back pressure @500 psi), the respective biodegradable acid system was pumped through the core at 1 mL/min.

Metal coupons were cut, polished and rinsed using butyl glycol prior to corrosion testing. Weight loss of the metal sample was determined after an exposure time of two to four hours in the respective fluid system at the actual bottomhole temperature. All tests were performed at a differential pressure of 1000 psi Nitrogen. Here, the fluid volume / metal surface area ratio was held constant at 5.7 mL/cm².

Weight increase of elastomers were measured after an exposure time of 24 h at bottomhole temperature. Fluid compatibility with synthetic formation water (composition in accordance with the customer) was tested with live and spent acid.

Targeting Clay Minerals in Sandstone / Granite Formations

The primary objective of acidizing geothermal wells in fractured sandstones and granites is to remove scales blocking the pathway of water, thus increasing the productivity or injectivity of the formation. For this purpose, hydrochloric acid- based fluids are commonly applied. At high temperature, however, the fierce reactivity of hydrochloric acid (HCl) often hinders deep penetration of the formation making stimulation of removed damaged zones difficult to attain [1, 2]. Selection of chemicals to reduce reactivity adds to the difficulties en-

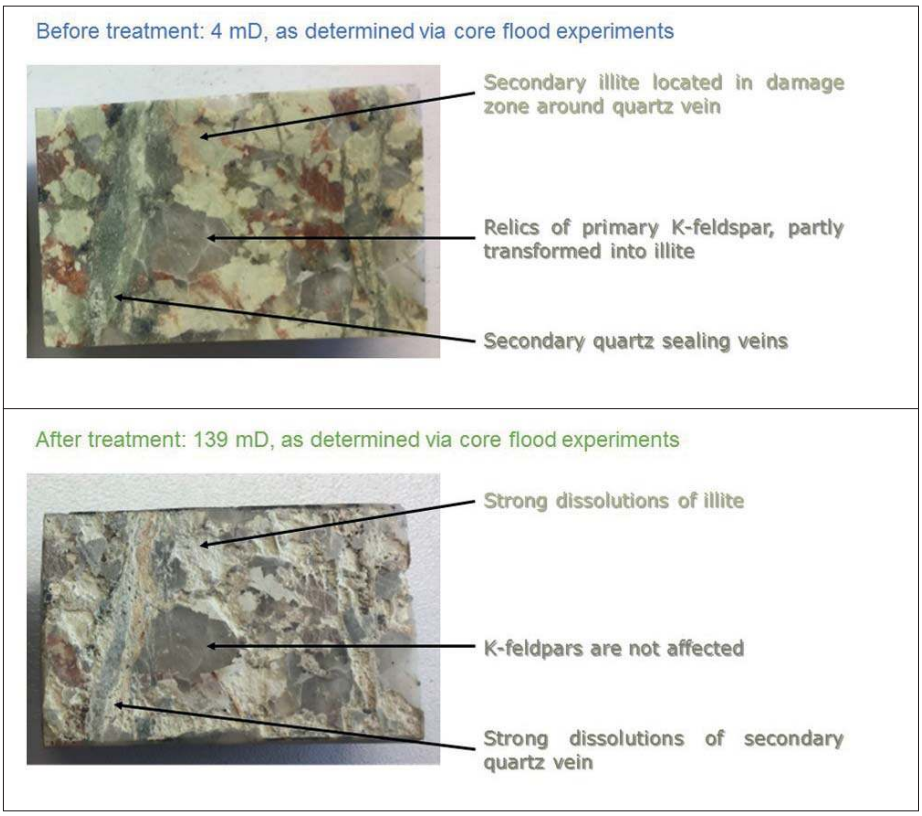

Fig. 1 Results of core flooding with granite sample employing biodegradable acid system I

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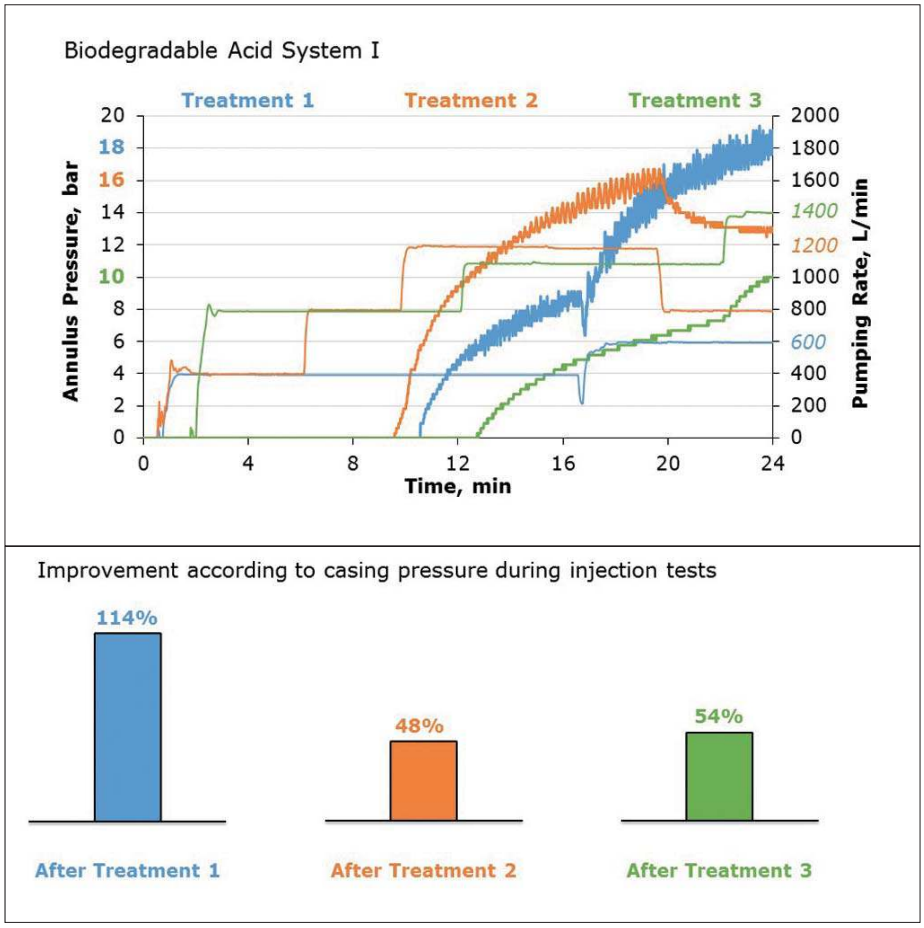

Fig. 2 Injectivity increase of granite formation through treatment with biodegradable acid system I

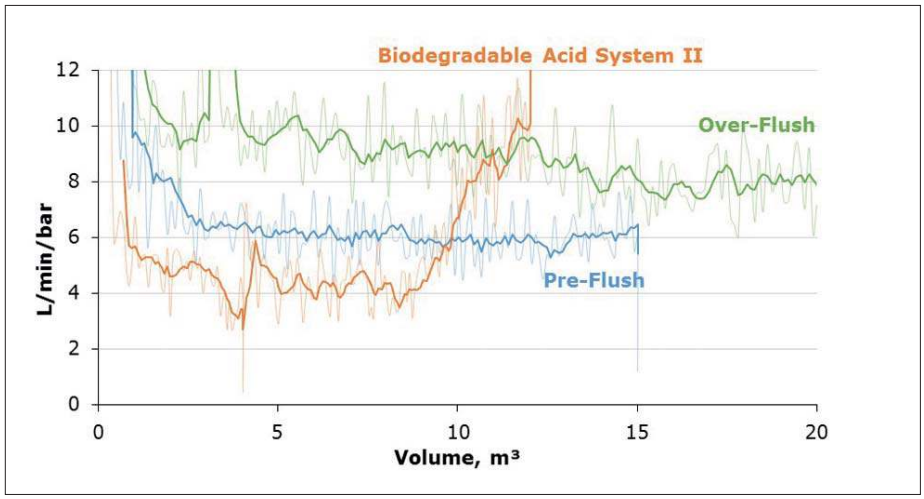

Fig. 3 Injectivity increase through lead-scale dissolution employing biodegradable acid system II (dashed line ≡ fluid reaches formation)

countered in the acceptance by mining and water authorities.

Furthermore, the extreme corrosion tendency of hydrochloric acid requires high concentrations of corrosion inhibitors and intensifiers [3, 4]. Another problem often encountered during acidizing sandstones with HCl-based formulations is their incompatibility with clay minerals. Core flood experiments and field results indicate that high temperature illitic sandstone is sensitive to conventional mud acid treatments. Here, the commonly employed HCl pre-flush degrades illite and chlorite leading to fines migration and formation damage [5].

An innovative fluid system is introduced, which is based upon a naturally retarded, biodegradable acid system and highlights its first field trial in a granite formation. Here, demanding borehole conditions (195 °C BHT, vast open-hole section, and a high concentration of illite) were encountered.

Preparing the application, core flood experiments with actual granite and sandstone samples (Fig. 1), as well as solubility tests with cuttings from the target zones were performed. In contrast to HCl-based fluids, this state-of-the-art acid system has supreme dissolving capacity against carbonates and silicates. Furthermore, it shows a low corrosion tendency and an excellent compatibility profile with illite, even at high temperature.

For the first field trial, three target zones (MD: 4900–5300 m) in the open-hole section were selected for chemical injection via tubing. The superior chemical properties of this treatment system lead to a greatly enhanced injectivity of the well (Fig. 2).

Dissolving Lead Scale

Scale formation may decrease flow potential of geothermal wells reducing project profitability. For premium results, remedial treatments, as well as fluid recipes should be diverse and optimized according to the respective reservoir conditions. Nonetheless, it is often common practice to employ standard hydrochloric acid-based solutions, even for persistent and more complex precipitates.

Here the development of an innovative fluid system specially customized for dissolving lead (Pb^{2+}) scales and highlights its field trial in a geothermal well. The first component of this new system is a salt dissolved in water providing clay control and pH-adjustment. The second is a biodegradable acid, which shows low environmental impact [6]. Lab research regarding the solubility of actual Pb^{2+}-scale samples, the compatibility with elastomers and synthetic formation water, as well as the corrosion tendency of metal coupons preceded the first application.

The following results were observed: In hydrochloric acid, dissolved lead-ions form $PbCl_2$-precipitates at lower temperature. In contrast, Pb^{2+} remains highly soluble in the new system rendering it most preferable for descaling purposes. This innovative fluid provides compatibility with elastomers and synthetic formation water. Additionally, it is extremely low corrosive (< 0.05 lbs/ft²).

Chemical injection via tubing targeted eight different zones in the perforated liner section of the Bunter sandstone formation (TVD: 2500–2600 m; BHT: 60 °C). In the course of the three treatment steps planned for this application, cup tools provided fluid separation and diversion.

The superior chemical properties of this biodegradable treatment fluid combined

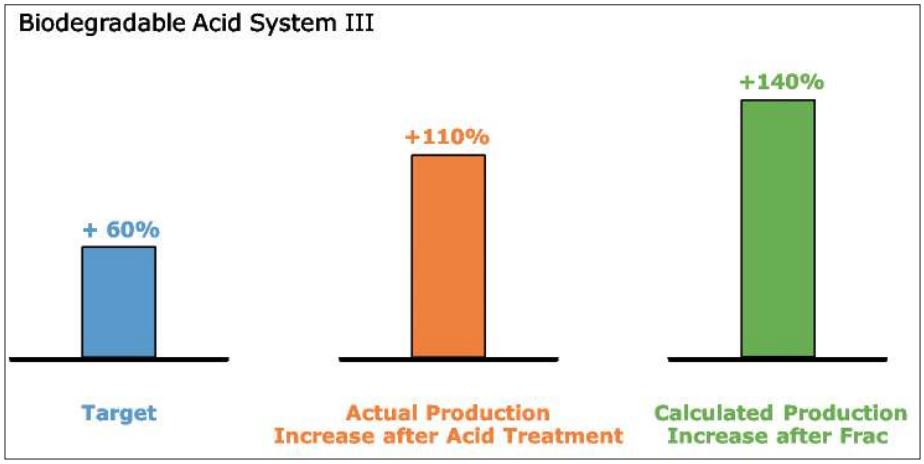

Fig. 4 Results of treating a sour, high temperature, tight gas well with biodegradable acid system III

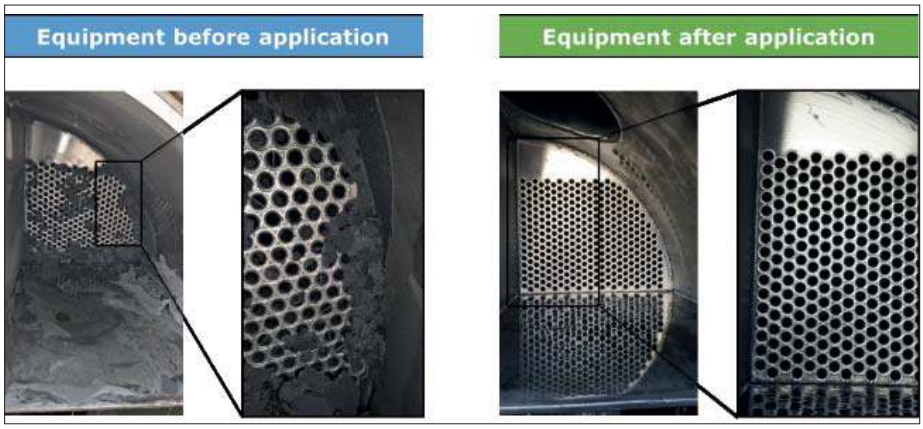

Fig. 5 Heat exchanger before (left) and after (right) application with biodegradable acid system IV

Tab. 1 Advantages of innovative biodegradable acid systems

Biodegradability and Low Toxicity	Ensures acceptance by mining and water authorities
Naturally Retarded Reactivity	Enables deep penetration into the formation
Low Corrosion Tendency	Minimizes corrosion inhibitor concentration
Excellent Compatibility with	
Swellable Clays	Reduces concentration of potassium chloride
Elastomers	Facilitates the use of inflatable packers and cup tools
Formation Water	Counteracts formation damage and ensures long-term efficiency

with an optimized pumping schedule resulted into an improved injectivity of the geothermal well. As an example, Figure 3 depicts the results for the second step. Here, the injectivity index increased from 6 to 8 L/min/bar.

Acidizing in Carbonate Formations under H_2S-Conditions

For matrix acidizing of carbonate wells, hydrochloric acid is usually employed. HCl simply dissolves the formation and creates wormholes when pumped at the optimum rate, thus by-passing the damaged zone and increasing well productivity. However, at high temperature, hydrochloric acid reacts vigorously with carbonates. Additionally, the corrosion rate of metal material is high, especially in wells completed with Cr-based alloys. In these cases, hydrochloric acid dissolves the protective layer (Cr_2O_3) and can severely corrode well tubulars. To address the corrosive nature of HCl at high temperatures, an increase of corrosion inhibitor loading, as well as the use of intensifier may be necessary. Another option is to employ a large volume of pre-flush to reduce bottomhole temperature of the treated well. In the following the results of the first field application of a biodegradable fluid to acidize a sour, high temperature, tight gas well completed with high chrome content tubulars are presented. The sour carbonate reservoir was damaged during workover. Previous matrix acidizing employing HCl and a chelating solution was not successful and below expectations.

The well produces sour gases with 19 mol% H_2S and 9 mol% CO_2. The target zone contains dolomite and calcite minerals with an average porosity of 11.5 vol% and permeability of 0.4 mD. The length of the target zone is 25 m. The well tubular consists of L-80, a low carbon-steel, with some internals made of Incoloy 925, and Alloy 28. After the application with biodegradable acid system III, gas production of the well improved by 110%. The treatment efficiency was excellent, as the result exceeded the target set for the stimulation. Here, the resulting production rate nearly equaled the one expected for a frac-treatment (Fig. 4).

Cleaning of Geothermal Plants

In the Molasse basin, phosphoric acid (H_3PO_4)-based fluids are the most commonly used systems for de-scaling geothermal plants. In comparison to other acids, however, H_3PO_4 dissolves carbonates (e.g. $CaCO_3$) only slowly hence unnecessarily lengthening each application. At high concentrations of Ca^{2+}-ions, phosphoric acid also tends to form Ca-Apatite precipitates further counteracting its efficiency as scale-dissolver. Additionally, due to environmental concerns regarding phosphonates, spent H_3PO_4 may require special disposal treatments and generate additional costs.

This part of the article presents the evaluation of biodegradable acid system IV and focuses on the optimization of the corresponding treatment program, both specially customized for de-scaling geothermal plants. Intensive lab research regarding the solubility of actual scale samples, as well as the corrosion tendency of metal coupons resulted into a customized fluid recipe.

An optimized treatment plan employing specially adapted field equipment ensured turbulence flow further accelerating the reaction rate of the fluid and hence the actual de-scaling procedure. The combination of biodegradable acid sys-

tem IV and state-of-the-art equipment resulted into great results (Fig. 5).

Conclusion

Based upon excessive lab testing and vast filed experience, the biodegradable acid systems presented here were specifically customized to meet unique project-related demands. In the course of numerous applications, they have shown their excellent efficiency improving the productivity of geothermal, as well as oil & gas wells. Their biodegradability, low corrosion tendency and excellent compatibility profile complement these state-of-the-art treatment fluids. Table 1 summarizes their benefits. ■

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