Review of Chemical Cleaning Methods in Geothermal Wells

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ABSTRACT

We have reviewed technologies and techniques applied to geothermal well cleaning to recover lost productivity from wells using chemical cleaning methods. We have undertaken a review of the publicly available literature on geothermal well cleaning and adjacent technologies in the petroleum industry. Whilst many hypothetical solutions are proposed in laboratory-based studies, we found that the predominance of real-world applications is limited to the use of simple Hydrochloric (HCl) and Hydrofluoric (HF) acid blends.

Acid treatments are usually accompanied by mechanical cleaning operations using drilling rigs and coiled tubing units as part of well intervention programmes. To decouple pure chemical cleaning from mechanical cleaning is difficult as the combined effects are intended to achieve more than a pure chemical or pure mechanical treatment alone.

The predominant use of HCl and HF acids for chemical cleaning is likely due to the availability of these chemicals, the cost of transport and the relatively well-known and understood reactions that take place between scale materials and these acids. On reviewing more than 112 well workover examples, 89 of these cases used a blend of HCl/HF. The rest of the wells were cleaned using blends of either Sodium Hydroxide (NaOH), Formic Acid, proprietary organic acids, condensate waters, or acetic acids.

As a corollary, the global petroleum well cleaning industry is also dominated by the use of HCl/HF acids for cleaning scale and stimulating production formations, even though many proprietary acid blends are offered through service providers; we found no evidence that exotic chemical blends have achieved significant uptake in cleaning geothermal wells.

1. INTRODUCTION

We have explored technologies applied to geothermal well cleaning to recover lost productivity from wells. The focus was on the remediation of scaling in geothermal wells through chemical cleaning methods. To achieve this, we undertook a review of the publicly available literature on geothermal well cleaning and adjacent technologies in the petroleum industry. Whilst many hypothetical solutions are proposed in laboratory-based studies, we found that the predominance of real-world applications is limited to the use of simple Hydrochloric (HCl) and Hydrofluoric (HF) acid blends.

Acid treatments are usually accompanied by mechanical cleaning operations using drilling rigs and coiled tubing units as part of well intervention programmes. To decouple pure chemical cleaning from mechanical cleaning is difficult as the combined effects are intended to achieve more than a pure chemical or pure mechanical treatment alone. For this study, we have attempted to decouple chemical cleans from mechanical cleans.

The predominant use of HCl and HF acids for chemical cleaning is likely due to the availability of these chemicals, the cost of transport and the relatively well known and understood reactions that take place between scale materials and these acids. There are occasional reports of workovers using more exotic acid blends reported in the literature. We investigated more than 112 well workover examples and 89 of these cases used a blend of HCl/HF. The rest of the wells were cleaned using blends of either Sodium Hydroxide (NaOH), Formic Acid, proprietary organic acids, condensate waters, or acetic acids.

There are many other chemical blends that are proposed in laboratory-based studies, but none of these appear to have been used in the geothermal industry. If operator(s) have adopted a special blend for extensive use, then it is likely to have appeared in promotional activity or discussed amongst the sector as this is a significant and widespread issue and the geothermal industry is a relatively small well-connected market.

The global petroleum well cleaning industry is also dominated by the use of HCl/HF acids for cleaning scale and stimulating production formations, even though many proprietary acid blends are offered through service providers, we found no evidence that exotic chemical blends have achieved uptake in cleaning geothermal wells. This may be due to the cost and complexity of applying more exotic blends and the relatively well-established use of HCl and HF from the petroleum industry.

2. GEOTHERMAL WELL CHEMICAL CLEANING METHODS AND TECHNOLOGIES

This section summarizes the technologies used to clean geothermal wells with a specific focus on cleans using fluid chemistries. We comment on the method of application (drilling rigs, coiled tubing units and through-wellhead) and compare how extensively they have been used. Note that we are talking to only publicly available information.

2.1 Well Intervention Using Drilling Rigs and Drillpipe

The use of drilling rigs to apply acid/workover processes is well known throughout the geothermal industry and has seen wide uptake in cleaning of scale from wells. They allow the use of other mechanical cleaning during the implementation as well as the ability to directly target each zone needing chemical stimulation. However, rigs are costly to mobilize, take long periods to set up and run (into and out of the hole); they are the most expensive way to work over geothermal wells. This cost is balanced with flexibility throughout the

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process to allow multiple different types of intervention (mechanical/chemical/logging etc.) to be applied. Overall, using drilling rigs combined with acid dosing, operators see improvements on average of 157% of total output from the pre-workover state (ranging from 13%-650% improvement after), Injectivity index improvements are also observed to range from -5% (loss in injectivity) to nearly 650% of regained injectivity as a result of using rigs to clean wells (Flores-Armenta et al.,2006.; Mahajan et al., 2006.; Pasikki et al., 2010.; Morales Alcala 2012).

2.2 Coiled Tubing Units (CTU)

Coiled tubing units (CTU) are emerging as the preferred way to perform geothermal well workovers, allowing for continuous running in and out of hole as well as the ability to run multiple types of tools down the hole. CTU provides the most accurate spot treatment of scale in zones of interest and also offers the most operational flexibility in terms of application of different fluid and mechanical cleaning abilities (Pasikki et al, 2010). Downsides to CTU are that pump rates are lesser than drilling rigs so acid volumes may have to be injected over longer time periods which can potentially compromise the tubing itself and downhole equipment due to long exposure times to treatment fluids which can lead to corrosion. However, the balance of the interruption of well operation of using a CTU is much less than a drilling rig but still requires significant site setup and works (Malate et al, 2015).

2.3 Through Wellhead Injection (Bullheading)

Injection directly through the wellhead or bullheading is a stimulation technique that requires the least amount of effort to set-up and has the least disruption to down-hole mechanical integrity, thus reducing the risk of getting stuck or having tools lost in the hole. Bullheading also allows for the highest available pumping rates of CTU and drilling rigs. However, Bullheading is the least directed in terms of down-hole isolation and does not target specific zones like the other two technologies. Barrios et al, 2012 reported that bullhead cleaning results in an average improvement of 40% compared to pre-treatment conditions. We find in our study of 16 well documented histories (Fernanda et al, 2014, Fukuda et al, 2010, Suryanta et al 2015, Barrios et al, 2007, Ventre et al, 1998 and Goh et al, 2020) that the average improvement in injectivity is around 63% and an increase of 48% mass-flow capacity compared to pre-treatment values.

2.4 Permanent Down-hole Tubing (or Hang-down Strings)

This review did not identify any specific technologies that apply to the removal of scales as a corrective measure in active wells using down-hole tubing. The application of down-hole tubing is mainly related to the prevention of scaling through inhibition of scale formation. In New Zealand, Calcite Inhibition Systems (CIS) or similar technologies are applied widely at fields such as Wairakei, Kawerau and Ngatamariki. This review did not consider the use of these systems and are excluded from detailed review here (see Rock 2000, Duran et al, 2020).

Table 1: Summary of Applications of Chemical Cleaning in Geothermal Wells.

Method	Treatment Volumes (Range)	Average Flow improvement (kg/s,l/s)	Chemicals Employed	Average Injectivity Index Improvement Over Pre-Workover	Number of Wells Known using technique
Drilling Rig	79,500 – 556,00 litres	157% (range 13% to 650%)	HCl+HF; NH4CL+High Temp Organic Clay Acid	171% (range = -5% to 647%)	56 (reported using a mix of Drilling rigs, CTU, and bullhead)
CTU	150,000 – 352,000 litres	144% (range 0% to 540%)	HCl + HF; Sandstone Acid (acetic + hydrochloric + hydrofluoric)	231% (range -% to 811%)	39 (only using CTU)
Bullheading	10,000 – 600,000 litres	48% (range 33% to 94%)	HCl + HF, EDTA, NaOH, Formic Acid	63% (range -15% to 275%)	15 (bullhead only)

2.5 Chemicals Employed

There are many possible chemical blends that are identified as theoretically possible for employment in cleaning of geothermal wells which are predominantly based in laboratory analyses and desktop reviews. However, HF (and derivatives), HCl and only a few others are readily identified in the literature as being widely used in geothermal well intervention. Several other researchers have proposed using different blends, but these have not seen wide uptake in geothermal applications. This may be due to the fact that other acids are more costly, difficult to handle and have uncertain effects on the reservoir. As noted by Flores in 2005, a failed acidizing of well LV-3 at Las Tres Virgenes was discussed in detail as such:

"It was found that several retarded or slow reacting HF acids such as fluoroboric, fluroaluininic and hexa-flurophosphonic were also developed to increase the depth of permeability improvement (Gdanski, 1985; Ayorinde et al., 1992). Most of these acid systems rely on the use of weak organic acids and their secondary reactions to slowly generate HF acid. Stimulation results using these acid systems were found to be better but were not substantial, since it is believed that live acid penetration is marginally increased, and separation and precipitation effects are slightly retarded. The marginal reduction of reaction rate of these acid systems could not overcome the large contrast in surface area between clays and quartz minerals. Various 'in-situ generated' HF acids were also developed with questionable to poor results due to the premature or improper mixing of solutions, both in the tubes and in the formation (Malate et al, 1998)."

These blends could provide an opportunity for further development of better chemical stimulation techniques if operators have the desire to explore more experimental processes on their assets.

Several authors highlight the potential that EDTA and other acetic acid blends may have in the cleaning of scale from geothermal facilities and the application in wells. Muller and Rodman (2014) present practical application of caustic and

EDTA in an above-ground study that compares this blend against Nalco's GEO907 and GEO991 for removal of silica that shows promising results but do not provide any significant detail on their use in wells.

Many other researchers have pointed to the use of chelants coupled with EDTA as a potential pathway to silica dissolution in down-hole applications (Xu et al, 2021, McCartney et al, 2017, Sutra et al, 2017, Phillips et al, 1976). This technology has been widely used in the cleaning of steam boilers to remove silica deposits and has found uptake in cleaning of geothermal assets on the surface (Al Saadi and Al Haddabi, 2019, Demadis et al, 2021). Only one example of EDTA use in geothermal well cleaning was in NF-12 at Mori field in Japan as highlighted from Fukuda et al, 2010 and was described as a good alternative to HCl/HF cleaning.

Table 2: Summary of Known Chemical Cleaning Blends Applied

Chemical Abbreviation/ Common Name	Full Name/ Product Name / Descriptor	# of actual uses in geothermal application	Locality of Use	Reference
HCl	Hydrochloric Acid	69	Multiple	Multiple
HF	Hydrofluoric Acid	87	Multiple	Multiple
NaOH	Sodium Hydroxide	1	Matsukawa, JP	Phillips et al, 1976, Fukuda et al, 2010
HCOOH	Formic Acid	1	Kawerau, NZ	Goh et al, 2020
EDTA	Ethylenediaminetetraacetic acid	1	Multiple	Portier et al, 2007, Fukuda et al, 2010, Muller and Rodman, 2014
Solenis Method	Acid, Chelant, Caustic, Surfactant	5	Wairakei, Ohaaki, Domo San Pedro	Muller et al, 2012, , Rodriguez et al, 2021
GEO991	Online Chemical Cleaning Approach	1	Anonymous- Silica Scaling	Ecolab 2018
OCA	Organic Clay Acid	2	Soultz-Sous Forets	Portier et al, 2009, Flores 2005
GEO980	Silica Inhibitor	1	NZ, Uncertain	Ecolab 2013
Geogard SX	Geogard	1	Central America	Guidetti et al,2022

3. DISCUSSION

In this analysis, we have found only a few chemical methods for chemically cleaning geothermal wells that differ from blends of HCl/HF acids. The widespread adoption of HCl/HF acids suggest that operators may be happy with these offerings or are unwilling to risk potential damage to operational assets by trying new blends.

There are emergent technologies that appear novel and promising. Particularly the use of formic acid at well KA44 in Kawerau as discussed by Goh et al, 2020 where formic acid was used in lieu of HCl. The authors attributed its use as a space, volume and cost beneficial exercise but the application yielded similar results to traditional methods, albeit with significant improvement in health and safety considerations.

Two notable examples from the literature that are a deviation away from the standard practice of HF-based acidizing to target silica scale were found to be applied at Mori, Japan (Fukkuda et al 2010) on two production wells:

- Well NF-12 had 445 m^3 of EDTA (Ethylenediaminetetraacetic acid) injected to address Anhydrite ($CaSO_4$) scaling in the wellbore. This EDTA solution was supplemented by NaOH to raise the pH of the fluid to greater than pH 12 and was injected at rates of 5-20 tonnes/hour over several days. This resulted in a 51% improvement over the pre-treatment mass flow from the well.

- Well NF-1 had 600 m^3 of NaOH solution injected (no EDTA applied) to treat magnesium-silicate scaling in the wellbore. The solution used was a pH 12-13 blend that was injected at a rate of 13-15 tonnes/hour also over several days. This procedure improved the output of the well by 25% and successfully dislodged scale as noted by sampling downstream of the production flow lines.

Solenis have detailed the results of several wells showing improvement in capacity in both production and injection that have been treated using their proprietary method (Muller et al, 2021A, B, Rodriguez et al, 2021) of cycling acid and alkaline solutions while wells are still online. This method is one of the more interesting in that it deviates from the application of HF to address silica which is the dominant method presented in the global geothermal literature.

Nalco (Ecolab) presents their GEO991 as a compelling example of a solution that can be injected into wells without taking them out of service and not using an HCl/HF blend (Nalco, 2018). The case study presented is opaque in nature and only details that it was used on an injection well suffering from silica scaling. While the results presented are interesting, there is little public facing information to support a critical interrogation of their proposed solution.

There is a global interest to try more exotic chemistries to clean geothermal wells, however, most do not appear to advance past laboratory-based studies. Ameri et al, 2016 detail that blends such as GLDA, MSA and HEDTA have theoretical basis to outperform traditional acidizing in high temperatures. They temper their enthusiasm by acknowledging that these blends are costly to produce and have relatively unknown efficacy in the very high-temperature environments such as those seen in geothermal applications. Further work by Leong et al (2018), Amjad and Zuhl, 2008 and Portier et al, 2007 detail the theoretical merits of using exotic acid blends.

In summary, there is a large volume information detailing the chemical cleaning of geothermal wells which are predominantly HCl, and HF based. There are opportunities for new, novel chemicals to make headway in reducing cost and complexity of geothermal chemical cleaning.

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