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Formation damage during stimulation of sandstone reservoir

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Abstract

Formation damage is critical factor in reducing production of oil and gas. This damage effects production at any stage during life of the a well. There could be many reasons of formation damage but this work is describing formation damages in sandstone reservoir during stimulation jobs. This damage took place due to precipitation of colloidal silica, swelling clays, iron bearing cements formed in results of reaction with quartz, iron minerals and clay particles with acid. Reaction products enter into porous media and adversely affect well performance of reservoir. Such damages are necessarily irreversible; the substance get into porous media not necessarily come out. Combination of HCl and HF acids is used to stimulate sandstone acid that have variable sensitivity to different grains of minerals and clay particles. Therefore, sandstone reservoirs need a meticulous designing and execution of acid stimulation job. Good knowledge of reservoir minerals and stimulation solution is valuable information to avoid formation damage during stimulation. This paper describes reactions of acid with different mineral grains. Further explains how to reduce or avoid these reactions.

Keywords: Formation Damage, Acid Stimulation, Sandstone Reservoir, Clay properties, Precipitation, Minerology

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Introduction

Formation damage is one of the significant factors in oil industry effecting economy of projects by decreasing significant production or injection due to reduction in permeability and porosity around borehole. Formation damages take place during drilling, cementation, perforation, completion, etc. by moving fines, excluding deposition of paraffin or asphaltenes etc., Porter (1989) [1] quotes; “What gets into porous media, does not necessarily come out.”

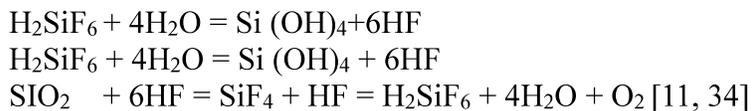
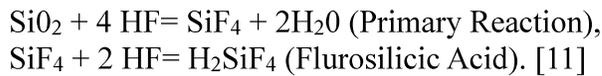
This paper discusses formation damage occur during stimulation of sandstone reservoir by stimulation fluids. Further process of damaging is discussed along with avoiding formation damage in such reservoirs. It is difficult to assess extent of formation damage during stimulation but qualitative evaluation of damage can be assessed by using information such as production and pressure data, pressure transient data, etc. during acid job in sandstone reservoirs acids react with sandstone and form sharp zones due to local thermodynamic equilibrium. HCl/HF form colloidal silica and AlF_3 precipitation may cause reduction in permeability. High reservoir temperature (generally more than 200°F) products of stimulation job resist to remove precipitate form the formation [2].

Reactions during chemical action

The purpose of acid job is to remove fines and improving permeability and porosity around borehole for the last eight decades. Enhancement in porosity up to 56% and permeability up to 156% has been recorded with acidizing job [4, 5]. HF reacts with sand grains and cement, feldspar and clays quickly due

to its corrosive nature and action of fluoride ion (F⁻) with siliceous material. Fluoric acid reacts with different minerals rapidly resulting precipitation from colloidal quartz [6] beside this secondary and tertiary reactions took place [7].

Three types of reaction take place with rock grains; first is primary reaction around borehole dissolves fast reacting minerals into silica fluoride (SiF₄) and aluminous fluoride without any significant precipitations [2,3,4]. Secondary reaction takes place when silica gel is formed as result of reaction of acids with quartz in slow reaction. Third type of tertiary reaction takes place further away forms silica gel. During these reactions many minerals alter into many new compounds those are formed such as fluorides, alumina silicates, fluor-aluminate, fluorosilicate, colloidal-silicate, iron compound etc. [8]. This is well known that mud acid (HCl:HF) job may fail if the rate of secondary and tertiary reactions increase rapidly due to high temperature. Smith and Hendrickson (1965) [9] also describe similar products are formed in reaction with fluoric acid as potassium and sodium silicate precipitates; calcium fluoride precipitates and hydrated silica precipitates those can be damaging for reservoir. Colloidal silica formed in results of reaction of sandstone (silica SiO₂) with hydrofluoric acid (HF) is complex as SiF₄ but HF again reacts with tetrafluoride (SiO₄) turned into fluosilicic acid (H₂SiF₆) and silica precipitate [10]. Reactions taking place in stimulation are given below:

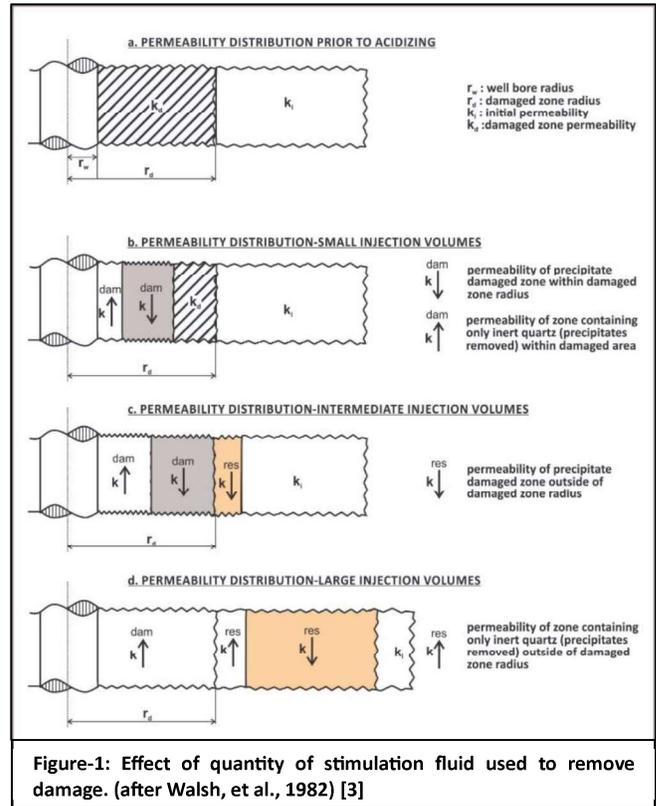


Al Harbi et al., (2011) [4] mentions that mud acid reaction with SiO₂ generates low concentration HF in reversible reaction and silica precipitates.

Discussion

A pile of literature is available on sandstone stimulation since 1940 [12]. Different combination of acids and ratio of HF and HCl is used to improve permeability and porosity but in some cases stimulation of sandstone reservoirs restrict the flow of hydrocarbons and reduce permeability around the wellbore [13,14]. The most commonly used acid system is Mud Acid, a mixture of hydrochloric and hydrofluoric acids in variable proportions. These compositions are prepared by diluting concentrated formulations or by reacting ammonium bi-fluoride with hydrochloric acid. This stimulation fluid is used to remove pore filling by overgrowth of quartz. Simple stimulation jobs cannot create new flow paths but removing damaging material (skin) to improve permeability, occasionally form worm holes that improves vertical permeability. Besides removal of filled material wormholes can also be created due to excessive leak of etching penetration. This process was defined in literature based on laboratory tests conducted on cores [15]. Where it is also shown that chemical action formed channels in about 15 seconds or more whereas

channels became deep within 20 seconds when gel followed by acid but after 15-20 minutes further channels started to reduce due to precipitation of silica. Another issue of migration of fines those formed and flow towards wellbore and bridge in the pore throat, fractures or the channels created through stimulation therefore after dissolution of the damage remaining undissolved fines need to be stabilized. Schematic diagram in Figure-1 illustrates the importance of quantity of stimulation fluid (acids) in homogenous permeable sandstone media depends on scale of stimulation job [16]. Prior stimulation job damage zone is around borehole and beyond this uninvaded zone with original permeability is preserved (Fig. 1a). If stimulation job is carried out in sandstone reservoirs with small volume of acid, permeability will improve around borehole but beyond this damage zone will be further damages and further deteriorate due to precipitation of quartz and fines and original damages zone will remain intact outside this. In case of intermediate volume of stimulation fluid is used (Fig-1b), zone around borehole will be improved and widened but damaged zone permeability will further deteriorate but original damaged zone will be disappeared (Fig. 1c). If stimulation fluid is used in large amount, then wider zone permeability will be improved but colloidal quartz it participates further away (Fig. 1d).



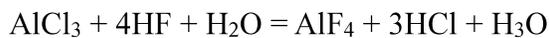
Most of these damages are due to rate and or size of stimulation fluid used in job. To avoid this damage different workers used different combinations of acids and retarding agents to reduce rate of reaction of HF with quartz (SiO_2) to avoid precipitation into colloidal silica. Fast reaction of corrosion in HF acid with quartz reacts rapidly and consumed quickly. Retarder, organic acid emulsified acid and chelating agents are used reduces reaction.

Civan (2007) [17] explains formation damage as Impairment of reservoir permeability by adverse processes around well bore. Yildiz (2002) [18] explains it as mechanical skin by reduction in porosity and permeability by migration of fines in-situ in rock or mud filtrate, acid job scaling, rock compression etc. Mineral oxides (SiO_2 , Al_2O_3 , etc.), swelling and non-swelling clays (detrital and authigenic) and substance induced in rocks such as mud particles cement, and debris [19],[20],[21]. Clay mineral are generally hydrous aluminum silicates containing, Kaolinite group in which clay breaks apart into fine particles, smectite or montmorillonite group those are hydrophilic swells and choke pore throats and Illite group clays and mixed-layer clay minerals breaks apart in lumps and form bridges across pores. Hill et. Al., (1994) [22] explains interaction of fluids with rocks causes mobilization, migration, and deposition of fine particles (internal or external) into pore throat and reducing permeability and porosity that change porous media as particle surface by absorption, adsorption, wettability change, and swelling and processes fluids imbibition, grinding and mashing of solids, surface glazing, etc.

To prevent above situation, retarded mud acids, organic acids, emulsifiers, chelating agents are used to retard corrosive acid reactions, organic-HF acids, emulsified acids, chelating agents have shown their

effectiveness at different conditions. These acids proved to be alternative to mud acid in sandstone acidizing, but the reaction mechanism and experimental analysis have not yet been investigated. Reaction with clays and iron bearing minerals (siderite) as cement also form precipitate. Even residual carbonate level remaining after pre-flushing, there is a maximum allowable HF acid concentration for each HCl acid concentration. The maximum is independent of the quantity of clay in an argillaceous sandstone.

During main job usage of boric acid (H_3BO_3), aluminum chloride ($AlCl_3$) and phosphonic acid were also used to decrease reaction rate. Gadanski (1985) [21], Thomas et al. (2002) [23] and Gomaa et al. (2013) [24] and in high temperature conditions potassium tetrafluoro-boron (KBF_4) precipitate when the flu-boric acid reacted with feldspar. Flu-boric acid has been produced when boric acid reacts with HF acid. Aluminum hydro acid ($Al.HF$) also works as retarder when it reacts with aluminum chloride ($AlCl_3$) to form into AlF_3 . Aluminum fluoride reacts with aluminum chloride reacts with HF. Zhou and Nasr-El-Din (2014) [25] added $AlCl_3$ as a retarding agent for regular mud acid and found it suitable in controlling AlF_3 precipitation.



As HF spends on siliceous minerals, AlF_4 hydrolyzes to regenerate HF.



Phosphoric acid (H_2O_3P) is also used as retarder to HF, as it reacts with ammonium bifluoride ($NH_4F \cdot HF$) to produce ammonium phosphate ($(NH_4)_3PO_4$) and HF. The fluoride ions are provided by the ionization of dissolved ammonium bifluoride [26]. In high temperature reservoirs Ethylenediamine-tetra acetic acid (EDTA) and hydroxy-ethylene diamine-tetra acetic acid (HEDTA) are used as chelating agent to improved production without using of HF. Addition of Na_3HEDTA as chelating agent increases reaction to add wormhole at temperatures up to 400°F and more effective than mud acid used. Many studies conducted in last two decades showed better results in increasing permeability compared to mud acid at high temperatures [21],[24],[25]. Mahmoud et al. (2011) [8] also showed that HEDTA, diethylenetriaminepentaacetic acid (DTPA) and disodium EDTA (Na_2EDTA) are effective in acidizing sandstone formations.

To avoid formation damage other acids and their combination is also used. Acetic acid (10%) proved better 10% HCl in sandstone [26]. Non-HF-based system is used to stimulate sandstone in two injector wells in off-shore Brazil in 1999 [8],[3]. Single-stage sandstone acid has been developed by Gomaa et al. (2013) [24], which consists of boric acid (H_3BO_3), ammonium bifluoride ($NH_4H.HF$) and HCl to generate flu-boric acid. This system eliminates the use of pre-flush and after-flush stages. GLDA has been applied by Reye et al. (2015) [26], Rignol et al. (2015) [27], and found it effective in increasing sandstone permeability at high temperatures. It is highly admirable that many researches had focused. Organic acids with HF in matrix acidizing to decrease reaction rate.

Gomaa et al., 2013 [24] mentioned on the basis of their laboratory work about new acid system to avoid usage of HCl in pre-flushing and post-flushing to remove Ca and Mg to prevent damaging of formation by precipitation of CaF_2/MgF_2 .

Despite of several issue related to acidizing still it is preferred over hydraulic fracturing as hydraulic fracturing especially like high permeability formation with loose packing, naturally fractured reservoirs and removing damage around wellbore [2],[28]. In past few years failure of expensive hydraulic fracturing is much higher than acid jobs. Collier (2013) [29]; Shafique and Mahmud (2017) [2] improves

chances of success in acid job if acid-removal skin is known, fluid concentrations and volume of treatment are well known, additives execution of job and post job evaluation is properly done.

Concentration of acids, reservoir temperature, pressure, permeability and porosity of the formations play vital role in success of job. Reaction of acid with sandstone is directly proportion to Concentration of acid [30]. Higher temperature also increased reactivity whereas the pressure increases the solubility of by-product gases, carbon dioxide and silicon tetra fluoride and CO₂ entrapped in fluid. McCune et al. (1975) [31] mentioned that ‘rock permeability less than 100 mD have better improvement than good permeability of rocks.

In sandy reservoirs silicate and fluorides precipitation and colloidal silica prevention is required therefore HCl should be used as pre-flushing of borehole [32],[33] to wash carbonates and cement grains in perforations. Pre- job flushing requires HCL 10% however some workers recommend to add acetic acid and ammonium chloride for more effective flushing by avoiding formation of silicates and fluorides [22].

Design of job

Table-1: Guide line for sandstone stimulation job.

Mineralogy	100 mD	20–100mD	<20 mD
< 10% silt and <10% clay	12%HCl and 3% HF	8% HCl and 2% HF	6%HCl and 1.5% HF
>10% silt and >10% clay	13.5% HCl and 1.5% HF	9% HCl and 1% HF	4.5% HCl and 0.5% HF
>10% silt and <10% clay	12% HCl and 2% HF	9% HCl and 1.5% HF	6% HCl and 1% HF
>10% silt and >10% clay	12% HCl and 2% HF	9% HCl and 1.5% HF	6% HCl and 1% HF

Designing of acid stimulation job planning is key to the success. Production improves if job is design properly considering all factors that can affect the job. Important rock factors are mineralogy including silt and clay presence, iron bearing minerals, porosity and permeability, formation temperature and pressure. Shafiq and Mahmud (2017) [2] improved Mcleod et al, (1983) [32] guidelines to improve results of stimulation for Pre-job flushing.

Mahmoud et al., (2011) [8] also proposed a scheme that suggests that good permeable (>100mD) rocks having >20% solubility, then HCl 15% form main job without any pre-flushing. In case permeability is >100mD and clay is less than 5% and quartz is more than 80% then pre-flushing with 15 % HCl and main acid job with 12% HCl with 3% HF is recommended. In presence of feldspar greater than 20% pre-flush is same but main acid requires 13.5% HCl and 1.5% HF. In case clays contents exceed 10% then 6.5% HCl and 1% HF is recommended to use in main job but sequestered 5% HCl is recommended in Pre-job flushing. In case iron chlorite clays are in rocks then pre job flushing is recommended with sequestered 5% HCl and main job is recommended with 3% HCl and 0.5%HF. However, in low permeable rocks (less than 10mD permeability).

Many workers suggest to use organic acids such as HCl and HF with addition of an organic acid like citric acid, formic acid or acetic acid to prevent the hydrated silica precipitation [5],[6],[33] (Shafiq, 2016, 2013; Yang et al. (2012). Gomma et al., (2013) [24] proposed new single stage acid system for sandstone

by changing equal ratio of HCl and HF but it was never tested in high temperature wells. Hartman et al. (2003) [35] effectively used 10% acetic in high temperature wells. Few authors stressed to avoid use of HF due to its corrosive nature in used Flu-silicic acid (H_2SiF_6) successful in laboratory and field [36], [7],[34] (Martin; 2004; Da Motta and Dos Santos, 1999; Kaflyan and Mctcalf, 2001). Some laboratory studies show 200% increment by using these acids Shafiq (2013) [6] proposed Phosphoric and HF acid and Fluoroboric–formic acid due to less corrosion and effective to increase permeability but its reaction mechanism is not well understood

Conclusion

Sandstone stimulation is not a forthrightly job, although usage of HCl / HF is in common in industry but good knowledge sandstone mineralogy, proper stimulation fluids preparation and proper planning of job acquisition Including pre-flushing, main job and post flushing are key to achieve the target. This is irony that many ill planned jobs instead of improvement in porosity and permeability damages reservoir. Therefore, the best practice to treat stimulation fluids and their by-products. Pre-flushing with HCl acid removes the accessible carbonates and shale that is helpful in reducing or eliminating AlF_3 precipitation but if reservoir is containing large carbonate concentrations than it needs larger volumes of pre-flush than normal. Similarly post job flushing and recipe for main job are equally important.

Many researchers developed different acid combinations, applied different chelating agents to get the best results related to permeability, porosity and precipitation, but still there are some limitations like fast spending of acid, precipitation reactions, less penetration of acids and corrosion of hardware of wells.

Industry also tried many other chemicals to avoid mud acid due to its hazardous and corrosive nature such as modified as combinations such as ($\text{HF}:\text{H}_3\text{PO}_4$ and $\text{HBF}_4:\text{HCOOH}$) as suggested by Shafiq et al. (2016) [5], Shafiq and Mahmud (2017) [2]. New chemicals are required in sandstone acid stimulations because of limitation at high temperature and corrosive nature of fluids and cost effective. Some combinations are not developed completely as their mechanisms are not yet known and poorly understood. Further research is required to develop cheaper stimulants that can work at high temperature and avoiding formation of precipitates due to reaction. Challenges in acidizing of sandstone reservoirs are many to secure high production by removal of fines from pores or by making new path ways.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research.

References

1. Porter, K. (1989): "An Overview of Formation Damage," paper SPE 19894, Journal of Petroleum Technology, 780.
2. Shafiq, M.U., and Mahmud, H. B. (2017): Sandstone matrix acidizing knowledge and future development. Journal of Petroleum Exploration & Production Technology. DOI: 10.1007/s13202-017-0314-6.
3. Walsh, M.P., Lake, L.W., Schechter, R.S. (1982): A description of chemical precipitation mechanisms and their role in formation damage during stimulation by hydrofluoric acid. SPE Journal, 2097-2112.

4. Al-Harbi, B.G., Al-Khaldi, M.H., AlDossary, K.A. (2011): Interactions of organic-HF systems with aluminosilicates: lab testing and field recommendations. Society of Petroleum Engineers, SPE-144100-MS.
5. Shafiq, M. U., et al. (2016): New acid combination for a successful sandstone acidizing. Presented in 29th Symposium of Malaysian Chemical Engineers (SOMChE), Miri, Sarawak, Malaysia.
6. Shafiq, M. U., Kyaw, A., Shuker, M. T. (2013): A comprehensive research to find suitable acid for sandstone acidizing. *Advanced Materials Research*, 787, 274–280.
7. Motta, D. E. P., Dos Santos, J. A. (1999): New fluorinic-silicic acid system removes deep clay damage. Society of Petroleum Engineers, SPE-54729-MS.
8. Mahmoud, M. A., Nasr-El-Din, H. A., De Wolf, C., Alex, A. (2011): Sandstone acidizing using a new class of chelating agents. Society of Petroleum Engineers, SPE-139815-MS.
9. Smith, C.F., Hendrickson, A.R. (1965): Hydrofluoric acid stimulation of sandstone reservoirs. Society of Petroleum Engineers, SPE-980-PA.
10. Al-Dahlan, M.N., Nasr-El-Din, H.A., Al-Qahtani, A.A. (2001): Evaluation of retarded HF acid formic acid. Society of Petroleum Engineers, SPE-65032-MS.
11. Li, C. (2004): Fine scale sandstone acidizing core flood simulation. University of Texas at Austin, Austin.
12. Shaughnessy, C.M., Kunze, K. R. (1981): Understanding sandstone acidizing leads to improved field practices. Society of Petroleum Engineers, SPE-9388-PA.
13. Lehnhard, P.J. (1943): Mud Acid - its theory and application to oil and gas wells. *Petroleum Engineer Annual Issue*, 82.
14. Crowe, C., Masmonteil, J., Touboul, E., Thomas, R. (1992): Trends in matrix acidizing. *Oil Field Review*, 4(4), 24–40.
15. Lindsay, D.M. (1976): An experimental study of sandstone acidization. University of Texas at Austin, Austin.
16. Coulter, G. (2012): Technology focus: well stimulation. Society of Petroleum Engineers, Dallas.
17. Civan, F. (2007): Formation damage mechanism and their phenomenal modeling. Paper presented at SPE Formation Damage Conference, Scheveningen, Netherlands, May 30 - June 1, 2007, 1–12, SPE-107857.
18. Yildiz, T. (2002): Productivity of selectively perforated vertical wells. *Society of Petroleum Engineers Journal*, 7(2), 158.
19. Civan, F. (2007): *Reservoir Formation Damage*, 2nd ed. Elsevier, 1089p.
20. Ezzat, A.M. (1990): Completion Fluids Design Criteria and Current Technology Weaknesses. SPE Formation Damage Control Symposium, SPE-19434.
21. Gadanski, R.D. (1985): AlCl₃ retards HF acid for more effective stimulation. *Oil & Gas Journal*, 83, 111–115.
22. Hill, A.D., Sepehrnoori, K., Wu, P.Y. (1994): Design of the HCl preflush in sandstone acidizing. Society of Petroleum Engineers, SPE-21720-PA.
23. Thomas, R.L., Nasr-El-Din, H. A., Mehta, S., Hilab, V., Lynn, J. D. (2002): The impact of HCl to HF ratio on hydrated silica formation during the acidizing of a high temperature sandstone gas reservoir. Society of Petroleum Engineers, SPE-77370-MS.

24. Gomaa, A. M., Cutler, J., Qu, Q., Boles, J., Wang, X. (2013): An effective single-stage acid system for sandstone formations. Society of Petroleum Engineers, SPE-165147-MS.
25. Zhou, L., Nasr-El-Din, H. A. (2014): Acidizing sandstone formations using a sandstone acid system for high temperatures. Society of Petroleum Engineers, SPE-165084-MS.
26. Reyes, E.A., Smith, A.L., Beuterbaugh, A., Calabrese, T. (2015): GLDA/HF facilitates high temperature acidizing and coiled tubing corrosion inhibition. Society of Petroleum Engineers, SPE-174264-MS.
27. Rignol, J., et al. (2015): Improved fluid technology for stimulation of ultrahigh-temperature sandstone formation. Society of Petroleum Engineers, SPE-173755-MS.
28. Mancini, E.A. (1991): Characterization of sandstone heterogeneity in Carboniferous reservoirs. *Progress Review*, 64, 79–83.
29. Collier, R. (2013): Fracking's more dangerous bed flow: acidizing. *The Next Generation*.
30. Bennion, D.B., Thomas, F.B., Sheppard, D.A. (2002): Formation damage due to mineral alteration. *Journal of Canadian Petroleum Technology*, 41(11), 39–36.
31. McCune, C.C., Ault, J.W., Dunlap, R.G. (1975): Reservoir properties affecting matrix acid stimulation. Society of Petroleum Engineers, SPE-4552-PA.
32. McLeod, H.O. Jr., Ledlow, L. B., Till, M. V. (1983): The planning, execution, and evaluation of acid treatments in sandstone formations. Society of Petroleum Engineers, SPE-11931-MS.
33. Yang, F., Nasr-El-Din, H.A., Al-Harbi, B.M. (2012): Acidizing sandstone reservoirs using HF and formic acids. Society of Petroleum Engineers, SPE-150899-MS.
34. Kalfayan, L.J., Metcalf, A.S. (2001): Successful sandstone acid design case histories. Society of Petroleum Engineers, SPE-63178-MS.
35. Hartman, R.L., Lecerf, B., Frenier, W., Ziauddin, M., Fogler, H.S. (2003): Acid-sensitive aluminosilicates: dissolution kinetics and fluid selection. University of Michigan.
36. Kalfayan, L.J. (2008): Production Enhancement with Acid Stimulation. PennWell, Tulsa.
37. Frenier, W. W., M. Hardly and S. Al-Harthy (2004) Hot oil and gas wells can be stimulated without acids, SPE-86522-PA, <https://doi.org/10.2118/93805-PA>
38. Ali, S., Ermel E., Clarke J., Fuller M.J., Xiao Z., Malone B. (2008) Stimulation of High-temperature sandstone formations from west Africa with chelating agent-based fluids. Society of Petroleum Engineers, Dallas, <https://doi.org/10.2118/93805-PA>
39. Abdelmoneim, S., Nasr-El-Din, H.A. (2015) Determining the optimum HF concentration for stimulation of high temperature sandstone formations. Society of Petroleum Engineers, SPE- 174203-MS, <https://doi.org/10.2118/174203-MS>.