Use of chelators and hydrofluoric acid for the improvement of well productivity

Le Viet Khai¹, M M Veliev¹, V Sh Mukhametshin², E M Veliev², K T Tyncherov², A V Andreev²

¹ JV „Vietsovpetro”, 105, Le Loi St., Thang Nhi Ward, Vung Tau, Ba Ria – Vung Tau City, S.R. Vietnam
² Ufa State Petroleum Technological University, Branch of the University in the City of Oktyabrsky, 54a, Devonskaya St., Oktyabrsky, Republic of Bashkortostan, 452607, Russian Federation

E-mail: vsh@of.ugntu.ru

Abstract. The paper presents the results of microscopic analysis of the content of elements on the surface of clay samples after treatment with an acidic mixture of HV:HF. The analysis showed that as a result of the dissolution of clay and quartz, quartz dissolves faster, the Si/Al ratio on the sample surface decreased, which indicated the formation of a protective film of aluminum phosphate silicate. The studies of the ability of chemical reagents to dissolve clay by the method of weight loss showed that in the HV:HF system, the dissolution rate of clays is much lower due to the formation of a coating layer. The stage of the increase in the rate of dissolution occurs when a part of this layer is dissolved. The studies of the ability of the HV:HF chemical reagent system to dissolve silicon showed that the amount of dissolved silicon varied linearly with the exposure time and the rate of silicon dissolution was proportional to the HF concentration in the system. The dissolution rate of silicon in the HV:HF system is much higher than in the HCl:HF system at the same HF concentration. This is a significant advantage of the proposed system of chemical reagents HV: HF in comparison with the traditional HCl:HF system. HV: HF system dissolves calcium carbonate much more efficiently than traditional hydrochloric or acetic acid systems.

Key words: high temperature, hydrofluoric acid, chelator, non-acidic components, reaction, protective film.

1. Introduction

The possibility of the increase in well productivity by acidizing the bottom hole area (BHA) has been known for a long time, almost from the first days of the oil industry [1-4]. This method leads to the opening of pores that previously existed in the reservoir by dissolving the material that clogged them or to the creation of new channels by dissolving the reservoir rock.

Well interventions, such as acid formation treatment, significantly help oil companies maximize production in their fields. The reactions with the participation of traditionally used mineral acids, at elevated temperatures above 93°C occur at too high a rate, as a result of which the acid is completely consumed in a too short time, which reduces the processing efficiency and can provoke other complications [5–8].

Moreover traditionally used mineral acids require special safety measures, corrode well pipes and equipment and must be neutralized when returned to the surface. As the temperature at the bottom of the well rises, the cost of corrosion inhibitors increases rapidly due to the need to increase their concentration.

Secondary sediments provoke clogging of the porous space and reduce the permeability of the formation. In many cases, due to the formation of secondary sediment, acid treatment has a negative effect, i.e. the permeability of the bottom hole area decreases after treatment. The main types of secondary sediments in acid treatment of a sandstone formation are iron hydroxide gel, silicon gel, etc. In order to prevent their formation or reduce the negative impact, it is necessary to select the appropriate composition of the solution
and processing technology [9–12]. To solve these problems in JV Vietsovpetro it was proposed to use non-acidic components with the formation of an acid composition at the bottom hole in order to increase the productivity of producing wells of the fields. Due to the formation of hydrofluoric acid (HF) inside the formation from injected non-acidic components from the surface, a reaction occurs between HF with sediments within the formation, which increases the permeability of the bottom hole area.

Successful treatment requires solutions to achieve the maximum required penetration depth. One of the ways to increase the penetration depth is the use of systems that promote the generation of HF in the formation. Such a system can be presented by the use of chelates and salt containing fluorine for the formation of HF.

2. Methods and Materials
The use of chelators (chelating agents) is one of the possible solutions to the problem of flow stimulation in high-temperature wells.

As a rule, chelators with ions and metal cations form complex compounds - chelates - in which the captured ion is bound immediately to two or more atoms of the same chelator molecule (similar to how the caught prey is held on both sides by the predator's claw, hence the name "chela", which means "claw" in the Greek language). Chelators are used to prevent the precipitation of metal compounds and dissolve the deposits. Stimulation of high temperature wells is their new application.

Chelators commonly used in the oil and gas industry are complex organic acids. These compounds not only bind metals, but can also serve as active dissolving agents during acid treatment of BHA.

The process of stimulation with chelators has a number of advantages, including slower stimulation, low corrosion rate and better compliance with health, safety and environmental requirements.

The method of formation of hydrofluoric acid within the formation using chelates and ammonium hydrofluoride (inorganic compound, acid salt of ammonium and hydrofluoric acid, colorless crystals, soluble in water with the formula NH₄HF₂) is a simultaneous solution to two problems associated with high temperature and the formation of secondary sediments. This method allows increasing the penetration depth of the solution and high pH level of the system limits corrosion. Chelate compounds are capable of keeping Ca²⁺, Si⁴⁺, Fe³⁺ ions in a dissolved state and does not allow the formation of secondary sediments.

The chelating compound has an abbreviated chemical formula C₈H₈O₁₇P₂ called Oxyethylidene diphosphonic acid (international name: 1-Hydroxyethylidene-1,1-Diphosphonic Acid) and has weak acidic properties. In the works, HEDP is also referred to as HV.

The chemical mixture that forms as a result of the reaction between an HV acid and NH₄HF₂ is commonly referred to as an HV: HF acid system. This reaction produces HF and ammonium sulphate.

As in the case of clay-acid solutions (HCl: HF system), using the HF: HV system, after the dissolution of the clay layer, a shell is formed by the adsorption mechanism. This shell, measured in micrometers, is formed from aluminum-silicon phosphate. It preserves the surface of the clay or excessive dissolution. This mechanism reduces acid losses so that the remaining amount of acid can penetrate into the depth of the formation. The shell also preserves the cement layer and limits the clogging of pores with fine particles.

The HV:HF system, obtained as a result of the reaction between chelate compounds (HV) and hydrofluoric acid (NH₄HF₂), has low acidity and can create a buffer effect that maintains a high pH, reduces corrosion, has low toxicity and fully meets the requirements of environmental safety of JV Vietsovpetro.

The experiments were carried out in the laboratory of NIPmorneftegaz, JV Vietsovpetro in order to study the protective film on the surface of clay minerals and the regularities of the interaction of chemical reagents with typical minerals of the sandstone formation such as silicon, clays and carbonates.

The composition of the primary minerals of the rocks of the White Tiger deposit consists of illite and quartz. Secondary minerals include: chlorite, montmorillonite, feldspathoid and goethite. In addition, there is also calcite, dolomite, rutin and organic matter with a mass content of <3%.

For laboratory studies, rock samples were taken from a horizontal well. No. 815 / MSP8 (the first horizontal well on the Vietnamese shelf, drilled by JV Vietsovpetro in February 1996) of the White Tiger deposit at a depth of 3000 m.

Clay samples are loaded into a flask filled with a solution of various compositions. The immersion time is 30 minutes. Then the samples are removed and thoroughly air dried to prevent cracking. Then the samples undergo microscopy (SEM - Scanning Electron Microscope) in order to obtain an image of the object surface with a high (up to 0.4 nanometer) spatial resolution, as well as information on the composition, structure and some other properties of the near-surface layers.

The chemical reagents used in research are HV: HF systems with various HF concentrations: 1, 1.5, 2 and
For comparison, chemical reagents of the HCl:HF systems are also used with HF concentrations of 1, 1.5 and 2%, respectively.

According to the analysis results of the elements on the surface of the samples before and after treatment with a mixture of HCl:HF with an HF concentration of 1, 1.5 and 2%, respectively, the following conclusions can be drawn:

- The sample before acid treatment (series 8) has the ratio Si:Al=2.45, which is typical for the clay, quartz component in the sample of clay minerals from the White Tiger deposit;
- After the treatment with HCl:HF solution (series of experiments M5-M7), as a result of dissolution of clay and quartz, it was revealed that quartz dissolved more slowly, the Si:Al ratio increased;
- After the treatment with a solution of HCl:HF, F element appeared on the surface of the sample (the atoms of which have the valence electrons with the highest energy occupy the f-orbital).
- There is no P element (chemical elements the atoms of which have the electron with the highest energy occupying the p-orbital) is absent on the sample surface;
- Element P appeared on the surface of samples of the M1-M4 series. The content of element P is equivalent to the concentration of HF in the acid mixture (the concentration of HF is 0.07; 0.31; 1.28 and 4.82%).

After the treatment with an HV:HF solution (a series of experiments M5-M7), as a result of the dissolution of clay and quartz, quartz dissolves faster, the Si:Al ratio on the sample surface decreased.

Thus, the appearance of P element on the sample surface and a decrease in the Si:Al ratio is the evidence of the formation of a protective film of aluminum phosphate silicate.

Laboratory studies of the ability of the proposed system of HV:HF reagents to dissolve clay, silicon (SiO₂) and calcium carbonate (CaCO₃) were carried out.

The ability to dissolve silicates (minerals, which are silica compounds) is one of the important requirements for chemical reagents during the treatment of sandstone formation. However, chemicals containing HF usually have common disadvantages — strong dissolution of clay, but very weak dissolution of silicon in the form of quartz. The reason for this phenomenon is the very large specific surface area of clay in comparison with silicon. Thus, a chemical system with a low clay dissolution rate and a high silicon dissolution rate is considered to be more successful.

The study of the ability of chemical reagents to dissolve clay is carried out using the weight loss method. The experiments are carried out in the following order:

- to prepare identical clay samples 2-3 mm in size and acid-insoluble bags to contain the samples;
- put a number of samples in a bag and weigh the mass m0;
- to prepare acid by pouring it into different glasses with equal volumes;
- to put the bags with samples in water for 1 minute to wet the surface of the samples, then remove the bags for weighing and measure the mass m2;
- to put samples in test acids;
- to remove the bags after a certain period of time (5, 10, 20 and 30 minutes), drain the liquid from the bags and weigh the mass of samples m5; m10; m20; m30;
- to build a graph of the dependence of the amount of dissolved clay from time to time.

The clay for the experiments was taken from the White Tiger deposit (well No. 815, depth 3000 m). Clay samples were prepared in the form of a flat block with relatively uniform dimensions and mass. In order to determine the advantages of the studied system of chemical reagents, similar experiments were also carried out in the traditional system of acids HCl:HF (based on clay-acid solutions).

The HF concentration for experiments in the HV:HF system was calculated in such a way that the concentration of HF formed in the corresponding experiments was 1.0; 1.5; 2 and 3%; and the concentration of HF for the experiments in the HCl:HF was 0.5; 1; 1.5 and 2%. According to the experimental results obtained in the HV:HF and HCl:HF systems at various HF concentrations, the graphs of the ability of the HV:HF and HCl:HF systems to dissolve clays in time were drawn (Fig. 1).
3. Results and Discussion

The comparison of the kinetics of dissolution of clays of two systems of chemical reagents (HV:HF and HCl:HF) at different concentrations of HF shows that, in the general case, the HV:HF system dissolves clays more slowly than the HCl:HF system. The dissolution rate of clays of the HCl:HF system at an HF concentration of 0.5% is equal to the dissolution rate of clays of the HV:HF system at an HF concentration of 2% (within 30 minutes of being in acid, the mass of dissolved clays in the HCl:HF system at 0.5% HF is 0.039g, and in the HV:HF system at 2% HF is 0.034g).

In the HV:HF system, the rate of clay dissolution in the first 10 minutes (inductive time) is low, then it slightly increases with slow acceleration. After the stage of the decrease in the dissolution rate, the stage of the increase in the rate begins. This phenomenon justifies the formation of a layer of aluminum phosphate silicate. The stage of slow decrease in the dissolution rate occurs due to the formation of a coating layer, when a part of this layer is dissolved, the stage of the increase in the dissolution rate begins.

The slow rate of clay dissolution (3.5 times less than in the HCl:HF system) allows the proposed system of chemical reagents to penetrate deeper into the bottom hole area. This factor is very important for the increase in the efficiency of treatment of the bottom hole area, especially in the conditions of high formation temperatures of the White Tiger and Dragon deposits.

The experiments to study the ability of the proposed system to dissolve silicon (SiO2) were carried out by the mass loss method, as for other systems. For the experiments, silicon samples were taken in the form of flat glasses with a size of 25 x 50 x 3 mm.

In order to ensure accuracy, the experiments were carried out with different concentrations of HF and similar experiments were carried out in the traditional HCl:HF system.

The results of the experiments show that the amounts of dissolved silicon over time in the systems of chemical reagents HV:HF at various concentrations of HF (1.0; 1.5; 2 and 3%) are linear, which shows the accuracy of the experiments.

According to the results of the HV:HF experiments, at various concentrations of HF (0.5; 1.0; 1.5 and 2%), a graph of the kinetics of silicon dissolution over time is drawn (Fig. 2). Figure 2 shows that if the amount of silicon is small compared to the volume of chemical reagents HCl:HF, then the amount of dissolved silicon changes linearly during the contact time and the rate of silicon dissolution is proportional to the concentration of HF in the system.

The comparison of the kinetics of silicon dissolution in the HV:HF and HCl:HF systems shows (Fig. 3) that the dissolution rate of silicon in the HV:HF system is much higher (1.6 - 1.8 times) than in the HCl:HF system at the same concentration of HF. This is a significant advantage of the proposed system of chemical reagents in comparison with the traditional HCl:HF system.

The experiments to study the ability of the proposed system of chemical reagents to dissolve calcium carbonate (CaCO3) were carried out using the weight loss method. CaCO3 samples were processed in cubic...
blocks with dimensions of 20 x 20 x 50mm. HF concentration in the HV:HF system for experiments was 1; 1.5; 2 and 3%.

![Figure 2. Kinetics of silicon dissolution in the HCl:HF system at various HF concentrations](image)

For a relative comparison, similar experiments were carried out in the following systems:
- Hydrochloric acid with a concentration of 6, 8, 12 and 15%;
- Hydrochloric acid-hydrofluoric acid-acetic acid (HCl:H F:CH₃COOH) with a concentration of 12, 3 and 5%;
- Acetic acid (CH₃COOH) with a concentration of 3, 4 and 5%.

According to the results of the experiments, a graph of the kinetics of dissolution of calcium carbonate at different concentrations of HF (1; 1.5; 2 and 3%) in the HV:HF system was drawn (Fig. 4). The effect of the HF concentration in the HV:HF system on the amount of dissolved CaCO₃ at different contact times (30; 60 and 120 min) is shown in Figure 5.

According to the results of the experiments, a graph of the kinetics of CaCO₃ dissolution in the HCl and HCl:HF:CH₃COOH systems at various concentrations of HCl (1; 1.5; 2 and 3%) and HCl: HF:CH₃COOH (12: 3: 5%) was drawn (Fig. 6). The effect of HCl concentration on the amount of dissolved CaCO₃ at different contact times (30, 60 and 120 min) is linear, which proves the accuracy of the research results.

According to the results of the experiments, a graph of the kinetics of dissolution of calcium carbonate in acetic acid at various concentrations of CH₃COOH (3; 4 and 5%) was drawn (Fig. 7). As in the HV:HF system, the effect of HCl concentration on the amount of dissolved CaCO₃ at different contact times (30, 60 and 120 min) is linear, which proved the accuracy of the research results.

As a result of too big range of dissolution of calcium carbonate in different systems of chemical reagents:
HLV:HF; HCl and CH₃COOH, it is impossible to draw the dissolution kinetics in the same coordinate system. Therefore, in order to compare the dissolution of calcium carbonate in different systems, the amounts of dissolved CaCO₃ at different points in time in HVL:HF; HCl and CH₃COOH at various concentrations were used (Table 1).

![Graph 1](image1.png)

**Figure 4.** Kinetics of CaCO₃ dissolution in the HVL:HF system at various HF concentrations

![Graph 2](image2.png)

**Figure 5.** Dependence of the amount of dissolved CaCO₃ on the concentration of HF in the HVL:HF system
Figure 6. Kinetics of dissolution of CaCO3 in the HCl chemical reagent at various concentrations

Figure 7. Kinetics of dissolution of CaCO3 in the chemical reagent CH3COOH at various concentrations

Table 1. Amount of dissolved calcium carbonate in different chemical reagent systems

| Chemical reagents | The amount of dissolved CaCO3 in time, g |
|-------------------|-----------------------------------------|
|                   | 10 min | 30 min | 60 min |
| HCl 15%           | 37.541 | 54.532 | 61.298 |
| HCl 12%           | 26.974 | 41.332 | 46.964 |
| HCl 8%            | 16.961 | 27.534 | 31.006 |
| HCl 6%            | 12.179 | 20.719 | 23.255 |
| CH3COOH 5%        | 0.626  | 1.360  | 2.177  |
| CH3COOH 4%        | 0.529  | 1.160  | 1.844  |
| CH3COOH 3%        | 0.404  | 0.805  | 1.319  |
| HV:HF 3%          | 0.034  | 0.053  | 0.075  |
| HV:HF 2%          | 0.023  | 0.037  | 0.057  |
| HV:HF 1%          | 0.012  | 0.021  | 0.034  |

Table 1 shows that at the same concentration, the dissolution of calcium carbonate in acetic acid is 15-20 less than when dissolved in hydrochloric acid and 12-18 times less in the HV:HF system than when dissolved in acetic acid. In turn, the dissolution of calcium carbonate in the HV:HF system is approximately 290 times less than when dissolved in hydrochloric acid at the same concentration. This confirms that the HV: HF system dissolves calcium carbonate more effectively than traditional hydrochloric or acetic acid systems.
In general, the results of laboratory tests of rock samples from JV Vietsovpetro deposits showed progress in the solution of the problems associated with acid treatment at high temperatures.

4. Conclusions

1. The results of microscopic analysis of the content of elements on the surface of clay samples after acid treatment with HV:HF showed that as a result of dissolution of clay and quartz, quartz dissolved faster, the Si/Al ratio on the sample surface decreased, which indicated the formation of a protective film of aluminum phosphate silicate.

2. The studies of the ability of chemical reagents to dissolve clay using the weight loss method showed that in the HV:HF system, the dissolution rate of clays was much lower due to the formation of a coating layer. The stage of the increase in the rate of dissolution occurred when a part of this layer was dissolved.

3. The studies of the ability of the HV:HF chemical reagent system to dissolve silicon showed that the amount of dissolved silicon varied linearly with the exposure time, and the rate of silicon dissolution was proportional to the HF concentration in the system. The dissolution rate of silicon in the HV:HF system was much higher than in the HCl:HF system at the same HF concentration and this was a significant advantage of the proposed system of chemical reagents HV:HF in comparison with the traditional HCl:HF system.

4. HV:HF system dissolves calcium carbonate more effectively than traditional hydrochloric or acetic acid systems.

References

[1] Xie X, Weiss W W, Tong Z J, Morrow N R 2005 Improved Oil Recovery from Carbonate Reservoirs by Chemical Stimulation, SPE Journal, 10(3) DOI: 10.2118/89424-PA
[2] Soloviev N N, Mukhametshin V Sh, Safiullina A R 2020 Developing the efficiency of low-productivity oil deposits via internal flooding, IOP Conf. Ser.: Mater. Sci. Eng. 952, 012064 DOI: 10.1088/1757-899X/952/1/012064
[3] Mukhametshin V V, Andreev V E 2020 Search and argumentation of decisions aimed at increasing the efficiency of bottom-hole zone stimulation in oil accumulations with challenged reserves, SPE Russian Petroleum Technology Conference (16–18 October 2017, Moscow) DOI: 10.2118/187785-MS
[4] Economides M, Oligney R, Valko P 2002 Unified Fracture Design: bridging the gap between theory and practice (Ora Press, Alvin, Texas, 2002)
[5] Mukhametshin V Sh 2020 Rationale for the production of hard-to-recover deposits in carbonate reservoirs, IOP Conf. Ser.: Earth Env. 579, 012012 DOI: 10.1088/1755-1315/579/1/012012
[6] Mukhametshin V V 2017 The need for creation of a unified comprehensive method of geological and field analysis and integration of data on effective influence on the bottom-hole formation zone, Oil Industry, 4 DOI: 10.24887/0028-2448-2017-4-80-84
[7] Gonzalez I J F, Gammiero A, Llamedo M A 2012 Design of a Neural Network Model for Predicting Well Performance after Water Shutoff Treatments Using Polymer Gels, SPE Latin America and Caribbean Petroleum Engineering Conference (Mexico City, Mexico, 16–18 April 2012) DOI: 10.2118/153908-MS
[8] Mukhametshin V Sh 2020 Justification for increasing the performance of hydrochloric acid treatment in wells with carbonate reservoir, IOP Conf. Ser.: Mater. Sci. Eng., 905 DOI: 10.1088/1757-899X/905/1/012083
[9] Mukhametshin V V 2017 Eliminating uncertainties in solving bottom hole zone stimulation tasks, Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, 328(7)
[10] Olarte J D, Haldar S, Said R, Ahmed M, Burov A, Stuker J, Kherrat W, Wortmann H 2011 New Approach of Water Shut off Techniques in Open Holes - and World First Applications of Using Fiber Optic Services With Tension-Compression Sub, SPE/DGS Saudi Arabia Section Technical Symposium and Exhibition (Al-Khubar, Saudi Arabia, 15-18 May 2011 DOI: 10.2118/149116-MS
[11] Rogachev M K, Mukhametshin V V 2018 Control and regulation of the hydrochloric acid treatment of the bottomhole zone based on field-geological data. Journal of Mining Institute 231 DOI: 10.25515/PML.2018.3.275
[12] Gdanski R D 2000 Kinetics of the Primary Reaction of HF on Alumino-Silicates, SPE Production & Facilities, 15(4) DOI: 10.2118/66564-PA