Research and application of multi-hydrogen acidizing technology of low-permeability reservoirs for increasing water injection

Mengmeng Ning, Hang Che, Weizhong Kong, Peng Wang, Bingxiao Liu, Zhengdong Xu, Xiaochao Wang, Changjun Long, Bin Zhang, Youmei Wu
Engineering Technology Research Institute of Huabei Oilfield Company, Renqiu, Hebei, China
cyy_ningmm@petrochina.com.cn

Abstract. The physical characteristics of Xiliu 10 Block reservoir is poor, it has strong reservoir inhomogeneity between layers and high kaolinite content of the reservoir, the scaling trend of fluid is serious, causing high block injection well pressure and difficulty in achieving injection requirements. In the past acidizing process, the reaction speed with mineral is fast, the effective distance is shorter and It is also easier to lead to secondary sedimentation in conventional mud acid system. On this point, we raised multi-hydrogen acid technology, multi-hydrogen acid release hydrogen ions by multistage ionization which could react with pore blockage, fillings and skeletal effects with less secondary pollution. Multi-hydrogen acid system has advantages as moderate speed, deep penetration, clay low corrosion rate, wet water and restrains precipitation, etc. It can reach the goal of plug removal in deep stratum. The field application result shows that multi-hydrogen acid plug removal method has good effects on application in low permeability reservoir in Block Xiliu 10.

1. Introduction
Xiliu 10 block reservoir locates at Xiaowangguozhuang country of Gaoyang county in Hebei province. Its main oil bearing formation is the 3rd member of the Shahejie Formation. It possesses complicated oil-water relation and poor physical characteristic. The porosity of Gao 43 well area is 14.9% and the permeability is 8.7×10-3μm2. Therefore, it belongs to a typical low or extra low-permeability reservoir. Fluids are hard to flow in the reservoir and pressure-transmitting capacity is poor because of the small throat radius [1]. The damage of reservoir would increase if the pore blockage is formed. The content of kaolinite is relatively high and up to 77% in Xiliu 10 block reservoir. In addition, due to the serious sensitivity to water, it is prone to produce various contamination in exploration process, which leading to the further decrease of permeability. The content of calcite is also relatively high and the average value is 18% in cements. The increase of the concentration of Ca2+ ion provides the source for scaling inside the reservoir by the slowly dissolution of calcite during the long-term water injection. The above conditions lead to the continuous increasing of the pressure and difficulty of water injection. Mud acid plug removal technology was commonly employed before in order to remove the blockage in the oil flow passage, increase permeability and reduce skin factor [2]. However, the regular mud acid acidizing has two disadvantages. First, most of the acid is consumed at the vicinity of the wellbore on account of fast reaction rate between acid and mineral, which reduces the effective distance of acidizing and causes the damage of wellbore [3]. Second, secondary precipitation results in new
damage of formations. Therefore, regular mud acid acidizing does not meet the current requirement\textsuperscript{[4]}. The multi-hydrogen acid is a suitable pressure decrease and injection increase technique for Xiliu 10 block reservoir since it can realize slow releasing and deep penetration acidizing and prevent secondary contamination.

2. Acidizing mechanism of multi-hydrogen acid

Multi-hydrogen acid is a mixture of phosphate complex and villiaumite and contains multiple hydrogen ions. In the multi-hydrogen acid system, phosphate complex plays the same role as hydrochloric acid in hydrochloric-hydrofluoric acid system\textsuperscript{[5]}. Phosphate has multiple hydrogen ions, and releases hydrogen ions sequentially by multi-stage ionization under different stoichiometric ratios. The concentration of released hydrogen ions remains at a lower level, which prevents the corrosion of rock and the recompression of formation near wellbore by excessive acid concentration.

Sandstone mainly consists of sand and cement. The main components of sand include quartz-feldspar and various rock debris. The main constituents of cement include clay, carbonates, siliceous cements and ferruginous cements. The acidizing of sandstone is different from limestone and is controlled by surface reaction instead of diffusion mass transfer, indicating that once acidizing begins, the reaction rate would be fairly fast. The faster the acidizing reaction rate is, the shorter the penetration distance of acid fluid is and the worse the acidizing performance is. Hence, the retardance of sandstone acidizing is critical.

Experimental equipments.

Multi-hydrogen acid fluid formulation is the phosphate complex reacts with villiaumite to yield HF. HF is actually the substance reacting with the sandstone reservoir. The hydrogen ions produced by the ionization of phosphate complex keeps at a lower level at low PH value. Phosphate complex and villiaumite form a buffering system. The equilibrium of the buffering system is broken when HF is consumed partially by rock mineral. The equilibrium moves towards the direction of HF formation, and the concentration of hydrogen ions of the system decreases. Meanwhile, the ionization equilibrium of phosphate complex is broken. The phosphate complex continuous releases hydrogen ions until a new equilibrium is established. Consequently, the concentration of HF of acidizing fluid and the reaction rate between acidizing fluid and rock mineral maintain constant as long as the concentration of acidizing fluid is large enough.

3. Technical characteristics of multi-hydrogen acid

3.1. Slow releasing of hydrogen ions

A interlayer made of aluminium silicate-phosphate film with the thickness less than 1 μm is formed at the clay surface for the chemical absorption at the beginning of the reaction between multi-hydrogen acid and formation. Weak acid (HF acid / carbonic acid) has poor solubility of this film followed by organic acid. While the film dissolves fast in HCl solution. This thin film can block the reaction between clay and acid, reduce the solubility of the clay and prevent the decomposition of the formation. The surface layer of clay is soluble in acid. Therefore, the solubility of clay can be adjusted by adding small amount of hydrochloric acid and formic acid to achieve optimal design.

3.2. Reaching distant formation

The acidizing for far bore zone formation can be achieved using multi-hydrogen acid because of the sustained releasing effect of multi-hydrogen acid and high speed injection during acidizing process. The treatment radius of multi-hydrogen acid is 2.5 m, while the treatment radius of regular acid is lower than 2 m.

3.3. Strong reactivity with quartz

The reaction between HF and quartz can be catalyzed because multi-hydrogen acid has extremely high absorption capability and water-wet characteristic. The solubility of quartz will increase over time.
3.4. **Inhibiting secondary precipitation**

Multi-hydrogen acid is a good dispersing agent and has substoichiometric chelate property. It is also an excellent scale inhibitor and can inhibit the formation of the precipitate effectively in near borehole zone. The titration experiment of multi-hydrogen acid and silicate shows that no precipitate is formed. The active acid still exists in the formation pores when stop injecting multi-hydrogen acid. The delayed acid fluid flows backwards and keeps reactivity. The acid can only react with quartz because the clay is protected by the thin film. In consequence, the permeability of the formation is further improved.

Multi-hydrogen acid also has complexing ability to polyvalent metal ions. Even at low concentration of multi-hydrogen acid, the metal ions are chelated and can not form precipitate in the solution. Meanwhile, multi-hydrogen acid has strong absorption ability to Ca\(^{2+}\), Na\(^+\) et al. Consequently, they can not react with F\(^-\), SiF\(^4-\) to form precipitates, thus inhibiting secondary precipitation and avoiding secondary contamination.

4. **Lab experimental study on the acidizing effect of multi-hydrogen acid system**

4.1. **The concentration of multi-hydrogen acid optimization**

The concentration of multi-hydrogen acid was optimized by erosive experiment using the core of Xiliu 10 block reservoir. The result indicates that the corrosion ratio is highest at the optimum concentration with the value of 7%. The formation grain is not damaged at this concentration.

![Figure 1. The variation curve of core corrosion rate versus multi-hydrogen acid concentration (90°C)](image)

4.2. **The concentration of hydrochloric acid optimization**

The release time of multi-hydrogen acid can be delayed to some extent by increasing the concentration of hydrochloric acid properly and lowering PH. In addition, properly increasing the concentration of hydrochloric acid can decrease the formation of calcium fluoride because of the high limy content (18 %) in the cement of Xiliu 10 block reservoir. The experimental result shows that the optimum concentration of hydrochloric acid is 10 %.
Figure 2. The variation curve of core corrosion rate versus hydrochloric acid concentration (90°C)

Taking full account of conditions of Xiliu 10 block reservoir, clay stabilizer, ferric ion stabilizer, corrosion inhibitor and multi-effective additive were selected as additives for multi-hydrogen acid acidizing fluid of Xiliu 10 block reservoir.

5. Field application

Xiliu 10 block reservoir has 26 water injection wells. Because of lacking of clay stabilization treatment for a long time, 22 wells has different level of under injection problems. Among these 22 wells, 9 wells can not inject water. The average injection pressure was 30 MPa. 13 wells are under injection wells. The average injection allocation was 40m³/d and the average injection pressure was 28 MPa. The actual average injection was only 17.5 m³/d, which is far from the requirement of reasonable and effective reservoir exploration.

The multi-hydrogen acid pressure decrease and injection increase Technique has been applied to 10 water injection wells at Xiliu 10 block reservoir. One time success rate and effective rate were both 100%. The average increment of injection allocation was 23.1 m³/d per well. The decrement of the average injection pressure at early stage was 10.1 MPa. The current decrement of the average injection pressure was 3.2 MPa. The average validity was over 6 months so far. The total amount of injection increment was 29916m³. The performance of decreasing injection pressure and increasing injection is excellent.

XL-109 is a water injection well corresponding 6 production wells at 43 well area of Xiliu 10 block reservoir. It started injecting water at Dec.,2009. The injecting capability was 17.9m³/d at the beginning of injection. The oil pressure was 18.17 MPa. The injection pressure increased up to 31.5 MPa gradually for the poor physical characteristic of reservoir. The injection capability was 4.2 m³/d, while the injection allocation was 30m³/d. The fracturing was implemented at Feb.-Mar.,2011. The injection capability was 20.4 m³/d at the early stage and the oil pressure was 29.02 MPa. However, the effect reduced fast. The injection capability dropped down to 14.2 m³/d and the pressure remained at 33 MPa after 6 months. And then the injection capability fell to 7.3 m³/d and the pressure kept constant.

The multi-hydrogen acid acidizing technique has been applied to XL-109 at Oct. 2, 2013. The injection pressure reduced 27%. The injection capability increased 300%. The validity was 25 months. The total increment of water injection was 16390m³. The dynamic responses of the corresponding oil wells were obvious, such as the increasing of oil and fluid amounts and the decreasing of water content. The total increment of oil was 3173 t.
6. Conclusions

i. The multi-hydrogen acid pressure decrease and injection increase technique is a suitable broken down technique for water injection well of sandstone reservoir. It has several advantages, such as slow releasing acidizing, long effective distance, long effective duration and inhibiting secondary precipitation. Comparing to regular clay acid, it also possesses the advantages, such as wide applicability, low cost, excellent performance and easy implement et al.

ii. The result of field acidizing experiment of Xiliu 10 block reservoir shows that the pressure reduction and the increase of injection were significant. It played an active role in sustaining the reservoir pressure and block productivity. The multi-hydrogen acid acidizing technique can be applied to other similar reservoirs.

Author information
Mengmeng Ning was born in 1986 and is an engineer mainly working on the research of Reservoir Stimulation now. Phone: 0317-2728489, E-mail: cyy_ningmm@petrochina.com.cn.

Acknowledgements
The study was supported by PetroChina Science and Technology Major Project “The Study of Reducing Injection Water Pressure and Improving Injection Capacity of Low Permeability Sandstone Reservoir of Huabei Oilfield” under Grant No. Kt2017-18-08.

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