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Study on Improvement of Acidizing Fracturing Formula in Carbonate Reservoir

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ABSTRACT

The acidizing fracturing is a kind of stimulation technology for oil and gas reservoir. This technology has been applied to the geothermal well and become an effective means to raise the production of hydrothermal geothermal reservoir. In this paper, we focus on the geothermal wells of carbonate reservoirs in Tianjin, which have the problem of poor acid fracturing effect and large consumption of hydrochloric acid. We have improved the acidification reagent formulation to achieve the goal of increasing production and saving reagents. The acidizing reagent formula is improved to achieve the purpose of increasing production and saving reagents. The acidification formula and construction scheme were tested in a geothermal well in Jinghai District, Tianjin. After acidification, the production of the well increased by 8 times. The acidification effect of the new formulation and acidification scheme is increased by more than 3 times compared with the traditional acidification scheme while saving more than half of the hydrochloric acid.

1. INTRODUCTION

As a kind of zero-emission, sustainable development of green energy, geothermal resources are increasingly favored by society. The development and utilization of geothermal resources in Tianjin has a long history. The carbonate reservoir thermal storage of the Ordovician group and Wumishan group of the Jixian System are the main thermal reservoir. In the development of geothermal resources, it is very common that the production of geothermal wells cannot meet the needs of utilization. In order to increase production, the acid fracturing stimulation technology that using in oil and gas wells have been applied in geothermal wells by technicians , and achieved good results and promoted.[1]~[6] The acidification fracturing technology has been used in Tianjin area several times for the purpose of increasing production of carbonate thermal storage geothermal wells[1][3].

Generally, the carbonate reservoir acidizing solution formula is: A Certain Concentration of Hydrochloric Acid + Corrosion Inhibitor + Iron ion stabilizer + Clear water.[1][3][7] Rough construction methods are often used to achieve the goal of increasing production, such as higher concentration of hydrochloric acid, increasing the amount of hydrochloric acid, and multiple acid fracturing. These methods have a poor effect on increasing the production of reservoir with poor thermal fissures. At the same time, the construction cost is increased. Excessive residual acid emissions also cause some pollution to the environment.

2. ANALYSIS OF ACID FRACTURING MECHANISM

The purpose of acid fracturing is to form acid-etched cracks in the wellbore formation that can effectively improve the seepage of geothermal fluids. The length of the crack and the conductivity are two important factors affecting the acid fracturing.[8]

Acidified fracturing consists of acidification and fracturing. Carbonate rocks are formed by chemical and biochemical aqueous phase deposition or by debris transport. The main mineral components are calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$]. Carbonate thermal reservoirs are usually acidified with a hydrochloric acid solution, and the $CaCl_2$ and $MgCl_2$ formed after the reaction are easily dissolved in water and break through the cracks. In the acidification reaction, the mass transfer rate of hydrogen ions, the reaction rate of hydrogen ions with the rock mineral surface, and the rate at which the reactants leave the mineral surface all affect the rate of the acidification reaction.[9] The acidification reaction chemical equation is listed as follows:

$$2HCl+CaCO_3=CaCl_2+H_2O+CO_2\uparrow$$

$$4HCl+CaMg(CO_3)_2=CaCl_2+MgCl_2+2CO_2\uparrow+2H_2O$$

Fracturing is the artificial pressure, which increases the fluid pressure at the bottom of the well. When the fluid pressure is greater than the rock fracture pressure, new cracks are generated or the original cracks are enlarged. In summary, cracks are generated by acid fracturing, the seepage area is increased, the flow pattern of geothermal fluid is improved, the seepage capacity of the well thermal reservoir is increased, the influence of reservoir pollution near the borehole is eliminated, and the fractures near the wellbore and the deep reservoir are communicated.

3. THE KEY OF ACIDIZING SOLUTION FORMULATION IMPROVEMENT AND PROCESS

3.1 Acidification solution formulation improvement

The biggest difference between geothermal wells and oil well construction processes is cost control. Since geothermal wells are far less profitable than oil and gas wells, the cost must be strictly controlled in geothermal well construction projects, so the construction process of oil and gas wells cannot be completely copied, as is acid fracturing. In order to control the cost, some geothermal wells are acidified using only hydrochloric acid or a small amount of corrosion inhibitor, drainage aid, iron ion stabilizer and anti-swelling agent. This formula has some effect on some strata with better development fracture, but the effect on the fracture with poor development is not obvious. The geothermal well fracturing pressure is generally 10-20 MPa, which has certain damage to the rock around the wellbore, the main function is to drive the acidification liquid to react with the reservoir farther away from the wellbore and expand the fissure. Hydrochloric acid is a strong acid, it reacts fast with carbonate rocks, especially geothermal wells with high temperature, and its reaction is very fast. When the predetermined fracturing distance is not reached during the acidification process, the basic reaction is complete and the treatment range is limited. The acid fracturing only acts to enlarge the crack around the wellbore, and it is impossible to establish communication with the distant fissures, and the effect on crack improvement is not obvious. Therefore, many geothermal well acid fracturing must be applied several times to achieve the desired effect.

The transfer rate of H^+ controls the reaction speed of carbonate rock. Therefore, by changing the formulation of acidification solution, reduceing the transfer speed of H^+ and carbonate rock as to reduce the reaction speed and increase the effective working distance of acid solution. Therefore, this article introduces formic acid based on the original acidification formula. Formic acid is a slow organic acid with weak ionization reaction. It reacts slowly with carbonate rock, has weak corrosivity, and has slow and corrosion inhibition effect at higher temperature. The reaction chemical equation is listed as follows:

$$2HCOOH+CaCO_3=Ca(COOH)_2+H_2O+CO_2\uparrow$$

$$4HCOOH+CaMg(CO_3)_2=Ca(COOH)_2+Mg(COOH)_2+2CO_2\uparrow+2H_2O$$

However, the reaction product of formic acid and carbonate is easy to precipitate and block the percolation channel, so the higher concentration of formic acid cannot be used, and the recommend concentration is generally below 10%.

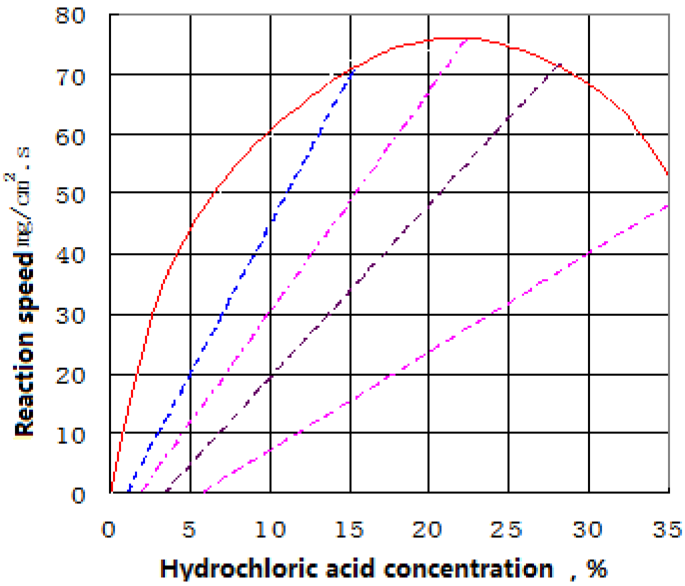

Figure 1: Curve of hydrochloric acid concentration and reaction rate

The relationship between hydrochloric acid concentration and reaction rate is shown in Figure 1. When the concentration of hydrochloric acid is below 20%, the reaction rate has a positive correlation with concentration; when the concentration of hydrochloric acid is above 20%, the trend becomes slower; when the concentration of hydrochloric acid reaches 22-24 %, the reaction speed reaches the maximum value. When the concentration exceeds this value, with the concentration increases, the reaction rate decreases. If concentrated acid is used as the acidifying solution, when it becomes a residual acid, the reaction rate is much slower than that of the same concentration of fresh acid. Due to the high viscosity of high concentration hydrochloric acid, it helps to reduce the fluid loss. Therefore, the optimal concentration of hydrochloric acid in the acidified solution is about 20%. The specific hydrochloric acid concentration can be determined according to the cuttings acid corrosion test.

Corrosion inhibitor and iron ion stabilizer can effectively reduce the acid corrosion of the wellbore, reduce the generation of hydrogen, and ensure construction safety.

The new acidification solution is: hydrochloric acid + 10% formic acid + corrosion inhibitor + iron ion stabilizer

3.2 The key of acid fracturing process

The acid fracturing construction process has a significant impact on the acid fracturing effect. The following process key points should be noted in the construction:

(1) Pre-liquid. The role of the pre-liquid is to generate cracks and reduce the temperature of the surrounding cracks. Generally, the NH_4Cl solution is used as the pre-liquid, and the pre-liquid should be fully replaced below the packer.

(2) Replacement fluid. The role of the replacement fluid is to replace the acid in the column and push it forward along the fracture and into the stratum to increase the penetration distance of the acid.

(3) Returning in time. Since the solubility of the formic acid reactant is low, precipitation is likely to occur after the reaction of the high concentration hydrochloric acid, so the faster the reflux, the better the effect. A large amount of CO_2 is produced during the acidification reaction. The physical properties of CO_2 are shown in Fig. 2. The critical point temperature and pressure are 31.1 °C and 7.38 MPa. When CO_2 reaches critical condition and the temperature is higher than the critical temperature of 31.1 °C, the

pressure increases, CO_2 does not convert into liquid, but becomes a state in which the viscosity and the gas are close, the density is close to the liquid, and the CO_2 in this state has a very strong solubility. Therefore, the flow-back liquid can not eliminate the residual impurities and CO_2 in the formation, we should also promptly carry out gas lift back. When performing gas lift back, the tracheal inflow depth should meet the conditions of destroying the critical point of CO_2, and reduce the pressure in the well below 7.38 MPa to facilitate CO_2 discharge and avoid secondary precipitation.

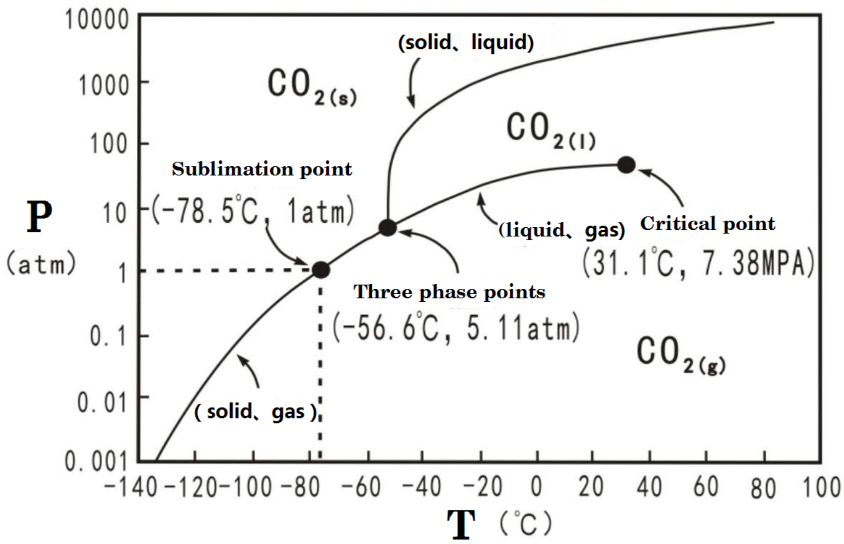

Figure 2: Physical properties of CO_2

Whether the acidified liquid can be back flow in time will seriously affect the acid fracturing effect, but it is often ignored by the technicians. There is another geothermal well near the test well, the well structure, geological conditions, acid fracturing formula and construction process are basically the same, but due to weather reasons, the gas lift is delayed for 2 days, and its acid fracturing effect is poor. The effect of increasing production is not obvious.

4. ACID FRACTURING TEST AND EFFECT ANALYSIS

4.1 Test well profile

This test uses the new formula for acid fracturing in a geothermal well in Jinghai, Tianjin. The geothermal well has a depth of 3800m and is a four-stage directional well,The reservoir is the wumishan group in the Jixian System, exposing more than 270 meters of Dolomite in the wumishan group. Theoutflow rate is 12.33m^3/h before the acid fracturing. The dynamic water level is 250m and the liquid temperature is 62°C. Through borehole logging, the fracture development is shown in Table 1. Among them, there are 2 fracture in the first and second types, the total length is18.3m, 3 fracture in the third types, the total is 15.3m, and the fracture development is poor.

Table 1: Logging fracture interpretation table

NO.	Starting depth（m）	End depth（m）	thickness（m）	Porosity(%)	Permeability($10^{-3}\mu m^2$)	Mud content(%)	Temperature(℃)	Interpret conclusion
26	3545.5	3548.7	3.2	4.02	0.35	1.64	87.1	三类裂缝层
27	3600.1	3608.4	8.3	3.13	0.22	1.57	87	三类裂缝层
28	3627.5	3632.4	4.9	3.81	0.35	1.94	87.6	二类裂缝层
29	3637.8	3641.9	4.1	4.56	0.74	1.66	88.1	三类裂缝层
30	3648.4	3661.8	13.4	6.29	1.65	1.90	88.8	一类裂缝层

4.2 Construction materials

Pre-liquid: 450kg NH_4Cl + 15m^3 water

The concentration of the hydrochloric acid solution was determined to be 20% by laboratory rock dissolution experiments. Acidizing solution formula: 100t 20% hydrochloric acid + 10t 10% formic acid + 2t corrosion inhibitor + 2t iron ion stabilizer

Replacement solution: 31m^3 clear water

4.3 Analysis of acid fracturing effect

We use three 700-type pump trucks and one 300-type pump truck. When pumping acid, the maximum pumping pressure is 15MPa, and the average discharge rate is 1.3m^3/min. If the carbonate fractures are acidified and fractured, and there is good communication with the surrounding cracks, the pressure will suddenly drop during the pumping process. During the acid fracturing process, the pressure suddenly decreased from 15 MPa to 1 MPa, which indicates that acid fracturing achieved good results. After the blowout, we put up the splitter and the tubing, and then we put in the 800m duct for gas lift back. In order to prevent the occurrence of secondary precipitation, we try to keep the acid fracturing end to the beginning of the gas lift release within 10-20 hours.

Through the pumping test, the outflow rate of the test well after acid fracturing was 100.4 m^3/h, the dynamic water level was 158.85 m, and the liqiuid temperature was 90 °C. This experiment shows that this acidification scheme and formulation successfully opened the well and surrounding formation fractures. The acidification of the new acidification formula has increased the acid production by more than three times comparing to the traditional acidification scheme, while saving more than half of the hydrochloric acid usage.

5. CONCLUSIONS AND RECOMMENDATIONS

(1) In this paper, experiments show that the acidizing radius can be increased by using the acidizing solution formula . The effect of acidification is more than three times higher than that of traditional acidification scheme, and the amount of hydrochloric acid used is saved by more than half.

(2) One of the key factors affecting the acid fracturing effect is whether it can be back flow in time, and the technician must pay attention to it. After acid fracturing the gas lift and back flow should be implement as soon as possible to gain high production. , the more obvious the yield increase effect.

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REFERENCES

[1]MA Zhong-ping,DU Bin,Applications of Acid-fracture Technology in Geothermal Well Construction[J], Exploration Engineering(Rock & Soil Drilling and Tunneling),2007,34(2):45-47;

[2]LIN Tianyi ,KE Bolin, The Acid-Fracturing Stimulation Mechanism and Application in Hydrothermal-Carbonate Geothermal Reservoir[J], Urban Geology,2018,13(3):21-26;

[3]LV Dian-chen，Application of acid fracturing technology in geothermal well stimulation[J], China Petroleum and Chemical Standard and Quality, 2013，（22）：156-156；

[4] KE Bai-lin,ZHAO Lian-hai, Application of Perforation and Acid Fracturing in Geothermal Well[J], Exploration Engineering(Rock & Soil Drilling and Tunneling), 2007，34（8）：21-23；

[5] LIU Xing-hao,YANG Chun-hua, Application of acid fracturing process in carbonate reservoir[J], China Petroleum and Chemical Standard and Quality, 2011，31（7）：83，17；

[6] ZHU Li-jun ,LIU Guo-liang, Summary of Acidizing Fracturing Technology[J], Anhui Chemical Industry, 2015，41(2):9-12;

[7] Pan Xiannian, Acid fracturing in high temperature deep layer carbonate reservoir[J], Petrochemical Industry Technology, 2016，23(3):97;

[8] ZHANG Yu, The Research and Application of Sand-adding Acid Fracture in Carbonate Reservoir[J], Journal of Chongqing University of Science and Technology(Natural Sciences Edition), 2014，16（3）：4-7;

[9] Chen Gengliang, Huang Ying, An Analysis of Acidizing Reaction Mechanism of Carbonates[J], NATURAL GAS INDUSTRY, 2006，26(1) : 104-108.