Study on Formula of Retarded Acid for Acidizing and Blocking of Coalbed Methane Wells

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Abstract. Acid plugging removal technology is an effective measure to remove the pollution in the near-well zone of oil and gas reservoirs and restore the productivity of oil and gas wells. It is to use the chemical dissolution of acid solution to dissolve formation plugs, expand or extend formation fractures and holes, so as to restore and improve formation permeability, reduce oil inflow resistance or water injection resistance, thus achieving the purpose of increasing oil well production and water injection. Therefore, the acid formula is particularly important. The commonly used acid formula is the soil acid formula. However, due to the shortcomings of the Soil Acid Formula itself, as well as higher safety risks and construction costs, this paper has studied a new acid formula. X-ray diffraction analysis was carried out on the experimental slime samples from 8 wells in Linfen block of Shanxi province, and it was found that the main mineral composition of the blockage was a mineral that can react with acid. The dissolution rate and corrosion rate of the blockage were tested with Southwest Solid Acid and Soil Acid Formula. The advantages and usability of Southwest Solid Acid were found by comparing the experimental results. Through a large number of experiments, the formula of retarded acid liquor with excellent performance, economy and effectiveness has been selected.

1. Introduction
Acid plugging removal technology can effectively solve the problem of reservoir pollution and improve reservoir production. Lu Baoqiang analyzed and studied the derivative acid system, thus analyzing the acidification effect of various acid liquid systems. Wei Ziyang studied the problem of polymer flocculation plugging in the study and successfully developed a flocculation acid plugging removal system [1]. Jiang Guancheng has developed an autogenous acid system, which has a strong acid plugging removal effect [2]. Gu Na determined the acidizing residual liquid treatment agent composed of neutralizer and complexing agent through the experiment of optimizing the formulation of acidizing and plugging removal agent suitable for Chaoyanggou Oilfield, and solved the potential safety and environmental protection problems brought by the drainage after acidizing [3].

In this paper, a large number of plugging material composition tests, acid solution experiments, corrosion experiments and so on have been completed, and a good performance, economic and effective formula of retarding acid for acidizing and plugging removal of coalbed methane wells has been formed [4].

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2. Experimental Part

2.1. Experimental Samples and Instruments

The experimental slime samples were taken from 8 wells in Linfen block of Shanxi province. Experimental instrument: The experimental instrument adopts X-ray diffractometer. Each mineral has its specific X-ray diffraction pattern, and the content of a mineral in the sample has a positive correlation with its diffraction peak and intensity. In the mixture, the diffraction pattern of one substance component has nothing to do with the existence of other substance components, which is the basis of phase quantitative analysis by X-ray diffraction.

![Figure 1. X-ray diffractometer.](image)

2.2. Experimental Scheme

X-ray diffraction analysis was carried out on slime samples from 8 wells in Linfen block of Shanxi province, and the main mineral components of the blockage and minerals that can react with acid were obtained.

1. Start the pump. Observe the water condition on the pump truck.
2. Pressure test. On-site pressure test shall be conducted according to the design requirements. Generally, it is qualified to hold the pressure for 3~5 minutes without puncture or leakage.
3. Substitute acid. The displacement of displacing acid should not be too large, the well setting the packer should not expand and unseal the packer, and the displacement of displacing acid should not be too large. For wells with unsatisfactory wellbore, fill them with clear water before replacing acid.
4. Squeezing acid. After replacing the acid, close the casing gate. Under the condition that the water exceeds the formation fracture pressure and the allowable pressure of tubing and casing (and the allowable pressure difference of packer), the acid solution and other working fluids shall be squeezed into the formation as soon as possible according to the designed displacement and injection sequence. When the construction pressure is close to the above pressure limit value, the construction displacement shall be reduced. When the construction pressure difference of the well running the packer is close to the allowable pressure difference of the packer, the pump truck shall be used to pump the balancing fluid from the casing. The balancing pressure depends on the construction pressure difference.
5. Replacement. After squeezing the acid, squeeze in the designed amount of displacement fluid immediately, and do not stop the pump in the middle. The construction pressure and displacement are the same to squeeze acid.
6. Shut-in reaction.
7. Acid fluid return. Generally, the total amount of discharged liquid should be 4~5 times of the total amount of squeezed acid, or until the PH value reaches 7~8.
2.3 Experimental Principle
The chemical dissolution of acid solution is used to dissolve formation plugs, expand or extend formation fractures and holes, so as to restore and improve formation permeability and reduce oil inflow resistance or water injection resistance, thus achieving the purposes of increasing oil well production and water injection [5].

3. Experimental Results and Discussion

3.1. Sample Composition Analysis
In the experiment, slime samples from 8 wells were collected from Linfen block. X-ray diffraction analysis was carried out on slime samples from these 8 wells respectively, as shown in table 1. The X-ray diffraction analysis results of slime samples show that the mineral components of the blockage are mainly dolomite, siderite, hematite, silicic acid rock, etc., which can react with acid. However, there are also special circumstances, such as the slime sample of Well 4.

| Well Number | Quartz (%) | Calcite (%) | Dolomite (%) | Gypsum (%) | Barite (%) | Siderite (%) | Hematite (%) | ... | Clay (%) |
|-------------|------------|-------------|--------------|------------|------------|--------------|--------------|-----|----------|
| Well 1      | 28.88      | 10.77       | 16.83        | 2.37       | 1.86       | 7.53         | 27.53        | ... | 1.26     |
| Well 2      | 24.80      | 6.96        | 18.17        | 0.95       | 3.32       | 8.49         | 31.20        | ... | 4.94     |
| Well 3      | 20.24      | 12.22       | 21.18        | 1.43       | 5.22       | 7.56         | 26.56        | ... | 3.48     |
| Well 4      | 1.82       | 1.42        | 1.58         | 31.67      | 58.38      | 0.55         | 2.07         | ... | 1.47     |
| Well 5      | 25.54      | 9.86        | 17.93        | 2.16       | 2.50       | 8.93         | 25.73        | ... | 3.47     |
| Well 6      | 24.82      | 13.82       | 10.59        | 1.97       | 1.97       | 7.72         | 32.66        | ... | 3.52     |
| Well 7      | 32.77      | 8.95        | 13.21        | 0.78       | 1.24       | 9.59         | 24.65        | ... | 4.76     |
| Well 8      | 34.18      | 14.75       | 1.36         | 1.09       | 1.46       | 7.83         | 35.31        | ... | 2.90     |

3.2. Study on Formulation of Retarded Acid
In the early days, the National Engineering Research Center carried out dissolution experiments and corrosion experiments on slime samples from 5 wells to form a formula of soil acid (hereinafter referred to as central soil acid). However, due to the shortcomings of the central earth acid itself, as well as higher safety risks and construction costs, a new acid formulation must be studied. In this paper, the formulation of solid retarded acid is studied, and its indexes are mainly required to meet the requirements of high dissolution, low corrosion, low cost and less influence on the propping fracture formed by early fracturing.

3.2.1. Corrosion Rate performance evaluation. Dissolution experiment is to investigate the dissolving ability of acid solution to the blockage (slime) in wellbore, and is the primary index for selecting acid solution. For the first batch of slime samples from Well 1, Well 2 and Well 3, various acid formulations were adjusted to make the dissolution rate of slime reach about 50%. The dissolution rate results under various concentrations, different wells and drug combinations are shown in figure 2 to figure 7 (part).
It can be seen that under a certain acid content, the longer the shut-in time, the smaller the dissolution rate; Under the condition of constant shut-in time, the higher the acid content, the smaller the dissolution rate. For the first batch of slime samples from Well 1, Well 2 and Well 3, the dissolution capacity of southwest solid acid is 11.06% higher than that of central soil acid, with an average dissolution rate of 47.96%, indicating that southwest solid acid can effectively remove blockage and achieve the purpose of restoring production capacity.

3.2.2. Evaluation of Corrosion Rate performance. Corrosion experiment is to investigate the corrosion ability of acid solution to casing, rod and pipe in production well, and is an important index for selecting acid solution. The corrosion ability of different concentrations of drugs to N80 steel sheet is shown in figure 8 and figure 9 (part). It can be seen that the corrosion ability of southwest solid acid is very low.
and almost has no influence on casing, rod and pipe in the production well, which is 40.11% lower than that of central soil acid, reaching the first-class standard.

Figure 8. Corrosion Rate at different concentrations.

Figure 9. Comparison chart of Corrosion Rate between Central Soil Acid and Southwest Solid Acid.

3.2.3. Optimization of acid formulation. The composition tests of slime samples from 8 wells, 36 kinds of acid solutions and 856 times of corrosion experiments and corrosion experiments have been completed, and an economical and effective retarding acid solution for coalbed methane wells has been formed. When the retarding acid solution is 4% SWA-1+4% SWA-2+2% SWA-3+1%SWA-4+1%SWA-5+1%SWA-6, its dissolution rate reaches 50%, and its dissolution capability is strong. The corrosion rate is lower than 3, which is the level 1 standard. But also in solid form, and has the advantages of easy procurement, transportation, preparation and safety.

4. Conclusion

(1) When the shut-in time is fixed, the higher the acid content, the smaller the dissolution rate; When the acid content is constant, the longer the shut-in time is, the smaller the dissolution rate is.

(2) The solubility of southwest solid acid is higher than that of central soil acid, which indicates that southwest solid acid can effectively remove blockage and restore production capacity. Compared with the central soil acid, the southwest solid acid has lower corrosion ability, reaching the first-class standard.

(3) When the formula of retarded acid liquor is 4% SWA-1+4% SWA-2+2% SWA-3+1%SWA-4+1%SWA-5+1%SWA-6, its dissolution rate reaches 50% and its dissolution ability is strong. The corrosion rate is lower than 3, which is the level 1 standard. But also in solid form, and the solubility of southwest solid acid has the advantages of easy procurement, transportation, preparation and safety.

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