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Research Article

Research and performance evaluation on an HA integrated acid system for sandstone acidizing☆,☆☆

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Abstract

When the conventional sandstone acidizing technologies are adopted, many slugs are needed in the injection of prepad fluid, treatment fluid and postpad fluid, and consequently the production and operation suffers inconveniences and difficulties. In view of this, a kind of HA integrated acid system which is mainly composed of organic polybasic acids (HA)+HCl + HF and an efficient organic solvent was developed in this paper based on the idea of integrated acid replacing "multiple steps" and high efficiency and intensification. Via this HA integrated acid system, the complicated blockage in sandstone reservoirs can be removed effectively. Then, experiments were carried out on this system to evaluate its performance in terms of its retardance, organic blockage dissolution, chelating and precipitation inhibition. It is indicated that this new system can not only realize the acidizing of conventional integrated acid, but also present a good retarding performance by controlling H^+ multi-stage ionization step by step and by forming silica acid-aluminum phosphonate film on the surface of clay minerals; that via this new HA integrated acid system, the organic blockage can be removed efficiently; and that it is wider in pH solution range than conventional APCs (amino-polycarboxyliates) chelants, stronger in chelating capacity of Ca^{2+}, Mg^{2+} and Fe^{3+} than conventional chelants (e.g. EDTA, NTA and DTPA), and better in precipitation inhibition on metal fluoride, fluosilicic acid alkali metal, fluoaluminic acid alkali metal and hydroxide than multi-hydrogen acid, fluoboric acid and mud acid systems. These research results provide a technical support for the plugging removal in high-temperature deep oil and gas reservoirs.

Keywords: Organic polybasic acid; Integrated acid; Retardance; Chelating; Precipitation; Acidizing; Sandstone; Reservoir

Acidizing is an important method for removing plugging and increasing production in sandstone reservoirs [1–5]. It is intended to dissolve the near-wellbore blockage, relieve the damage, restore the reservoir permeability, and increase the production/injection volume of target wells. However, when the conventional acid system is used, multiple slugs are needed in the injection of prepad fluid, treatment fluid and postpad fluid, in order to relieve various damages, prevent secondary precipitation and enhance the acidizing effect. This will inevitably lead to problems such as complicated pump injection procedure, massive use of equipment and high cost of construction, which brings inconvenience and trouble to production and operation [6–9].

In 2004, Chike et al. [10] unprecedentedly proposed an innovative idea of replacing "multiple steps" with one-step integrated acid system. Since then, extensive researches have been carried out by a lot of researchers. Uchendu et al. [11]

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used a chelate system based on HV complexes as the integrated acid to successfully relieve the damage to the Nigeria delta sandstone reservoirs with the domination of particle invasion. Nasr-El-Din et al. [12] proposed the solution of a new acid system based on a new chelant + HF acid, which pointed out a new direction for the development of acid system. Wang et al. [13] proposed an integrated acid system based on the retarded acid system of boric acid (H_3BO_3), ammonium hydrogen fluoride ($NH_4F{\cdot}HF$) and organic acids, but the application range of this kind of acid system was limited since the pH was required to be less than 2 in the whole acidification process. The organic integrated (HA) acid system proposed in this paper is a new kind of integrated acid composed of HA + HCl + HF and an efficient organic solvent. With multiple functions integrated, this HA integrated acid system can not only reduce the complexity of the acidizing process, but also have better performance in inhibiting corrosion and secondary and tertiary precipitation, as well as excellent retarding performance, so it is applicable for plug removal in high pressure deep oil and gas reservoirs.

1. Development idea of the new integrated acid system

The new composite acid system based on HA is mainly composed of HA (organic polybasic acid), HCl and HF acid as well as an efficient organic solvent. Among them, the efficient organic solvent can quickly dissolve some organic blockage that the acid cannot dissolve; HF acid is a strong acid, mainly used to dissolve the quartz, clay and other minerals in the sandstone, but generally HF acid is not used alone for acidization for two reasons [14–17]. First, HF acid will preferentially react with carbonate rock and be consumed substantially, and thus cannot effectively remove mud clogging. Second, HF acid can not only dissolve quartz, clay and other minerals, but also quickly dissolve carbonate to generate CO_2 and insoluble metal fluoride precipitation, resulting in secondary and tertiary damage. The hydrochloric acid in the HA integrated acid system can rapidly dissolve carbonates and protect HF acid from being consumed substantially, so that HF can effectively dissolve argillaceous components and some quartz particles. HA maintains the acid at a certain pH value through multistage ionization, to inhibit the secondary and tertiary precipitation damage. Specifically, the new HA composite acid system can realize retardance in the following two ways.

1.1. Controlling the ionization of H^+ to achieve retardance

The system is a mixed system composed of organic polybasic acid and mud acid. It controls the ionization of HA organic phosphonic acid via hydrochloric acid to achieve a retardance effect of mixed acid system. The HA in the system is a polybasic acid with ionization constant smaller than that of hydrochloric acid. After the acid system enters the formation, hydrochloric acid reacts with the rock minerals. When the effective H^+ content in the acid is reduced, HA begins to ionize to generate hydrogen ions and react with the rock minerals, thereby prolonging the action time of the active acid and increasing the acidification distance, to achieve the purpose of deep acidification.

1.2. Controlling the reaction between H^+ and rock surface to achieve retardance

When the acid reacts with the formation, HA is adsorbed on the clay due to physical adsorption. Because HA is an anionic organic polybasic acid, it can achieve chemical adsorption with Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} and other metal ions on the clay surface, thus forming a silica acid-aluminum phosphonate film on the surface of clay and fillings (Fig. 1), which is acid soluble with a thickness of less than 1 μm. The results of scanning electron microscopy (SEM) showed that the film had a low solubility in weak acid (hydrofluoric and carbonic acids) and water, so it could prevent further reaction of hydrofluoric acid with clay and restrict clay dissolution, and thus protect the near-wellbore base rock from damage and realize retarded acidizing.

2. Performance evaluation of the new integrated acid

2.1. Retarding performance

Dissolution experiments on four kinds of monominerals (Fig. 2) were designed to study the retarding performance of

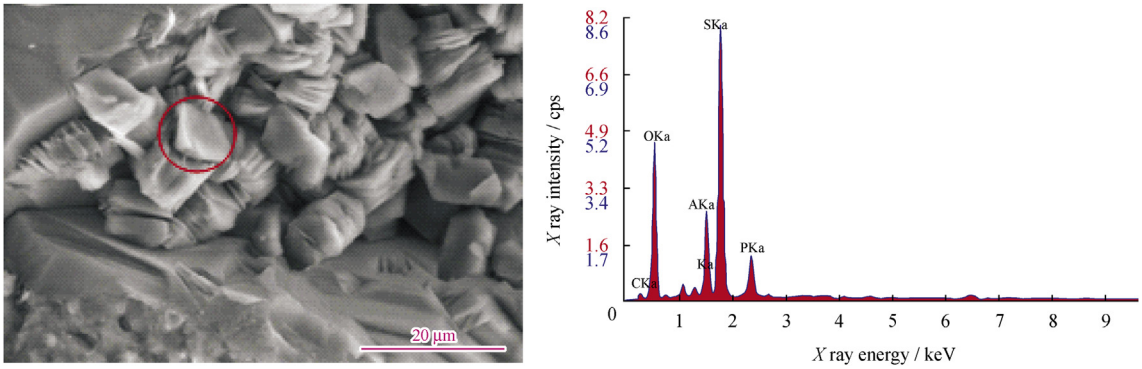

Fig. 1. SEM and energy spectrum analysis of HA film on the surface of kaolinite.