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PK-OFTA In-situ Acid Generation Process Adaptability Evaluation

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Abstract

Currently, there are various types of in-situ acids, but they all encounter different problems during on-site construction, such as excessive hydrolysis time, strong construction odors, and goods prone to moisture degradation. To address these issues, this study evaluates the adaptability of PK-OFTA in-situ acid, which is prepared by mixing 25% A reagent and 0.6% B reagent, through a comparison of in-situ acid performance and indoor experiments. The experimental results show that A reagent in PK-OFTA exhibits multiple acid releases. As the H+ concentration increases, the acid generation rate gradually decreases. Furthermore, PK-OFTA can be uniformly dispersed in the solution through dissolution and suspension. Combining the on-site construction data, it is observed that A reagent does not show significant settling when the displacement is greater than 1 m3, meeting the construction requirements.

Keywords

PK-OFTA; Performance Comparison; Indoor Experiments; On-site Construction.

1. Introduction

In-situ acidizing technology refers to the use of two or more acidizing agents mixed in the formation, which slowly react under the catalytic effect of temperature or inducers to form acidizing working fluid. Based on the acid generation mechanism, acid-rock reaction mechanism, main functions, and differences of acid liquids, researchers have classified in-situ acids into self-generated hydrofluoric acid, self-generated organic acid, self-generated hydrochloric acid, and composite self-generated acids. Self-generated hydrofluoric acid refers to the hydrolysis of fluorinated acidizing agents or the formation of self-generated acid systems with HF as the main component through hydrogen bonding. The development of self-generated organic acids can be traced back to 1975 when Temploton et al. first introduced HCOOCH3 and NH4F as the main components of self-generated acid systems in field tests, generating an effective combination of hydrofluoric acid and organic acids. The addition of self-generated organic acids solves the problem of ineffective treatment of sandstone deep blockages by single acid and has certain economic benefits. One of the raw materials for self-generated acids is chlorinated hydrocarbons, but chlorinated hydrocarbons can penetrate the skin and cause severe damage to the central nervous system and internal organs. Therefore, most chlorinated hydrocarbons do not meet the safety requirements of the production process.

2. PK-OFTA Performance Evaluation

2.1 PK-OFTA Acid Generation Mechanism

The A reagent of OTFA in PK-OFTA (Figure 1) is composed of a combination of various substances that are soluble in water. The main component is trifluoromethylnitrate, which has a functional group with a chemical formula of CF3NO3-. For example, trifluoromethylnitrate butyl ester can be written as CH3CH2CH2CH2OTF. It is a strong acid ester that can hydrolyze in the presence of an activator to form the corresponding organic acid.

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Figure 1. Sample of A reagent

2.2 PK-OFTA Hazard Evaluation

The hazardous nature of the self-generated acid system has been determined through goods hazard identification, proving that it is non-hazardous.

As shown in Table 1, trifluoromethylnitrate butyl ester is safer compared to polyoxymethylene, with low harm to water and no significant irritating odor. The decomposition product is non-toxic n-butane, which meets the requirements of construction.

Table 1. Hazard Comparison of OTFA and Polyoxymethylene

	Trifluoromethylnitrate butyl ester	Polyoxymethylene
Harm to water	Low (WGK-1)	High (WGK-2)
Toxicity	None	Low toxicity
Irritability	Weak	Strong
Volatility	Moderate	High
Decomposition	Weak	Moderate
Decomposition products	n-Butane	Formaldehyde
Toxicity	None	Low toxicity

2.3 Performance Advantages of PK-OFTA

(1) Easy transportation, storage, and scalable use: A significant breakthrough of this technology is the change in the form of the acid, allowing for convenient on-site use in large doses.

(2) Excellent corrosion inhibition performance, minimal damage to pipelines: It has minimal corrosion on ground equipment and operation tubulars at low temperatures. At high temperatures, it can be used in combination with specialized organic acid corrosion inhibitors.

(3) Achieving deep acidizing in remote areas, improving acid penetration depth: Conventional acids have fast reactions, which can easily create a low-conductive crack. PK-OFTA has a lower acid-rock reaction rate, enabling a broader acid etching range and enhancing acid etching for increased production.

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(4) Non-uniform etching on fracture walls, improving conductivity: Experimental evidence shows that the acid precursor of PK-OFTA forms a rougher and non-uniform etching on the fracture walls, thus improving the conductivity of acid-etched fractures.

3. Experimental Procedure for PK-OFTA

In this experiment, the formulation of PK-OFTA consists of 25% A reagent and 0.6% B reagent. The B reagent is prepared by mixing two types of substances in a 1:1 ratio by mass to obtain a 0.6% B reagent solution. During the experiment, the 25% A reagent is poured into the B reagent and stirred thoroughly.

(1) Acid concentration

Prepare the self-generated acid system according to the proportion and place it in a blue-sealed bottle. Heat the system in a water bath at a temperature of 95°C. At 0 min, 30 min, 60 min, 90 min, 120 min, and 180 min, take approximately 1 ml of self-generated acid and transfer it to a conical flask. Add 2-3 drops of phenolphthalein indicator to the flask and place it in a 95°C magnetic stirring water bath. Titrate the solution with 0.1 mol/L NaOH standard solution until the solution turns red and remains unchanged for 5 minutes, indicating the endpoint of titration. Calculate the concentration of the self-generated acid solution.

(2) Solubility

Weigh the A reagent of PK-OFTA and add it to 100 ml of water with stirring at 300 rpm at room temperature. Observe the dissolution process and consider it as completely dissolved if no visible solute particles are observed.

(3) Settling Rate

Based on the settling rate measurement method of individual particle sedimentation using a supporting agent, determine the settling rate of the A reagent of PK-OFTA in a saturated solution of the B reagent of A reagent.

4. Analysis of PK-OFTA Experimental Results

4.1 Analysis of Acid Concentration

As shown in Table 2, when the concentration of the A reagent is 25%, the hydrochloric acid equivalent concentration exceeds 10% at 30 minutes, and reaches approximately 16.15% hydrochloric acid equivalent concentration at 2 hours. It reaches close to the endpoint of acid concentration around 90 minutes (Figure 3). The results indicate that the A reagent exhibits multiple acid release characteristics, and the acid production rate gradually decreases as the H+ concentration increases.

Table 2. Acid Concentration Statistical Table

Agent A concentration	25%	
Time	Equivalent concentration of hydrochloric acid (%)	H^+ (mol/L)
0	8.38	9.45
30	10.94	11.54
60	13.63	14.16
90	15.48	16.37
120	16.15	19.58
180	16.25	20.33

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Comparison of PK-OFTA with other researched self-generating acid systems, including polyoxymethylene and organic carboxylic acids, was conducted to compare their acid concentrations within 2 hours (Table 3). The acid concentration of PK-OFTA has been found to exceed that of other self-generating acid systems.

Table 3. Comparison of Experimental Data with Other Self-Generating Acid Systems

data sources	Types of self-generating acids	Temperature (℃)	Reaction Time (h)	Hydrochloric Acid Equivalent Concentration (%)
Liu, Yongquan	Organic acid ester + ethyl chloride salt	150	7	3.81
Li, Yongshou	Organic carboxylic acid ester	110	5	＜0.4
Xu, Zhipeng	Ethyl lactate + polyoxymethylene + ammonium chloride	90	2	11.5
Hou, Fan	Polyoxymethylene + ammonium chloride	90	2	14
Ma, Xueli	Hydrogen-containing organic compound + chlorinated organic compound + fluorinated organic compound	130	3	11
The present experiment	Self-generating nitric acid	95	2	16.15

4.2 Solubility Analysis

By conducting measurements at room temperature, the solubility of PK-OFTA was found to be 0.158g/ml. Other particles were observed to be suspended in the solution. The solubility of PK-OFTA increased when heated, and after heating for 30 minutes, no visible particles were observed. Therefore, through dissolution and suspension, PK-OFTA can be uniformly dispersed in the solution.

4.3 Sedimentation Rate and Process Parameter Calculation

Based on multiple single-particle sedimentation times, the average sedimentation rate of A agent was determined to be 0.095 cm/s. According to Stokes' law, in combination with the pipe diameter and an approximate depth of 3500m, when the displacement exceeds 1m3, A agent reaches the crack without significant sedimentation. The specific displacement needs to be determined based on construction design and factors such as the power of the auger.

Table 4. Experimental Data for Sedimentation Rate

Settlement time (s)	Settlement distance (cm)	Settlement rate (cm/s)
105	10.3	0.098
94	8.9	0.097
107	9.5	0.089

5. Summary

(1) PK-OFTA is easy to transport, store, and use on a large scale. It has low harm to water, no noticeable irritating odor, and its decomposition products are non-toxic compounds, meeting the requirements for construction.

(2) When the concentration of A agent in PK-OFTA is 25%, the hydrochloric acid equivalent concentration exceeds 10% at 30 minutes and reaches 16.15% at 2 hours. Comparing the acid generation concentration at 2 hours with other self-generating acid formulations such as polyoxymethylene and organic carboxylic acids, PK-OFTA has a higher acid generation concentration.

(3) The solubility of PK-OFTA is 0.158g/ml, and the other particles are suspended in the solution. The solubility of PK-OFTA increases when heated, and after heating for 30 minutes, no visible particles are observed. The average sedimentation rate of A agent is 0.095 cm/s. When the displacement is greater than 1m3, A agent reaches the crack without significant sedimentation, satisfying the requirements for on-site construction.

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