Parametric and Item Study of Major Principles in the Pre-Treatment Process of Drilling Wastewater

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Abstract: The performance assessment of nano ferric oxide and mixtures of it (10 and 15 gr/lit) which contain mineral coagulants (5 and 10 mg/lit for evaluation of acidity of wastewater and 15 and 20 mg/lit for measuring of zeta potential) as auxiliary coagulants in pre-treatment of drilling waste water was considered, in this pilot scale experimental work. Major parameters in coagulation and flocculation such as initial and final pH, zeta potential and resident time were evaluated in two pre-treatment reactors.

Keywords: Environmental Pollution, Nano Ferric Oxide, Coagulation, Treatment.

INTRODUCTION

Drilling fluids are applied extensively in the upstream oil and gas industry, and are critical to ensuring a safe and productive oil or gas well. During drilling process, a large volume of drilling fluid is circulated in an open or semi enclosed system, at elevated temperatures, with agitation, preparing an important potential for chemical exposure and subsequent health effects [1-3]. When deciding on the type of drilling fluid system to use, operator well planners require conducting comprehensive risk assessments of drilling fluid systems, considering health aspects in addition to environmental and safety aspects, and strike an suitable balance between their potentially conflicting requirements [4-5]. The results of these risk assessments require to be made available to all employers whose workers may become exposed to the drilling fluid system [6].

Functions of Drilling Fluid

In the early days of rotary drilling, the primary function of drilling fluids applied to bring the cuttings from the bottom of the hole to the surface [7]. Today it is recognized the drilling fluid has at least ten important functions: A). Assists in making hole by: A-1). Removal of cuttings, A-2). Cooling and lubrication of bit and drill string, A-3). Power transmission to bit nozzles or turbines. B). Assists in hole preservation by: B-1). Support of bore hole wall, B-2). Containment of formation fluids. C). It also: C-1). Supports the weight of pipe and casing, C-2). Serves as a medium for formation logging. D-It must not: D-1). Corrode bit, drill string and casing and surface facilities, D-2). Impair productivity of producing horizon, D-3). Pollute the environment [8-10].

The Role of Drilling Fluid

Undoubtedly, the drilling fluid has vital role in drilling process [11, 12]. Two basic items included; frictions and in the recycling cycle.

Customized Solutions

Despite the excellent track record demonstrated by invert emulsion fluids, operators continued searching for a water-based system that will give comparable performance [13-15]. Increasing concern is placed on environmental impact of operations, making water-based alternatives more attractive [16-18].

Baroid has engineered high-performance water-based fluids that emulate the performance of an invert emulsion fluid. Each fluid system is customized to address specific drilling challenges [19-21].

MATERIALS AND METHOD

NaOH and Na₂CO₃ as auxiliary coagulants
were used in coagulation reactor. The mixing rate of mixer in the first reactor is 120rpm. Totally, two reactors as pretreatment unit were applied in this work. Both of reactors were made from, stainless steel-316. In addition, three chemical compounds as mineral coagulants were used in the pretreatment unit. \( \text{Al}_2(\text{SO}_4)_3 \), \( \text{Fe}_2(\text{SO}_4)_2 \) and \( \text{FeCl}_3 \) applied in the experimental runs. The purity of all of the chemical compounds were 99.98% and its brand is Merck. The all of the runes were held in the two poly vinyl chloride series tanks equipped by adjustable agitator. Also, the treatment process was done in two series mixed reactors. In addition, the 450 ml of NaOH and 600 ml of \( \text{Na}_2\text{CO}_3 \) was inserted in the drilling mud feed line.

The first reactor is a fast mixing reactor to insert a coagulant during 5 min with 120 rotations per minute. Also, the second slow mixing reactor vessel (60 rpm, 20 min). Feed was 4 litters watery drilling mud.

Three auxiliary mineral coagulants, Aluminium Sulphate, \( \text{Al}_2(\text{SO}_4)_3 \), Ferric Sulphate, \( \text{Fe}_2(\text{SO}_4)_2 \) and Ferric Chloride, \( \text{FeCl}_3 \), were used in the pre-treatment process of waste stream of drilling. Moreover in softening process Sodium Carbonate and Sodium Hydroxide were added to the waste drilling fluid. To prepare the NaOH and \( \text{Na}_2\text{CO}_3 \) solution, 10 gr \( \text{Na}_2\text{CO}_3 \) and 10 gr NaOH solutes in one litter distilled water and then the appropriate volume of the solution was taken to the first reactor. So the appropriate fraction of these additives to coagulant was is consideraded. Nano ferric oxides (5 to 20 gr/lit) was as coagulant and gather the sulphur and salts which are situated around the structure.

The first reactor used as coagulation step and the second reactor was used as flocculation step. In addition, the third step is applied as sedimentation unit. After sedimentation and at the constant final pH, the clear water was withdrawn from the tank.

**Operating Functions for Prediction of Treatment Performance**

The some functions which were evaluated in the treatment units are listed at the below. These functions state the quality of treatment process.

**Operating Variables of Treatment Performance**

The pH, time, zeta potential are the basic variables which were measured in this study. These variables were measured several times according to the Figures 1, 2 and 3.

1. **Fourier Transform Infrared Spectroscopy (FTIR)**

   This is a proper and confident technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of fluid. The FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The used FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy. Figure 1 show the FTIR photo of produced ferric nano particles.
Figure 2 shows the scanning electron microscopy pictures of ferric nano particles. In addition, the pictures of transmission electron microscopy are shown in the Figure 3. The scale of this picture is 10 nm, 20 nm and 100 nm.

2. Zeta Potential

Zeta potential as a scientific term is applied for electro kinetic potential in this study. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta (ζ), hence ζ-potential. From a theoretical viewpoint, the zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. In fact, the zeta potential shows the stability of a treated solution. The reference number for this measurement is 25m Volt. The decreasing and increasing in the amount of zeta potential can be cause by the quality of coagulation and flocculation steps. The zeta potential is a good reference for determination the colloidal solution from the other solutions. Zeta meter can measure this variable and stated the electricity difference between the bulk molecules and the outer layer of coagulants.

RESULTS AND DISCUSSION

Effect of Concentration of Nano Ferric Oxide and Time on the pH of Solution

The Figure 4 shows the effect of amount of nano ferric oxide flocculants (5 and 10 g/lit) on values of pH. The pH values changes during time if the reactions weren't completed. So, according to the experimental results, the lower amount of nano ferric oxide, 5 gr/lit, presents unstable conditions during times. The pH decreases to 10.37 till 21 hrs and then increases to 10.4 till 25 hrs. However, the amount of 10 g/lit of nano ferric oxide presents more stable pH
condition during 5 hrs to 25 hrs with value of about 10.5. This seems that 10 gr/lit is the proper amount of nano ferric oxide to complete flocculation reaction so this produces stable compounds with magnesium and calcium.

![Fig-4: pH versus time in different concentration of Nano ferric oxide](image)

The Effect of Initial pH and Time on the Final pH of Solution

The pH values are important keys in chemical reactions such as flocculation and coagulation. The separation and formation of flocs complexes depends on initial pH value of solution and time. The Figure 5 shows the amount of final pH versus sedimentation time. The final pH of solution then can show the produced compounds and the quality of treatment. The solutions with initial value of pH of 7 and 8 during 19 hrs, were examined. Solutions with initial pH value of 8 showed the more stable compounds with final pH value around 8. The pH value around 7.8 is obtained applying solutions with initial value of 7 however; there is fluctuation in pH value of final solution after 7 hrs and the value of final pH decreases to 7 which may be an error of experiment.

![Fig-5: pH versus time in different initial pH value](image)

Zeta Potential Versus pH

The effect of flocculants on value of zeta potential is shown in the Figure 6. Two different amounts of nano ferric oxide 15 and 20 gr/lit were used. The higher amount of nano ferric oxide, 20 g/lit, shows the higher value of zeta potential at the same value of final pH. Final pH values were changed in amounts of 8, 8.5, 9, 9.5, 10 and 10.5. Zeta potential values in final pH of 9 and 9.5 were higher than those are obtained at the other pH values. Minimum value of
Concentration of nano ferric oxide is 15 gr/lit. Concentration of nano ferric oxide is 20 gr/lit.

**CONCLUSION**

Nano ferric oxide coagulation capability was evaluated in comparison with mixtures include this poly coagulant and three common mineral coagulants of ferric chloride, ferric sulphate and aluminium sulphate. The pre-treatment of drilling complex with these coagulants in two series reactors is investigated experimentally. Below results are deduced from the experimental work. The better capability of nano ferric oxide in pollution reduction as a coagulant was obvious for all materials than other combined coagulants. This can be described by the proper molecular weight and ion charges of this poly coagulant which affect the interaction between the molecules of poly coagulants and undesirable compounds. The experimental results show the pH values decreases to 10.37 till 21 hrs and then increases to 10.4 till 25 hr. In addition, the amount of 10 g/lit of nano ferric oxide presents more stable pH condition during 5 hrs to 25 hrs with value of about 10.5. The lowest molecular weight and amount of ion charges of ferric chloride influences the performance of it in combined mixtures. The increase in the coagulation power of combined coagulant was affected by amount of ferric chloride in lowest amount of it, 5 gr/lit. The pH, zeta potential and transmittance were also investigated in this work.

**REFERENCES**


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