Characterization and Source Analysis of Suspended Solids in Chemical Flooding Sewage

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Abstract. The oilfield sewage from chemical flooding was analysed in this paper. It showed that the sewage contained high concentration of suspended solids, organic acrylamide polymer, multivalent metal ions. IR and Electron microscope measurement showed the value of suspended solids measured by membrane filtering method was much higher than the real value due to polymer absorption and plugging on membrane. The suspended solids in filtered sewage increased due to formation of fine inorganic scale and colloidal particles under certain conditions. The zeta potential showed the sewage was much negatively charged. At pH value 3~4, the zeta potential of sewage shifted to -5.0mv quickly and much precipitate of polymer gel appeared in sewage. Above all, the negatively charged polymer and high viscosity of sewage played an important role in dispersing and stabilizing suspended solids.

1. Introduction

In recent years, various chemical flooding technologies have been developed to enhance oil recovery. Polymer flooding technology has been applied successfully on an industrial scale in Daqing oilfield and obtained satisfied stimulation effect[1-2]. On polymer flooding basis, Alkali-surfactant-polymer (ASP) flooding pilot test has been performed in Daqing Oilfield. By using strong or weak alkali, surfactant and polymer in the injected water, ASP flooding technology can improves recovery rate dramatically. However, produced sewage from ASP flooding became more difficult to treat for it contained much emulsified oil, suspended solids and residual chemicals[3-4]. In particular, the fine suspended solids were very stable and difficult to remove. The effective treatment for ASP flooding sewage became urgent and important for its industrial application.

Engineers and researchers are eager to know the Characterization, source and stability of suspended solids (SS) in ASP flooding sewage[5]. In this paper, various measurement including Zeta potential, Size distribution, IR and SEM were applied to suspended solids of ASP flooding sewage from Daqing oilfield. The study would help understand the characteristics of suspended solids and improve the treatment efficiency of ASP flooding sewage.

Liu, G., Li, X., Zhang, F., Qu, Y., Qi, N., Lu, Y. and Su, H.
Characterization and Source Analysis of Suspended Solids in Chemical Flooding Sewage.
In *Proceedings of the International Workshop on Materials, Chemistry and Engineering (IWMCE 2018)*, pages 77-82
ISBN: 978-989-758-346-9

2. Experimental

2.1. Materials

JCXG-03 Suspended solids Measurement, Harbin Jin Boda Electrical Co., Ltd; X650 Scanning Electron Microscope, Japan Hitachi Company; Nexus 670 Infrared Spectrophotometer, USA Nicolet Company; EA940, The Thermo Orion; ICAP- 9000 Jarrel-ASH Company.

ASP flooding sewage was taken from wastewater treatment station in Daqing oilfield. Microporous membrane (pore size 0.45μm, diameter 50mm) was purchased from Beijing Huada Liming membrane material Co.; Hydrochloride and sodium hydroxide were all analytical grade and supplied by Sinopharm Chemichal Reagent Beijing Co, Ltd; PAC was industrial grade.

2.2. Suspended solids content measurement and particle size analysis

Suspended solids content was measured with the microporous membrane filtration method recommended by SY/T 5329-2012 standard. The particle size was analysized by Mastersizer 2000 laser particle sizer.

2.3. Zeta potential measurement

The zeta potential of suspended solids was measured by Nano Z zeta electric potential analyzer at 35℃.

2.4. SEM observation and elemental analysis

First, the blank membrane and membrane filtering sewage were dried at 60℃ and sprayed platinum. Then, the membrane was fixed on the SEM sampler for micro-morphology observation of retention matter on membrane. Moreover elemental analysis was carried out by EDAX.

2.5. IR analysis

The dried retention matter on membrane filtering sewage was comminuted and ground with dried KBr powder. The KBr disk was dried again and subjected to the IR spectrophotometer.

3. Results and discussion

3.1. Suspended solids content and particle size distribution

The sewage sample of ASP flooding was taken from Daqing oilfield. The water quality data including suspended solids content, ions and chemicals was shown in Table 1.

Table 1. The water quality of ASP flooding sewage from Daqing oilfield (mg/L).

Item	Ca^{2+}	Mg^{2+}	Al^{3+}	Fe^{3+}	HCO_3^-	CO_3^{2-}
Data	36.8	27.51	0.94	0.68	920	32.5
Item	pH Value	Soluble silicon	Suspended solids	Total solid	HPAM	Surfactant
Data	8.6	32.1	123.5	6940	575	46.2

According to Table 1, the suspended solids content in ASP flooding sewage was above 120mg/L measured with membrane filtering method. And there were much HCO3- and HPAM in sewage with high pH value of 8.6. Meanwhile, there were multivalent metal ions such as Ca^{2+}, Mg^{2+} and soluble silicon. Overall, the water quality of ASP flooding sewage was very complicated.

Figure 1 showed that the median grain diameter of suspended solids, namely D(0.5), was 2.2μm. The D(0.1) and D(0.9)were0.085μm and 9.561μm respectively. According to the peaks of particles size distribution, there were various size particles in ASP flooding sewage.

According to water quality standard in SY/T5329-2012(Water quality standard and practice for analysis of oilfield injecting waters in clastic reservoirs), the suspended solids content of ASP sewage was much higher than standard value about 10mg/L.

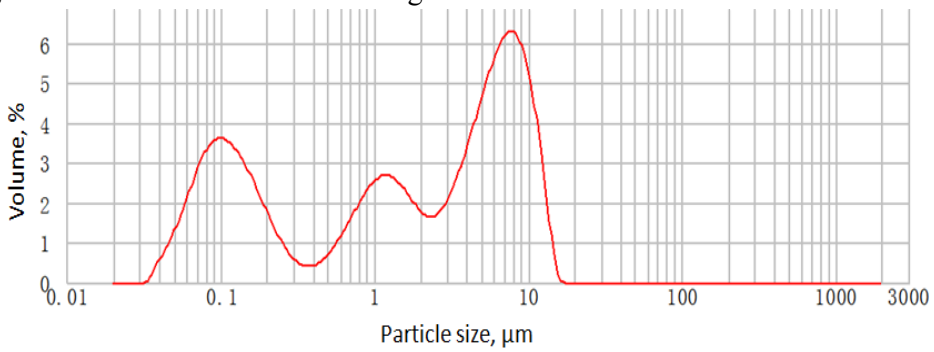

Figure 1. Size distribution of suspended solids in ASP flooding sewage from Daqing oilfield.

3.2. Zeta potential studies of suspended solids

The suspended solids in sewage was always charged, which can be characterized with zeta electric potential. Usually the stability of suspended solids increased with the increase of zeta potential absolute value. Figure 2 and Figure 3 showed the influence of PAC flocculant or pH value on zeta potential of suspended solids in sewage.

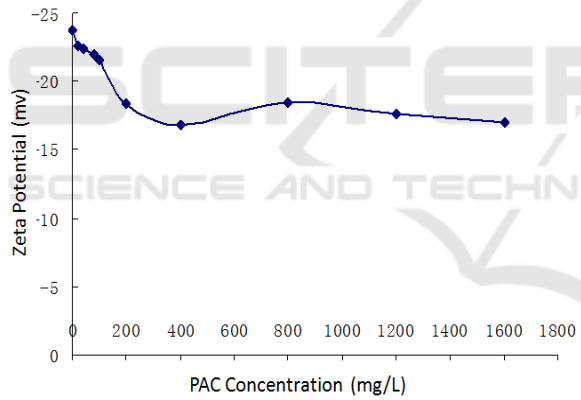

Figure 2. Influence of PAC on zeta potential.

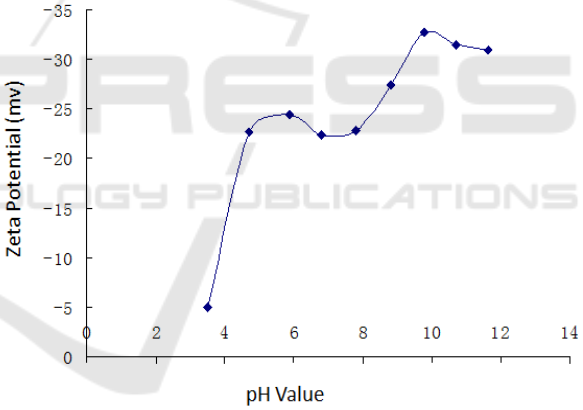

Figure 3. Influence of pH Value on zeta potential.

Figure 2 showed that the zeta potential of ASP flooding sewage was -23.8mv, indicating the suspended solids was much negatively charged. The main reason for negative zeta potential was that ASP flooding sewage contained much base, negatively charged HPAM and anionic surfactant, which enhanced the stability of suspended solids. The zeta potential positively shifted when adding PAC flocculant and keep -18.3mv finally, which showed that the PAC flocculant could decrease the stability of suspended in ASP flooding sewage in some extent. The hydrolysate of PAC was positively charge and changes the zeta potential of suspended solid by electric neutralization.

Figure 3 showed that pH value influenced zeta potential of sewage greatly. The zeta potential positively shifted significantly with the increase of pH value with the maximum value of -32.7mv. And the zeta potential positively shifted with the decrease of pH value. At pH value 3~4, the zeta potential shifted to -5.0mv quickly and much precipitate appeared. Meanwhile the suspended solids content decreased significantly to less than 20mg/L. At low pH values, negatively charged polymers formed gels to improve the zeta potential of sewage. Although adding acid could make the suspended

solids precipitation and decrease its content, it was not feasible considering economical and technology factors for the precipitation pH value of suspended solids must be less than 4.

3.3. IR of the retention matter on microporous membrane

In order to determine the composition of suspended solids in ASP flooding sewage, the IR of retention matter on microporous membrane was measured and analysized. The results were shown at Figure 4.

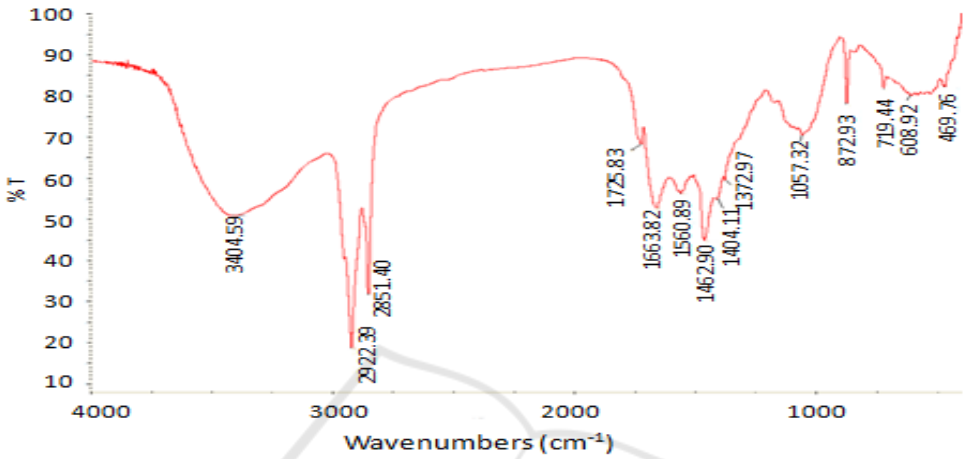

Figure 4.IR of retention matter on membrane after filtering sewage.

The Figure 4 showed that the composition of retention matter on microporous membrane was very complicated. The HPAM (hydrolyzedpolyacryamide) was evidenced by peaks at 3404cm-1, 1725 cm^{-1}, 1663cm^{-1}, 608cm^{-1}. The -CH_3 and -CH_2- functional groups were evidenced by peaks at 2922cm^{-1}, 2851 cm^{-1}, 1462 cm^{-1}, 719 cm^{-1}. The clay and inorganic salts were evidenced by peaks at 1560 cm^{-1}, 1057cm^{-1},872cm^{-1}.

The results showed that the retention matter on microporous membrane contained not only suspended solids but also organic matters such as HPAM, hydrocarbons, etc.

3.4. SEM of the retention matter on microporous membrane

In order to study the composition and microstructure of suspended solids further, SEM measurement and elemental analysis were carried on to retention matter on microporous membrane.

According to the SEM micrographs presented in Figure 5 (A), the blank membrane appeared as network structure with multilayer connected by cellulose. Its pore diameter was 2~5μm and the main elementals were C, O, Zr. As presented in Figure 5.(B) and Figure 5 (C), much fine particles(particle size<1μm) with various shapes were intercepted and Na, Cl, Ca and Si elements content increased, indicating existence of clay, inorganic salt or scale.

However, as presented in Figure 5 (D), there were much sticky and amorphous matters adsorbed on membrane skeleton and the C content increased significantly, which also proved that the retention matter on microporous membrane contained much organic matters such as HPAM in addition to suspended solids.

The water-soluble HPAM shouldn't be regarded as suspended solids according to the definition of suspended solids in SY/T 5329-2012. However HPAM could make the value of suspended solids measured by membrane filtering method much higher than the real value. The HPAM absorption on membrane increased the mass of retention matter directly. On the other hand, HPAM absorption resulted in the decrease of microporous membrane pore size, intercepting more suspended solids.

Therefore, measurement method of suspended solids content suitable for ASP flooding sewage should be established to decrease the effect of HPAM to measurement result.

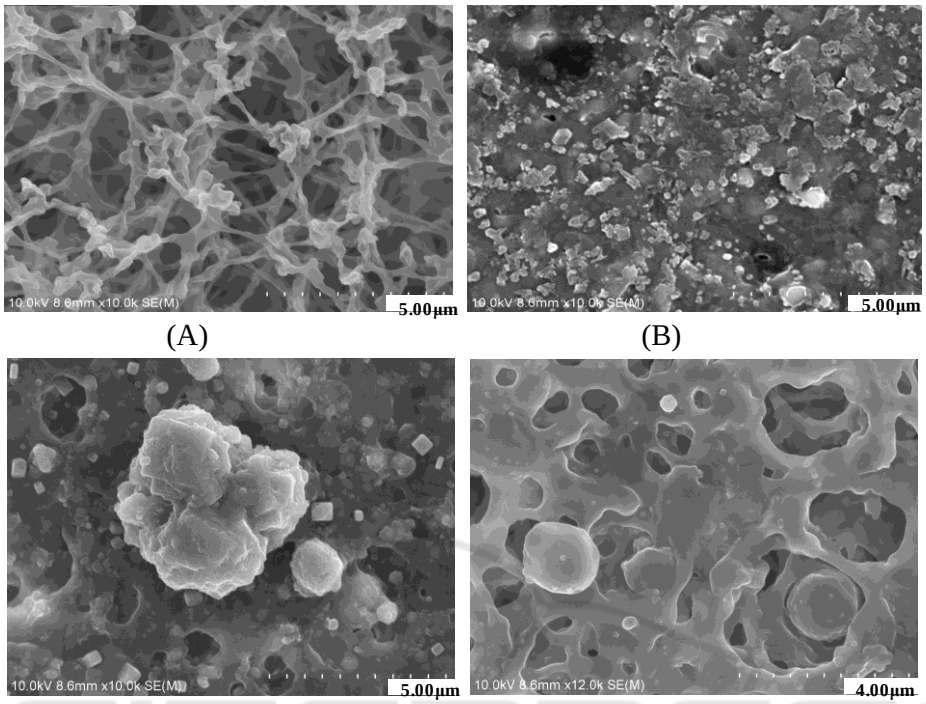

Figure 5.SEM images of the blank membrane (A); Membrane after filtering sewage(B);Membrane after filtering sewage and solvent extraction(C); Membrane after filtering sewage, solvent extraction and removing surface layer(D).

3.5. Suspended solids increase of filtered sewage with scale formation

It was found that the sewage of removing suspended solids through microporous membrane filtration gradually became cloudy when keeping at 45℃ of reservoir formation temperature. The turbid matter could react with hydrochloric acid and release bubbles, which indicated that it contained much carbonate scale. From Figure 6, the SS content of sewage increased from 82mg/L to 160mg/L after 24hat 45℃because of scale formation.

During ASP flooding process, the scale of calcium carbonate and hydroxide and silicate scale was formed as followed:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O \quad (1)$$

$$Ca^{2+} + HCO_3^{-} \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O \quad (2)$$

$$Ca^{2+} + SiO_3^{2-} \rightarrow CaSiO_3\downarrow \quad (3)$$

$$SiO_3^{2-} + H_2O \rightarrow H_mSiO_4^{m-4} \rightarrow \text{Polysilicic acid} \rightarrow \text{Silicic acid gel} \rightarrow SiO_2 \quad (4)$$

Because of the reaction between strong alkali in the ASP flooding system with formation fluid and minerals, the produced sewage contained OH-, HCO_3^-, CO_3^{2-}, Ca^{2+}, SiO_3^{2-} and other scaling ions. Under certain conditions, there would be various inorganic carbonate scales and silicon colloidal particles. On the other hand, a large number of negatively charged HPAM adsorbed on the scale of sewage would play a role in dispersing and stabilizing scale and particulate matters. The high viscosity of sewage made the particles deposition very slow and suspended in water.

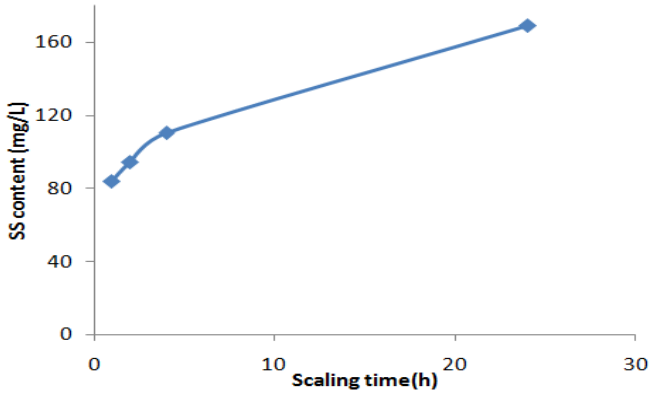

Figure 6. Scaling and suspended solids (SS) content variation(45℃) for ASP flooding sewage after membrane filtration

4. Conclusions

(1) The ASP flooding sewage contained high concentration of suspended solids and much HCO_3^-, HPAM, multivalent metal ions such as Ca^{2+}, Mg^{2+} and soluble silicon. And there were various size particles in ASP flooding sewage.

(2) The zeta potential showed suspended solids in ASP flooding sewage was much negatively charged due to negatively charged HPAM. PAC could make the zeta potential positively shifted with a finite limit. But the pH value influenced zeta potential of sewage greatly because HPAM changed to gel and precipitate at pH value 3~4.

(3) IR and SEM measurement showed that the HPAM influenced the measurement and stability of suspended solids greatly. This was different from usual suspended solids, such as clay and corrosion products. It is necessary to eliminate the influence of polymers by means of degradation and other measures.

(4) The suspended solids in filtered sewage increased due to formation of inorganic scale and silicon colloidal particles under certain conditions. Scaling prevention are needed to avoid the formation of suspended solids again.

Acknowledgement

The authors thank the financial support of PetroChina Ministry of science and technology and Research Institute of Petroleum Exploration and Development. This work is also supported by Daqing Oilfield Engineering Co., Ltd. and Testing Center of USTB Co.,Ltd.

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