Influencing Factors in the Test Procedure of Hydrated Microsphere Particle Size

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Abstract: Microsphere profile control is a new deep profile control technology in oilfield, which has developed in recent years. The particle size distribution of hydrated microsphere is an important basis for its application in formation pore throat, which has direct influence on the effect of profile control. First, the existing problems in current particle measurement of hydrated microsphere were studied through analyzing the results of the hydrated particle size, which were obtained from the static laser particle size analyzer. Results showed that there were two main problems in the current test methods of hydrated particle size. One was the poor reproducibility of the test results, and the other was the unrecognized particle size distribution of the truly hydrated microsphere. In addition, the test factors of hydrated microsphere particle size were studied through analyzing the morphology and the composition of microsphere. Results showed that the main influential factors of the hydrated particle size testing were the organic solvent and the emulsifier, which existed in the aqueous solution of microsphere with a variety of forms. Finally, some specific suggestions were put forward about the measurement of testing the hydrated particle size, which was removing the organic solvent and emulsifier from the aqueous solution of microsphere before measuring the hydrated particle size..

1. Introduction

Microsphere flooding is a new deep flooding technology in oilfield, which has developed in recent years.[1-2] Only when the particle size of microsphere and the core pore throat match well with each other, can the flooding effect of microsphere will be approving.[3] Therefore, the size and distribution of microsphere size is an important basis for its application in the pore throat size, which directly affects the displacement control effect of microsphere.[4-5]

The research shows that most domestic oil fields, including Huabei Oilfield, universities, as well as enterprises and other units related to the production of microsphere,[6-11] use laser particle size distribution analyzer to obtain the microsphere hydrated size value by testing microsphere water solution sample of microsphere, which is used to guide the microsphere application in oil fields.

In this paper, problems existed in the test procedure of hydrated microsphere particle size was analyzed, which was based on summarizing the experimental results. Besides, influencing factors during the test procedure of hydrated microsphere particle size were analyzed and definite. On the above basis, the improvements in the current test method of laser particle size distribution tester were given.

2. The experiment

2.1 Experimental equipment and materials

2.1.1 Experimental equipments. LA-950S laser particle size analyzer, Horiba company of Japanese. Olympus U-RFL-T microscope, Olympus company of Japanese. JK-MSH-PRO-6B magnetic agitator, scientific instrument company of Shanghai. H-101 electrothermal constant temperature drying box, Yao instrument equipment factory of Shanghai..

2.1.2 Experimental materials. Technical white oil, Jingshan of Hebei petrochemical plant. Emulsifier A and emulsifier B, industrial grade, Jiebote energy technology Co. Ltd of Beijing. Microsphere samples used in profile control of Huabei oilfield.

2.2 Experimental steps

Shake fully the microsphere samples with distilled water. Formulate aqueous solution of microsphere, whose mass fraction is 1%. Sub-package to seal the stainless steel drums. Take the microsphere solution sample out from the electric thermostatic drying oven for a period of time. Place at room temperature for cooling. Then, a small amount of microsphere solution was taken to be observed under the microscope oil mirror, which could get the effect of 1000 times magnification.

Turn on the laser particle size, preheat 30 minutes, and then calibrate the instrument according to the operating procedures. Test the distilled water as the empty sample to deduct the background value. Fully shake the microsphere sample after the check amount in the beaker with distilled water, and then adjust the sample concentration to transmittance falls in the range of suitable instruments (red semiconductor laser to meet 80%~90%, the blue LED light meet 70%~90%). Finally, test the size and distribution of dispersion medium in particle samples using laser particle size analyzer at room temperature (refractive index: 1.33; particle refractive index: 1.50).

3. Experimental results and discussion

3.1 Problems existing in the test of hydrated microsphere particle size

The indoor test prepared 4 different aqueous solutions of microsphere samples, which were used in profile control. The microsphere samples were hydrated at 70℃ for 4 days, and then were tested the particle size and the distribution by using the laser particle size analyzer. Besides, the median particle size was characterized by D_{50}, which was the corresponding particle size when the cumulative frequency reached to 50%. The D_{50} data of four samples were shown in table 1.

From table 1, it can be seen that the D_{50} repeatability of the same microsphere sample were poor. Besides, the test data even appeared in the order of magnitude of nanometer and micron. Moreover, the relative standard deviation was up to 136%.

Table 1 diameter of 1% solution prepared by different microsphere samples hydrated at the condition of 70℃ for 4 days

sample number	particle size of microsphere hydrated at 70℃ for 4 days(μm)							deviation	
	determination times						mean value	standard deviation(μm)	relative standard deviation(%)
	1	2	3	4	5	6			
1#	0.158	0.145	3.60	0.146	3.31	0.167	1.25	1.71	136
2#	0.319	0.164	8.06	0.186	8.53	8.27	4.25	4.42	104
3#	0.159	0.158	2.69	2.54	0.153	2.82	1.42	1.39	98
4#	13.41	12.95	18.78	1.48	25.58	2.13	12.39	9.39	76

3.2 Influencing factors during the test of hydrated microsphere particle size

In order to clarify the reasons for the above problems of laser particle size analyzer in testing microsphere hydrated size in the process, this paper analyzed the influencing factors during the test of hydrated microsphere particle size, which was based on the composition, the synthesis process of microsphere samples, as well as the hydrated size detection steps of analysis.

(1) Organic solvent and emulsifier

The investigation of the microsphere synthesis was shown that there were some organic solvents in the synthesis process of microsphere, including white oil, kerosene, as well as diesel oil, et cl, which was as the dispersing agent of the microsphere sample.

In addition, the microsphere also contained special emulsifiers, such as Tween, span, CTAB, as well as SDBS, and other surfactants, which can stabilize microsphere sphere in the organic solvents. More importantly, organic solvents and emulsifiers accounted for as much as 70%~80% in the microsphere samples, which severely affected the true size of the microsphere in a variety of forms.

① The organic solvent and emulsifier in the aqueous solution of microsphere was of the emulsion droplet form, which could form a small sphere (figure 1(c)) or the cluster (figure 1 and figure 2(a) (b)). Furthermore, the droplet diameter was ranged from one hundred nanometers to tens of microns. And then, after agglomeration, the particle size could up to several hundred micrometers, even the millimeter level. All the above could direct the interference measurement of the real particle size in aqueous solution.

② The amphiphilic emulsifier adsorbed on the surface of the microsphere, forming an emulsion layer, which directly affected the real size of the microsphere.

It was found that the microsphere used in oilfield was mostly the acrylamide polymer microsphere. That was to say, most of the monomers used in profile modification were acrylamide (AM). The sphere surface of the microsphere was the hydrophilic group, the amide group (-CO-NH-). According to the principle of similar dissolution, the hydrophilic group of the emulsifier can adsorb the amide group on the surface of the microsphere. Thanks to the steric effects of the amide groups, the particle size value measured was bigger than its true size value. On the other hand, the lipophilic groups of the emulsifier adsorbed on the surface of microsphere were toward the outside of the sphere, which can wind with the organic solvent drops. Further, because of the amphiphilic property, the emulsifying agent could make the microsphere sphere connect with the organic solvent drops of the microsphere sample. And then, they were gathered together, as shown in Figure 5, which could greatly affect the measurement of the real microsphere particle size.

③ The emulsifier could produce bubbles in the test of the microsphere particle size, which affected the testing result of the microsphere particle size.

To ensure the accuracy of particle size test and the comprehensive, the laser particle size analyzer needed cycle the microsphere solution in the testing. Furthermore, the emulsifier/surfactant of the microsphere sample could form bubble with the air in the testing process. Still further, the bubble can reach a few microns, or even tens of thousands of microns. All the above led to the multi peak and doublet phenomenon in the particle size distribution curve, which affected the hydrated particle size test.

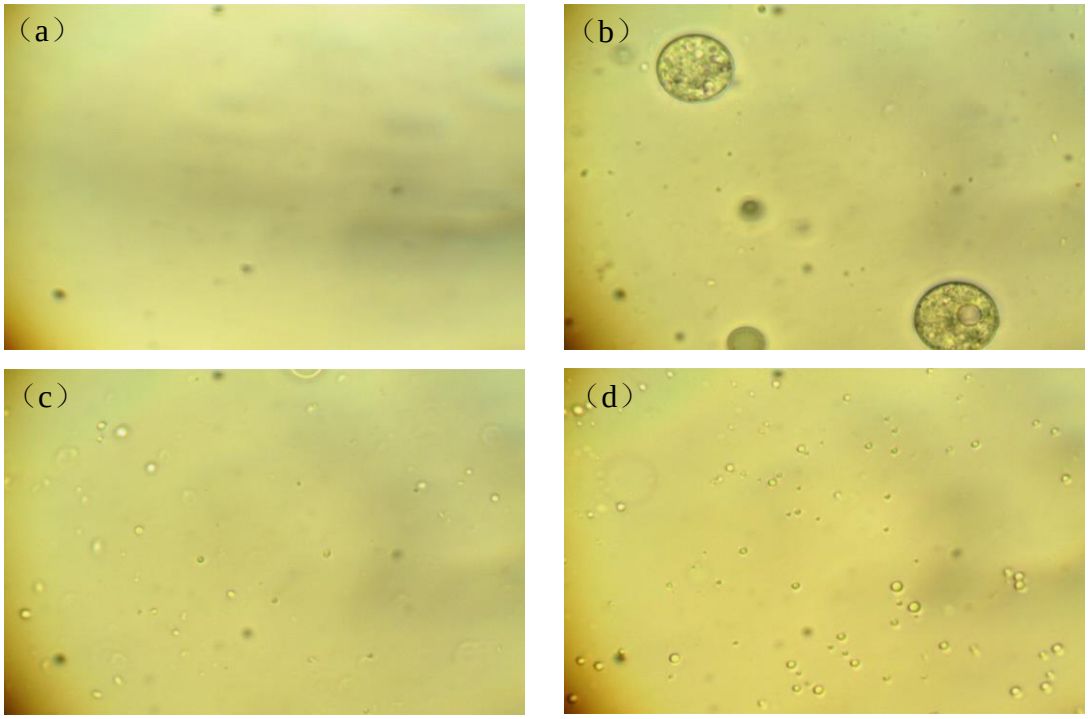

Figure 1. The micrographs of solutions at 70 ℃ for 4 days (×1000)
(a) The blank samples (b) and (c) the mixture of organic solvents and emulsifiers (d) microsphere solutions of the sample 1#

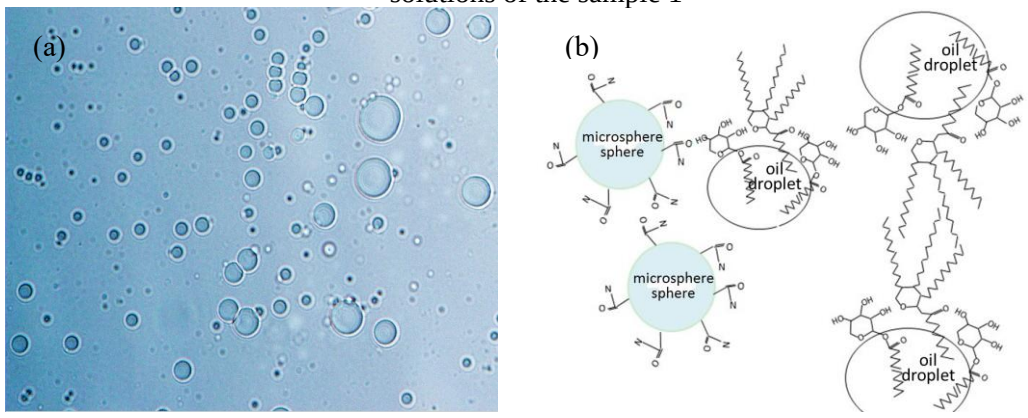

Figure 2. The micrograph of microsphere aqueous solution (a) and the microscopic diagram (b)
(a) the micrograph of microsphere samples 4# placed in aqueous solution at 70 ℃ for 4 days (×1000)
(b) the presence schematic diagram of organic solvents and emulsifiers in microsphere solutions

(2) The microsphere sphere itself

The density of water at room temperature is 0.997mg/L. It was inferred that the density of acrylamide microsphere sphere itself and the density of water may exist certain differences, the microsphere sphere in aqueous solution may be sinking sphere (figure 3(a)) or floating (figure 3(b)) and so on, resulting in the microsphere hydration particle appeared and the testing size in the process of testing for micron level, and sometimes the test results for the nanometer level.

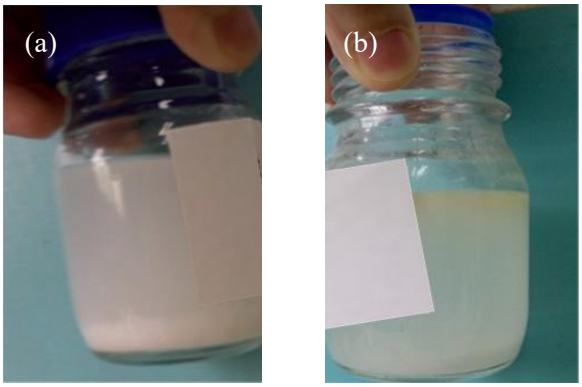

Figure 3. The aqueous solution figures of two microsphere samples had the same mass concentration at 70 ℃ for 4 days

3.3 The improvement suggestions

Considering that the organic solvent and emulsifier in microsphere components were the important factors, which affected the authenticity of the particle size measurement, it was suggested that choosing an appropriate solvent for extraction of microsphere in aqueous solution preparation, and then testing the hydration diameter. The solvent should meet the organic solvent and emulsifier, as well as the microsphere solids (effective components, such as acrylamide, et cl.) had different solubility in microsphere solution. And then, combined with the flow difference of microsphere solids, the organic solvent, as well as the emulsifier, the effective components could be extracted from the microsphere samples. Furthermore, prepare new microsphere samples by the soluble in water solution. Finally, use the laser particle size analyzer test the new microsphere samples prepared well before, which can obtain the true particle size of microsphere solid.

4. Conclusions

The indoor test result with laser particle size analyzer microsphere hydrated size numerical and optical microscope observation of the morphology of microsphere, laser particle size analyzer in the microsphere hydrated size test problems existing in the process and influence factors are analyzed, and gives suggestions for improvement, the main draw the following conclusions:

i.The current testing methods of microsphere size mainly had two problems. One was the poor reproducibility of testing results, and the other was the not real particle size distribution of microsphere samples.

ii.The important factors affected the affect the authenticity of the measured size of the hydrated particle size were the organic solvent and emulsifier in the microsphere fraction.

iii.The appropriate solvent extraction was recommended on the selection of the effective components. And then, the preparation of aqueous solution to test the microsphere hydrated size, in order to weaken or eliminate the effects of organic solvent and emulsifier. Finally, the laser particle size analyzer was used obtain the true particle size of microsphere solid.

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