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Study on Preparation and Performance of High Swelling Bentonite

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ABSTRACT

For improving the expansibility of natural Ca-based bentonite (Ca-Bent), the Ca-Bent was modified with sodium dodecyl benzene sulfonate(SDBS)-Na_2CO_3 complex agent by microwave semi-dry method. And the ratio of Na_2CO_3 to SDBS, microwave power, radiation time and initial temperature on the modification were studied. Furthermore, X-ray diffraction (XRD) patterns and infra-red spectrum (IR) were carried out to characterize , which obtain microstructure of samples. The result showed that the optimized experimental parameters are obtained as follows: Na_2CO_3 to SDBS ratio 1:1, radiation time 2min, microwave power 600W and initial temperature 120K. Besides, under the optimization conditions, the modified bentonite has swelling volume of 68.5mL/g, cation exchange capacity of 56.2mmol/10^2g and yield point and plastic viscosity ratio of 1.67, respectively. A comparison of the single factor experiment and orthogonal experiment indicates that the SDBS and Na_2CO_3 have synergistic effect in the process of modification, especially, under the optimum microwave condition, Na_2CO_3 increased the anion activity of SDBS, which enhanced the hydrophilicity of modified bentonite. The experimental result show that the process improves the swelling volume of bentonite and the comprehensive performance. So, the modified bentonite was a perfect additive in water drilling mud.

Keywords: Ca-Bent, SDBS-Na_2CO_3 complex agent, high swelling.

1. INTRODUCTION

Bentonite is a non-metallic mineral, montmorillonite($(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{16}(OH)_2\_xH_2O$) as the main mineral component, and a sandwich structure composed of silicon oxygen tetrahedron and alumina eight surface, monoclinic. Because of this special layered structure, it has a large specific surface area, so it has strong adsorption. Bentonite has strong hygroscopicity and expansibility, and it can absorb 8~15 times the volume of water. Bentonite is a colloidal and suspended in aqueous solution, the suspension has viscosity, thixotropy and lubricity, especially, there is strong ion exchange capacity and adsorption capacity for gas, liquid and organic matte.[1]

The natural bentonite is divided into two types: Ca-based bentonite(Ca-Bent) and Na-based bentonite(Na-Bent). There are abundant resources of bentonite in the world, but the distribution is not balanced, bentonite resources are mainly distributed in the Pacific Rim belt, India ocean belt and Mediterranean Sea-Black Sea belt. China, the United States, the Commonwealth of Independent States, Germany, Italy, France, Japan and Greece is the main resource country. Although the reserves of bentonite in the world are large, more than 70% bentonite is inferior Ca-Bent. However, the Ca-Bent is limited to be used in divese fileds, the natural Ca-Bent is modified because Na-Bent takes on high properties of water swelling, so it have extensive applications in the different industrial fields such as ceramic, paints, food, drug manufacturing, treating polluted water, such as the adsorption of toxic organic compounds and stabilization of oil–water emulsions. The Na-Bent dispersions are widely used in industrial processes because of their exceptional colloidal and rheological properties. [2]

The physical and chemical properties of Ca-based bentonite are mainly characterized by good adsorbability and cohesiveness, but little swelling. Sodium bentonite or organic bentonite shows excellent swelling and colloidal properties. Due to the structural of bentonite, Ca^+ of bentonite layers can be exchanged to other cations, which achieve the purpose of modification.

Huang et al.[3] studied the Ca-based bentonite was modified by Na_2CO_3, which in order to improve per-

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formance of metallurgical pellet bentonite. Kumararaja et al. [4] studied bentonite clay was pillared with polyhydroxy aluminum complexes, and pillared bentonite could potentially be used for solving heavy metal pollutions by immobilising the metals in the contaminated soil. Zhou et al. [5] presented a method that groundwater was filtered with mixtures of sodium bentonite and clay, the result showed excellent adsorption effect for ammonium and phosphate was attributed to the addition of sodium bentonite. Ahmed S. Mohamed[6] discovered that iron oxide nanoparticles(nanoFe_2O_3) modified bentonite, the modified bentonite improved rheological properties of drilling mud. Lisi et al[7] studied the talc was modified with surface active agent by microwave, it's found that the microwave modified silicate minerals was better. However, most of the bentonite was modified by inorganic sodium salt or sodium modification after organic. And anionic surfactant and inorganic salt composite modified natural Ca-Bent wasn't reported. So in order to modify Ca-Bent effectively, modification experiment of Ca-Bent was carried out with SDBS-Na_2CO_3 complex agent by microwave semi-dry method.

2. MATERIALS AND METHODS

2.1 Materials and Equipments

The following materials and instruments were used for the experiments: bentonite (325mesh) for preparing the modified bentonite was supplied by Lingshou County Xing Yuan mineral powder processing plant (Hebei, China); sodium carbonate, sodium dodecyl benzene sulfonate and absolute ethanol (analytical reagent) from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China) were used in this study. Na-based bentonite was used to prepare drilling fluid from PetroChina Liaohe Oilfield Company (Liaoning, China).

The equipment included MAS-ⅡPLUS type microwave synthesis/extraction reaction workstation(Shanghai Xinyi Microwave Chemical Technology Co., Ltd.), PHSJ-5 laboratory *pH* meter(Shanghai Jinpeng Analysis Instrument Co., Ltd.), ZNN-D6B electronic six speed rotary viscometer(Qingdao Hongxiang Petroleum Machinery Manufacturing Co., Ltd.), 78-1 magnetic heating stirrer(Jintan Jiangsu Hengfeng Manufacturing Co., Ltd.), FTIR-660+610 Fourier transform infrared spectrometer (Agilent Technologies) and D8 Advance X ray diffractometer (Brukcr, Germany).

2.2 Pretreatment of calcium bentonite

The calcium bentonite samples were treated before using in the experiments as follows. 325 mesh sizes of calcium bentonite were mixed with 300mL distilled water, and the mixtures were stirred for 1h. After stirring, all mixtures were stood for 1 h and the small impurities suspended in the supernatant were removed with a pipette. This process was repeated until the supernatant was clear. The resulting products were then dried at 221K.

2.3 Modification.

First, SDBS and Na_2CO_3 were mixed in different proportions, and mixtures of Na_2CO_3 and SDBS dissolved in 50% ethanol, we obtained required modified agent. The 5g Ca-based bentonite was mixed with the modifying agent, which was the semi-dry reaction material. The mixture is placed evenly on bottom of flask, and keep still for 30 minutes before microwave treatment. Then, the flask with the reaction material was put into microwave apparatus and different parameter of microwave was set. The parameters of microwave included time, initial temperature and microwave power. In particular, the electromagnetic stirring speed should be controlled at 500r/min. After the reaction material was placed in digital display blast drying box and dried at 176K.Finally, the reaction material was ground and sieved so that 140 mesh powder were obtained.

According to the order of Na^+, K^+, Mg^{2+} and Ca^{2+}, the ability to exchange was increasingly smaller. When the SDBS was added into Ca-bent, Na^+ of SDBS exchange the Ca^{2+} of bentonite, but $C_{18}H_{29}O_3S^-$ was adsorbed on the surface of bentonite and inserted into the bentonite interlayer. The reaction process is as follows:

$$\text{Ca-Bent} + 2Na^+ \rightarrow Na_2\text{-Bent} + Ca^{2+}$$

The single factor experiment and orthogonal experiment were used to study the process of modification. Firstly, under the condition of constant microwave parameters, the ratio of Na_2CO_3 to SDBS was changed. This experiment would fix the amount of sodium carbonate, and gradually increased the amount of SDBS then we change the ratio of Na_2CO_3 to SDBS. Then the ratio of SDBS to Na_2CO_3 was controlled in the best

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ratio in order to investigate the effect of microwave conditions on the modification. Finally, on the basis of single factor experiment, the orthogonal experiment of 3 levels and 4 factors were designed. Especially, in order to study the interaction between various factors, the select scope of orthogonal factors level in range of normal fluctuations of the influential factors in the single factor experiment. The fluctuation indicated the interaction of among the factors, so the interaction effect between all factors could be found by the orthogonal experiment.

2.4 Measurement

The modified bentonite and Na-based bentonite for drilling were measured according to API SPEC 13A-2010 Specification for Drilling Fluid Materials. [8] The test parameters included viscosity, swelling volume and *pH*, etc. The basic indicators of original Ca-Bent was showed in Table 1.

Table 1: The basic indicators of original Ca-Bent..

NAME	DIMENSION	UNIT
Type	Ca-Bent	
Granularity	325	mesh
pH	6	
Swelling volume	20	mL/g
Montmorillonite	>85	%

The modified bentonite and Liaohe drilling grade bentonite were characterized by X-ray diffractometer and Fourier transform infrared spectrometer, the X-ray parameter was tube voltage 40 kV, current 40 mA, wavelength 1.54056, the 2-theta rage of 5-80°, and 001 planes were tested to obtain the distance between 001 layers. Besides Fourier transform infrared (FTIR) analyses were performed at room temperature in the spectral range of 4000–400 cm^{-1} using a FTIR spectrometer by KBr tabletting. Then the spectra were observed and analyzed.

3. RESULTS AND DISCUSSION

3.1 Effect of the ratio of Na_2CO_3 to SDBS on modified bentonite

In the preparation of modified agent, the work will fix the amount of sodium carbonate, and gradually increase the amount of SDBS, then the ratio of Na_2CO_3 to SDBS changed. It can be seen from Figure 1 that the swelling volume of bentonite increased gradually with the increase of SDBS. It is presumed that the Na_2CO_3 promoted the anionic surface activity of SDBS, so that the cation exchange was continuously shifted toward the positive. [9] When the ratio of Na_2CO_3 to SDBS was 1:0.5, the swelling volume of bentonite reached the high value of 66mL/g. Then the amount of SDBS increased, the swelling volume of bentonite decreased a little. It is probably that there will be notmore space for inhaled water molecule because sodium ions and organic ions have occupied the interlayer of bentonite, which results in the decrease of the swelling capacity. Finally, the optimum ratio of Na_2CO_3 to SDBS was chose as 1:0.5.

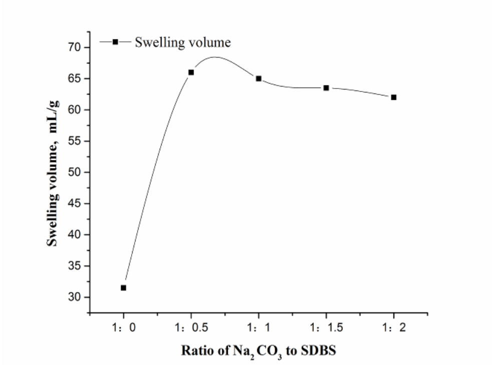

Figure 1: Effect of ratio of Na_2CO_3 to SDBS on sodium modification

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3.2 Effect of microwave on Modified Bentonite

In the process of microwave-assisted modified bentonite, the most critical parameters are microwave temperature, microwave irradiation time and microwave power. Meanwhile in the selective experiment of the parameters, the values of each parameter were selected according to the rated value of microwave apparatus.

It can be seen from Figure 2, when the initial modified temperature of microwave was 80K, the swelling volume of bentonite was 66 mL/g. It showed that the Na^+ in Na_2CO_3 can exchange with Ca^{2+} in bentonite. With the increase of temperature, the swelling volume of bentonite slightly increased. When the temperature reached 140K, swelling volume of bentonite had a maximum value 69mL/g. Subsequently, with the increase of temperature, the swelling volume of bentonite slowly declined. It is proposed that. When the initial temperature was up to 180K, the experiment failed.[10]

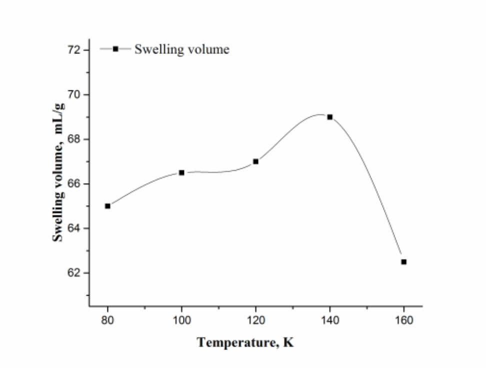

Figure 2: Effect of microwave temperature on sodium modification

As can be seen from Figure 3, With the increase of power, the swelling volume of bentonite suddenly increase, then when the microwave power was 500W, the maximum swelling volume is 68mL/g. Then the swelling volume of bentonite abruptly decreased, ultimately the swelling volume of bentonite slightly decreased. This phenomenon may be because the main function of microwave radiation that eliminate effect of in-diffusion on sodium-modification process. Within a certain range of microwave radiation intensity, the indiffusion have been eliminated, the influencing factors of reaction occupies the dominant position. Therefore, unit mass of Ca-Bent was modified, it needs to microwave power about 80W/g.

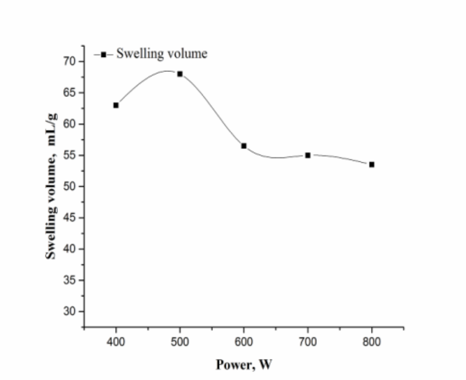

Figure 3: Effect of microwave radiation power on sodium modification

As can be seen from Figure 4. At first, the curve showed a slow upward trend, and then the rate of rise suddenly accelerated, when the microwave time was 3min, the maximum capacity was 65mL/g, afterwards the curve suddenly dropped, the downtrend is slow at length. It is probably that the surface was modified at the beginning of the process, With the increase of time, temperature of reaction sharply increased, which lead to strong molecular thermal motion. If the time continue to extend, ion exchange equilibrium reaction will be breached.

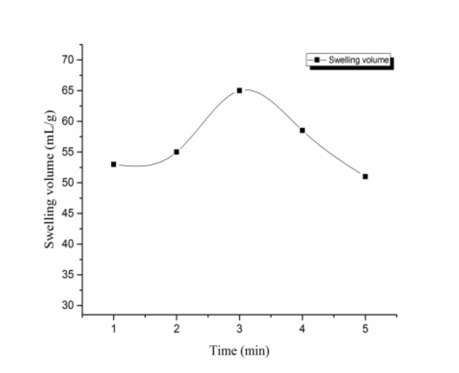

Figure 4: Effect of microwave irradiation time on sodium modification

3.3 Orthogonal experiment

Some factors were studied by single factor experiment, and then orthogonal experiments were carried out. The experimental factors were shown in Table 2, and the results were shown in Table 3.

Table 2: Experimental factor table

FACTOR	PROPORTION A	TIME/min B	TEMPERATURE/K C	POWER/W D
1	1：0.5	1	100	500
2	1：1	2	120	600
3	1：1.5	3	140	700

Table 3: Data for orthogonal test

NUMBER	A	B	C	D	SWELLING VOLUME mL/g	CEC mmol/10^2g
1	1	1	1	1	61	50.7
2	1	2	2	2	67.5	58.7
3	1	3	3	3	65	20
4	2	1	2	3	68	53.3
5	2	2	3	1	69	36
6	2	3	1	2	69.5	40
7	3	1	3	2	18	32
8	3	2	1	3	20.5	26.7
9	3	3	2	1	22	37.3
K_1	193.5	147	151	152		
K_2	206.5	157	157.5	155		
K_3	60.5	156.5	152	153.5		
R	146	10	6.5	3		

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K_1`	12.94	13.6	11.74	12.04		
K_2`	12.93	12.14	14.93	13.07		
K_3`	9.6	9.73	8.8	10		
R`	3.34	3.87	6.13	3.07		

There, CEC was cationic exchange capacity; K_i was sum of the same level; R represented range of swelling volume; K_i` was was sum of the same level of CEC; R` represented range of CEC.

As shown in Table 3, the main influencing factors of sodium-modification bentonite are the ratio of Na_2CO_3 to SDBS(A>B>C>D) and temperature. The best modification condition was $A_2B_2C_2D_2$, that is, the optimized experimental parameters are obtained as follows: Na_2CO_3 to SDBS ratio of 1:1, radiation time of 2 min, microwave power of 600W and initial temperature of 120K.

3.4 Measure analysis

The *pH*, swelling volume, yield point and plastic viscosity ratio of Na-based bentonite is 8, 46mL/g and 0.8, respectively. Under the optimization conditions, the modified bentonite has a swelling volume of 68.5mL/g, *pH* of 9 and yield point and plastic viscosity ratio of 1.67, respectively. Thus, it can be seen, the modified bentonite has well expansibility and rheological, and it is substantial foundation for later organic modification, because under the condition of weak alkali, Na-Bent was effectively modified with organics.

3.5 Characterization of bentonite and its mechanism

3.5.1 IR spectra

As shown in Figure 5, the characteristic absorption peaks were showed in the IR spectra of the original Ca-Bent: a broad and strong -OH stretching vibration peak in $3650cm^{-1}$~$3600cm^{-1}$, and the -OH stretching vibration peak near $1640cm^{-1}$, both of them are the representation of crystalline water in bentonite lattice. And the modified bentonite by Na_2CO_3 and original Ca-Bent have associating -OH absorption peak in $3440cm^{-1}$ and 3471 cm^{-1}, it is sign of absorbed water in bentonite layer, but the absorption peak disappeared on spectra of composite modified bentonite. According to the IR spectra of modified bentonite by SDBS-Na_2CO_3 compared with modified bentonite by Na_2CO_3, a pronounced C-H asymmetric stretching vibration and symmetric stretching vibration peaks in the $2950cm^{-1}$~$2830cm^{-1}$ are present to the IR spectra, furthermore the peak belongs to SDBS. What's more, there is the strong absorption band of Si-O near 1030 cm^{-1}, and it has bending vibration peaks of Al-O and Si-O in $400cm^{-1}$~$600cm^{-1}$. In summary, the rest of modified bentonite spectrum and Ca-Bent spectrum are similar, but there are also differences, which also shows that the structure of three different substance, these positions of absorption peak indicate that SDBS entered into the layers of bentonite, it was successful intercalation.[11]

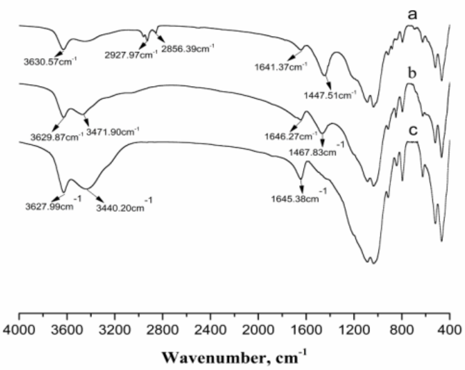

Figure 5: IR spectra of the modified bentonite by SDBS-Na_2CO_3 (spectrum a), the modified bentonite by Na_2CO_3 (spectrum b) and unmodified bentonite (spectrum c).

3.5.2 X-Ray diffraction

The results of characterization by XRD of unmodified Ca-Bent and modified Ca-Bent are presented in Figure. 6. SDBS and Na_2CO_3 not only modified raw bentonite, but also smoothed surface of bentonite. There is a certain distance between the bentonite cell, which is generally called the layer spacing, and the 001-surface spacing is represented by d_{001}. When 2θ=5.729°, d_{001} of unmodified bentonite is 1.53nm, when 2θ=7.061°, d_{001} of modified bentonite is 1.25nm. By the modified bentonite compared with those of the unmodified bentonite, the intensities of diffraction peaks were significantly decreased, Because the constitutional water of interlayer is lost, and the layer structure was slightly recombined under the microwave radiation. Moreover, the Na^+ radius is small, it can only adsorb water molecules of a layer while Ca^{2+} absorb water molecules of two layers, so the modified bentonite layer spacing is smaller, it illustrates that Na^+ has exchanged Ca^+ in Ca-Bent. Besides, the crystallinity of modified bentonite becomes significantly worse, but its activity, purity and colloidal properties are enhanced, because SDBS promoted ion exchange between Na_2CO_3 and Ca-Bent.[12]

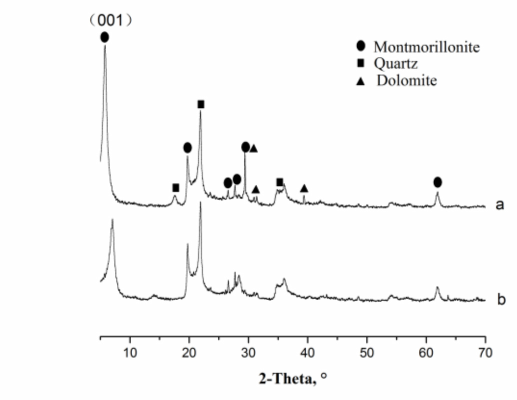

Figure 6: XRD patterns of unmodified bentonite(a) and modified bentonite(b)

4. CONCLUSIONS

In this work, Ca-Bent was modified with SDBS and Na_2CO_3 by microwave. The chemical bonds, phase constitution and morphology of the unmodified and modified Ca-Bent were studied by FTIR and XRD, respectively. It was found that the ratio of Na_2CO_3 to SDBS, initial temperature and radiation time and microwave power had influences on the modification process of bentonite. And SDBS and Na_2CO_3 modified Ca-Bent by microwave, which made synchronization between sodium-modification and organic-modification, besides, it obtained a high swilling bentonite of 68.5mL/g. SDBS and Na_2CO_3 have synergistic effect in the process of modified bentonite, and Na_2CO_3 increased the anion surface activity of SDBS, which enhanced the hydrophilicity of modified bentonite, besides, SDBS promoted ion exchange between Na_2CO_3 and Ca-Bent. So, The modified bentonite has superduper rheology, activity and colloidality than modified bentonite by single inorganic sodium salt. Particularly, the Na_2CO_3/SDBS-bentonite was a novel high swelling bentonite, and it would be applied in water based drilling fluid.

5. ACKNOWLEDGEMENTS

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