

Influence of Carbon Dioxide on Colloidal Properties of Bentonite Suspensions

Mezhidov V.Kh.

Research Center of Nanotechnologies and Nanomaterials
Grozny State Oil Technical University
named after academician M.D. Millionshchikov
Grozny, Russia
nizkp@mail.ru

Dadashev R.Kh.

Laboratory of Theoretical and Experimental Physics
Complex Research Institute named after Kh.I. Ibragimov
Grozny, Russia
raykom50@mail.ru

Dadasheva Z.I.

Grozny, Russia
Department of Physical, Mathematical
and Chemical Sciences
Academy of Sciences of the Chechen Republic
Grozny, Russia
Zarema-69-69@mail.ru

Gatsaev Z.Sh.

Research Center of Nanotechnologies and Nanomaterials
Grozny State Oil Technical University
named after academician M.D. Millionshchikov

Talkhigova Kh.S.

Department of Physical, Mathematical and Chemical Sciences
Academy of Sciences of the Chechen Republic
Grozny, Russia
talhigova@mail.ru

Abstract – The influence of carbon dioxide on swelling, size of particles, intensity of sedimentation, jellification time, pH value, chemical composition of sediments from suspensions is studied bentonites of two types NaM and CaM in the field of the Chechen Republic for. It is shown that carbon dioxide is well absorbed by both types of bentonites. At the same time the swelling index, pH value and sedimentation time decrease, while the size of particles and concentration of soluble salts in the dispersion medium increases. The obtained results can be used to manage colloidal properties of bentonite suspensions of the considered types and to assess the swelling index of clays in productive collectors of oil and gas industry. The ability of bentonite water suspensions to absorb carbon dioxide can be used to regulate its concentration in water and in air with biological objects.

Keywords – bentonite; swelling; sedimentation; carbon dioxide; dispersion medium; particle size.

I. INTRODUCTION

Bentonite has high adsorptive and ion-exchange properties, big specific surface and considerable specific volume of pores. These properties are caused by the crystal lattice structure of montmorillonite forming the basis of bentonite clay [1]. The specified properties can be changed by the activation of bentonite mechanical [2–5], thermal [6], chemical (addition of acids of various concentration) [7], ion exchange [8], etc. Similar external influences may be applied to manage rheological and thixotropic properties of bentonite water

suspensions. The studies [9] showed that the rheological behavior of water bentonite dispersions in the field of small concentrations strongly depends on the concentration of clay particles and an electrolyte. Electrohydrodynamic action leads to the dispersion of bentonite particles in water dispersion medium thus affecting rheological properties and thixotropy [10]. Analyzing electrophysical activation methods of clay minerals suspensions the authors [11, 12] came to similar conclusions. The reduction of the swelling index of clays within productive collectors in a wellbore zone together with a drilling mud filtrate, as well as during drilling, repair works, water flooding seems a relevant task of the study. This clay swells thus decreasing oil and gas production and sometimes leads to production shut down [13, 14]. To suppress such swelling, carbon dioxide is injected into the well, however it does not always solve the problem since the change of the structure of bentonite colloidal systems in the presence of CO₂ is not well studied. Therefore, the study of colloidal properties of bentonite suspensions in the presence of carbon dioxide seem relevant [13-15].

II. METHODS AND MATERIALS

The influence of carbon dioxide on colloidal properties of activated bentonite of sodium (NaM) and calcium (CaM) montmorillonite within fields of the Chechen Republic is studied. The concentration of carbon dioxide (C_{cd}) in water dispersion medium was defined via two methods: using INS-

210 tool and through titration using 0.1N of sodium hydroxide solution, as well as 1% of alcoholic phenolphthalein. Sparkling water by Kubay manufacturer and distilled water received in the laboratory were used as the dispersion medium. The pH value of the dispersion medium was defined by PH-150 MI device. The size of bentonite particles in the suspension was studied by the analyzer of submicron particles HORIBA LB-550 (Japan). The chemical composition of bentonite samples was studied through energy dispersive X-ray analysis (EDAX) using scanning electron microscope QUANTA 3D 200i (USA).

III. RESULTS

1.50g of powdered bentonite was added into 6 hermetically sealed numbered ampoules (each 50 ml). The ampoules No. 1-5 were filled with distilled and sparkling water at a temperature of 3-5°C increasing the concentration of carbon dioxide (Ccd) as the number of an ampoule was increasing. One control ampoule No. 6 had the dispersion medium of distilled water without CO₂ gas. The reliability of sealing was ensured through sampling after test at high pressure of the sparkling water. The ampoules with bentonite and sparkling water were stirred up within three minutes and put for observation at 25°C. Within the first 30 minutes all sparkling suspensions in ampoules formed gray sediments and translucent columns over them. The change of sediment volumes in time was registered visually according to scales on ampoules. In the control carbon dioxide-free water suspension (ampoule No. 6) sediments are not formed within 24 hours. Fig. 1 (curve 1) shows the dependence of the swelling index of daily sediment on the concentration of carbon dioxide in water 3% bentonite suspension of NaM (curve 1) and CaM (curve 2). It is apparent that the swelling index of NaM bentonite drops twice with the increase of gas concentration in the suspension, and the swelling capacity of clay almost does not react to the specified changes of Ccd values (curve 2, Fig. 1).

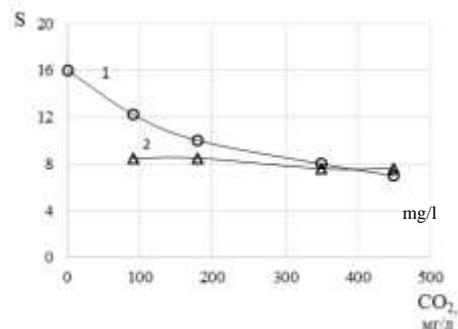


Fig. 1. Dependence of the swelling index of NaM (1) and CaM (2) bentonites on CO₂ concentration in water suspension

The process of sedimentation ends with slow sedimentation of fine bentonite particles. Fig. 2 (curve 1) shows the diameters of these particles depending on the concentration of carbon dioxide in 3% water suspensions of NaM bentonite. It is seen that the size of bentonite particles is increasing in suspensions with the increase of gas concentration. The pH value of the dispersion medium goes down (curve 2, Fig. 1) since the CO₂ surplus in water increases the concentration of carbonic acid in the dispersion medium.

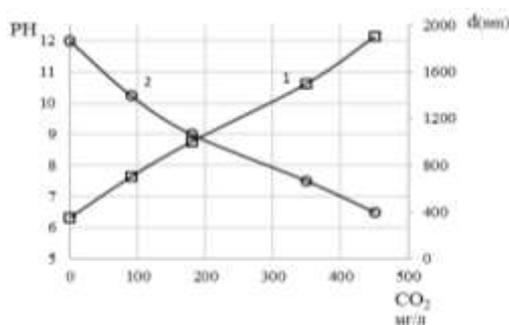


Fig. 2. Dependence of the particle size of NaM bentonite (1) and PH (2) of the water dispersion medium on CO₂ gas concentration

A. Absorption of carbon dioxide injected into the water dispersion medium by particles

It is known that the molecules of carbon dioxide are adsorbed on water surface. According to data [17], the dissolution of carbon dioxide in water is considered an absorption process where liquid acts as an adsorbent and gas – as an absorbate. The hydrophilic surface of bentonite absorbs water, it gets between montmorillonite packages moving them apart and sometimes destroying them. Such spontaneous dispersion of bentonite increases the specific surface and thus creates favorable conditions for the absorption of a considerable volume of carbon dioxide by clay. Five samples (ampoules) were prepared to test this assumption (Table 1).

TABLE I. COMPOSITION OF SAMPLES

No. ampoule	1	2	3	4	5 Control
Concentration of NaM and CaM in % wt	2	4	6	8	4
Concentration of gas in mg/l	367	293	220	147	0
Sedimentation volume in ml					
NaM	4.0	6.2	10.0	12.5	--
CaM	2.4	6.1	6.2	7.8	11.0

Bentonite powder of 1, 2, 3 and 4 grams respectively was placed into ampoules No. 1-4 (each 50 ml) and 2 grams into No. 5. At a temperature of 3-5°C these ampoules were filled in a similar way with distilled and sparkling water thus receiving the concentration of bentonite specified in the second line of the table and the concentration of carbon dioxide marked in the third line of the table. The ampoules were hermetically sealed, stirred up for 3 minutes and put for observation at 25°C. In the course of observation, the growth of sediment volumes was recorded, as well as the mobility of their surface at ampoule inclination by ~ 8 degrees, as in [18]. The fourth line of Table 1 shows the sedimentation volumes in 24 hours. They were recorded visually on scales of ampoules, and the CO₂ concentration in them was defined through titration. Fig. 3 shows the dependence of the sedimentation volume (Vsed) on bentonite concentration (Cb). It is seen that the sedimentation volume increases almost linearly depending on Cb. With the increase of bentonite concentration, the curves differ since the NaM swelling index is higher than that of CaM. In the control

ampoule with 4% NaM bentonite suspension without CO₂ in the dispersion medium the sedimentation is not complete in 24 hours.

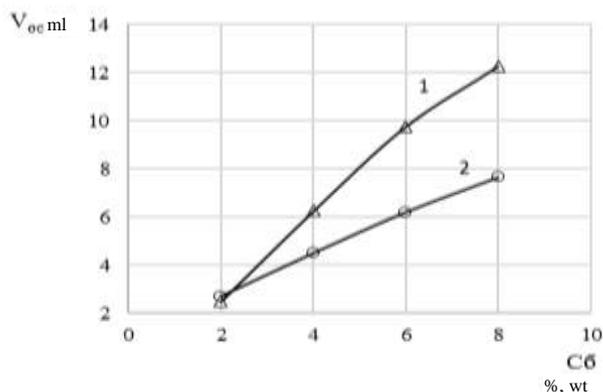


Fig. 3. Dependence of sedimentation volume (V_{sed}) on bentonite concentration (C_b) for NaM (1) and CaM (2)

The jelling time (τ) was defined by fluidity of suspension [18]. On Fig. 4 the curve 1 for NaM bentonite is located above that for CaM. At small bentonite concentration τ weakly depends on bentonite concentration, which is typical for CaM type.

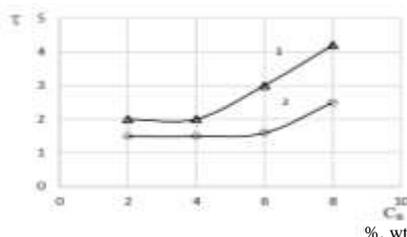


Fig. 4. Dependence of jelling time (τ) on bentonite concentration (C_b) for NaM (1) and CaM (2)

To study of the absorption of carbon dioxide by NaM and CaM bentonites in ampoules, as shown in Table 1. The powders of these clays were introduced and filled with Kubay sparkling water with known concentration of CO₂.

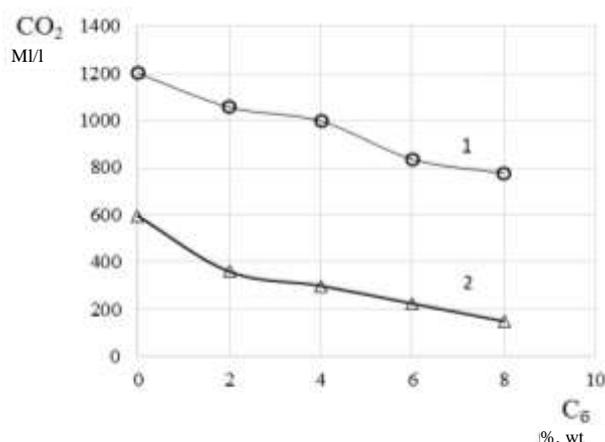


Fig. 5. Decrease over 24 hours of CO₂ concentration (mg/l) in water dispersion medium depending on bentonite concentration for CaM (1) and NaM (2)

At the same time suspensions with various concentration of bentonites in the sparkling dispersion medium were obtained. Hermetically sealed ampoules were stirred up for 3 minutes and kept for 24 hours at 25°C. Then the CO₂ concentration was determined through titration. Fig. 5 shows the obtained results. It is shown that irrespective of the type of bentonite, carbon dioxide is more active and is equally absorbed at low concentration. With C_b increase the rate of carbon dioxide concentration drop slows down.

To determine the influence of carbon dioxide on chemical composition of sediments we prepared 1% of bentonite suspension of NaM type. The Kubay water with carbon dioxide concentration of 0.20 % wt was used as the dispersion medium. It was filled in at a temperature close to zero, into a 140 ml glass container with 1.4 g of NaM bentonite powder. Hermetically sealed suspension was mixed by a magnetic mixer thus controlling pressure in it. In the absence of bentonite in the container the gas pressure increases at the rate defined by the intensity of magnetic mixer rotation and reaches its constant value of 290 mm Hg. In the presence of 1% bentonite the growth of gas pressure in suspension also depends on the intensity of mixer rotation, however it reaches only 104 mm Hg, i.e. 1% of bentonite particles in water suspension reduces the pressure of 290 mm Hg of carbon dioxide by 2/3. Therefore, according to Clapeyron-Mendeleev equation, 1% of NaM bentonite reduces 2/3 of carbon dioxide mass due to its adsorption on the surface of water molecules and interaction with clay elements.

Table 2 shows the chemical analysis of sediments in 3% water suspensions of NaM bentonite with various concentrations of carbon dioxide.

The element structure was defined for upper and lower sediment surface and then for powdered state.

Table 2 shows that at 470 mg/l concentration of carbon dioxide, the concentration of calcium on the upper sediment surface with the thickness of ~ 2 mm is 4 times higher than that on the lower surface and is 3 times less than on a powdered surface. This is caused by the fact that during water evaporation the concentration of salts dissolved in the dispersion medium is increasing over bentonite sediment. The concentration of magnesium on the upper sediment surface is higher up to 60% irrespective of carbon dioxide concentration. Sodium was the most sensitive to carbon dioxide concentration in bentonite suspension.

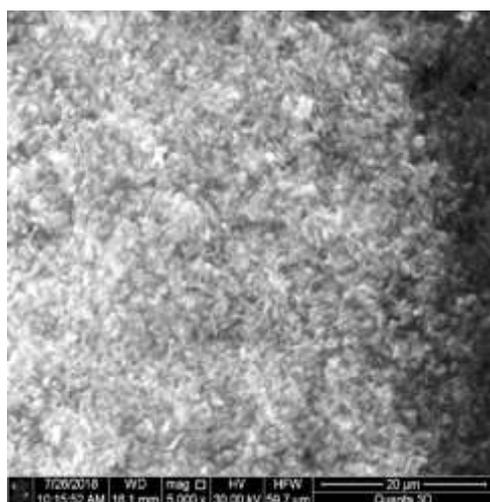
In the presence of CO₂ all values of sodium concentration are reduced with the increase of gas concentration. This is caused by the interaction of sodium and CO₂ with further formation of soluble hydrocarbonates, which are removed together with the dispersion medium.

The role of chemical reactions is also evident during the observation of sediment surfaces in suspensions (Fig. 6). The surface of bentonite sediment a) is obtained at carbon dioxide concentration of 0.088%, and b) for CO₂ = 0.176%.

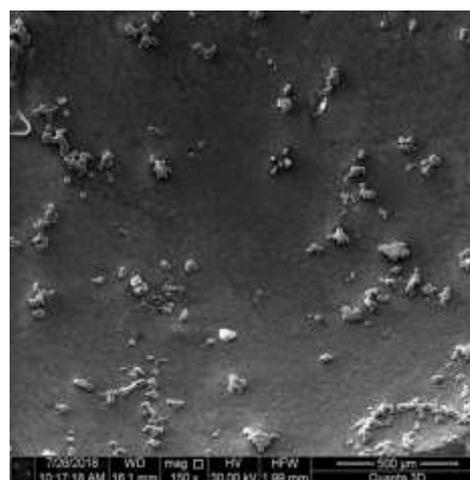
At small concentration of carbon dioxide, the sedimentation of fine particles created a uniform surface (Fig. 6 a). At high CO₂ concentration in the dispersion medium the carbonate particles were formed.

TABLE II. CHEMICAL COMPOSITION OF SAMPLES

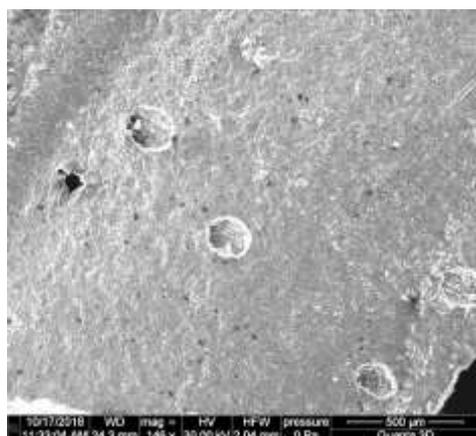
Samples Elements	Gas-free			Gas 191 mg/l			Gas 470 mg/l		
	Powder	Lower sediment surface	Upper sediment surface	Powder	Lower sediment surface	Upper sediment surface	Powder	Lower sediment surface	Upper sediment surface
C	0.58	1.04	1.45	0.46	1.41	1.18	0.37	1.01	1.56
O	52.3	52.81	47.96	52.59	51.01	51.88	52.95	49.24	49.4
Na	1.56	1.44	1.47	1.09	1.02	1.03	0.72	0.72	0.57
Mg	0.95	0.98	1.37	0.86	0.96	1.24	0.9	0.88	1.12
Al	8.38	8.92	10.46	8.49	8.68	9.46	8.45	9.28	8.93
Si	25.71	24.07	26.98	25.22	26.42	24.38	25.95	27.57	24.55
K	2.77	2.73	2.56	2.93	2.8	2.78	2.85	3.06	3.2
Ca	1.54	1.49	1.08	1.52	1.47	1.57	1.18	0.93	3.83
Ti	0.67	0.6	0.52	0.61	0.68	0.61	0.6	0.64	0.8
Fe	5.31	5.62	5.79	5.99	5.31	5.69	5.78	6.32	5.79
Co	0.23	0.29	0.36	0.23	0.24	0.22	0.24	0.34	0.24



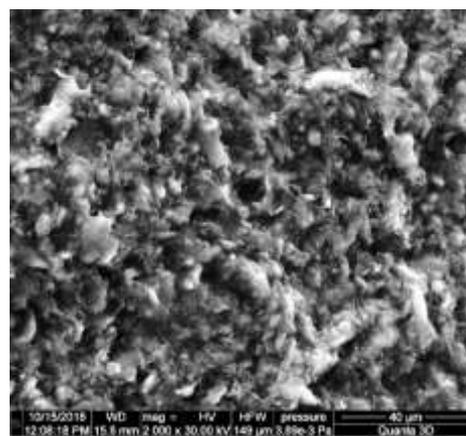
a)



b)



c)



d)

Fig. 6. Images of solid sediments from suspensions aerated by carbon dioxide a) and b). The surfaces formed by the presence of gas in solid sediment c) and d).

Their concentration increased during water evaporation from sediment. This led to the formation of a crystal phase of Na, Ca and other salts. These phases are shown in Fig. 6 b. Fig.

6 (images c and d) shows holes and pores formed by carbon dioxide on the lower (c) and upper (d) parts of sediment.

IV. CONCLUSION

1. In water suspensions of bentonite the molecules of water are distributed along a huge specific surface of hydrophilic particles that creates favorable conditions to increase the amount of absorbed carbon dioxide. Therefore, bentonite gel is a good absorber of carbon dioxide.

2. Carbon dioxide in bentonite suspension reduces the swelling index, pH value and sedimentation time, increases the sizes of particles and concentration of soluble salts in the dispersion medium.

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