The simulation study on montmorillonite and its effecting to borehole stability *

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Abstract.

Borehole instability is one of the most complex downhole problems in the drilling process. In order to study the micro-mechanism of inorganic salts on shale hydration, a micro-crystal structure model of Na-montmorillonite was established using the MS software. The shale hydration mechanism, mechanical strength change due to hydration and the inhibition mechanism of inorganic salts were studied by molecule dynamic simulation. The simulation results showed some basic microscopic property, and agreed with the experiment.

Keywords: Molecular simulation; Mechanical properties; Inorganic salt; Swelling

Introduction

The rock strength reduction due to hydration depends on the clay content and the component of clay minerals, especially the content of montmorillonite. Shale inhibitors have an inhibition effect on clay hydration and swelling. Different content and type of shale inhibitors have different inhibition effects[1-3]. Experiments can show the macroscopic mechanism between drilling fluid chemicals and rocks, but they are difficult to reveal microscopic mechanism. Monte-Carlo dynamic simulation showed that the diffusion coefficients of both Na^+ and water molecule were sharply decreased with KCl added into the Na-montmorillonite crystal structures[4]. Fangui Zeng, et al studied the microscopic hydration process of Na-montmorillonite, and gave an interlayer space curve changing with absorbing water molecule number[5]. Ping Na, et al found that different type and number of interlayer cation made the montmorillonite showing different swelling behaviors[6]. In this paper, a Na-montmorillonite model was established using the Material Studio（MS） software. The hydration process and mechanism were studied as well as the

effects of these inorganic salts on montmorillonite strength, and the chemistry and mechanics were coupled together to show how the chemical aspect affected on rock mechanics property. The simulation results showed a good agreement with experiments.

1 Optimization of Na-montmorillonite model

According to the basic structure properties of montmorillonite, a Na-montmorillonite crystal model with 8 unit cell (4×2×1) was established. The crystal lattice substitutions were made at the same time, and the negative charges produced by substitution were compensated by Na^+.

The Na-montmorillonite interlayer spaces was increased with the addition of water. According to the change of montmorillonite interlayer spaces and unit cell parameters, and considering X-ray diffraction, we found that when water molecules reach 48, 72 and 96, c is 1.25nm, 1.55nm and 1.85nm respectively, the first, second and third saturated water molecule layer were formed.

2 Simulation on inorganic cation inhibition mechanism

2.1 Ion type

In this study, seven types of salts were used, which are NaCl, KCl, $CaCl_2$, NH4Cl, $MgCl_2$, $AlCl_3$ and $FeCl_3$. The coordinate number, hydration number and hydration radius of these cations were calculated. At the same time, the mechanical parameters were analyzed. The results were shown in Table1, Fig.1 and Table2.

Table1 The inorganic cations coordination number, hydration number and hydration radius change with Montmorillonite hydration

Ion type	Hydration layers	Ion coordinate number	Ion hydration number	Ion hydration radius, nm
Na^+	1	8.03	5.57	3.41
	3	5.26	3.63	3.00
K^+	1	5.00	2.00	2.43
	3	3.29	1.32	2.06
NH_4^+	1	5.55	2.18	2.46
	3	4.26	1.56	2.17
Ca^{2+}	1	5.24	4.08	3.08
	3	3.01	2.12	2.50
Mg^{2+}	1	5.26	4.12	3.10
	3	3.00	2.23	2.55
Al^{3+}	1	5.27	4.55	3.28
	3	4.54	3.90	3.14
Fe^{3+}	1	6.08	5.00	3.29
	3	2.92	2.40	2.58

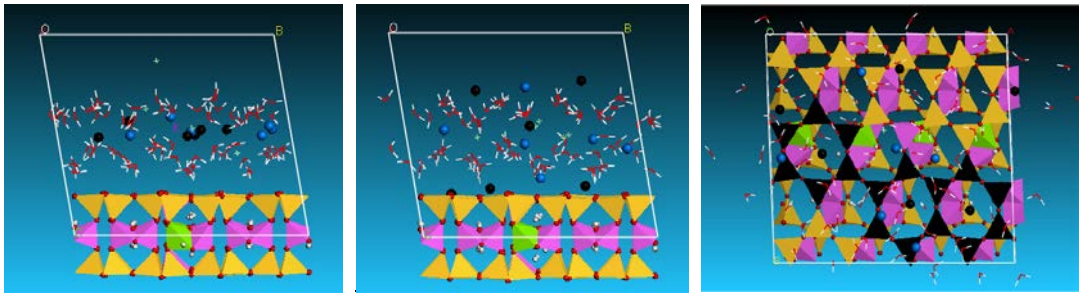

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Fig.1 The position of K^+ and Na^+ adsorbed in the layers of Montmorillonite (" ● " is K^+; " ●" is Na^+)

Table2 Elastic parameters of Na-montmorillonite with inorganic salts （E for Young's modulus, K for Bulk elastic modulus, G for Shear modulus, v for Poisson ratio, C for Compressibility, λ for Lame's constant）

Inorganic salt	Hydration layers	K GPa	G GPa	C 1/TPa	E GPa	v	Wave velocity km/s	λ GPa
Water /Na-montmorillonite	1	50.34	26.66	39.79	18.61	0.7	2.73	25.68
	3	38.75	17.15	76.62	11.88	0.3	1.37	19.
NaCl/Na-montmorillonite	1	73.28	37.34	30.21	21.78	0.5	2.83	35.24
	3	56.18	30.66	43.73	15.11	0.2	1.9	26.30
KCl/Na-montmorillonite	1	72.81	36.79	34.88	38.38	0.3	2.73	37.73
	3	59.93	32.47	36.19	24.98	0.1	1.58	24.87
NH_4Cl/Na-montmorillonite	1	63.42	33.40	29.04	41.19	0.4	1.88	31.52
	3	50.15	26.71	65.75	12.10	0.2	1.58	22.72
$MgCl_2$/Na-montmorillonite	1	63.92	38.35	31.55	20.92	0.2	2.41	35.11
	3	56.63	28.20	58.54	16.22	0.4	2.01	21.6
$CaCl_2$/Na-montmorillonite	1	87.48	35.16	19.42	58.00	0.3	1.74	43.64
	3	61.40	27.54	35.33	25.26	0.0	0.80	19.45
$AlCl_3$/Na-montmorillonite	1	69.48	35.76	37.29	23.94	0.1	2.50	29.16
	3	56.93	26.19	44.70	13.04	0.3	1.94	19.03
$FeCl_3$/Na-montmorillonite	1	68.83	38.32	28.66	28.51	0.2	2.83	36.78
	3	45.99	21.58	69.93	13.47	0.0	0.98	24.65

From the simulation results of the Table1 and Fig.1 we can learn that both the hydration number and the hydration radius of K^+ and NH_4^+ are smallest among all the seven inorganic cations. Since these two inorganic cations can embed into the hexatomic ring of silicon-oxygen tetrahedron, they can weaken the montmorillonite hydration and reduce the interlayer swelling tendency. However, the other cations, such as Na^+, are hanging on the top of tetrahedron charges, they can only reduce the repulsion forces between the negative charges in montmorillonite interlayers, therefore their hydration number and hydration radius are relatively large.

As a whole, the elastic modulus, Lame's constant and acoustic wave velocity will reduce with the increase in water molecule number, and the compressibility will increase, which means that the crystal stability of montmorillonite become poorer. As to inorganic salt type, $CaCl_2$ and KCl have the best inhibition effect, and NaCl is almost same as NH_4Cl which are better than $MgCl_2$, $AlCl_3$ and $FeCl_3$.

3.2 Ion concentration

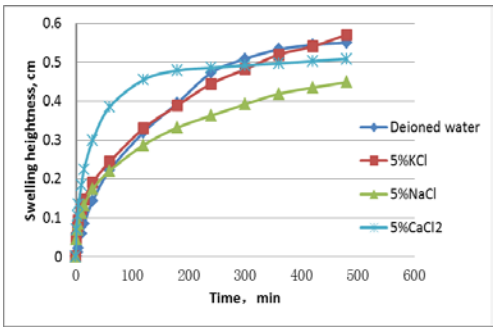
In order to understand how the ion concentration affects on elastic mechanics parameter of montmorillonite, the different concentration of NaCl, KCl and $CaCl_2$ solutions were added into montmorillonite interlayers. The simulation results were listed in Table3.

Table3 The effect of cation concentration on montmorillonite elastic parameters

Cation type	Hydration layers	Concentration w/w	Young's modulus GPa	Bulk elastic modulus GPa	Shear modulus GPa	Compressibility factor 1/TPa
NaCl	1	6.34	23.70	86.05	64.15	26.50
		11.93	33.89	77.76	47.03	36.20
		16.88	39.26	82.45	44.71	29.87
		21.31	40.47	89.58	95.70	33.60
		25.29	21.78	73.28	37.34	30.21
KCl	1	8.00	19.69	79.44	36.73	63.37
		15.00	27.98	83.11	52.77	33.93
		20.00	42.45	76.07	36.95	31.52
		25.00	38.38	72.82	36.79	34.88
$CaCl_2$	1	11.38	26.97	73.82	34.48	43.45
		20.44	28.26	75.97	38.52	27.49
		27.82	42.06	39.16	50.28	39.54
		33.94	52.97	85.14	45.94	30.34
		39.11	62.82	88.67	36.41	7.45
		43.50	58.00	87.48	35.16	19.42

For KCl, if Young's modulus, bulk elastic modulus, shear modulus and compressibility are at their ideal conditions when one layer is water saturated, KCl concentration is 14.7%-25.65%, 8%-20.55%, 8%-20.55% and 14.7%-25.65% respectively. Therefore, 8%-20.0% is selected as the best concentration range for montmorillonite crystal stability. Similarly, we can find the best concentration ranges of NaCl and $CaCl_2$, which are 15.0%-20.0% and 37.0%-43.0% respectively.

4 Experiments



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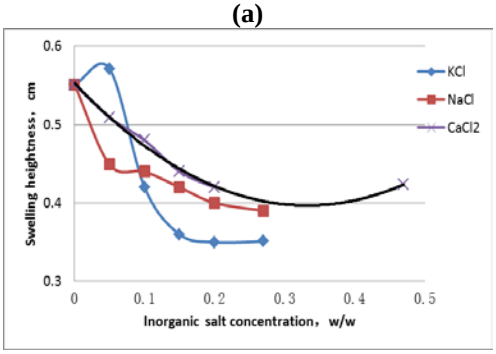


(b)

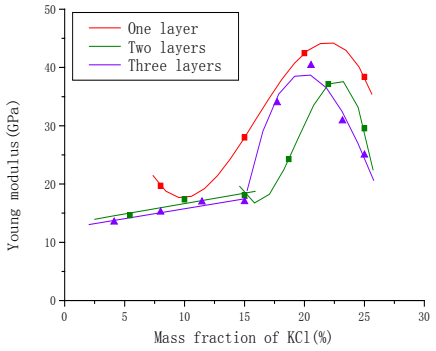
Fig.2 The swelling results of Montmorillonite in different concentration salt solutions

It can be seen from Fig.2 that the inhibition of the inorganic salts is enhanced with the concentration increase. The inhibition of KCl and $CaCl_2$ are in good agreement with the simulation results. The inhibition of NaCl is weakened after its concentration is over 20% w/w, which conforms to simulation conclusion. The experiment results showed that the inorganic ions can exchange intensely when the concentration of inorganic salt solutions is high. Such exchange changed the interior structure and ion composition of montmorillonite, which is harmful to the borehole stability.

The acoustic velocity experiments results were listed in Table 4. And the comparison between simulated results and experiment result of the Young's modulus were shown in Fig.3.

Table4 Change of montmorillonite mechanical parameters with inorganic salt concentration

	NaCl w/w，%					KCl w/w，%					$CaCl_2$ w/w，%				
	5	10	15	20	25	5	10	15	20	25	10	20	30	40	45
ρ ×10^3kg/m^3	2.55	2.54	2.55	2.56	2.56	2.54	2.55	2.56	2.55	2.56	2.55	2.56	2.56	2.57	2.57
C_P，km/s	1.70	1.73	1.75	1.76	1.74	1.72	1.73	1.74	1.75	1.72	1.71	1.73	1.75	1.76	1.73
C_T，km/s	0.86	0.87	0.88	0.95	0.92	0.84	0.86	0.9	0.93	0.88	0.85	0.87	0.91	0.92	0.87
E，MPa	49.14	50.20	51.60	58.68	55.52	47.24	49.43	53.60	56.40	51.45	48.29	50.59	54.68	55.99	50.79
σ	0.33	0.33	0.33	0.29	0.31	0.34	0.34	0.32	0.30	0.32	0.34	0.33	0.31	0.31	0.33
R，MPa	5.76	5.88	6.03	6.15	6.10	5.68	5.66	5.90	6.16	6.02	5.90	5.92	6.04	6.03	6.02



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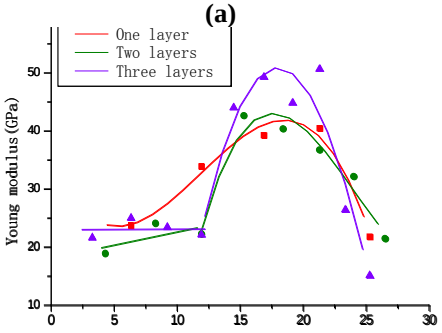

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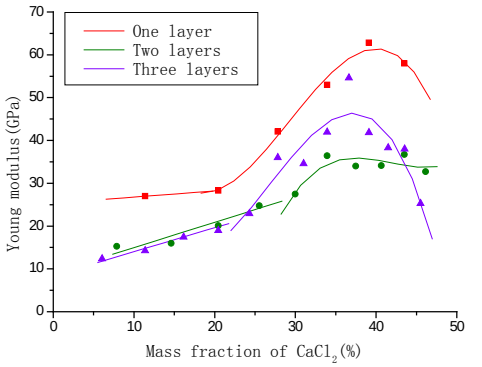

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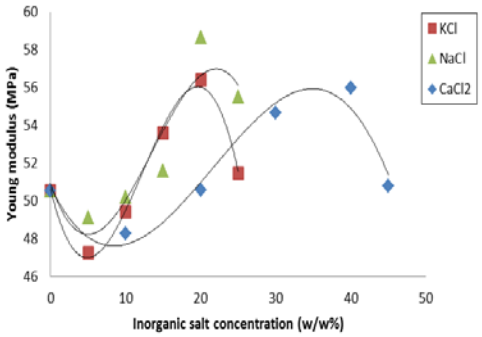

（d）

Fig.3 The fitting curves of Montmorillonite Young modulus with the amount of inorganic salts

The results shown in Table 4 and Fig.3 demonstrated that the strength parameters of montmorillonite depend on not only water content but also the different inorganic salt type and concentration. The appropriate salt concentration is favorable to improve the rock strength, rather than the greater the concentration, the better. The experiment results with various water content and inorganic salt concentrations verified the validity of the simulation results.

5 Conclusions

1. The simulation results showed that the first, second and third saturation hydrate layers were formed when the absorbing water molecules amount to 48, 72 and 96 irrespectively. From the radial distribution functions we can conclude that the ion coordinate, ion hydration number and ion hydration radius of interlayer balance cation Na^+ in montmorillonite all reduced with the increase in interlayer absorbed water, which indicated that montmorillonite hydration was weakened.

2.The simulation results showed that $CaCl_2$ and KCl have the best borehole stability effect among seven simulated chloride salts. Montmorillonite is salt sensitive. The best concentration range of $CaCl_2$, NaCl and KCl which can keep montmorillonite stable are given.

3. The swelling and acoustic velocity experiments are in good agreement with the simulation conclusions. The results provide a good means for further studying borehole stability with coupling chemistry with mechanics.

Acknowledgements

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References

[1] Chenevert ME. Adsorptive Pore Pressure of Argillaceous Rocks[R]. The llth Symposium on Rock Mechanics. June16-19, 1969.

[2] Jiafang Xu, Zhengsong Qiu. Journal of China University of Petroleum(Edition of Natural Science), 2006, 30(3): 63~66.

[3] Jingyin Wang. Chemical-Mechanical Modeling of Borehole Stability in Shale [D]. Qingdao of Shandong Province: China University of Petroleum, 2007.

[4] Skipper NT, Chang FR, Sposito G.. Clays Clay Miner, 1995, 43: 285~293.

[5] Jin Wang, Fangui Zeng. Journal of Chinese Ceramic Society, 2005, 33(8), 995～1001.

[6] Ping Na, Fan Zhang, Yanni Li. Acta Physico-Chimica Sinica, 2006, 22(9), 1137～1142.