Sedimentation Characteristics of Kaolin and Bentonite in Concentrated Solutions

Abdulah Obut [1]

Charakteristika sedimentácie kaolínu a bentonitu v koncentrovaných roztokoch

The sedimentation characteristics of two clays, namely kaolinite and bentonite, were determinated at high clay (5 % wt/vol) and electrolyte (1 N) concentrations using various inorganic-organic compounds. It was observed that the settling behaviour of kaolinite (1:1 clay) and montmorillonite (2:1 clay) is quite different due to the structural differences between these minerals. Although, similar initial settling rates and final sediment volumes were obtained after 24 hours of settling time for kaolin suspensions, the corresponding rates and volumes for bentonite suspensions varied greatly with the used chemical compound. According to the experimental results, a further intensive theoretical and experimental investigation is needed to reveal the mechanism underlying the sedimentation characteristics of clay minerals at high clay and electrolyte concentrations.

Key words: *Industrial minerals; Fine particle processing; Dewatering*

Introduction

The coagulation-flocculation characteristics of clay mineral suspensions, especially montmorillonite and kaolinite, were extensively investigated by several workers in the presence of various inorganic and organic compounds (Swartzen-Allen and Matijević, 1976; Melton and Rand, 1977; Oster et al., 1980; Goldberg and Glaubig, 1987; Keren et al., 1988; Pierre and Ma, 1999; Duan and Gregory, 2003; Petzold et al., 2003; Proskurina et al., 2003). In these studies, generally, the critical coagulation concentration (c.c.c.) values of clay suspensions, which are low with respect to the concentrations used in this study, have been determined at different pH values. The NaOH and HCl used in these studies for the pH adjustments also affect the corresponding c.c.c. values.

Although the coagulation behaviours of clay suspensions for low electrolyte concentrations have been determined, there is no study found in the literature that compares the effects of various inorganic-organic substances at high concentrations on the settling behaviours of the same clay suspensions under same physical conditions. Such kind of information is useful in some type of mineral processing operations that includes clays and in the preparation of new types of inorganically or organically modified clay minerals. So, this study has been performed to find out the effects of inorganic-organic compounds at high concentrations on the sedimentation characteristics of kaolin and bentonite suspensions.

Experimental

Materials

The original high grade kaolin and bentonite samples (Turkish Republic) were sieved through 38 µm sieve and the sieve undersizes (<38 µm fractions) were used in the sedimentation experiments. The clay samples were identified using XRD patterns of randomly oriented <38 µm fractions (Fig. 1.) and specially prepared (normal, glycolated, heated and Li-250 treated) clay fractions (Lim and Jackson, 1986; Wilson, 1987).

XRD studies showed that the kaolin sample is nearly pure kaolinite and the bentonite sample contains mainly montmorillonite (>90 % Na-montmorillonite, d_{001}=12.3 Å) with little amounts of zeolite, feldspar, calcite and opal-CT.

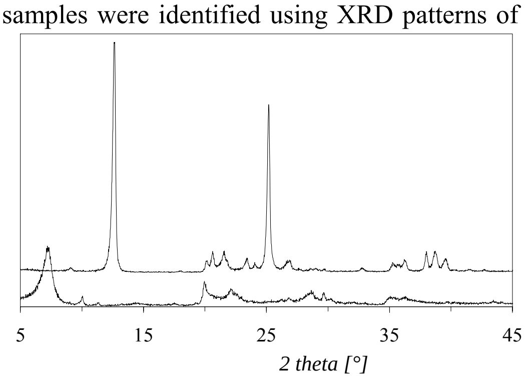

Fig. 1. Randomly oriented XRD patterns of <38 µm kaolin and bentonite samples (k: kaolinite, m: montmorillonite, z: zeolite, f: feldspar, c: calcite).

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(Recenzovaná a revidovaná verzia dodaná 16. 8. 2005)

Methods

Test tubes were used in the settling experiments. After filling each test tube with concentrated solutions of different inorganic or organic compounds, the clay was added to each tube providing a solids concentration of 5 % by wt/vol. After mixing each tube for the same period of time, the settled volumes for the tubes which has a sharp solid-liquid interface and clear supernatant were recorded against time to determine the sedimentation curves of the used clays. There were no pH adjustments done on the test tubes, because the acids and bases themselves also affect the sedimentation behaviors of the clays due to their dissolving and/or ion exchange properties.

All the chemicals used in the sedimentation experiments were chemically pure. All the used solutions, except boric, oxalic and citric acids, had concentrations of 1,0 N. Due to the low dissolution values in water, only boric, oxalic and citric acid solutions were prepared at 0,5 N concentration. The clay was directly added to the liquids when organic liquids such as carbon tetrachloride, nitrobenzene or alcohols vere used. The initial volume (settling time is zero) of clay suspensions was constantly 10 cm^3.

Results and discussion

At first, the chemical susbstances were grouped as “acids”, “salts” and “organic liquids”. Acids and salts were chosen due to their dissolving or ion exchange effects on the used clays. Pure organic substances like carbon tetrachloride, ethanol etc. were used to collect data about the dispersion and settling behaviours of the used clays in pure organic substances. The settling curves of kaolin and bentonite samples in the presence of “acids” are given in Fig. 2. and 3., respectively.

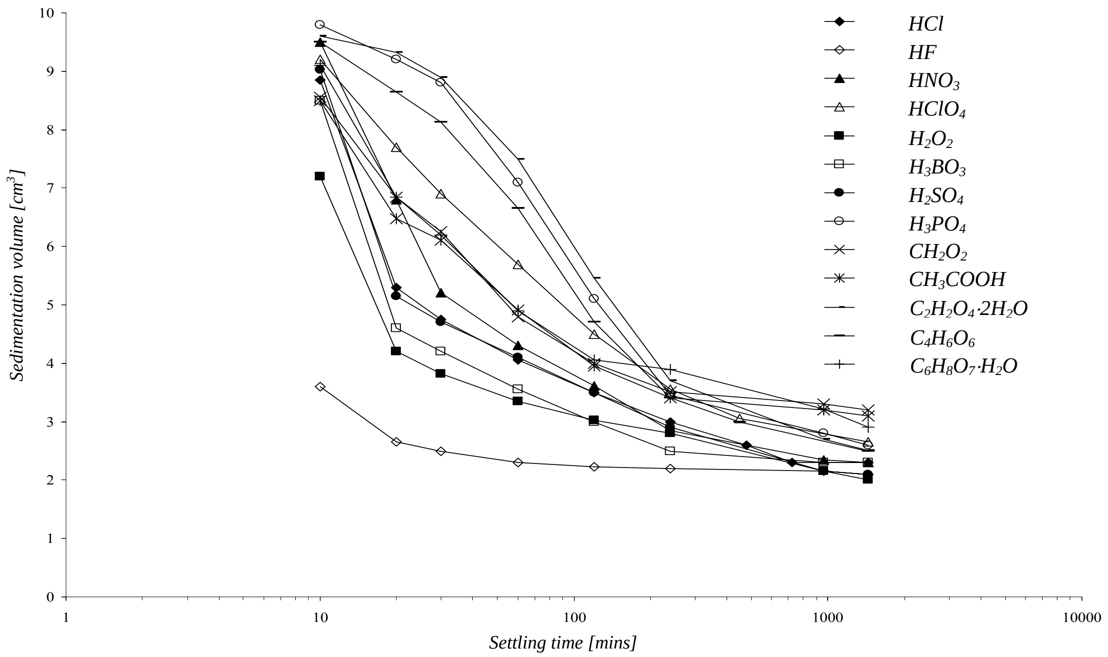

Fig. 2. Sedimentation volume vs. time curves of kaolin suspensions in “acids”.

For the kaolin suspensions (Fig. 2.), except with HF, the settling curves follow a similar pattern in each case. The HF (which can dissolve the silicate structure) containing kaolin suspension settles in first 10 minutes at a faster rate and then the rate diminishes greatly.

Considering the bentonite suspensions (Fig. 3), only suspensions containing $HClO_4$, HCl and HNO_3 show settling with a clear solid-liquid interface up to 10th minute and no settling was observed, interestingly, for the suspensions including HF, H_2O_2, H_3BO_3 and $C_2H_2O_4{\cdot}2H_2O$ (oxalic acid) for a 1440 minutes of sedimentation time.

In “salt” solutions, all the kaolin suspensions settle following a very similar pattern (Fig. 4). In CCl_4 (carbon tetrachloride) and $C_6H_5NO_2$ (nitrobenzene). On the other hand, according to the Fig. 5, the bentonite suspensions that show similar settling patterns can be grouped as; ‘Li^+’ – ‘K^+, Cs^+, NH_4^+’ – ‘Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}’ – ‘CCl_4, $C_6H_5NO_2$’.

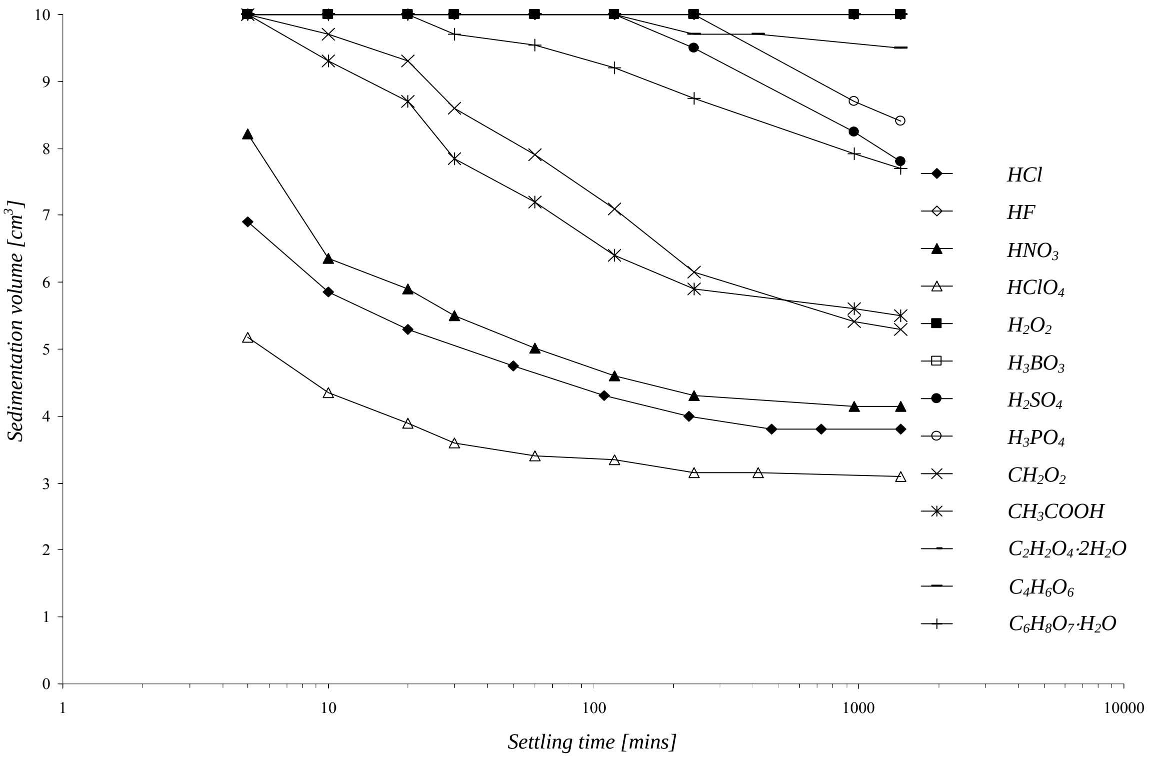

Fig. 3. Sedimentation volume vs. time curves of bentonite suspensions in "acids".

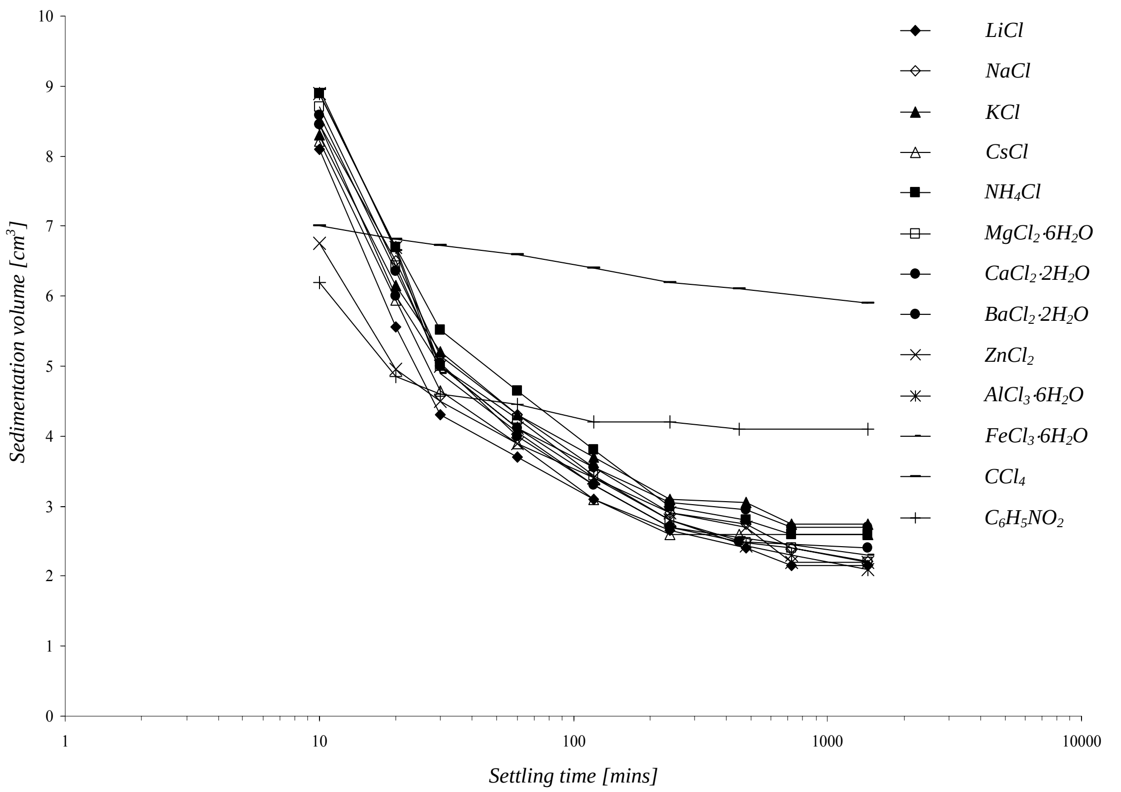

Fig. 4. Sedimentation volume vs. time curves of kaolin suspensions in "salts" and "organic liquids".

Tab. 1. shows the initial sedimentation rates of clay suspensions in the first 10 minutes and the final sediment volumes of suspensions. For kaolin suspensions, the fastest settling rates were observed for HF, $C_6H_5NO_2$, $ZnCl_2$, CCl_4 and H_2O_2 and the slowest rates were observed for $C_6H_8O_7{\cdot}H_2O$ (citric acid),

$C_2H_2O_4$·.2H_2O, H_3PO_4 and HNO_3 containing suspensios. The settling rates of bentonite suspensions are generally higher than the kaolin suspensions.

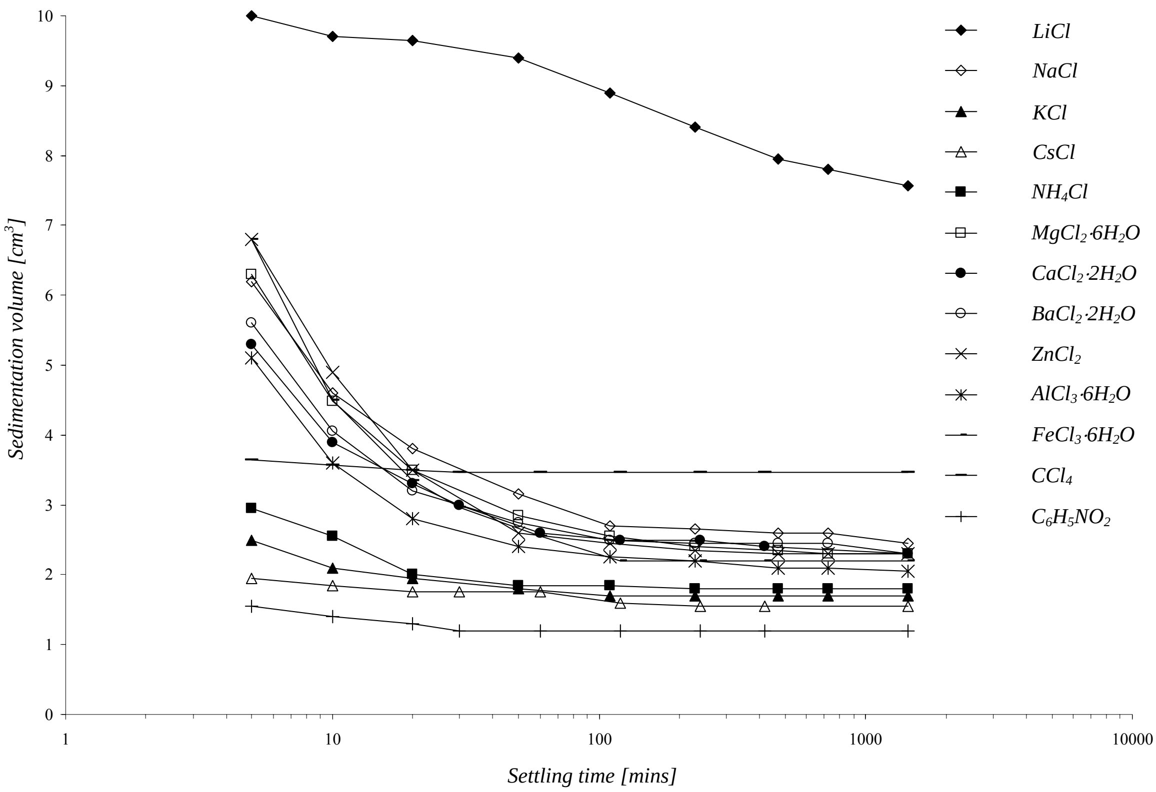

Fig. 5. Sedimentation volume vs. time curves of bentonite suspensions in "salts" and "organic liquids".

For bentonite suspensions, the nitrobenzene and CsCl containing suspensions were settled at a fastest rate while the acetic acid and LiCl suspensions settle at a slowest rate. No settling was observed in the first 10 minutes for the suspensions containing HF, H_2O_2, H_3BO_3, H_2SO_4, H_3PO_4, $C_2H_2O_4 \cdot 2H_2O$ and $C_6H_8O_7 \cdot H_2O$. When salt solutions are considered, although the final sediment volumes for +2 and +3 valence cations (Mg, Ca, Ba, Zn, Al, Fe) were nearly same, the final sediment volumes of +1 valence cations (Li, Na, K, Cs) differ greatly. The pictures showing final sediment volumes of kaolin and bentonite suspensions for some of the +1 valence cations are given in Fig. 6. and 7., respectively.

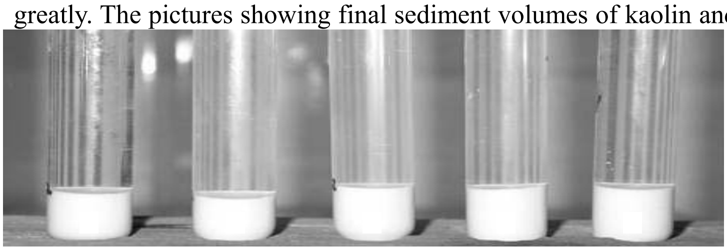

Fig. 6. The final sediments of kaolin suspensions in the presence of a.HCl, b.LiCl, c.NaCl, d.KCl and e.NH_4Cl.

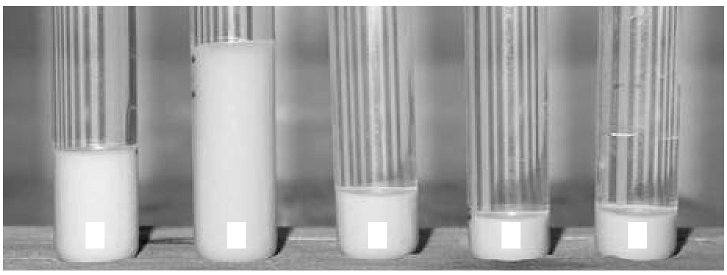

Fig. 7. The final sediments of bentonite suspensions in the presence of a.HCl, b.LiCl, c.NaCl, d.KCl and e.NH_4Cl.

Since no sharp solid-liquid interfaces and clear supernatants were observed, the settling curves in some organic liquids (alcohols, acetone etc.) were not included in Fig. 4. and 5. Only final settled volumes of these suspensions are given in Tab. 1. When comparing the experimental results, it should be remembered that there were no pH adjustments done in the test tubes due to the effects of acid or bases on the sedimentation behaviors of the used clays. Whereas the pH values of the kaolin suspensions were nearly the same after the sedimentation experiments, the pH values of corresponding bentonite suspensions generally increased by 2. Maximum pH increase after sedimentation was observed for the boric acid containing bentonite suspension, from pH 4 to 7.

Tab. 1. Initial settling rates and final sediment volumes of kaolin and bentonite suspensions.

Group	Compound	Settling rate (for the first 10 mins, mm/min)		Sediment vol. (at 1440th minute, cm^3)	
		Kaolin	Bentonite	Kaolin	Bentonite
Acids	HCl	0.72	2.58	2.30	3.80
	HF	3.98	0.00	2.10	10.00
	HNO_3	0.31	2.27	2.30	4.15
	$HClO_4$	0.50	3.52	2.65	3.10
	H_2O_2	1.74	0.00	2.00	10.00
	H_3BO_3	0.93	0.00	2.30	10.00
	H_2SO_4	0.61	0.00	2.10	7.80
	H_3PO_4	0.12	0.00	2.60	8.40
	CH_2O_2	0.90	0.19	3.20	5.30
	CH_3COOH	0.93	0.44	3.10	5.50
	$C_2H_2O_4{\cdot}2H_2O$	0.00	0.00	2.50	10.00
	$C_4H_6O_6$	0.31	0.84	2.50	9.50
	$C_6H_8O_7{\cdot}H_2O$	0.00	0.00	2.90	7.70
Salts	LiCl	1.18	0.19	2.15	7.60
	NaCl	0.97	3.36	2.20	2.45
	KCl	1.06	4.92	2.75	1.70
	CsCl	1.11	5.07	2.60	1.55
	NH_4Cl	0.68	4.64	2.60	1.80
	$MgCl_2{\cdot}6H_2O$	0.81	3.44	2.20	2.30
	$CaCl_2{\cdot}2H_2O$	0.88	3.80	2.40	2.30
	$BaCl_2{\cdot}2H_2O$	0.97	3.70	2.70	2.30
	$ZnCl_2$	2.02	3.18	2.20	2.30
	$AlCl_3{\cdot}6H_2O$	0.68	3.98	2.10	2.05
	$FeCl_3{\cdot}6H_2O$	0.65	3.42	2.30	2.20
Organic liquids	CCl_4	1.87	4.00	5.90	3.45
	$C_6H_5NO_2$	2.37	5.35	4.10	1.20
	CH_3OH	n.a.	n.a.	2.50	1.20
	C_2H_5OH	n.a.	n.a.	2.35	1.20
	C_3H_8O	n.a.	n.a.	1.20	1.00
	CH_3COCH_3	n.a.	n.a.	3.10	1.35
	$(CH_3)_2NOCH$	n.a.	n.a.	1.90	3.65

n.a.: not applicable

Conclusion

In this study, it was showed that sedimentation behaviour of clay in a concentrated suspension, both high electrolyte and high clay concentrations, is very different from the corresponding behaviour in dilute suspensions reported in the literature. Although similar sedimentation volumes after 24 hours of settling time (2-3 cm^3) and initial settling rates for the first 10 minutes (from 0 to ~4 mm/min, average 1.0 mm/min) were observed for the kaolin suspensions, the correspoding volumes (1 cm^3 to no settling) and rates (from 0 to ~5 mm/min, average 2,3 mm/min) of bentonite suspensions are varying greatly with the used reagent.

It was shown that at high bentonite content of, one can hold the clay in suspension without settling for 24 hours using hydrofluoric acid, hydrogen peroxide, boric acid and oxalic acid. On the other hand, one can easily separate bentonite at a fastest rate from its concentrated suspension with KCl, CsCl and NH_4Cl because of the high sedimentation velocities reached.

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