THE pH OF AQUEOUS BENTONITE SUSPENSIONS

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Abstract—The pH of aqueous bentonite suspensions is known to be influenced by carbonates present even in minor amounts. On the other hand, at high solid:liquid ratios (at standard pH measurement conditions: 2% w/w suspension), the type of exchangeable cation in the smectite is also known to determine pH (particularly Na^+ or Ca^{2+}). By cation-exchange tests we proved that exchanging the Ca^{2+} for Na^+ results in an increase in the pH. However, this increase in pH was only found if excess salts were removed from the system (by washing or dialysis, respectively). The effect of the type of exchangeable cation can, at least partially, be explained by hydrolysis of Ca^{2+}. On the other hand, a pronounced alkalinity of Na bentonites is observed which can, at least partially, be attributed to the hydrolysis of montmorillonite (Na^+ is exchanged for H^+ of water). The increase in the volume of the Stern layer, caused by increasing the degree of delamination, is also suggested to play a role. H^+ and Na^+ are concentrated in the Stern layer. Hence, increasing the Stern layer volume decreases the amount of H^+ and Na^+ in solution and thus increases pH. Unfortunately, both processes, montmorillonite hydrolysis and delamination, depend on the ionic strength. Distinguishing the processes quantitatively, therefore, is an analytical challenge, and impossible based on the data presented here.

To model the pore-water chemistry of clays and clay stones, all of the above-mentioned processes have to be considered. It is possible that other reactions, not identified in the present work, contribute toward the pH values of aqueous bentonite suspensions.

Key Words—Bentonite pH, Carbonate Content, Clay-water Interaction

INTRODUCTION

The 'pH' of soils and clays is commonly determined by electrometric measurement of the pH value of a clay suspension (*e.g.* 2% w/w), or of the clear supernatant after centrifugation or filtration. The pH of a clay suspension strongly influences its technical applications and some essential properties including, *e.g.* adsorption and rheological properties (Tombácz and Szekeres, 2004). Analytical variations and problems were summarized by Thomas (1996).

The significance of soil pH is discussed in detail by Ulrich (1981) and Thomas (1996) among others. The pH value can be used to predict the dominant cations on soil-cation exchangers (pH 2−3: free mineral acids, pH 4−5: exchangeable Al^{3+} and Fe^{3+}, pH > 5.5: Al hydroxide ions/polymers, pH 7.6−8.3: $CaCO_3$, pH > 9: Na_2CO_3). This classification refers mainly to Al speciation and the presence of carbonates and does not take into account possible effects of Na^+ compared to Ca^{2+} at the surfaces of swelling clay minerals.

pH is believed to depend mainly on minor constituents such as carbonates, zeolites, and sulfides. In particular, any carbonates present influence the pH in many geological environments. On the other hand, interlayer cations possess a certain acidity (Benesi and Winquist, 1978) which in turn influences pH. Thus, the pH of a bentonite suspension is determined by at least two parameters. The effect of carbonate dissolution on the pH of a solution is well known and can be calculated easily. In addition, Ca^{2+} is known to be more acidic than Na^+, due to hydrolysis. However, the extent to which the pH is influenced by each of these constituents is not yet clear. Kamil and Shainberg (1968) and Bar-on and Shainberg (1970) investigated the hydrolysis of montmorillonite, caused by an exchange of Na^+ for H^+ from water molecules, which leaves OH^- in solution and thus increases the pH. Those authors also discussed the instability of the resulting H-montmorillonite, an argument readily acknowledged nowadays (Janek and Komadel, 1999). This process is referred to as auto-transformation and can be the cause of pH measurements not reaching a stable end-value (Bar-on and Shainberg, 1970).

Kaufhold and Dohrmann (2008) investigated 38 bentonites (some calcareous and some non-calcareous) and identified a correlation between pH and the amount of exchangeable Na^+. This indicates that the type of interlayer cation of swelling clay minerals (particularly Na^+) is more important with respect to pH than the carbonate content. Therefore, in the present paper we systematically investigate the effect of carbonate content

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and the type of different cations on the pH value of bentonite suspensions. The main objectives of this study are therefore to: (1) examine the extent to which the pH of bentonites is determined by carbonate content or type of exchangeable cation; and (2) investigate whether the measured pH can be attributed to these two parameters unequivocally.

MATERIALS AND METHODS

Thirty eight bentonite samples were investigated with respect to the pH of a 2% w/w suspension. Except for samples B24−B28 (which were dried and ground using industrial means), only unprocessed materials were considered. None of the samples contained any soda ash. Most of the samples were kindly provided by bentonite-producing companies and so sample localities cannot be mentioned. The samples were dried under air, broken down to ~5−20 mm, dried at 60ºC, and then ground to <0.25 mm using a hammer mill. The water content was determined by oven drying at 105ºC up to constant weight (~1 week). To determine the suspension pH, 1.00 g of the material dried at 60ºC plus the weight loss between 60 and 105ºC were weighed (*e.g.* 1.05 g, 60ºC in the case of 5% water content between 60º and 105ºC) and immersed in 50.0 mL of deionized water (pH 6), followed by end-over-end shaking for 24 h. The tubes were sealed carefully in order to prevent contact with air. The pH was measured using a WTW Inolab pH-meter (WTW GmbH, Weilheim, Germany) equipped with a WTW pH electrode SenTix 81. The electrode was calibrated using buffer solutions of pH 4, 7, and 10. The pH of the suspensions was measured with continuous stirring in closed beakers in order to prevent CO_2 contamination. The pH values were recorded after 5, 10, and 15 min in order to ensure that equilibrium was attained.

The chemical composition of the bentonites was given by Kaufhold and Dohrmann (2008) and the mineralogical composition was investigated by Ufer *et al.* (2008). However, Ufer *et al.* (2008) did not consider samples 30 and 35 as they contain mixed-layer minerals. Therefore sample assignment is different (see Table 1). The cation exchange capacity (CEC) was determined according to Meier and Kahr (1999) and results were published by Kaufhold and Dohrmann (2008). The carbonate content was determined by LECO analysis (LECO CS-444) and recalculated to the calcite content. A few samples contain minor amounts of carbonates other than calcite. The relevant mineralogical data are presented in Table 1.

For selected experiments, natural calcite material (clear crystals) from the Sauerland region, Germany, was used. This calcite was ground in different ways: crushing to (1) <1 mm; (2) <250 μm using a hammer mill (the same mill was used for all bentonites); or (3) < 20 μm, using a McCrone mill.

RESULTS AND DISCUSSION

Carbonates, if present, are known to determine the pH of various geochemical systems. That they determine the pH of bentonites also is therefore assumed. It was important to study the effect of calcite on pH under the experimental conditions applied in this study. Calcite reference samples were investigated. In addition, two Ca^{2+}- and two Na^+-bentonites, both containing calcite, were investigated with respect to pH at different solid:liquid ratios (⩽2% w/w). The solid:liquid ratio was adjusted in such a way that the amount of calcite within the system was below and above the maximum calcite solubility, finally attaining standard conditions (2% w/w suspension). The results are presented in Figure 1 from which we conclude that: (1) the pH of all samples at low solid:liquid ratios depends significantly on calcite dissolution; (2) calcite dissolution depends on grain size, at least if very coarse material is compared with powder; (3) within the bentonite sample set, calcite grain size is not supposed to play a role since all materials were ground to <250 μm using the hammer mill; and (4) Ca^{2+}- and Na^+-bentonites behave differently: after attaining maximum calcite solubility: Na^+-bentonites are still basic, while Ca^{2+}-bentonites show a slightly more acidic reaction.

Figure 1 proves that the type of exchangeable cation (Na^+ or Ca^{2+}) influences the aqueous pH, particularly in the case of 2% w/w suspensions. This corroborated the results of Kaufhold and Dohrmann (2008) who described the correlation of exchangeable Na^+ and pH (as shown in Figure 2).

From Figures 2 and 3 it can be concluded that both the exchangeable Na^+ content and the calcite content influence the suspension pH. Figure 3 indicates that calcite, if present, provides substantial alkalinity. However, Figure 3 also demonstrates a significant pH variation for calcite-free samples with varying exchangeable Na^+ concentrations (Figure 4). The calcite contents were calculated from elemental carbon analyses providing values accurate to 0.1% w/w. It is conceivable that trace amounts of carbonates, below the detection limit, are present in those samples and these influence the pH. However, Figure 4 clearly proves that the pH of non-calcareous bentonite suspensions increases with increasing exchangeable Na^+.

The typical pH of Ca-bentonite suspensions ranges from 7 to 8 in contrast to Na-bentonites with pH values ranging from 9 to 10. This trend is valid regardless of the carbonate concentration. In conclusion, the effect of the type of clay mineral, or to be more precise, the exchangeable cations, on pH at high solid:liquid ratios (*e.g.* 2% w/w suspension) dominates over the effect of carbonate content.

In order to prove the effect of the type of exchangeable cation on pH, additional tests using selected bentonites were performed. Samples B16 and B32

Table 1. pH, carbonate, carbon (C), and sulfur (S) contents, CEC, and exchangeable cations of the 38 bentonite samples.

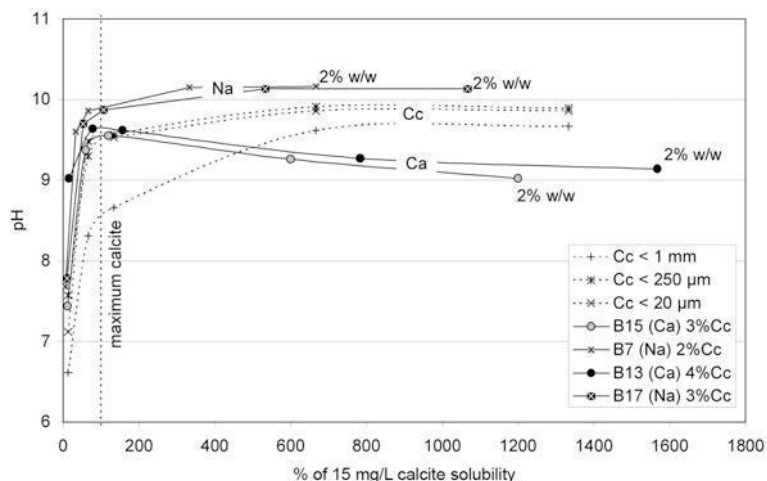| Sample assignment This study	Ufer et al., 2008	pH	Calcite	Other carbonates	C total (% w/w)	C organic (% w/w)	C inorganic (% w/w)	Sulfides	S total (% w/w)	Na^+ ICP (meq/100 g)	Na^+ (%)	K^+ ICP (meq/100 g)	Mg^{2+} ICP (meq/100 g)	Ca^{2+} ICP (meq/100 g)	Sum of cations (meq/100 g)	CEC ICP (meq/100 g)	Sum-CEC (meq/100 g)	CEC VIS (meq/100 g)
B1	1	8.5	+		0.2	0.0	0.1		0.0	17	17	2	45	52	116	97	19	102
B2	2	7.7			0.1	0.0	0.0		0.0	13	13	2	47	42	104	103	1	102
B3	3	7.5			0.0	0.0	0.0		0.0	12	11	2	35	53	102	105	−3	104
B4	4	7			0.0	0.0	0.0		0.1	19	17	2	46	38	105	108	−2	107
B5	5	7.3	+		0.6	0.0	0.6	Pyrite	0.7	14	14	3	33	67	117	100	17	100
B6	6	8.6			0.0	0.0	0.0		0.0	17	16	2	36	52	107	107	1	110
B7	7	9.9		Dolomite	0.2	0.0	0.2		0.1	66	67	5	5	33	109	98	11	99
B8	8	9.9	+		0.2	0.0	0.2		0.1	69	100	0	1	16	86	69	17	72
B9	9	9.6	+		0.3	0.1	0.3		0.2	62	91	1	2	31	95	68	27	70
B10	10	9.2	+		0.1	0.1	0.1		0.0	28	29	2	22	54	105	96	9	96
B11	11	9.2	+		0.1	0.0	0.1		0.0	63	65	1	17	34	115	97	18	99
B12	12	9.2	+		0.1	0.0	0.1		0.1	56	51	1	26	41	124	108	16	110
B13	13	8	+		0.5	0.1	0.5		0.0	1	1	2	38	75	116	84	32	87
B14	14	7.8	+		0.2	0.1	0.1		0.0	1	1	3	41	48	93	84	9	86
B15	15	7.8	+		0.4	0.1	0.4		0.0	1	2	2	31	54	87	66	21	68
B16	16	7.2			0.1	0.1	0.0		0.1	0	0	2	22	53	77	67	10	69
B17	17	9.9		Dolomite	0.4	0.1	0.3		0.1	68	68	7	4	38	116	99	17	103
B18	18	9.3	+		0.2	0.1	0.1		0.0	28	27	3	37	46	114	105	9	107
B19	19	9.4	+		0.4	0.0	0.3		0.0	20	24	3	33	47	102	83	20	85
B20	20	9.5	+		0.3	0.1	0.2		0.3	58	71	2	8	35	102	82	20	85
B21	21	7.9			0.0	0.0	0.0		0.0	42	47	3	29	30	104	91	13	93
B22	22	8.8	+		0.0	0.0	0.0		0.0	66	71	1	3	27	97	93	4	98
B23	23	9			0.0	0.0	0.0		0.0	68	68	1	2	33	105	101	4	104
B24	24	9.4			0.1	0.0	0.0		0.1	46	47	2	27	36	112	98	14	101
B25	25	7.4			0.1	0.1	0.0	Pyrite	0.0	0	0	2	15	41	57	63	−6	62
B26	26	9.5	+		0.2	0.1	0.1		0.0	20	22	3	16	49	88	93	−5	88
B27	27	9.7	+		0.9	0.1	0.9		0.2	62	68	2	5	31	101	92	9	89
B28	28	7.4			0.1	0.1	0.0		0.0	1	1	2	3	70	75	82	−7	82
B29	29	6.4			0.1	0.1	0.0		0.0	0	0	1	23	44	68	76	−8	77
B30	30	7.3			0.5	0.4	0.1		0.1	27	72	3	3	8	41	38	4	36
B31	31	9.7	+		0.2	0.0	0.2		0.0	51	62	1	12	31	95	82	13	81
B32	32	7.4		Dolo.+sider.	0.1	0.1	0.0		0.0	1	1	2	6	73	82	87	−5	85
B33	33	9.4			0.1	0.1	0.1		0.0	57	69	2	5	33	97	82	15	81
B34		7.7			0.1	0.1	0.0		0.0	5	6	1	29	55	90	85	5	85
B35		7.7	+	Dolomite	0.0	0.0	0.0		0.0	0	0	3	10	32	45	40	4	38
B36	34	7.1			0.1	0.1	0.0		0.0	0	1	2	17	36	54	56	−1	53
B37	35	6.5	+		0.3	0.2	0.1		0.2	1	1	1	27	56	84	85	−1	80
B38	36	9	+	Dolomite	1.3	0.3	1.0		0.0	14	21	3	21	46	84	67	17	65

Figure 1. pH of four calcareous bentonites at different solid:liquid ratios, given in percentage above maximum calcite solubility (calculation based on calcite content and calcite solubility) and of the calcite reference material (1% w/w calcite and 99% w/w quartz) ground to different grain sizes. The final data point refers to the highest solid:liquid ratio (2% w/w) representing standard conditions for pH measurements.

(carbonate-free, no exchangeable Na^+) were suspended in water (1.000 g/50 mL = 2% w/w suspension) and the initial pH was recorded (Figure 5). The water was then separated by centrifugation and 50 mL of a 2 M NaCl solution were added and the pH was recorded again ('NaCl' in Figure 5). This procedure led to a decrease in pH, probably caused by desorption of protons from variable-charge sites and the Stern layer, caused by the high ionic strength (competitive adsorption). Two subsequent washing steps led to an increase in pH to values greater than initially recorded. A similar experiment was conducted, applying a stepwise (semi-continuous) procedure (Figure 6). A suspension (2% w/w) of sample B32 was kept in a dialysis tube immersed in a water bath and the pH monitored *in situ*. After equilibration of the pH to 7.4, solid NaCl (20 times the CEC) was added. As observed previously, initially the pH decreases significantly, but then starts to increase. Significant increases in pH were observed after each

change of the water in the dialysis bath which, of course, decreases the ionic strength.

The influence of the exchangeable Na^+ or Ca^{2+} content on the pH can probably be explained by the acidity (hydrolysis) of Ca^{2+} compared to Na^+ (*e.g.* Benesi and Winquist, 1978). In order to investigate the effect of Ca^{2+} on pH, a 1 M NaCl solution (no clay) was prepared and adjusted to pH 9.9−10 by addition of NaOH. Subsequently, $CaCl_2$ (salt) was added, corresponding to 100 meq/100 g of Ca^{2+} of a theoretical bentonite in a 2% w/w suspension. The pH decreased to 9.3 which is still greater than the typical Ca bentonite range (pH 7−8).

This indicates that the significant correlation of pH and Na^+ content cannot be explained by the hydrolysis of Ca^{2+} alone. Our hypothesis is that at least one additional process is involved. On the other hand it is possible that the interlayer Ca^{2+} is more acidic than dissolved Ca^{2+} (Yariv and Michaelian, 2001). The data presented in
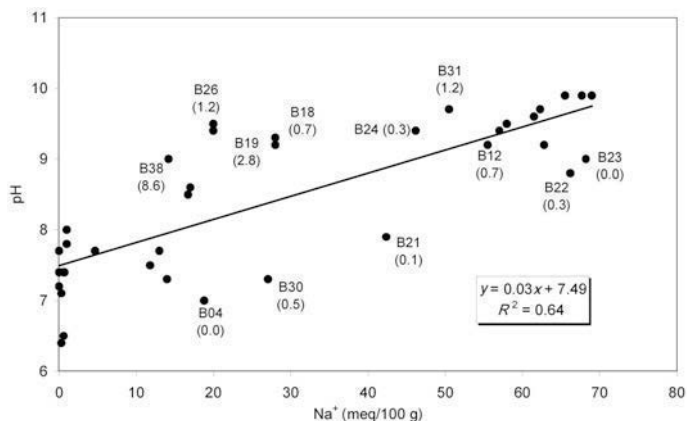

Figure 2. Amount of exchangeable Na^+ and pH of 38 bentonites (in parentheses: calcite content calculated from elemental analysis; black line: regression curve).
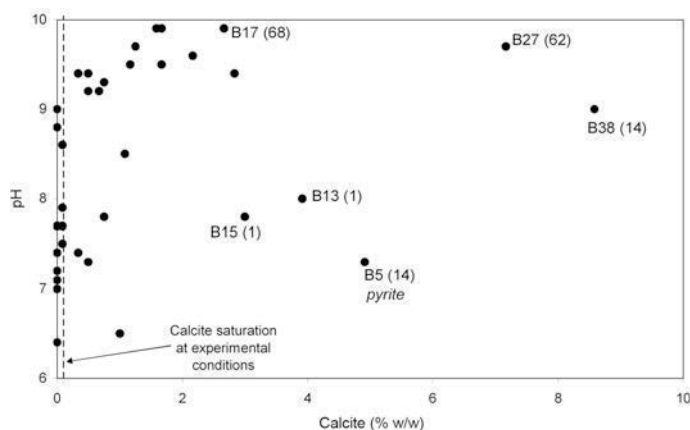
Figure 3. Calcite content and pH of the 38 bentonite samples (in parentheses: amount of exchangeable Na^+ in meq/100 g). Sample B5 contains ~1.5 % w/w pyrite.

Figure 1 support our hypothesis: after exceeding calcite solubility, the alkalinity of Na-bentonites continues to increase and the alkalinity is even greater than that of pure carbonates. This clearly proves that a proton-consuming reaction takes place which increases pH (in the absence of Ca^{2+}). At least some of this alkalinity can be attributed to the hydrolysis of Na^+-montmorillonite (as suggested by Kamil and Shainberg, 1968, and Bar-on and Shainberg, 1970). The Na^+ is exchanged for H^+ (sufficient present in neutral water) which leaves OH^- in solution, thereby increasing the pH. The reaction can be expressed as:

$$H_2O + \text{Na-montmorillonite} \rightleftharpoons$$
$$OH^- + \text{H-montmorillonite} + Na^+$$
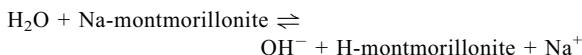
This cation-exchange process could also occur with Ca^{2+}-montmorillonite but is probably suppressed by the greater adsorption energy of Ca^{2+}, resulting in greater cation-exchange selectivity compared to Na^+. Nevertheless, Bar-on and Shainberg (1970) admit that the montmorillonite hydrolysis process alone does not explain the high pH values ($\geqslant 9.5$). They propose an additional effect of oxyhydroxides, possibly present on the clay surfaces. The present authors propose a different process, based on the different degree of delamination of
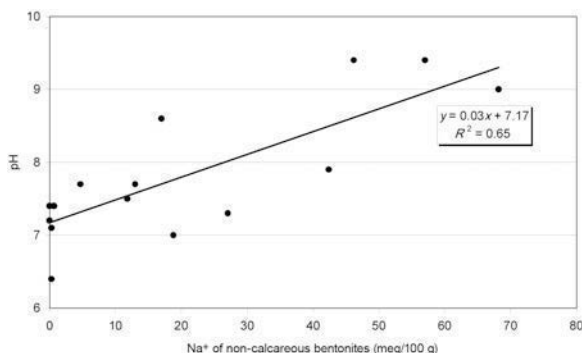
Ca^{2+}- and Na^+-montmorillonites. Na^+-montmorillonites are known to at least partly delaminate in aqueous suspensions. Of course, delamination does not affect the total surface area of the clay surfaces but increases significantly the outer surface area of the montmorillonite in suspension. The interlayer space is accessible to water, regardless of the degree of delamination. Therefore, the water−basal plane interaction is not supposed to be significantly affected by the degree of delamination. On the other hand, delamination increases the volume of the Stern layer in which H^+ and Na^+ are concentrated. In conclusion, increasing the volume of the Stern layer can potentially contribute to the total alkalinity (by binding of H^+). Unfortunately, both processes, montmorillonite hydrolysis and the delamination, depend on ionic strength. Distinguishing the two processes quantitatively, therefore, is an analytical challenge and impossible based on the data presented here.

SUMMARY AND CONCLUSIONS

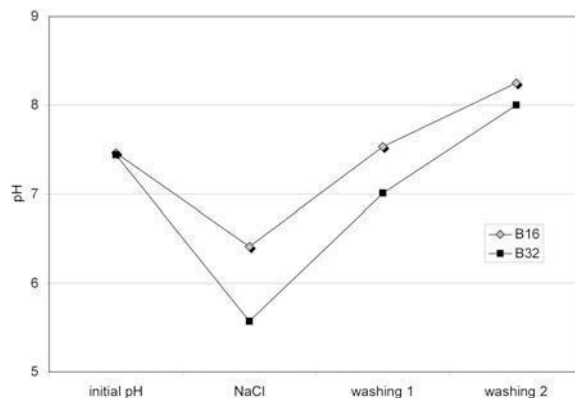The pH of bentonite suspensions is known to be affected by carbonates; this was found to be important

Figure 4. Exchangeable Na^+ and pH value of non-calcareous bentonite samples.

Figure 5. Effect of NaCl addition and two subsequent washing steps on the pH of two Ca^{2+}-bentonite suspensions.
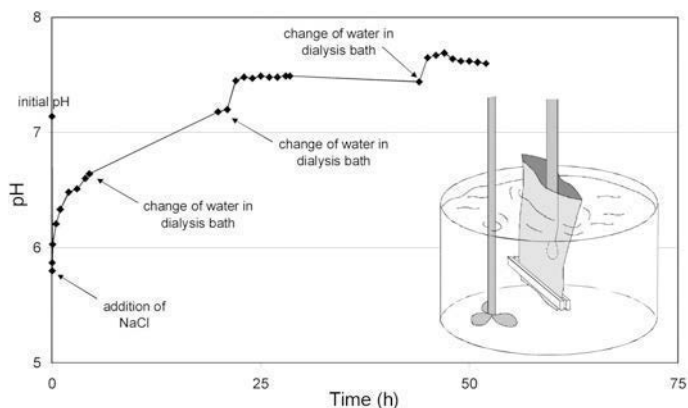
Figure 6. Effect of NaCl addition and subsequent washing steps (dialysis) on the pH of the suspension of the Ca-bentonite sample B32.

only in case of small solid:liquid ratios. Under standard conditions for pH measurements (2% w/w suspensions) the type of exchangeable cation has a strong influence on suspension pH. This effect is, to a certain degree, influenced by the hydrolysis of Ca^{2+}, providing some acidity. The alkaline reaction of Na^+-montmorillonite is tentatively attributed to: (1) the hydrolysis of montmorillonite; and (2) the increase of the Stern-layer volume caused by delamination. To model the pore-water chemistry of clays and clay stones, these processes, all depending on ionic strength and solid:liquid ratio, have to be considered. Other reactions, not previously identified, may contribute to the pH value of aqueous bentonite suspensions.

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