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Utilization of Na-bentonite to Improve pH-buffering Capacity of Acid Sulfate Soils in Natural Gas Transmission Pipeline Rights-of-Way, Thailand

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Abstract. Na-bentonite, non-hazardous material usually uses as a drilling mud in Horizontal Directional Drilling (HDD) technique. Its alkalinity may reduce severe acidic conditions of acid sulfate soils (ASS) in natural gas transmission pipeline Rights-of-Way in Thailand (RoW). This study focused on the effects of Na-bentonite on pH buffering capacity (pHBC) of ASS. Five major acid sulfate soils in RoW were collected and incubated with incremental amounts of 0.4 M $Ca(OH)_2$ and 0.4 M HCl to determine their pHBC. Hydroxyl equivalent alkalinity derived from pHBC curves was used to define the appropriate rate of Na-bentonite. The various soil:Na-bentonite ratios of 1:0.1, 1:0.15, 1:0.2, 1:0.3, 1:0.4, 1:0.5, 1:1 were prepared to examine their pH change. The results showed that active acid sulfate soils especially in subsoil had very high pHBC and Na-bentonite can increase soil pH to the optimal pH of 6.0, implying that Na-bentonite was beneficial for acid sulfate soils.

1. Introduction

PTT Public Company Limited is a national oil and gas company that has played an important role in strengthening national energy security of the Kingdom of Thailand by transporting natural gas via pipeline system to customers, industrial and commercial sectors since 1981. PTT has been constructing and operating natural gas pipeline system network for more than 4,500 kilometers, including both onshore and offshore areas. Recently, there is the new project, named the 5th Transmission Natural Gas Pipeline Project (5TP) with approximately 415 kilometers length from eastern to central part of Thailand laid through various kinds of soils and land uses.

Acid sulfate soil is one of major soil types in the Rights-of-Way (RoW) of 5th Transmission Natural Gas Pipeline Project. Most of them occurred in the lower central plain of Thailand [1]-[3]. Generally, acid sulfate soils can be divided into i) potential acid sulfate soils which contain sulfide minerals near the soil surface, ii) active acid sulfate soils, where sulfuric acid is produced by oxidation of sulfide minerals and their pH become ultralow (pH < 4.0), and iii) post active acid sulfate soils, where sulfuric acid is neutralized and soil pH has risen above 4.0 by liming or drainage [3]. In addition, wetland rice is a major crop grown on these soils [4]. So, the disturbance of these soils by excavation causes exposure of severe acid and aluminium toxicity [5] to surface soils.

In general, the construction of natural gas transmission pipeline in some area needs Horizontal Directional Drilling (HDD) technique and Na-bentonite, an alkaline material, is usually used as a

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drilling mud. This alkalinity may be useful for reducing severe acidic conditions of major agricultural acid sulfate soils in natural gas transmission pipeline RoW. However, there are only few scientific reports demonstrating the utilization and impact of Na-bentonite on agricultural soils [6]-[7], and there are no any scientific reports on utilizing Na-bentonite to improve acid sulfate soils in Thailand. Therefore, the objective of this study mainly focused on the effects of Na-bentonite on pH buffering capacity (pHBC) of acid sulfate soils in natural gas transmission pipeline RoW of Thailand. Our research is therefore novel to investigate an effective estimation of the appropriate rate of Na-bentonite and management of acid sulfate soils on the pipeline RoW.

2. Materials and Methods

2.1. Acid Sulfate Soil Samples and Na-bentonite

Selected topsoil and subsoil samples from three active acid sulfate soils namely Sena series (Se), Ongkharak series (Ok) and Rangsit series (Rs), and 2 potential acid soils namely Chachoengsao series (Cc) and Bang Nam Priao series (Bp) were collected in the natural gas transmission pipeline Rights-of-Way (Figure 1). Some physicochemical properties of the studied soils were analyzed according to the standard methods of National Soil Survey Center [8] and are given in Table 1. Commercial grade Na-bentonite was used in this study. Basic properties of Na-bentonite including pH, calcium carbonate equivalent (CCE) and alkalinity were analyzed and given in Table 2. Na-bentonite used in this study had a pH of 9.26 and very low CCE, indicating that Na-bentonite was not a carbonate liming material, but its alkalinity mostly derived from hydroxyl ion [OH^-] from its structure. Commercially, bentonite is a rock term used to designate a naturally occurring, very fine grained, light weighted, and opacity material, largely composed of clay minerals, i.e. montmorillonite with a small proportion of feldspar, calcite, silica and gypsum. Chemically, montmorillonite is a hydrous aluminosilicate containing small amounts of alkali and alkaline earth metals. Montmorillonite has very high cation exchange capacity (CEC) and water holding capacity with large expansion [9]-[10].

Table 1. Physicochemical properties of acid sulfate soils

Soil series	Soil horizon	Depth (cm)	pH 1:1 Soil:H_2O	EC 1:5 dS m^{-1}	Clay content (%)	Organic carbon (%)	CEC ($cmol_c\ kg^{-1}$)
active acid sulfate soils							
Se	Ap	15	4.12	0.6	58.8	1.8	33.2
	Cg	100	2.76	2.49	32.8	5.0	36.5
Rs	Apg	7.5	4.99	0.21	48.0	2.5	29.8
	Cg	85	2.58	2.85	47.2	4.4	34.9
Ok	Apg	18	4.41	0.54	50.4	3.1	29.7
	Cg	85	2.68	3.29	33.2	4.7	36.1
Potential acid sulfate soils							
Bp	Apg	8	5.10	0.35	59.2	2.0	31.6
	Cg	75	6.75	0.56	63.6	0.5	29.6
Cc	Apg	15	6.79	0.14	47.2	2.4	28.8
	Cg	100	5.06	0.48	58.8	1.1	31.5

Remarks: pH 1:1 by pH meter in soil:water of 1:1, EC 1:5 by electrical conductivity meter in soil:water of 1:5, clay content by pipette method, organic carbon by Walkley and Black titration method, Cation exchange capacity (CEC) by 1 M NH_4OAc pH 7.0 method.

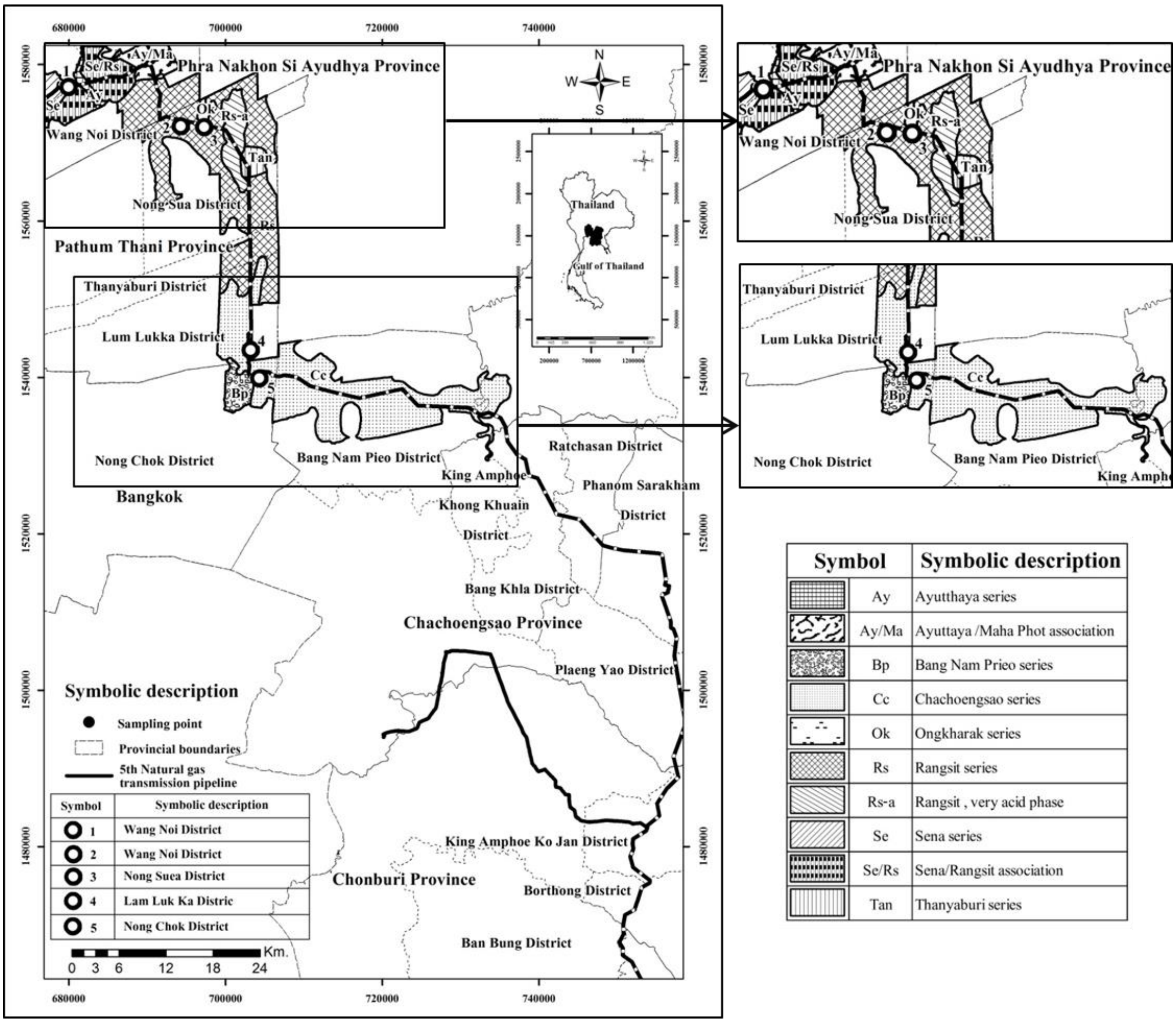

Figure 1. Soil sampling sites in the 5th transmission natural gas pipeline Rights of Way.

Table 2. Some selected properties of Na-bentonite

Properties	Analytical values
pH	9.26
CCE (%)	22
Alkalinity (mmol OH kg^{-1})	962

Remarks: pH by pH meter, CCE (calcium carbonate equivalent) and alkalinity determined by HCl dissolution and black titration.

2.2. pH Buffering Capacity Measurement

Soil pH buffering capacity (pHBC) of soil samples in Table 1 were determined by the modified method of Aitken and Moody [11] by adjusting concentration of alkaline ($Ca(OH)_2$) and acid (HCl) from 0.04 M to 0.4 M. The adjustment was made to meet target pH 6.0. Four grams of soil samples were incubated with the incremental amounts of 0.4 M $Ca(OH)_2$ and 0.4 M HCl of 0, 0.1, 0.25, 0.5, 1, 2.0, 4.0, 8.0 ml or being equally to 0 , 20, 50, 100, 200, 400, 800, 1600 mmol $OH^- kg^{-1}$ soil, and 0, 10, 25, 50, 100, 200, 400, 800 mmol $H^+ kg^{-1}$ soil, respectively. The incubation was conducted for 6 days prior to measure their pH.

Soil pHBC was calculated by fitting with sigmoid function according to the method described by Nelson and Su [12] and Luo *et al.*[13] as the following equation

$$pH = pH_{min} + \frac{a}{1+e^{\frac{-(A-A_{mid})}{b}}} \qquad \text{(Eq. 1)}$$

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Where A is the amounts of acid added (inserted as a negative value) and alkaline added (and inserted as a positive value) A_{mid}, a, b and pH_{min} are fitted constants, was fitted to the pH measurement data by iteration using Solver in Microsoft Excel 2013. To calculate pHBC for the studied soils fitted with the sigmoid function, Eq. 1 was rearranged to obtain A as a function of pH, and then differentiated to the following Eq.2.

$$pHBC = \frac{dA}{dpH} = \frac{\mathrm{ab}}{(\mathrm{a}+\mathrm{pH_{min}}-\mathrm{pH})(\mathrm{pH}-\mathrm{pH_{min}})} \qquad \text{(Eq. 2)}$$

The fitting parameters from sigmoid function (Eq.1) were then used to calculate the amounts of OH^{-1} (mmol kg^{-1}) to raise soil pH to pH 6.0 by Eq. 3. The calculated amounts of OH^- from Eq.3 was used to further calculate as the bentonite equivalent.

$$\mathrm{A} = \mathrm{A_{mid}} - \mathrm{b} \times \mathrm{Log}\left(\frac{\mathrm{a}}{\mathrm{target\ pH}-\mathrm{pH_{min}}} - 1\right) \qquad \text{(Eq. 3)}$$

2.3. Determination of the Effects of Na-bentonite on pH Change of Acid Sulfate Soils in Natural Gas Transmission Pipeline Rights-of-Way

The selected soil samples were incubated with dried Na-bentonite at the rates of 0, 100, 200, 300, 400, 500, 600, 700, 800, 900 g kg^{-1} soil for 6 days at 25 C° then pH of each soil mixture was determined. The linear regression model was used to fit between logarithmic pH (Log[pH]) and bentonite rates (Log[bentonite]). The bentonite rates derived from the regression model were compared with those derived from the pHBC model.

3. Results and Discussion

3.1. Soil pHBC of Acid Sulfate Soils in Natural Gas Transmission Pipeline Rights-of-Way

The sigmoid function was well fitted with pH curve in this study indicated by high coefficient of determination (R^2) values (Table 3). The sigmoid fitting parameters and pHBC at pH_{mid} of acid sulfate soils in Table 3 revealed that all parameters are in diverse values among studied soils. However, the active soil series (Se, Rs and Ok soil series) had high pHBC values ranged from 51-159.3 mmol kg^{-1} pH $unit^{-1}$ and higher than potential acid sulfate soils (Bp and Cc series) (40.4-78.5 mmol kg^{-1} pH $unit^{-1}$) indicated that these soils needs more alkaline or acid to change one pH unit at pH_{mid} or infection point of slope in the sigmoid curve. High pHBC values of these soils are affected by acidity from oxidation of pyrite indicating by very low pH value especially in subsoil samples (Table 1). On the other hand, the pHBC of soils is depended on mineral phase, organic matter content and the concentration of Al^{3+} in soil solution, taking into account the increase in pHBC at low pH [14][15]. In addition, the studied acid sulfate soils have similar high clay content, high cation exchange capacity but quite different in organic content and pH values. So, the variations in organic carbon and soil pH made these soils different in their pHBC. This is due to organic carbon and Al^{3+} directly related to effective cation exchange capacity which was closely correlated with pHBC [12] [15].

Moreover, the pHBC of studied acid sulfate soils varied considerably with pH (Figure 2) and markedly increased at pH = 3.0 and pH = 10.0. These characteristics are due to their nature of permanent charges of soil clay which markedly differ from the study of Nelson and Su [12] who reported the lower pHBC of variable charge acid soils from Australia and Papua New Guinea than the acid sulfate soils in our study. However, there are considerably different in the magnitudes of pHBC between the studied acid sulfate soils (Figure 2), that is due to very low pH and higher organic contents especially in the subsoil horizons of Se, Rs and Ok series.

Table 3. Sigmoid fitting parameters and pHBC of acid sulphate soils

Soil series-genetic horizon	a	b	A_{mid}	pH_{min}	Adj. R^2	pH_{mid}	pHBC at pH_{mid} (mmol kg^{-1} pH $unit^{-1}$)
Se-Apg	9.97	127.1	79.4	1.57	0.999	6.56	51.0
Se-Cg	10.53	350.3	565.7	1.00	0.991	6.27	133.0
Rs-Apg	10.53	167.6	73.4	1.25	0.933	6.51	63.7
Rs-Cg	11.04	323.9	617.7	1.26	0.874	6.78	117.4
Ok-Apg	10.37	151.1	142.3	1.47	0.988	6.66	58.3
Ok-Cg	10.24	407.5	631.3	0.98	0.986	6.10	159.3
Bp-Apg	10.56	207.3	122.8	1.08	0.870	6.36	78.5
Bp-Cg	9.98	100.8	7.9	1.30	0.977	6.29	40.4
Cc-Apg	10.54	130.9	16.3	1.39	0.955	6.66	49.7
Cc-Cg	9.39	145.6	59.5	1.44	1.000	6.14	62.0

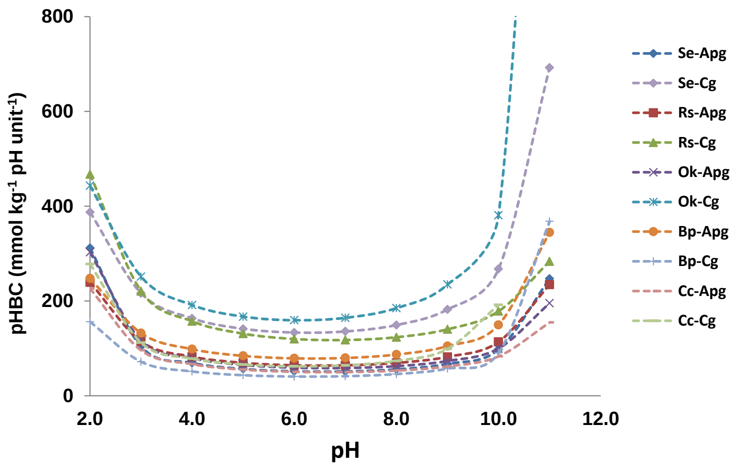

Figure 2. The relationship between pH buffer capacity (pHBC) and pH for acid sulfate soils.

3.2. Effects of Na-bentonite on pH Change of Acid Sulfate Soils in Natural Gas Transmission Pipeline Rights-of-Way

The well fitted linear regression (R^2 range of 0.90-0.99) between the logarithmic of pH and bentonite added rate for acid sulphate soils (Figure 3 and Table 4) indicated that bentonite significantly increased pH of acid sulfate soils especially in the subsoil layers of Se, Rs and Ok series which have higher slope than the topsoils, and the slopes of potential acid sulfate soils (Bp and Cc series). These results demonstrated that alkalinity from Na-bentonite (approximately 962 mmol OH^{-1} kg^{-1}) had a capacity to raise pH up to 6.0 which is in normal rage. This pH value is recommended for liming requirement that restricts to dissolution of aluminium which is toxic to plant root. The predicted bentonite rate is strikingly different among soil samples. The higher application rate was in the subsoils of Se, Rs and Ok series due to these soils had very high pHBC values.

The bentonite rates derived from pHBC (Eq. 3) and those from the incubation method were both able to increase pH to 6.0 of each acid sulfate soil sample in the similar order of magnitude (Table 5). Our results imply that the parameters derived from sigmoid equation can be used to predict the optimal bentonite rate for reducing severe acidic pH, allowing to apply into each acid sulfate soil series in the natural gas transmission pipeline Rights-of-Way.

Table 4. Linear model for prediction of Na-bentonite to adjust pH up to 6.0

Soil series	linear regression model	R^2	Log (bentonite) at pH 6.0	Bentonite rate at pH 6.0 (g kg^{-1})
Se-Ap	Log pH= 0.0871Log(bentonite)+ 0.6435	0.9871	1.55	35.15
Se-Cg	Log pH= 0.2674Log(bentonite)+ 0.0004	0.9717	2.91	810.16
Rs-Apg	Log pH= 0.0187Log(bentonite)+ 0.8093	0.9072	-1.67	0.02
Rs-Cg	Log pH= 0.2558Log(bentonite)+ 0.0591	0.9643	2.81	647.13
Ok-Apg	Log pH= 0.0737Log(bentonite)+ 0.6414	0.9813	1.86	71.70
OK-Cg	Log pH= 0.251Log(bentonite)+ 0.041	0.9829	2.94	864.68
Bp-Apg	Log pH= 0.0719Log(bentonite)+ 0.736	0.9933	0.59	3.86
Bp-Cg	Log pH= 0.0595Log(bentonite)+ 0.7285	0.9863	0.83	6.83
Cc-Apg	Log pH= 0.0597Log(bentonite)+ 0.7701	0.9588	0.13	1.36
Cc-Cg	Log pH= 0.0749Log(bentonite)+ 0.6667	0.9934	1.49	30.76

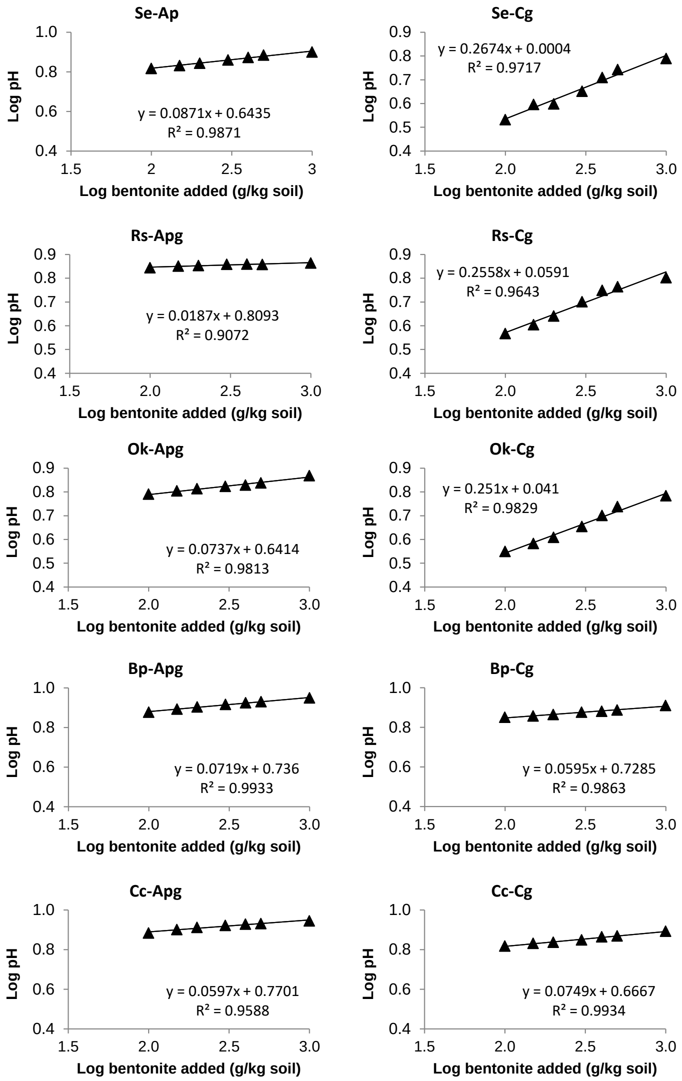

Figure 3. Linear regression of logarithmic pH [Log pH] and bentonite rates [Log bentonite].

Table 5. Comparison on Na-bentonite rate derived from incubation and pHBC prediction

Soil series	Bentonite rates (g kg^{-1}) needed for increasing soil pH to 6.0	
	incubation	pHBC
Se-Ap	36	70
Se-Cg	811	572
Rs-Apg	0.02	62
Rs-Cg	648	601
Ok-Apg	72	130
OK-Cg	865	649
Bp-Apg	4	115
Bp-Cg	7	3
Cc-Apg	2	2
Cc-Cg	31	58

4. Conclusions

The active acid sulfate soils with sulfuric materials (Rs, Ok, Se series) in the natural gas transmission pipeline RoW of Thailand have very high pHBC that require more OH^-/H^+ to change their pH, and relatively higher than the potential acid sulfate soils i.e. Bp and Cc soil series. The sigmoid function can be used to precisely predict soil pHBC of acid sulfate soils. Alkalinity derived from Na-bentonite could improve pHBC and raise soil pH up to the desired pH range, and also mitigate severe acidic conditions of these soils. Our findings imply that drilling mud Na-bentonite was beneficial to acid sulfate soils especially in the active acid sulfate soils at the natural gas transmission pipeline RoW, Thailand.

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