EFFECT OF CHLORIDES AND SULPHATES ON LIME TREATED MARINE CLAYS

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ABSTRACT

Soft marine clay deposits are present in many coastal regions of the world and they are usually enriched with chlorides and occasionally with sulphates. The use of lime to improve the properties of soft clay deposits is not new. A test program was carried out to study the changes in the particle level of soil systems attributed to lime in a marine environment. The formation of various new reaction products due to soil-lime reactions were identified by X-Ray Diffraction (XRD) and the same was investigated using Scanning Electron Microscope (SEM). The test results indicate that the presence of chlorides encourage the efficiency of lime stabilization, but the presence of monovalent sulphates affect the improvement of the soil system due to the formation of the swelling compound, ettringite. It is suggested, that the lime injection technique can be conveniently used to improve the behavior of soft marine clay deposits.

Key words: cementation compounds, engineering properties, lime injection, marine clays, soil-lime reactions (IGC: F2/K6)

INTRODUCTION

Soft marine clay deposits are located in many parts of the world and it is common to find them in coastal regions, on continental shelves and in offshore areas. The design and construction of many coastal and offshore structures in these deposits are confronted with many geotechnical problems (Bjerrum, 1973). It is necessary therefore to improve the engineering behavior of marine clays using appropriate soil improvement techniques. Conventional soil stabilization techniques are not effective because of severe wave conditions and large depths of water in the ocean environment. It is possible however to use some chemical injection techniques to improve underwater soft clays.

Many investigators reported the successful application of lime stabilization of soft clays (Yanase, 1968; Kitsugi and Azakami, 1982; Kamon and Bergado, 1991; Rajasekaran, 1994). Deep lime mixing was attempted to improve the engineering properties of soft marine clays in a Japan harbor area (Okumura and Terashi, 1975; Terashi et al., 1977). The successful use of the lime injection technique to improve the behavior of upland clays was reported by several researchers (Joshi et al., 1981; Sargunam et al., 1980; Kamon, 1992). The addition of inorganic additives like calcium sulphate, calcium chloride

and fly ash with lime improves the efficiency of lime stabilization of soft clays much better than lime alone (Kujala, 1983; Wu et al., 1983; Shanmuganathan and Oades, 1983). It has been proven that for land based soils containing sulphates, lime treatment causes severe distress problems to the various structures founded on them. The drop in pH and the formation of high swelling compounds such as ettringite and thaumasite due to lime-sodium sulphate reactions cause several adverse effects on the engineering behavior of the soil (Mitchell, 1986; Hunter, 1987). There is a necessity however to bring out the effectiveness of the lime injection technique in a marine environment with excessive monovalent (sodium) ions present in the pore water. It is also necessary to investigate the effect of lime stabilization in a marine environment which is rich with chlorides and sometimes with sulphates due to heavy industrial effluent to the sea.

For this investigation, an attempt was made to stabilize soft marine clays using lime injection technique. A testing program has been planned accordingly and carried out in order to establish the changes occurring in the soil system due to lime-inorganic additive stabilization. The details of the experimental setups adopted, soil and chemical additives used in the lime injection technique are presented below.

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EXPERIMENTAL INVESTIGATION

Soil Samples and Chemicals Used

The soil used in this investigation was obtained from the east coast of India (from Madras and Nova ports) and designated as soil 1 and soil 2, respectively. Soil samples were collected from shallow water depths and care was taken to remove the water by continuous pumping. The samples were air dried, powdered and properly stored. The untreated soil properties and the mineralogical composition of soils are given in Table 1. Commercially available hydrated lime ($\text{Ca(OH)}_2=82\%$) was used for all types of treatment. The other chemical additives such as chlorides and sulphates of sodium, potassium, calcium and magnesium of the same manufacture were used in an equal ratio (1:1) for the experimental program to study their effects with lime in a marine environment.

Test Programme

The soil samples were mixed with sea water to the required soft to medium stiff consistency and the natural moisture contents of soil 1 was 72% whereas for soil 2 it was 31%. These were placed in a test tank of size, 0.5 m $\times$ 0.5 m $\times$ 0.7 m in 25 to 50 mm layers and compacted lightly with a wooden tamper to remove the air voids. Hydrated lime slurry of 30% concentration was injected into the soil at predetermined points as shown in Fig. 1. The lime-inorganic additives slurry was injected into the soil bed under a pressure of 0.2 to 0.3 N/mm² by pushing a perforated injection pipe of 1.0 m length at predetermined points as shown in Fig. 1 into the refusal stage. Different tests carried out using grouts (injection slurries) made of various additives with lime have been attempted in the same type of experimental setups. Sea water of 50 mm depth was always maintained on top of the soil bed to avoid evaporation loss of water.

In this test program chemicals such as lime and inorganic additives were used in equal amounts to investigate the effect of these additives on lime stabilization of soils and their subsequent effects on the microchanges have been studied. Air dried powdered samples were used for the XRD analysis of soil samples (both untreated and treated) and the samples were scanned at a speed rate of 2°/minute using a standard Philips diffractometer for $2\theta=3^\circ$ to 50° . After 15 days treatment, undisturbed samples were collected from treated soil samples at a depth of 0.3 m to investigate the microchanges occurring at the

PLAN

Depth of the tank = 0.7 m

O - Injection point

* - Sampling point

Fig. 1. Schematic diagram of test tank used

particle level of the treated soil systems. Cubical specimens of size, 10 mm were placed in carbowax (polyethylene glycol 6000) solution at 55°C (Wilson, 1987). The samples were then air-dried and the fractured surface (horizontal plane) of the specimens were gold coated to view the soil structure and the nature of the products formed due to different chemicals treatment. The micrographic details of the samples obtained are discussed in the following sections.

RESULTS AND DISCUSSIONS

XRD Studies

Samples were taken at the locations marked as shown in Fig. 1 and an XRD analysis was carried out. The obtained XRD patterns were compared with the standard ASTM (1991) powder diffraction file. The mineralogical analysis of untreated soil samples (both soil 1 and soil 2) indicate the presence of high swelling minerals such as montmorillonite, chlorite, vermiculite with traces of low swelling mineral, kaolinite (Fig. 2). The presence of non-clay mineral such as quartz in significant amount is also

Table 1. Physico-chemical properties of soils

Soil type	Liquid limit (%)	Plasticity index (%)	pH	Particle size distribution (%)			c.e.c* (m.eq/100 g of the soil)	Clay minerals composition (%)				
				0.075 mm-0.425 mm	0.002 mm-0.075 mm	<0.002 mm		M	C	K	V	Q
soil 1	76	48	7.36	4	49	47	46	27	12	22	8	31
soil 2	33	21	7.12	7	72	21	32	11	30	28	4	27

M-montmorillonite, C-chlorite, K-kaolinite, V-vermiculite, Q-quartz

*-cation exchange capacity

M - montmorillonite, K - kaolinite, C-V-M - chlorite-vermiculite-montmorillonite, Q - quartz, CA - calcium aluminate, CAH - calcium aluminate hydrate, CSH - calcium silicate hydrate, CASH - calcium aluminate silicate hydrate

Fig. 2. Untreated samples

Fig. 3(a). Lime-calcium chloride treated samples

Fig. 3(b). Lime-sodium chloride treated samples

seen. Figures 3(a) and 3(b) represent the typical XRD patterns of lime-calcium chloride and lime-sodium sulphate injected soil systems after 45 days treatment. The formation of various new reaction products due to soil-lime reactions are summarized and given in Table 2. In most of the cases, the formation of new reaction products such as calcium silicate hydrate (CSH), and calcium aluminate hydrate (CAH) and calcium aluminate silicate hydrate (CASH) groups can be seen. These compounds help in the formation of aggregates which bind the particles together and result in the overall improved behaviour of the soil (Ingles and Metcalf, 1972; Kawamura and Diamond, 1975). The formation of high swelling compound, a needle shaped calcium sulphaaluminate (E-ettringite) can be seen in lime-sodium sulphate treated soil system (Fig. 3(b)) and this produce adverse effects in the lime treated soil systems such as reduction in strength and increase in compressibility as reported by earlier investigators (Mitchell, 1986; Hunter, 1987).

Table 2. Reaction products formed/modified for different lime treated soil systems

S. No	Type of treatment	Soil 1		Soil 2	
		Basal spacing, d (Å)	Product formed	Basal spacing, d (Å)	Product formed
1.	Lime with sodium chloride	1.99	CSH	1.99	CSH
		2.10	CA	2.10	CA
		2.81	CSH	—	—
		3.42	CAH	3.42	CAH
		3.65	CAH	3.65	CAH
2.	Lime with potassium chloride	4.22	CASH	4.22	CASH
		1.99	CSH	1.99	CSH
		2.10	CA	2.10	CA
		2.81	CSH	—	—
		4.22	CASH	4.22	CASH
3.	Lime with calcium chloride	1.91	CaCO ₃	—	—
		1.99	CSH	1.99	CSH
		2.10	CA	2.10	CA
		2.81	CSH	—	—
		3.06	CSH	—	—
		3.42	CAH	3.42	CAH
		3.65	CAH	3.65	CAH
		4.22	CASH	4.22	CASH
4.	Lime with magnesium chloride	4.40	CASH	—	—
		1.99	CSH	1.99	CSH
		—	—	2.10	CA
		2.81	CSH	—	—
		3.42	CAH	3.42	CAH
5.	Lime with sodium sulphate	—	—	3.65	CAH
		4.22	CASH	4.22	CASH
		9.73	E	—	—
		—	—	20.62	E
		1.99	CSH	1.99	CSH
		—	—	2.10	CA
		2.62	E	2.62	E
		2.81	CSH	—	—
6.	Lime with potassium sulphate	3.42	CAH	3.42	CAH
		—	—	3.65	CAH
		3.79	E	—	—
		—	—	4.22	CASH
		—	—	—	—
		9.73	E	—	—
		—	—	20.62	E
		—	—	—	—
7.	Lime with calcium sulphate	1.91	CaCO ₃	—	—
		1.99	CSH	1.99	CSH
		2.10	CA	2.10	CA
		—	—	—	—
		3.06	CSH	—	—
		3.42	CAH	3.42	CAH
		—	—	3.65	CAH
		4.22	CASH	4.22	CASH
8.	Lime with magnesium sulphate	4.40	CASH	—	—
		8.92	CAGH	—	—
		1.91	CaCO ₃	—	—
		1.99	CSH	—	—
		2.10	CA	2.10	CA
		—	—	—	—
		3.06	CSH	—	—
		3.42	CAH	3.42	CAH
		—	—	3.65	CAH
		4.22	CASH	4.22	CASH
		4.40	CASH	—	—
		8.92	CAGH	—	—
		—	—	—	—

CAH-calcium aluminate hydrate, CSH-calcium silicate hydrate, CASH-calcium aluminate silicate hydrate, CA-calcium aluminate, CaCO₃-calcium carbonate, E-ettringite, CAGH-calcium aluminate gypsum hydrate

SEM Studies

The micrographs of the untreated soil samples at a depth of 0.3 m at a radial distance as marked in Fig. 1 are discussed in the following sections of this paper. In the present investigation, the samples obtained from Cuddalore are designated as soil 1 and the samples obtained from port Nova designated as soil 2. Figure 4(a) shows the micrograph of soil 1 which indicate the presence of carbonates (porous like material) on the top left hand corner. Figure 4(b) shows large cusp like crystals in a joined fashion with fuzzy arrangement of individual particles. These micrographs indicate the presence of highly crumpled and curled flakes of soil particles. This is the characteristics of montmorillonite minerals and this type of partially flocculated arrangement of particles can usually be seen in sea water sedimented soils. The poorly crystalline kaolinite particles with thin swirl like fabric can be seen in Fig. 4(c), and the enlarged view of the same sample (soil 2) indicates thin platelet of the same mineral, kaolinite (Fig. 4(d)).

The micrographs of the lime treated samples were collected after 45 days treatment at a depth of 0.3 m the same as that of the untreated samples. Flocculated and aggregated mass with quartz packets can be seen in the

lime and sodium chloride treated soil 1 system (Fig. 5(a)). The highly magnified view of the same sample is seen in Fig. 5(b) which indicates the formation of fused clay particles to form concentrations and floccules at several places of the micrograph. Figure 5(c) shows the micrograph of the marine clay (soil 2) treated with sodium chloride and the C-S-H gel like vesicular formation extending into the pore system with a well knit frame work between the aggregated fused soil units can be seen. The formation of these cementation compounds in soil-lime treated systems was reported earlier by Kawamura and Diamond (1975).

Reaction of lime with soil fused the clay particles and formed crystal lumps in soil 1 treated with lime and potassium chloride. The edge to face flocculated arrangement of particles due to higher concentration of calcium can be seen at several places of the micrograph (Fig. 6(a)). The magnified view of the fused aggregated mass of the previous micrograph can be seen in Fig. 6(b). The micrographic view of lime-potassium chloride treated sample (soil 2) is shown in Fig. 6(c) and the reaction products coating the fabric elements result in a uniform distribution of aggregates. The magnified view of the above sample with a stable fused clay particles can be seen in Fig.

Fig. 4(a). Micrograph of untreated marine clay (soil 1)

Fig. 4(b). Micrograph of untreated marine clay (soil 1)

Fig. 4(c). Micrograph of untreated marine clay (soil 2)

Fig. 4(d). Micrograph of untreated marine clay (soil 2)

6(d).

Figures 7(a) and 7(b) show the microfabric view of the lime-calcium chloride treated soil system which indicate

clay aggregates at several places of the micrograph and the formation of well formed aggregates is due to the vigorous action of lime and calcium chloride on soil parti-

Fig. 5(a). Micrograph of lime and sodium chloride treated marine clay (soil 1)

Fig. 6(a). Micrograph of lime and potassium chloride treated marine clay (soil 1)

Fig. 5(b). Micrograph of lime and sodium chloride treated marine clay (soil 1)

Fig. 6(b). Micrograph of lime and potassium chloride treated marine clay (soil 1)

Fig. 5(c). Micrograph of lime and sodium chloride treated marine clay (soil 2)

Fig. 6(c). Micrograph of lime and potassium chloride treated marine clay (soil 2)

Fig. 6(d). Micrograph of lime and potassium chloride treated marine clay (soil 2)

Fig. 7(a). Micrograph of lime and calcium chloride treated marine clay (soil 1)

cles (Fig. 7(b)). The fluffy coating over the soil particles with a kind of spongy appearance can be seen in soil 2 system treated with lime and calcium chloride (Fig. 7(c)).

Highly flocculated aggregates with an indiscriminate coating can be seen in soil 1 treated with lime and magnesium chloride (Fig. 8(a)). The magnified view of the sample indicates the presence of well fused aggregates all over the micrograph (Figs. 8(b) and 8(c)). Figure 8(d) shows the microfabric view of the soil 2 system treated with lime and magnesium chloride, and the micrograph shows fabric elements masked together to form large flocules. The magnified view of this sample indicates the indiscriminate fusion of elements (Fig. 8(e)) to form well knit work and these compounds are nothing but the cementation compounds such as CAH and CSH as confirmed previously by XRD in the earlier section.

The curled dispersive nature of the aggregates in soil 1 treated with lime and sodium sulphate can be seen in Fig. 9(a). Figure 9(b) indicates the formation of needle shaped ettringite particles in between the aggregates of lime-soil reaction products. Figures 9(c) to 9(e) show the dispersive nature of soil 2 treated with lime and sodium sulphate. It has been already well established that the presence of monovalent sulphates induce the formation of ettringite (calcium sulphotoaluminate) which is expansive in nature. The formation of ettringite and its adverse effects on the soil system was reported in sulphate enriched land based soils (Kujala, 1983; Kamon and Nontananandh, 1991). The micrographs of the lime and potassium sulphate treated soil systems (soil 1 and soil 2) are shown in Figs. 10(a) to 10(b) which indicates a dispersive nature of aggregates. The effects of lime stabilization in the presence of potassium sulphate is not serious compared to the lime-sodium sulphate treated system.

The severe attack of lime on the surface of soil particles can be seen in soil 1 and soil 2 systems treated with calcium sulphate (Figs. 11(a) and 11(b)). Aggregates with a spongy and fluffy like mass can be seen in several places on the micrograph due to the vigorous attack of lime on the soil particles. Figure 12(a) shows the nonuniform size

Fig. 7(b). Micrograph of lime and calcium chloride treated marine clay (soil 1)

Fig. 7(c). Micrograph of lime and calcium chloride treated marine clay (soil 2)

of fused aggregates which is the result of the severe attack of lime in soil 1 treated with magnesium sulphate. This resulted in highly flocculated aggregates with in-

Fig. 8(a). Micrograph of lime and magnesium chloride treated marine clay (soil 1)

Fig. 8(b). Micrograph of lime and magnesium chloride treated marine clay (soil 1)

Fig. 8(c). Micrograph of lime and magnesium chloride treated marine clay (soil 1)

Fig. 8(d). Micrograph of lime and magnesium chloride treated marine clay (soil 2)

Fig. 8(e). Micrograph of lime and magnesium chloride treated marine clay (soil 2)

discriminate coating of reaction products and similar flocculent structure can be seen in the soil 2 treated soil system with lime and magnesium sulphate (Figs. 12(b) and

12(c)).

These test results indicate that the addition of different inorganic chemicals with lime accelerates the soil-lime reactions favorably in the formation of cementitious compounds except in the sulphate environment. The reaction of lime with the soil in a monovalent (sodium) sulphate environment increases the double layer thickness of the soil particles which result in the formation of a swelling compound such as calcium sulfoaluminate (ettringite). Due to the lateral growth of these crystals with time, adverse swelling effects to the engineering structures resting on these deposits are produced. Due to the fully submerged and saturated condition of the marine clays, however the problems due to ettringite formation are not severe.

Strength and Deformation Behaviour of Soils

The soil-lime reactions contributed to several changes of the engineering behavior of different lime treated systems and a test program was carried out by conducting several laboratory vane shear tests based on ASTM D 4648-87 (1987) procedure. Several tests were conducted

Fig. 9(a). Micrograph of lime and sodium sulphate treated marine clay (soil 1)

Fig. 9(b). Micrograph of lime and sodium sulphate treated marine clay (soil 1)

Fig. 9(c). Micrograph of lime and sodium sulphate treated marine clay (soil 2)

Fig. 9(d). Micrograph of lime and sodium sulphate treated marine clay (soil 2)

Fig. 9(e). Micrograph of lime and sodium sulphate treated marine clay (soil 2)

Fig. 10(a). Micrograph of lime and potassium sulphate treated marine clay (soil 1)

on samples collected after 45 days of treatment and the test results are presented in Table 3. A strength improvement of 2 to 4 times that of the untreated soil system was

obtained, and the improvement in the strength of the soil was due to the formation of new cementation compounds such as calcium silicate hydrate (CSH) and calci-

Fig. 10(b). Micrograph of lime and potassium sulphate treated marine clay (soil 2)

Fig. 12(a). Micrograph of lime and magnesium sulphate treated marine clay (soil 1)

Fig. 11(a). Micrograph of lime and calcium sulphate treated marine clay (soil 1)

Fig. 12(b). Micrograph of lime and magnesium sulphate treated marine clay (soil 2)

Fig. 11(b). Micrograph of lime and calcium sulphate treated marine clay (soil 2)

Fig. 12(c). Micrograph of lime and magnesium sulphate treated marine clay (soil 2)

um aluminate hydrate (CAH). The lime induced changes that occurred in the compressibility properties of the soil were investigated by conducting several Oedometer tests

based on ASTM D 2435-80 (1989) procedure. There was an appreciable decrease in the compressibility up to 1/2 to 1/3 of the original values due to lime treatment (Table

Table 3. Strength and deformation behavior of soils

Test No	Type of treatment	Water content (%)		Dry density (g/cm ³)		Shear strength(kN/m ²)		Cc	
		Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2
1.	Untreated samples	72	31	1.06	1.2	34	37	0.79	0.72
2.	Lime and sodium chloride	51	25	1.26	1.41	109	102	0.57	0.55
3.	Lime and potassium chloride	49	25	1.28	1.43	103	107	0.54	0.53
4.	Lime and calcium chloride	41	18	1.57	1.54	149	153	0.46	0.41
5.	Lime and magnesium chloride	46	23	1.46	1.47	138	142	0.52	0.49
6.	Lime and sodium sulphate	67	26	1.1	1.25	46	42	0.82	0.79
7.	Lime and potassium sulphate	66	24	1.2	1.23	56	51	0.72	0.69
8.	Lime and calcium sulphate	42	19	1.54	1.48	146	142	0.53	0.51
9.	Lime and magnesium sulphate	48	21	1.57	1.53	136	131	0.59	0.57

3).

The use of calcium chloride with quicklime is the best additive for improving soil behavior however for soils rich with sodium sulphate, the lime stabilization technique is not effective. The addition of calcium sulphate and calcium chloride with quicklime increases the shear strength with a corresponding decrease in compressibility of the soil system, much better than other lime treated systems. This is due to the diffusion of additional calcium ions within the soil system resulting in concentration of cations near the soil particles and resulting in a better formation of the reaction products. The test results reveal that the presence of sea water does not affect the development of strength and reduction in compressibility in lime treated marine clays. In the quicklime-sodium sulphate treated soil system, however the improvements in the engineering properties are not encouraging.

CONCLUSIONS

The following conclusions were drawn from the experimental program carried out. The formation of aggregates/concentrations of particles of different sizes can be seen in all lime treated soil systems, and the addition of chlorides with lime result in a better formation of pozzolanic compounds. Adverse effects were induced for lime treated soils predominant with sodium sulphate, and this is due to the formation of the expansive nature of mineral, ettringite. For other sulphate treated soil systems, lime induced changes are similar to that of chloride salts. The formation of cementation compounds such as CAH and CSH due to soil-lime reactions can be seen in all lime treated soil systems and the same has been confirmed using XRD and SEM techniques. The results

of this investigation have established that the presence of excessive sodium ions in sea water do not retard the formation of these compounds. For weak marine clays encountered deep below water, the lime injection technique is better suited but one has to be cautious in using lime stabilizing technique in soils saturated with sodium sulphate.

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