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On suitability of stabilizer based on chemical analysis of the liquid from stabilized soil

L'analyse chimique du liquide sortant du sol stabilisé et la discussion sur le stabilisateur

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ABSTRACT: The stabilizers for soft soil mainly consist of cement, gypsum and active material in different proportion. Each stabilizer has its own suitability respectively. Stabilized soil samples were subjected to a series of tests, including chemical analyzing composition of the liquid squeezed from them. It was revealed that there exist great difference among the concentration of CaO and OH^- in the stabilized soils. It is the concentration that governs the quantity and behavior of the stabilizer's hydrates and therefore defines the suitable scope of the stabilizers.

RESUME: Les stabilisateurs pour le sol mou consistent principalement en ciment, gypse et matériel actif dans une proportion différente. Chaque stabilisateur a respectivement sa propre convenabilité. Les échantillons du sol stabilisé sont soumis à une série de tests, y compris l'analyse chimique de la composition du liquide pressé depuis le sol stabilisé. Ce qui révèle qu'il existe une grande différence dans la concentration de CaO et de OH^- , parmi ces sols stabilisés. C'est cette concentration qui régit la quantité et le comportement des hydrates du stabilisateur, donc définit aussi la portée convenable des stabilisateurs.

1 INTRODUCTION

The stabilizer for stabilizing soft soil may be composed of cement, gypsum and active material, etc. in different proportion. Each stabilizer has its own suitable scope respectively. For instance, to some kinds of soil, the strength of stabilized soil is much higher when the cement-gypsum stabilizer is used than that when cement only is used, but for some other soil, the result may be contrary.

In this study, stabilized soil samples were subjected to following tests: (1)chemical analyzing the composition of the pore water squeezed from them, (2)observing the hydrates of the stabilizer in them, (3)testing the strength of them. Besides the amount of CaO and OH^- consumed by the soil was measured.

The disparity of the concentration of the liquid in stabilized soils made from different soil samples and its influence on the yield and behavior of the hydrates in the stabilized soil were the main point to be interested in; and based on that, the suitable condition for the stabilizer was discussed.

2 METHODS USED IN THE TEST

The properties of the selected soil samples are shown in table 1. 425# Portland cement, gypsum lime mortar ($CaSO_4 \cdot 1/2H_2O$) and city water were used if not claimed.

Table 1. Properties of soil samples

No.	Name	γ (kN/m^3)	ω (%)	e	pH	Organic coontent (%)
1	Mucky clay	17.0	55	1.48	6.7	6.24
2	Mucky clay	17.6	50	1.43	6.8	4.77
3	Mucky loam	18.0	34	1.03	7.2	5.01
4	Mucky sandy loam	18.1	36	1.01	7.3	5.11

Stabilized soil samples were made by mixing stabilizer slurry (stabilizer / water = 0.6, in weight) with the selected soil samples. Some of them were tested to obtain unconfined compressive strength. The others were sealed into plastic pocket for fear being dehydrated and carbonated, and then squeezed to schedule to get pore water that was analyzed immediately. Hydrates of the stabilizer in the stabilized soil were observed by SEM and X-ray on the 15th day. Ethanol was used to cease the hydration in stabilized soil.

20g air-dried soil powder (passed 0.2mm sieve) was blended with 100 ml saturated $Ca(OH)_2$ solution. Then the filtrate was taken to measure the amount of CaO and OH^- consumed by the soil samples.

The details of the test methods could be seen in reference (Hung 1990).

3 THE RESULTS

Part of the strength test results are shown in table 2, where sample i-k was made from soil i (i=1, 2, 3, 4); $A_w = (\text{dry weight of stabilizer} / \text{wet weight of soil}) \times 100\%$, $B = (\text{weight of gypsum} / \text{weight of whole stabilizer}) \times 100\%$. For convenience, in the following, the stabilizer composed of cement and gypsum was called CG stabilizer; the stabilized soil stabilized by cement was called cement soil, and that stabilized by CG stabilizer called gypsum soil. The B in the table 2, for soil 1 and soil 2, were the optimal ones according a series of test; for soil 3 and soil 4, as soon as $B > 5$, the strength of gypsum soil would be lower than that of corresponding cement soil. Even if fixing the amount of cement and adding gypsum, instead of substituting cement by gypsum, the result was same.

Table 2. Unconfined compressive strength of stabilized soil

Sample	A_w (%)	B (%)	Compressive strength q_u (kPa)	
			15d	30d
1-1	10	0	536	818
2-1	10	0	778	1038
3-1	10	0	1254	1479
4-1	10	0	1289	1574
1-2	10	25	1323	1642
2-2	10	15	1003	1297
3-2	10	5	1021	1328
4-2	10	5	1072	1410

The results show that: to the different soils, the strength of cement soil with same A_w differed greatly, so did the stabilizing effect of CG stabilizer. If name increase of strength = strength of gypsum soil - that of cement soil, then plus increase of strength would be obtained for soil 1 and soil 2, but minus ones for soil 3 and soil 4, which was also proved by the results of about a hundred sets of test.

The analysis results and calculated value of pH and $(Ca^{++}) \cdot (OH^-)^2$ of the liquid in cement soil samples are

shown in table 3. The solubility product of saturated $\text{Ca}(\text{OH})_2$ liquid

$$K_{sp} = (\text{Ca}^{++}) \cdot (\text{OH}^-)^2 = 4.44 \times 10^{-5}$$

From table 3, it can be seen that the liquid in the cement soil was not saturated. That is essentially different from cement plaster and concrete, in which the liquid are always $\text{Ca}(\text{OH})_2$ saturated. The liquid of sample 1 and sample 2 were far below $\text{Ca}(\text{OH})_2$ saturated point, while that of sample 3 and sample 4 were close to it.

Table 3. Composition of liquid in cement soil

Sample	Age	Calculation Value		Composition (mmol / l)	
		pH	$(\text{Ca}^{++}) \cdot (\text{OH}^-)^2$	(OH^-)	CaO
Sample 1—1	5h	12.18	1.41×10^{-6}	15.88	7.86
	2d	12.26	2.41×10^{-6}	18.23	10.18
	5d	12.18	8.67×10^{-6}	15.29	5.19
	10d	12.25	1.51×10^{-6}	17.65	6.79
Sample 2—1	5h	12.46	1.15×10^{-5}	29.41	18.57
	2d	12.50	8.49×10^{-6}	31.76	11.79
	5d	12.45	3.16×10^{-6}	28.23	5.54
	10d	12.48	4.47×10^{-6}	30.00	6.96
Sample 3—1	5h	12.51	2.06×10^{-5}	32.35	27.50
	2d	12.35	2.28×10^{-5}	22.35	8.21
	5d	12.81	9.25×10^{-6}	65.29	3.04
	10d	12.73	8.78×10^{-6}	53.53	4.29
Sample 4—1	5h	12.55	2.96×10^{-5}	35.88	32.14
	2d	12.88	4.48×10^{-5}	75.29	11.07
	5d	12.79	1.09×10^{-5}	62.35	3.93
	10d	12.87	2.07×10^{-5}	74.71	5.18

Note: h—hour. d—day.

Figure 1 are the photos of SEM of the stabilized soil. Photo 1—Photo 4 are for cement soil sample 1—1~4—1. The hydrates in it were mainly fibre like CSH adhered to the wall of voids to cement the soil particles together. Photo 5—6 are for gypsum soil sample 2—2 and 4—2. It can be seen that ettringite appeared in the hydrates, but the shape of them were different in the samples made from different soils. In the sample 1—2 and 2—2, large amount of needle shaped ettringite grew in the void, they intersected mutually forming spatial structure with CSH , which braced and filled up the void, as shown in Photo 5. While in the sample 3—2 and 4—2, the size of ettringite crystal were much smaller than that in sample 1—1 and 2—2, and the tiny ettringite crystal mostly grew in group right on the surface of the particles, instead in voids, as shown in Photo 6.

The X-ray graphs of the gypsum soil were similar to that of the cement soil, except that the characteristic peak of ettringite appeared. The strength of the peak at $d=5.61\text{\AA}$, which was scarcely interfered by other peaks, took such order: sample 1—2's > sample 2—2's > sample 3—2's \approx sample 4—2's.

The amounts of CaO and OH^- consumed by different soil samples were different, so was the ratio of OH^- / CaO , as shown in table 3.

Table 4. Quantity of CaO , OH^- consumed by soil

Soil No	Consumed quantity (mg/100g)		
	OH^-	CaO	OH^- / CaO
Soil 1	322.3	520.9	0.619
Soil 2	289.4	481.7	0.601
Soil 3	274.3	471.4	0.582
Soil 4	265.9	458.2	0.580

4 DISCUSSION

4.1 Particularity of hardening environment in stabilized soil.

Hardening process of stabilized soil is that in which the physical and chemical reaction proceed between stabilizer and

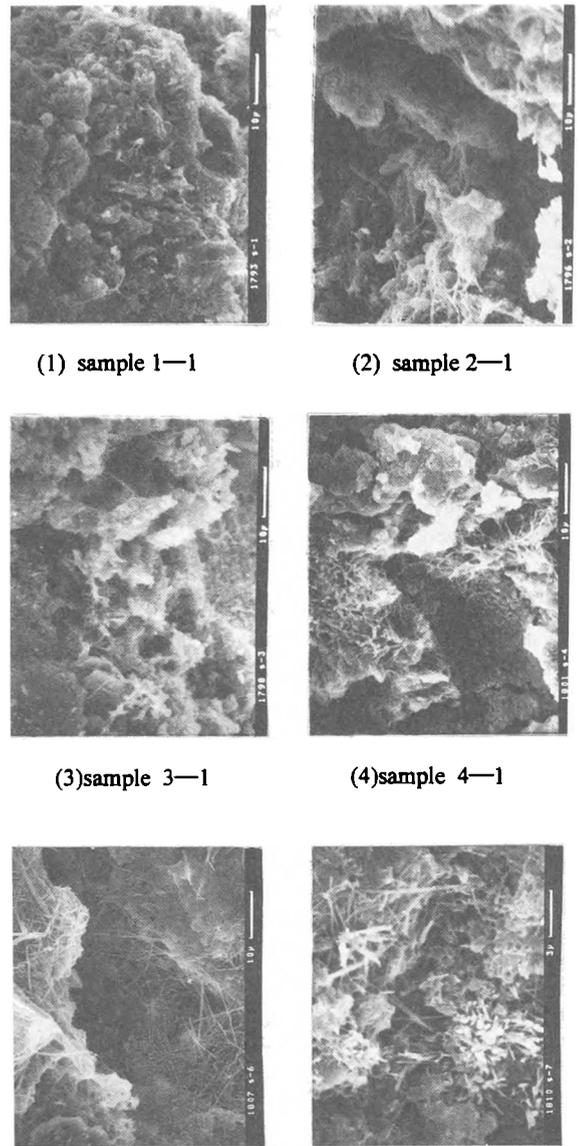


Figure 1. Photos of SEM of stabilized soil

soil. Clay mineral, organic matter, cation exchange and many other factors will participate in the reaction, so they have great influence on the environment of hydrating and hardening in the stabilized soil.

Soil and stabilizer being taken as an entire complex system, comprehensive influence caused by all factors of the soil on the hydrating and hardening environment was studied by analyzing the composition of the liquid squeezed from stabilized soil.

Mixed with wet soil, cement release $\text{Ca}(\text{OH})_2$ that may exist in the form of Ca^{++} , OH^- and CaO . There is about 20% $\text{Ca}(\text{OH})_2$ in cement hydrates. Meanwhile, because of physical absorption, cation exchange, neutralization reaction, etc., soil may consume large amount of Ca^{++} , OH^- and CaO within minutes or hours (Diamond 1966). As the test results in this study shown, in many cases, the pore water in stabilized soil may not be saturated with $\text{Ca}(\text{OH})_2$, for the $\text{Ca}(\text{OH})_2$ released by cement may not be enough to meet that consumed by soil. the more the amount of Ca^{++} , OH^- and CaO consumed by soil, the lower the concentration of those in the stabilized soil.

It is obvious that the amount of Ca^{++} , OH^- and CaO consumed by soil and the concentration of those in the stabilized soil has correlation with the pH value of the soil. The pH of the soil used in the test were in the range of 6.7~7.3 only. Such a

little difference of pH resulted in tens times of difference of concentration of OH^- and CaO in the stabilized soil, so it can be inferred that the difference in the concentration of OH^- and CaO in stabilized soil would be much larger in practice.

As we shall see later on, it is the difference of the concentration of OH^- and CaO in stabilized soils made from different soil, especially when the liquid is not saturated with $Ca(OH)_2$, that determine the suitable scope of each stabilizer.

4.2 Influence of the concentration on CSH growing

In cement hydrates, calcium silicate hydrate (CSH) possessing cementing function makes chief contribution to strength. It showed that (Kazutaka 1985) : CSH formed in liquid has a certain Ca/Si ratio of about 1.2, and the thermodynamic equation of CSH formation was as following:

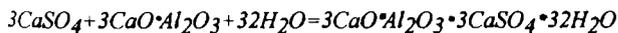


Initial Ca/Si and OH^-/Si ratios of the liquid affect the species of hydrate. If the ratios were rather low, silicate gel having no binding function would be predominant in hydrates; as the ratios increased, the proportion of CSH increased also.

In stabilized soil, when the liquid is not saturated with $Ca(OH)_2$, the soil will continue to consume Ca^{++} and OH^- that would otherwise have been used to form CSH, which, of course, reduces the amount of CSH in cement soil. Soil consuming Ca^{++} , OH^- and cement releasing $Ca(OH)_2$ take place simultaneously. Ca^{++} , OH^- and CaO being consumed at early age results in rather low initial Ca/Si and OH^-/Si ratio of the liquid. That lead to an increase of the yield of silicate gel, which further consume Ca^{++} , OH^- and decrease the amount of CSH too. Because it is cement hydrates such as CSH that make chief contribution to strength of stabilized soil, the difference in the amount of Ca^{++} , OH^- and CaO consumed by soil will cause the difference in yield of hydrates such as CSH and eventually result in difference in strength of stabilized soil, which was fully demonstrated by the test results: when the liquid in cement soil was not saturated with $Ca(OH)_2$, the concentration of OH^- and CaO in the cement soil and the value of $(Ca^{++}) \cdot (OH^-)^2$ took such order: sample 1—1's < sample 2—1's < sample 3—1's < sample 4—1's, and yield of hydrates in the cement soil and strength of the cement soil were also took such order. While the amount of OH^- and CaO consumed by soil took opposite order. That is to say, the higher the concentration of OH^- and CaO in cement soil, the more the yield of hydrates and the higher the strength, vice versa. And there exist minus relevant relation between the concentration of OH^- and CaO in stabilized soil and the amount of OH^- and CaO consumed by soil.

4.3 Influence of the Concentration on the Behavior of Ettringite

When CG stabilizer was mixed with wet soils, in addition to CSH, some amount of ettringite appeared, which was produced by the reaction between gypsum and calcium aluminate in cement, that was also verified by the x-ray and SEM observation. The reaction is as following:



There exist different shapes of ettringite, most properties of them are almost same, the volume of their solid phrase will expanding by 120% during its forming. But the expansion behavior of ettringite is determined by the concentration of OH^- and CaO of the liquid where the ettringite grow in (Xue 1985). When the liquid is $Ca(OH)_2$ saturated, the equilibrium concentration of Al_2O_3 is very low, and supersaturated degree of ettringite crystal separating is high, so ettringite separate in tiny crystal in group right at the surface of solid phrase involving aluminum. They support on solid phrase, with one end having a certain fixation, so they grow orientally. If they encounter obstacle during growing, the crystal growing will build up stress, which will destroy the existing link among particles, and result

in decrease of the strength. When the concentration of OH^- and CaO in liquid is very low, the equilibrium concentration of Al_2O_3 is rather high and supersaturated degree of ettringite crystal separating is rather low, so the single larger ettringite crystal will separate away from solid phrase and grow nonorientally in voids, such kind of ettringite do not fix on solid and grow freely in the voids, so the crystal growing stress will scarcely build up. The ettringite fill up voids in the structure, so increase the strength of it.

Based on the analysis result of the liquid in sample i—1, it could be deduced that the concentration of OH^- and CaO in the pore water of the gypsum soil sample 3—2 and 4—2, which were made from soil 3 and soil 4, were rather high, closing to the saturated point, while that of the sample 1—2 and 2—2 made from soil 1 and soil 2 were rather low. The test result showed that: in the sample 1—2 and 2—2, ettringite in larger crystal grew in voids in the stabilized soil and the strength increase of stabilized soil was plus; while in the sample 3—2 and 4—2, the ettringite in tiny crystal grew in group right at the surface of solid particles and the strength increase were minus.

Above analysis suggested that the stabilizer containing gypsum suit to stabilize the soil that consume large amount of OH^- and CaO , but can't be used to the soil that consume few OH^- and CaO .

4.4 Suitable Condition for the Stabilizers

Strength of the soil to be stabilized is very poor because the links among the soil particles are very weak and there are too many voids in the soil. In order to make stabilized soil acquire high strength, the stabilizer should has both functions of cementing soil particles together and filling up voids in the soil. As we know now, the hydrate having cementing function is mainly CSH come from cement hydrating and active material hydrating, the hydrate that can fill up voids at high efficiency is ettringite come from reaction between cement and gypsum.

Now we know that: (1) there exist great difference of the concentration of OH^- and CaO in the stabilized soil made from different kinds of soil, because the amount of OH^- and CaO consumed by different soil differ greatly, (2) the concentration of OH^- and CaO in the medium determine the yield and behavior of hydrates, that is the yield of CSH is large at high concentration of OH^- and CaO and decreases as the concentration of OH^- and CaO decrease; and only the ettringite growing in low concentration of OH^- and CaO can increase the strength of stabilized soil, (3) high concentration of OH^- and CaO in the medium is the prerequisite for active material to hydrate. Based on these, we can discuss the available scope of various stabilizers.

Mixed with soil, cement hydrates and generates $Ca(OH)_2$ and hydrates such as CSH. A certain amount of $Ca(OH)_2$ is consumed by soil as soon as it is released.

If the soil consumes little OH^- and CaO , the liquid in stabilized soil is still oversaturated with $Ca(OH)_2$. In such case, the cement hydrates such as CSH will not be influenced by surrounding medium and grow normally and amply; and for existing surplus $Ca(OH)_2$, active material added and active substance in soil can hydrate fully and produce hydrates such as CSH. Therefore, in such case, the stabilizer such as cement and cement-active material will obtain good stabilizing effect; but CG stabilizer can't be used for ettringite growing in high concentration of OH^- and CaO will destroy the structure having formed in stabilized soil.

As some OH^- and CaO will be consumed when active material hydrates, which reduce the concentration of OH^- and CaO , the stabilizer composed of cement, active material and gypsum can be used at some case in which concentration of OH^- and CaO is not very high.

If soil consumes more OH^- and CaO , the liquid of stabilized soil is not $Ca(OH)_2$ saturated, as the concentration OH^- and CaO reduce, the amount of hydrates produced by cement will decrease and pozzolantic reaction between active material and $Ca(OH)_2$ can not proceed because of lack of $Ca(OH)_2$. But as the concentration decrease, the shape of ettringite will be

beneficial to the strength of stabilized soil. Therefore to such kind of soil, CG stabilizer is a favorite one while the stabilizing effect of the stabilizer such as cement or cement and active material must be poor.

If the concentration of OH^- and CaO in stabilized soil is very low, alkaline material should be added to increase them. Of course, alkaline material can be added in every stage according to the practical condition of soil and stabilizer.

It was emphasized that the soil and the stabilizer should be taken as an entire system to investigate. In addition to the kinds of soil, many factors such as the kind and amount of cement, property of active material added, etc. can influence the concentration of OH^- and CaO in the system, and therefore influence the available scope of stabilizer.

5. CONCLUSION

1. Taking the soil and the stabilizer as an entire system, investigating the comprehensive influence caused by the various factors of the soil on the hydrating and hardening environment in stabilized soil by using the method of chemical analysis of the liquid squeezed from stabilized soil. It was revealed that, because the amount of OH^- and CaO consumed by different kinds of soil are greatly different, the concentration of OH^- and CaO in the stabilized soil differ greatly, in many cases, the liquid in the stabilized soil may not be saturated with $Ca(OH)_2$. It is the difference of the concentration of OH^- and CaO in the stabilized soil, that governs the yield and behavior of hydrates in stabilized soil and therefore determine the suitability of various kinds of stabilizer.

2. The principle of stabilizing soft soil is that the hydrates such as CSH cement soil particles together and ettringite fill up voids in soil. When the concentration of OH^- and CaO in the stabilized soil is high enough to maintain the liquid oversaturated with $Ca(OH)_2$, CSH from cement and active material hydrating grow amply, but ettringite growing in such condition will destroy the structure existing in stabilized soil.

When the concentration of OH^- and CaO is lower than the $Ca(OH)_2$ saturated point, the prerequisite for active material hydrating lost, and as the concentration of OH^- and CaO in the stabilized soil decrease the yield of hydrates such as CSH decrease for short of OH^- and CaO , but ettringite growing in such case can fill up the voids in stabilized soil to increase the strength of it.

3. In stabilizer, the proportion of the substance such as that produce CSH, that produce ettringite, alkaline material and active material, should be adjusted according to amount of OH^- and CaO consumed by the soil to be stabilized.

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