Determination of Sulphate Content in Marine Clays

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ABSTRACT

Improving the engineering behavior of soft clays using lime has been used for several decades. Even though chemical stabilization of clays has proved to improve the engineering properties, problems arise when calcium – based stabilizers are used in soils rich in sulphate bearing minerals. Therefore lime stabilization technique should be cautiously applied in sulphate enriched environment or in marine clays containing sodium sulphate. Sulphate content is thus clearly the most important property to consider when evaluating such soils as foundation medium or for construction purposes. Thus the key issue in deciding how to properly stabilize sulphate bearing soils using lime is to efficiently determine the sulphate content of soils and to determine the threshold quantity of sulphate likely to cause damage. This paper focuses on a comparison of different methods used to quantify sulphate in soils.

***Keywords* - ** Cochin Marine Clay, Sodium Sulphate, Sulphate Determination

1. INTRODUCTION

Lime stabilization is known to create long – term chemical changes in unstable clay soils, to create strong, but flexible, permanent structural layers in pavement systems and other foundations. When lime is added to soil, pozzolanic reactions take place to form Calcium Silicate Hydrate (CSH) and Calcium Aluminate Hydrate (CAH).These compounds form the matrix that contributes to the strength of lime – stabilized soil layers. As the matrix forms, the soil is transformed from its highly expansive, undesirable natural state to a more granular, relatively impermeable material that can be compacted into a layer with significant load bearing capacity. But when soluble sulphate is present in soil in high concentrations, it reacts with calcium from lime and alumina from soil to form Calcium – Aluminate – Sulphate – Hydrate i.e., ettringite (CASH) and (or) thaumasite. The sequence of reactions reactions can be summarized as follows [1]:

$6Ca^{2+} + 2Al(OH)^{-}_{4} + 4(OH)^{-} + 3(SO_4)^{2-} + 26H_2O = Ca_6[Al(OH)_6]_2 \, . \, (SO_4)_3 \, . \, 26H_2O$ (formation of ettrigite)

$Ca_6[Al(OH)_6]_2 \, . \, (SO_4)_3 \, . \, 26H_2O + 2H_2SiO_4^{2-} + 2CO_3^{2-} + O_2 = Ca_6[Si(OH)_6]_2 \, . \, (SO_4)_2 \, . \, (CO_3)_2 \, . \, 24H_20 + 2Al(OH_4)^{-} + (SO_4)^{2-} + 4OH^{-} + 2H_2O$ (isostructural substitution as ettringite changes to thaumasite)

Studies conducted on sulphate attack in lime stabilized marine clays have revealed that formation of ettringite in lime-sodium sulphate-clay system adversely affects the engineering behaviour of marine clay [2].

If the concentration of sulphate is not high, then monosulphoaluminate may form instead. Ettringite, which tends to form very small (µm), fibrous crystals, damages the soil structure through mineral expansion during its precipitation. [3]. Thus the presence of sodium sulphate in lime treated marine clay can adversely affect its properties. Sulphate content is thus clearly the most important parameter to be considered when evaluating such soils for construction purposes. It is possible for marine clays to be enriched with sulphates, either by nature or due to the discharge of nearby industrial waste containing sulphates [2]. The quantity of sulphates present generally dictates the extent to which ettringite will form. Or in other words, the greater the content of soluble sulphates in soil, the greater the potential for the growth of ettringite [4].

Marine clay found along Coastal belt are characterized by large compressibility and poor shear strength. Studies, conducted on Cochin marine clay, have proved that lime is the most effective stabilizing agent for marine clays of Cochin[5]. But like any other marine clay, presence of sulphate can adversely affect the strength behaviour of these clays also. The only fool proof way to know whether or not sulphates will be a problem is to test the soil for presence of sulphates.

If the total level of soluble sulphates is below 0.3%, or 3,000 parts per million (ppm), by weight of soil, then lime stabilization should not be of significant concern and the potential for a harmful reaction is low. Total soluble sulphate levels of between 0.3% (3,000 ppm) and 0.5% (5,000 ppm) are of moderate concern. Generally, these sulphate levels do not result in harmful disruption, but on occasions have caused localized distress. Localized distress is often due to seams of higher sulphate concentration not detected in testing. Total soluble sulphate levels between 0.5% (5,000 ppm) and 0.8% (8,000 ppm) present are moderate to high risk. Total soluble sulphate levels of greater than 0.8% (8,000 ppm) are generally of high risk to stabilize with lime. Soils with total soluble sulphate contents greater than 1.0% (10,000 ppm) generally are not suitable for lime stabilization because of the high risk of sulphate-induced disruption and failure [6].

Even sulphate content of 0.03 to 0.05% in soils can induce severe swelling conditions favourable for the formation of ettringite [2].

2. MATERIALS AND METHODS

2.1 Soil Sample

Sample collected for the present study was from Panampilly Nagar in Cochin. Boring was carried out using shell and auger method with the sides protected by casing pipes. The top layers at this location consist of sand/clayey sand followed by soft clay. Clay sample was collected from a depth of 5m, transferred to polythene bags and were sealed immediately. The samples were later mixed thoroughly to get a uniform sample and were again transferred back into polythene bags. The physical properties of the sample taken for study is as given in Table I

Table I Physical Properties of Soil

	Property	Test Values
1.	Natural Moisture Content(%)	157.3
2.	Liquid Limit (%)	166.7
3.	Plastic Limit (%)	40.6
4.	Plasticiy Index	126.1
5.	Shrinkage Limit(%)	14.4
6.	Grain Size Distribution	
	i) Clay size(%)	50
	ii) Silt size(%)	45
	iii) Sand size(%)	5
7.	Free swell Index(cc/g)	4.45
8.	pH	8.00

2.2 Test Programme

Soluble sulphates present in water are measured in parts per million (ppm) and often expressed either in ppm or percent.10,000ppm are equivalent to 1.0%. Therefore 3,000ppm are equivalent to 0.3% and 5,000ppm to 0.5%. The soluble sulphate content should be reported on a dry soil basis to ensure consistency of test results [6].

IS 2720 Part XXVII [7] lays down the procedure for determining the total soluble sulphate content of soils by: (a) precipitation method or Standard Method (b) volumetric method or Subsidiary Method, and (c) Calorimetric or Turbidimetric method.

2.2.1 Precipitation Method (Standard Method)

The method depends upon preparing an aqueous extract of the soil and determining the sulphate content of this extract or an aliquot portion of it by the precipitation of sulphate as barium sulphate, filtering off the precipitate and weighing it. The soil sample shall be brought to a state in which it may be crumbled, if necessary, by drying it in an oven maintained at 105 to 110°C. The aggregations of particles shall be broken up in mortar with rubber covered pestle or the mechanical device. The sample shall be thoroughly mixed and then sub-divided by quartering

2.2.1.1 Procedure

Take 10 g of soil from the sample prepared, in a 250-ml bottle with 100 ml of distilled water. Give occasional shaking for 2 hours by means of the mechanical shaker. Allow the soil suspension to stand overnight Filter and take 25 ml of filtrate in a beaker and add concentrated hydrochloric acid to just neutralize the solution if it is found alkaline to phenolphthalein indicator. Add further 4 ml concentrated hydrochloric acid to make the solution acidic. Boil the solution. Remove the solution from the source of heat and add hot barium chloride solution in a fine stream with constant stirring, till there is no precipitation with a further addition. Place the beaker on a steam-bath for a minimum period of 4 hours and allow the precipitate to settle. Filter the precipitate through ashless filter paper, wash free from chloride ions,dry and ignite. The filteration may also be done through a preweighed sintered glass crucible or a Gooch crucible. In the case of filter paper, after drying, ashing shall be done on a low flame and the precipitate then ignited over a burner or in a muffle furnace at 600 to 700°C for half an hour. Cool in a desiccator, weigh and note the weight of the residue. This is the weight of barium sulphate. A corresponding weight of sodium sulphate should be calculated and thus its percentage determined.

Calculate as follows:
a) Sulphates (as SO_4), percent by mass
$= 41.15\ W1/W2$
b) Sulphates (as Na_2SO_4), percent by mass
$= 60.85W1/W2$
where, W1 = mass in g of the precipitate, and
W2 = mass in g of the soil contained in the solution taken for precipitation.

2.2.2 Volumetric Method (Subsidiary Method)

The volumetric method depends upon insoluble barium sulphate forming and settling rapidly when barium chloride solution is added to the sulphate solution. The barium chloride reagent is added in excess and the excess is determined by the standard solution of barium chromate. With the formation of potassium chromate, the slight excess of chromate reagent becomes evident from the resultant yellow color of the supernatant solution. The end point can be further tested (confirmed) by silver nitrate solution used as an external indicator. A brick red colouration is obtained when a drop of silver nitrate is added to a drop of the chromate solution.

2.2.2.1 Procedure

Weigh 10 g of the soil specimen, in a beaker and add about 50 ml water. Stir well, allow decanting, filtering, washing the soil on filter paper with a small quantity of water and making the filtrate to 100 ml. Pipette out 10 ml of the water extract in a conical flask, make it slightly acidic by adding concentrated hydrochloric acid and heat to boiling. While boiling, add barium chloride solution (N/4) from the burette till the precipitation is complete and barium chloride solution is in slight excess. Neutralize the solution with ammonium hydroxide and titrate the excess of barium chloride against potassium chromate solution (N/4). The end point may be confirmed if considered necessary, by using silver nitrate solution as an external indicator.

Calculate as follows:

Sulphates as sodium sulphate in soil, percent by mass
$= 0.0177 \times 100(x-y)$
Where,
x = volume of N/4 barium chloride added, ml;
y = volume of N/4 potassium chromate solution used in back titration; and

x - y = N/4 barium chloride actually used for precipitating sulphate.

2.2.3.Colorimetric or Turbidimetric Method (Subsidiary Method)

2.2.3.1 Procedure

Weigh 20 g air-dry soil specimen in a 250-ml conical flask. Add 100 ml of Morgan's extraction solution. Shake the suspension for one-half hour and filter through Whatman's No. 42 filter paper or equivalent. Take 10 or 20 ml aliquot and transfer to a 25-ml volumetric flask. Add 1 g of barium chloride crystals (ground to pass 50-micron IS sieve and to be retained on 250-micron IS sieve) to the aliquot in the flask and shake for 1 minute. Add 1 or 2 ml of 25 percent gum acatia, Pour distilled water up to the mark of volumetric flask and shake for a minute. Precipitate the suspension and take the reading between 5 to 30 minutes after precipitation either by photoelectric calorimeter using blue filter or by turbiditimeter. Sulphate is then determined by the standard sulphate curve.

2.2.3.2 Preparation of Standard Sulphate Curve

a. *Stock Solution* - Dissolve 0.888 g anhydrous sodium sulphate Na_2SO_4/m1 alcoholic, ammonium chloride (NH_4Cl). This gives a concentration of 0.60 mg of SO_4/ml. Absolute alcohol should be used for the preparation of the solution.

b. *Working Standard Solution* - Dilute 0.60 mg SO_4/ml stock solution with alcoholic (N) ammonium chloride to give 0.06 mg SO_4/ml. Take 2, 4, 6, 8, 10 ml of this to give a range of 0.12 – 0.60 mg of SO_4.

c**.** The standard curve should be prepared by taking readings with photoelectric calorimeter using blue filter or by turbiditimeter using the working standard solution.

2.3 Test Results and Discussions

Test for the determination of sulphate content was conducted on the marine clay sample as per procedure detailed above. The obtained value of sulphate content using three methods suggested in IS 2720 Part 27 is summarized in Table II

Table II Comparison of Sulphate Content by Various Methods

Sl No:	Method Used	Total Soluble Sulphate(%)
1.	Precipitation Method	0.49%
2.	Volumetric Method	0.49%
3.	Calorimetric Method	0.47%

The results indicate that Sulphate content obtained by three methods are comparable. Errors are likely to creep in most, in Precipitation method of determination of total soluble sulphates.

3. CONCLUSION

In this paper, the importance of assessing the sulphate content in soil has been reviewed. A laboratory study has been carried out to determine the sulphate content of clay sample by different methods and the following conclusions have been drawn.

1. Sulphate content of the order of 0.5% obtained for the marine clay sample is of serious concern while considering stabilization of these clays using lime.

2. All the three methods give comparable results.

3. As per easiness of conducting the test especially when large number of representative samples have to be tested, the order of preference is as follows, i)Calorimetric method by use of Nephelometer, ii)Volumetric Method, and iii) Precipitation Method.

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