

The Role of Carbonates in Sulfuric Acid Waste Management

B. Guru Prasad¹, P.V. Sivapullaiah², and M. M. Allam³

^{1, 2, 3} Department of Civil Engineering, Indian Institute of Science,
Bangalore, India, Email: gurubpch@lycos.com

ABSTRACT: The addition the waste carbonates to the acid sulfate soils are examined by using the oedometer swell tests. Swell under nominal surcharge, in oedometer, till equilibrium is reached and subsequent consolidation behaviour with standard load increment ratio has been studied. The soils treated with 5-10% of carbonate, after interaction with sulfuric acid showed considerable difference in their volume change behaviour. Once the consolidation tests are completed the soil samples are diagnosed through X-ray and SEM studies. The high swelling has been attributed to the formed new minerals. The conducted studies will gives an idea to the geo-environmental engineer for better utilization of the waste materials in the contaminated scenario to construct the buildings.

Keywords: sulfuric acid, neutralization, sustainable technology, mineralogy, contamination

1. INTRODUCTION

Acid sulfate soils, whose occurrence is on the rise due to oxidation of pyrites, are the focus of many investigations recently. It is known that 1 ton of iron sulfide minerals can produce about 1.5 tones of sulfuric acid naturally. The generated sulfuric acid percolates into the soil media, leads to the acidification of pore water in soil matrix, mobilization of mineral dissolution, release of harmful metals like aluminum and other elements into the water, and adverse effects on man made structures. To overcome the above problems the current research is going on the avoidance of pyrite oxidation prevention, active and passive acidity barriers, neutralization systems, and utilization of corrosive construction materials, etc. In consequence of this better utilization of waste sulfuric acid has become

a concern to environmental and geotechnical engineers.

Carbonates, exists in abundance in earth's crust is proposed to use to neutralize acid in contaminated soils. Carbonate behaviour differ from common silica-rich materials due to several fundamental and important ways. First, carbonates are predominantly produced and deposited by biological process. Second, because of the form in which we often find them, carbonates are comparably softer than the constituents comprising most terrigenous soils. Third, they are much more susceptible to post-depositional alteration at normal surface temperatures and pressures. Due to these fundamental differences, the geotechnical engineer should not routinely extrapolate experience found to be valid in a terrigenous soil to a situation involving carbonate soils.

1.1 Importance of Swell in Soils

Swell is one of the important properties of expansive soils that occur when water is imbibed into the layers of mineral structure in the natural environment. As it is given in the literature the soils gets contaminate due to generated sulfuric acid solutions. Thus the studies on volume change behaviour of contaminated soils are plays vital role. The importance and the need of volume change is summarized as, a) the details are needed in design of foundations for various structures; b) volume changes in soils are vital because of their relation to settlements due to compression, heave due to expansion, and their contribution to deformations caused by shear stresses. Large volume changes in soils results in extensive structural damage; c) volume change behaviour of soils cause changes in strength and deformation properties that in turn, influence the stability;d) the swell behaviour plays an important role in the design of permeable reactive barrier (PRB) in acid sulphatic soils, to control and improve the water quality.

1.2 Importance of Mineralogy

Clay minerals are sheet silicates, thus they have a crystalline structure that allows them to break easily along parallel sheets. These minerals are formed by alteration of other minerals during the process of chemical weathering. Soil colloids also carry negative or positive charges on their external and internal surfaces. The presence of charge influences their ability to attract or repulse charge ions to or from surfaces. The silicate clays are layers of tetrahedral and octahedral sheets. The basic building blocks of tetrahedral and octahedral sheets are the silica tetrahedron and the aluminum octahedra. The Si^{4+} cation occurs in fourfold and tetrahedral coordination with oxygen whilst the Al^{3+} is generally found in six fold or octahedral coordination.

1.3 Use of Carbonates in Neutralizing the Acidity

Mixing the soil with carbonates is essentially due to binding of soil particles with the hydrated calcium compounds of carbonate in alkaline environment. In the literature the use of carbonates control the sulfate induced heave is not reported, while the double lime addition has been reported [1, 2]. Carbonate stabilization may not be effective in acidic environment. Nevertheless the addition of carbonate in excess quantities to acid sulfate soils may be useful. Thus an attempt is made to check the effectiveness of 5% and 10% carbonate as an admixture to reduce the swell in acid sulphatic soils.

2. MATERIALS AND METHODS

2.1 Selected Carbonate Soils

Carbonate soils prepared by mixing the two natural soils, viz., black cotton soil and red earth with known amounts of 5 and 10% of carbonate, are used to study the effect of varying concentration of waste sulfuric acid solutions. Table 1 gives the average chemical composition of the two chosen soils.

2.2 Experimental Fluids

To mimic the sulfate in acidic conditions, the waste sulfuric acid solutions of 1 and 4N are used in the study.

2.3 Tests Performed

2.3.1 Swell Tests

The one-dimensional free swell tests were conducted on soil specimens compacted to Proctors maximum dry density at optimum water content using fixed-ring oedometer test. The required soil was mixed with required quantity of fluid, packed in watertight polyethylene bags, and kept in desiccators to allow for uniform moisture distribution (for about 7 days). The soil was statically compacted to a required dry unit weight to a thickness of 14 mm in a 60-mm diameter and 20-mm high well-polished stainless steel consolidation ring. A thin smear of silicon grease was applied

inside the ring to minimize the friction between the specimen and ring. Two porous stones each of 10-mm thick were placed below and above the soil specimen. Then, the consolidation cell was positioned gently with compacted soil specimen in the consolidation equipment. At a seating pressure of 6.25 kPa, the specimen was soaked with the sulfuric acid solution of 1 and 4N. The 0.002 mm accuracy dial gauge attached to the set-up was used to monitor the change in the height of the specimen.

Table 1: Chemical Composition of BC Soil and Red Earth

Property	BC Soil (%)	Red Earth (%)
Silica (SiO ₂)	41.05	62.35
Alumina (Al ₂ O ₃)	14.31	18.05
Ferric (Fe ₂ O ₃)	21.96	2.61
Titanium (TiO ₂)	-	0.21
Potassium (K ₂ O)	0.04	0.42
Sodium (Na ₂ O)	0.60	0.32
Magnesium (MgO)	1.66	1.67
Calcium (CaO)	-	5.91
Traces	3.17	-
Loss on ignition	17.13	8.41

The percent swell was calculated as the ratio of percent increase in the thickness to the actual thickness of specimen. A load increment ratio of one, with increment duration of 24 h or until completion of primary consolidation was adopted. The loading cycle was continued up to a pressure of 800 kPa and then unloading was carried

out. Then the samples were removed and oven-dried, powdered to carryout mineralogical studies.

2.3.2 Mineralogical Tests

2.3.2.1 X-Ray Diffraction (XRD) Analysis

The presence of crystals in soils needs thorough X-ray diagnosis. XRD analysis was carried out on radiation generated at 40 kV and 40 mA using a Philips diffractometer (Pw 3710). The scanning speed was 0.02° 2θ/s with scanned angle range of 3°–70°. Randomly oriented samples were prepared by manual grinding of oven-dried material in a glass slide using silica gel as adhesive. To identify mineral types, qualitative assessment was made by comparing the diffraction pattern of each sample with standard patterns prepared by the Joint Committee of Powder Diffraction Data Service [3].

2.3.2.2 Scanning Electron Microscope Study

The Scanning Electron Microscope is one of the most versatile instruments available for the examination and analysis of the micro structural characteristics of the soil. Then SIRION (XL40, series) machine is used to study the morphology of the soil samples at a voltage range of 0.2--30 KV. The oven-dried (105 ± 5° C) treated soil samples were placed on an aluminum stub covered with double-sided carbon tape. The surface of the sample was coated with fine gold film by vacuum sputtering to prevent charging effect over the sample.

3. RESULTS AND DISCUSSION

3.1 EFFECT OF CARBONATE ON OEDOMETER FREE SWELL BEHAVIOUR

3.1.1 Upon the Interaction with Carbonatic BC Soil

The equilibrium swelling obtained was about 17% for the sample containing 5% CaCO₃. This shows that the swelling in soil

increases in the presence of 5% carbonate in 1N H_2SO_4 solution. The swell further increases in the soil with 10% CaCO_3 in 1N H_2SO_4 solution. The equilibrium swelling in soil containing 10% CaCO_3 was about 27%. Higher swelling in the presence of 10% carbonate indicates the qualitative and quantitative alterations to be different. The reactions with 1N acidic solutions might have accelerated and/or modified by the presence of carbonate leading to increase in swelling in soils. The role of acidity appears to be less as high swelling is observed even with 1N solution.

The equilibrium swelling obtained was about 27% for the sample containing 5% CaCO_3 with 4N acid solution. This is essentially due to mineralogical alterations leading to formation of new minerals. The swelling increases further with 10% CaCO_3 in 4N H_2SO_4 solution. This supports that the increased swelling is due to newly formed minerals. The equilibrium swelling in soil containing 10% CaCO_3 was about 38%.

Higher swelling in the presence of 10% carbonate indicates both qualitative and quantitative alterations. The swelling in the soil containing carbonate with 4N acid solution occurs in two stages. The first one in the sample with 5% carbonate occurs is about 15%. This might be due to the exchangeable ions. There was some time lag before the second stage swell initiated. The relatively slower rate of swelling continued for about 70 days and the maximum swelling observed was about 25%. This might be due to mineralogical alterations. Similar behaviour is observed in the sample containing 10% CaCO_3 in 4N acid solution. However, the swelling in this soil is slightly higher and is about 31%.

3.1.2 Upon the Interaction with Carbonatic Red Earth

The equilibrium swelling obtained was about 15% for the sample containing 5% CaCO_3 . This shows that the swelling in soil increases in the presence of 5% carbonate in 1N H_2SO_4 solution. This is further increased

in the soil with 10% CaCO_3 in 1N H_2SO_4 solution. The equilibrium swelling in soil containing 10% CaCO_3 was about 20%. The equilibrium swelling obtained was about 37% for the sample containing 5% CaCO_3 . This is essentially due to mineralogical alterations leading to formation of new minerals. The swelling decreases further with 10% CaCO_3 in 4N H_2SO_4 solution. The equilibrium swelling in soil containing 10% CaCO_3 was about 23%. Soil treated with carbonate has shown two stages of swelling indicating formation of new minerals.

3.2 EFFECT OF CARBONATE ON VOLUME CHANGE BEHAVIOUR

3.2.1 Upon the Interaction with Carbonatic BC Soil

The void ratio--pressure relationships of the BC soil with 5 and 10% CaCO_3 by 1N H_2SO_4 solution are compared in Table 2. It can be seen that the natural BC soil undergoes relatively high compression compared to the soil containing carbonate. This might be due to high swelling that has taken place in the soil with carbonate.

Table 2 compares void ratio--pressure relationships of BC soil with 5 and 10% CaCO_3 inundated with 4N H_2SO_4 solution. Though the soil containing carbonate has swollen considerably, the reduction in the void ratio with increase in pressure is very less. This is because the swelling in soil with sulfuric acid is more due to the mineralogical changes than due to increase in swelling potential of the soil.

Table 2: Mode of Fluids Usage on Volume Change Behaviour

Soil	CaCO_3 %	H_2SO_4 Normality	Max. Swell at 6.25 kPa, %	Change in Void Ratio Δe

BC soil	5	1	17.34	0.16
	5	4	27.22	0.38
	10	1	26.89	0.07
	10	4	34.37	0.24
Red earth	5	1	19.78	0.17
	5	4	37.31	0.03
	10	1	14.54	0.12
	10	4	22.65	0.15

3.2.2 Upon the Interaction with Carbonatic Red Earth

The void ratio--pressure relationships of the red earth with 5 and 10% CaCO₃ by 1 and 4N H₂SO₄ solutions are compared in Table 2. It can be seen that the natural red earth undergoes relatively lower compression compared to the soil containing carbonate. Though the soil containing carbonate has swollen considerably, the reduction in the void ratio with increase in pressure is very less. This is because of swelling in soil with sulfuric acid is more due to mineralogical changes than due to increase in swelling potential of the soil.

3.3 EFFECT OF CARBONATE ON MINERALOGICAL CHANGES

3.3.1 Upon the Interaction with Carbonatic BC Soil

The peaks of new minerals, yavapaiite (K Fe(SO₄)₂) (d-spacing of 7.83 Å) and krausite (potassium iron sulfate hydrate) (K Fe(SO₄)₂ H₂O) (3.09 and 2.23 Å) are observed in BC soil mixed with 5% CaCO₃ inundated with 1N acid after completion of consolidation. The observed peaks of montmorillonite-(d-spacing 15.0, 5.01 and 1.88 Å), mullite (Al_{4.95}Si_{1.05}O_{9.52}) are shown in BC soil mixed with 5% CaCO₃ inundated with 4N

sulfuric acid solutions after completion of consolidation.

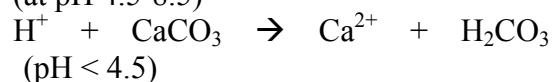
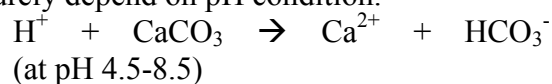
The peaks of yavapaiite, other minerals such as rankinite and sillimanite are formed in the soil containing 10% CaCO₃ in BC soil mixed with 10% CaCO₃ inundated with 1N acid. Rankinite (Ca₃Si₂O₇) (2.72, 3.18, 4.48 Å) is formed by the presence of high calcium content and sillimanite- aluminum silicate (Al₂SiO₅) (d-spacings of 3.38, 2.22, 2.9, 2.1, 1.60 Å), one of three aluminosilicate polymorphs, due to reformation of other minerals. Apart from montmorillonite, the presence of voltaite (K₂Fe₅Fe₃ Al (SO₄)₁₂ (H₂O)₁₈) (5.56, 3.41 Å), and monticellite (Ca Mg SiO₄) (3.58, 1.69 Å) are observed BC soil mixed with 10% CaCO₃ inundated with 4N H₂SO₄ after completion of consolidation.

3.3.2 Upon the Interaction with Carbonatic Red Earth

Apart from kaolinite (7.1, 3.56, 4.41 Å), muscovite (KAl₃Si₃O₁₀(OH)₂) (4.24, 3.95, 2.28 Å), and quartz (3.37, 1.37, 1.81 Å) are present in red earth mixed with carbonate and inundated with sulfuric acid solutions after completion of consolidation. The presence of muscovite indicates that the soil containing potassium can undergo reactions to produce this mineral.

3.4 MECHANISMS OF CARBONATE WITH HYDROGEN ION

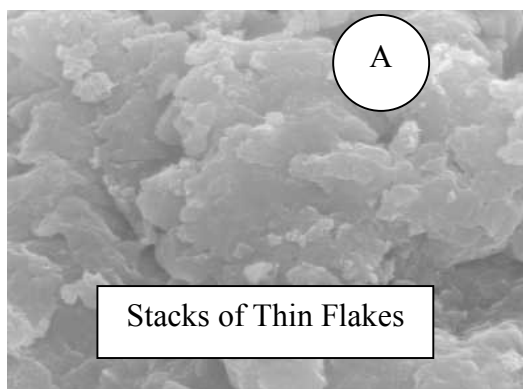
The disassociated hydrogen ions in sulfuric acid upon reacting with calcite, lead to following reactions. These reactions purely depend on pH condition.



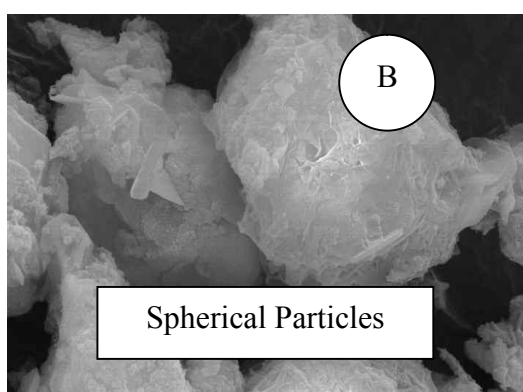
3.5 EFFECT OF CARBONATE ON MORPHOLOGICAL CHANGES

3.5.1 Upon the Interaction with Carbonatic BC Soil

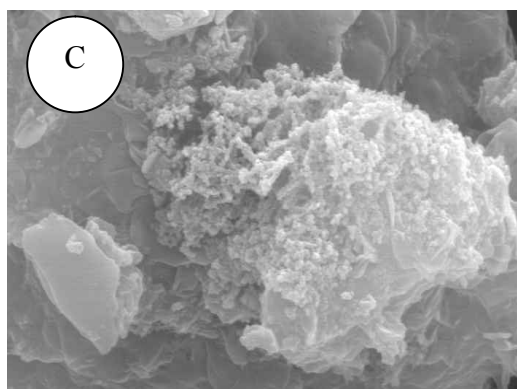
The scanning electron microscope images of soils treated with carbonate is presented in Figs. 1 A to 1H. The SEM image of soil treated with 5% CaCO_3 shows an intricate configuration lacking any definite structural pattern. The BC soil mixed with 5% CaCO_3 and inundated with 4N sulfuric acid after completion of consolidation shows the spherical particles. The SEM image of BC soil mixed with 10% CaCO_3 inundated with 4N sulfuric acid after completion of consolidation shows the thin lath clusters. The SEM Images of ASS Soils after the consolidation is presented below Fig 1:



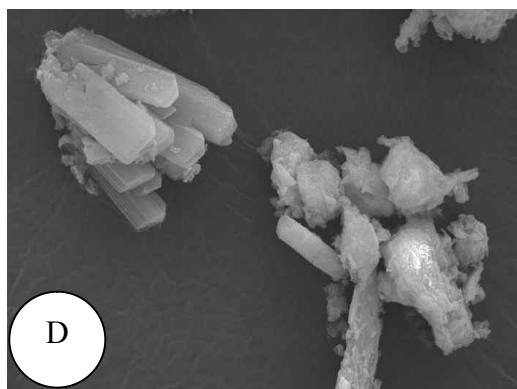
A) BC Soil Mixed with 5% CaCO_3 and Inundated with 1N H_2SO_4 .



B) BC Soil Mixed with 5% CaCO_3 and Inundated with 4N H_2SO_4 .



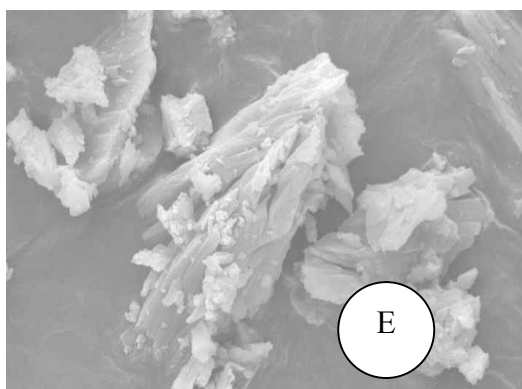
C) BC Soil Mixed with 10% CaCO_3 and Inundated with 1N H_2SO_4 .



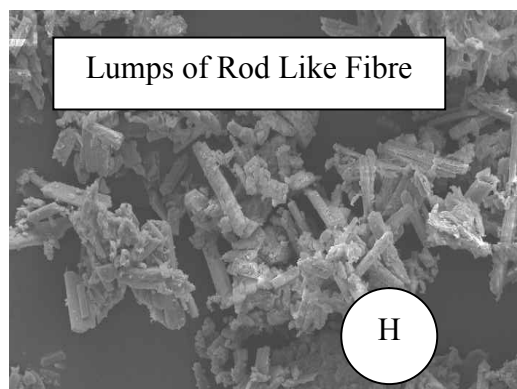
D) BC Mixed with 10% CaCO_3 and Inundated with 4N H_2SO_4 .

3.5.2 Upon the Interaction with Carbonatic Red Earth

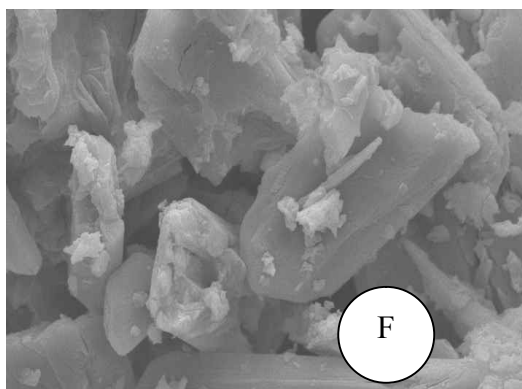
The SEM micrograph of red earth mixed with 10% CaCO_3 inundated with 1N sulfuric acid, after the completion of consolidation, is given in Fig. 1G, reveals, with the existence of aggregates of rod shape, the surface texture resembles flocculants nature. Figure 1H shows the existence of aggregates of rod shapes in red earth mixed with 10% CaCO_3 and inundated with 4N sulfuric acid



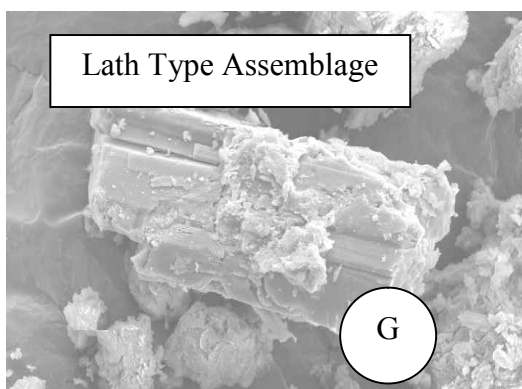
E) Red Earth Mixed with 5% CaCO_3 and Inundated with 1N H_2SO_4 .



H) Red Earth Mixed with 10% CaCO_3 and Inundated with 4N H_2SO_4 .



F) Red Earth Mixed with 5% CaCO_3 and Inundated with 4N H_2SO_4 .



G) Red Earth Mixed with 10% CaCO_3 and Inundated with 1N H_2SO_4 .

4. CONCLUSIONS

1. The swell in both black cotton soil and red earth containing different amounts of carbonate increases in the presence of acid sulfate. Generally, the swell increase with increases in carbonate content and the concentration of sulfuric acid.

2. The mineralogical changes that occur due to soil acidic sulfate reactions are accelerated and/or modified in the presence of carbonate leading to increase in swelling in soils.

3. The minerals present in soils upon the addition of carbonate in the presence of sulfuric acid solutions are transformed to new minerals.

4. In case of carbonatic black cotton soil with 4N acid solutions the new minerals such as, mullite, coesite, voltaite, and monticellite are observed and these may be a delayed occurrence. With 1N acid solutions, the formed minerals are yavapaiite, krausite, rankinite, and sillimanite.

5. The high leaching in the presence of 4N acid leading to the removal of potassium and consequently most of the potash minerals are reduced in soil leading to very high swelling compared to 1N acid solution.

Yavapaiite (potassium iron sulfate mineral) and voltaite (potassium iron aluminum sulfate hydrate mineral) are the iron sulfate minerals.

6. In carbonatic red earth calcium sulfate and the muscovite are the new minerals formed.

REFERENCES

[1] Kota, P. B. V. S., Hazlett, D., and Perrin, L., 1996, Sulfate-Bearing Soils: Problems With Calcium Based Stabilizers, TRR 1546, Transportation Research Board, Washington, DC.

[2] Puppala A.J., Griffin; J. A., Hoyos L.R., and Chomtid. S. 2004. Studies on Sulfate-Resistant Cement Stabilization Methods to Address Sulfate-Induced Soil Heave, Journal of Geotechnical and Geo environmental Engineering, ASCE, Vol.130, pp391–402.

[3] JCPDS.1999, Joint committee for powder diffraction studies, The powder diffraction file, — International centre for diffraction data (ICDD), Newtown Square, PA,USA.