Understanding the effect of acid rain on physico-chemical and engineering properties of black cotton soil

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ABSTRACT

Population outburst have forced over exploitation of natural regimes of biosphere. Rapid urbanization and industrialization are posing constant threat to environment. Continuous addition of air pollutants like sulfur dioxide and oxides of nitrogen etc. not only pollutes the atmosphere but also indirectly causes degradation of lithosphere. These gases are major source of acid rain whose pH may be as low as 3 to 4. The frequent, persistent and growing intensity of acid rain will certainly exceed buffering cation exchange capacity of soil which will enhance the rate of leaching of cations from the soil to a great extent. Absorption of H+ , SO42-, NO3- and CO32- by the soil particles will alter physico-chemical and engineering properties of soil which cannot be ignored. Therefore it is imperative to examine the properties of soils eroded due to acid rain in order to augment understanding of its influence on geotechnical engineering. To monitor the degree of variation in the texture, physico-chemical and the engineering properties of soil of different plasticity on exposure to acid rains of varying strength have been taken up. The present paper focuses on the findings observed on black cotton soil.

The soil fraction passing 4.75 mm sieve was shaken for eight hours with varying probable simulated strength of acid rain equivalent to normality 0.005N, 0.01N, 0.02N and 0.04N of H2SO4, HNO3 and 1:1 mixture of H2SO4 / HNO3 (expected composition of acid rain) to study influence of acid rain on soil properties. The acidification lowers the cation exchange capacity, affects the grain size distribution and alters the consistency as well as strength properties of the soil. The paper presents the observed degree of variation in these properties under varying strengths of acid rain.

Keywords: Acid rain; pH; Index Properties; Erosion; Consolidated undrained.

1. Introduction

The gaseous pollutants released during volcanic eruptions and industrial exhausts are continuously adopting alarming proportions. These when absorbed by rain water reduces its pH (Chandrawanshi C K et al 1997). The direct effect of acid rain (AR) on various types of soils needs to be evaluated. Although the H+ content of AR falling for a short duration is very low compared to the cation exchange capacity (CEC) of the soil yet its influence on the physico-chemical and engineering properties of soil will be alarming in near future as ever growing industrialization/pollution will keep on decreasing its pH. The enhanced rate of
leaching of cations and absorption of $\text{H}^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{CO}_3^{2-}$ will alter its physicochemical and engineering properties (Kamon et al. 1997). It is thus one of the most influential environmental factors which directly affect the properties of soil (Yamaguchi et al., 1993). Environmental Geo-technology is emerging as an interdisciplinary science, aiming at forecasting, analyzing and solving the geotechnical problems involving the influence of environmental factors (Manassero and Deangeli, 2002).

The city is an industrial town located at the southern fringes of the Malwa Plateau. It is situated at 75° 48' East longitude and 22° 48' North latitude, perched at an average height of
550 meters above the sea level. It covers an area of 214 square kilometers. The soil stratum is mainly composed of high plastic black cotton soil.

2. Experiment

2.1 Materials

The soil sample was oven dried & sieved using 4.75 mm IS sieve. The down size material was used for further experimental work. The consistency, strength and chemical characteristics of the samples were determined for the soil fraction passing 425 µm sieve. The results are summarized in Table 1.

| Characteristic | Result |
|----------------|--------|
| pH             | 8.16   |
| Liquid limit (W_L) % | 54.90 |
| Plastic limit (W_P) % | 24.00 |
| Plastic Index (Ip) % | 30.90 |
| Shrinkage limit % | 6.42  |
| Free Swell Index % | 60.57 |
| Particles finer than 0.002mm % | 23.40 |
| Particle 0.002mm-0.075mm % | 66.00 |
| Particle 0.075mm-0.425mm % | 3.50  |
| Particle 0.425 mm-2.00 mm % | 4.20  |
| Particle 2.00 mm - 4.75 mm % | 2.90  |
| Extractable Ca cmol/kg | 40.0 |
| Extractable Mg cmol/kg | 5.1  |
| Extractable Na cmol/kg | 0.4  |
| Extractable K cmol/kg | 0.7  |
| CEC, cmol/kg | 45.14 |
| EC, dS/m | 0.123 |
| Organic Matter, % | 1.82 |
| CaCO3 Content, % | 9.70 |
| Effective cohesion (c’), kg./cm² | 0.44 |
| Effective angle of internal resistance (Ø’), degree | 16.20 |

2.2 Experimental Methods

1 kg of soil sample was shaken for 8 hours with 1 liter of distilled water. Simultaneously the sample was also shaken separately with H2SO4, HNO3 and 1:1 mixture of H2SO4 / HNO3 of 0.005N, 0.01N, 0.02N and 0.04N strengths as detailed in Table 2. These sample were then kept undisturbed over night. The treated sample were filtered and air dried which were then used to find their consistency, strength and chemical properties as per Bureau of Indian Standards (IS 2720, BIS 1987 & 1988).

| Sl. No. | Description | Strength of acid | Sample Designation |
|---------|-------------|-----------------|-------------------|

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3. Results and Discussions

3.1 Physico-Chemical Properties of Soil before and after Acid Treatment

The physico-chemical characteristics such as pH value of used acid (pHₐ), effluent obtained after agitation (pHₑ), treated soil extract (pHₛₑ), concentration of exchangeable cation (EC), CEC, electrical conductivity, organic matter and CaCO₃ Content of the original soil sample as well as the acid treated sample are presented in Table 3 and 4.

Table 3: Physico-Chemical properties of soil before and after acid treatment

| Sample  | pHₐ  | pHₑ  | pHₛₑ | EC Left in the Treated Soil | CEC of Treated Soil |
|---------|------|------|------|-----------------------------|---------------------|
|         | cmol/kg soil |
| B       | 8.16 | 40   | 0.4  | 0.7                         | 45.14               |
| Bₛ - 1  | 4.71 | 5.98 | 7.75 | 4.6                         | 41.37               |
| Bₛ - 2  | 4.49 | 5.64 | 7.32 | 4.2                         | 39.52               |
| Bₛ - 3  | 4.28 | 5.17 | 6.90 | 3.7                         | 37.71               |
| Bₛ - 4  | 4.04 | 4.95 | 6.20 | 3.5                         | 36.22               |
| Bᴺ - 1  | 4.67 | 6.07 | 7.82 | 4.8                         | 41.37               |
| Bᴺ - 2  | 4.42 | 5.84 | 7.40 | 4.5                         | 39.52               |
| Bᴺ - 3  | 4.21 | 5.42 | 7.01 | 3.8                         | 37.71               |
| Bᴺ - 4  | 4.10 | 5.05 | 6.50 | 3.7                         | 36.22               |
| Bᴺˢ - 1 | 4.34 | 5.58 | 7.95 | 4.6                         | 40.12               |
| Bᴺˢ - 2 | 4.25 | 5.14 | 7.50 | 4.1                         | 39.20               |
| Bᴺˢ - 3 | 4.16 | 4.96 | 6.99 | 3.6                         | 38.16               |
| Bᴺˢ - 4 | 4.02 | 4.42 | 6.01 | 3.5                         | 37.26               |

Table 4: Physico-Chemical properties of soil before and after acid treatment

| Sample  | Electrical Conductivity of Effluent dS/m | Electrical Conductivity of Soil Extract dS/m | Organic Matter % | CaCO₃ Content, % |
|---------|----------------------------------------|-------------------------------------------|------------------|-----------------|
| B       | 0.123                                  | 0.123                                     | 1.82             | 9.70            |
3.1.1 pH Values

The pH value of Acid used (pH_A), Elluent obtained (pH_E) and Treated Soil Extract (pH_SE) for the soil sample treated with different strengths of H_2SO_4, HNO_3 and 1:1 mixture of H_2SO_4 / HNO_3 are presented in Table 3. It is observed that in all the cases

\[ \text{pH_E} > \text{pH_A} \]

and

\[ \text{pH_SE (Sample B)} > \text{pH_SE (Sample BS –1)} > \text{pH_SE (Sample BS –2)} > \text{pH_SE (Sample BS –3)} > \text{pH_SE (Sample BS –4)} \]

\[ \text{pH_SE (Sample B)} > \text{pH_SE (Sample BN –1)} > \text{pH_SE (Sample BN –2)} > \text{pH_SE (Sample BN –3)} > \text{pH_SE (Sample BN –4)} \]

\[ \text{pH_SE (Sample B)} > \text{pH_SE (Sample BNS –1)} > \text{pH_SE (Sample BNS –1)} > \text{pH_SE (Sample BS –1)} > \text{pH_SE (Sample BS –1)} \]

3.1.2 Exchangeable Cations and CEC

The concentration of the exchangeable cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ in the soil samples and the CEC values of respective samples are presented in Table 3. It is observed that on acid treatment the concentration of these cations as well as the CEC value goes on reducing as the intensity of AR increases.

The pH_E > pH_A because the exchangeable cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ in the soil samples got exchanged by H^+ ion in the artificial AR and leached to effluent water during agitation. The decrease in pH values of soil sample was caused by leaching of cations and adsorption of H^+ ions due to ion exchange reaction. A quantity of exchangeable cations in the samples was exchanged rapidly by H^+ ions in higher AR. This resulted in larger decrease in pH values of the sample.

3.1.3 Electrical Conductivity (EC)

The observations as presented in Table 4 indicate an increase in EC of the effluent (EC_EFF) obtained after agitation and decrease in EC of treated soil water extract (EC_TSWE) as intensity of acidification increased. The exchangeable cations in the soil got exchanged by H^+ ions in the artificial AR and became water soluble cations in the effluent, this increased the EC_EFF.
As the intensity of AR increased more exchangeable cations got leached off in the effluent. This reduced their concentration in treated soils. The \( ECTSWE \) values corresponding to more intense AR are found to be lesser.

### 3.1.2 Organic Matter (OM)

The observations as presented in Table 4 indicate that on acid treatment, the OM got digested and thereby its percentage reduced. More intense AR can completely digest the OM.

### 3.1.3 Calcium Carbonate (CaCO_3) Content

CaCO_3 present in the soil reacted with acid, its concentration got reduced with intensity of AR. The observations are presented in Table 4.

### 3.2 X-Ray Diffraction (XRD) Pattern of Original and Treated Samples

XRD pattern of original soil samples is presented in Figure 3. XRD pattern for the soil samples treated with 0.04 N H\(_2\)SO\(_4\), HNO\(_3\) and 1:1 mixture of H\(_2\)SO\(_4\) / HNO\(_3\) are presented in Figure 4-6 respectively.
The XRD pattern of the acid treated soil shows clear difference in certain peaks. This is due to change in mineralogy as a result of reaction with acid. The XRD analysis of all the treated samples clearly shows more mineralogical changes as the intensity of AR increased.

3.3 Soil Texture

The soil samples were analyzed before and after acid treatment using scanning electron microscope (SEM) for finding the texture of the soil crystals. The result of SEM analysis (Mag. 300 x ) for the original soil samples and for the sample treated with 0.005N and 0.04 N of H₂SO₄, HNO₃ and 1:1 mixture of H₂SO₄ / HNO₃ are presented in Figure 7, Figure 8 – 9, Figure 10 – 11 and Figure 12 – 13 respectively.
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**Figure 7:** SEM analysis of original soil (Sample B)

**Figure 8:** SEM analysis of soil treated with 0.005 N H₂SO₄ (Sample B₅⁻1)

**Figure 9:** SEM analysis of soil treated with 0.04 N H₂SO₄ (Sample B₅⁻4)

**Figure 10:** SEM analysis of soil treated with 0.005 N HNO₃ (Sample B₅⁻1)

**Figure 11:** SEM analysis of soil treated with 0.04 N HNO₃ (Sample B₅⁻4)

**Figure 12:** SEM analysis of soil treated with mixture of 0.005 N HNO₃/0.005 N H₂SO₄ (Sample B₅NS⁻1)

**Figure 13:** SEM analysis of soil treated with mixture of 0.04 N HNO₃/0.04 N H₂SO₄ (Sample B₅NS⁻4)
It is observed that angularity of the particles is increased which can be attributed to leaching of the cations and subsequent deflocculation.

### 3.4 Mechanical Analysis

The results of mechanical analysis of the soil samples before and after acid treatment are presented in Table 5. The results clearly show that if the intensity of AR is more it will reduce the clay percentage. It may be attributed to reduction in ionic forces due to cationic leaching. The percentage of the fractions more than 0.075 mm also reduces. The percentage of silt sizes increases as intensity of acidification increases.

**Table 5:** Results of grain size analysis of soil before and after acid treatment

| Soil Sample | Particle Size (mm) | Below 0.002 (%) | 0.002 to 0.075 (%) | 0.075 to 0.425 (%) | 0.425 to 2.0 (%) | 2.0 to 4.75 (%) |
|-------------|-------------------|-----------------|--------------------|--------------------|-----------------|----------------|
| B           |                   | 23.40           | 60.00              | 9.50               | 4.20            | 2.90           |
| B_S - 1     |                   | 22.00           | 65.40              | 6.20               | 3.90            | 2.50           |
| B_S - 2     |                   | 20.80           | 68.50              | 4.90               | 3.70            | 2.10           |
| B_S - 3     |                   | 19.40           | 71.80              | 3.60               | 3.40            | 1.80           |
| B_S - 4     |                   | 18.20           | 75.10              | 2.40               | 2.90            | 1.40           |
| B_N - 1     |                   | 21.30           | 66.80              | 5.90               | 3.80            | 2.20           |
| B_N - 2     |                   | 19.60           | 70.70              | 4.30               | 3.50            | 1.90           |
| B_N - 3     |                   | 18.00           | 73.40              | 3.10               | 3.00            | 1.50           |
| B_N - 4     |                   | 17.60           | 76.80              | 1.90               | 2.60            | 1.10           |
| B_NS - 1    |                   | 22.20           | 65.60              | 6.30               | 3.60            | 2.30           |
| B_NS - 2    |                   | 19.80           | 71.90              | 3.00               | 3.40            | 1.90           |
| B_NS - 3    |                   | 18.60           | 74.30              | 3.00               | 2.80            | 1.30           |
| B_NS - 4    |                   | 17.80           | 76.40              | 2.80               | 2.40            | 0.60           |

### 3.5 Consistency Characteristics

The values of Liquid limit (W<sub>L</sub>), Plastic limit (W<sub>P</sub>), Plastic Index (I<sub>p</sub>), Shrinkage limit and Free Swell Index for the soil samples before and after acid treatment are presented in Table 6. The degree of variation in the consistency characteristics of the soil depends on factors like type of soil, electrical charge of exchangeable cations absorbed by soil particles and concentration of cations in soil water (Kamon et al. 1997).

Due to the leaching of cations the consistency characteristics of the soil reduced except shrinkage limit. The increase in values of shrinkage limit is attributed to increase in interparticulate distances due to reduction in the forces between soil particles.

**Table 6:** Results of consistency characteristics of soil before and after acid treatment

| Sample | W<sub>L</sub>, % | W<sub>P</sub>, % | I<sub>p</sub>, % | Shrinkage limit, % | Free Swell Index, % |
|--------|------------------|-----------------|-----------------|--------------------|---------------------|
| B      | 54.90            | 24.00           | 30.90           | 6.42               | 60.57               |
| B_S - 1| 51.80            | 23.40           | 22.60           | 8.61               | 50.81               |
| B_S - 2| 50.60            | 22.60           | 28.00           | 8.97               | 48.94               |
3.6 Strength Characteristics

The strength characteristics of soil are affected extensively by soil’s internal structure and interaction between soil particles. The strength of soil originates mainly from the soil skeleton and electric attractive force between the electric charges absorbed by the soil particles.

The results of the effective cohesion (c’), kg/cm² and Effective angle of internal resistance (Ø’), degree for untreated and acid treated soil samples is presented in Table 7. The values of effective cohesion (c’) and Effective angle of internal resistance (Ø’) are observed to be lesser for acid treated soil samples. This is mainly due to reduction in the electric forces as concentration of exchangeable cations reduced on acid treatment.

Table 7: Strength Characteristics of soil samples before and after acid treatment

| Sample | Effective cohesion (c’), kg./cm² | Effective angle of internal resistance (Ø’), degree |
|--------|-------------------------------|-----------------------------------------------|
| B      | 0.44                          | 16.20                                         |
| BS - 1 | 0.34                          | 15.90                                         |
| BS - 2 | 0.29                          | 15.60                                         |
| BS - 3 | 0.26                          | 15.10                                         |
| BS - 4 | 0.26                          | 14.40                                         |
| BN - 1 | 0.28                          | 15.40                                         |
| BN - 2 | 0.30                          | 14.80                                         |
| BN - 3 | 0.28                          | 14.10                                         |
| BN - 4 | 0.21                          | 13.20                                         |
| BN - 1 | 0.37                          | 15.60                                         |
| BN - 2 | 0.32                          | 14.80                                         |
| BN - 3 | 0.25                          | 13.60                                         |
| BN - 4 | 0.23                          | 12.90                                         |

4. Conclusions

AR results in changes in physico-chemical characteristics of soil due to cations exchange. pH of the soil decreases. Grain size distribution of the soil will shift towards silt fractions when subjected to AR. The angularity of individual particles will also increase. AR affects the consistency properties of the soil. Leaching of cations will reduce the attractive forces between the soil particles which will lower the overall strength of the soil. The data obtained during the
experiments is useful in gauging the damages to the soil that could occur due to the AR in future. However the magnitude of the deterioration will depend on persistence and strength of AR.

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