

# Effects of Chemicals on Compacted Clay Liner

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## ABSTRACT

Engineering properties of bentonite soils get modified upon contamination with different chemicals from industrial waste. Bentonite soil is often used as a material for clay liner. But its engineering properties change when it is contaminated. To see the effect of inorganic & organic chemical on bentonite soil, two chemicals (Aluminium hydroxide and Acetic acid) that are generally found in municipal solid waste were selected. The effect of these chemicals on Bentonite soil has been studied in a controlled condition in the laboratory. The optimum values of these chemicals are evaluated and added separately to Bentonite soil. The engineering properties such as Differential Free Swell, Hydraulic Conductivity and Swelling Pressure were found out. The result of differential free swell indicate that with Acetic acid and Aluminum hydroxide the free swell decreases by 47 % and 49 % respectively. The hydraulic conductivity results show that it decreases by 12% with Aluminum hydroxide and 17% by Acetic acid. Tests were also carried out to evaluate Shear strength parameters of Bentonite soil upon contamination with chemicals. The result of swelling pressure indicated that it decreased by 82% when Aluminum Hydroxide was added and increased by 20% when Acetic Acid added was added, Maximum Dry Density decreased by 14.8 % when Aluminum hydroxide was added & 7% with Acetic acid, The strength parameters cohesion 'c' and the angle of internal friction ( $\phi$ ) were also evaluated and was observed that cohesion decreases by 50% with Aluminum Hydroxide and 43% with Acetic Acid, and angle of internal friction almost remain same. The selected soil is considered to be highly expansive in nature. In addition to these tests some test were also carried out to study the fabric of soil such as Scanning Electron Microscope (SEM), Cation Exchange Capacity (CEC), Infra-Red Spectroscopy (IR), X-Ray Diffraction (XRD) and Specific Surface Area.

**KEYWORDS:** Clay liner, Acetic acid, Aluminium hydroxide, Soil fabric, Engineering behavior.

## INTRODUCTION

Compacted clay has gained wide acceptance as part of the barrier systems for municipal or industrial waste disposal site (Rowe et al, 1995; Daniel & Koerner 1995; Rowe 2001). However, this acceptance is largely based on experience in North America & Europe. There has been much less work conducted to examine the use of clay found in other part of world. Any such examination must involve consideration of factors such as hydraulic conductivity, compaction, swelling pressure and shear strength characteristics etc.

The bentonite-based material being evaluated in several countries as potential barriers and seals for a nuclear waste disposal system In order to investigate whether local Korean bentonite could be useful as a buffer or sealing material in an high level waste repository system.( Jongwon Choi et al,2001).

The interaction of minerals in bentonite soil with organic materials may result in changes of their surface properties and microstructures. Such changes are critical for the environment and should be taken into consideration during treatment of wastewater by clay materials. In the repositories of municipal waste, in addition to stable waste materials, some organic acids and bases are formed as products of chemical, photochemical and biological reactions (Acher and Saltzman, 1989; Lee Wolfe, 1989; Perry et al., 1989). Leakage waters trickling through municipal repositories contain organic bases and other polar water-soluble organic compounds, often accompanied by water insoluble aliphatic or aromatic hydrocarbons (Yaron, 1989).

A considerable amount of information related to contaminant has been published for constant charged soils formed in cold and temperate climates. However, there is only limited data on variable charged soils formed in tropical regions. In the present study an attempt has been made to have a better understanding about the behavior of compacted clay upon contamination with different chemicals.

Bentonite soil is used as the compacted clay liner and the chemicals used in the present study are Aluminum hydroxide (inorganic chemical) and Acetic acid (organic chemical). Aluminum hydroxide [Al(OH)<sub>3</sub>] is widely used in the manufacture of fire retardants, fillers, pigments, adsorbents, catalysts etc. and also available in the waste generated during the manufacturing process. Similarly, Acetic acid [CH<sub>3</sub>COOH] is available in the waste product during the fermentation of organic substances. The properties of Bentonite soil is presented in Table 1.

**Table 1:** Properties of Bentonite Soil

Silica	50.73 %
Alumina	20.40 %
Ferric Oxide	5.78 %
Titanium Dioxide	1.30 %
Magnesium Oxide	1.74 %
Calcium Oxide	1.07 %
Magnous Oxide	Nil
Sodium Oxide	2.12 %
Potassium Oxide	0.92 %
Loss on Ignition	15.90 %
Gel Index	18%
pH(2% suspension )	7.2%

## EXPERIMENTAL PROGRAM

Commercially available Bentonite soil is used for the entire tests. The samples for all the tests were prepared by mixing optimum dose of the chemical and then compacting the mixture at optimum moisture content (OMC). To simulate field condition, all the tests were carried out following the procedure for the heavy compaction test. A comprehensive laboratory testing was then carried out on the samples prepared in order to determine its mineralogical composition, geotechnical properties and physico-chemical properties. Following laboratory tests were conducted on soil to determine its index properties and compaction, strength, and volume change characteristics:

Determination of the fabric by the scanning electron microscopy (SEM) technique.

X-ray (XRD) technique has been used for the determination of possible phases present in the soil.

IR spectroscopy was carried out to get an information on fundamental vibrational modes of the constituent units of the soil.

Cation exchange capacity (CEC) and pH were carried out to study the physico-chemical nature of the soil .CEC was done according to IS 2720 ( Part 24)-1987 and pH according to IS 2720 ( Part 26)-1987.

The consistency behavior was determined by the evaluation of Atterberg limits: as per IS-2720 (Part 5)-1985.

Heavy compaction test was carried out to investigate the compaction characteristics IS-2720 (Part 8) – 1983.

Unconsolidated Undrained Triaxial compression tests on cylindrical specimens 3.81 cm in diameter and 7.62 cm long, for strength evaluation of soil IS-2720 (Part 11)-1971

One dimensional consolidation test on samples 6.0 cm in diameter and 2.0 cm in thickness, for Hydraulic conductivity analysis

The percentage of swell test was carried out in a consolidation ring of 6.0 cm diameter and 2.0 cm thick, to determine the volume change behavior of the soil. IS 2720(Part 40)-1977

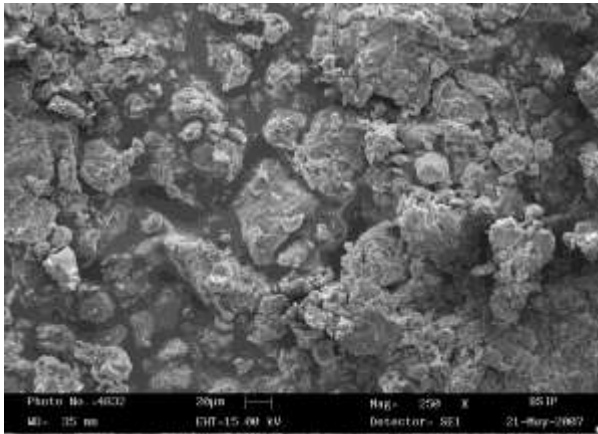
The swelling pressure test was performed using a constant volume condition using proving ring method. Test was carried out on samples of height 128 mm and 100 mm in diameter. The volume of the sample was kept constant after flooding the soil with water as per IS (Part 41)-1977

## RESULTS AND DISCUSSION

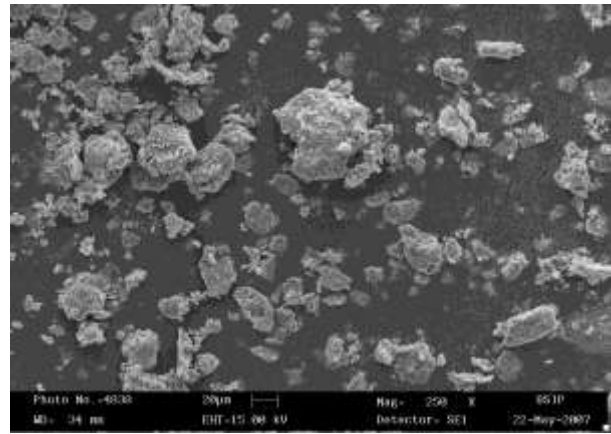
### Mineralogical properties

#### *Fabric*

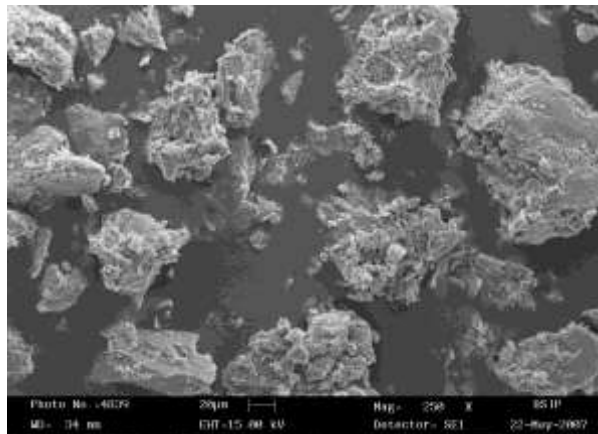
Geometric arrangement of particles in the soil is referred to as fabric of the soil. The fabric plays a crucial role in controlling the engineering parameters of soil. The scanning electron microscopy technique was used to study the fabric of the soil at a magnification of 250X.



(a) Bentonite



(b) Bentonite + Aluminium Hydroxide



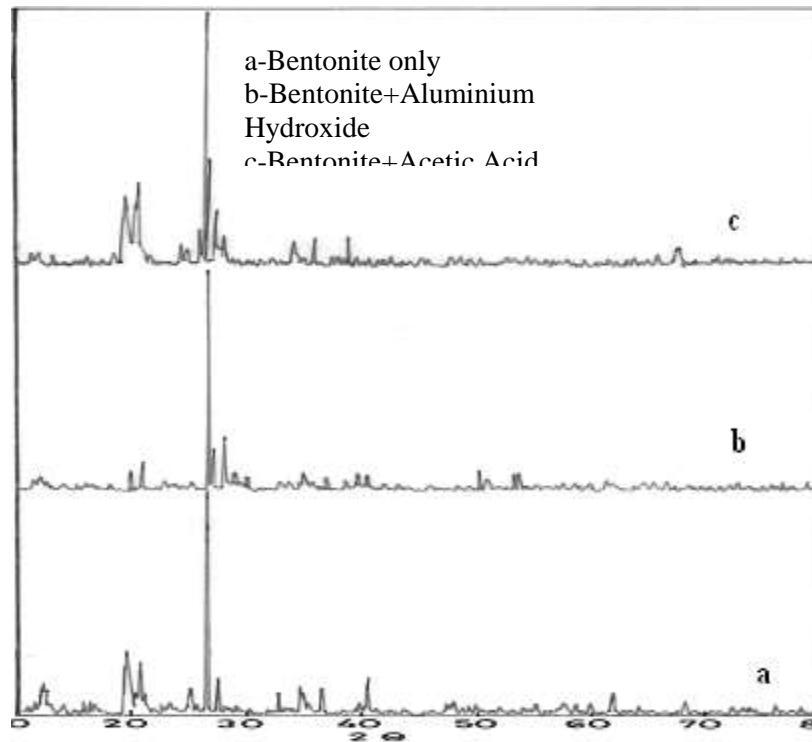
(c) Bentonite + Acetic Acid

**Figure 1: SEM micrograph**

Fig. 1(a) shows the micrograph of the Bentonite soil added with distilled water, Fig. 1 (b) shows the micrograph of soil added with Aluminum hydroxide, and Fig. 1(c) shows of soil added with Acetic acid. By studying the micrograph, it was observed that flocks are formed due to Acetic acid. In case of Aluminum hydroxide it forms crystalline silicates hydrates due to partial dissolution of  $\text{Al}(\text{OH})_3$ , which make the soil hydrophobic, which is significant in micrograph.

### X-Ray Diffraction (XRD)

The XRD test was done on SIEFERT MZ VI. The mineralogical identification was based on the XRD studies carried out for identifying the reaction products formed.



**Figure 2:** XRD of Bentonite with Chemicals

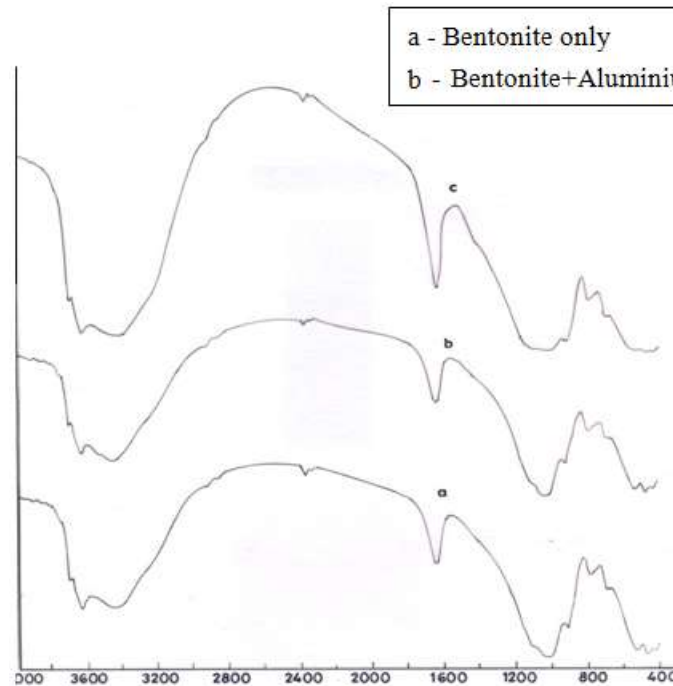
The XRD of bentonite soil alone is shown in 2(a). The XRD pattern of untreated bentonite indicate the presence of montmorillonite, quartz etc.

The XRD of bentonite soil mixed with  $\text{Al}(\text{OH})_3$  is shown in Fig.2 (b) and with acetic acid is shown in Fig.(2(c)).

The XRD of bentonite soil mixed with  $\text{Al}(\text{OH})_3$  and with  $\text{CH}_3\text{COOH}$  does not show any marked departure in peaks when compared to XRD of bentonite soil alone. This shows that mineral phase remains same upon treatment with both  $\text{Al}(\text{OH})_3$  and  $\text{CH}_3\text{COOH}$ .

### Infrared Spectra (IR)

The IR test was done on Varian 3100 FT-IR (Excalibur Series). Fig.3 shows the graphs of IR spectra in region  $4000\text{-}400\text{ cm}^{-1}$  that provides information on fundamental vibrational modes of the constituent units of these materials. Graph-a shows IR obtained for bentonite only, graph-b is for bentonite + Aluminium hydroxide and graph-c is for bentonite + Acetic acid. OH stretching and bending vibrations occurs in the spectral region of the  $3750\text{-}3500$  and  $950\text{-}600\text{ cm}^{-1}$ , respectively. Si-O and Al-O stretching modes are found in the  $1200\text{-}700\text{ cm}^{-1}$  range, while Si-O and Al-O bending modes dominate the  $600\text{-}400\text{ cm}^{-1}$  region.



**Figure 3:** IR-Spectra of Bentonite with Chemicals

The IR spectra indicate that montmorillonite is the dominant mineral phase in this clay. The absorption band at  $3624\text{ cm}^{-1}$  is due to stretching vibrations of structural OH groups of montmorillonite. A complex band at  $1032\text{ cm}^{-1}$  is related to the stretching vibrations of Si–O groups, while the bands at  $529\text{ cm}^{-1}$  are due to Al–O–Si bending vibration. The band at  $690\text{ cm}^{-1}$  was assigned to coupled Al–O and Si–O out-of-plane vibrations. Water in montmorillonite gave a broad band at  $3446\text{ cm}^{-1}$  corresponding to the H<sub>2</sub>O-stretching vibrations, due to an overtone of the bending vibration of water observed at  $1639\text{ cm}^{-1}$ . The changes in the Si environment after acid activation process were reflected in both the position and the shape of the Si–O stretching band near  $1032\text{ cm}^{-1}$ . A slight shift of this band to higher frequencies indicates alteration of the structure. The IR spectrum of the Bentonite +Al(OH)<sub>3</sub> shows, in addition to the tetrahedral Si–O band near  $1033\text{ cm}^{-1}$ , absorption band at  $1120\text{ cm}^{-1}$ , assigned to Si–O vibrations of amorphous silica with a three-dimensional framework. The spectrum of the Bentonite +Al(OH)<sub>3</sub> sample, has all absorption bands characteristics of amorphous silica ( $1120, 791$  and  $467\text{ cm}^{-1}$ ) confirms a high degree of structural decomposition. Almost same type of spectra is seen in Bentonite + Acetic acid. The broad band near  $1032\text{ cm}^{-1}$ , assigned to complex Si–O stretching vibrations in the tetrahedral sheet, upon saturation process moved to  $1026\text{ cm}^{-1}$  in the Fig. 3c, but some broadening and a decrease in intensity of the Si–O band was observed.

## PHYSICO-CHEMICAL PROPERTIES

These properties are related to the physical and chemical interaction of the soil particles with each other and with their environment such as the pore fluid and dissolved salts etc. For fine-grained soils, the physical interaction is of little importance. However, the behavior of fine-grained soils is entirely dependent on how the particles interact chemically with each other or with their environment. Various physico-chemical properties have been determined for uncontaminated and contaminated bentonite soil and are presented in Table2.

## Cation Exchange Capacity (CEC)

CEC of a clay can be defined as the amount of exchangeable ions, expressed in milliequivalents, per 100g of dry clay. The CEC of bentonite alone was determined by Ammonium acetate saturation method and is found to be 54.84 meq/100g where as CEC of Bentonite found by Yurdakoc, M. (2007) is 92 meq/100g of clay. This difference in CEC may be due to variation in the mode of formation of bentonite. The CEC of bentonite alone and bentonite with chemicals is shown in Table 2. The CEC of bentonite + Aluminium hydroxide is 55.05 meq/100g and of bentonite + Acetic Acid is 43.05. There is a marked reduction in the CEC of the Bentonite when added with Acetic acid. However, with Aluminum hydroxide it remains almost same.

### *Specific Surface Area*

The surface of clay particles per unit mass is generally referred to as specific surface, usually expressed in  $\text{m}^2/\text{g}$ . BET surface area was determined by nitrogen adsorption and desorption data acquired on a Micromeritics ASAP 2020 apparatus. The sample was pretreated overnight under vacuum of  $5 \times 10^{-3}$  Torr @  $350^\circ\text{C}$  for 15 hrs. Surface area measurement had an error of  $\pm 2 \text{ m}^2/\text{g}$ . The specific surface area of bentonite + Aluminium hydroxide is  $136.33 \text{ m}^2/\text{g}$  and of bentonite + Acetic Acid is  $68.79 \text{ m}^2/\text{g}$ . It was observed that there is an increase in surface area of bentonite + Aluminium hydroxide and bentonite + Acetic acid over bentonite alone, which is also evident in micrograph of SEM. The results of specific surface are presented in Table 2.

### *pH*

pH of the samples was measured by a pH meter. The results showed that there is a slight increase of pH, showing the basic nature of the chemical.

**Table 2:** Summary of Various Physico-chemical properties of bentonite soil and bentonite with chemicals.

Property	Bentonite	Bentonite+ Al(OH) <sub>3</sub>	Percentage increase(+)/ Decrease(-)	Bentonite+ Acetic acid	Percentage increase(+)/ decrease(-)
CEC (meq/100g)	54.84	55.05	(+)0.38	43.05	(-)21.5
Specific Surface Area ( $\text{m}^2/\text{g}$ )	54.02	136.33	(+)152.37	68.79	(+)27
pH	6.56	7.66	(+)16.77	8.18	(+)24.70

## GEOTECHNICAL PROPERTIES

The geotechnical properties were determined for bentonite, bentonite + Aluminium hydroxide and bentonite + Acetic acid. The geotechnical properties have been used to investigate the influence of microstructure and physico-chemical changes on the physical and mechanical behavior of the bentonite soil under investigation.

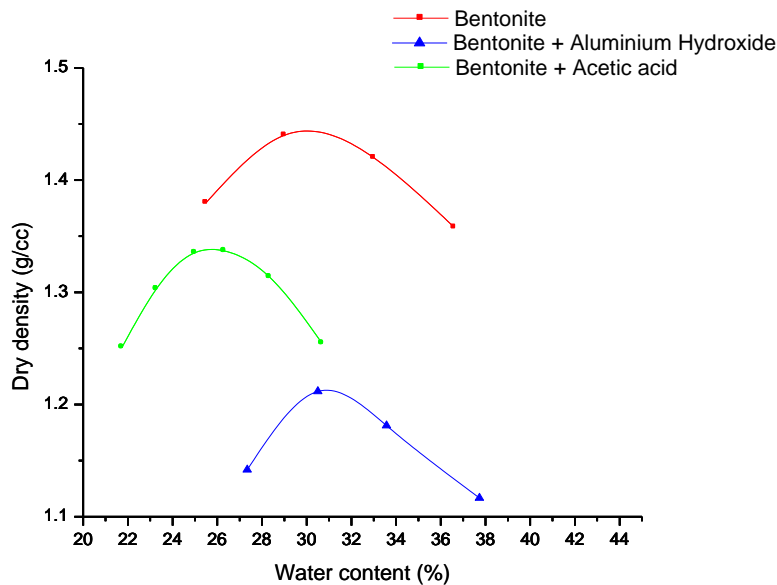
### *Atterberg Limits*

The optimal dose of the chemicals to be added is evaluated using Atterbergs Limits. When the plasticity index is decreasing the hydraulic conductivity increases and is maximum at minimum value of plasticity index (Brandal H.,1992).The percentage of chemical corresponding to minimum plasticity index is taken as optimum dose of chemical.

### *Compaction Test*

Heavy Compaction test results indicate that addition of Acetic acid causes reduction in both OMC and MDD whereas addition of Aluminium hydroxide causes increase in OMC but reduction in MDD.

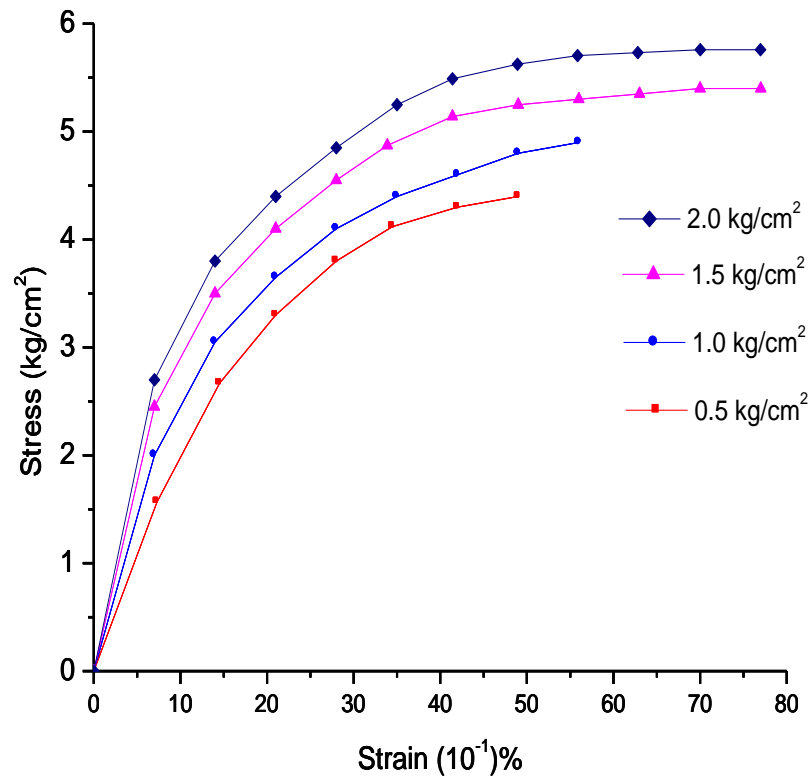
Relative change in OMC and dry density will depend on the effect of resistance offered by soil particles during compaction. This behavior can be explained in context of diffuse double layer. With the addition of Acetic acid, diffuse double layer tends to depress; this allows particles to come closer under the same amount of compactive effort leading to increase in density. On the other hand, with the addition of Aluminium hydroxide, maximum dry density decreases whereas OMC increases. Addition of  $Al(OH)_3$  forms crystalline silicate hydrates due to partial dissolution of  $Al(OH)_3$ . This is due to the dissolution of  $Al(OH)_3$  that gives free ions which combine with alumina or silica to initiate complex Aluminium silicate reaction that will make the soil hydrophobic and an increase in OMC (Gutschick, 1978).



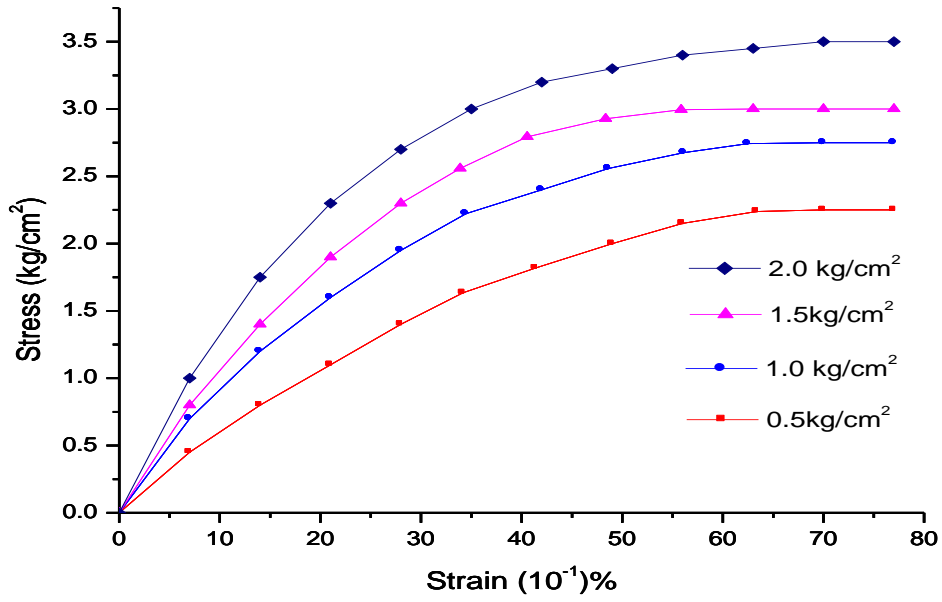
**Figure 4:** Influence of Chemicals on Compaction of Bentonite

## Shear Strength Parameters

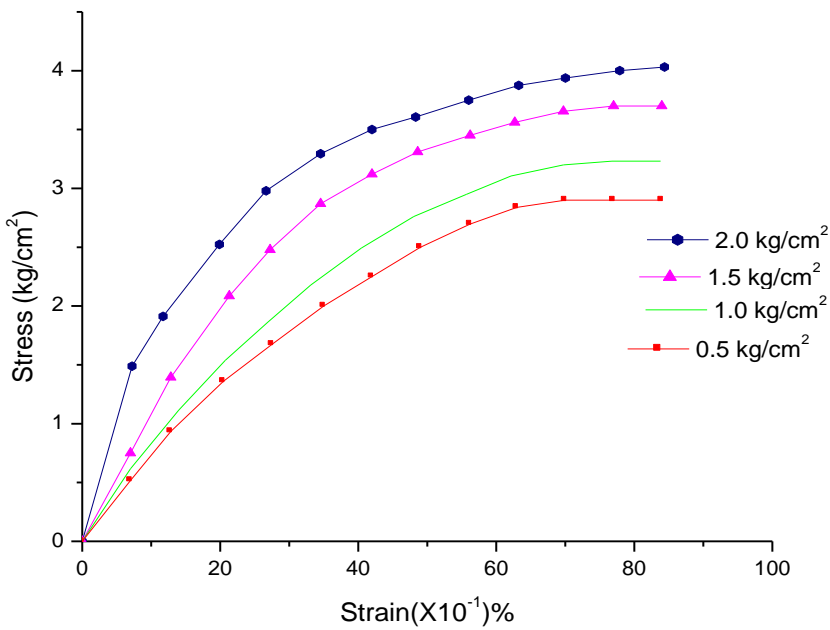
The results of undrained triaxial test performed on the samples prepared at OMC are presented in Table 3. Typical stress versus strain curves are presented in Figs. 5(a) to 5(c). Results indicate that with the addition of Aluminium hydroxide, the cohesion ( $C_u$ ) decreased by about 50% whereas the angle of internal friction ( $\phi_u$ ) remained unchanged. With the addition of Acetic acid, the behavior of bentonite was almost same as that with Aluminium hydroxide.



**Figure 5(a):** Stress-Strain Curve of Bentonite alone



**Figure 5(b):** Stress- Strain Curve of Bentonite + Aluminium Hydroxide



**Figure 5(c):** Stress-Strain Curve of Bentonite + Acetic Acid

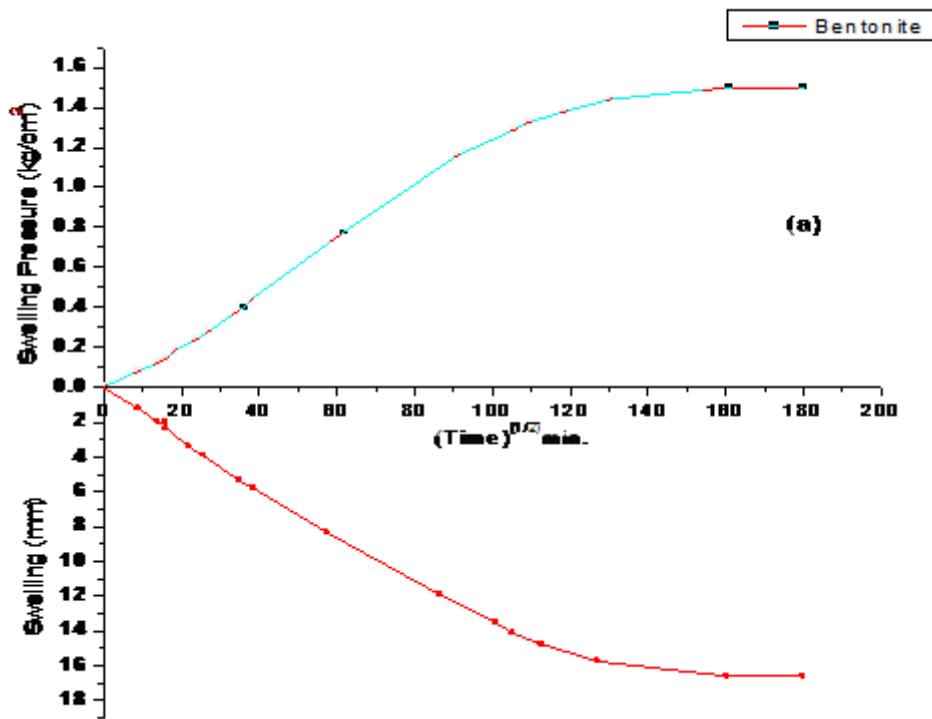
Differential Free Swell (DFS)

When compared with Bentonite DFS decreases by 49% with addition of Aluminium hydroxide and by 47% with the addition of Acetic acid. . The results are presented in Table 3.

Swelling Pressure

Swelling pressure is the pressure applied by the swelling clays when their volume change is prevented. A load cell was used to record the increase in pressure after the addition of water. The sample was then inundated by water. Since the sample was being prevented from undergoing any change in its volume, in reaction, it applies pressure to the load cell, which was recorded and is presented in Table3.

It is observed that swelling pressure tends to decrease when Aluminium Hydroxide is added to bentonite soil and the behavior is same with Acetic acid also. Relationship between swelling & swelling pressure versus square root of time has been plotted and shown in Figs.5 (a) to 5(c).



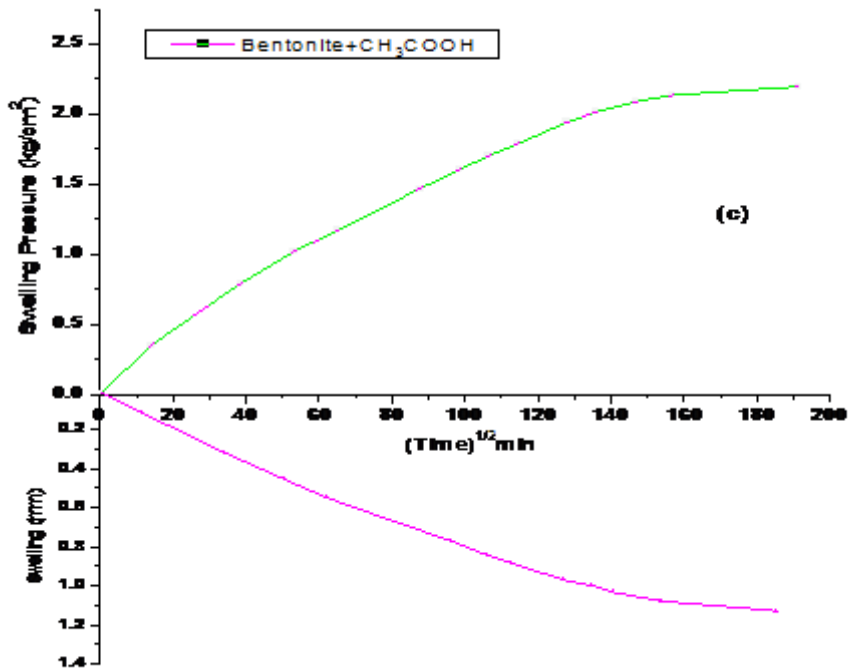
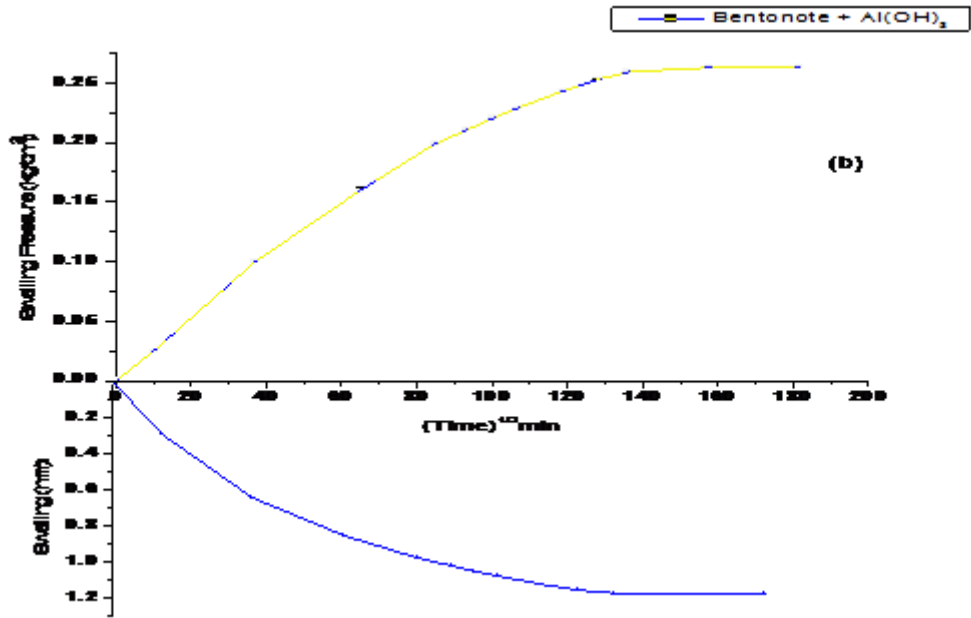


Figure 6: Influence of Chemicals on Swelling Pressure and Swelling of Bentonite soil

The swelling pressure of bentonite only was  $1.46 \text{ kg/cm}^2$ , whereas swelling pressure of bentonite + Aluminum hydroxide was  $0.22 \text{ kg/cm}^2$  and for bentonite + Acetic acid was  $1.55 \text{ kg/cm}^2$ . There is a decrease of 85% when Aluminum hydroxide was added and when Acetic acid was added there is an increase of 6%. It is observed that the above relationships are more or less mirror image of each other. This suggests that during the ingress of moisture, development of swelling pressure corresponds to that of swelling tend to stabilize with time. Swelling pressure is related to development of diffuse double layer. Less value of swelling pressure is in case of Aluminum Hydroxide and can be considered as an indication of well-developed diffuse double layer.

The rate of swelling in the initial stages was very high. This behavior is probably due to the dispersed soil fabric. Individual particle surfaces were open to adsorb water. The water around the sample come in contact with the top and bottom surfaces of the sample. This interaction caused the fabric to change slowly.

## HYDRAULIC CONDUCTIVITY

The hydraulic conductivity of bentonite soil is normally in the range of  $10^{-4}$  to  $10^{-6} \text{ cm/sec}$  and is said to be impervious/slightly pervious soil. As such, the hydraulic conductivity is obtained by indirect method from the results of oedometer test.

The test results indicate that, the hydraulic conductivity of bentonite is  $1.06 \times 10^{-5} \text{ cm/sec}$ . With the addition of the chemicals, the hydraulic conductivity decreased slightly in both the case.

**Table 3:** Summary of Various Geotechnical properties of contaminated and uncontaminated bentonite soil

Property	Bentonite	Bentonite+ Al(OH) <sub>3</sub>	Percentage increase(+)/ decrease(-)	Bentonite+ Acetic acid	Percentage increase(+)/ decrease(-)
Liquid Limit (%)	220	345	(+)57	115	(-)48
Plastic Limit (%)	53	50	(-)6	35	(-)34
Plasticity Index (%)	167	295	(+)77	80	(-)52
Heavy MDD (g/cc)	1.44	1.29	(-)10	1.34	(-)7
Compaction Test OMC (%)	29.0	30.5	(+)5	25.5	(-)12
Shear Strength Cu (kg/cm <sup>2</sup> )	1.5	0.75	(-)50	0.85	(-)43
Strength parameters Φu (Deg.)	16	16	--	17	(+)6
DFS (%)	976	500	(-)49	516	(-)47
Swelling pressure (kg/cm <sup>2</sup> )	1.46	0.22	(-)85	1.55	(+)6
Hydraulic Conductivity (cm/sec)	$1.06 \times 10^{-5}$	$0.932 \times 10^{-5}$	(-)12	$0.88 \times 10^{-5}$	(-)17

## COMMENTS

The results of the above tests show that Aluminum Hydroxide is probably creating much more separation between diffuse double-layer of clay particles, which is causing breaking of the particles into smaller pieces and hence particle size is decreasing. This may be incursion of cations in double

layer causing repulsion due to positive charge of double layer. However Acetic acid is not showing this type of effect, and just causing increase of the particle size and appears that probably hydration is taking place in soil. This is also supported by XRD graph, which shows that some type of hydration is taking place, which is causing more ordered geometry in comparison to bentonite

## CONCLUSIONS

The following conclusions can be drawn from the above discussion:

- Acetic acid upon contact with bentonite soil leads to the formation of flocs. This is also evident from the reduction in hydraulic conductivity by about 17%. But when Aluminum hydroxide is in contact with bentonite soil, flocs reduced in size. As such the specific surface area increased.
- XRD diffractogram of bentonite with Aluminum hydroxide and Acetic acid does not show any marked departure in peaks when compared with XRD diffractogram of bentonite soil alone. Hence, it can be concluded that the mineral phases remain same, i.e. mainly montmorillonite and quartz.
- IR spectra of bentonite with Aluminium hydroxide and Acetic acid does not show any marked change in fundamental vibrational modes of the constituents units. However in case of bentonite + acetic acid the peak at  $1026\text{ cm}^{-1}$  is missing. This is probably due to some new bonding.
- CEC decreases in case of bentonite + Acetic acid by 21.5% over bentonite alone. However in case of bentonite + Aluminium hydroxide there is negligible increase of 0.38%.
- OMC and MDD, both show a reduction when bentonite is added with Acetic acid. But upon addition with Aluminium hydroxide, MDD reduces but OMC shows an increase by 5%.
- Strength parameter 'c' decreased by 50% upon addition of Aluminum hydroxide to bentonite and by 43% with Acetic acid. There is practical no change in the strength parameter ' $\Phi_u$ ' in both the case, i.e. bentonite + Aluminum hydroxide and bentonite + Acetic acid.
- When compared with bentonite, DFS decreases by 49% with addition of Aluminium hydroxide and by 47% with addition of Acetic acid. It is observed that swelling pressure tends to decrease when Aluminium Hydroxide is added to bentonite soil and the behavior is same with Acetic acid also. This is also evident from Specific surface data.
- Hydraulic conductivity decreases by 12% with Aluminum hydroxide and 17% with Acetic acid. This is also evident as the specific surface is increasing in both the case.

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