Characterization of Swelling Clays as Buffer/Backfill Material for Geological Repositories of Immobilized Radioactive Liquid Waste


Abstract

After gaining considerable expertise in establishing and exercising waste management strategy by immobilization of high-level radioactive liquid waste (HLW) in borosilicate glass matrix followed by its interim storage, it is envisaged to focus on geologic disposal of radioactive waste packages. The multi barrier disposal system is considered one of the options for isolation of radioactive waste from human environment for an extended period of time. The engineered barrier comprises of waste form, canisters, over packs, buffer and backfill material whereas host rock serves as the natural barrier.

The buffer and backfill materials play an important role because it can retard the migration of radionuclides by delaying the contact with ground water and associated sorption. Characterization and demonstration of efficacy of swelling clays in repository condition forms an integral part of studies ensuring the safe disposal of high level radioactive waste. Natural clays may be used solely or as a phase in a buffer/backfilling mixture because of its low hydraulic conductivity, high specific surface area and in some cases swelling ability. Long term performance of these materials has to be assessed with respect to their suitability as candidate backfill material.

Twenty six nos. of swelling clay samples were collected from the natural deposits of different locations from western zone of the country. Samples collected have been taken up for detailed characterization of clay with respect to mineralogical, physico chemical, microscopic and geotechnical properties. From the X-ray diffraction patterns presented and the d-values associated with the patterns, montmorillonite and quartz have been identified as major phases present in all the samples of swelling clay. Energy Dispersive X-Ray (EDX) analysis of the swelling clay samples mainly indicated presence of Si, Al, Na, K, Mg supporting thereby the X-Ray diffraction data. SEM micrographs of two typical clay samples at different magnifications indicate flake like surface morphology. The clay samples were found to be having swelling ability indicating smectite rich composition and optimum CEC. While chemical analysis indicates the presence of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, Na$_2$O, CaO as major elements, higher amount of chlorides is
attributed to the marine origin of the clay. Present paper given an account the experimental studies carried out to evaluate the potentiality of using swelling clays as buffer/backfill material for geological repositories of immobilized high-level radioactive liquid waste.

Keywords Cesium; Clays; Sorption; HLW; Backfill; Repository.

1. INTRODUCTION

In nuclear technology the management of nuclear waste is a mandatory requirement. Stepwise, the management entails the immobilization of high-level radioactive liquid waste (HLW) in a suitably designed glass matrix, interim storage for some period and the surveillance of the waste glass confined within sealed canisters, and finally, the disposal of the conditioned product in geological repositories. The last step involves meticulous planning for secured isolation of the radioactive waste from human environment taking measure for the activity confinement during naturally occurring premeditative evolution, both normal and off normal at and around the selected site. In order to materialize the safe disposal of the wastes, the identification and characterization of suitable geological repository sites is an issue in the nuclear waste management of every country adopting nuclear technology for power production. In India, after gaining considerable expertise in establishing and exercising waste management strategy of immobilization followed by surveillance of HLW in borosilicate glass matrix in sealed cans, it is envisaged to focus research on the rock and clays of candidate geological repository sites within this country.

Geological repositories (GR) as well as Near Surface Disposal Facilities (NSDF) generally use the concept of multi-barrier system for the waste confinement over ages against possible natural calamities. The multi barrier disposal system buried inside host rock is considered as one of the options for isolation of radioactive waste from human environment for an extended period of time. The engineered barrier comprises of waste form, canisters, overpacks, buffer and backfill material. Host rock of selected site serves as the natural barrier for isolation of radioactive waste from human environment. Buffer and backfill material play an important role as an engineered barrier in any repository concept. They are suitably selected to fulfill various functions summarized below.

Natural clays may be used solely or as a phase mixture with buffer/backfilling materials because of their low hydraulic conductivity, high specific surface area and in some cases swelling ability [Paula Keto et al, 2004 and Pusch R., 1998]. They are used to bury the sealed and over-packed canisters of the immobilized waste inside the host rock. Besides filling any voids around the waste package and in excavated areas for increasing the structural stability, the buffer and backfill have other important roles: they reduce the ground water’s volume movement as well as channeling within the repository, provide chemical buffering around the waste packages, retard oxygen inflow and outward migration of radio nuclides released from over-packs, and allow sufficient heat conduction. Because of their swelling characteristics any fracture, joint and other pathways get blocked mechanically, the migrating radionuclides can only make delayed contact with ground water and lead to associated sorption, and the
impeded oxygen inflow slows down the canister’s corrosion. Characterization and demonstration of efficacy of swelling clays in repository condition forms an integral part of studies to ensure the safe disposal of high-level radioactive waste. Long-term performances of these materials are thereby assessed in terms of their suitability as candidate backfill material.

India has good reserves of the swelling clays located in various parts of the country. Smectite rich deposits of about 20 million ton have been identified in western zone of the country. Unlike most of the world deposits, clays from India’s western region are alteration products of older volcanoes. The naturally available swelling clay deposits of this country are seemed to be the potential candidates as the buffer/backfill materials. This study focuses on the characterization of a large numbers of swelling clay samples collected from the natural deposits of different locations from western zone of the country to evaluate their suitability as the buffer/backfill materials in the geological repository for disposal of high level radioactive waste. In order to find out the promising one among the collected deposits, the samples were characterized for their different physico-chemical, mineralogical, geotechnical properties and swelling behaviors. Experimental studies carried out and observations gathered with respect to the above said micro and macroscopic properties are presented in the paper.

2. EXPERIMENTAL

2.1. Sample Dressing & Screening Criteria

Twenty-six numbers of swelling clays samples were collected from different locations from western zone of the country. Sample collection was mainly based on quadruple sampling methodology. The drying of the soil samples was carried out in the air/sun. The clods were broken with wooden mallet to hasten the drying. The organic matter, like tree roots, pieces of bark and shells were removed from the main soil mass. The noting of these removals was taken into consideration for estimation of organic content. A portion of each sample was soaked in water to breakdown clay lumps and then subjected to sieve and hydrometer test to determine the particle size distribution. Adequate amount of samples were pulverized to pass through a 425 mesh (ASTM) sieve and tested as per the standards procedures [Indian Standard: 2720].

The geotechnical properties of swelling clays depend on the mineralogy, smectite content and smectite type of the material together with the density and porosity. Criteria adopted for screening of available mineral deposits to see its suitability as buffer/backfill material is based on characterization for a set of properties. A candidate material should have smectite rich clay, low hydraulic conductivity, good swelling ability and adequate thermal & radiation stability having retention potential for different radionuclide. All the samples have been analyzed for physico-chemical properties including sorption behavior, and were found to have the properties almost in comparable range.

Based on above observation, few swelling clay samples selected arbitrarily were taken up for mineralogical examination using X-Ray Diffraction (XRD) technique,
microscopic examination using Scanning Electron Microscope (SEM) and were also subjected for heat treatment at 400°C and 600°C for 8 hours to see temperature based mineralogical transformation. These heat-treated samples were also subjected for X-ray diffraction study to check thermal stability of various mineralogical phases. In order to confirm the presence of different minerals, Energy Dispersive X-Ray (EDX) analysis of these samples were also carried out.

The smectite content of the swelling clay samples was determined by using Methylene Blue (MeB) indicator method [Richard Gunderson et al]. Experimental procedure essentially consists of taking known weight of sample, treating with sulphuric acid and then titrating with 0.01N Methylene Blue dye solution (3.74g/L of MeB in water). The selective adsorptive property of the above indicator for smectite clay has been used for the estimation. Paper chromatographic technique was used to ascertain the end point of the titration. Each ml of 0.01N MeB added per gram of soil was equivalent to 1% increment of smectite content and is reported in percentage.

2.2. Sample Preparation for Mineralogical Characterization

In order to get maximum diffraction planes contributing to the XRD patterns of the swelling clay samples, powdered and sieved (425 mesh) particles were used. For microscopic examination using Scanning Electron Microscope, the powdered samples were dried to remove the moisture present. The dried powdered was sprinkled on the aluminum stub with a fine layer of carbon glue so as to facilitate sticking the sample on the surface. Samples for the microscopic examination were coated with 10 nm gold using BALTEC-SCD-050 sputter-coater.

2.3. Mineralogical Examination

2.3.1. X-Ray Diffraction & Energy Dispersive X-Ray Studies

Six numbers of swelling clay samples were taken up for mineralogical examination using X-Ray Diffraction (XRD) technique. A few samples were also subjected for heat treatment at 400°C and 600°C for 8 hours to see temperature based mineralogical transformation. These samples were subjected for X-ray diffraction study to understand thermal stability of various mineralogical phases.

The details of the XRD patterns, including the inter-spacing of crystal planes (d-values) are presented in Figure 1 & 2.

2.3.2. Microscopic Examination

The details of the SEM scans and EDX analysis of the selected few samples of the swelling clays that were subjected for the microscopic examination using Scanning Electron Microscope (SEM) are presented in the Figure 3 to 10.

2.4. Chemical Composition

After having a proper dressing and pretreatment which involved soaking the sample in water to allow breakdown of the bigger lumps, the materials were oven dried at 110°C and then pulverized to size of 425 mesh ASTM to get homogeneous and
Figure 1: XRD Pattern of Three Swelling Clays from Western Region

Figure 2: XRD Pattern of a Particular Swelling Clay Sample at Different Temperature
representative powder. Known weight of the sample powder was fused with requisite amount of sodium carbonate and the fused mass was dissolved in water for chemical analysis using inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

Figure 3: SEM Micrograph of Swelling Clay-1 from Western India

Figure 4: Magnified (10KX) View of Swelling Clay-1
For the sake of comparison, chemical composition reported for MX-80, Na-bentonite, is also presented in the table [Pusch R., 1999]. All sample analysis was done in triplicate and average value has been presented.

![Figure 5: SEM Micrograph of Swelling Clay-2 Indicating Flake Morphology](image1)

![Figure 6: Magnified View (20KX) of Swelling Clay-2](image2)
Figure 7: EDX Spectra of Bigger Particle (Q) Shown in SEM Micrograph

Figure 8: EDX Spectra of Smaller Particle (M) Shown in SEM Micrograph
Figure 9: EDX Spectra of Swelling Clay-1 from Western India

Figure 10: EDX Spectra of Swelling Clay-2 from Western India
Organic contents of the clay samples were analyzed by standard procedure, which involves digestion of the samples with hydrogen peroxide followed by weighing the residue left. The chemical composition of clay samples in oxide form of various elements is presented in Table 1.

Table 1
Chemical Composition of the Typical Clay Sample

<table>
<thead>
<tr>
<th>Major Element</th>
<th>Typical soil sample</th>
<th>MX-80 reference material*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48–56</td>
<td>63.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15–20</td>
<td>21.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3–6</td>
<td>3.3</td>
</tr>
<tr>
<td>MgO</td>
<td>3– 4</td>
<td>2.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1–2</td>
<td>2.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14–0.42</td>
<td>0.7</td>
</tr>
<tr>
<td>Organic matter</td>
<td>4–6</td>
<td>–</td>
</tr>
</tbody>
</table>

Soluble constituents of swelling clay were also analyzed by equilibrating the samples with a solution of pH 2 for four hours. The solution was filtered and analyzed for total soluble salts, Na, Ca, F and Cl using appropriate analytical procedures. Results are presented in Table 2.

Table 2
Soluble Inventories of Swelling Clays

<table>
<thead>
<tr>
<th>Major Element</th>
<th>Typical soil sample</th>
<th>MX-80 reference material*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble salts (%)</td>
<td>1–3</td>
<td>–</td>
</tr>
<tr>
<td>Na⁺</td>
<td>10–16</td>
<td>0.0196</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>3–6</td>
<td>0.0470</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1–3</td>
<td>0.0036</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
<td>2.303</td>
</tr>
<tr>
<td>F⁻</td>
<td>&lt; 0.005</td>
<td>–</td>
</tr>
</tbody>
</table>


2.5. Physicochemical Properties

2.5.1. Moisture Content (Indian Standard: 2720, Part-II, 1973)

Clay samples were analyzed for moisture content following the standard test procedures. Samples were taken in suitable Stainless Steel (SS) planchets and kept for drying in oven maintained at 110°C for 48 hours. After complete drying to constant weight, the samples were removed from the oven and cooled to room temperature in the desiccators and weighed, and moisture contents of the samples were computed [Yong R. N. et al, 1975].
2.5.2. Bulk Density (Indian Standard: 2720, Part-III, Section-2, 1980)
About 2-3 g of each sample was filled in the calibrated cylinder with gentle packing and the volume occupied by sample was noted and bulk density was computed.

2.5.3. True Density (Indian Standard: 2720, Part-III, section-2, 1980)
Known amount of bentonite sample were taken in weighed specific gravity bottle. The bottle was then filled with DM water and again weighed without any air bubble with cap. The bottle was then filled with only water and weighed and true density was computed. Porosity and void ratio were determined by using data collected during bulk and true density determination.

2.5.4. pH Value (Indian Standard: 2720, Part-XXVI, 1973)
About 10 gm of the soil specimen was taken in 50 ml capacity beaker. Around 25 ml of DM water was added to it and the suspension was stirred. The beaker was then covered with a watch glass and allowed to stand for one hour with occasional stirring. It was again stirred well immediately before testing its pH. The pH value of the soil suspension was recorded to the nearest 0.1 pH units.

2.5.5. Total Soluble Salts (Indian Standard: 2720, Part-XXI, 1965)
The determination of total soluble solids in soils was carried out by gravimetric method. A representative sample was dried to constant weight in an oven at a temperature of 110°C. About 10 g of soil was accurately weighed and transferred to a 250 ml capacity glass bottle. 100 ml of distilled water was added to it and shaken overnight for 15 hrs. The soil was then allowed to settle and filtered through Whatman-42 paper. Accurately measured 50ml of clean filtrate was taken in a porcelain dish and concentrated by evaporating in the water bath before drying in oven at 105°C. The dish was allowed to cool and weighed. The percentage soluble solid in soil was then computed.

Cation exchange capacity (CEC) of the swelling clay samples were evaluated by equilibrating with sodium acetate solution followed by exchanging with aqueous solution of calcium chloride. The exchanged Ca ions were replaced by means of sodium acetate solution. The replaced Ca was estimated by titrating with standard EDTA solution. CEC was then computed and expressed as meq /100 g soil.

2.5.7. Distribution Coefficient (K_d value)
Distribution coefficient of swelling clay samples were determined by equilibrating about 1 g of accurately weighed soil samples with 100 ml of the spiked solution of radionuclides. Prior to K_d value estimation, optimum time for equilibration was experimentally determined. The optimum time of equilibration was found to be 24 hrs for fission products and 2 hrs for actinides. The K_d value for swelling clay was checked for 90Sr, 137Cs and 241Am. The concentration of the radionuclide was arbitrarily kept in the range of 1 nCi/mL. About 5 ml of decant was centrifuged for 15 to 20 min
and supernatant was analyzed for activity. Distribution coefficients were computed by knowing initial and equilibrium concentration of radionuclides. The results obtained during physico-chemical characterization studies are presented in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (% w/w)</td>
<td>10–12</td>
</tr>
<tr>
<td>pH</td>
<td>7.01–8.68</td>
</tr>
<tr>
<td>True density (g/mL)</td>
<td>2.04–2.58</td>
</tr>
<tr>
<td>Bulk density (g/mL)</td>
<td>1.19–1.29</td>
</tr>
<tr>
<td>Porosity (% v/v)</td>
<td>43–50</td>
</tr>
<tr>
<td>Void ratio</td>
<td>0.74–0.99</td>
</tr>
<tr>
<td>Cation Exchange Capacity (meq/100g)</td>
<td>50–65</td>
</tr>
<tr>
<td>Kd (90Sr)</td>
<td>245–350</td>
</tr>
<tr>
<td>Kd (137Cs)</td>
<td>400–580</td>
</tr>
<tr>
<td>Kd (241Am)</td>
<td>280–400</td>
</tr>
</tbody>
</table>

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Mineralogical Characterization

From the X-ray diffraction patterns presented and the d-values associated with the patterns, montmorillonite and quartz have been identified as major phases present in all the samples of swelling clay. Presence of Kaolinite in small amount has also been identified. Attempts were made to distinguish between Kaolinite and Chlorite mineral phases because many of the diffraction peaks of the above two phases coincides. It is often necessary to conduct further test to distinguish between the two. This problem was resolved by taking the diffraction pattern of the swelling clay sample after giving a heat treatment at 600°C, where Kaolinite looses its crystalline character. On the other hand, diffraction peaks corresponding to Chlorite gets intensified because of dehydration. As seen from the diffraction pattern (Figure 2), diffraction peak of 7.20 Å at 2θ of 12.5 which is the strongest peak of Kaolinite gets disappeared in the case of clay-2 sample heated at 600°C. This observation indicates presence of Kaolinite rather than Chlorite.

Energy Dispersive X-Ray (EDX) analysis of the swelling clay samples mainly indicated presence of Si, Al, Na, K, Mg supporting thereby the X-Ray diffraction data. As seen from the SEM micrographs of two typical clay samples at different magnifications, flake like surface morphology is present. In order to know the finer details of the constituents in the sample, the probe beam was spotted at different locations and corresponding EDX analyses were carried out to check their elemental compositions. As seen from the micrograph (Figure 3), position indicated at “Q”, EDX spectrum indicated the presence of Si and O only showing the existence of quartz. Whereas positions indicated at “M”, EDX spectrum shows the presence of Si, Al, Na, Mg, O etc reflecting the signature of montmorillonite.
Smectite content of the swelling clay samples determined by Methylene Blue method were found to be in the range of 50–65% which is comparable to the reported value in the literature [3].

3.2. Chemical Composition
The chemical composition of swelling clay reveals the information about the nature of parent material. The chemical composition of the swelling clay samples have also been compared with the chemical analysis reported data of MX-80 sodium bentonite. Chemical analysis of the samples indicates presence of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O, MgO, CaO and TiO$_2$. Studies pertaining to soluble inventories of swelling clays showed marked presence of chlorides & sodium. Presence of higher amount of chlorides may attribute to the marine origin of the clay.

3.3. Physicochemical Properties
Physicochemical Characterization of the swelling clay samples collected from different locations of western region of the country indicated comparable results in terms of properties like moisture content, true & bulk density, porosity, organic content etc. CEC of the samples were also found in the range of 50–65 meq/100 g of sample. Sorption behavior of the clay samples with respect to different radionuclide at given experimental conditions were also is in a close range in terms of distribution coefficient values (Table 3) indicating by and large uniform composition of the clay deposits. Results indicate noticeable variation in the Fe$_2$O$_3$ content. Studies pertaining to soluble inventories of swelling clays did not indicate noticeable presence of fluorides, however all the swelling clay samples are characterized by comparatively large amounts of chlorides and sodium. Presence of higher amount of chlorides is attributed to the marine origin of the clay. The chloride content and other properties will vary in the clay samples from different depths.

4. CONCLUSIONS
The clay samples are having swelling ability indicating smectite rich composition and optimum CEC. Chemical composition indicates the presence of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, Na$_2$O, CaO as major elements. The high Fe content is one of the noticeable difference with respect to other reported values. Presence of higher amount of chlorides is attributed to the marine origin of the clay. XRD patterns of different clay samples show principal phases of Montmorillonite and Quartz along with minor phase of Kaolinite. XRD pattern of heat treated (400 & 600°C) clay samples show a change in d-value corresponding to Montmorillonite phase indicating temperature dependent transformations of the mineral. PDF No. 07-0304 corresponds to montmorrilonite heated (Na-Mg-Al-Si$_4$O$_{10}$) showing the absence of bounded water. The SEM micrographs and EDX spectra of the clay show the assemblage of montmorillonite and quartz phases. These further reveal that clay is rich in montmorillonite. SEM micrographs of the clay samples taken at higher magnifications (10KX – 40KX) show lumpy aggregate, extremely thin laths or stacked irregular sheets giving an impression of flake like surface morphology.
References


