American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-6, Issue-5, pp-253-260
www.ajer.org
Research Paper Open Access

The Possibility of Usage Iraqi Bentonite in the Nuclear Waste Disposal Repositories

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ABSTRACT: *This research describes a quality analysis for the Iraqi bentonite material to use in a nuclear waste disposal repositories. Some physical, chemical, and mineralogical methods, which may be applied in quality control of bentonite are reviewed. Many of the presented control analysis were performed for local calcium bentonite and sodium activation bentonite samples. X-ray diffraction is the best method to identify smectite minerals and general characteristics of bentonite can be obtained by rapid indicator tests, which can be done on the place of reception. These tests are methylene blue test giving information on the cation exchange capacity, swelling index and determination of water absorption.*

I. INTRODUCTION

Natural Na-bentonite (both natural and sodium-exchanged or sodium-activated), and calcium bentonite have a high dry strength and good high-temperature durability which means that bonding properties are not destroyed by moderate heating. The ease of dispersion of Na-bentonite in water to produce a fluid with high viscosity and thixotropic properties (the development of a rigid structure when shear stress is removed) is widely employed in water-based drilling fluids particularly for the petroleum industry [1]. Ca-bentonites have a lower durability than sodium bentonites, although this property can be improved by sodium-exchange. Natural Na-bentonites and Na-exchanged calcium bentonites are used to improve the performance of clay liners in engineered landfill sites for solid and liquid waste [2].

Bentonite clay has been adopted as a key material in the production of buffer and backfill materials by most international nuclear waste isolation concepts. Various national programs have examined differing contents of bentonite and compacted densities for their buffer and backfilling materials but in all cases the buffer material contains 50% (Canada) or more (70% Japan, 100% Finland, Sweden and Switzerland), of this clay product. The backfill material proposed in the various national concepts vary considerably in the bentonite content and overall composition [3-8]. The main properties relevant to this application are the low hydraulic conductivity of the compacted bentonite (which serves to isolate the radioactive waste canisters from circulating groundwater) and the cation-exchange capacity (to capture any radionuclides escaping from the canisters) [9 & 10]. In this paper we intended to understand the bentonite barriers roles in controlling the migration of radionuclides after canister failure and providing both mechanical and chemical buffering conditions to the waste package through studying the behavior and desirable properties of the bentonite; chemical, mechanical and thermal roles of bentonite on its radionuclide removal and adsorption.

II. CHARACTERISTICS NEEDED IN A SAFE REPOSITORY

The most widely accepted concept of a nuclear waste repository is that of a deeply buried one, which places the waste at a great distance from the biosphere. The challenge is to build repositories that will remain stable and without any leaks for such long periods of time and avoiding radionuclides transport away from the repository; as shown in Figures 1. Thus, the required characteristics of the facility where the waste will be buried that it should be able to adsorb the small amount of water that might be present in a 'dry' repository, hinder any water flow to or from the repository and transmit the heat generated in the canisters to allow heat dispersion and avoid steep temperature gradients.

The clay mineral that most fulfils the characteristics listed above is smectite and that type of clay is named bentonite; a clay which, despite having a rather large range of chemical compositions, maintains basic physical and chemical properties that are valuable to its role [12]. Studies carried out on the sealing properties and chemical stability of smectite in the conditions foreseen of a nuclear waste repository are providing satisfactory results and indicate that it is possible to use this material as a safe and stable barrier against leaching and transport [13- 14].

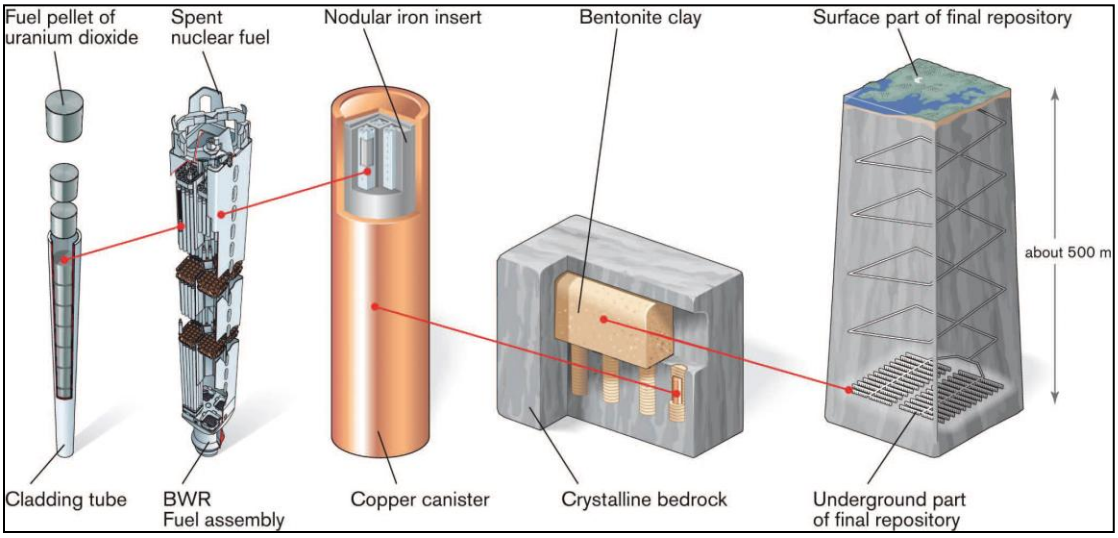


Figure (1). The KBS-3 method involves encapsulating the spent fuel in copper canisters which are then emplaced, surrounded by a buffer of bentonite clay, in deposition holes in a tunnel system at a depth of 400-700 m in the bedrock BWR: boiling water reactor [15].

III. MATERIALS AND METHODS

Reference Bentonite: The bentonitic smectite used in this study is from Wyoming bentonite (USA) as a reference. It contains 90 wt% of montmorillinite, 4 wt% quartz, 2 wt % albite; and trace amounts of calcite, cristobalite and pyrite. The total cation exchange of the montmorillonite is between 0.78 and 0.85 meq/g.

Local Calcium Bentonite: It is obtained from Iraq Geology Survey Authority and was used with or without chemical treatment for the present studies. The laboratory works involve a variety of chemical and physicochemical assessment techniques. These are used to characterize the bentonite and to assess grade and quality. Figure (2) illustrates a scheme which used to suspect bentonite quality for adsorption toxic metals. Local bentonite samples from the field (Ca-FB) was dried in the oven at 55 ^{o}C for four hours until reach moisture content less than 10%. Then the sample was crushed using grinding machine till it became powder. Later the experiments showed that grinding of bentonite samples cause an increase in cation-exchange capacity. The experiments were carried out in a rubber-lined ball mill, using polished agate balls.

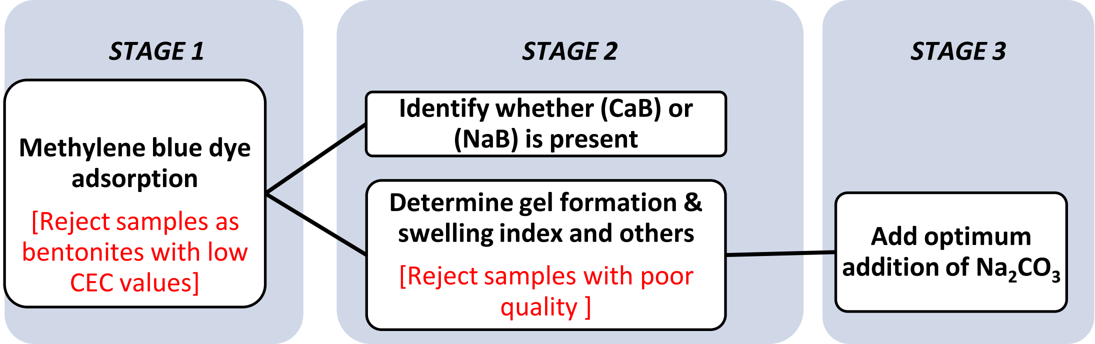


Figure (2). Scheme used for suspecting bentonites

The physical and chemical analysis were performed for CaB including the determination of density, specific surface area, linear shrinkage and others. The density of CaB was measured according to the ASTM D 854-83 test. The total surface area of bentonite sample was measured by using 2-Ethoxy Ethanol technique suggested by Carter [16]. Linear shrinkage test was carried out by British Standard Institution, BS 1377 [17]. Swelling power for powdered clay mineral was tested after drying to constant weight at 105 °C. pH values of dispersed bentonite samples were and fall to (8.9 – 9.3). Determination of methylene blue cation-exchange capacity for bentonite was measured according to the ISO 11260 or ASTM C837-99 (2003). The end-point was reached which produced a dark blue spot of clay absorbed dye surrounded by a blue halo of excess dye. When this pale-blue halo was obtained leave to stand for 5 minutes and then repeat spotting. If the pale-blue halo disappeared added a further 2 ml increment of dye. If it still present after a period of 25 min. then the end-point had been reached and the volume of dye was recorded dry weight.

Calculation the concentration of methylene blue chloride solution (MB_{conc}) :
MB_{conc}= ($D*P_{MB}$) / 319.9 ……. (1)

D: actual weight of methylene blue (g)
P_{MB}: % dry weight of methylene blue
Molecular weight of anhydrous methylene blue = 319.9

Calculation of CEC values:
CEC (meq/100g) = [(100*F/ (P_s*E)]* MB_{conc} ……. (2)
P_s: percentage dry weight of sample
MB_{conc}: concentration of methylene blue chloride solution
E: weight of sample as received
F: volume of methylene blue

The mineralogical and chemical examination were done for characterization of bentonite. Sample will be grinded with agate mortar to less than 50 μm. The chemical composition was determined by X-ray fluorescence analysis (Shimadzu-1800), whereas the minerals present were identified by XRD using Shimadzu-7000 diffractometer. The generator setting were 40 kV and 30 mA, and the wavelength (λ) was 1.54 ^{o}A, using Cu-kα radiation. X-ray diffraction patterns were then recorded as shown in Figure (3). The chemical analysis results are given in Table (1), based on weight percentage oxide of the dry sample.

Activation Calcium Bentonite: The bentonite as an adsorbent must possess high surface area per unit mass and must have an active surface. During activation, the structure of the raw clay is opened and becomes porous. However, to get higher properties in usage and to increase its productivity, bentonites must be manually reformed. This reformation could be achieved by utilizing the cation exchanging feature of montmorillonite structure, which replace Ca^{2+} , Mg^{2+} etc. in the bentonite. The process of this replacement is as follows:

$$\text{Ca-Bentonite} + Na_2CO_3 \xrightarrow{H_2O,\ \Delta} \text{2Na-Bentonite} + CaCO3 \qquad (3)$$

Chemical material used in reforming bentonite was 3-4% of sodium carbonate powder into the raw bentonite with water content over 30%, blended and mixed thoroughly, crushed and aged for ten days, then dry and grinding into finished product.

IV. RESULTS AND DISCUSSION

The X-ray diffraction of the natural material shows high content of CaO (5.50) and Na_2O/CaO ratio is less than 1, which indicates the presence of Ca-bentonite, as shown in Table (1). Local Ca-bentonite samples are relatively silica-rich (~ 57% SiO_2), but it should be noted that they contain Al_2O_3 (14.5%). It is rich in Fe_2O_3 (5.5 %). The ferric iron in the repository can lead to an increase in clay layer charge and a decrease in swelling [18]. Also it is relatively rich in carbonate (> 2% CO_3) compared with the other bentonites (< 1% CO_3). Higher carbonate contents are associated with a higher pH buffer capacity [19]. Sulphide (0.45 % S) can contribute both to buffering of redox potential and act as a supply of corrodants for the copper canister.

Table (1). Chemical analysis of calcium bentonite

Material Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO	TiO2	SO_2	Cl	LOI	CEC
Ca-B (%wt)	57.0	14. 50	5.50	5.50	0.48	1.30	3.30	0.80	0.45	0.90	10.27	0.65 Meq/g

The mineralogical analyses of the bulk materials is shown in Figure (3). This shows that smectite content is highest in the local bentonites 70%) and lowest in the and also has high Quartz content. Ignition loss value indicated the ability of bentonite to absorb a specified amount of water, it means that sodium base bentonite have a higher value of ignition loss as compared to untreated local bentonite. XRD examination of Ca-bentonite shows the basal spacing, d_{001}, of a divalent cation-saturated semectite is 15.72 ^{o}A, whereas for a monovalent cation-saturated semectite (Na-B) it is 12.823 ^{o}A. With semectites having a mixed monovalent/divalent exchangeable cation, the d_{001} spacing is between 15.4 and 12.6 ^{o}A. All Na^{+} to Ca^{2+} cation-saturated show d_{001} spacing variety between 10 and 15.4 ^{o}A in the air- dried state.

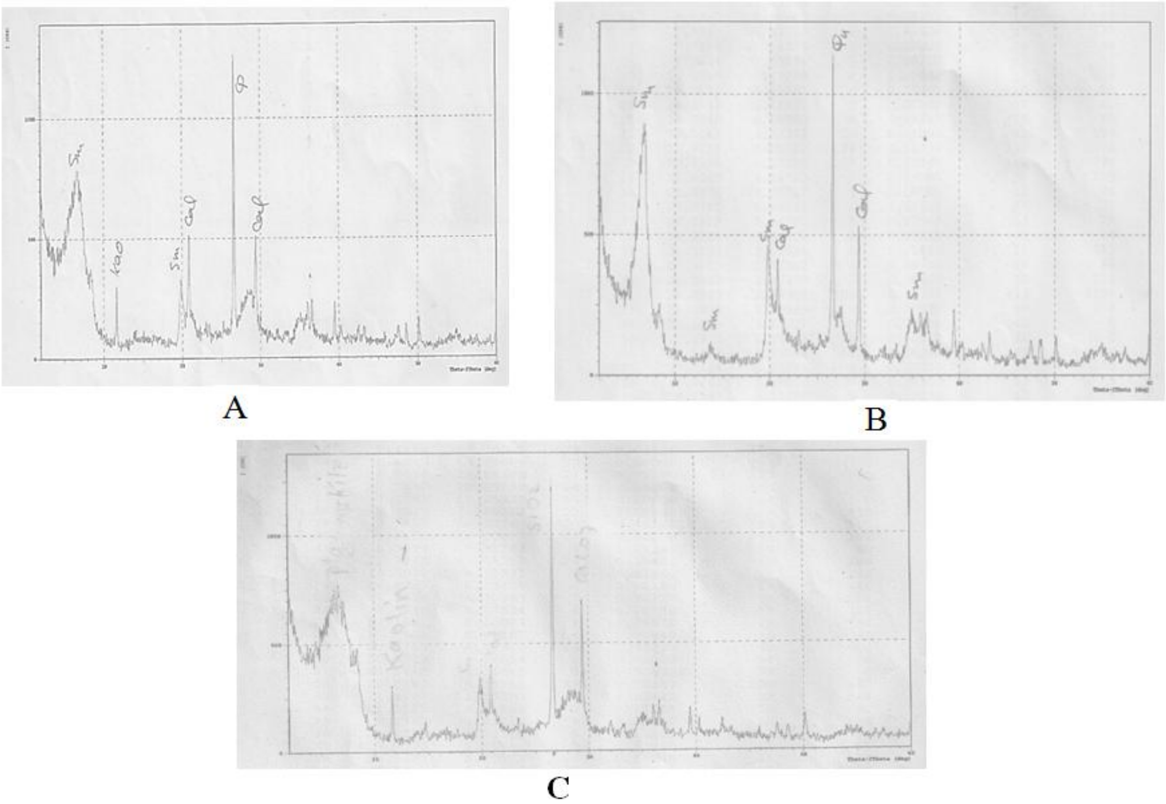


Figure (3). XRD Patterns of field raw bentonite (A), reference Na- bentonite (commercial) (B), and sodium activated bentonite (C)

Table (2). Preliminary required values for the buffer bentonite [20].

Required average value			
	High-grade Na-bentonite	**High-grade Ca-bentonite**	**Test Standard/ Reference**
Water content	≤ 13 %	≤ 13 %	ASTM D2216-05, ASTM D4643-00
Swelling index	≥20 ml/2g	≥ 15 ml/2g	ASTM D5890-06
Smectite content	≥75 %	≥75 %	XRD
Liquid limit	≥250 %	≥80 %	ASTM D4318-05 CEN ISO/TS 17892-12:2004
Cation exchange capacity (CEC)	≥70 mEq/100 g	≥60 mEq/100 g	ISO 11260, ASTM C837-99 (2003)
Hydraulic conductivity*	≤10^{-12} m/s	≤10^{-12} m/s	ASTM D5084-03
Swelling pressure*	≥1 MPa and ≤ 10 MPa	≥1 MPa and ≤ 10 MPa	ASTM D4546-03
Thermal conductivity**	≥ 1.0 W/m/K	≥ 1.0 W/m/K	ASTM D5334-05

* dry density of buffer blocks 1655 – 1754 kg/m3 ** In dry density of 1655 kg/m3, water content 17 % and degree of saturation 70 % or in dry density of 1754 kg/m3, water content 17 % and degree of aturation 81 %. After saturation thermal conductivity of buffer block should be 1.3 W/m/K.

Quality requirements for the bentonite depend on purpose (buffer on backfill) and used material. Preliminary required values for the buffer bentonite are presented in Table (2). The values are set based on current knowledge. The required values may be updated along with increasing amount of information and test data on suitable buffer bentonites [20].

In Table (3), the swelling volumes relative to the addition of 1-6 % by weight Na_2CO_3 to the dry clay after crushing and screening through 250 µm and leaving the samples for 24 hours the data indicated that the typical swelling volume for NaB is higher than that for CaB. The swelling volume for non-swelling material is 10-12 ml, for CaB is 25-35ml and for natural Na-bentonite 100-150 ml. Therefore, maximum swelling volumes are obtained with high- grade CaB after artificial Na-exchange with 3-4% Na_2CO_3 additions. Figure (4) indicated the ability of bentonite to absorb a specified amount of water.

Table (3) the relative quantities of clay and Na_2CO_3 required and swelling volumes.

Weight of clay (g)	4.00	3.96	3.92	3.88	3.84	3.80	3.76
Weight of Na_2CO_3 (g)	0.00	0.04	0.08	0.12	0.16	0.20	0.24
% Na_2CO_3	0.0	1.0	2.0	3.0	4.0	5.0	6.0
Swelling volumes (ml)	8-10	40-55	40-80	60-95	60-110	60-85	60-80

Mechanical treatment by grinding of clay minerals produces important changes of powdered materials and influences their behavior in further processing steps. The grinding causes a variation in particle size, an increase in surface, and an increase in the number of broken bonds. In Figures (3 & 5), X-ray examinations of the raw field bentonite sample (Ca-FB) and the ground materials showed a progressive broadening and diffuseness of the diffraction bands with final disappearance after long grinding indicating a gradual breaking down of the structure. Also, it was found that the kaolinite structure has been destroyed at grinding and heating.

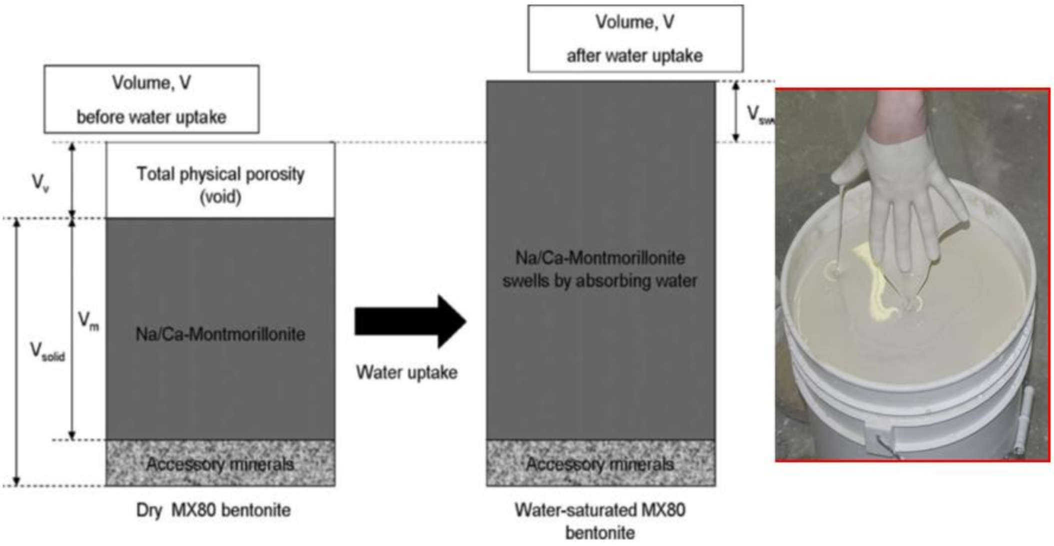
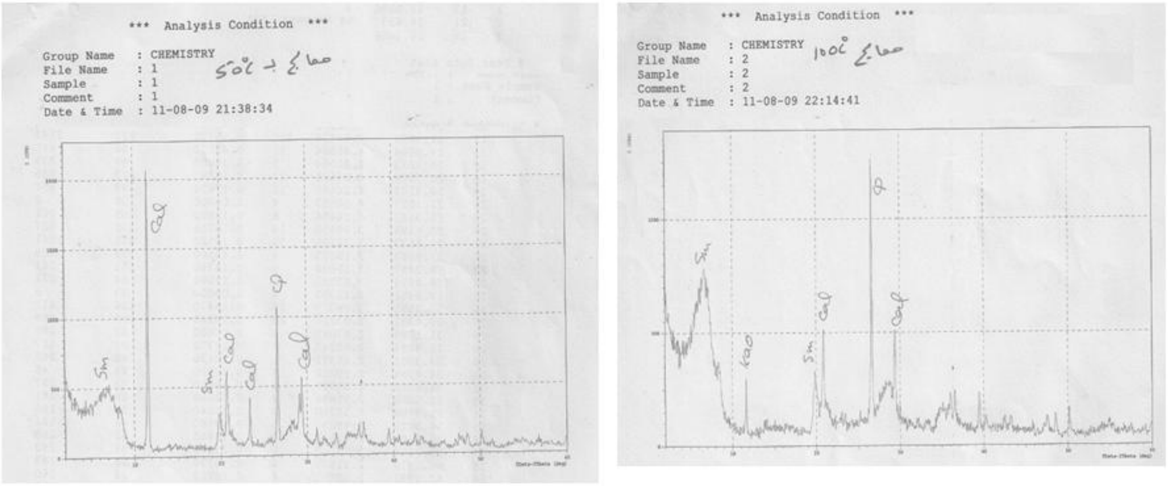


Figure (4). Definition of commercial bentonite barrier at water-saturated conditions [21].

The exchange capacity is reduced on heating, but the reduction is not uniform and varies with the cation present. So, the ca-montimorillonite shows a gradual loss of cation-exchange capacity on heating to 250 °C (82 to 50 meq per 100 g) which the inner crystalline swelling is lost. Na-montimorillonite unlike the calcium variety, shows in Table (4) only a slight drop in exchange capacity up to 250 °C (90 to 85 meq. Per 100g).

Table (4) Variations in Time grinding of Ca-FB samples with their Cation- exchange capacity

Mineral	Ground 4 hr	Ground for 24 hr	Ground for 48hr
Field Raw Sample (Ca-FB)	0.65 meq/g	0.70 meq/g	0.76 meq/g



(A) **(B)**

Figure (5) XRD Patterns of treated bentonite and heated to 50 °C (A) and to 100 °C (B)

In many repository designs, bentonite would be used in engineered barrier systems, to retard radionuclide migration and/or to control groundwater flow. Depending upon the design, cement could physically contact the bentonite [14] but there is a cement dissolution that releases mainly Na, K, OH (early), and Ca, OH (later) to increase porosity and permeability and to lower compressive strength [22]. However, these effects are countered by cementation processes (e.g. carbonation/calcite precipitation), which can lower the effective porosity, and therefore the permeability, to almost zero [23]. While in bentonite, clay layers bear a permanent negative charge compensated by counter ions located between them (interlayer space). These counter ions are the origin of two features of clay behavior: swelling; and cation exchange. The former refers to the entrance of water into the clay, while the latter involves the replacement of natural counter ions like Na^+ by other ions initially in the aqueous solution in contact with the mineral, and the concomitant release of Na^+ to the solution. In principle, the following law of various cations replacement power applies [10]: Li < Na < K < Ca < Mg < NH_4.

Therefore, the experimental results show that the property of exchange capacity is measured in terms of milliequivalents per gram or per 100 g at neutrality (pH 7.0). Titration curves showing the relation between pH and milliequivalents of added NaOH are giving in Figure (6 left). It can be seen from the data that the cation – exchange capacity of Bentonite was vary with the concentration of the clay, mainly at high concentrations. Therefore, the cation-exchange capacity based on NaOH for bentonite calculated at the inflection point of its potentiometric-titration curve is vary from 90 to 110 meq per 100 g as the bentonite concentration increased from 0.3 to 9.0%.

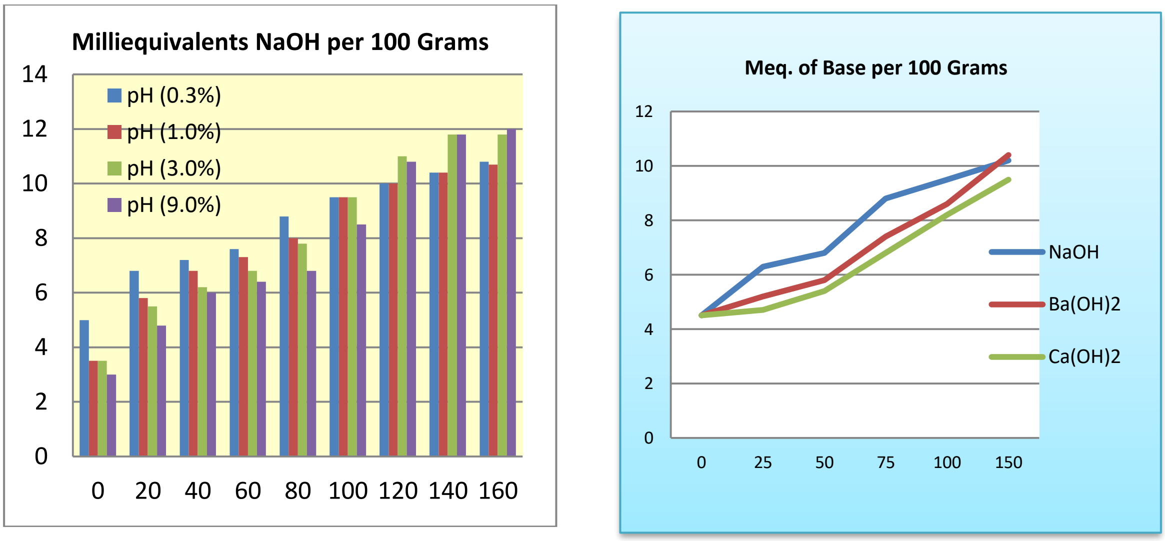


Figure (6). Cation-Exchange Capacity vary with the bentonite clay different concentration (left). And with the nature of the cation (Base) (right).

It was noted that the solubility of NaOH and Ca(OH)2 in pure water is of quite a different order: at 20°C, concentration (44 mol/L) and concentration (0.04 mol/L), respectively. Hence experiments with NaOH solutions can reach much higher pH values/OH^- ion concentrations.

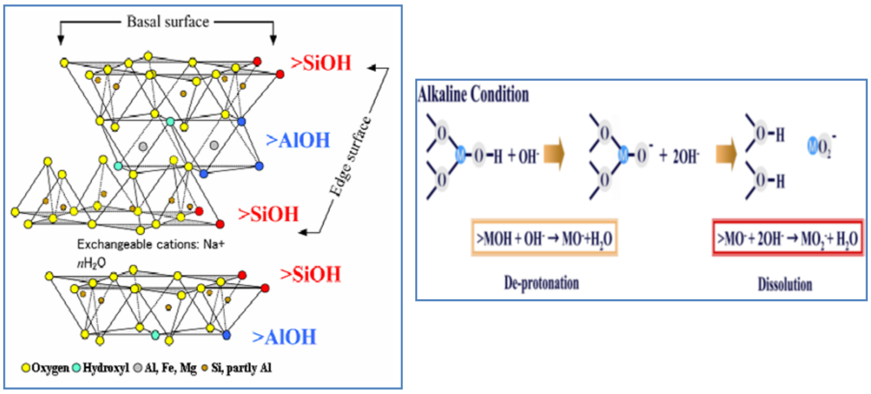


Figure (7). Layered structure of montmorillonite (left) and proposed two step dissolution mechanism of montmorillonite under high pH conditions (right) [24].

Also the Figure (6 right) showing the titration curves for bentonite with cations of different valences; monovalent and divalent cations. In both cases the exchange capacity is considerably larger when determined with Ca^{2+} than with Na^{2+}. There are three causes of the cation-exchange capacity of the clay minerals; broken bonds around the edges of the silica-alumina would give rise to unsatisfied charges, which be balanced by adsorbed cations. The broken bonds would tend to be non-cleavage surfaces. Therefore, the bentonite degradation is one of the most predictable changes that cause an increase in the pH of the buffer pore water. This increase influences significantly both the chemical and physical properties of the buffer [24]. In Figure (7 left) layered structure of montmorillonite where Al ions are sandwiched between two inward pointing sheets of linked SiO_4 tetrahedra. The basal surface runs parallel to the ilicate sheets whereas the edge surface is perpendicular to the sheets. The dissolution of montmorillonite is along the edge surface, reactive sites are shown in color. A two- step mechanism for the dissolution of montmorillonite is shown in Figure (8B). Sato et al. suggest the dissolution of montmorillonite is congruent based on the concentrations of silicon and aluminum in both NaOH and KOH solutions corresponding to the stoichiometry of montmorillonite [25 & 26].

V. CONCLUSION

Bentonite is a candidate buffer material for radioactive waste disposal which mainly consists of micrometer scale quartz particles and nanometer scale smectite clay minerals such as montmorillonite and beidellite and the interactions are dominated by ion exchange processes, whereas at high temperatures the mineral dissolution-precipitation reactions become more important. Thus, different determination methods must be also done in bentonite future studies like (liquid limit, plastic limit and plasticity index).

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