

DETERMINATION OF THE CATION EXCHANGE CAPACITY OF BENTONITE EXPOSED TO HYPERALKALINE FLUID

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ABSTRACT

The hyperalkaline fluid that could be generated by cementitious degradation in a repository, can affect important properties of backfilling materials, host-rocks and soils. It is well known that mineralogical characteristics of materials can change with the exposition to high pH conditions, such as found in a disposal installation. These modifications are likely to cause deterioration in physical and chemical properties of these materials, e.g., hydraulic conductivity, radionuclides sorption (K_d), diffusivity and cation exchange capacity (CEC). This paper presents the preliminary results for bentonite exposed to alkaline solutions in order to establish the time for mineralogical modifications to occur. The property of bentonite used as an indicator of the modification was CEC. A commercial bentonite was treated with NaOH 1 mol/L at 30°C, for different periods of time that varied from 4 hours to 28 days. After that, the CEC was determined by the conventional methylene-blue adsorption titration method. Although the methylene-blue titration has given fast results, it has not demonstrated confidence, due to the semi-quantitative nature of this technique. Generally, the values of CEC decreased from 68 meq/100g to 42 meq/100g with the time of contact showing that hyperalkaline conditions provide significant changes in the CEC. Additionally, a second group of samples was modified with moderate alkaline solution and had the CEC determined by Centrifuge Method, reported in Soil Survey Laboratory Methods Manual, nº 42. The second group presented an increase in the CEC in few hours of alteration, which can be explained by the formation of zeolites when an alkaline solution containing K and Ca is used.

1. INTRODUCTION

Large amounts of cement including waste matrices, construction elements, and backfill materials, are used in a storage facility for radioactive waste of low and intermediate levels of activity. These cementitious materials are likely to induce highly alkaline environments in radioactive waste repositories, since the concrete will begin to produce an alkaline plume as soon as it become saturated with pore water from geological formation or infiltration water from rain. The alkaline plume, released from the concrete materials, will be in contact with geological formations and the bentonite barriers. Due to its very aggressive nature, alkaline fluid will disturb these materials chemically. Mineralogical changes and modifications are expected to occur in the barrier and geological formation during the time required for radioactive wastes to reach non-hazardous radioactivity levels.

Depending on the overall design, the engineering barriers can be determinant to ensure the safety of the repository. Since bentonite is the most common and suitable material to be used as backfilling in a repository, the assessment of the bentonite stability under alkaline

conditions is a key topic. Therefore, the effect of alkaline solutions on clay materials has recently become a subject of many studies [1,2, 5-15].

The smectites are the main group of minerals in bentonites, highlighting among them the montmorillonites. The studies, related to mineral modifications under alkaline conditions, generally have interest on bentonites rich in montmorillonites due to their excellent sorption properties. Generally the results obtained in these studies shows that the first modification in montmorillonites is in their sorbed cation population, followed by beidellitization or illitization [6]. The dissolution of montmorillonite and illitization tends to reduce the cation exchange capacity (CEC), while beidellitization and formation of zeolites tends to result in a CEC increase [12,13]. Therefore, the variations in the CEC of bentonites, when submitted to alkaline conditions, usually can be related to a mineralogical modification.

The alkaline solutions used in these studies consisted of NaOH [1,2], KOH [11], Ca(OH)₂ [13] or a mix of these three hydroxides [12, 17], simulating the cementitious degradation fluids. Some of these solutions are strongly alkaline [1, 2], with pH 14 and NaOH concentration of 1 mol/L, however, many studies are carried out in more realistic conditions, with pH around 13 and smaller hydroxide concentration [11-13,17].

In this work it was investigated the effect of two different alkaline solutions on the CEC of a commercial bentonite. The CEC was used as an indicator property to identify that the transformations in mineralogical phases were completed. Additionally, it was proposed a relationship between the behavior of CEC and mineralogical exchanges observed in bentonite.

2. EXPERIMENTAL

Two samples groups of a commercial bentonite were altered by different alkaline solutions and then had their CEC analyzed. An X-rays diffraction analyses, using a diffractometer Rigaku d-max ultimate, were carried out to clarify the mineralogical changes. In each group, subsamples were kept in contact with alkaline solutions for specific intervals, then separated from the alkaline fluid and analyzed. Hereafter, the specific experimental details of each group of samples are presented.

2.1. Group 1 – Alteration with NaOH 1 mol/L

The first experiments were planned to represent hard alkaline conditions, applying a 1 mol/L NaOH solution as the alteration fluid. The goal of these experiments was to evaluate the changes in CEC under high alkaline media, thus accelerating the reactions in order to study the phenomenon in a short time.

According of the manufacturer information, the bentonite was chemically composed of: 62% of SiO₂, 15% of Al₂O₃, 8.6% of Fe₂O₃, 1.6% of CaO, 2.6 % of MgO, 2.1% of Na₂O, and less than 1% of K₂O and TiO₂.

Twelve bentonite subsamples (6 g each) were kept in contact with 300 mL of the 1 mol/L NaOH solution (solid/solution ratio 1:3) in a polyethylene bottle for a specific time, as shown in the table 1. For each time interval, two replicates were analyzed.

Table 1: Samples Group 1 and alteration intervals

Sample code	Alteration time (hours)
BGEL 01	0
BGEL 02	4
BGEL 03	8
BGEL 04	12
BGEL 05	24
BGEL 06	48
BGEL 07	72
BGEL 08	168
BGEL 09	264
BGEL 10	384
BGEL 11	504
BGEL 12	672

After the alteration, the bentonite samples were filtered washed with water, dried and ground. Afterwards, the samples had their CEC determined by conventional methylene-blue adsorption titration method [3], and were also analyzed by x-rays diffraction.

2.1.1. Determination of CEC by Methylene Blue Method

The determination of CEC followed the Standard Test Method for Methylene Blue Index of Clay, according to the ASTM C 837 -81 [3]. This test is based on the linear relationship between the methylene blue index and fundamental clay properties such as cation exchange capacity (CEC) and specific surface. The procedure consist in placing 2.00 g of clay in a 600 mL beaker, adding 300 mL of distilled water and sufficient sulfuric acid to bring the pH within the range of 2.5 to 3.8. After adjusting the pH, the burette was filled with the methylene blue solution and 5 mL of the solution was added to the slurry, and stirred for 1 to 2 min. Following, a drop of the slurry was placed on the edge of a filter paper. 1.0 mL increments of the methylene blue solution were added to the slurry with 1 to 2 min of stirring after each addition, and then a drop was added to on filter paper [3]. The end point was indicated by the formation of a light blue halo around the drop, as shown in figure 1 [16].

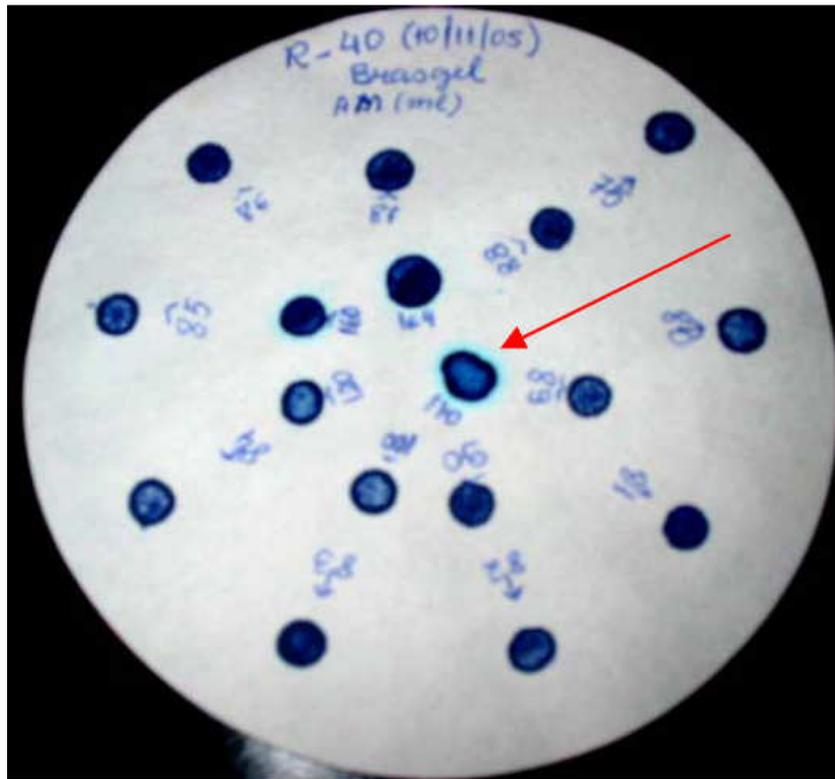


Figure 1: Filter paper showing the end point in CEC determination by titration with methylene blue: a light blue halo around the drop [16].

The CEC can be calculated as follows:

$$CEC = \frac{EV}{W} 100 \quad (1)$$

where:

CEC = cation exchange capacity in meq/ 100 g of clay

E = milliequivalents of methylene blue per milliliter

V = milliliters of methylene blue solution required for the titration, and

W = grams of dry material

2.2. Group 2 – Alteration with NaOH, KOH, Ca(OH)₂ solution

The second group of experiments was planned to represent a more realistic alkaline condition, in place of the high alkaline condition applied in the first group. A NaOH / KOH / Ca(OH)₂ solution was prepared by weighing 4.630 g of NaOH, 11.494 g de KOH, dissolving in 1 L of distilled water, and then saturating the solution with Ca(OH)₂. This solution was used to alter the second group of bentonite samples, according with the alteration times showed in table 2. Just as for the first group, these experiments were carried out in duplicate.

Table 2: Samples Group 2 and alteration intervals

Sample code	Alteration time (hours)
1BGEL 0	0
1BGEL 1	8
1BGEL 2	12
1BGEL 3	24
1BGEL 4	48
1BGEL 5	72
1BGEL 6	120
1BGEL 7	168
1BGEL 8	264
1BGEL 9	384
1BGEL 10	504
1BGEL 11	672

Once the alteration time was completed, the solids were separated from the solution by centrifugation and washed with ethanol until the electrical conductivity of wash solution had reached 55 $\mu\text{S}/\text{cm}$. In this case, the CEC was determined by Centrifuge Method according Solid Survey n°42 [4] instead of conventional titration with methylene blue.

2.2.1. Determination of CEC by Centrifuge Method

According to the procedure 5A2 of Soil Survey Laboratory Methods Manual n°42 [4], 5 g of each sample were kept in contact with 33 mL of NaOAc 1 N, shaken for 5 minutes, centrifuged and the supernatant phase had the K and Ca concentration determined by Atomic Absorption Spectroscopy (AAS) using a Atomic Absorption Spectrometer Agilent AA 240 FS. This step was repeated four times, in order to exchange all cations in bentonite for Na^+ . After the last saturation, the samples were washed with ethanol until the electrical conductivity of the supernatant liquid reached between 55 to 40 $\mu\text{S}/\text{cm}$. Finally, the absorbed sodium was replaced by extracting with three 30-mL portions of NH_4OAc 1 N. The concentration of K, Ca and Na was determined in former solution by AAS.

The CEC was calculated using the expression:

$$CEC = \frac{A}{W} \text{dilution } 10 \quad (2)$$

where:

CEC = cation exchange capacity in meq/ 100 g of clay

A = Na concentration (meq/L) and,

W = sample weight (g)

Additionally, the CEC was calculated taking in account the sum of all the cations analyzed in the NH_4OAc solution: K, Ca and Na, instead of just Na concentration.

3. RESULTS

The contaminant retardation factor includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. In many systems, the extent of sorption is controlled by the electrostatic surface charge of the mineral phase and its ability to exchange with contaminant species. The changes are mainly related to cations, thus the cation exchange capacity of materials is an important property to predict their sorption capacity [17].

The table 3 presents the estimated CEC values for Group 1 samples in each time interval. The results were also put in a graphic, as shown in figure 2.

Table 3: CEC results for Group 1 samples

Sample Code	Time of alteration	CEC (meq/100g)	Standard Deviation (meq/100g)
BGEL 01	0	67.32	0.30
BGEL 02	4	73.15	0.25
BGEL 03	8	60.18	7.28
BGEL 04	12	52.32	0.93
BGEL 05	24	56.37	0.52
BGEL 06	48	60.83	0.13
BGEL 07	72	55.16	4.48
BGEL 08	168	45.84	1.18
BGEL 09	264	54.00	0.42
BGEL 10	384	41.67	0.47
BGEL 11	504	52.40	4.33
BGEL 12	672	46.50	1.48

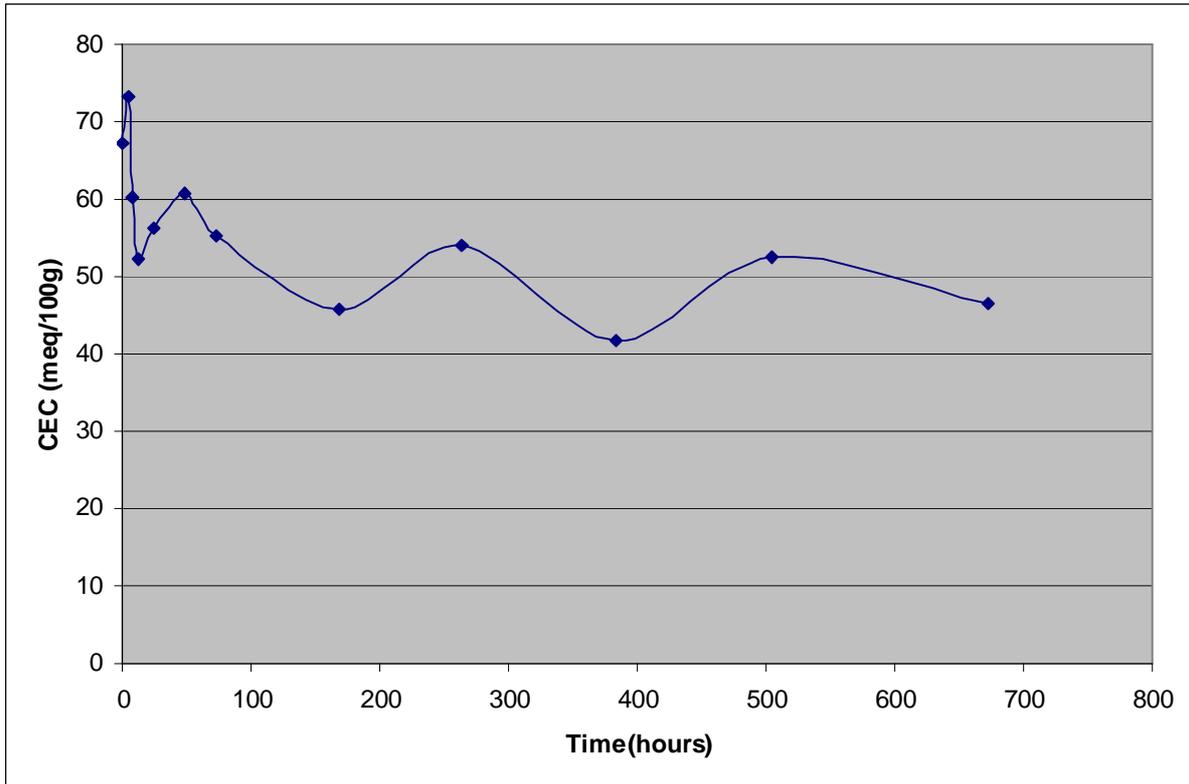


Figure 2: CEC versus time of alteration – sample of group 1.

It is noticed that the CEC values decrease with the increase of alteration time, although it is not possible to ensure that the stabilization time was reached, since the CEC was still varying even in the last two intervals.

The values of initial CEC for bentonites depend on their mineralogical composition. Generally bentonites with high content of montmorillonite (more than 80%) present CEC values around 75 meq/100g [6], which is in agreement with the results found for the BGEL material: 67.32 meq/100g using Methylene Blue Method.

In order to investigate the modifications in mineralogy of the material, X-rays diffraction analyses were carried out for the material before and after reacting with alkaline solution. The diffractogram for sample without alteration is presented in figure 3, and, for the sample after 28 days of alteration, in figure 4. It was chosen just the diffractogram after 28 days of reaction because the results were very similar in other conditions.

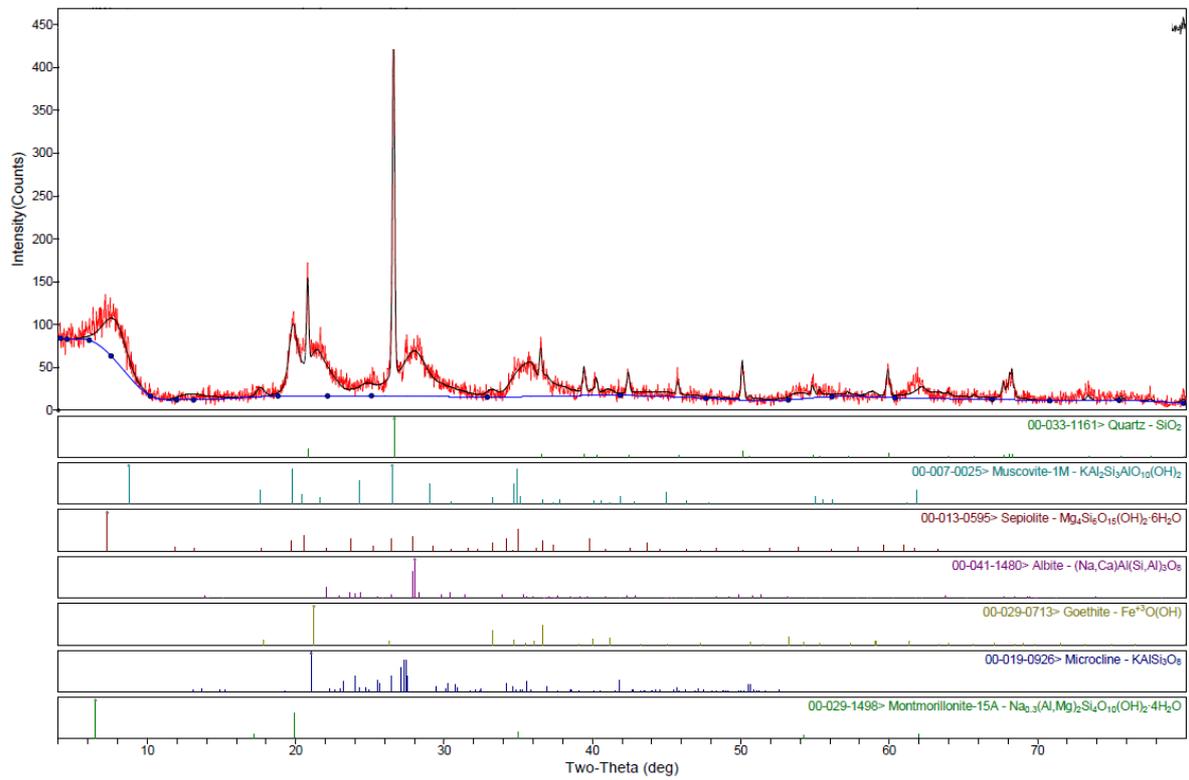


Figure 3: X-rays diffraction analyses for clay BGEL without alteration.

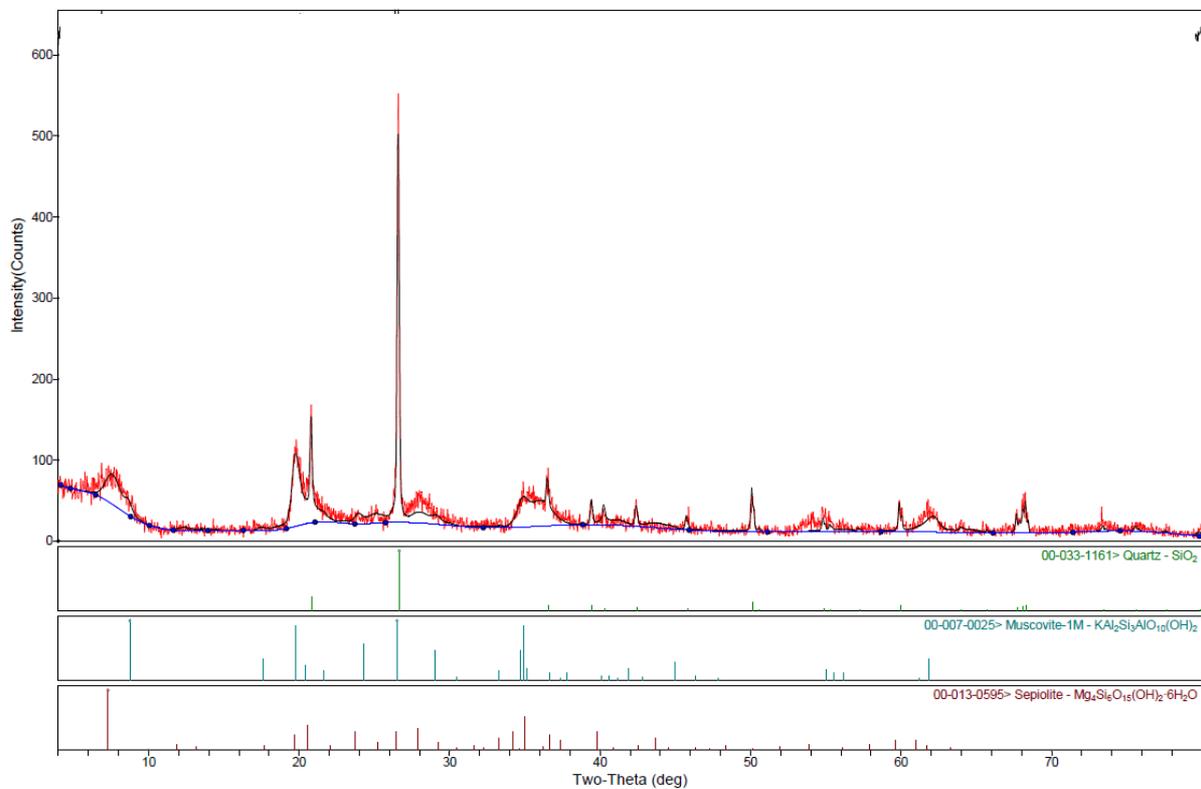


Figure 4: X-rays diffraction analyses for clay BGEL after 28 days of alteration.

Before alteration, it is noticeable that quartz is an important mineral, since their characteristic peaks are easily identified. With the best adjustment, it was also identified the presence of montmorillonite and sepiolite, as clay minerals, albite and microcline as feldspars, besides muscovite and goethite.

Figure 4 shows that after 28 days of alteration, among the minerals initially identified, it was noticed just quartz, sepiolite and muscovite, which indicates that the montmorillonite was dissolved. These results are in agreement with the CEC values, since it is expected a decrease in montmorillonite amounts once the CEC values decrease [2].

The table 4 presents CEC-Na and the CEC-total values obtained for Group 2 in each time interval. The CEC-Na considers the cation exchange capacity just related to Na species whereas the CEC-total considers the cation exchange for Na, K and Ca.

Table 4: CEC results for Group 2 samples

Sample Code	Time of alteration (hours)	CEC - Na (meq/100g)	Standard Deviation – Na (meq/100g)	Total CEC (meq/100g)	Standard Deviation – Total (meq/100g)
1BGEL 0	0	66.62	3.85	77.15	3.91
1BGEL 1	8	78.33	0.78	116.95	3.48
1BGEL 2	12	82.33	2.66	119.81	3.62
1BGEL 3	24	83.46	0.84	124.00	0.64
1BGEL 4	48	72.82	1.05	108.86	3.45
1BGEL 5	72	79.05	1.11	115.90	5.83
1BGEL 6	120	72.31	8.85	109.91	6.87
1BGEL 7	168	80.22	8.96	121.09	7.77
1BGEL 8	264	77.63	3.32	119.84	1.04
1BGEL 9	384	75.80	0.83	117.77	3.46
1BGEL 10	504	80.84	1.30	124.01	4.16
1BGEL 11	672	82.08	1.12	121.69	1.83

Figure 5, shows the results also, in a graphic way.

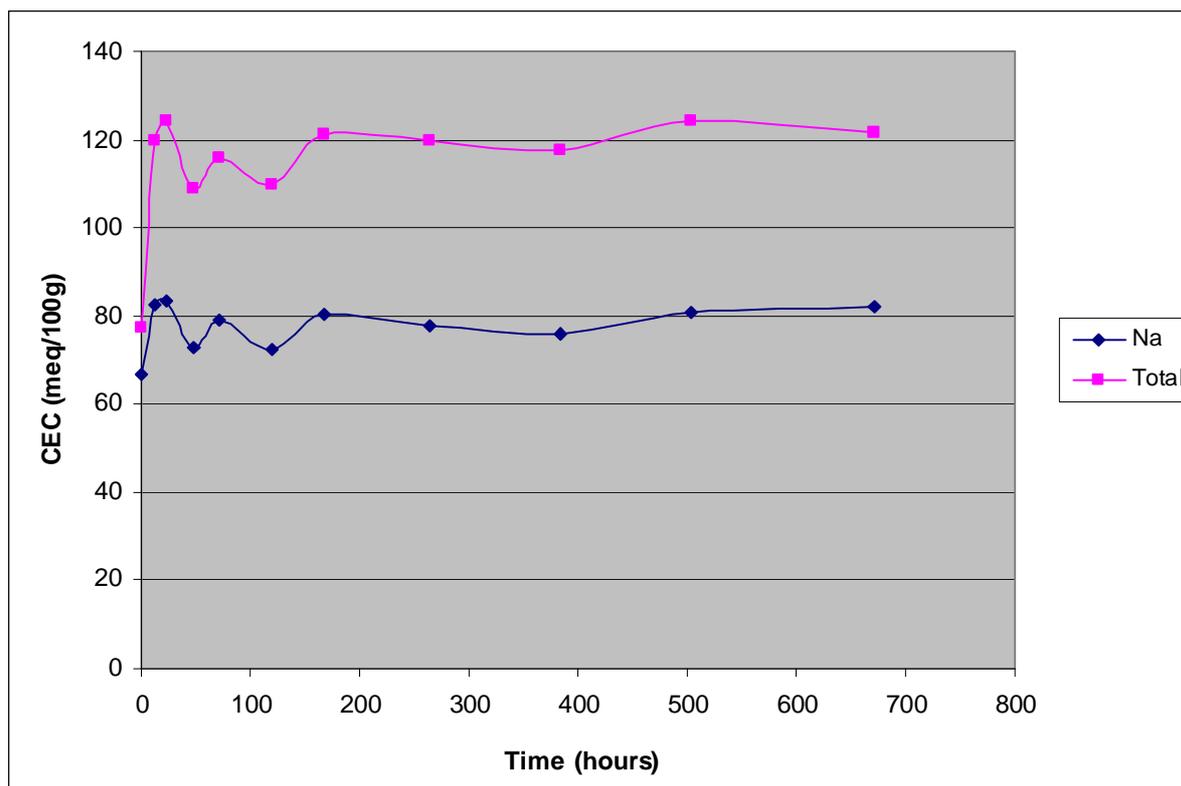


Figure 5: CEC Na and CEC total versus time for the second group of samples: NaOH/ KOH/ Ca(OH)₂ alteration solution.

Figure 5 shows that the values for CEC-total and CEC-Na are not the same, although they present the same behavior, i.e., a marked increase in the first 12 hours followed by a slight decrease, and after a period of instability they tend to stabilize in a value around 120 and 80 meq/100g, respectively. In short, the CEC increased from 66 to 80 meq/100g considering just Na, and from 77 to 120 meq/100g considering the total cations. Bouchet et al. [18] obtained an increase from 75 to 110 meq/100g, using similar conditions and materials, which is in agreement with the results of the present work.

The evolution of bentonites CEC during alkaline alteration is related with the initial mineralogical composition and also with the chemistry of alkaline solution. The presence of high content of K and Ca ions in the alkaline fluid can provide appropriate conditions for modification of the absorbed cation population of the bentonite, i.e., given the greater affinity of these cations for clay, they can replace the Na initially present [6].

According with previous works, it is conclude that the increase in CEC in the beginning of alteration process could be due to the zeolite formation, mainly philipsite and analcime types from accessory minerals, as volcanic glass and K-feldspars, and also from montmorillonite. The zeolite crystallization is controlled basically by chemical composition of the alteration solution [12]. X-rays diffraction analyses are being carried out to confirm this result.

4. CONCLUSIONS

A different behavior was observed when the samples were treated with the two types of alkaline solution: a CEC decrease was observed in the treatment with NaOH 1 mol/L while a CEC increase was noticed in a treatment with the moderate alkaline solution NaOH/KOH/Ca(OH)₂. The alkalinity and the composition of the solutions of alteration seem to play an important role in the CEC evolution of the material.

For the second group of samples it was concluded that the stabilization time for CEC was 200 hours. Although some small variations are observed after this time, they are not significant. For the first group of samples, although after 28 days of alteration no montmorillonite was identified, it is not possible to assure that the CEC reached the stabilization, since the values still varies even in the last points.

Future studies of X-rays diffraction will help to clarify the mechanism of alteration for the second group of samples, in which alteration was performed using a most realistic alkaline condition.

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