

Activation of Mirsid Volcanic Tuff with NaOH Solutions

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The purpose of this article is to study the activation of the Mirsid volcanic tuff with NaOH solutions at various concentrations. To be more specific, the work investigated the evolution of the concentrations of species that passed from the tuff into the activating solutions and the quantities of dissolved species from 100 g tuff. The species found in the activating solution were: potassium, magnesium, aluminium and silicon. The shape of the curves - a sudden increase followed by a plateau or a second stage of slower increase - allowed for setting up the optimal activation time at a half-hour. Another finding was the optimal concentration of 1 N for the activating solution. X-ray diffractograms showed the increase of clinoptilolite content in the tuff, thus improving the adsorbent as well as ion exchange properties by activation with NaOH solutions.

Keywords: Mirsid volcanic tuff, alkaline activation, dissolved species, optimum activation time, optimum activating concentration

Volcanic tuff is a sedimentary rock coming from volcanic ash. An important component of this ore is the mineral class called zeolites (in Greek zein means boiling and lithos - stone). They are hydrated aluminosilicates of various alkaline metals (Na^+ and K^+) and alkaline earth metals (Ca^{2+} , Mg^{2+} , Ba^{2+} and Sr^{2+}) [1- 3]. More specifically, zeolites are formed from $(\text{SiO}_4)^{4-}$ tetrahedra where silicon is partially replaced by aluminium, which results in a positive charge deficiency. That is neutralized by the alkaline and alkaline earth metal ions. These cations are hydrated and the hydrating water (also called constitutive water) is eliminated at well-defined temperatures. It should be noted that $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedra form channels and cavities filled with the so-called zeolitic water, which is weakly bonded and is continuously eliminated by heating.

Depending on zeolite content of a volcanic tuff, it can be classified into rich zeolite tuff (more than 50 % zeolite), medium zeolite tuff (20-50 % zeolite) and zeolite-depleted tuff (20 % zeolite) [1].

The tuff of Mirsid (a locality in Sălaj county in the northern part of Romania), which is the subject of this study, is characterized by the fact that the dominant zeolite is clinoptilolite, which can be accompanied by quartz, feldspat, calcite, montmorillonite, etc. The chemical composition of this tuff is given in Table 1 [1].

Table 1
CHEMICAL COMPOSITION OF THE MIRSID VOLCANIC TUFF [1]

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Content [%]	68.1-70.1	11.8-12.6	0.7-1.1	3.4-4.8	0.6-0.8	2.2-3.5	0.4-0.6

The most important applications of the volcanic tuff are based on the adsorbent and ion exchange properties of zeolites. As a consequence, a determinant role in these properties is played by the zeolite content of the tuff. More specifically, the adsorbent properties come from the channels and cavities within the zeolite structure. Since the channel diameter limits the size of the molecules adsorbed into cavities, zeolites act as sieves, hence their other name of molecular sieves. As regards the ion exchange property, this is ensured by the alkaline metals (especially Na^+ and K^+) and alkaline earth metals (especially Ca^{2+} and Mg^{2+}) within the zeolite, so it is determined by the ratio of aluminium to silicon. In addition, also in this case, the dimension of the channels and cavities plays an important role.

Commonly, zeolites within volcanic tuff can be transformed to Z-H structure by treatment with acid solutions or to Z-Me by using base solutions or metal (Na^+ , Ag^+ , Cu^{2+} , etc.) salts. The result of this approach is the improvement of adsorbent and ion exchange proprieties of the tuff (both ion exchange capacity and selectivity towards a certain cation) [1, 4, 5, 6, 7] and also bactericide properties (e.g., Cu^{2+} , Ag^+ - doped tuff) [8, 9], catalytic and photocatalytic characteristics (TiO_2 - doped tuff) [10], etc.

This study focused on chemical activation with NaOH of the Mirsid volcanic tuff. The evolution of potassium, calcium, magnesium, iron, aluminium and silicon quantities that passed from tuff into the activating solutions (various concentrations) was monitored over time. Optimum activation time and NaOH concentrations were established based on the shape of these time dependencies. In addition, the influence of the NaOH concentrations on the clinoptilolite content of the tuff was determined by using X-ray diffractograms.

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Experimental part

The experiments aimed at activating the Mirşid volcanic tuff with sodium hydroxide solutions at concentrations of 0.1, 1 and 2 N followed by analysis of both solutions used for activation and the activated tuff. For activation, 15 g of less than 63 μm granulation tuff and 200 mL of NaOH solutions were mixed at 23⁰ C by using a vertical stirrer. At 15 minute intervals, samples were taken with a syringe and immediately filtered on a G4 filtering crucible. To minimize the contact time between tuff and solution after sampling, filtration was carried out under vacuum. The resulting filtrates were stored in plastic bottles.

Given the chemical composition of the tuff (Table 1), potassium, calcium, magnesium, iron, aluminium and silicon concentrations were determined in the activating solution.

Potassium concentration was determined by flame photometry, with a Flapho 4 device of Carl Zeiss Jena [11].

The determination of calcium and magnesium concentrations were carried out by titration with EDTA (ethylenediaminetetraacetic disodium salt) [11, 12]. Actually, the calcium concentration and the sum of the calcium and magnesium concentrations were determined directly. Thus, for the determination of calcium concentration, the pH was set at 12 and murexide was used as an indicator, when the colour turned from pink to purple. To determine the sum of calcium and magnesium concentration the pH was set at 10 (ammonium buffer solution) and Eriochrome Black T was used as an indicator. The equivalency was marked by the colour turn from red to blue.

Quantitative determination of iron (sum of Fe^{2+} and Fe^{3+} concentrations), aluminium and silicon was done spectrophotometrically by using a Shimadzu UV 1240 device.

The determination of the total iron concentration was based on the reaction between Fe^{2+} (Fe^{3+} was previously reduced to Fe^{2+} with hydroxylamine hydrochloride) and o-phenantroline. The resulting complex was characterized by a maximum absorption at 510 nm [11].

Aluminium was determined as its complex with Eriochromcyanine R, which was characterized by a maximum absorption at 535 nm [11].

The starting point for determining silicon concentration was its reaction with ammonium heptamolybdate that led to the formation of some yellow heteropolyacids. To increase the sensitivity of the method, methol (photorex) was added when the colour of the sample turned into blue. Quantitative analysis was performed at $\lambda = 810 \text{ nm}$ [13].

The characterization of the raw and activated Mirşid volcanic tuff was made by X-ray diffraction. A Philips PW 3020 XRD device was used for this purpose [14- 16].

Results and discussions

This section consists of two parts. The first part deals with the evolution of the concentrations of species that pass from the tuff into the activating solutions at various concentrations. Considering the composition of the Mirşid volcanic tuff (Table 1), the determinations were made for: potassium, calcium, magnesium, iron, aluminium and silicon. The second part of the study followed the influence of the concentration of activating solutions on X-ray diffractograms. The two investigated aspects allowed the determination of the optimal activation time and solution concentration.

Of the listed species, Ca^{2+} and $\text{Fe}^{2+, 3+}$ were found below the limit of detection of the methods used: 6 μM and 9 μM . This was not a surprise because the alkaline medium contributed to strengthening the position of these ions within the crystalline lattice. Unlike alkaline activation, in the case of acid activation (with H_2SO_4), these species were found in the activating solutions, calcium concentration was much higher than that of the total iron [17].

Figures 1, 2, 3 and 4 show the dependencies of K^+ , Mg^{2+} , Al^{3+} and SiO_2 concentrations in the activating solutions with time (left y - axis) and their released quantities from 100 grams of tuff (right y – axis).

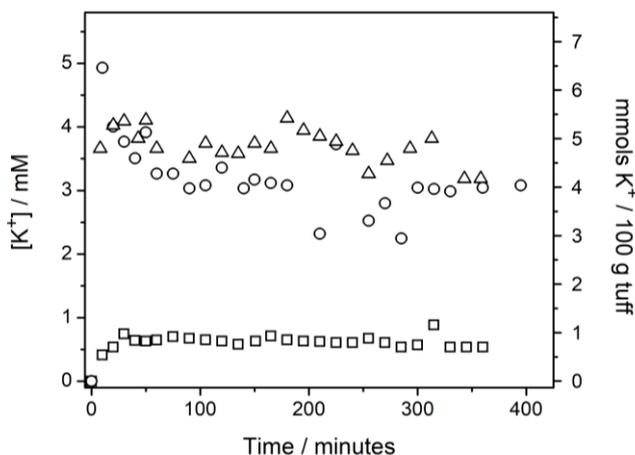


Fig. 1. Dependence of K^+ concentrations in the activating solutions (left y – axis) and of dissolved K^+ from 100 g Mirşid volcanic tuff (right y – axis) on activation time. (Activation with NaOH: squares – 0.1 N; circles – 1 N and triangles – 2 N, $t = 25^\circ\text{C}$)

Regarding K^+ concentrations (Figure 1), they suddenly increased at the beginning and after 30 minutes oscillated around average values. For the three NaOH activating solutions (0.1 N; 1 N and 2 N), the average K^+ concentration within solution (expressed in mM) and the K^+ released from 100 g tuff (expressed as mmol / 100 g) were: 0.6 / 0.8 - for 0.1 N; 3.0 / 4.0 - for 1 N and 3.7 / 4.9 - for 2 N. It was noted that with the increasing of NaOH concentration from 0.1 N to 1 N, the K^+ concentration in the solution increased by about 5 times while the increasing from 1 N to 2 N NaOH, resulted in an increase of K^+ concentration by only 23 %. This proved that the 1 N activating solution was the most effective what the replacement of K^+ by Na^+ concerned.

When comparing the evolution of K^+ concentrations for the alkaline activation with those for the acid activation [17], it was firstly noted that the shape of the curves was the same and secondly that the concentrations corresponding to the plateau are higher than those of acid activation: 1.1 mM (0.1 N); 6.4 mM (1 N) and 9.4 mM (2 N). The corresponding quantities of K^+ dissolved from 100 g tuff (acid activation) were: 1.5 (0.1 N); 8.5 (1 N) and 12.5 (2 N).

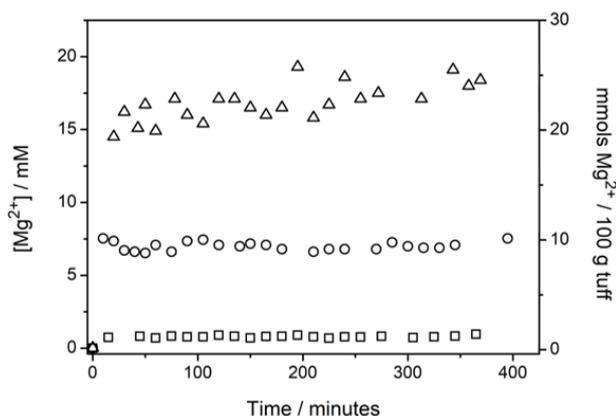


Fig. 2. Dependence of Mg^{2+} concentrations in the activating solutions (left y – axis) and of dissolved Mg^{2+} from 100 g Mirsid volcanic tuff (right y – axis) on activation time. (Activation with NaOH solutions: squares – 0.1 N; circles – 1 N and triangles – 2 N, $t=25^{\circ}C$)

The evolution of Mg^{2+} concentrations in the activating solutions and the released Mg^{2+} from 100 g tuff (Figure 2) were similar to those reported for K^+ : rapid increase in the first 15 minutes followed by a plateau. The plateau values for the three concentrations of the alkaline activating solutions were (cation concentration expressed in mM / cation quantity released from 100 g tuff): 0.8 / 1.0 - for 0.1 N; 7.0 / 9.3 - for 1 N and 16.9 / 22.6 - for 2 N.

The values obtained for activation with 2 N NaOH solutions (16.9 / 22.6) were comparable to those for activation with 2 N H_2SO_4 (14 / 18.7), while the values resulting from activation with NaOH 0.1 N and 1 N (0.8 / 1.0 and 7.0 / 9.3) were lower than those corresponding to acid activation with H_2SO_4 of the same concentration (9 / 12 and 15 / 20) [17]. It should be noted that we did not expect Mg^{2+} to pass from tuff into the solution as for the alkaline activation, because the position of Mg^{2+} cations in the crystal lattice should have been strengthened, as in the case of Ca^{2+} and $Fe^{2+, 3+}$. In addition, Mg^{2+} content in the Mirsid volcanic tuff was lower (0.6 - 0.8 % MgO) than that of Ca^{2+} (3.4- 4.8 % CaO) and $Fe^{2+, 3+}$ (0.7 – 1.1 % FeO_3). A possible explanation for the presence of Mg^{2+} in the activating solution was breaking of some O–Al bonds and passing into the solution as an Al^{3+} and Mg^{2+} block. This hypothesis was also sustained by the fact that the dissolved Al^{3+} and Mg^{2+} quantities from 100 g tuff were similar, as one can see from Figure 2 and 3 (of a few mmols / 100 g tuff in the case of activation with NaOH 0.1 N solution and tens of mmols / 100 g tuff – for activation with NaOH 1 N and 2 N solutions). The fact that aluminium concentration was higher than that of magnesium was in line with the previously mentioned hypothesis as the electroneutrality of aluminium tetrahedra, $(AlO_4)^{5-}$, could be also provided by other cations than magnesium and aluminium was in the crystal lattice also as an exchangeable cation.

With respect to aluminium and silicon, these were dissolved by the alkaline activation solution, as it was anticipated.

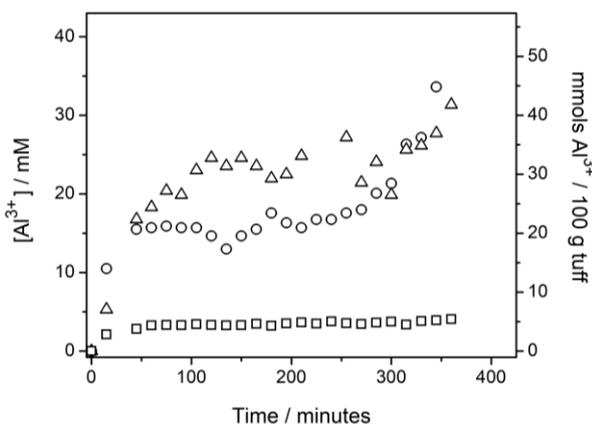


Fig. 4. Dependence of silica concentration (as SiO_2) in the activating solution (left y – axis) and of dissolved silica from 100 g Mirsid volcanic tuff (right y – axis) on activation time. Activation with NaOH solutions: squares – 0.1 N; circles – 1 N and triangles – 2 N, $t=25^{\circ}C$)

In the case of Al^{3+} (Figure 3), the shape of the curves that showed the time dependence of cation concentration within the activating solutions was a function of their concentrations. Thus, for the most dilute NaOH solution (0.1 N), the dissolved Al^{3+} concentration suddenly increased to 2 mM - in the first 15 minutes and continued to 4 mM slowly - for the next 6 hours. This evolution was similar to that seen for activation with H_2SO_4 0.1 N, when the sudden increase was up to about 4 mM and the slow one to about 5 mM. For concentration of NaOH solutions of 1 N and 2 N, the evolution of Al^{3+} concentrations showed two strong increases interleaved with a plateau. The average values of plateaux (concentration of Al^{3+} within the activating solutions, expressed in mM, or quantity of Al^{3+} released from 100 g tuff, expressed in mmol / 100 g) were: 15.7 / 20.9 (1 N) and 23.9 / 31.9 (2 N). It should be stressed that for activation with 1 N and 2 N H_2SO_4 , the shape of the curves was similar to that obtained for the activation with 0.1 N solutions (both H_2SO_4 and NaOH) while the Al^{3+} concentration obtained after 6 hours of activation was higher, of about 20 mM.

In summary, Al^{3+} concentrations within alkaline activating solutions were comparable to those recorded for acidic activation (for the same acid / base concentrations) [17]. Another important aspect was that the values obtained were higher but comparable to those established for K^+ - which is an exchangeable cation. This observation can be explained by the fact that aluminium is found in clinoptilolite both as an exchangeable cation, Al^{3+} , and as an anion, $(\text{AlO}_4)^5-$ [1, 2, 3]. In addition, the high content of aluminium in the Mirşid tuff, ranging from 11.8 to 12.6 % Al_2O_3 (Table 1), also explained the high dissolved aluminium concentration.

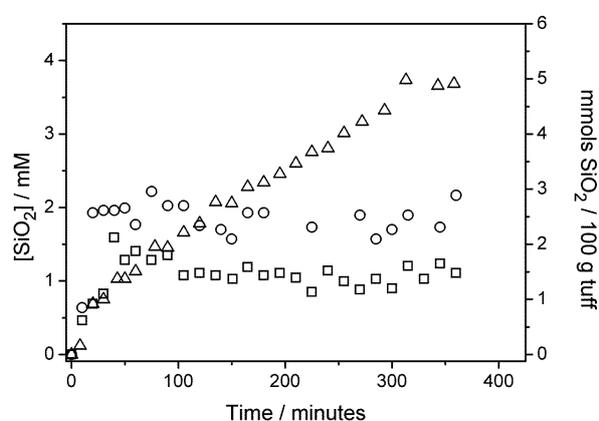


Fig. 3. Dependence of Al^{3+} concentration in the activating solution (left y - axis) and of dissolved Al^{3+} from 100 g Mirşid volcanic tuff (right y - axis) on activation time. (Activation with NaOH solutions: squares - 0.1 N; circles - 1 N and triangles - 2 N, $t=25^\circ\text{C}$)

As it can be seen in Figure 4, the shape of time dependence of the concentrations of silicon, expressed as $\text{mmol}\cdot\text{L}^{-1}$ SiO_2 , was determined by the concentration of the activating solutions. Thus, when activation was done with 0.1 N and 1 N NaOH solutions, a sudden increase of silicon concentrations was recorded in the first 15 minutes followed by a plateau. The average plateau values for 0.1 N / 1 N solutions were: 1.1 / 1.9 mM SiO_2 within the activating solution and 1.5 / 2.5 for the quantity of SiO_2 released from 100 g tuff. For the activation with 2 N NaOH solution, the sudden increase up to 0.7 mM SiO_2 (0.9 mmols SiO_2 / 100 g tuff) was followed by a second stage of increase to about 3.7 mM SiO_2 (5.0 mmols SiO_2 / 100 g tuff) after 6 hours of activation. It was noteworthy that the concentration increase of NaOH solution by one order of magnitude (from 0.1 N to 1 N) led to an increase by only 66% (from 1.1 to 1.9 mM) of SiO_2 dissolved after 6 hours of activation. A further two fold increase of NaOH concentrations (from 1 N to 2 N) almost doubled the concentration of the dissolved silica (from 1.9 to 3.7 mM). These observations showed that the destruction of $(\text{SiO}_4)^4-$ tetrahedral lattice was important and in addition it becomes a continuous process when activation was done with 2 N NaOH solution.

By comparing the quantities of dissolved silicon from 100 g tuff after 6 hours of activation when either sodium hydroxide or sulphuric acid were used as activating solutions, it was noted that these were in the order of (2 ± 0.5) mmol / 100 g tuff for all acid concentrations (around 2.5 mmol / 100 g tuff), for sodium hydroxide solutions 0.1 N (1.5 mmol / 100 g tuff) and for sodium hydroxide solutions 1 N (2.5 mmol / 100 g tuff) and increased to 5 mmol / 100 g tuff for 2 N sodium hydroxide solution [17].

Figure 5 shows X-ray diffractograms of the raw and activated (for 1 hour with solutions of 0.1 N, 1 N and 2 N NaOH) Mirşid volcanic tuff. By comparing these diffractograms, it followed that by the alkaline activation, clinoptilolite peaks increased in intensity suggesting an improvement of adsorbent and ion exchange properties of the Mirşid volcanic tuff. It should be mentioned that notable differences were only observed by comparing the raw and activated samples; comparison of diffractograms for the activated samples with various NaOH concentrations led to only small differences.

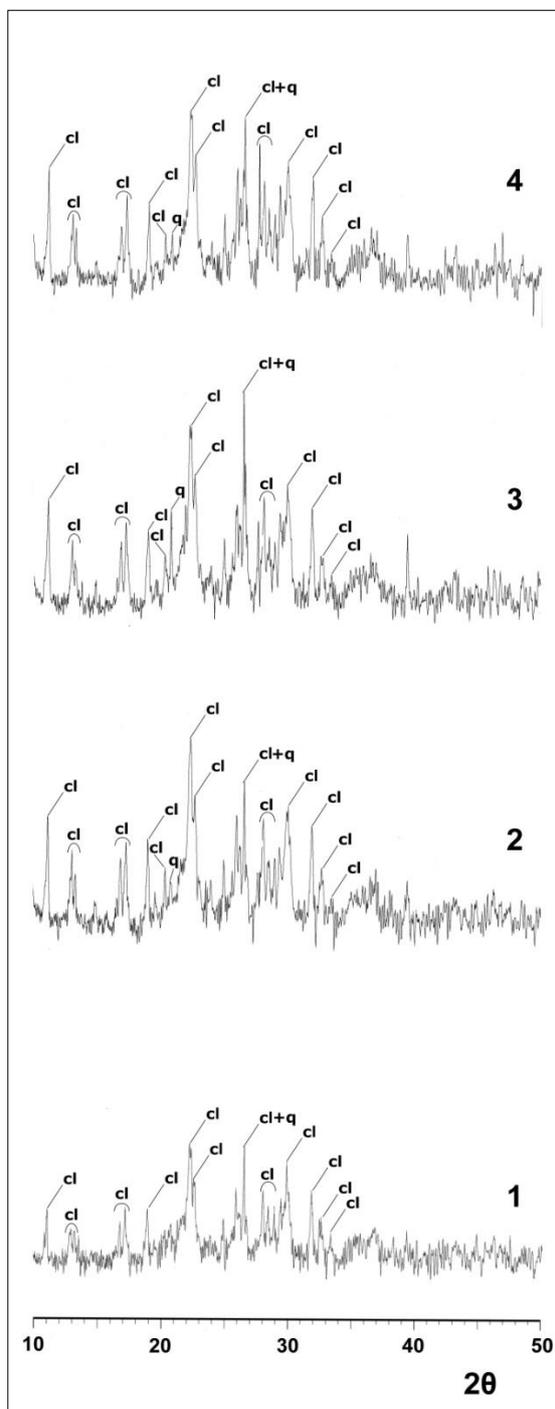


Figure 5. X-ray diffractograms of Mirsid volcanic tuff: (1 – raw 2, 3, 4 – activated (for 1 hour with solutions of 0.1 N, 1 N and 2 N NaOH Symbols used: “cl” - clinoptilolite and “q” – quartz)

Conclusions

Of the six main components of the investigated tuff: potassium, calcium, magnesium, iron, aluminium and silicon, only potassium, magnesium, aluminium and silicon were found in the activating sodium hydroxide solution. It should be noted that the time-variation of the concentrations of these species can take three forms, namely:

- sudden increase followed by a plateau for K^+ and Mg^{2+} - for all concentrations of NaOH solution and also for SiO_2 for activating solutions of 0.1 and 1 N;
- sudden increase followed by a second stage of slower increase - in the case of Al^{3+} - for 0.1 N NaOH solution and in the case of SiO_2 - upon activation with 2 N NaOH solution;
- sudden increase followed by a plateau and then again a sharp increase - in the case of Al^{3+} - for concentrations of 1 and 2 N NaOH solutions.

In the case of K^+ , the sudden increase at the beginning was explained by replacement with Na^+ from the activating solution. The sudden increase at the beginning with respect to Mg^{2+} , was explained by passing of certain aluminium – magnesium aggregates into the solution following the cleavage of some O–Al bonds within the crystal lattice. This phenomenon as well as the replacement of Al^{3+} with Na^+ from solution explained the increase of aluminium concentration in the solution at the beginning. For silica, the initial increase observed was small (up to 1.1 mM (0.1 N), 1.9 mM (1 N) and 0.7 mM (2 N) and could be explained by the dissolution of very small silica particles.

The second sudden increase observed for Al^{3+} (1 and 2 N NaOH solutions) could be explained by breaking up of some aggregates from which aluminium then dissolves more easily. The second stage of SiO_2 concentration increase at the activation with NaOH 2 N solution showed that SiO_2 tetrahedral lattice was practically destroyed continuously. This finding suggested that activation with NaOH 2 N solution was too aggressive.

It follows from this study that for almost all species and activation solution concentrations, the equilibrium concentration was practically reached after about 30 min. This showed that basically after this time, activation could be considered completed. These findings differed considerably from those in the literature, where the activation times ranged from one to tens hours [1, 4]. In addition, based on the dissolved species concentrations after about 30 min of activation, the optimal activating concentration was 1 N.

Further work will focus on experiments that determine the time evolution of the ion exchange capacity and specific surface area for various concentrations of sodium hydroxide solutions (0.1 N, 1 N and 2 N). These experiments aim at acknowledging the optimal activation time (of half hour) and NaOH concentration (1 N) based on the evolution of the concentrations of the dissolved species in case the tuff is to be used either as an ion exchanger or as an adsorbent. In addition, similar experiments to those of acidic or basic activations will be carried out with salt solutions of various concentrations in order to compare the efficacy of the three types of chemical activation.

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