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## Study of Acid-base Properties of Alumina Used as a Stationary Phase in Technetium Generators

Sbai S<sup>1</sup>, Elyahyaoui A<sup>1</sup>, Sbai Y<sup>2</sup>, Bricha MR<sup>3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Sciences, Mohamed V, Rabat, Morocco

<sup>2</sup>Faculty of Sciences, University Mohamed V, B.P-1014 Rabat, Morocco

<sup>3</sup>National Center for Energy Sciences and Nuclear Technique Rabat, Morocco

### ABSTRACT

The acid-base properties of alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) of different particle size classes are studied at room temperature by potentiometric titrations. The obtained results show that the point of zero charge (PZC) is unstable at  $t \leq 75$  min for grain size classes below  $32\text{-}63 \mu\text{m}$  and varies between  $3.3 \pm 0.2$  and  $6.5 \pm 0.2$  for the classes  $63\text{-}200 \mu\text{m}$  and  $42\text{-}27 \mu\text{m}$ . The PZC is obtained respectively up to  $3.1 \pm 0.1$  and  $3.6 \pm 0.1$ . The isoelectric point (IEP) which is the intersection of the suspensions titrations curves at different contact times was obtained at  $9.5 \pm 0.1$ . However, the IEP is difficult to observe when the particle size is less than  $23\text{-}63 \mu\text{m}$ .

**Keywords:** Alumina, Potentiometric titration, Content of the active sites, Surface charge

### INTRODUCTION

Potentiometric titration experiences are simple in principle and their implementation is important for characterizing the surface charge and number of active sites of colloidal particles, such as alumina. The choice of kinetic conditions such as volume and the beginning of the acid additions must limit unwanted secondary reactions, while ensuring a balance between the surface and solution is actually achieved.

Titration curves very often depend on three parameters: the speed with which is performed the titration, the period between two acid additions and the volume of each addition. Note that the prior conditioning suspensions play a vital role in controlling the initial acid-base properties of the suspensions.

The surface of aluminum oxide is characterized by connections between the ions  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  as well as by the presence of hydroxyl group  $\text{OH}^-$ , except at high temperature heat treatment [1]. The  $\text{OH}^-$  surface groups are formed by the dissociation of water molecules adsorbed in the surface of the oxide. These hydroxyl surface groups affect the acid-base properties of the oxide surface. According to their environment, the hydroxyl groups may acquire a donor or acceptor character [2,3]. The varieties  $\alpha\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  are widely used in organic synthesis for their catalytic properties. These two alumina possess a low Brønsted acidity coming from surface isolated hydroxyl groups and partial dehydroxylation. It also shows a strong Lewis acidity at  $\text{Al}^{3+}$  sites level [1]. The surface acidity of the  $\alpha\text{-Al}_2\text{O}_3$  alumina has been extensively studied, in particular by FTIR spectrometry using adsorption of probe molecules [4,5]. Whereas, the surface acidity models have been proposed by Peri [6] and by Knözinger [7] in the case of  $\gamma\text{-Al}_2\text{O}_3$ . These models are based on the local charge density that depends on the environment of the hydroxyl groups. They especially show how the dehydroxylation reaction of a strong Lewis site near an  $\text{OH}^-$  group increases its acidity by inductive effect. These models have been restudied more recently by Raybaud et al. [8].

The  $\alpha$  and  $\gamma$  forms of  $\text{Al}_2\text{O}_3$  are not stable at atmospheric pressure and room temperature. In contact with distilled water, after 1 h, the surface of  $\alpha$ -alumina is transformed into a mixture of different oxides and hydroxides. Das and the Fevre [9,10] showed that the surface of  $\gamma$ -alumina, in suspension, evolves over time. In fact, titration curves of  $\gamma$ -alumina suspensions made by these authors were not reproducible and depended, in particular, on the hydration of the oxide duration.

The objective of this study is to determine surface characteristics of alumina (point of zero charge (PZC), isoelectric point (IP), and amount of active sites (Ns) in order to develop new technetium generators. Titration techniques are performed to study the acid-base properties of the sorbent according to the particle size and contact time.

## MATERIALS AND METHODS

### Materials

The titrator used in volumetric dosing experiments is a Mettler Toledo DL 53 type, calibrated by three buffer solutions 4, 7 and 10. The agitation operations are performed by a rocker agitator to avoid crushing the grain sizes of alumina by the magnetic bar. The stirring speed is of 300 rpm and the average titration period is estimated at 45 min.

### Methods

The employed alumina was classified according to six different particle size categories. A sample mass for 0.5 g of each alumina sample was suspended in 25 ml of KOH solution 0.1 N. After different contact times (*t*) ranging between 15 min and 2 h. The obtained suspension is then titrated by HNO<sub>3</sub> 0.1 N solution. In this study, the Blank used as reference to calculate the number of active sites is the result of acid-base titration of potassium hydroxide with nitric acid under the same experimental conditions without the addition of alumina.

The results are presented in the form of mixture pH variation curves as a function of the volume added of nitric acid.

### Calculation of the mass contents of active sites of the alumina

$$N_s = \frac{Ca(v_{ei} - v_e)}{1000 m}$$

Were, *m*: Mass of alumina in grams (g), *N<sub>s</sub>*: The content by mass of basic alumina sites (mol/g), *V<sub>a</sub>*=*V<sub>e</sub>*: The volume equivalence of the "Blank" (ml), *V<sub>ei</sub>*: The neutralization volume of suspensions of various contact times (ml), *Ca*: The initial concentration of the acid.

### Calculation of the surface charge of alumina

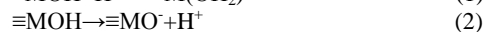
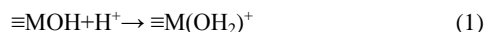
The surface charge *Q* is calculated in different experimental conditions, by using the conservation equations and electroneutrality.

The charge, *Q*, per g of suspension:  $Q = [>S-OH^{2+}] - [>S-O^-] = [NO_3^-] - [K^+] + [OH^-] - [H^+] = C_a - C_b + [H^+] - [OH^-]$  [NO<sub>3</sub><sup>-</sup>]: The concentration of nitrate ions in mol/l, [Na<sup>+</sup>]: the concentration of sodium ions in mol/l, [*>S-O*]: the concentration of basic sites of the alumina in mol/l, [*>S-OH<sup>2+</sup>*]: the concentration of acid sites of alumina in mol/l, *C<sub>a</sub>*: The initial concentration of the acid, *C<sub>b</sub>*: The initial concentration of the basic.

## RESULTS AND DISCUSSION

### Potentiometric titration

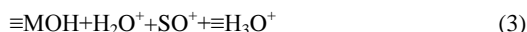
In general, the acid-base properties of α-alumina were described assuming the protonation and deprotonation reactions:



Figures 1 and 2 have the blank titration results and the suspensions of granulometric sizes 3-6, 7-12, 18-32, 32-63, 42-72 and 63-200 μm, at *t*=15, 30, 45, 60, 75, 90 and 120 min respectively. For particle size between 63-200, 42-7 and 32-63 μm, the titration curves (Figure 1) form two parts, the first between pH=11 and pH=8.5 corresponding to the neutralization of the basic active sites of the alumina. The curves of the other size classes have diagonal form indicating the homogeneity of the surface (Figure 2).

The equivalent volume (*V<sub>e</sub>*) of the acid base titration of the suspensions depends on the alumina particle size. In fact, the values of *V<sub>e</sub>* have decreased for granulometric sizes lower than 18-32 μm. This phenomenon is due to the consumption of OH<sup>-</sup> ions by deprotonation of the active sites ≡MOH<sup>2+</sup> and ≡MOH [11].

The zero point charge (PZC) is determined at the intersection of the suspension titration curves with the blank curve. Whereas, the isoelectric point (IPE) is determined at the intersection point between the titration curves suspension. Therefore, the (IPE) depends on the size of the alumina particles since it varies between 5.5 ± 0.2 and 9.5 ± 0.2. For the PZC we notice that it varies with the contact time (Figures 3-5), which is due to the absorption of electrolyte ions that has modified the surface charge of the oxide. This phenomenon was observed for particle size less than 32-63 μm. However, it should be noted that the PZC becomes stable at *t*>75 min for every particle size of the alumina. Consequently, the phenomenon of hydration reaches equilibrium conditions. It is also noted that the PZC increases with the particle size decreasing. To accurately determine all the variations in PZC following time, another complementary method was used, which shows the changes in the surface charge (*Q*) as a function of pH, the results show that the obtained charge of the alumina remains constant between pH=4 and pH=9 for the particle sizes 63-200, 42-72 and 32-63 μm (Figure 3). While the other classes of surface charge decreased continuously with increasing pH (Figure 4). These results indicate that (IPE) is observed at higher pH than the PZC. From these results, the isoelectric point (IPE) is higher than the (PZC) and it is associated to acidic character. As a result, this can lead to a deprotonation of the area with the formation of negatively charged ≡MOH groups on the surface, as observed previously for some oxides [12]. This suggests that adsorption and dissociation of water result in a negative surface charge according to:



The content of the active sites of alumina in basic solution does not depend on the contact time (Figure 6). However, it increases with increasing the particle size, especially for the grains sizes 18-32 and 32-63 μm, since it varies for 2,22 10<sup>-4</sup> mol/g to 5,44 10<sup>-4</sup> mol/g.

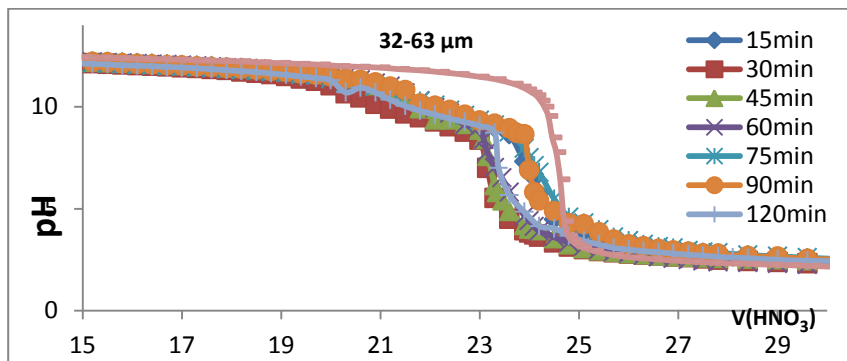
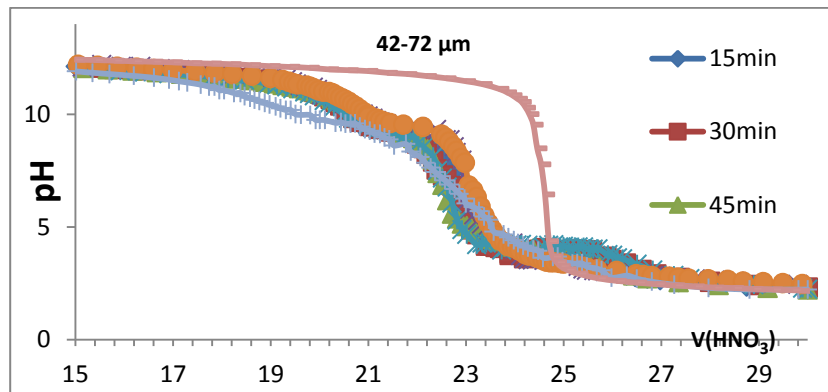
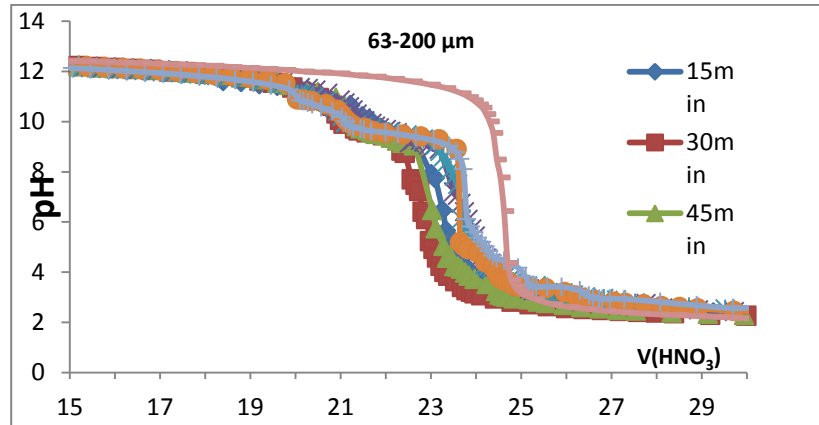
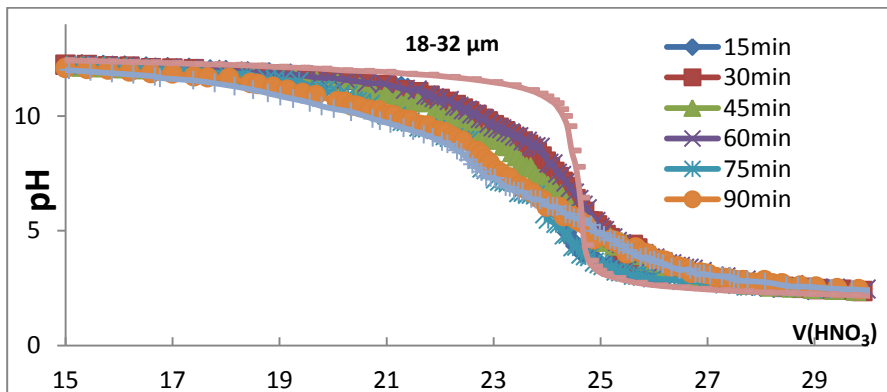


Figure 1: Variations in pH=f (V<sub>HNO<sub>3</sub></sub>) obtained for m=0.5 g, particle size 63-200 μm; 42-72 μm and 32-63 μm at contact times between 15 and 120 min



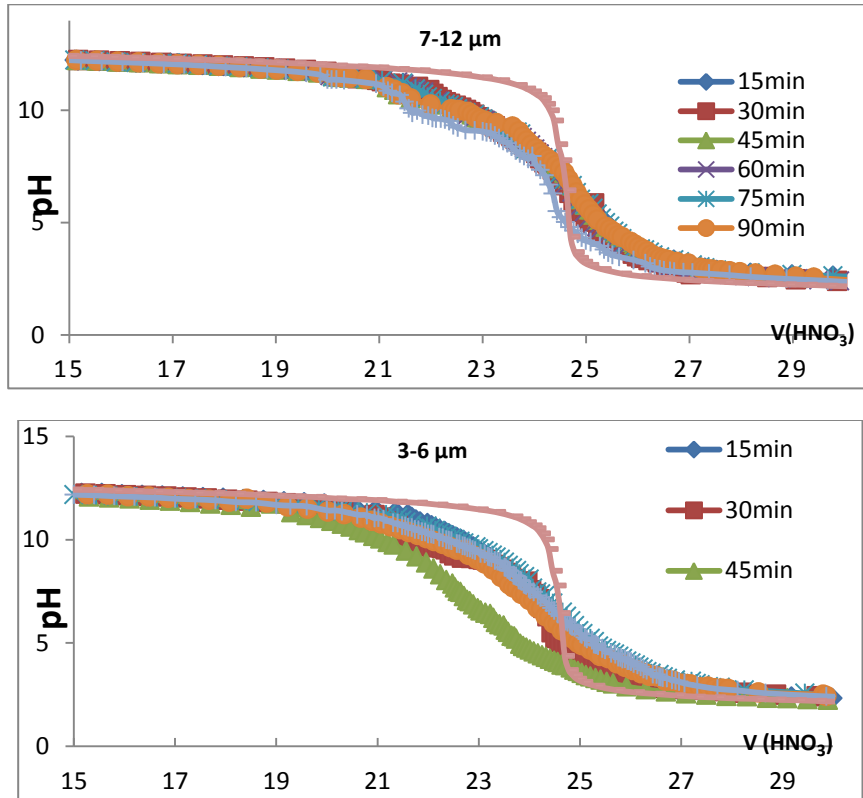
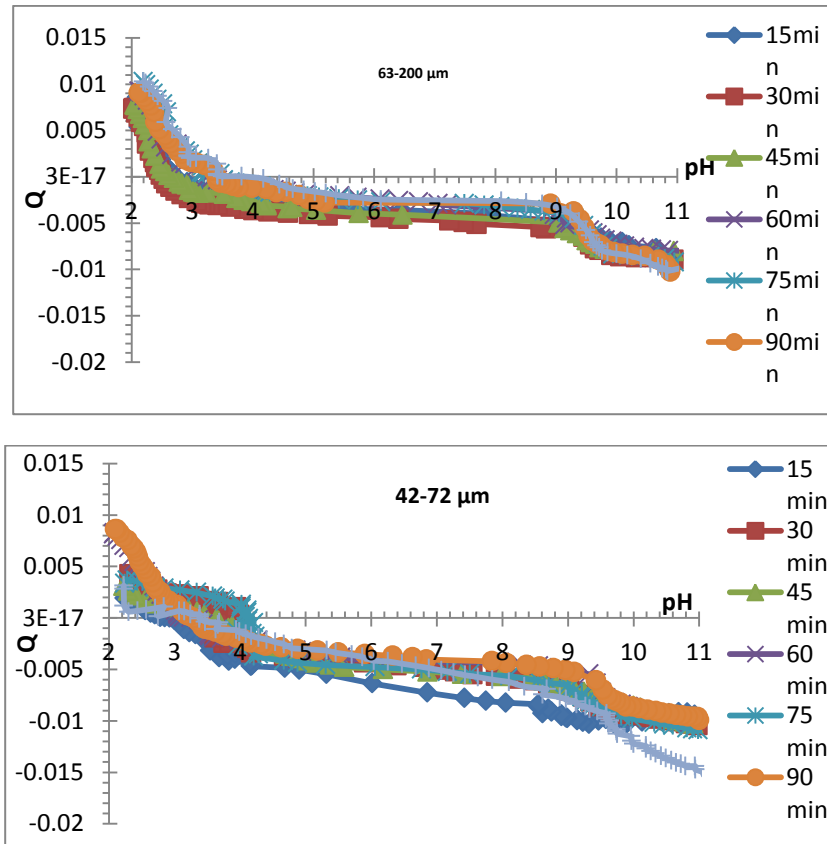


Figure 2: Variations in pH=f (V<sub>HNO3</sub>) obtained for m=0.5 g, particle size 18-32 μm; 7-12 μm and 3-6 μm at contact times between 15 and 120 min



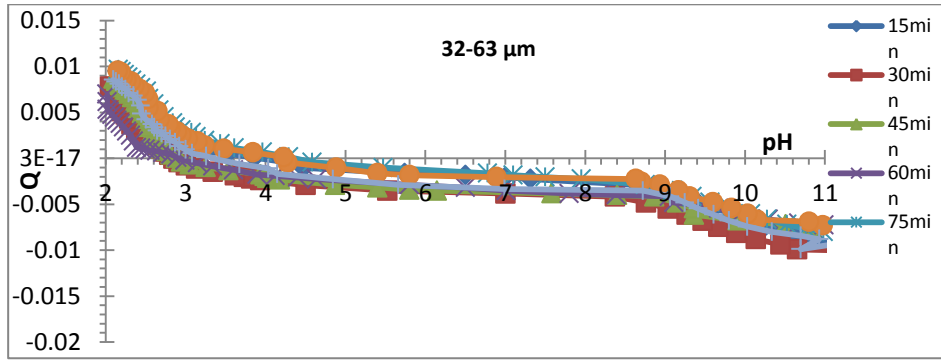


Figure 3: Changes in the surface charge of alumina depending on pH for the classes of alumina particle size: 63-200 μm; 42-72 μm and 32-63 μm

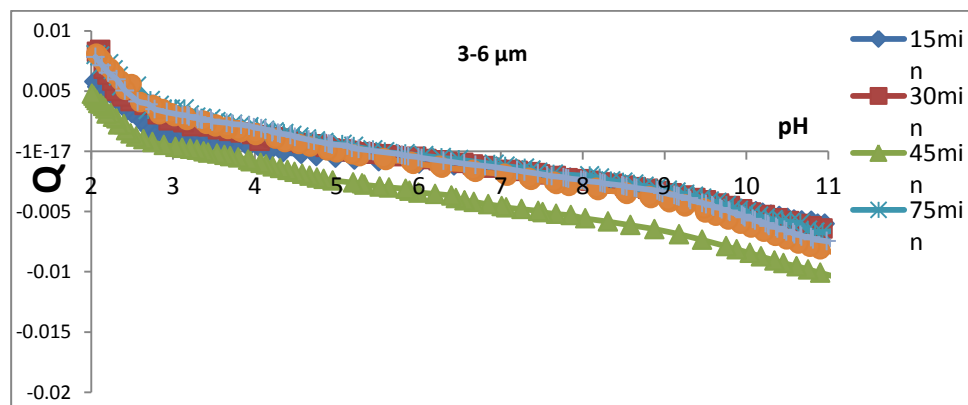
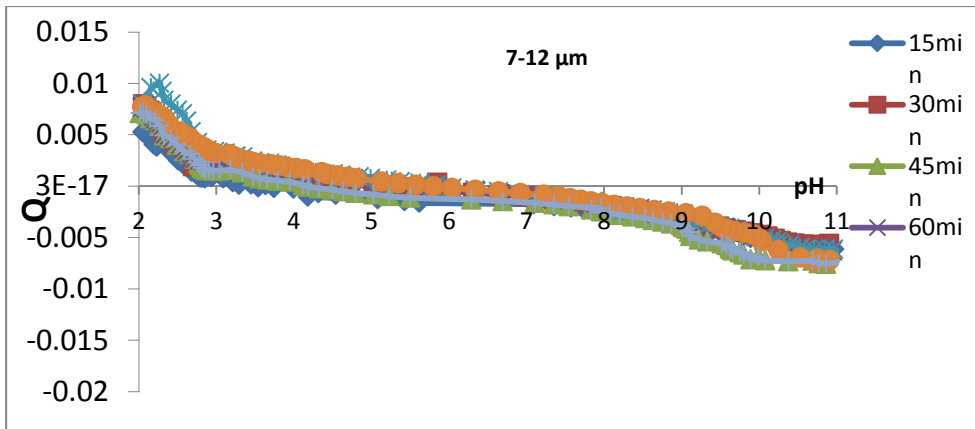
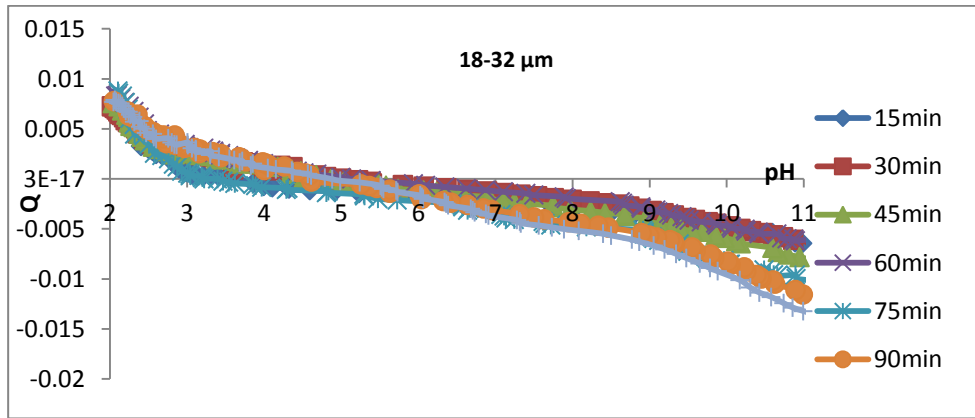


Figure 4: The variations in the surface charge of alumina depending on pH for classes of alumina particle size: 18-32 μm; 7-12 μm and 3-6 μm

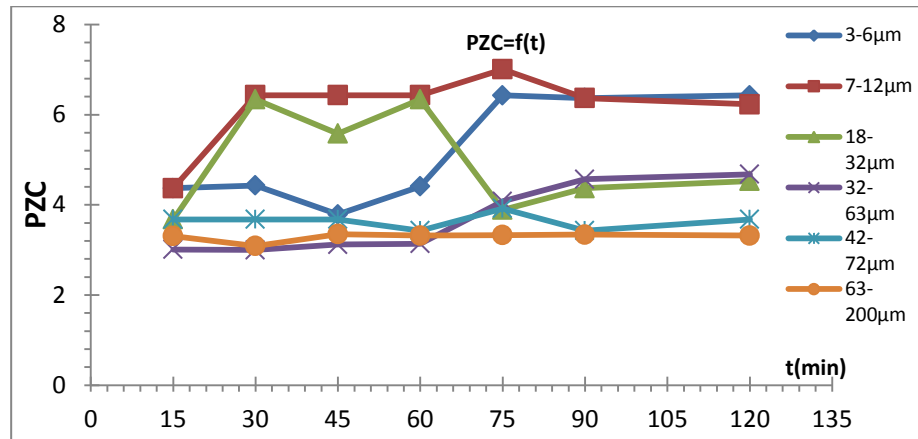


Figure 5: The zero charge point PZC plotted over the time (min) for different particle sizes of alumina

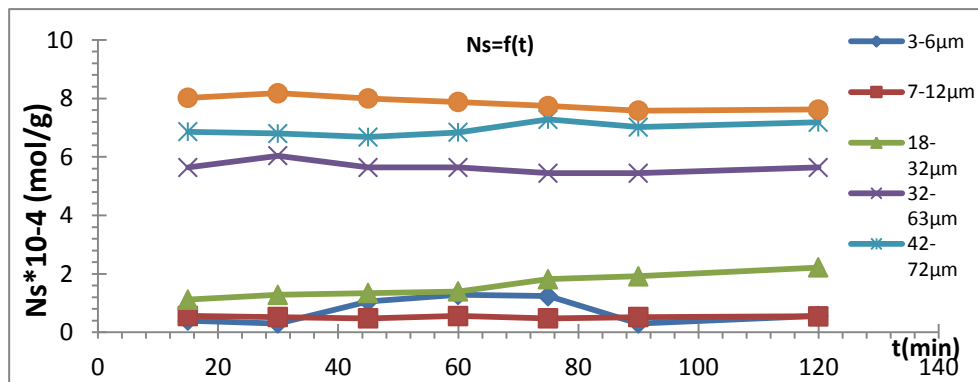


Figure 6: The variations in the content of active sites of alumina in a basic environment according to the contact time and the particle size

## CONCLUSION

The study of acid base properties of alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) used in technetium generators as a stationary phase was carried out by a simple method of potentiometric titration. The main parameters characterizing the surface of this oxide are the point of zero charge (PZC), the isoelectric point (IEP) and the active sites content which decreases as the grain size becomes finer.

The results obtained show that the (PZC) of alumina sizes varying between 63-200 and 42-72  $\mu\text{m}$  remains stable during the hydration time, but for the other sizes, the PZC is unstable since it varies between  $3.02 \pm 0.2$  and  $6.35 \pm 0.2$  and becomes stable after 75 min of hydration. The isoelectric point is obtained at  $9.5 \pm 0.3$  for the size 63-200, 42-72 and 32-63  $\mu\text{m}$ . The (IEP) is obtained towards the acidic pH range between  $5.5 \pm 0.2$  and  $6.7 \pm 0.2$ , however, it is noted that this last parameter is difficult to observe when the particle size decreases.

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