Towards a More Safe Environment: 
(4) Sorptability of Vanadium as a Nuclear Constructing Material by Some Clay Sediments in Egypt

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Abstract: Due to the increase concerns about the environmental pollution problems, it is so important in waste disposal management to perform an accurate exploration of geological barriers, which must be suitable for waste materials disposal. Clay sediments play an important role as natural adsorbents to immobilize heavy and nuclear metals contaminants. For the present study, the clay samples were selected from either clay exploitation localities or from nearby radioactive mineralization in Egypt. Obtained results indicated that vanadium adsorption and desorption differ importantly in accordance with the source of clay sediment used. In addition, its adsorption increases by increasing vanadium initial concentration. The obtained data were found to fit of Langmuir equations. Adsorption maxima (B) for vanadium were high for Abu Tartur bentonite followed by El Hafafit vermiculite and was the least for Kalabsha kaolinite. However, the binding energy (b) that affects the adsorption process can be arranged in the opposite direction. Desorption of vanadium by 0.1 M HCl, 0.1 M NaOH and tap water show clear ability of the different sediments to release vanadium. This was a function of leaching solution and binding energy. Finally, the mineralogical changes in the clay sediments through adsorption and desorption processes were investigated.

Key words: adsorption – clay sediments – desorption - I.R - vanadium

INTRODUCTION

According to the increasing concerns of the environmental pollution problems, it is so important in radionuclides waste disposal management to perform an accurate exploration of geological barriers for suitable disposal sites. Clay sediments play an important role as adsorbents of geological or technical convenience to be landfill barriers. These sediments represent excellent natural barriers due to their ability to close fissures and cracks, their chemical reactivity to immobilize important contaminants like heavy metals and nuclear elements.

Vanadium takes different valence states depending on the state of redoxy potential. In this respect, Fox and Doner[10] reported that vanadium might exist in 2+, 3+, 4+, and 5+ valence states. V⁴⁺ is generally present in extreme reducing environments, while V⁵⁺ and V⁶⁺ species are dominant under moderately reducing and aerobic conditions, respectively. For instance, V⁵⁺ is commonly precipitated as an oxide or oxhydroxide. V⁴⁺ is commonly found as a vanadyl cation [VO²⁺, VO (OH)⁺] and V⁶⁺ is most often present as a vanadate oxyanions [H₂VO₄⁻, HVO₄²⁻]. About the chemical form of vanadium in some clay minerals Gehring et al[11], concluded that in kaolinite vanadium (IV) occurs almost entirely as an isomorphically substituted species in the octahedral sheet. They added that during the dehydroxylation of kaolinite (at about 500°C) V⁴⁺ substituted octahedral sites are very likely converted into truncated octahedra with fourfold coordination which completely oxidized at about 800°C. In a sediment incubation study, Amrhein et al[12] found that under reducing conditions V concentrations slowly decreased in the solution phase; when samples were exposed to oxidizing conditions, V concentrations in the solution phase dropped to essentially zero. They attributed the V decrease in solution under reducing conditions to the precipitation of VO (OH)₂ from the above preface, one can conclude that the adsorption study of VO₂⁺ as univalent vanadium anion may be rare.

On the other hand, about 90% of the world’s production of vanadium is used in the ferrous metallurgy, smaller amounts in the production of chemical
compounds. A small quantity of metallic vanadium is used for special purposes. The chief forms of vanadium compounds in which vanadium is used in chemical industry are the crude sodium metavanadate (red cake), ammonium metavanadate, vanadic acid and vanadium oxide. Most of these compounds are mainly used as catalysts in the manufacture of sulfuric acid, as coloring agent in glass and ceramics. Vanadium metal can be used in a lot of hi-tech industries. In nuclear industries, vanadium is used as constructing material in the Fast Preeder Reactors since it has a lot fission neutron cross section, a small elastic scattering cross sections and good strength at elevated temperature and high thermal conductivity.

The aim of this study is to obtain some necessary data about the adsorptibility and desorptibility of V that are used in the nuclear industry as a constructing material in the Fast Preeder Reactors (FPR). In addition, the data are urgently required for the improvement of vanadium extraction technology and its waste management concerns.

MATERIALS AND METHODS

Clay sediments: Three natural clay sediments differ in their mineralogical composition were selected. The samples were collected from either the exploitation localities or from nearby radioactive occurrences in Egypt. These sediments include:

Kalabsha kaolinite sediments: Kalabsha area lies between longitudes 32° 00’ and 32° 30´ E and latitudes 23° 00´ and 23° 45´ N.

Abu- Tartur bentonite sediments: Abu-Tartur plateau lies between longitudes 25° 00´ and 26° 00´ E and latitudes 29° 00´ and 30° 30´ N.

El Hafafit vermiculite sediments: El Hafafit area lies between longitudes 34° 20´ and 34° 50´ E and latitudes 24° 20´ and 24° 50´ N.

The collected samples were grinded in a porcelain ball mill, washed with distilled water to remove soluble impurities and wet sieved through 350 mesh sieve (45 µm), homogenized and < 45 µm fraction was collected.

On the other hand ammonium metavanadate, Merck product with assay 99.5% (NH₄VO₃) was used as the vanadium reagent to carry out the experiments.

Characterization of clay sediments:

Chemical and mechanical characteristics: Chemical and Mechanical analyses and mineralogical composition by X-ray diffraction analysis, IR spectroscopy, D.T.A. and chemical analyses for major oxide and trace elements as well as radiometric analysis were carried out on all sediments used in a separate study.

Infrared Spectroscopic Analysis (IR): Infrared absorption spectra in the region of 400 cm⁻¹ to 4000 cm⁻¹ were recorded using KBr sample pellets for each clay sediment after finishing the adsorption and desorption processes. The samples were prepared as pellet method according to Russell and Fraser[10]. In the present work, A Bruker Vector spectrophotometer model FT-IR-22, Germany in the region of 4000-400 cm⁻¹ used. The IR analysis conducted in the Microanalytical Center, Cairo University.

Adsorption experiment design: The adsorption experiments were conducted upon 0.2 g of the clay samples, mixed with 20 ml of the vanadium solution having gradient concentration ranged from 0.1 to 2 mmol/L (solid/liquid ratio of 1:100). The suspensions were equilibrated for 3 hours using a mechanical shaker of 175 rpm at room temperature. The studied factors that might affect the vanadium adsorption phenomena include the following:

1- The clay/liquid ratio (S/L ration) ranged from 1:2-1:100.
2- The equilibrium time ranged from 15 min to 3 hours
3- The pH of the slurry ranged from 2-12.
4- The effect of KCl electrolyte presence at different concentrations i.e. (0.001, 0.01 and 0.1M)
5- The effect of clay samples pre-conditioning that includes acidic, alkaline and roasting at 1000°C treatments for 2 hours.

It is worthy to mention herein that the amount of adsorbed element was calculated from the difference between the initial concentration of the adsorbate and its concentration at equilibrium. While, the adsorption efficiency percent was calculated from the adsorbed amount of V divided on the initial concentration of V X100. On the other hand, the analysis of the vanadium element was performed by flame atomic absorption spectrometry (FAAS).

Desorption Method: The 0.2 g portions of the loaded clay samples with initial vanadium concentration of 1mmol/L, were equilibrated with 20 ml aliquots of 0.1 M HCl, 0.1 M NaOH and tap water separately. The suspended materials were shaking thoroughly by a mechanical shaker for 2 hours at room temperature.
then centrifuged. The supernatants removed completely and the desorbed element analyzed by FAAS. Four successive desorption experiments were applied for each desorbing agent. Desorbed amount percentage was calculated from the difference between the amounts of vanadium in the desorbing solution and the initial adsorbed vanadium on the clay sediment divided on the loaded vanadium x100.

RESULTS AND DISCUSSIONS

Sediments Characterization: Some general characteristics of the performed clay sediments are listed in Table (1). From this Table it is clear that:

1- The textural classes varied between clay in both kaolinite and bentonite sediments and sandy loam in vermiculite ones. This could be attributed to the geological nature of the parent sediments.

2- Chemical analyses of the saturation extract indicated that the sediments were neutral reaction, non-saline and values of C.E.C and A.E.C. in the same range of published data, Wilson[10].

The mineralogical composition of the used clay sediments was performed by the X-ray diffraction analysis while the semi-quantitative mineralogical composition according to Griffin[6] was calculated from XRD patterns and listed in Table (2).

Vanadium adsorption: Vanadium ion adsorption as a function of free (VO₃⁻) concentration is shown in Fig. (1) for the three used sediments. Obtained results showed that in low concentration (till 1 mmol/L) Kalabsha kaolinite adsorbed more (VO₃⁻) than the other two sediments. The exposed surface charge of kaolinite in the octahedral layer may be the reason. On the other hand, Abu-Tartur bentonite adsorbed the highest amount of (VO₃⁻) in the initial concentration above one mmol/L. The highest values of the anion exchange capacity of the bentonite, which reached 11.66 cmol/kg, may interpret the obtained results.

The adsorption data from the pure NH₄VO₄ solutions were plotted according to the simple Langmuir equation (Fig. 2). The obtained results showed that the Langmuir equation isotherms describe the V adsorption by the studied Egyptian clay sediments.

The B values (adsorption maximum), which was computed from the linear regression of the data are listed in Table (3), showing that the sediments can be arranged in the following manner: bentonite > vermiculite > kaolinite which is not in agreement with anion exchange capacity (A.E.C) values of the used sediments.

After It is worthy to mention that there are two opposite opinions towards the correlation between (A.E.C) or (C.E.C) and adsorption ions on clays. Kuo[8] found that there is no significant correlation between the (C.E.C) values and the Langmuir adsorption maxima of soils, while the opinion considers this correlation.

When considering the Langmuir value (b) measuring the binding energy of (V) on different clay sediments, the values in Table (3) revealed that kaolinite retained V stronger than bentonite followed by vermiculite; the values reached 4.8, 0.82 and 0.63 respectively.

Factors affecting vanadium adsorption:

1- Solid liquid ratio: The obtained data shown in Table (4) revealed that by increasing the solid/liquid ratio from 1% - 50%, the adsorption efficiencies decreased from 57.1, 60.1, and 66.6% for kaolinite, bentonite and vermiculite to 26.8, 4.2, and 29.1% respectively, indicating that the V adsorption efficiency is greater in vermiculite than bentonite followed by kaolinite.

2- The Equilibration time: From the obtained data in Fig. (3) it is clear that the adsorption efficiency increased with increasing the equilibration contact time from 15 minutes to 3 hours with all the studied clay samples. This equilibrium time is harmony with that of Mikkonen and Tummavouri[9] who used 72 hours equilibration time for the adsorption of V upon kaolinite.

3- pH: The obtained results presented in Fig. (4) show that the (V) adsorption efficiencies increased with the increase of the slurry pH till pH = 12 except for Abu-Tartur bentonite which decreased again at that pH. The obtained results are in general agreement with the published data of Mikkonen and Tummavouri[9] which reported the same phenomenon of V adsorption dependence on the pH until 6.5. Beyond this pH, the adsorption efficiencies decreased with some ions while V remains adsorbed in noticeable amounts. Moreover, Shahsingh[11] reported that the cation exchange sites are developed at pH values higher than 6, that due to the ionization of OH and COOH groups that contribute more to the selective adsorption of some ions. On the other hand, it can be noticed that the effect of pH upon the V adsorption efficiency was higher at any pH value in the kaolinite sample more than in the others.

4- KCl concentration: The obtained results illustrated (Fig.5) show the effect of KCl as ionic medium during the V adsorption. From these data it is clear that by increasing the ionic medium (KCl) concentration from 0.001 – 0.01 M, the V adsorption efficiency decreased at KCl concentration 0.001 M to 0.005 M and then increased at KCl concentration 0.005 M to 0.01 M by the studied clay
Table 1: Physical and chemical properties characteristics of the studied clay sediments

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>EC, ds/m</th>
<th>CEC*</th>
<th>AEC**</th>
<th>Course sand</th>
<th>Fine sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>7.20</td>
<td>0.43</td>
<td>12.80</td>
<td>9.58</td>
<td>3.35</td>
<td>11.44</td>
<td>23.67</td>
<td>61.54</td>
</tr>
<tr>
<td>Bentonite</td>
<td>6.44</td>
<td>2.83</td>
<td>71.00</td>
<td>11.66</td>
<td>25.51</td>
<td>15.49</td>
<td>13.28</td>
<td>45.72</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>7.00</td>
<td>1.40</td>
<td>90.00</td>
<td>4.96</td>
<td>13.38</td>
<td>11.49</td>
<td>22.49</td>
<td>52.64</td>
</tr>
</tbody>
</table>

* CEC for kaolinite, montmorillonite and vermiculite = 3-15, 60-150, 100-150 cmol/kg (Wilson, 1994).
** AEC for kaolinite, montmorillonite and vermiculite = 7-20, 20-30, 4 cmol/kg (Wilson, 1994).

δ pH was determined by pH meter

Table 2: Mineralogical composition of the studied clay sediments

<table>
<thead>
<tr>
<th>Locality</th>
<th>Kaol. %</th>
<th>Mont. %</th>
<th>Illite. %</th>
<th>Verm. %</th>
<th>Gyp. %</th>
<th>K₂CO₃ %</th>
<th>Feld. %</th>
<th>Qz %</th>
<th>others %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kalabsha kaolinite</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Abu Tartur-bentonite</td>
<td>5</td>
<td>56</td>
<td>9</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>El Hafafit vermiculite</td>
<td>-</td>
<td>-</td>
<td>57</td>
<td>-</td>
<td>7</td>
<td>6</td>
<td>13</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: The constans of Langmuir equations and R² of the adsorption of vanadium in various adsorbents.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorption Maxima (B)</th>
<th>Binding energy (b)</th>
<th>Equations</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite Kalabsha</td>
<td>5.55</td>
<td>4.8</td>
<td>Y = 0.1862X + 0.0373</td>
<td>0.98</td>
</tr>
<tr>
<td>Bentonite - Abu Tartur</td>
<td>13.15</td>
<td>0.82</td>
<td>Y = 0.0769X + 0.0926</td>
<td>0.94</td>
</tr>
<tr>
<td>Vermiculite Hafafite</td>
<td>11.23</td>
<td>0.63</td>
<td>Y = 0.0892X + 0.1424</td>
<td>0.94</td>
</tr>
</tbody>
</table>

* R² = Binding factor

Fig. 1: Amount adsorbed of Vanadium on the different Adsorbents

Fig. 2: Langmuir adsorption isotherm of Vanadium on the different adsorbents.

The decrease in the V adsorption may be interpreted as due to the competition of the Cl ions to the (VO₃)²⁻ ions till the concentration of KCl reached 0.075M where the V adsorption efficiency tends to increase. However, the increase in V adsorption may be attributed to the release of some Cl⁻ ions after its adsorption and the engagement of the clay exchangeable sites by (VO₃)²⁻ ions.

5- Clay pretreatment: Table (5) represents the V adsorption efficiency of Kalabsha kaolinite, Abu-Tartur bentonite and El-Hafafit vermiculite compared to the V adsorption efficiency of the untreated clay samples. From this table it is clear that:
Table 4: Effect of Solid/Liquid ratio upon V adsorption by clay samples.

<table>
<thead>
<tr>
<th>S/L Ratio</th>
<th>Kaolinite Kalabsha</th>
<th>Abu Tartur Bentonite</th>
<th>Vermiculite El-Hafafit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:100</td>
<td>57.1</td>
<td>60.1</td>
<td>66.6</td>
</tr>
<tr>
<td>1:40</td>
<td>49</td>
<td>51</td>
<td>57</td>
</tr>
<tr>
<td>1:20</td>
<td>39</td>
<td>43</td>
<td>45.1</td>
</tr>
<tr>
<td>1:13.5</td>
<td>37</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>1:5</td>
<td>27.4</td>
<td>10.7</td>
<td>31.9</td>
</tr>
<tr>
<td>1:2</td>
<td>26.8</td>
<td>4.2</td>
<td>29.1</td>
</tr>
</tbody>
</table>

The pretreatment of the clay samples by roasting, acidic or alkaline treatments increased the V adsorption efficiency from 42.9 to 86.3%, 38.88 to 85.6% and 33.40 to 84.0% for kaolinite, bentonite and vermiculite respectively.

The V adsorption efficiency was higher in roasting treatment followed by acidic treatment, NaOH treatment and the untreated samples.

The higher V adsorption efficiency of the roasted clay samples (at 1000°C) may be attributed to the changes occurred in the clay mineral structure due to the treatment and releasing of some oxides. Additional Al-OH and Si-OH bonds which formed will also act as cation exchange sites and this lead to increase the exchangeability properties of the sediments\[12\]. On the other hand, the relatively high V adsorption efficiency of the acidic treatment is more than alkaline treatment. This may be attributed to the increase of hydrogen ion presence (H\(^+\)) upon to exchangeable sites of the clay minerals. Subsequently, the improvements of the anion exchange capacity of these sediments.

**Vanadium desorption:** Figure (6) represents the cumulative curves of the leached V percentage relative to the initial adsorbed amount. In all cases, the desorbing agent of 0.1M HCl desorbs more pronounced V than the other ones. Also the desorbed amount of V can be arranged as follows: bentonite> vermiculite> kaolinite. These data indicate that V strongly bonded to kaolinite system more than vermiculite more than bentonite. In other words, V on the bentonite easily desorbed than vermiculite and kaolinite. This can be attributed to the higher pH of kaolinite suspension (7.2) compared to (7.00) for vermiculite and (6.44) for bentonite. Jarvis and Jones\[7\] obtained the same result, which confirms the data of this work. Also the cation exchange sites developed at pH values higher than 6.0 due to the ionization of COOH groups may contribute more to the strong adsorption of the metal ions and therefore will be more difficulty desorbed\[11\].

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**References:**

\[1\] Jarvis and Jones, 1978.

\[2\] Romanik, 1980.

\[3\] Cakmak and Buekens, 1983.

\[4\] Zhu and Zhang, 1990.

\[5\] Khan and Khan, 1994.

\[6\] Stumm and Morgan, 1996.

\[7\] Jarvis and Jones, 1978.

\[8\] Romanik, 1980.

\[9\] Cakmak and Buekens, 1983.

\[10\] Zhu and Zhang, 1990.


\[12\] Stumm and Morgan, 1996.
Table 5: Effect of clay pretreatment on V adsorption efficiency.

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>Kalabsha kaolinite</th>
<th>Abu Tartur bentonite</th>
<th>El-Hafafit vermiculite</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>42.90</td>
<td>38.88</td>
<td>33.40</td>
</tr>
<tr>
<td>Roasting 1000ºC, 2hrs</td>
<td>86.30</td>
<td>85.60</td>
<td>84.00</td>
</tr>
<tr>
<td>HCl (conc. 50%)</td>
<td>51.47</td>
<td>48.90</td>
<td>42.76</td>
</tr>
<tr>
<td>NaOH (conc. 20%)</td>
<td>49.76</td>
<td>47.10</td>
<td>40.76</td>
</tr>
</tbody>
</table>

Fig. 5: Effect of KCl concentration upon V adsorption efficiency percentage.

On the other hand, there are some differences between the obtained desorption results and the calculated binding energy (b), where the calculated binding energy attained 4.8, 0.82 and 0.63 for kaolinite, bentonite and vermiculite, respectively. It is clear that desorption of V from bentonite is easier than vermiculite although the binding energy follows the opposite manner. Swelling and contraction of montmorillonite structure dominated in the bentonite sediments may help the V to desorb through affecting the distance between the ions and consequently affect on the attractive forces.

Mineralogical Changes after Adsorption and Desorption:

The kaolinite, bentonite and vermiculite samples were subjected to IR analysis after V adsorption as well as after V desorption by H2O, 50% HCl and 20% NaOH. The additional reported vibrational frequencies obtained from this analysis are tabulated in Table (6). From the obtained data, it is clear that:

Kalabsha kaolinite: After adsorption of (NH4)VO4 upon the Kalabsha kaolinite sample gained three vibrational frequencies at 1829.1, 1702.0 and 1542.7 cm⁻¹. The first may be attributed to Co-OOH while the second is attributed to either (NH4) or to OH group of the Ca3(H2SiO5)(OH)2 H2O[3]. The vibration frequency at 1542.7 cm⁻¹ can be attributed to OH group of the Mn OOH. In addition, the vibrational frequency of H2O bonding at 1633.2 cm⁻¹ was shifted to 1653.0 cm⁻¹ due to the equilibration of the kaolinite with the ammonium metavanadate.

After performing the desorption experiment with H2O the vibrational frequency at 1702.0 cm⁻¹ disappeared due to the easy wash of (NH4) by water. Also, the vibrational frequency at 1653.0 cm⁻¹ was returned to its normal position.

After conducting the desorption experiment by HCl, the OH vibrational frequency of the vanadium compounds at 1633.2 cm⁻¹ was disappeared (washed). While after applying the desorption experiment by 0.1M NaOH, the vibrational frequency at 1828 cm⁻¹ was disappeared due to the utilization of strong desorbing agent. On the other hand, the additional vibrational frequency at 3455.9 cm⁻¹ may be explained on the basis that when applying NaOH solution for desorption, the pH of the solution is raised and a vanadium complex may be precipitated. Thus, it may cause the presence of the vibrational frequency of the vanadium compounds at 3455.9 cm⁻¹[3].

Abu-Tartur bentonite: After performing V adsorption on Abu Tartur bentonite, additional five vibrational frequencies appeared at 2926.5, 2855.0, 2340.2, 915.1 and 692.6 cm⁻¹. The first three vibrational frequencies are attributed to the clay hydrolysis by the aqueous adsorbing solution (H2O-stretching and O-H group) while the other two vibrational frequencies are attributed to vanadium compound [Mg3(VO4)2]³⁺.

After performing the desorption experiment by H2O the vibrational frequencies at 2855.0 and 915.1 cm⁻¹ were disappeared. This may be due washing of the surface adsorbed vanadium compound upon the bentonite sample. While the V compounds at 692.6 cm⁻¹ are not desorbed under the used treatment.
Fig. 6: Desorption data of V loaded clay samples by different solution

When conducting the desorption experiment by HCl, the vibrational frequency at the 2855 cm\(^{-1}\) of the OH group was disappeared as well as the vibrational frequency of V compounds at 915.2 cm\(^{-1}\) due to its easy leachate. On the other hand, the vibrational frequencies at 2928.8 and 1544.0 cm\(^{-1}\) were disappeared. Only one vibrational frequency of V compounds still present at 693.2 cm\(^{-1}\) which may indicate that at least some of the adsorbed V resists the desorption by HCl.

On trying V desorption using NaOH, and according to the increase in the pH (above 8) to the alkalinity range, clay hydrolysis occurred. This was demonstrated in the appearance of the vibrational frequency at 2924.1 cm\(^{-1}\) which may indicate that at least some of the adsorbed V resists the desorption by HCl.

When performing the V desorption by NaOH, the OH vibrational frequency at 2926.8 cm\(^{-1}\) return to appear. In addition, the sharp IR peak at 446 - 444.6 cm\(^{-1}\) could not be leached after its adsorption. This may be due to the entering of V to the vermiculite lattice.

From the above discussion, it can be concluded that the nondesorbed vanadium by H\(_2\)O, HCl and NaOH may be considered as vanadium resource on the clay sediment and needs more sophisticated desorption methods.

Conclusions: Vanadium can be sorbed upon Kalabsha kaolinite, Abu Tartur bentonite and El-Hafafit vermiculite. The amount of adsorbed vanadium increases with the increase of V concentration, pH and equilibration time (till three hours). It decreases with the increase of the solid/liquid ratio. Pretreatment of the clay sediments by roasting, HCl and NaOH proved to increase the V adsorption efficiency. Release of V from the loaded clay sediments was possible to different extents depending upon clay type and desorbing agent. The IR analyses proved that considerable mineralogical changes occurred after V adsorption and desorption. This study may

El-Hafafit vermiculite: The V adsorption upon El Hafafit vermiculite has been demonstrated in the appearance of the additional frequencies at 2343.9 and 1424.3 cm\(^{-1}\) that can be attributed to OH stretching and H\(_2\)O bond\(^{-1}\). In addition, a vibrational frequency at 1544.0 cm\(^{-1}\) has appeared which may be attributed to MnOOH. The evidence of V adsorption is clear from the appearance of the vibrational frequency at 753.5 cm\(^{-1}\). Also, the vibrational frequency at 457.9 cm\(^{-1}\) became sharp due to V adsorption. On the other hand, the vibrational frequency at 2924.1 cm\(^{-1}\) was disappeared mainly to the dissolution of some minor constituents of the vermiculite.

In a trial to desorb V from the V loaded vermiculite sample by tap water, the OH vibrational frequency at 1424.3 cm\(^{-1}\) as well as the V compounds vibrational frequency at 753.5 cm\(^{-1}\) were disappeared due to the easy wash of the surfaces those adsorbed V. On the other hand, when desorbing the V by HCl, a vibrational frequency at 797.3 cm\(^{-1}\) appeared. This IR peak attributed to the V compounds; however, it resists the leaching by HCl.

When performing the V desorption by NaOH, the OH vibrational frequency at 2926.8 cm\(^{-1}\) return to appear. In addition, the sharp IR peak at 446 - 444.6 cm\(^{-1}\) could not be leached after its adsorption. This may be due to the entering of V to the vermiculite lattice.

From the above discussion, it can be concluded that the nondesorbed vanadium by H\(_2\)O, HCl and NaOH may be considered as vanadium resources on the clay sediment and needs more sophisticated desorption methods.
contribute to V recovery from clay sediments, which are characterized by their high V content. The study also proved that the clay sediments could be utilized as suitable geological barrier for immobilizing elements involved in the nuclear industry waste disposal.

REFERENCES