Extraction of Boron and Vanadium from Abu Hamata Alkali Leach Solution by Using Ion Exchange Resin

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Abstract-- This work is concerned with the recovery of boron and vanadium from an ore residue originally collected from Abu Hamata mineralized sandy claystone ore material. The latter was previously treated to selectively extract its uranium and lanthanides contents through applying H_2SO_4 acid agitation leaching step. These two metal values which were left behind in the spent residue was found to assay 0.123 and 0.186 % for boron and vanadium respectively. The present work involves alkali roasting of the spent residue with NaOH at the obtained optimum roasting conditions. This was followed by water leaching of the roasted matrix to bring out the dissolved boron and vanadium. The latter's were then extracted via Amberlite IRA_{743} anion exchange resin. Pure products of H_3BO_3 acid and V_2O_5 were obtained. A tentative technical flowsheet was proposed and described.

Keywords: Extraction, Boric acid, Vanadium oxide, Ion exchange resins, Abu Hamata sandy claystone

I. INTRODUCTION

Abu Hamata sandy claystone rock facies of Um Bogma Formation, which occurs at Abu Zeneima area, Southwestern Sinai, Egypt, is considered as one of the most important occurrences of U mineralization beside the associated economic metal values e.g. Ln, B, V, Zn, Cu,…. etc [1]. Either uranium and lanthanides or boron and vanadium were found in relatively reasonable grades, 0.183, 0.137, 0.11 and o.175 % respectively. It is worthy to mentioned herein that, the authors have studied in detail the mineralogical and chemical composition of the raw ore material as well as the optimum conditions for selective recovery of uranium and lanthanides through applying H_2SO_4 acid agitation leaching process. These conditions involved 5% H_2SO_4 acid concentration, S/L mixing ratio of 1/2, leaching time of 1h and leaching temperature of 75^0C. In addition, The obtained results from the mineralogical study revealed that the study ore material consists mainly of montmorillonite as the main clay mineral $(K,Ca)Al_2SiO_4$ together with quartiz (SiO_2), hematite (Fe_2O_3) and the secondary uranium mineral renardite $Pb(UO_2)_2(PO_4)_2.8H_2O]$. On the other hand, the study ore material shows no specific minerals for either lanthanides, boron or vanadium. This is probably due to their adsorption upon clay mineral of the study ore material.

With respect to boron and vanadium recovery studies, several authors have been studied the recovery of both boron and vanadium from their leach liquors via anion exchange resins [2-9].

In this context, the ore material left after uranium and lanthanides can be probably processed for the dissolution and recovery of the other contained metal values namely; boron and vanadium. The latter would be greatly facilitated after U and Ln recovery. However, the present work aims to prepare pure H_3BO_3 and V_2O_5.

II. EXPERIMENTAL

A .Materials

The bead-type ion exchange resin, Amberlite IRA_{743} (Rohman and Hass ion exchange resins) is a macroporous styrenic resin with methyl glucamine functionality. It is commonly known that boron and vanadium are retained, borate and vanadate ions are complexed by two sorbitol groups, and a proton is retained by a tertiary amine site, which behaves as a weakly basic anion exchanger. The characteristics of Amberlite IRA_{743} are listed in table (1). The chemicals used during the experiments and analysis were reagent-grade Merck products.

Table(1): Characteristics of ion exchange resin Amberlite IRA_{743}

Parameter	Amberlite IRA_{743}
Matrix	Macroporous polystyrene
Functional group	N-Methylglucamine
Physical form	Beige-coloured beads
Ionic form as shipped	Free Base (FB)
Total capacity	0.8eq/L
Moisture holding capacity	48 to 54 % (FB form)
Shipping weight	700 g/L (43.7 lbs/ft3)
Particle size	
Harmonic mean size	0.500 – 0.700 mm
Uniformity coefficient	1.6
< 0.300 mm	1 % max

B. Alkali roasting of the ore residue

The alkali roasting process was conducted by mixing solid NaOH with the spent residue at slightly high temperature for different periods of times. After that the cooled roasted matrix was then undergoes water leaching to dissolve its boron and vanadium contents. All the experimental roasting procedures were conducted by using constant weight (10g) of the dried ore residue. While boron and vanadium in all the alkaline solutions were analyzed by using the Flame Atomic Absorption Spectrophotometer (FAAS), Unicam 969, England at their proper wave lengths.

C. Extraction of boron and vanadium from the alkaline leach liquor

In the present work, trials to recover boron selectively from accompanying vanadium in the pre-processed ore material under consideration have been performed during extraction process. In this respect, alkali roasting process was first accomplished upon 200 g of the ore residue by using pellets of NaOH in a sample/ reagent (S/R) weight ratio of 1/1 at roasting temperature of 140 °C for 1.5 h. The roasted matrix was then left to cool and leached with distilled water for 0.5 h at room temperature to bring out the dissolved boron and vanadium metal values.

On the other hand, with respect to boron and vanadium recovery, the prepared alkaline solution (pH >12) was firstly treated with drops of conc. H_2SO_4 to precipitate its content of the interfering SiO_2 from one hand, and to adjust its pH value to pH 8.5 which is very suitable for loading of boron and vanadium, from the other hand. Moreover, the precipitate of Si-gel should be washed with 1% H_2SO_4 solution to bring out any loaded boron or vanadium again to the alkaline solution. After filtration, the filtrate and the washing solution were closed up to volume of 2L. The latter was then directed to the ion exchange unit which consists of a column of 100cm in height and 0.7cm in diameter packed with 65ml of wet settled resin (wsr) Amberlite IRA_{743} in its hydroxide form. The applied flow rate was 2.5 ml/min. The collected effluent solutions of 100ml bed volumes was analyzed for both boron and vanadium and their extraction efficiencies were calculated.

The saturated loaded resin was subjected to the elution process to regenerate both of the loaded boron and vanadium. The former was firstly regenerated by using 400 ml of hot distilled H_2O at a working flow rate of 1ml/min while the latter was then regenerated by using 100 ml of 4% H_2SO_4 at an applied flow rate of 1.5 ml/min. Fractions of 40ml bed volumes were collected and its boron content was estimated to determine the relative elution efficiency of boron. With respect to vanadium, 10 ml bed volume fractions were collected to estimate vanadium elution efficiency. The eluate rich boron was subjected to evaporation to prepare pure H_3BO_3 while pure V_2O_5 was precipitated from vanadium rich eluate solution at pH value 2.5.

III. RESULTS & DISCUSSION

As mentioned previously, the present feed sample is an ore residue originally collected from Abu Hamata sandy claystone ore material. The latter was previously treated to selectively extract uranium and lanthanides through applying H_2SO_4 agitation leaching step. This ore residue was thus upgraded and found to assay 0.123% B and 0.186% V. However, due to the vital importance of both boron and vanadium, it was decided to study their recovery by using anion exchange resin Amberlite IRA_{743} from the obtained alkali leach liquor of the study ore residue.

A. Alkali roasting of the ore residue

The spent ore residue was firstly prepared for chemical analysis to recalculated its content of the upgraded boron and vanadium metal values after removing uranium and lanthanides together with other deleterious constituents e.g. Mg, Ca, Na, K,…etc. From the latter, boron was found to assay 0.123% while vanadium assaying 0.186%. Several

alkaline roasting parameters such as: sample/NaOH mixed weight ratios, roasting time and roasting temperature were studied. The expected reactions of the alkaline leaching process were illustrated in the following equations:

$$B_2O_3 + 8NaOH \rightarrow 2Na\,B(OH)_4 + H_2O + \quad (1)$$

$$2VO_2^+ + 4NaOH \rightarrow Na_4V_2O_7 + H_2O + H^+ \quad (2)$$

$$V_2O_5 + 2\,NaOH \rightarrow 2\,NaVO_3 + H_2O \quad (3)$$

$$VO_2^+ + 3NaOH \rightarrow Na_3VO_4 + H_2O + H^+ \quad (4)$$

1. Effect of ore residue / NaOH weight ratios (S/ R):

The effect of ore residue /NaOH weight ratios upon the dissolution efficiencies of boron and vanadium were studied by mixing different ratios in the range between 4/1 to 1/2. The mixed material was roasted in a porcelain crucible at 140 °C for 1 h. The roasted matrix was left to cool and then subjected to water leaching for 0.5 h at room temperature. After filtration and washing the total volume was closed to 100 ml. Both of boron and vanadium were determined and their dissolution efficiencies were calculated.

The obtained data table (2) emphasized that the dissolution efficiencies of the metals of interest increased with decreasing the ore /NaOH ratio from 4/1 to 1/1, where for boron it is increased from 57 to 89.4% and for vanadium it is increased from 51.2 to 90.1%. The ore/NaOH ratio less than 1/1 decreases the dissolution efficiency of boron while increasing that of vanadium. Therefore, the mixed ratio of 1/1 was found to be suitable for applying the other roasting parameters.

Table (2): Effect of Ore/NaOH weight ratio upon dissolution efficiencies of boron and vanadium.

Ore/NaOH Wt. ratio	Dissolution efficiency (%)	
	B	V
4/1	57.0	51.2
3/1	59.4	61.7
2/1	87.9	70.8
1/1	89.2	90.1
1/2	75.0	94.0

2. Effect of roasting temperature

The effect of roasting temperature upon the dissolution efficiencies of both boron and vanadium was studied in the temperature range from 90 to 300 °C. The applied ore/NaOH weight ratio was kept at 1/1 and 1h as roasting time. Data in table (3) shows that, by increasing the roasting temperature from 90 to 140°C the dissolution efficiencies of boron and vanadium show a significant improvement. However, with respect to boron the dissolution efficiency increased to its maximum value of 89.2% at 140°C. Further increase in roasting temperature to 300 °C shows an opposite effect. This might be due to the formation of insoluble borosilicate compounds at high temperature which might be complicate the subsequent recovery [10]. This emphasized the association of boron with clay minerals. On the other hand, with respect to vanadium, it is almost dissolute at 200 °C while at the temperature of 170 °C it is slightly improved to 94.6%. Therefore, the roasting temperature at 140 °C would represent the optimum one for dissolution of both boron and vanadium.

Table (3): Effect of roasting temperature upon the dissolution efficiencies of boron and vanadium.

Temperature (ºC)	Dissolution efficiency (%)	
	B	V
90	27	78.5
140	89.2	90.1
170	85.6	94.6
200	79.8	100
300	45.7	100

3. Effect of roasting time

The effect of roasting time upon the dissolution efficiencies of boron and vanadium from the study ore residue was studied in the range between 0.5h to 3h. The other roasting factors were fixed at roasting temperature of 140 ^{0}C and ore/NaOH weight ratio of 1/1. The obtained data represented in table (4) emphasized that, the roasting time of 1.5h can be considered as the more suitable to attain satisfactory dissolution efficiencies for both of boron and vanadium which achieved 94.1 and 97% respectively.

Table (4):Effect of roasting time upon the dissolution efficiencies of boron and vanadium.   .

Time (h)	Dissolution efficiency (%)	
	B	V
0.5	71.2	85.0
1	89.2	90.1
1.5	94.1	97.0
2	94.5	98.4
3	90.1	95.1

In the light of the foregoing mentioned alkali roasting process of Abu Hamata ore residue, it can be concluded that, the optimum roasting conditions required for dissolving 94.1% of boron and 97 % of vanadium are as following:

Ore/NaOH wt. ratio : 1/1

Roasting time : 1.5 h

Roasting temperature : 140 ^{0}C

These determined optimal roasting conditions are used to prepare the pregnant leach liquor for subsequent recovery of both boron and vanadium. Accordingly, 200 g of the ore residue was used to yield 2 liters of alkaline leach liquor. The latter was found to assay 0.116 g/l of B, 0.18 g/l of V, 10.2 g/l of Si and pH value of > 12 .

B. Extraction of boron and vanadium from the alkaline leach liquor

In this context, Amberlite IRA$_{743}$ anion exchange resin was used. The latter has a macro porous poly-styrene matrix, on which N-methyl glutamine functional groups (R-N(CH$_3$)-C$_6$H$_8$(OH)$_5$) are attached as represented by Fig. (1).
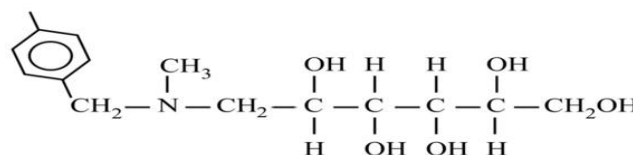
Fig.1. A scheme of building chemical structure of Amberlite IRA$_{743}$

In the alkaline solution, both of boron and vanadium were found in the anion species borates $[B(OH)_4]^-$ and vanadates (VO_3^-) at pH value over 8 [6]. The process of extraction depends upon the substitution reaction between the borate $[B(OH)_4]^-$, vanadates (VO_3^-) anions and anionic resin sites. Figs. (2, 3) describe the mechanism of the uptake of both boron and vanadium from the aqueous solutions. The uptake of boron as borate anion B $(OH)_4^-$ and vanadium as vanadates anion $(VO_3)^-$ is a curious mechanism, where it involves protonation of the amine, de-protonation of the ploy sugar tail. Boric acid dissociate in distilled H$_2$O to form the borate anion. While the protonation process of the amino group will be taken place as illustrated in equations below.
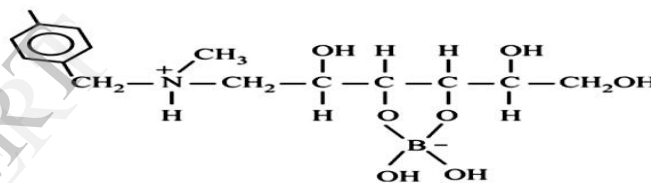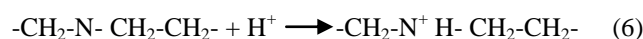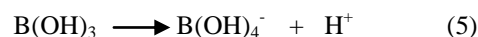
$$B(OH)_3 \longrightarrow B(OH)_4^- + H^+ \qquad (5)$$

$$-CH_2-N-\ CH_2-CH_2- + H^+ \longrightarrow -CH_2-N^+H-\ CH_2-CH_2- \qquad (6)$$

Fig. 2. A scheme of boron uptake mechanism from the aqueous solutions.

With respect to vanadium uptake upon the resin sites, VO$_3^-$ species has been adsorbed through electrostatic attraction and complexed with N$^+$ and OH groups of the resin sites.
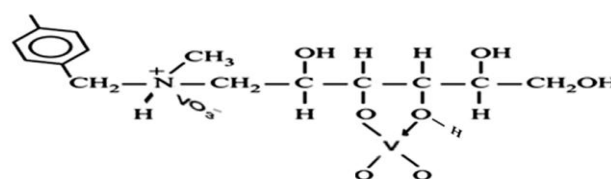

Fig. 3. A scheme of vanadium uptake mechanism from the aqueous solutions.

1. Si-gel precipitation before Loading of boron and vanadium

Before applying the loading process of boron and vanadium upon the resin, it is important to remove silica gel as by-product from the prepared alkaline leach liquor. The purpose is to avoid coating of the exchange sites of the resin. This was carried out by adjusting the pH value of the prepared alkali leach liquor via conc. H$_2$SO$_4$ to be 8.5. The precipitated silica in the form of SiO$_2$-gel should be washed with dilute H$_2$SO$_4$ (1%) during filtration to avoid the loss of any dissolved boron and vanadium by adsorption on its outer surface. The precipitate of SiO$_2$-gel was then ignited at 850$^°$C for 1h and left to cool and then washed. After dryness, SiO$_2$ was recovered with recovery efficiency up to 99%. The produced

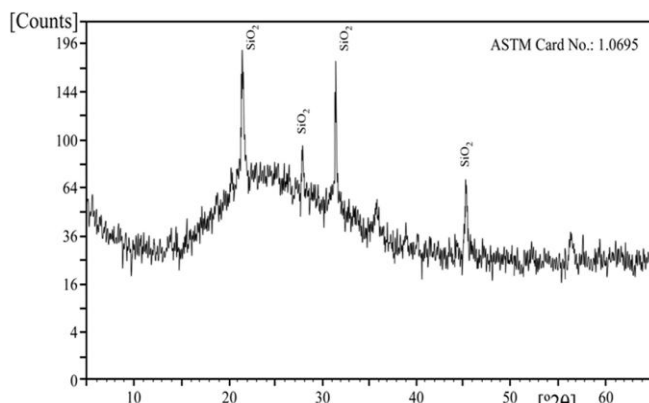SiO_2 was identified by means of XRD technique as shown in Fig. (4).

Fig. 4. XRD pattern for the identification of the produced SiO_2.

It is important to mentioned herein that, the chosen pH value of 8.5 represent the optimum value for uptake of both boron and vanadium [3, 11-12]. At pH values higher than 9, boron extraction efficiency decreased because an amount of other interfering species especially the excess $(OH)^-$ could be retained by resin [13]. Also, at pH values below 7, H_3BO_3 is the dominant species which has a low extraction efficiency due to low electrical activity [14].

2. Loading process of both boron and vanadium

In the present work, 2 Liters of the prepared leach liquor was passed through the resin column packed with 65 ml wsr at a working flow rate of 2.5 ml/min. The obtained effluents were collected every 100 ml for boron and vanadium analyses. From the obtained results (Fig.5), it is evident that, the amount of loaded boron upon the resin was 0.203g realizing high loading efficiency of 87.5%. While the amount of the loaded vanadium was 0.255g with the loading efficiency of 70.46%. The calculated capacity of the working resin for both of both boron and vanadium represented about 79%. This relatively low capacities may be due to the competition of some anions in the resin sites especially OH^- ions. Finally, the saturated resin was rapidly washed with distilled H_2O to remove the remains of loaded ions before applying the elution process.
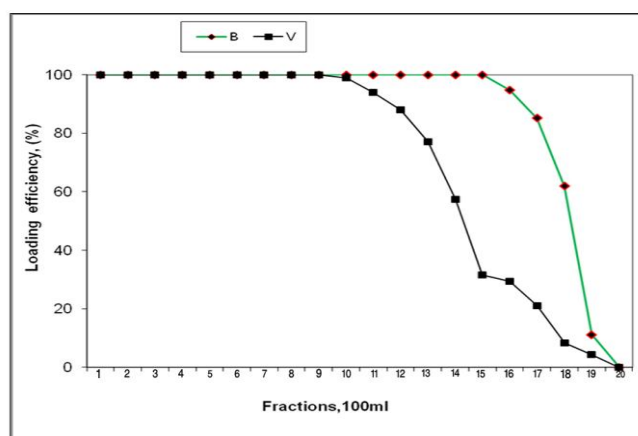

Fig. 5. loading curve of both boron and vanadium from the treated alkaline solution.

3. Elution process of the loaded boron and vanadium

Elution process is not only used to regenerate the loaded resin but also to prepared a concentrated solutions suitable for the subsequent precipitation process to prepare the final element products. Different elute solutions suggest good elution efficiencies for both of boron and vanadium e.g. dilute HCl, H_2SO_4 and NaOH. However, any of these eluants can be used for the elution of the loaded elements of interest.

In the present work, to avoid the problem of interfering the two elements of interest during elution, the loaded Amberlite IRA_{743} was firstly subjected to selective elution process of boron by using hot H_2O to regenerate $B(OH)_4^-$ anion species depending upon the high solubility of borate ions in distilled water [15]. This was followed by vanadium elution by using 4% H_2SO_4 acid.

3.1. Elution of boron and preparation of pure boric acid (H_3BO_3)

Accordingly, the loaded resin when treated with hot H_2O or very weak acid solution is being regenerated to its original structure (Fig. 6), as illustrated by the following:
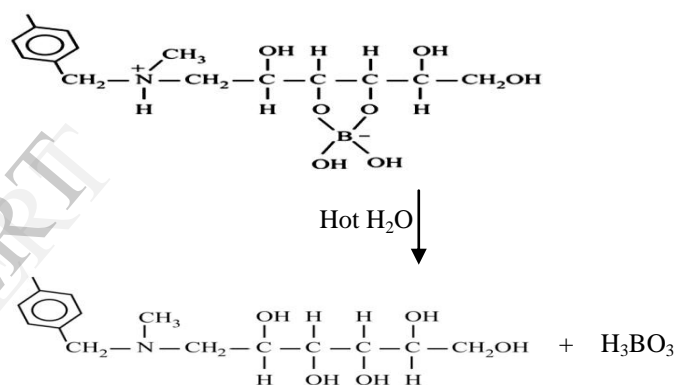

Fig. 6. A scheme of boron elution mechanism from the loaded resin

For this purpose, suitable volume of 400ml hot H_2O was used at working flow rate of 1m/min to regenerate almost loaded boron (95.3%). The eluate solution fractions each of 40ml bed volumes were collected to determine their boron content and to calculate the corresponding elution efficiency as plotted in Fig.(7).
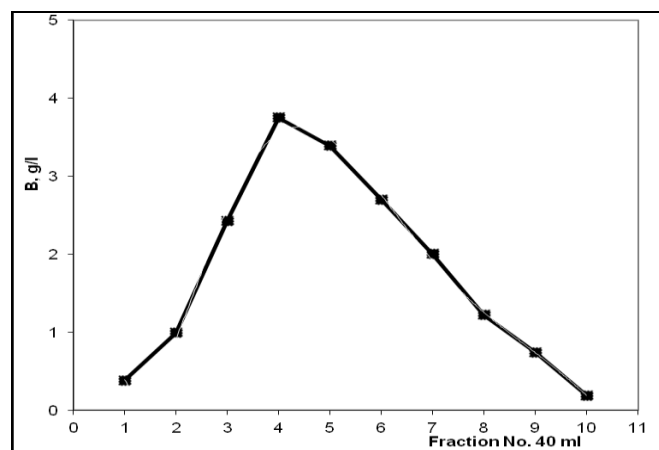

Fig. 7. Elution curve of boron from the loaded Amberlite IRA_{743}

The recovery of boron in the form of boric acid as pure crystals from boron eluate concentrated solution seems possible by partial evaporation. About 400 ml of the eluate solution contains 0.193 g boron was used for the preparation of 1.08 g boric acid (H_3BO_3). The obtained product has purity reached about 96.9% together with some trace of NaCl and V.

For further purification, the product was re-dissolved in distilled H_2O and then directed to the anion exchange unit. After loading and elution processes, the eluate rich boron solution was re-crystallized by evaporation to produce high pure H_3BO_3 acid as shown in Fig.(8).
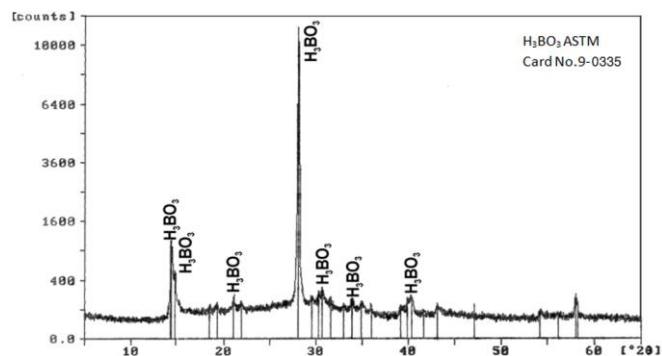

Fig. 8. XRD pattern of pure boric acid (H_3BO_3).

3.2. Elution process of vanadium and preparation of pure red cake (V_2O_5)

After eluting of almost boron content from the loaded Amberlite IRA_{743} anion exchange resin, vanadium elution process takes place. For this purpose 100 ml of $4\%H_2SO_4$ acid solution at flow rate of 1.5 ml/min was used. Fig. (9) shows the expected mechanism elution from the loaded Amberlite IRA_{743} anion exchange resin.
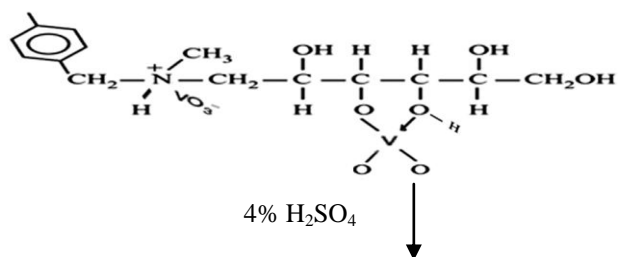

Fig. 9. A scheme of vanadium elution mechanism from the loaded resin.

The eluate solutions each of 10ml bed volumes were collected to determine their vanadium content. From the latter, it was found that, vanadium was eluted with elution efficiency of 96.8%.The corresponding elution results were plotted in Fig. (10).
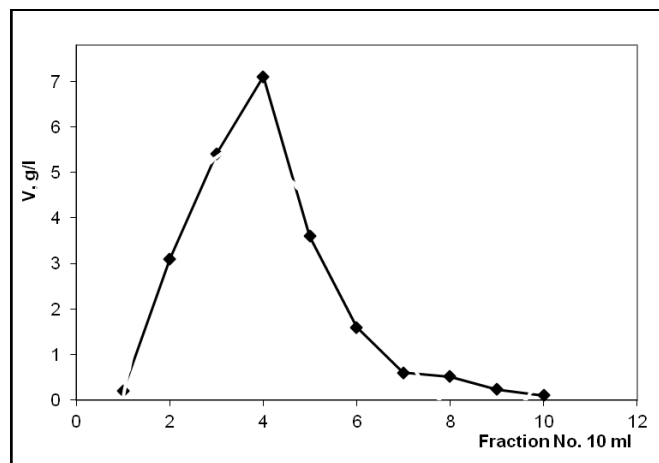

Fig. 10. Elution curve of vanadium from the loaded Amberlite IRA $_{743}$.

The eluate sulfate solution which assays 2.4 g/l of vanadium was used to prepare the final vanadium product. However, 100ml of vanadium rich solution was adjusted to pH 2.5 with NH_4OH solution and then oxidized by the addition of 0.25g $KClO_3$. Complete precipitation of vanadium (98.2%) as a red cake (V_2O_5) was obtained at 75 ^{0}C after 2h stirring time. The product was then filtrate and washed with distilled water to remove the associated salts. The obtained red cake was then dried in the oven at 120 ^{0}C for a suitable period of time. The latter was identified by means of EDX analysis as shown in Fig. (11). The chemical analysis proved that the purity of the final product (V_2O_5)was 95.9%.
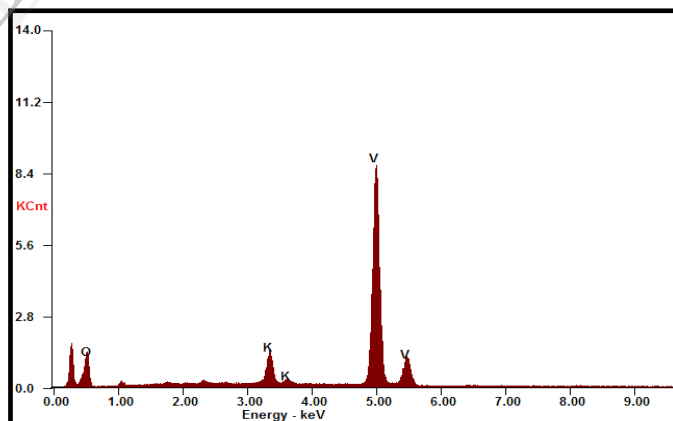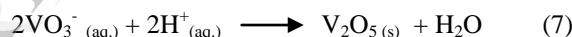
$$2VO_3^-{}_{(aq.)} + 2H^+{}_{(aq.)} \longrightarrow V_2O_{5\,(s)} + H_2O \qquad (7)$$

Fig. 11. EDX chart for the identification of pure red cake,(V_2O_5).

IV. CONCLUSION

From the forgoing study, the following general conclusion can be summarized:

1- A procedure for separating the loaded boron from the accompanying vanadium upon Amberlite IRA_{743} anion exchange resin can be achieved by using hot H_2O as an eluant for boron and 4 % H_2SO_4 acid for vanadium.

2- A procedure to prepare pure Si-gel as by-product was achieved by adjusting pH of the pregnant alkali solution to 8.5. The latter was found to be the suitable pH for boron and vanadium loading upon the Amberlite IRA_{743} resin.

3-Finally, a proposal technical flowsheet for processing Abu Hamata ore residue to obtain pure H_3BO_3 and V_2O_5 was designed Fig.(12).
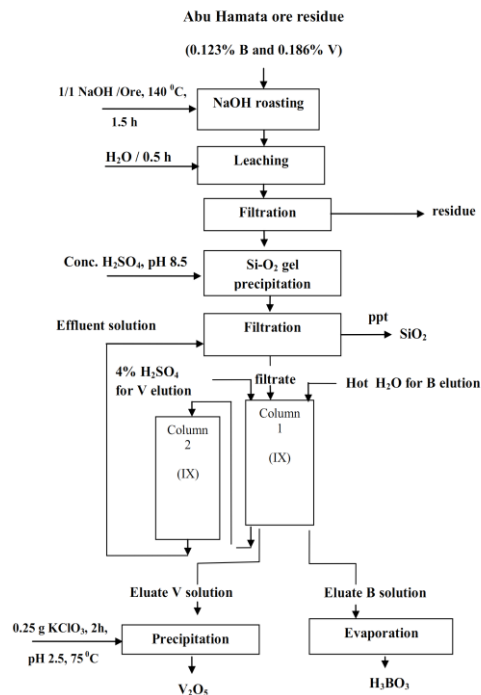

Fig. (12): Proposed technical flowsheet for the processing of Abu Hamata ore residue to produce pure H_3BO_3, V_2O_5 and SiO_2.

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