

Extraction study of Vanadium from Pre-Processed Gibbsite- bearing shale, Abu Thor area, Southwestern Sinai, Egypt, by using Amberlite IRA₇₄₃ anion exchange resin,

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Abstract

This work is concerned with study the affecting parameters on the recovery of V from pre-processed gibbsite bearing shale sample which assays 0.045% of V which obtained from Abu Thor area, Southwestern Sinai, Egypt. The original sample (0.05 % V) was previously treated to selectively extraction of Cu, Cd and U through applying H₂SO₄ acid agitation leaching. The present study work involves alkaline dissolution of the sample residue with NaOH solution at the obtained optimum conditions. However ion exchange process was applied by using anion exchange resin, Amberlite IRA₇₄₃.

About 97.25% of the extracted V was already regenerated by using 4% H₂SO₄. Not less than 98.2% of V was precipitated as hydrated V₂O₅ by using NH₄OH solution via strongly oxidation by the addition of 0.25g KClO₃ at 75 °C with continuous stirring for 2h. The latter was dried in the oven at 120 °C to prepare the final V product V₂O₅ (red cake). The overall process was designed in a technical flowsheet.

Keywords: *Extraction, Vanadium pentoxide, Ion exchange resin, gibbsite bearing shale.*

1-Introduction

Gibbsite bearing shale of middle member of Um Bogma Formation, which occurs at Abu Thor area, southwestern Sinai, Egypt, is one of the most important occurrences of low grade U beside the associated economic metal values e.g. Cd , Cu and V. U, Cd, Cu and V were found in low grades, 0.04, 0.014, 0.5 and 0.05 %, respectively. It is worthy to mention herein that, the authors have been applied acidic agitation leaching for recovering of Cu, Cd and U. The performed optimum conditions were acid concentration of 25% H₂SO₄, S/L mixing ratio of 1/3, leaching time of 2h and leaching temperature of 75 °C. On the other hand, the residual material left after carrying out the former acidic leaching would be alkaline processed for recovering its V content which assays 0.045%, **Abd El Wahab et al.**(2017).

Acidic leaching of V with H₂SO₄ from different ore materials has been already performed in commercial leaching procedures. **Haoran et al (2008)** studied the recovery of V from V bearing -clay minerals. The dissolved V was then precipitated with NH₄Cl solution after removing the present impurities by precipitation with NaOH solution. Also, **Zhang et al (2011)** leached up to 80% of V from the carbonaceous shale by using 8% H₂SiF₆ at 95 °C for 16 h at solid/liquid, (S/L) ratio of 1/1 together with 15% H₂SO₄. But **Chen et al (2010)** used 35% H₂SO₄ solution for dissolving about 95.8% of V from stone coal at a mixed S/L ratio of 1/3 and at temperature of 90 °C. On the other hand, **Mohamed (2011)** was used 15% H₂SO₄ solution at the mixed S/L ratio of 1/10 and leaching time of 3h at 50°C to dissolve 98% of V and 96% of Ni from the carbonate matrix of residual boiler fly ash of the Egyptian Power Stations. The prepared sulfate solution was used to prepare highly pure V₂O₅ (98.2%) and pure NiS by precipitation with H₂S solution at pH 4 and stir ring for 1h at 70°C.

Due to the interfering problems of the associated elements especially heavy metals e.g. Fe, Ni, Co, Mn... acidic leaching process has several disadvantages. Thus, the alkaline leaching method is more promising where the water soluble Na₄V₂O₇ or Na₃VO₄ were produced. These reactions probably occurred as following:

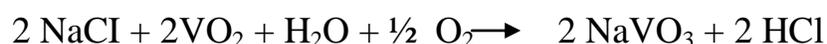
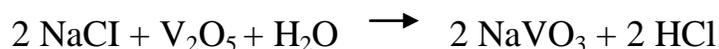


The obtained Na-V salts may contain small amounts of V⁴⁺, which can be easily oxidized to V⁵⁺ by using H₂O₂ solution. The prepared alkaline solution could be neutralized to pH 8 by using H₂SO₄ to precipitate the present Si⁴⁺ and other impurities. Where NH₄Cl or (NH₄)₂SO₄ were used for precipitating NH₄VO₃ as the following equation:



Stas et al (2006) used the alkaline leaching process for the recovery of V and Mo from the fly ashes produced from heavy oil-fired electrical power station. Also **Abbas (2008)** recovered pure V₂O₅ from the spent catalysts via alkaline chemical treatment by using 20 wt.% of NaOH at leaching temperature 85°C and leaching time of 8h. Moreover **Guirguis et al (2014)** have been extracted up to 99% of V content from the residual boiler fly ash of the Egyptian Power Stations by 2M KOH solution and 2% KClO₃ solution at S/L ratio of 1/5 for agitation time of 3h and agitation temperature of 95°C at 600 rpm.

Salt roasting leaching process was devised to extract V in the thirties of the last Century by alkaline leaching method. It is applied to produce water soluble V products and to separate between V and U, **Merritt (1971)**. The salt roasting process was performed by mixing the ground ore (-10mesh) with 6 -10% NaCl and roasting the mixture at a temperature ranging from 825 to 850°C for 1- 2h in a multiple roaster. The prepared matrix is then cooled rapidly and leaching with H₂O to extract the water soluble, NaVO₃. (**Holloway and Etsell, 2002**).were illustrated The leaching process as following equations:



Salt roasting to recover vanadium has been proposed in several studies, [**Hahn et al (1988)**, **Holloway and Etsell (2004)** and **Ming-yu et al (2011)**] using NaCl, Na₂CO₃, NaOH, or Na₂SO₄, Na₂CO₃-NaCl, Na₂CO₃-Na₂SO₄ or Na₂CO₃-KNO₃ mixtures as roasting additives. According to **Puhong et al (2012)** roasted a weight of 25 g of KFe₃(SO₄)₂(OH)₆ and HNaV₆O₁₆·4H₂O with 22.5 g NaOH at 170 °C for 1h. The roasted matrix was then dissolved in H₂O at mixed ratio of 3.3/1 mL/g where a percentage 97% of V was recovered. **Abdella et al (2014)** have been recovered 80% of V from the

alkaline solution of Abu Hamata sandy claystone ore material by using anion exchange resin, Amberlite IRA₇₄₃.

The aim of this work is extraction of V by using anion, thus, the residual left after Cd, Cu and U extraction would be under the alkaline processing used for study the parameters affecting on the recovery of its contained V. The anion exchange resin Amberlite IRA₇₄₃ was then used to extract V which regenerated by using diluted H₂SO₄ after extraction of Cd to obtain the prepared V rich solution which is adjusted to prepare pure product of V₂O₅.

2-Experimental

2.1. Materials

The present study work was conducted by using 500g of the fine ground residual left behind after carrying out the acidic agitation leaching of gibbsite bearing shale sample of Abu Thor area which assays 0.045% of V. Agitation alkaline leaching process by using NaOH solution was performed for dissolution of V which recovered by using anion exchange resin, Amberlite IRA₇₄₃. The element of interest V was analyzed spontaneously in all agitation leaching and extraction experiments by using the flame atomic absorption spectrophotometer, (FAAS), Unicam 969, England, to calculate its dissolution efficiency.

2.2. Optimization of alkaline agitation leaching

All the alkaline agitation leaching procedures were performed by mixing 10g of the present residual sample with NaOH solution. Different effective dissolution parameters such as: NaOH concentrations, solid/liquid (S/L), addition ratio, leaching time and leaching temperature were investigated.

2.3. Preparation of pregnant alkaline solution

The pregnant alkaline leach liquor of the head sample was prepared via leaching a weight of 450g of the latter at the obtained optimum leaching conditions. After filtration and washing with distilled water, the total volume of the prepared alkaline solution was

one liter. The latter was neutralized at pH value ranged between pH 8.5 to pH 9 by using conc. H_2SO_4 which is suitable for vanadate extraction process, **Abdella et al (2014)**. Neutralization process leads to the precipitation of $Si(OH)_4$ which was carefully washed and filtered. The alkaline solution containing low concentration of Si was then direct to the ion exchange resin unit for recovering V.

2.4. Extraction of V

The bead-type anion exchange resin, Amberlite IRA₇₄₃ (*Rohman and Hass company*) is a macro porous styrene resin with methyl glucamine functionality. Vanadate anions (VO_3^-) complexes with a tertiary amine site, which behaves as a weakly basic anion exchanger. The ion exchange unit consists of a column of 50cm in height and 0.7cm in diameter packed with 10mL of wet settled resin (wsr) in its hydroxid form. The collected effluent solutions of 50mL bed volumes were analyzed for V to calculate its extraction efficiency. On the other hand, the saturated loaded resin was subjected to the elution process to regenerate the loaded V. A volume of 100 mL of 4% H_2SO_4 was used for this purpose where fractions of 10mL bed volumes were collected and its V content was estimated to determine the relative elution efficiency. Pure V_2O_5 , (red cake) was produced via oxidation precipitation from V rich eluate solution by using $KClO_3$ at pH 2.5 and stirring for 1h. The operating conditions of Amberlite IRA₇₄₃ are listed in **table (1)**.

Table (1): Operating conditions of Amberlite IRA₇₄₃

Issue	Amberlite IRA ₇₄₃
Loading flowrate	1mL/min
Activation	4% NaOH or NH_4OH
pH	8-10
Elution	100 mL of 4% H_2SO_4
Elution flowrate	1mL/min

3- Results and Discussions

3.1. Alkaline agitation leaching of the head sample (residue)

The residue left behind the acidic leaching process of the gibbsite-bearing shale of Abu Thor area assays 0.045 % of V was processed via alkaline agitation leaching with NaOH solution for recovering its V content. Several alkaline leaching effective parameters such as: concentration of NaOH, solid / liquid ratio, leaching time and leaching temperature were studied for optimization of dissolution process. The expected reactions of the alkaline leaching process were illustrated in the following equations, **Abdella (2014)**.



3.1. 1. Effect of NaOH concentration

Different concentrations of NaOH solution ranged from 4% to 10% were used to investigate the effect of alkaline leaching upon dissolution efficiency of V from the present residual sample. The other leaching parameters were kept constant at S/L ratio of 1/3 and agitation time of 1h at room temperature. After washing, filtration and analysis, the obtained data (Fig.1) clarify that, the dissolution efficiency of V increased from 65 to 86% with increasing NaOH concentration from 5% to 8%. On the other hand, further increase concentration of NaOH solution resulted decreasing in dissolution efficiency of V up to 76%, this may be attributed to the consumptions of the alkaline solution in the dissolution of Si.

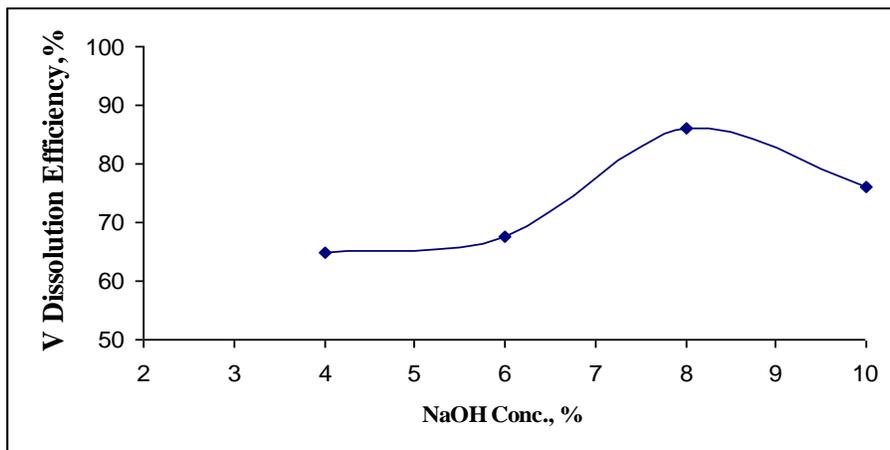


Fig. (1): Effect of NaOH concentration upon V dissolution efficiency of V at 1|3as S/L ratio of 60 min and RT.

3.1.2. Effect of solid/ liquid (S/L) ratio

This effect was studied by mixing 8% NaOH solution with the working sample at different S/L ratios ranged from 1/2 to 1/5 and stirring for 1h at room temperature. The obtained results (Fig.2) indicated that, decreasing S/L ratio from 1/2 to 1/5 increased V dissolution efficiency from 65% up to 90% .Also,by increasing the quantity of OH groups in the slurry which increase the dissolution efficiency of V from the residue wase incread .

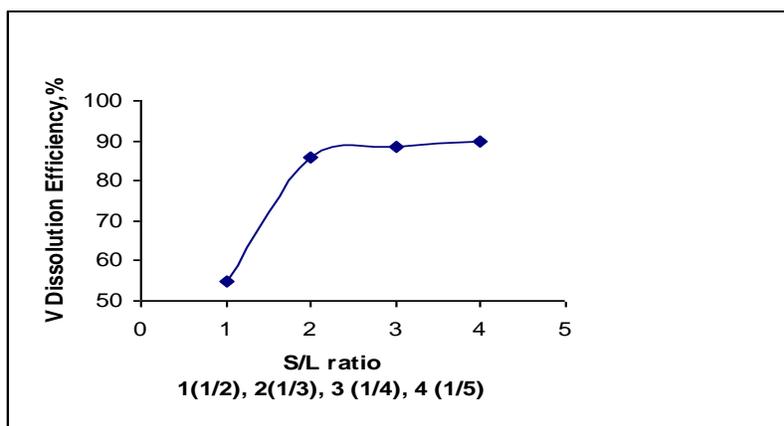


Fig. (2): Effect of S/L ratio upon V dissolution efficiency at NaOH concentration of 8%, dissolution time of 60 min and RT.

3.1.3. Effect of dissolution time

This effect was studied by mixing the residual sample with 8% NaOH solution at S/L ratio of 1/5 with stirring for different time periods ranged from 30 to 120 min at room temperature. Results (Fig.3), revealed that, dissolution efficiency of V increased from 78% to 92% by increasing the leaching time from 30min to 90min. Further time increasing to 120 decreased dissolution efficiency of V 88% due to the dissolution of Si.

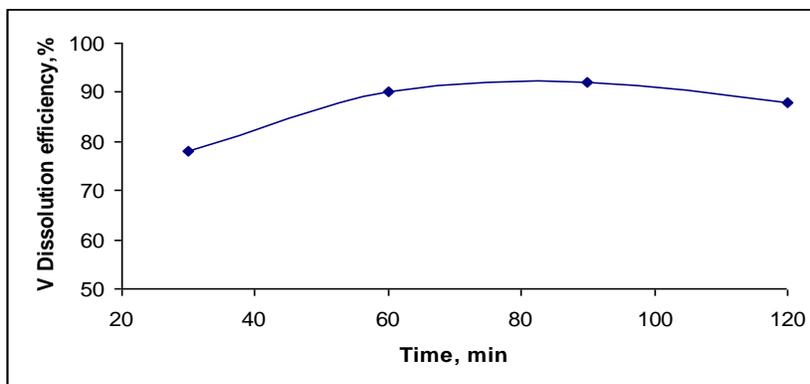


Fig. (3): Effect of leaching time upon V dissolution efficiency at 8% NaOH concentration of S/L ratio of 1/5 and RT.

3.1.4. Effect of dissolution temperature

Fig. (4) shows the effect of changing temperature from 25°C up to 100°C upon V dissolution efficiency from the working residual ore sample. The other dissolution conditions were kept constant at NaOH solution concentration of 8%, S/L ratio of 1/5 and 90min as leaching time. data showed that a remarkable improvement in V dissolution efficiency which achieved 97.5% at 80°C. Further increase in temperature to 100°C decreased dissolution efficiency of V to 91% due to the high dissolution of interfering elements especially Si.

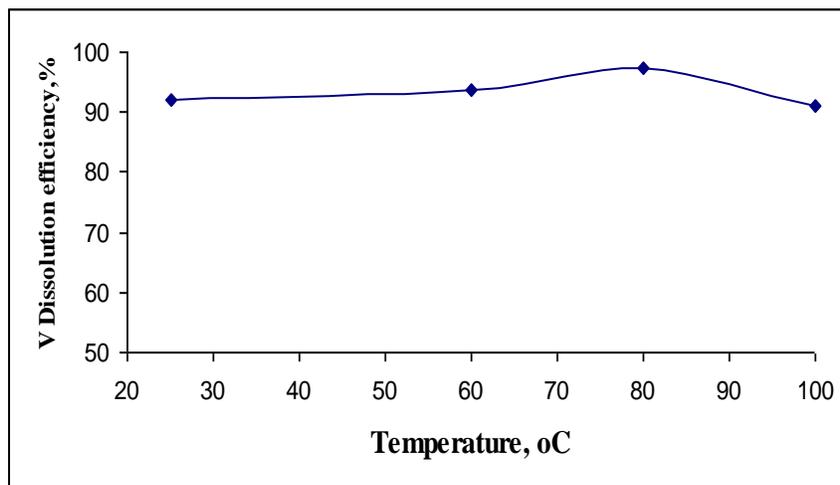


Fig.(4): Effect of temperature upon V dissolution efficiency at NaOH concentration of 8%, S/L ratio of 1/5 and time of 90 min.

From the foregoing dissolution study, it can be concluded that, the optimal dissolution conditions for dissolving about 97.5% of total V content from the residual sample of Abu Thor gibbsite bearing shale are summarized as following:

- NaOH concentration : 8%
- Solid/Liquid ratio (S/L) : 1/5
- Dissolution time : 90min
- Dissolution temperature : 80 °C

The mentioned optimal dissolution conditions were applied up on 200 g of the residue head sample to yield 1 liter of alkaline leach liquor which assays 0.11 g/L of V and 4.2 g/L of Si and its pH > 12. The latter was neutralized by using drops of conc. H₂SO₄ where Si-Gel, Si(OH)₄ is precipitated and the solution pH value attained pH 9. The alkaline solution which has low concentration of Si was directed to the ion exchange unit for recovering V.

3.2. Precipitation of Si-gel

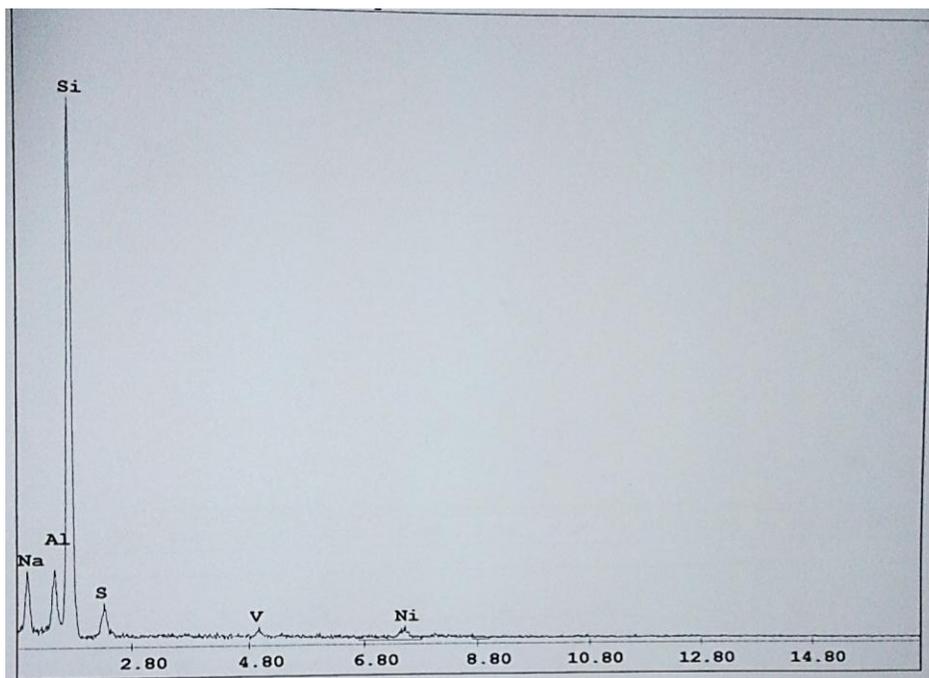


Fig. (5): SEM - EDAX chart of the produced SiO₂.

In the present alkaline solution, V was found as anion species (VO₃⁻), **Wang et al. (2010)** at pH>8. The process of extraction depends upon the substitution reaction between vanadate anions and OH groups of the anionic resin. Fig. (7) describes the mechanism of the uptake of VO₃⁻ species from the aqueous solutions through electrostatic attraction and complexed with N⁺ and OH groups of the anion resin.

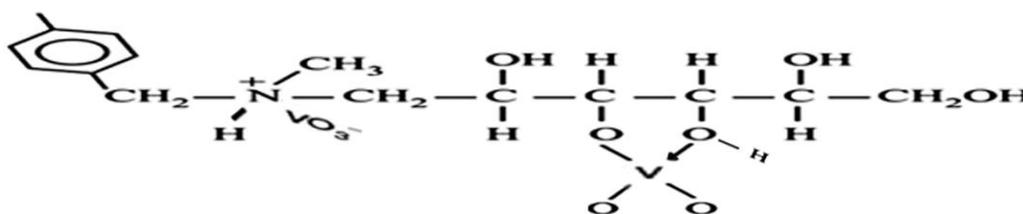


Fig. (7): Mechanism of anion VO₃ species uptake from the aqueous solutions, **Abdella, 2014.**

3.3.1. Loading process of V

The prepared alkaline solution was passed through the resin column packed with 25 mL of wsr at a working flowrate of 1 mL/min. Bed volumes of 50 mL of effluent solution was collected for V analyses where its extraction efficiency was calculated and plotted against number of bed volumes. Results, (Fig.8), clarified that the amount of the loaded V was 0.2g with 90% loading efficiency of After full saturation, the loaded resin was washed with distilled H₂O to get rid of the adsorbed impurities before applying the elution process.

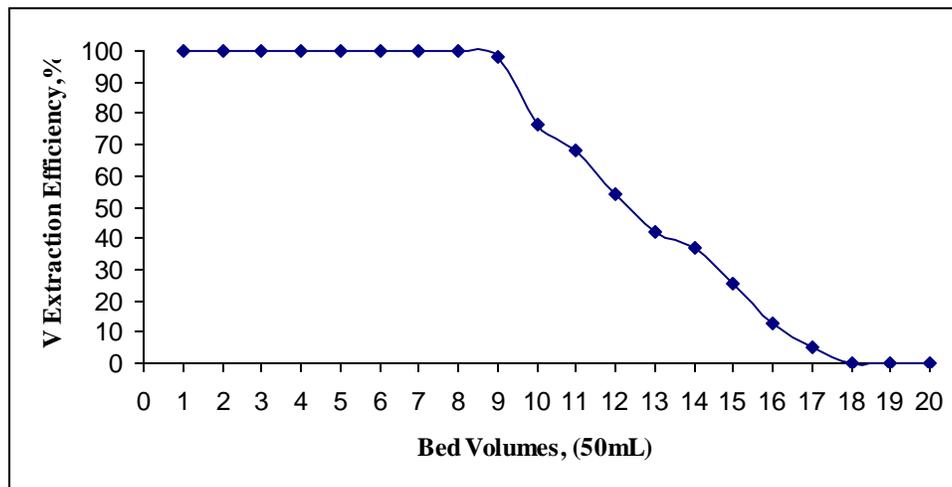


Fig.(8): Loading curve of V from the prepared alkaline solution.

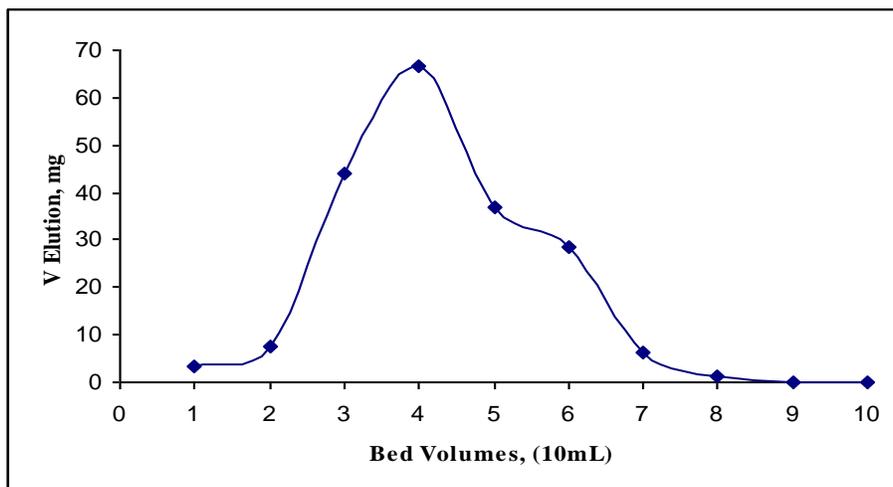


Fig. (10): Elution curve of V from the loaded Amberlite IRA ₇₄₃.

3.4. Precipitation of red cake

The eluate sulfate solution which assays 1.94 g/L of V was used to prepare the final V product. The latter was adjusted to pH 2.5 with NH₄OH solution and strongly oxidized by the addition of 0.25g KClO₃ at 75 °C with continuous stirring for 2h. Not less than 98.2% of V was precipitated as hydrated V₂O₅. The latter was dried in the oven at 120 °C to prepare the final V product V₂O₅ (red cake). The latter was identified by means of SEM - EDAX analysis as shown in Fig. (11). The chemical analysis proved purity of the final product (V₂O₅) which achieved as 95.9%.



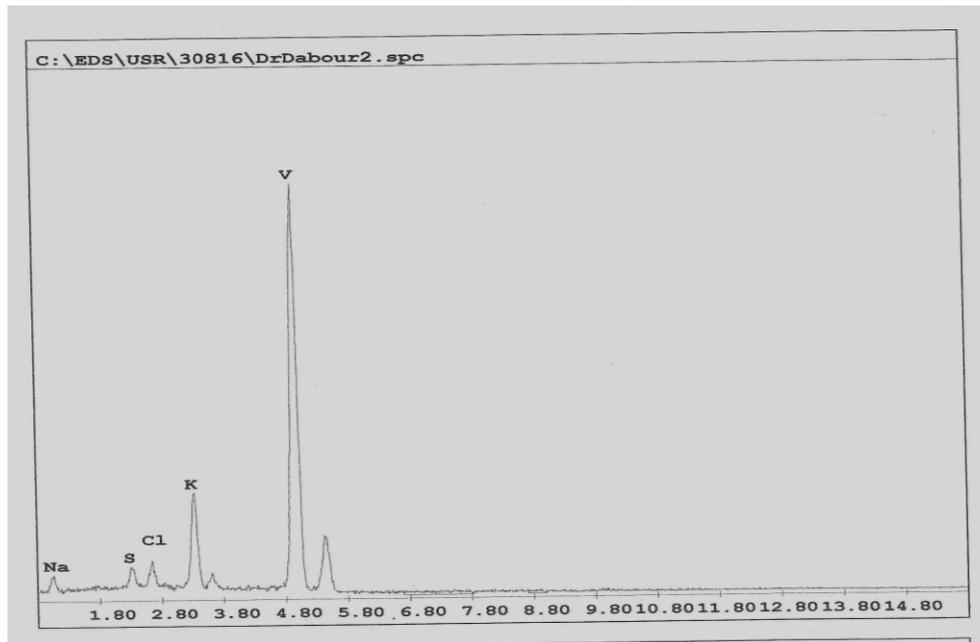


Fig. (11): SEM - EDAX chart for the identification of pure red cake (V_2O_5).

4-Conclusion

The potentiality of preparing highly pure V_2O_5 as well as the by-products of SiO_2 from the alkaline solution of the residual ore of Abu Thor gibbsite - bearing shale ore material has been proven. However, the alkaline agitation dissolution was effectively applied to dissolve V with achieved dissolution efficiencies of 97.5%. On the other hand, anion exchange resin, Amberlite IRA₇₄₃ in its OH form was successfully used for extraction of 90% of V from the prepared alkaline solution. About 97.25% of the extracted V was already regenerated by using 4% H_2SO_4 . Not less than 98.2% of V was precipitated as hydrated V_2O_5 by using NH_4OH solution via strongly oxidation by the addition of 0.25g $KClO_3$ at 75 °C with continuous stirring for 2h. The latter was dried in the oven at 120 °C to prepare the final V product V_2O_5 (red cake). Finally, a proposal technical flowsheet for processing the present ore residue to obtain pure V_2O_5 , (Fig.12).

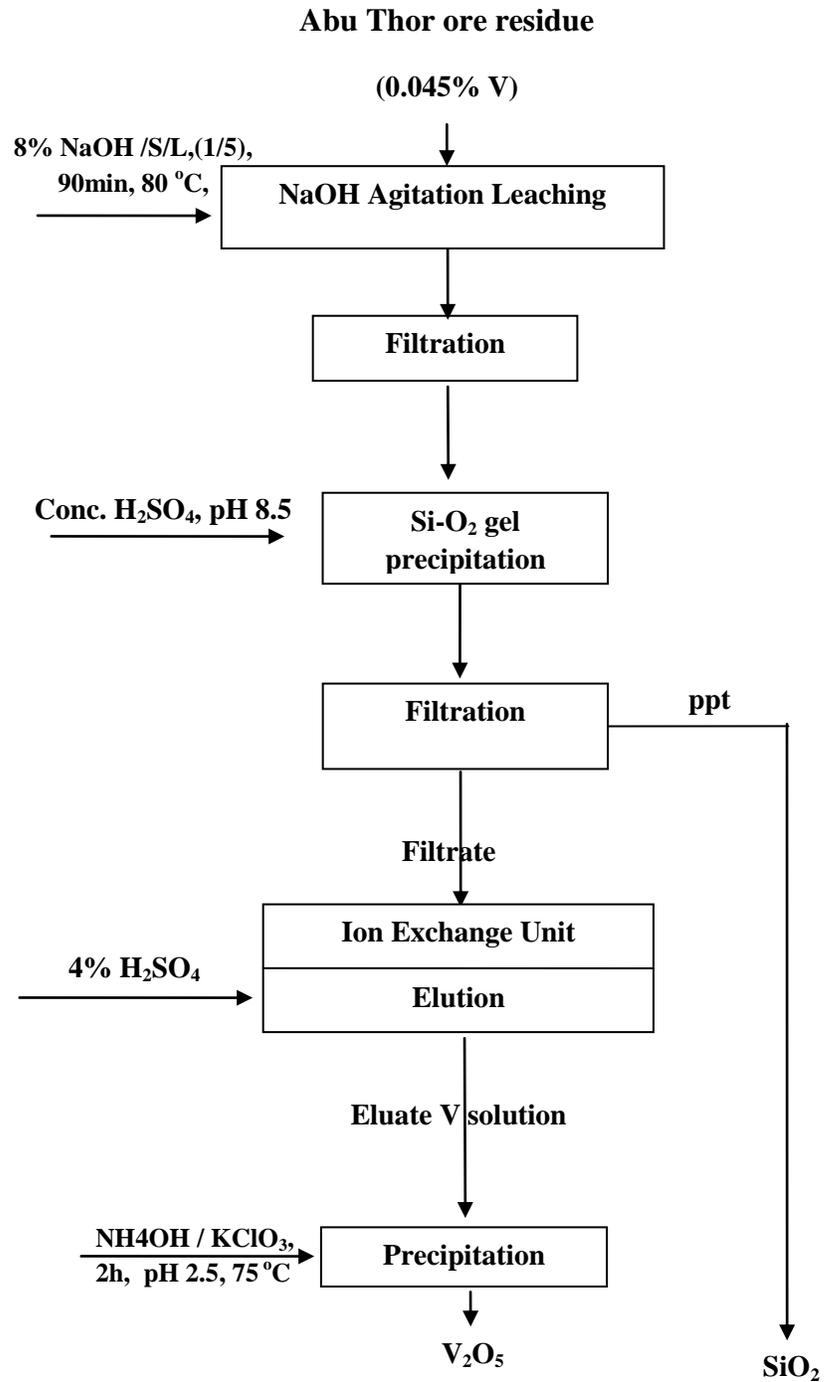


Fig. (12): Technical flowsheet describes the processing of Abu Thor ore residue for preparing pure V_2O_5 and SiO_2 .

5. References

- Abbs, F. O.** "Vanadium oxide recovery from spent catalyst by chemical leaching", *J. Enginerring and technology*, 26, P. (2008)
- Abdellah, W.M., Amer, T.E Abdel Wahab, G.M. and AlShami, A.S. El-Shahat, M.F.** "Extraction of boron and vanadium from Abu Hamata alkali leach solution by using ion exchange resin", *International Journal of Engineering Research & Technology*, Vol. 2, No.11, pp. 1255-1263, 2013. (2014)
- Abdella, W.M.** "Extraction of U and valuable elements from Abu Hamata poly-mineralized Sedimentary rocks, Southwestern Sinai, Egypt". PhD Thesis, Chem. Depart., Faculty of Sc., Ain Shams University, Cairo, Egypt. (2014)
- Chen, X. Y., Lan, X. Z., zhang, q. L., MaHong, Z. and Zhou, J.** "Leaching V by high concentration H_2SO_4 from stone coal", *Trans. Non Ferrous Met. Soc. Chaina*, 20, pp123-126. (2010)
- Guirguis, L. A., Mahmoud, A. H., Zahran, M. A., Sharaf, M. M.** "Leaching kinetics and recovery of Vanadium from Egyptian boiler ash under alkaline oxidizing conditions", 4th Conference on Radiation Science & Applications, Taba, Egypt, 13-17 February, PP. 67- 73. (2014):
- Haoran L., Yali, F., Jianglong, L., Xiaobing, L. and Zhuwei, D.** V. recovery from clay V minerl using an acid leaching method, *rare Metals*, 27, (2), pp.116-120. (2008)
- Holloway, P. and Etsell, T. H.** "Recovery of V from oil sands fly ash" In. Tanner, M. F., Riveros, P. A., Dutrizac, J. E., Gattrell, M., Perron, L. (Eds), *V, Geology, Processing and applications*, Proceedings of International Symposium on V, conference of Meatllurgists, Montr eal, Canda, aug.11-14, pp.227-242. (2002)

- Holloway, P. and Etsell, T. H.** (“Alternative reagents for roasting suncoar oil fly ash”). Mineral processing and extractive Metallurgy (Transactions of the Institution of Mining and Metallurgy), 113, pp.153-160. (2004)
- Hu, J., Song, S.G. and Zhang, B.Q.** (“Removal of vanadium from molybdate solution by ion exchange”), Hydrometallurgy, 95, pp. 203–206. (2009)
- Jin-Wen, H., Peng, S., Wen-Wei W., Sen L.;Hui-Quan, Q. , Xue-Hang W.** (“Concentration and separation of vanadium from alkaline media by strong alkaline anion-exchange resin₇₁₇”), Rare Metals, Vol. 29, No. 5, pp. 439-443(2010)
- Ming-yu, W. , Xue-wen, W. , Ji-feng, S. and Ri-na, W.** (“Extraction of vanadium from stone coal by modified salt-roasting process”), J. of Central South University of Technology, 18, (6), pp. 1940-1944. (2011):
- Mohamed, H. S:** (“Extraction of some economic elements from flay ash”), M Sc. Thesis , Chem. Depart., Faculty of Sc. Zagazeg University, Egypt. (2011):
- Puhong, Y., Xuewen, W., Mingyu, W., Yeye, F. and Xiaoyan, X:** (“Recovery of V from stone coal acid leaching solution by co-precipitation alkaline roasting and water leaching”), Hydrometallurgy, 117-118, pp.108-115. (2012).
- Wang, X. , Wang, M., Shi, L., Hug, J. and Qiao, P.** (“Recovery of vanadium during ammonium molybdate production using ion exchange”), Hydrometallurgy, 104, pp.317–321. (2010)
- Xiao-Hu H., Liu-Jia T. and Yan-Jin, F.** (“Concentration and separation of vanadium from alkaline media by strong alkaline anion-exchange resin₇₁₇”), Rare Metals, 29, (5), Pp. 439-443(2010)
- Zeng, L., Li, Q.G. and Xiao, L.S.** (“Extraction of vanadium from the leach solution of stone coal using ion exchange resin”), Hydrometallurgy, 97, P.194–197. (2009)
- Zhang, X., Yang, K., Tian, X. and Qin, W.:** Vanadium leaching from carbonaceous shale using Fluosilicic acid, International Mineral Processing, 100, pp.184-187. (2011)

الملخص العربي

استخلاص الفانديوم من خامات الطمي الحاملة للجبسيات المعالجه من منطقة ابو ثور ، جنوب غرب سيناء
باستخدام ال تبادل الايوني على راتنج امبرليت^{IRA743}

هذا العمل مهتم باستخلاص الفانديوم من خامات الطمي الحاملة للجبسيات السابق معالجتها والتي تحتوى على
عنصر الفانديوم والعينة الاصلية تركيزها 0.05 تم معالجتها مسبقا لاستخلاص النحاس والكادميوم واليورانيوم
باستخدام حمض الكبريتيك كمذيب حركى . هذا العمل يتضمن الازابه القلويه باستخدام محلول هيدروكسيد الصوديوم
عند الظروف المثلى . تم تطبيق طريقة التبادل الايوني على الراتنج امبرليت^{IRA743} 0.045%
لاستخلاص 90% من الفانديوم فى شكل اكسيد الفانديوم الخماسى النقى والذى تم الحصول عليه وقد تم عمل
بعض المعالجات لترسيب ثانى أكسيد السليكون ولتحميل الفانديوم ومن ثم ترسيبه باستخدام هيدروكسيد الأمونيوم
فى وجود عامل مؤكسد وهو كلورات البوتاسيوم لمدة ساعتين عند 75° م.