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RESEARCH ARTICLE

RECOVERY OF URANIUM AND ASSOCIATED ELEMENTS FROM FERRUGINOUS GIBBSITE-BEARING SHALE OF DABBET ABU THOR LOCALITY, SW SINAI, EGYPT.

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Abstract

Chemical processing of the ferruginous gibbsite-bearing shale ore material of southwestern (SW) Sinai, has been studied for the recovery of U, REEs and B together with the possible associated Cu, Zn and Al contents. A technological sample assaying 0.04 % U, 0.2143 % REEs, 1%Zn, 2.3% Cu, 38% Al₂O₃ and 0.1% B has thus been collected. U, REEs, Cu, Zn and Al have been leached upon their combined sulfate leach liquor. Under the optimum conditions, leaching efficiencies of about 100% for U, 88 % for REEs, 68.57 % for Cu, 66.52 % for Zn and 37.51 % for Al have been achieved.

The work was then shifted for the recovery of boron from the residue left behind. The latter was accomplished by roasting with sodium hydroxide to achieve 95% leaching efficiency. From the two adequately obtained leach liquors, marketable products have conveniently been prepared.

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Introduction:-

Recovery of uranium and possible associated valuable elements is one of the most important concerns of the Nuclear Materials Authority of Egypt. Among the discovered mineralization, the Carboniferous rocks sequence at SW Sinai represents indeed a promising terrain for uranium and other valuable economic metals in association with Um Bogma Formation. The latter includes mainly Cu, V, REE besides the famous Fe/Mn deposits in different concentrations in several localities and rock facies of this formation; viz, Allouga, Talatselim, Abu Thor, etc.

Mineralogically, Abu Thor Cu-U mineralization is essentially composed of the copper carbonate minerals malachite [Cu₂(OH)₂CO₃] and azurite [Cu₃(OH)₂(CO₃)₂] and to a much less extent the chloride mineral atacamite CuCl₂·3Cu(OH)₂. Amer (1997)⁽¹⁾. On the other hand, according to this author uranium in Abu Thor mineralization is essentially present either in the form of its secondary minerals uranophane, beta uranophane which is found in nearby mineralizations, however, in a finely-divided form or else adsorbed on the gangue minerals e.g. clays and iron oxides. Mira and Aita, (2009)⁽²⁾ identified Cu and U-bearing minerals include mainly: atacamite [Cu₂Cl(OH)₃], paratacamite (Cu,Zn)₂(OH)₃Cl or Cu_{1.5}Zn_{0.5}(OH)₃Cl, malachite [Cu₂(OH)₂CO₃], rosasite [(Cu,Zn)₂(CO₃)(OH)₂], monazite [(Ce,La)PO₄] and K- rich zippeite K₄(UO₂)₆(SO₄)₃(OH)₁₀·4(H₂O).

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The main target of the present work is to recover uranium and possible associated elements from the ferruginous gibbsite-bearing shale of Um Bogma Formation at Abu Thor locality. Actually, The gibbsite bearing shale occurs at different locations and besides its interesting Al content, it can be considered as a polymetallic ore as it is associated with varying amounts of U, Zn, Cu, Co, Ni, REE, V, et..... In this regard, for the recovery of the different contained metal values several studies have previously been done using sulfuric acid leaching upon Abu Zeneima mineralized ore material. Accordingly, **Amer (1993)⁽³⁾** and **(1997)⁽¹⁾** has applied the ion exchange and/ or solvent extraction techniques for the extraction of U using Amberlite IRA-400 anion exchange resin and/ or the organic solvent extractant almanine 336 and LIX-64N for Cu. **Mahdy (1995)⁽⁴⁾** has presented a number of flowsheets for the recovery of U, Cu and Mn using different methods such as precipitation, crystallization besides using the organic solvents as well as the anion exchange resin. Also, **Abdel Fattah (2003)⁽⁵⁾** has studied the leaching and extraction efficiency of Al, Cu, Zn and U from a gibbsite ore material of west central Sinai and proposed two flowsheets. In these flowsheets, the alkali one include both U and Al recovery by caustic soda containing some Na_2CO_3 ; then by passing CO_2 into this liquor, Al was precipitated while U could be recovered from the filtrate by anion exchange resin. The Cu and Zn left behind in the ore were then leached by dilute H_2SO_4 acid followed by metallic Cu precipitation by Zn dust. The dissolved Zn was recovered by precipitation at pH 8.4 after Fe(III) removal at pH 3.0–3.5. In the acid flowsheet; Al, Cu, Zn and U were leached by H_2SO_4 . After Cu recovery by metallic Zn at pH 1, U was recovered by anion exchange resin. The solution pH was then adjusted to pH 5.3 to precipitate Al (III) and Fe (III) for later separation by selective caustic soda leach of Al. The filtrate from the Al–Fe cake was treated for the recovery of dissolved Zn values by pH adjustment to 7.5. On other hand, **El Hazeek, et al., (2008)⁽⁶⁾** reported that the agitation acid leaching is preferred to leach most of the interested metal values namely; Al, Cu, Zn, Co, Ni, REE of the gibbsite shales belonging to the Paleozoic sequence of sedimentary rocks occurring at Abu Zeneima area of SW Sinai, The optimum acid agitation leaching conditions involves working at 800 g/L H_2SO_4 acid in a S/L ratio of 1/2 at 100 °C for 12 h and using an ore mesh size of –60 mesh. Under these conditions, it is possible to achieve the following leaching efficiencies: Al 100%, Cu 100%, Co 91%, Zn 84 %, Ni 100% and U 95%.

It is interesting to mention herein that, **Ibrahim and El-Sheikh(2011)⁽⁷⁾** have applied a proper bioleaching processing for a carbonate rich mineralized gibbsite ore material from Abu Zeneima area, SW Sinai. The metal values of this ore material included 0.34% Zn, 0.49 % REEs and 0.05% U beside 26.43% Al_2O_3 . In the bioleaching process, the columnar technique was applied upon non-sterilized material including the use of 5% *Acidithio bacillus ferrooxidans* bacteria and circulating the bioleach liquor for 30 cycles. Under these conditions, the obtained leaching efficiencies amounted to about 67.6, 55, 50 and 22.4 % for the REEs, uranium, zinc and aluminum respectively.

As previously mentioned, the main target of this study is to recover U, and REEs and B together with Cu, Zn and Al and Si from the study ferruginous gibbsite-bearing shale of Um Bogma Formation at Abu Thor locality. To realize this goal, a technological representative sample of Abu Thor mineralization was properly collected which was found to assay 0.04% U, 0.2143 % REEs, 1% Zn, 2.3% Cu and 38% Al_2O_3 . Acidic leaching was applied for U, REEs, Cu, Zn and Al recovery followed by alkali roasting for recovering B from the spent residue by using sodium hydroxide. Different parameters affecting the leaching processes such as acid / or alkali concentration, leaching time, solid / liquid ratio, and temperature of the system were investigated.

Experimental:-

Materials and methods:-

Characterisation of the working sample:-

Proper quartering of the technological sample was performed after its grinding to less than 200 mesh size to obtain a representative sample which was subjected to complete chemical analyses of both major and trace elements content. For the former, the conventional wet chemical technique was applied (**Shapiro and Brannock, 1962)⁽⁸⁾** where SiO_2 , Al_2O_3 , TiO_2 and P_2O_5 were determined using their relevant spectrophotometric methods while Na_2O and K_2O were assayed by the flame photometric technique. Total Fe as Fe_2O_3 , MgO and CaO were determined by titration methods against dichromate and EDTA solutions respectively. The loss on ignition (L.O.I) was gravimetrically determined at 550 °C for H_2O , H-O and organic matter as well as at 1000°C for CO_2 . The estimated error for these major constituents is not more than ± 1 %.

The trace elements V, Nb, Ni, Cu, Zn, Y, Zr, and Pb were also analyzed by means of the X-ray fluorescence technique (XRF) using Philips Unique II unit fitted with an automatic sample changer PW 1510 (30 position), connected to a computer system using X-40 program for spectrometry. The detection limit of the measured elements by means of XRF technique was estimated to be 5 ppm.

Leaching procedures:-

In this process, the ground sample (-200 mesh size) was well mixed by quartering to attain homogeneity. However, several sample portions were subjected to the leaching experiments.

In the present work, two leaching methods were subsequently performed; the first includes acidic agitation leaching by using H_2SO_4 acid upon the raw ore material to dissolve both of U, REEs and some of the associated elements such as Zn, Cu and Al, leaving behind B and Si in the residue. While the other includes the spent residue which was roasted with NaOH to dissolve the unleached B and Si.

 H_2SO_4 acid atmospheric agitation leaching:-

Each leaching experiment has been performed by agitating a weighed amount of the ground sample (10g) with H_2SO_4 acid of different concentrations, different solid/liquid ratios(S/L) for different periods of time at different temperatures. In these experiments, a hot plate with magnetic stirrer was used and precautions were taken to avoid evaporation. The obtained slurry was then filtered and the residue left behind was thoroughly washed with distilled water. Both of filtrate and washings were made up to volume before analysis of the leached metal values.

Alkali roasting of the spent residue :-

To recover boron from the spent residue, obtained after applying acidic leaching, 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 contents. It is worthy to mention herein that, all the roasting experiments were conducted by using constant weight (5g) of the working residual sample.

Recovery procedures:-**Recovery of U and REEs:-**

According to the chemical characteristics of the studied metal values, it can be mentioned that Al, Cu and Zn beside most of undesired metal impurities exist in sulfate liquors in their cationic forms except the uranium exist in both cationic and anionic forms. Therefore, anion exchange resin would be selective for uranium recovery from the obtained sulfate leach liquor. In order to improve recovery of uranium, without interference of other elements, especially Fe, the latter must be firstly removed at pH of 3. In the latter solution, the competing anions include mainly SO_4^{2-} and HSO_4^- and therefore uranium would be better adsorbed at pH value exceeding 1.8 while below this value, HSO_4^- would be strongly adsorbed. (Merritt, 1971⁽⁹⁾; Preuss and Kurrin, 1965)⁽¹⁰⁾.

In the present work the pH of the prepared pregnant solution was re-adjusted to pH 1.8 for U adsorption upon the anion exchanger resin Amberlite IRA-400 while the effluent was then used to precipitate Cu and Al as their hydroxides at pH of 5.5. The separation between copper hydroxide and aluminum hydroxide takes place by adding excess of 35% ammonia solution to dissolved the copper selectivity.

U, Cu and Al free solution was then directed to precipitate zinc. The latter was directly precipitated as its sulfide from the sulfate leach liquor after adjusting its pH to 2 using a 2 % Na_2S solution.

The Zn- free leach liquor was then subjected to the precipitation of the total REE as their oxalates by the addition of 30% oxalic acid at pH 1.

Recovery of B:-

In the present work, trials to recover boron from the pre-processed ore material under consideration have been performed. In this respect, alkali roasting process was first accomplished upon 500 g of the ore residue by using pellets of NaOH under the obtained optimum roasting conditions. 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 metal value. The recovery of boron has been performed via Amberlite IRA-743 anion exchange resin. Fractions of 100 mL bed volumes were collected and its boron content was estimated to determine the relative loading efficiency of boron upon the applied flow rate of 1.5 mL/min. The saturated loaded resin was subjected to the elution process to regenerate the loaded boron. Hot water was used to attain acceptable elution efficiency of B. For this purpose, suitable volume of 100 mL hot distilled H_2O was used at working flow rate of 1 mL/min to remove almost loaded B. The eluate rich boron was subjected to evaporation to prepare pure H_3BO_3 acid.

Analytical procedures:-

To follow the periodical analyses in the obtained leach liquors from the different stream solutions, oxidimetric titration method against ammonium metavanadate was used for uranium analysis after its reduction (Mathew et al., 2009)⁽¹¹⁾. While for copper and zinc, an atomic absorption spectrometer (AAS) Unicam 969, England was used. Total rare earth elements were spectrophotometer determined by the colored method using Arsenazo-III, as an indicator (Merczenko, 1986)⁽¹²⁾.

On the other hand, B analysis was performed by using prism ICP-OES, Teledyne technologies (Inductively Coupled Plasma Optical Emission Spectrometer). Also, the final obtained products of all study metal values have qualitatively been analyzed using the ESEM-EDX analysis.

Results And Discussion:-**Chemical characteristics of the working ferruginous gibbsite-bearing shale ore material:-**

The chemical composition of the working Abu Thor ore sample is given in **table (1)**. From this table, it is clear that the high level of the loss on ignition (attaining about 20%) reflect its high content of organic matter on the expense of carbonates as shown from its low contents of CaO and MgO $\approx 0.57\%$. Also, silica, alumina and iron oxide contents are also of high content, 21.75, 38.09 and 11.39% respectively together with 1.6% of P₂O₅ and TiO₂.

On other hand, X-ray fluorescence (XRF) analyses of some trace elements (**Table 2**) shows that U attains 404ppm besides interesting values of Zn, Ni, Y, B and Σ REEs; namely 10000, 1784, 69, 1000 and 2143 ppm respectively. Some of the corresponding minerals are included in the host rocks which essentially represented by hematite besides variable amounts of rutile, jarosite, goethite, crednerite (CuMnO₂), kaolinite, alunite, gibbsite, hausmannite, phosphosiderite and lawrencite (FeNiCl₂) (Aita, 1996)⁽¹³⁾.

Table (1):- Chemical composition of the working gibbsite bearing shale ore sample

Component	wt. %	Component	wt. %
SiO ₂	20.75	Na ₂ O	3.09
TiO ₂	1.10	K ₂ O	1.89
Al ₂ O ₃	37.09	P ₂ O ₅	1.69
Fe ₂ O ₃	11.39	*L.O.I.	20.02
CaO	0.34	Cu	2.3
MgO	0.23	Total	99.89

L.O.I**Total loss in ignition

Table (2):- Trace elements Content in the working gibbsite bearing shale ore sample.

Trace element	ppm	Trace element	Ppm
Ni	1784	V	203
Nb	29	U*	404
Zr	598	Σ REEs*	2143
Pb	3855	Zn*	10000
Y	69	B*	1000

*= Wet Chemical determination

Results of H₂SO₄ acid atmospheric agitation leaching:-**Effect of acid concentration:-**

The sulfuric acid concentration used for studying its effect upon the agitation leaching efficiency of U, REEs, Cu, Al and Zn values has been varied between 80 and 240 g/L. The other leaching conditions were fixed for only one hour at 70 °C within the S/L ratio of 1/2 and using an ore ground to -200 mesh size. The obtained results **Table.(3)** indicate that, increasing the acid concentration has a direct influence upon the leaching efficiencies of the studied metal values. Thus, as the acid concentration increased from 80 to 200 g/L, the leaching efficiency of U increased from 20% to 40% while the leaching efficiencies of REEs increased from 25.23 to 37.51% and Cu, Al and Zn increased from 20.29 to 30.44 %, 22.40 to 29.91% and 50.00 to 62.29% respectively. On the other hand, further increase in the acid concentration (i.e.240 g/L) slightly improved the leaching efficiencies of U, Cu, Zn, and Al to 45, 35, 81 and 32.41% respectively. It is important to mention herein that further increase in the acid concentration (i.e.240 g/L) has an adverse effect on the leaching efficiency of REEs. This may be due to partial precipitation of

LREEs as double sulfates. It can thus be mentioned that the 200 g/L sulfuric acid concentration that is optimum leaching concentration for different metal values. Also, it is evident that B dissolution has not been affected to any extent by increasing the acid concentration.

Table (3):- Effect of acid concentration leaching efficiency upon the study metal values of gibbsite-bearing shale ore material.

Acid Conc., g/L	Leaching efficiency, %					
	U	Σ REEs	Cu	Al	Zn	B
80	20	25.23	20.92	22.40	50.00	*ND
120	25	28.56	19.57	22.50	53.65	*ND
160	30	32.95	15.66	28.99	60.66	*ND
200	40	37.51	30.44	29.91	62.29	*ND
240	45	32.40	35.00	32.41	81.80	*ND

*ND= Non detected

Effect of Leaching Time:-

To study the effect of agitation time upon the leaching efficiencies of the metal values of Abu Thor gibbsite ore material, a series of leaching experiments were studied at different periods of time ranging from one hour to 4h under fixed conditions of 200 g/L H_2SO_4 acid at 70°C and using 1/2 S/L ratio. The leaching efficiencies of the interested metal values are given in **Table (4)**. From the obtained results it is clear that the leaching efficiencies of U and associated elements increased by increasing the agitation time from an hour to 4h from 40 to 75 % for U, from 30.44 to 54.51% for Cu, from 29.91 to 39.34 for Al and from 62.29 to 76.3 for Zn.

It is worthy to mention herein that REEs dissolution efficiency increased from 37.5 at 1h to 84.1 % at 3h. Increase leaching time to 4 or 5 h doesn't increase the leaching efficiency of REEs due to its precipitation as double sulfates. Finally, it can be stated that extending the leaching time to 4 h is quite beneficial where satisfied leaching amount of U and most of the other associated elements were achieved. In this context, it is noted that the B content of the study ore material does not change even when the leaching time was increased.

Table (4):- Effect of leaching time leaching efficiency upon the study metal values of gibbsite-bearing shale ore material

Time, h	Leaching efficiency, %					
	U	Σ REEs	Cu	Al	Zn	B
1	40	37.51	30.44	29.91	62.29	*ND
2	65	65.42	40.11	38.88	70.80	*ND
3	70	84.08	48.83	39.33	75.00	*ND
4	75	80.80	54.51	39.34	76.23	*ND
5	75	80.80	54.51	39.34	76.23	*ND

*ND= Non detected

Effect of leaching temperature:-

The effect of leaching temperature upon the dissolution efficiencies of the studied metal values was studied in the range from room temperature (25°C) up to 95°C. The other leaching conditions were fixed at 200 g/L H_2SO_4 acid, 4h agitation time and S/L ratio of 1/2. The obtained data which are shown in **Table (5)** indicated the importance of leaching temperature upon the study metal value leaching efficiencies from this ore material. Also, this effect is actually more pronounced in case of U, REEs, Cu and Zn which gave better results than those of Al in spite of using the same experimental conditions. This may be due to the hydrolysis effect that might have led to Al re-precipitation. Working at room temperature under the mentioned conditions did not leach more than 50% of U, 55.67% REEs, 37.58% of Cu and 26.83% of Al while that of zinc amounted to 60.15%. Increasing the leaching temperature to 65°C has increased the leaching efficiency of U, REEs, Cu, Al and Zn to 70, 75.71, 65.45, 38.34 and 75.0 % respectively. Further increase to 95°C increased the U, REEs, Cu, Al and Zn to leaching efficiency to 85, 80.87, 65.54, 39.35 and 85.00 %. It can thus be mentioned that the optimum leaching temperature using 200 g/L sulfuric acid under the above mentioned condition would be 95°C. Also, B dissolution was not affected by any increase in leaching temperature.

Table (5):-Effect of temperature leaching efficiency upon the study metal values of gibbsite-bearing shale ore material

Temperature, °C	Leaching efficiency,%					
	U	ΣREEs	Cu	Al	Zn	B
25	50	55.67	37.58	26.83	60.15	*ND
45	60	60.36	50.28	30.26	70.74	*ND
65	70	75.71	65.45	38.34	75.00	*ND
70	75	80.80	54.51	39.34	76.23	*ND
75	78	80.82	60.37	39.23	80.11	*ND
85	80	80.86	61.52	39.35	82.44	*ND
95	85	80.87	65.54	39.35	85.00	*ND

*ND= Non detected

Effect of S/L ratio:-

As the solid/liquid ratio in the leaching slurry would control its viscosity and hence efficient mixing; its effect was therefore studied in the range of 1/2 to 1/5. The other leaching conditions were fixed at 200 g /L H₂SO₄ and 4h agitation time at 95°C. From the obtained data shown in **Table (6)**, the dissolution efficiencies of all metal values increased by decreasing the solid liquid ratio from 1/2 to 1/4. In other words, the metal values leaching efficiency are increased with increasing the amount of acid input to the ore weight. It was found that after the S/L ratio of ¼ a perceptible decrease in the leaching efficiencies of U to 90 % and REEs to 80.77% took place. With respect to the other metal values a significant increase in the leach efficiency was achieved. Accordingly, a solid / liquid ratio of 1/4 would be considered as optimum for the high dissolution efficiency of U and REE.

Table(6):-Effect of the S/L ratio leaching efficiency upon the study metal values of gibbsite-bearing shale ore material

Solid/liquid, Ratio	Leaching efficiency,%					
	U	ΣREEs	Cu	Al	Zn	B
1/2	85	80.87	65.54	39.35	85.00	*ND
1/3	90	84.53	67.94	38.35	70.55	*ND
1/4	99	88.54	68.57	37.51	66.52	*ND
1/5	90.13	80.77	75.99	47.91	90.00	*ND

*ND= Non detected

From the forgoing study it can be concluded that the optimum leaching conditions for almost complete leaching of U and 88.54 % REEs and a satisfy amount of the other associated elements would be summarized as follows:

Grain size : -200mesh
 Acid concentration : 200g/L
 Leaching time :4h
 Leaching temperature : 95°C.
 Solid/liquid ratio : 1/4

Results of metal values recovery:-

For recovering of U, REEs and the associated metal values,a sulfate leach liquor was probably prepared by applying the above mentioned optimum leaching conditions upon 1kg of the provided working ore material. This resulted in 0.1, 0.45, 1.66, 3.9 and 35.71 g/L within leaching efficiencies for U, REEs, Zn, Cu and Al respectively.

Uranium recovery:-**Loading of U upon Amberlite IRA400 resin:-**

A resin sample of Amberlite IRA 400 equivalent to 4.35 ml wet settled resin (w s r) was packed over a glass wool plug in a pyrex glass column. The prepared 4000 mL sulfate leach liquor was then subjected to loading process by passing through the prepared resin bed at the flow rate of about 1.4 mL / min. The effluent was collected every 200 mL that and analyzed for its uranium content .The obtained results which are shown in **Fig (1)** reflects the loading efficiency of 75% from the theoretical capacity of the study Amberlite IRA 400.

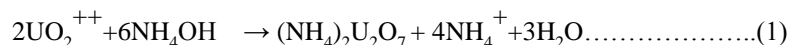
Uranium Elution:-

Before uranium elution, the resin column was first washed with distilled water displace of the pregnant solution. This

was followed by passing the eluant solution composed of 1N NaCl acidified with 0.25M sulfuric acid using a flow rate of 1.4 mL /min. and collecting the obtained eluate every 10 mL for uranium analyses. The obtained elution efficiency for U was found to be 96.4%. **Fig (2).**

Uranium Precipitation:-

Uranium from the collected eluate was precipitated at a pH of about 6.5 using 30 % NH_4OH solution in the form of ammonium diuranate as the following equation:



After filtration and washing, the produced crude yellow cake (Y.C.) was then dried at 110 °C and its uranium content was chemically determined assaying about 75%U. EDAX analysis of the latter indicate 98% purity as shown in **Fig. (3).**

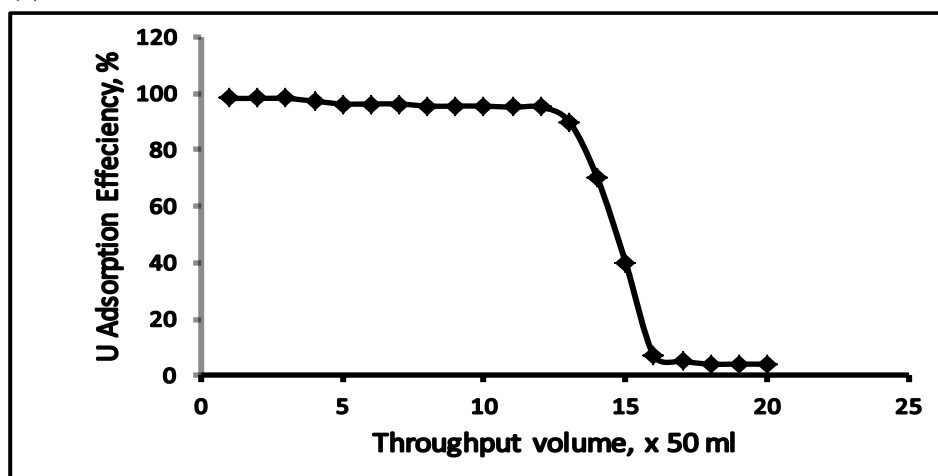


Fig. (1):- Adsorption curve of uranium from sulfate leach liquor.

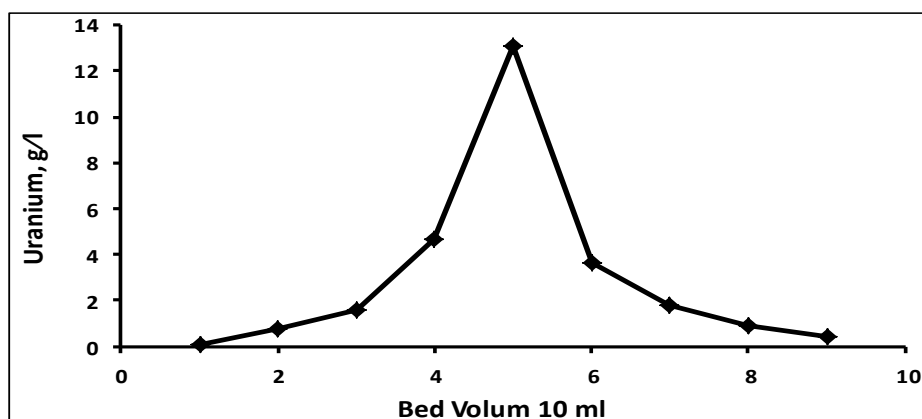


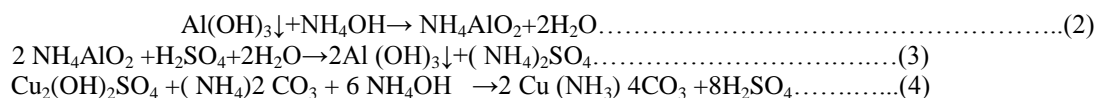
Fig. (2):- U elution curve of saturated Amberlite IRA 400 resin bed

Selective Recovery of Total REEs:-

As it is known either Cu or Zn greatly interfered during precipitation of the REE by using oxalic acid where it also forms an insoluble oxalate with those of the REEs. Therefore, Cu, Al and Zn should be first removed from the sulfate leach liquor before the recovery of the REEs as their oxalates.

Recovery of Al and Cu:-

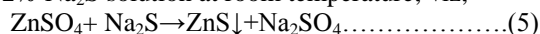
From the uranium effluent liquor, Cu and Al hydroxide crystals have been obtained by adjusting its pH to 5.5 using ammonia solution. The separation between copper hydroxide and aluminum hydroxide takes place by adding excess of 35% ammonia solution to dissolve the copper content selectively according to the following equation:



The obtained crystals of either Cu or Al have been calcined and the obtained oxides were then subjected to ESEM - EDAX analysis to confirm the degree of its purity which was found to attain up to about 100% of both Cu and Al as shown in Fig. (4, 5).

Selective recovery of Zn:-

After removing of U, Cu and Al from the prepared sulfate leach liquor, Zn was almost completely precipitated at pH 2 by using drop wise addition of 2% Na_2S solution at room temperature; viz,



After filtration, the gray ZnS precipitate was properly washed several times with distilled water to get rid of any included impurities. The obtained ZnS was identified by means of EDAX analysis with 90% purity (Fig. 6).

Finally, the U, Cu, Al and Zn-free leach liquor was then subjected to the selective recovery of the total REEs through selective precipitation of their oxalates. This is due to the fact that, the REEs form stable insoluble oxalates and thus can be used for their separation (Habashi, 1993)⁽¹⁴⁾. Therefore, a 30 % oxalic acid solution was used for this purpose after raising the pH value of the working effluent to 2.5. Almost complete precipitation of REEs was attained at pH 1. These conditions represent the optimum conditions for the REEs precipitation. The obtained white REE-oxalate product was filtered and properly washed with distilled water to get ride of any impurities. After drying it was ignited at 850°C for 2h to have the corresponding REE-oxides. The latter was subjected to EDAX semi-quantitative analysis to identify its individual REEs distribution as shown in (Fig.7)

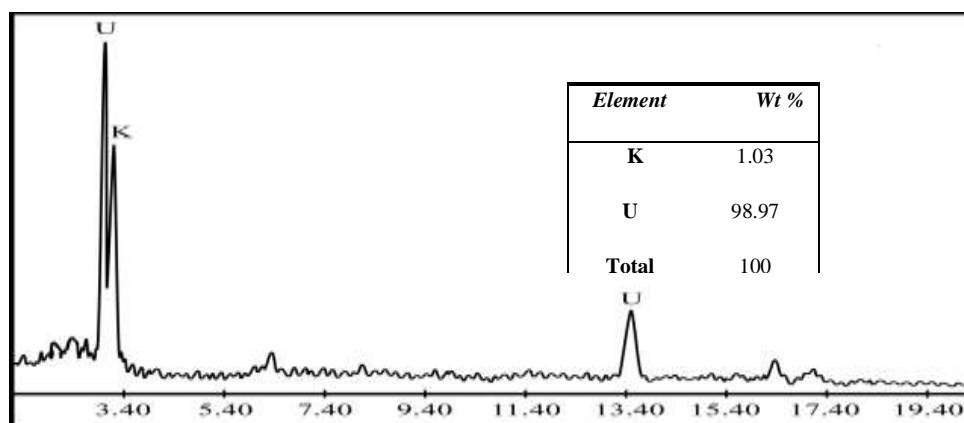


Fig. (3):- EDX analysis of the obtained crude yellow cake product.

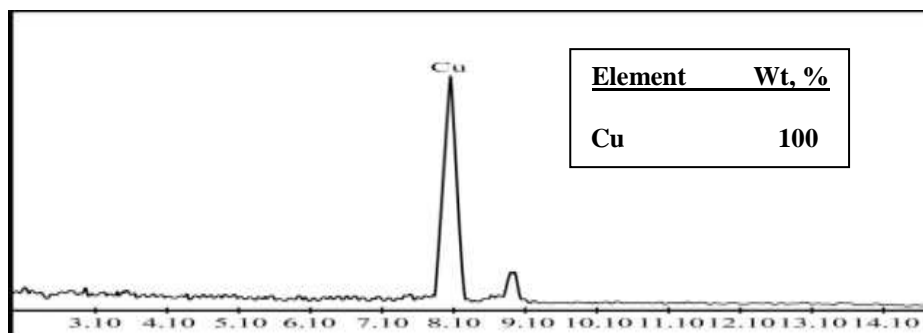


Fig. (4):- EDX analysis of the obtained pure copper

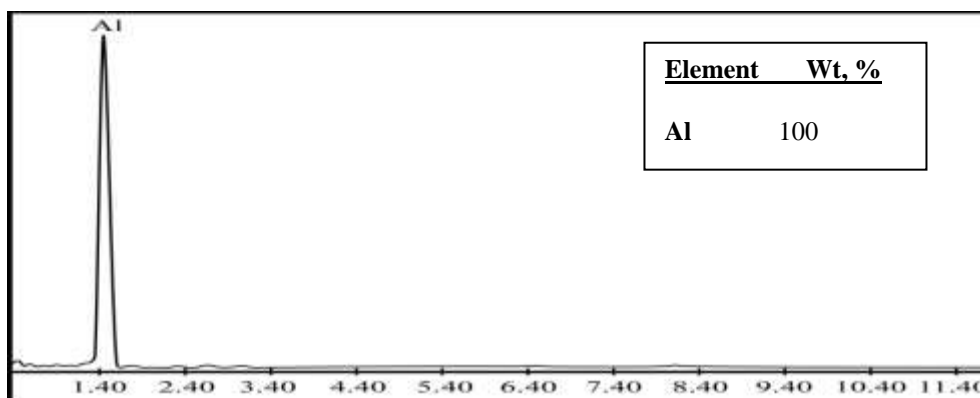
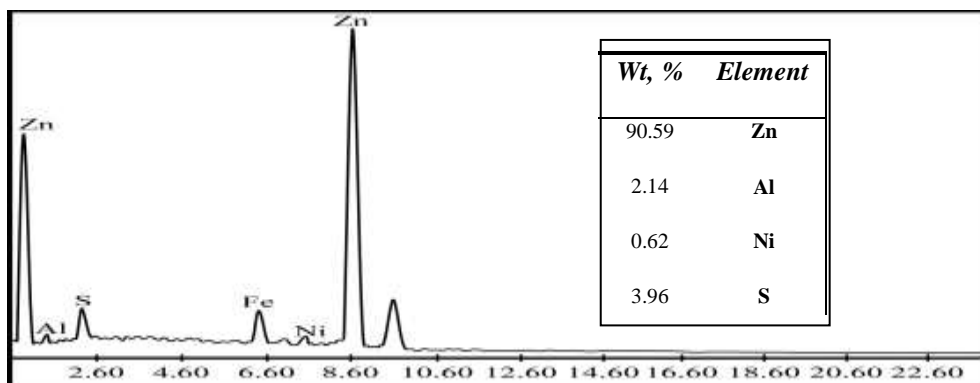
Fig. (5):- EDX analysis of obtained $\text{Al}(\text{OH})_3$.

Fig. (6):- EDX analysis of the obtained zinc sulfide.

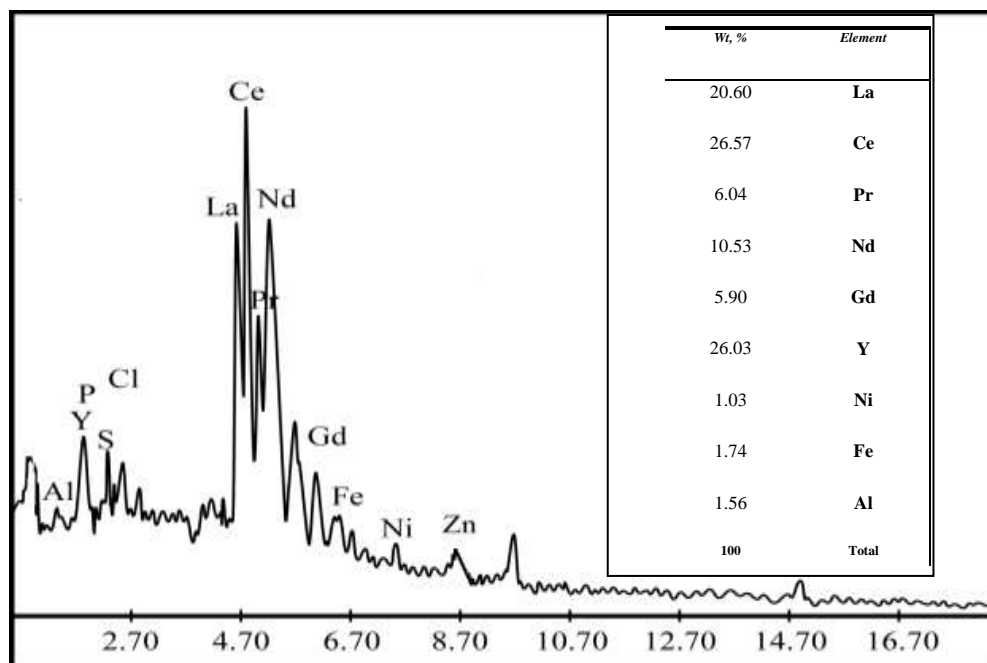


Fig. (7):- EDX analysis of obtained REE oxalate

Results of alkali roasting of the spent ore residue:-

As mentioned above, U and REEs, together with some of the associated metal values namely; Cu, Zn and Al have successfully been recovered from the study raw ore material, the spent residue will represent the feed material of

boron recovery. However, for this purpose alkali roasting process using NaOH was applied.

The main applicable alkali roasting conditions for recovering of B content include; effect of ore / NaOH weight ratios, roasting time and roasting temperature. Each experiment was performed on 5 g from the study ore residue.

Effect of ore / NaOH weight ratio:-

A set of experiments has been performed using different S/R (ore residue / NaOH) ratio ranging from 1:1 to 1:4 while the other roasting conditions were fixed at 400 °C for 2 h. The results plotted on **Fig. (8)** proved that the dissolution efficiency of B increased at 1/3 ore / NaOH ratio where 95.0% dissolution of B was achieved. Using 1/4 S/R ratio decreases the leaching efficiency of B to 87.23 %. This most probably due to hydrolysis effect.

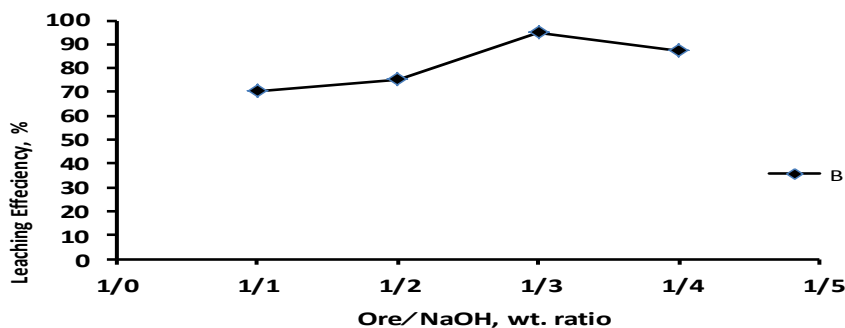


Fig. (8):- Effect of NaOH upon B dissolution efficiency of the working ore residue

Effect of roasting time:-

A set of roasting experiments was studied ranging from 1 to 3 h. Other roasting conditions were fixed at an ore / NaOH ratio of 1:3 and roasting temperature of 400 °C. The dissolution efficiency of B metal value is plotted in **Fig. (9)**. From the results, it is clearly evident that increasing the fusion time from 1 to 2 h increases the dissolution efficiency of B till reached 95%. Further increasing in the roasting time to 3 and 4 h has adversely affected the dissolution efficiency of B, most probably due to hydrolysis effect.



Fig. (9):- Effect of roasting time upon B efficiency of the working ore residue

Effect of roasting temperature:-

A series of roasting experiments has been studied at temperature ranging from 100 °C to 600°C. Other roasting conditions were fixed at ore / NaOH ratio of 1:3 for 2h. The dissolution efficiency of B, plotted in **Fig. (10)** indicated that increasing the roasting temperature to 400 °C increasing B dissolution to 95%. These data indicated the roasting temperature is the most important factor for B dissolution. However, increasing the roasting temperature to 500 and 600 °C has an adverse effect on the dissolution efficiencies of B where the dissolution efficiency decreased to 92.22 and 85.88 % respectively. This might be due to the formation of insoluble borosilicate compounds at high temperature which might be complicate its subsequent recovery (**Vickand Whittle, 1969**)⁽¹⁵⁾. This emphasized the association of boron with clay minerals (**Abdellah, 2014**)⁽¹⁶⁾.

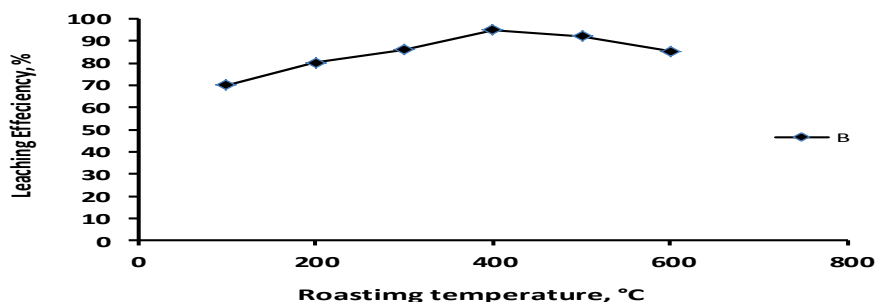


Fig. (10):- Effect of roasting temperature upon B of the working ore residue

In the light of the foregoing mentioned alkali roasting process of the working ore residue left, it can be concluded that, the optimum roasting conditions required for dissolving 95 % of B was as following:

Ore / NaOH, wt. ratio	:	1:3
Roasting time	:	2 h
Roasting temperature	:	400°C

After applying these optimal roasting conditions a proper pregnant leach liquor was prepared. The roasted matrix was then left to cool and leached with distilled water for 2 h at room temperature to bring out the dissolved boron. Accordingly, 500 g of the ore residue was used to yield 2 liters of alkaline leach liquor. The latter was found to assay 0.238 g/L of B, 12.0 g/L of Si and 39.2 g/L Al, 3.45 Cu and 1.5 g/L Zn within pH value of > 12 .

Recovery processes of silica and boron:-

In this context, Amberlite IRA-743 anion exchange resin was used for B recovery. The latter has a macro porous poly-styrene matrix, on which N-methyl glutamine functional groups (R-N (CH₃) -C₆H₈ (OH)₅) are attached as represented by fig. (11).

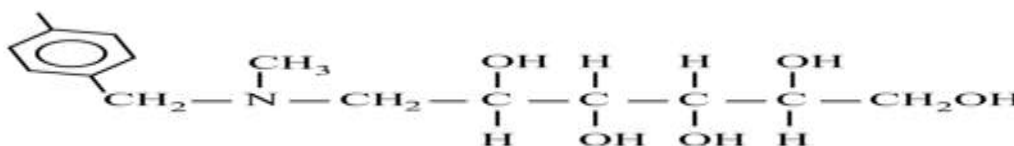
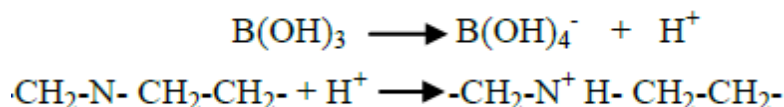


Fig. (11):- A scheme of building chemical structure of Amberlite IRA743

In the alkaline solution, boron was found in the anion species borates $[B(OH)_4]^-$ at pH value over 8 **Muetterties (1967)**⁽¹⁷⁾. The process of extraction depends upon the substitution reaction between the borate $[B(OH)_4]^-$ anions and anionic resin sites. **Fig.(12)** describe the mechanism of the uptake of boron from the aqueous solutions. The uptake of boron as borate anion $B(OH)_4^-$ is a curious mechanism, where it involves protonation of the amine, deprotonation of the ploy sugar tail. Boric acid dissociate in distilled H₂O to form the borate anion. While the protonation process of the amino group will be taken place as illustrated in equations below.



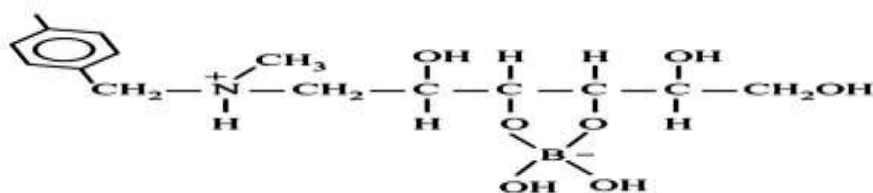


Fig. (12):- A scheme of boron uptake mechanism from the aqueous solutions

Si-gel precipitation before loading of Boron:-

Before applying the loading process of boron 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_2SO_4 to be 8.5. The precipitated silica in the form of SiO_2 -gel should be washed with dilute H_2SO_4 (1%) during filtration to avoid the loss of any dissolved boron 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%, Fig. (13).

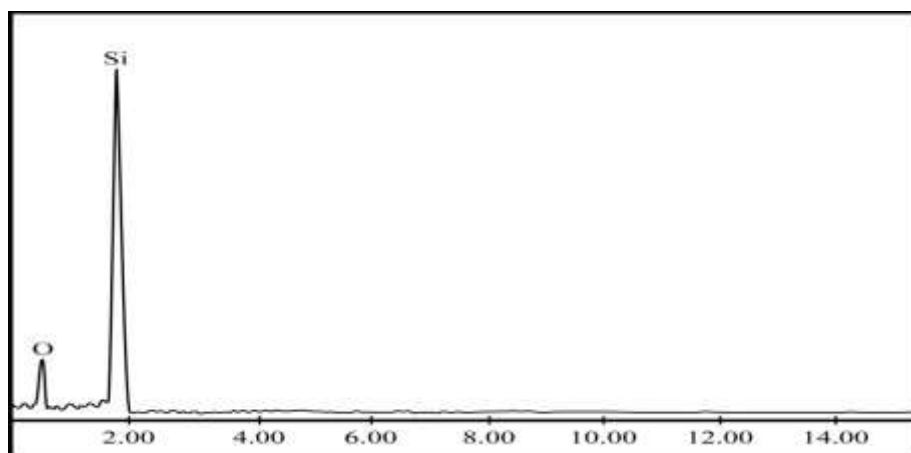


Fig. (13):- EDX analysis of obtained Si-gel product

Loading process of boron:-

In the present work, 2 Liters of the prepared leach liquor from 500 g residue left behind (mainly free from SiO_2) was passed through the resin column packed with 79 ml w.s.r at a working flow rate of 2 mL/min. The obtained effluents were collected every 100 mL for B analysis. From the obtained results (Fig. 14), it is evident that, the calculated capacity of the working resin for B represented about 68 % and this is 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 remained amount of loaded species before applying the elution process.

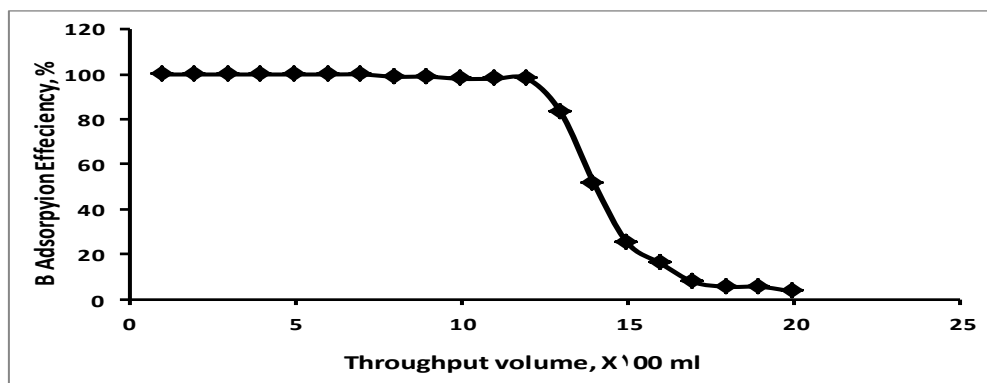


Fig. (14):- Adsorption curve of boron from alkaline leach liquor

Elution of the loaded boron:-

Different elute solutions suggest good elution efficiencies for B e.g. dilute HCl, H₂SO₄ and NaOH. In the present work, the loaded Amberlite IRA743 was subjected to selective elution process of B by using hot H₂O to regenerate B(OH)₄⁻ anion species depending upon the high solubility of borate ions in distilled water (Lahoda et al., 1995)⁽¹⁸⁾. The loaded resin when treated with hot H₂O or very weak acid solution is being regenerated to its original structure as illustrated in the Fig. (15).

For this purpose, suitable volume of 100 mL hot distilled H₂O was used at working flow rate of 1mL/min to remove almost loaded B. This is because, B(OH)₄⁻ anion species form slightly weak complexes with sorbitol hydroxyl groups of Amberlite IRA743. The eluate solution fractions each of 10mL bed volumes were collected to determine their boron content and to calculate the corresponding elution efficiency as plotted in Fig.(16). The obtained product was achieved through an evaporation process and then identified by means of XRD as shown in fig. (17).

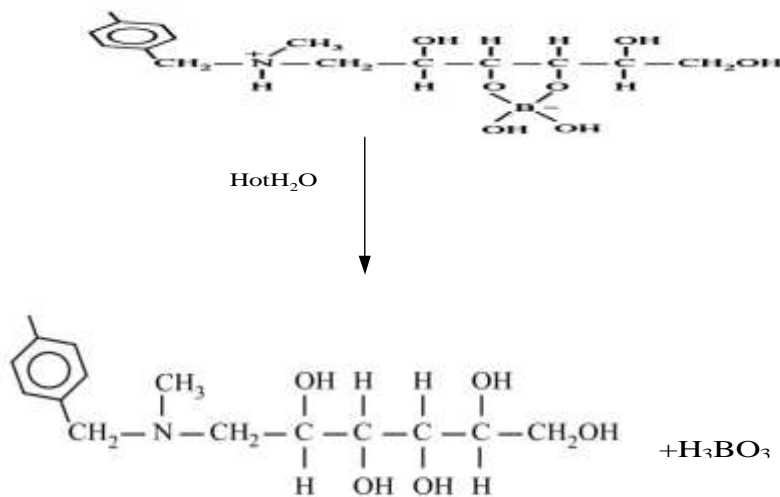


Fig. (15):- A Schematic diagram showing boron elution mechanism from the loaded resin.

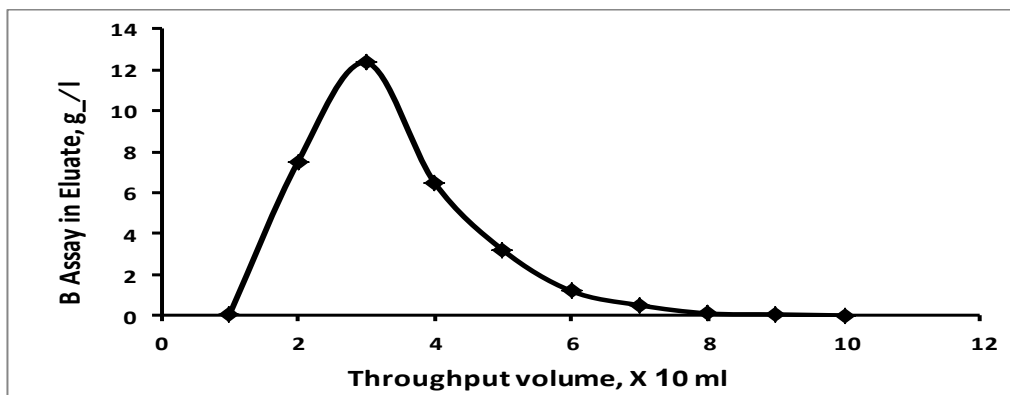


Fig.(16):- Boron elution curve of 40 ml saturated Amberlite IRA 743resin bed

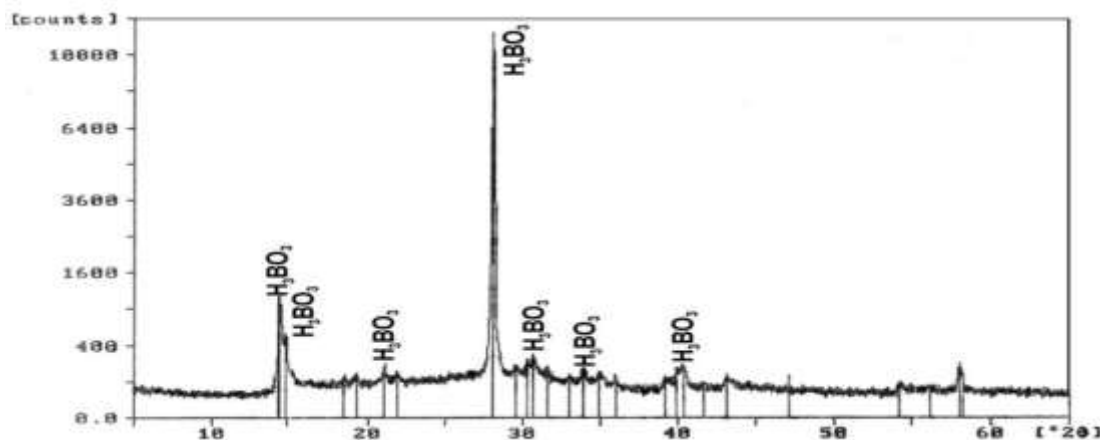


Fig. (17):- XRD pattern of obtained pure boric acid (H_3BO_3).

Conclusions:-

U, REE, Cu, Zn and Al leaching have been achieved upon their acidic leach liquor of the original raw ferruginous gibbsite-bearing shale of SW Sinai by using H_2SO_4 acid. The optimum leaching conditions were 200 g/L H_2SO_4 ; a solid/liquid ratio of 1/4, 4h and a particle size of -200 mesh, gave leaching efficiencies of about 100% for uranium and 88 % for REEs, 68.57 % for Cu, 66.52 % for Zn and 37.51 % for Al.

On the other hands, the remaining boron content which was left behind in the spent residue would be recovered via alkaline roasting process. From the two adequately obtained leach liquors, marketable products have conveniently been prepared.

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