RECOVERY OF CU, REES, U AND V FROM ABU ZIENEMA POLY-MINERALIZED CARBONACEOUS SHALE ORE MATERIAL, SOUTHWESTERN SINAI, EGYPT

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Abstract

Recovery of separated pure concentrates of Cu, REEs, U and V from sulfate leach liquor of southwestern Sinai poly-mineralized ore material was carried out by using different extraction techniques namely; cementation, direct precipitation and ion exchange. These techniques were applied upon the prepared sulfate leach liquor which assaying in g/L: 3.4 Cu, 0.33 REEs, 0.92 U, 0.19 V when using the optimum conditions of H$_2$SO$_4$ acid pug leaching (1.35 ton H$_2$SO$_4$/t ore, at 110°C as curing temperature and 2 h as a curing time). A tentative flow sheet for the overall treatment of Abu Zienema poly-mineralized ore material was also presented.

Keywords: Carbonaceous shale, Copper, REEs, Uranium, Vanadium, Leaching, Ion exchange.

Introduction

Abu Zienema area is situated at southwestern Sinai between longitudes 33° 20’ to 33° 25’ E and latitudes 29° 00’ to 29° 05’ N. Alloga carbonaceous shale facies of Um Bogma Formation is considered as one of the most important occurrences of U mineralization in Abu Zienema area. It is characterized by the presence of some interesting metal values namely; U, Cu, V, B, Ln, Zn, Co, Ni...etc. (EL Assy et al., 1986, 1996; Abdel Moneim et al., 1997; Al Shami, 2003).

Several recovery studies have been performed upon comparable Abu Zienema ore material from different locations, but with different constituents and grades of the economic metal values using either acidic or alkaline methods Amer (1993, 1997); Amer et al. (2000 &2010); Abdel Fattah (2003); Abdel Moneim (2005); El-Hazek et al. (2008);
Abdellah (2009 &2014); El-Sheikh et al. (2012a, b); El-Sheikh et al. (2015) and Abu khoziem (2017).

For Cu recovery, it is worthy to mention that, extraction of Cu from oxidized ores is quite different from those employed for the sulfide ores. The oxidized ores, consisting of the silicates, carbonates and sulfates, are treated by several methods. All involving leaching of the crushed ore with sulfuric acid to produce impure solutions of copper sulfate. The most important extraction techniques include adsorption (Morcali et al., 2014); chemical precipitation (Alonso-Gonzlez et al., 2013); ion exchange (Jun-jie et al., 2010); reverse osmosis (Csefalvay et al., 2009) and electrodialysis (Peng et al., 2011). Today, more than 13% of all copper is produced from leachates, which are normally concentrated using solvent extraction (SX) and stripped of their copper content by conventional electrowinning (EW), the so-called SXEW process.

Modern methods of extraction allow economic leaching and electrowinning of Cu from low-grade ores and extraction techniques are continuously being refined and developed to achieve the most efficient removal of Cu from a wide variety of ores from sources around the globe. Cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solutions and it is also used in electrowinning of metals to purify the leach liquor from impurities before electrolysis to produce a pure metal which does not need further refining (Bockman and Ostvold, 2000 a, b; Boyanova et al., 2004; Mubarak et al., 2004; Casaroli et al., 2005; Ahmed et al., 2011 and Nassef and El-Taweel, 2015).

On the other hand, for REEs recoveries various developed separation techniques of REEs from their leach liquor were employed namely; fractional crystallization, fractional precipitation as well as solvent extraction ion exchange and direct precipitation (Panturu et al., 2000 ; Zhou et al., 2007, Fernández and García, 2008, and Ahmed et al., 2015). The precipitation of REEs has been developed using oxalic acid (Habashi, 1993; Gupta and Krishnamurthy, 2005 and Khawaskek et al., 2015). This method is considered as a better method to produce rare earth oxalate precipitate free from the undesired sulfate and phosphate ions as well as separating from the majority of accompanying and troublesome elements as iron, aluminum, nickel, chromium, manganese, zirconium, hafnium, uranium, zinc and copper.

With respect to extraction of uranium from sulfate leach liquors several techniques such as direct precipitation, solvent extraction (SX) and ion-exchange (IX) were used. The choice of an economic suitable technique depends upon many factors such as the concentration of uranium in the
leach liquors, the amount and the concentration of the co-dissolved impurities as well as upon the desired final uranium product purity (Beltrami et al., 2013).

The U anion complexes in acidic solutions are directly precipitated by neutralization in two subsequent steps by using the suitable alkaline reagents e.g. NaOH, Ca (OH)$_2$, Mg(OH)$_2$ and NH$_4$OH. Hydrogen peroxide would be used to precipitate U in very high purity products. H$_2$O$_2$ has also become an important precipitating agent due to the superior physical properties of the precipitate. The uranium precipitation via H$_2$O$_2$ is more selective and has maximum recovery with minimum impurities. Precipitation of uranium as uranium tetrafluoride was also employed; almost complete precipitation of U (99.5%) was attained by using HF at pH 1.5 with stirring time 2h at room temperature (Sil1, 1987; Mousa et al., 2013 and Abdellah and Abu Khoziem, 2015).

For V recovery, the above mentioned extraction techniques were used for the recovery of V from the leach solutions. These techniques aim to selectively extraction of V and to obtain a concentrated V effluent. The ion exchange process is useful for the extraction of vanadium from the low V concentration leach liquors (Tokuyama et al., 2003; Zeng et al., 2009; Hu et al., 2009; Li et al., 2009; Xuewen et al., 2010 and Mingyu et al., 2011).

The present work aims to recovery some of the present valuable metals such as Cu, REEs, U and V with the highest possible purity from the study ore material. To achieve this goal, sulfate leach liquor was prepared from the study poly-mineralized ore sample using the pug leaching method (H$_2$SO$_4$ acid amount 1.35 ton H$_2$SO$_4$/t ore, at 110 °C as curing temperature and 2 h as a curing time). The produced pregnant solution assaying in g/L: 3.4 Cu, 0.33 REEs, 0.92 U, 0.19 V.

**Experimental**

**Analytical methods**

An atomic absorption spectrometer model (Unicame 969) fitted with the corresponding lamp was used for Cu, V, Co and Ni analyses at λ 365.4, 334.4, 271.5 and 360.1 nm respectively (Weltz and Sperling 1999). A spectrophotometric method was used for REEs determination where REEs formed stable colored complexes with Arsenazo III in weakly acidic media. In this method, the pH is adjusted at about 2.6 and the absorbance measured at wavelength 650 nm against a reagent blank solution using a double-beam UV-Visible Shimadzu (model 160A) spectrometer (Marchzenko,1986). For uranium analysis, an oxidometric
titration method against NH$_4$VO$_3$ was used in the presence of diphenyl amine-4-sulfonic acid sodium salt as indicator (Mathew, 2009). Concerning, the pure obtained products of Cu, RE$_2$O$_3$, V$_2$O$_5$ and U$_3$O$_8$ as well as the picked mineral grains, scanning electron microscope (SEM-EXL 30 Philips type) coupled with X-ray analyzer (EDX unit system) was used for conducting semi-quantitative analysis of the prepared products of Cu metal, RE$_2$O$_3$, U$_3$O$_8$ and V$_2$O$_5$.

Separation and extraction techniques
In these processes, the prepared sulfate leach liquor was firstly used to recover Cu through its precipitation as Cu metal using Fe powder. To optimize this process, different experiments were carried out to determine the amount of the added Fe powder, pH, reaction time and precipitation temperature. The Cu-free leach liquor was then subjected to the separation of REEs from U and V via their selective precipitation as oxalates by using 10% oxalic acid solution at ambient temperature at proper pH. The leach liquor free from either Cu or REEs was then subjected to fluoride precipitation of U using HF acid to produce uranium oxiflouride which associated with Al and Ca. The latter were removed by dissolving the former in a mixture of (NH$_4$)$_2$CO$_3$/NH$_4$HCO$_3$ solution.

An ion exchange resin Amberlite IRA$_{400}$ in its sulfate form was used for vanadium concentration and separation from the sulfate leach liquor free from Cu, U and REEs. For this purpose, a proper glass column was used and packed with 5 mL wet settled resin (wsr) of Amberlite IRA$_{400}$ at the working flow rate of 0.5 ml/min. The collected effluent solutions of 50 mL bed volumes were analyzed for vanadium and its extraction efficiency was calculated. The V loaded resin after washing with distilled water, was then subjected to the elution process to regenerate loaded vanadium. The latter was regenerated by using 100mL of 4% H$_2$SO$_4$ at the applied flow rate of 1mL/min. Fractions of 10mL bed volumes were collected and its vanadium content was estimated to determine its relative elution efficiency. The eluate rich vanadium fractions were then subjected to V precipitation by using NaOH solution at pH of 2.5.

Results and Discussion
Leaching process
A sulfate leach liquor of the provided Abu Zienema working ore material was prepared by using optimum conditions of H$_2$SO$_4$ acid pug leaching (1.35 ton H$_2$SO$_4$/t ore, at 110°C as curing temperature and 2 h as a curing time). After filtration and washing, the total volume of the obtained sulfate
leach liquor was adjusted to be 1.6 L/0.25Kg ore. The produced sulfate leach liquor was found to assay in g/L: 3.4 Cu, 0.33 REEs, 0.92 U and 0.19 V, figure (1). These obtained results indicate that the leach liquor has a specific relativity of major anions expressed essentially as SO$_4^{2-}$ (79 g/L) and to a lesser extent PO$_4^{3-}$ (30 mg/L).

![Chemical composition of the prepared Abu Zienema sulfate leach liquor](image)

**Fig. 1.** Chemical composition of the prepared Abu Zienema sulfate leach liquor.

**Selective extraction of Cu by using cementation process**

Copper was first recovered from the prepared sulfate leach liquor via its precipitation as copper metal by using cementation process. Cementation process can be described as electrochemical precipitation of a metal by another more electropositive metal. This process is one of the most effective and economic techniques for recovering valuable metals from industrial leaching solutions (Sousa et al, 2007). Cementation method has some advantages, such as recovery of metals in relatively pure metallic form, simple control requirements, low energy consumption and is in general low cost process. In this context, iron has been chosen as a sacrificial metal because of its availability and its low cost. The cementation of copper from the prepared sulfate aqueous solution is described by the reaction:

$$\text{Fe}^0_{\text{(powder)}} + \text{Cu}^{2+}_{\text{(aq)}} \rightarrow \text{Cu}^0_{\text{(cemented metallic copper)}} + \text{Fe}^{2+}_{\text{(aq)}} \quad (1)$$
The effective parameters of the optimum conditions of the cementation of copper from its sulfate leach liquor are pH values, reaction time, reaction temperature, and amount of Fe powder added respectively.

**Effect of pH value**

The effect of pH on the precipitation efficiency of Cu was studied at pH values ranging from 0.5 up to 2 by the addition of NaOH pellets to five prepared sulfate leach liquors. The other factors were kept constant at 7% excess stiometric amount of Fe powder with stirring time for 1h at 70 °C as precipitation temperature. From data summarized in Fig.2a, it's clearly evident that the extraction efficiency of Cu was increased from 92.5% to its maximum value of 99.5% by increasing the pH value from 0.5 up to 0.7 and then decreased to 78.9% with increasing the pH value to 2. This phenomenon may be attributed to the dissolution of the sacrificial metal into the solution, more critical at low pH values (pH 0.5) (Panão Ana et al., 2007). In addition, an increase of the pH values may cause the passivation of iron due to the precipitation of the metal hydroxides on its surface (Jackson, 1986). Therefore, pH value of 0.7 represented the optimum value for complete precipitation of Cu.

![Fig. 2. Effect of pH value (a), reaction time (b) temperature (c) and Fe powder dose added on Cu²⁺ precipitation efficiency (d).](image-url)
Effect of reaction time
To study the effect of reaction time upon the extraction of Cu from its sulfate leach solution, a number of cementation experiments were performed for a time varying from 30 up to 120 min. The other factors were kept constant at pH 0.7 and 70 °C with 7% excess stabiometric amount of added Fe powder. The obtained data show that almost complete cementation of Cu (99.6%) takes place after 30 min as shown in Fig.2b. This may be attributed to the fact that cementation reactions mostly follow first order kinetics and takes place rapidly (Agrawal and Kapoor 1982; Demirkiran et al., 2006; Ahmed et al., 2011; Nassef and El-Taweel, 2015).

Effect of temperature
The effect of temperature upon the precipitation efficiency of Cu was studied at different temperatures, 25±5, 60, 70, 80 and 90 °C while the other factors were fixed at 7% excess amount of Fe powder with stirring time 30 min and pH value 0.7. The obtained data (Fig.2c) shown that the reaction rate increases with the increase in temperature. Firstly, the raise of the temperature favours cementation kinetics, and also augments the amount of Cu removed, that the efficiency of Cu precipitation increased from 79.9% to 99.6% by increasing the temperature from room temperature up to 70 °C while more increasing in temperature has no effect on Cu precipitation (Amin et al., 2007; Nassef and El-Taweel, 2015).

Effect of amount of surfactant (Fe powder) added
Aqueous sulfate solutions, each composed of 100 mL of 3.4 g/L copper of pH 0.7 were shaken for 30 min. at 70 °C with different iron powder ratio in the range of 0.25–1 g. The results presented in Fig. 2d indicate that the cementation percent increases with the increase of iron ratio and a maximum cementation value of 99.6% was reached when using 0.3 g iron powder for each 100mL of sulfate leach liquor.
From the obtained results, it can be concluded that the optimal cementation conditions (pH 0.7, 30 min. 70 °C and Fe dose 0.3 g/100 mL sulfate solution) resulted in 99.6% precipitation efficiency of Cu. The obtained Cu product was confirmed by means of EDX analysis (Fig.3a) which show the purity of the recovered copper powder reaches 99.2%.
Fig. 3. Energy depressive X ray analysis (EDX) of the obtained Cu metal (a), impure total REEs concentrate (b) and purified total REE oxide concentrate (c).
Direct precipitation of REEs:
The reduced Cu-free leach liquor was then subjected to the recovery of the total REEs through its selective precipitation as oxalates. This is due to the fact that, REEs form stable insoluble oxalates and thus can be used for their separation (Habashi, 1993). In this regard, it has to be mentioned that the main problem during REEs precipitation as their oxalates was the co-precipitation of Fe$^{2+}$ as shown in Fig. 3. REEs were produced during Cu metal precipitation as a result of Fe$^{3+}$ reduction to Fe$^{2+}$ by adding Fe powder. Therefore, an oxidation step by using H$_2$O$_2$ was firstly applied to the reduced leach liquor to oxidize Fe$^{2+}$ to Fe$^{3+}$ prior to the REEs precipitation (Abdellah, 2009 and Xie et al., 2014). Therefore, a 10% oxalic acid solution was used for this purpose to attain almost complete precipitation of REEs at pH 1.1 after 45 min. stirring time at room temperature. These conditions represent the optimum conditions for the REEs precipitation. The following equation illustrates the precipitation reaction:

$$2\text{REE}^{3+} + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{RE}_2(\text{C}_2\text{O}_4)_3 + 6 \text{H}^+ \tag{2}$$

The obtained RE-oxalate cake was then dried at 120 °C and ignited to obtain their oxides at 850 °C for 2 h. The latter was confirmed by means of EDX analysis to identify the associated impurities, Fig. (3b&c)

Direct precipitation of uranium
After almost complete removal of copper and REEs from the prepared pregnant sulfate leach liquor, the latter was then subjected to the recovery of uranium (IV) as uranium tetra-fluoride. In this regard, almost complete precipitation of U (99.5%) was attained by using HF at pH 1.1 with stirring time of 2h at room temperature. The precipitate after filtration and washing was then subjected to EDX qualitative analysis as shown in Fig. (4a & b). The latter proved that the obtained uranium concentrate contains 59.6% U, 13.5% Al, 13.2 Ca and about 8.4% Fe. The obtained impure uranium oxy-fluoride cake was then subjected to further purification by dissolving it in mixed ammonium carbonate/bicarbonate solution. In this treatment, U would dissolve as carbonate complex while Fe, Ca and Al would remain insoluble as illustrated in the following equation:

$$\text{UO}_2^{2+} + \text{CO}_3^{2-} + 2\text{HCO}_3^- \rightarrow [\text{UO}_2(\text{CO}_3)_3]^+ + \text{H}_2\text{O} \tag{3}$$
The following conditions represented the optimum dissolution conditions for dissolving 98.5% of the U content from their combined Al-Fe fluoride cake (Abdellah and Abu Khoziem, 2015): (NH$_4$)$_2$CO$_3$/NH$_4$HCO$_3$ weight ratio is 3/1, (NH$_4$)$_2$CO$_3$/NH$_4$HCO$_3$ concentration 150 g/L, leaching time 2 h, leaching temperature 80 °C and solid/liquid ratio of 1/5.

The obtained carbonate solution of uranium was then boiled for suitable period of time to get rid of its carbonate and ammonium contents while uranium was directly precipitated as hydrated UO$_3$. After filtration and washing the obtained UO$_3$ cake was dried, ignited at 850 °C to produce U$_3$O$_8$ as shown in Fig. 4b.

![Fig. 4. Energy depressive X ray analysis (EDX) of the impure U concentrate (a), the obtained highly pure U$_3$O$_8$ (b) and the obtained V$_2$O$_5$ (c).](image)
Extraction of vanadium:
Amberlite IRA\(_{400}\) anion exchange resin in its sulfate form was used for concentration and separation of V (0.175 g/L) from the sulfate leach liquor free from Cu, REEs and U after its oxidation to its pentavalent state V (V). The extraction process of V from the sulfate solution involves two main subsequent stages namely; loading and elution.

Loading process of vanadium
In the present work, 1100 mL of the prepared leach liquor was passed through a resin column packed with 5 ml wrs at a working flow rate of 0.5 mL/min. at pH value 2.5. The obtained effluents were collected every 50 mL for V analysis. From the obtained results (Fig. 5a) it is evident that, the amount of the loaded V was 0.1612g with the loading efficiency of 82.66%. The relatively lower uptake of V upon the working resin was actually due to the competition of some anions in the resin sites especially SO\(_4^{2-}\) and Fe (SO\(_4\))\(_{2}^{2-}\) ions. Finally, the saturated resin was then rapidly washed with distillated H\(_2\)O to remove the remains of loaded materials before the elution process.

![Loading Efficiency vs. Fraction no.](image1)

![Vanadium conc. g/L vs. Fraction no.](image2)

**Fig. 5.** Vanadium Uptake by Amberlite IRA\(_{400}\) anion exchange resin at pH 2.5 and flow rate of 0.5 mL/min (a) and Vanadium elution from the loaded Amberlite IRA\(_{400}\) using 4 % H\(_2\)SO\(_4\) at flow rate of 0.7 mL/min and10 mL bed volume(b).

Elution process of the loaded vanadium
Elution process is not only used to regenerate the loaded resin but also to prepare a concentrated solution suitable for the subsequent precipitation process of the element. In the present work, the loaded Amberlite IRA\(_{400}\)
was eluted by using 4 % H₂SO₄ acid to obtain vanadium. For this purpose 100 mL of 4 % H₂SO₄ acid solution at flow rate of 0.7 mL/min was used. The eluate fractions each of 10 mL bed volumes were collected to determine its V content. The corresponding elution results were shown in Fig. 5b. From this figure, it was found that, V was eluted with elution efficiency of 96.7 %.

Finally, the eluate sulfate solution which assays 2.1g/L of vanadium was used to prepare the final vanadium product. However, 70 mL of vanadium rich solution was firstly oxidized by the addition of 0.2g NaClO₃ and then adjusted to pH 2.5 by using NaOH solution. Complete precipitation of V₂O₅ (98.3 %) as a red cake was obtained at 75 ºC after 2h stirring time. The product was then filtrates and washed with distilled water to remove the associated salts. The obtained red cake was then dried in the oven at 120 ºC for a suitable period of time. The latter was identified by means of EDX analysis as shown in Fig. 4c. Chemical analysis of the final product of (V₂O₅) proved the purity of 87.8 % with associated impurities of 8.1% Fe and 5.7% Na.

\[
2\text{VO}^{3+}(\text{aq.}) + 2\text{H}^+ (\text{aq.}) \rightarrow \text{V}_2\text{O}_5 + \text{H}_2\text{O} \quad (4)
\]

A generalized technical flowsheet summarizing the applied successive unit operations for the preparation of separated concentrates of Cu metal, REEs, U and V oxides schematically shown in Fig. 6.

**Conclusion**

Sulfate leach liquor was prepared by applying a sulfatization roasting process upon the study Abu Zienema poly-mineralized carbonaceous shale ore material. This pregnant leach liquor assays in g/L: 3.4 Cu, 0.33 REEs, 0.92 U, and 0.19 V while 0.03 for Co and 0.06 for Ni. Different extraction techniques were applied for the recovery of the metals of interest in highly pure forms.

**Acknowledgements**

Deep appreciation is due to **Prof. T. E. Amer**, Vice president of production sector for ores processing (NMA) for providing the working sample, faithful discussion during the progress of the present work, continuous help, valuable advices and critical reading of the manuscript. Also, the author is greatly indebted to **Dr. W. M. Abdellah** for his valuable advices, continuous help in the accomplishment of this work.
Abu Zienema carbonaceous shale ore material

\((2.4\% \text{ Cu, } 0.22\text{REEs, } 0.62\text{ U}\% \text{ and } 0.13\% \text{ V})\)

Fig. 6. Proposed technical flowsheet for processing of Abu Zienema carbonaceous shale ore material
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استخلاص النحاس، العناصر الأرضية النادرة، اليورانيوم والفانديوم من خامه الطفل الكربونية متعدده التعدينات بابو زنيمة جنوب غرب سيناء- مصر

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تهدف الدراسة الحالية إلى استخلاص كلا من عنصر النحاس والعناصر الأرضية النادرة واليوانيوم والفانديوم من خام الطفل الكربونية من منطقة العلوجه بابوزنيمه جنوب غرب سيناء- مصر.

وقد توصلت الدراسة إلى استخدام طريقه الاذابه بالتحميص للظروف المثلى للاذابه وتم تحضير محلول حامل لعناصر الاستخلاص بالتركيزات الاتيه:

3.4 جرام /اللتر للنحاس و 0.33 جرام /اللتر العناصر الأرضية النادرة و 0.92 جرام /اللتر اليورانيوم و 0.19 جرام /اللتر الفانديوم.

ثم استكملت الدراسة استخلاص هذه العناصر بطرق مختلفه فتم اولا استخلاص النحاس بطريقة الاكسدة/ الاختزال باستخدام بودره فلز الحديد وتباعد الخطوات لترسيب العناصر الأرضية النادرة عن طريق الترسيب المباشر باستخدام 10% حمض الاوكسالات وتم الحصول على اليورانيوم عن طريق الترسيب المباشر باستخدام فوق أكسيد الهيدروجين ثم استخلاص الفانديوم باستخدام الراتنج الأيوني.

وأخيرا تم التوصل إلى تصميم لوحة البيانات الخاصة بتشغيل خامة الطفل الكربوني بابو زنيمة.