

Liquid-liquid separation of Cd (II) from Cu-sulfide cake prepared from sulfate solution of Abu-Thor ore material, Southwestern, Sinai, Egypt

Elham Awny Gamil

Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt.

Abstract: The present work is concerned with the subsequent liquid-liquid separation of Cu, Zn, and Cd compounds from Cu-sulfide cake prepared from the sulfate solution of Abu-Thor Gibbsite-bearing shale ore material. This ore was found assaying 0.014% of Cd, 0.5% of Cu, and 0.55% of Zn as the elements of interest, by using 25% of H₂SO₄ solution at a solid/liquid ratio of 1/3 reaction time of 90 min at a temperature of 80 °C. About 96.5% of Cu (II), 99.3% of Cd (II), and 95.6% of Zn (II), respectively, were dissolved. After filtration, the prepared sulfate solution was treated with a suitable weight of Na₂S to prepare the working Cu-sulfide cake, which was then wholly re-dissolved in 10% of H₂SO₄ solution to prepare the working sulfate solution, which contained the elements of interest. This solution was gone out to the organic solvent process for complete separating between the Cu (II), Zn (II) ions in the organic phase, and Cd (II) ions in the aqueous phase. The effective extraction parameters such as pH value, LIX concentration, contact time, and organic/aqueous ratio were studied. The obtained data cleared that the pH value of 2.5 was found effective for separating Cd (II) in the aqueous phase and both Zn (II) and Cu (II) in the organic phase. Where Cd (II) ions were precipitated as CdS using Na₂S solution at pH 0.89, on the other side, both Zn (II) and Cu (II) were completely separated in the stripping process using Na₂CO₃ solution.

Keywords: Abu-Thor ore materials; Ion exchange; Organic solvent; Solvent extraction.

1. Introduction

Egyptian U and Cu-U mineralized ores of Um-Bogma Formation southwestern Sinai, Egypt was studied by many authors ^{1,2}. Recently ³ postulated that the Carboniferous strata bound Cu and U in the form of Cu-carbonate, chloride, silicate, sulfate, and phosphate minerals of supergene origin concentrated by pathogenic processes and latosol formation. Such U and Cu-U mineralized ores have been leached with sulfuric acid, as reported by ⁴.

Consequently, the concentration and purification of Cu were performed by either extraction with organic solvents or electro-winning. It was proved that solvent extraction is one of the most effective, simple, intensive, and applicable methods used for Cu (II) extraction from aqueous solutions in hydrometallurgical processes ^{5,6}. In this context, different oxime-based extractants. g. LIX 84 and LIX d973N were used to recover and purify Cu (II) from sulfate solutions. Also, several published papers have been stated the selective extraction of Cu (II) from aqueous solutions using different types of LIX extractants at other conditions ⁷⁻¹¹. Also, was successfully used the Schiff base 4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole for separating and determination of Cu (II)

from acetate buffer solution at pH 4.2, where Cu (II) complex with the ligand is instantly extracted into chloroform and shows maximum absorbance at λ_{max} 414nm which remains stable for >48h ¹². This reagent forms a yellow-colored complex with Cu (II) metal ion in acetate buffer solution at pH 4.2, where Cu (II) complex with the ligand is instantly extracted into chloroform and shows maximum absorbance at λ_{max} 414nm, which remains stable for >48h. Under optimal conditions, Cu (II) complex in chloroform adheres to Beer's law up to 17.5 $\mu\text{g}\cdot\text{mL}^{-1}$ of Cu (II), the best concentration range obtained from Ring boom's plot is from 5 $\mu\text{g}\cdot\text{mL}^{-1}$ to 17.5 $\mu\text{g}\cdot\text{mL}^{-1}$. On the other side, The synthesized chromogenic sulfur-containing reagent, 4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole was successfully applied for the determination of Cu (II) metal ion in various synthetic mixtures, complexes, fertilizers, environmental samples such as food samples, leafy vegetables, and water samples.

Moreover, developed a rapid and simple spectrophotometric method for separating and determination of Cu (II) using synthesized *N''*, *N'''*-bis [(E)-(4-fluorophenyl) methylidene]thiocarbonyl hydrazide [bis (4-fluoroPM)TCH] ¹³. The reagent is highly sensitive, and it forms a yellow-colored ternary

*Corresponding author: Elham Awny Gamil

Email address: Elhamawny76@yahoo.com

DOI: <http://dx.doi.org/10.13171/mjc02108231573awny>

Received February 21, 2021

Accepted March 21, 2021

Published August 23, 2021

complex with Cu (II) in the presence of pyridine in the acidic pH range. The absorption of the colored complex in amyl acetate is measured with reagent as a blank at λ_{\max} 375 nm. Beer's law was obeyed in the concentration range from 2.0 to 14 $\mu\text{g mL}^{-1}$ for Cu (II)-[bis (4-fluoroPM) TCH]-Py complex. Consequently, applied the mentioned reagent for simple ¹⁴, fast, and synergistic extractive spectrophotometric determination of Cd (II) metal ion, which forms stable faint yellow-colored ternary complex at room temperature with reagent and pyridine at pH 4.0. The absorbance of the colored organic layer in isoamyl acetate is measured spectrophotometrically at λ_{\max} 390 nm against the reagent blank. Beer's law is obeyed in the concentration range 10–40 $\mu\text{g mL}^{-1}$ of Cd (II) and optimum range of 15–35 $\mu\text{g mL}^{-1}$ of the metal as evaluated from Ring boom's plot.

In addition, applied a simple and selective spectrophotometric method for the determination of Cu (II) with 1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2,4-dinitro APTPT] as a chromogenic reagent based on extracting with forming green colored ternary complex in the pH range 8.7–10.5. The maximum absorption of the colored complex was attained at λ_{\max} 445- 645nm in chloroform against the reagent blank ¹⁵. Beer's law was followed in Cu (II) concentrations ranged between 10–80 gmL^{-1} and 20–70 gmL^{-1} , respectively.

Cadmium metal and salts have gained significant importance due to their wide applications in civil and navy purposes and the nuclear field. It is characterized by its ability to absorb thermal neutrons during the chain reaction inside the nuclear reactors. Cadmium is comparatively rare in almost Zn ores which are distributed in all Sinai ores, and Pb-Zn deposits, which are distributed along the Red Sea coast. About

0.1% of Cd and 15.3% of Zn were estimated in Pb- Zn deposits at Um-Gheig ore martial. Red Sea Coast, Egypt ¹⁶. Also, recorded 164g/t of Cd in the Pb-Zn deposits ore sample containing 0.17 % of Pb and 10.98% of Zn at Aladag ¹⁷, Turkey. Several studies were mentioned, including the leaching of Cd from both Pb-Zn deposits and Zn ores using sulfuric acid ¹⁶. However, at least 90% of Cd (II) metal ions were dissolved using 40% H_2SO_4 solution from Um-Gheig Pb-Zn deposits, Red Sea Coast, Egypt. So as too ¹⁸ dissolved about 96% of Cd from Ni-Cd scarps rechargeable batteries using 5M H_2SO_4 solution.

The goal of this work is to utilize an organic solvent, e.g., LIX973, for separating between Cd (II) metal ions and both Cu (II) and Zn (II) metal ions in sulfate solutions. Where both Cu (II) and Zn (II) metal ions were collected in the organic phase and the Cd (II) metal ions in the aqueous solution. Cd (II) metal ions were completely precipitated using Na_2S solution at pH 0.5, a pure CdS product. The novelty in this work appeared where both Cu (II) and Zn (II) were co-extracted and transferred to the organic phase. By using an alkaline solution (sodium carbonate) in the stripping process, it can be regenerate Zn (II) ions left behind Cu (II) alone in the organic phase. So it can be quickly prepared pure Zn products separated from Cu products.

2. Experimental

2.1. Chemical and mineralogical composition of ore martial

A representative sample weighted 50Kg was collected from the upper organic-rich gibbsite-bearing shale mudstone sub horizon of the latosol horizon of the Abu Thor area. A small portion of the representative quartered sample was ground and sent to Acme Labs in Canada for complete chemical composition [Table 1](#).

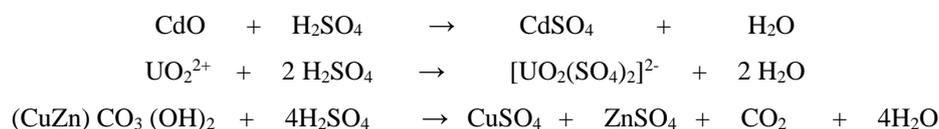
Table 1. Chemical composition of Abu Thor gibbsite bearing shale material, AcmeLabs, VAN13004169.1.

| Major oxides | Conc., (%) | Trace elements | Conc., ppm |
|--------------------------------|------------|----------------|------------|
| SiO ₂ | 40 | Co | 2700 |
| Al ₂ O ₃ | 27 | Ni | 1000 |
| Fe ₂ O ₃ | 6.87 | V | 500 |
| MnO | 1.3 | U | 400 |
| ZnO | 0.68 | ∑REEs | 356 |
| CuO | 0.62 | Cd | 140 |
| K ₂ O | 0.62 | | |
| CaO | 0.45 | | |
| MgO | 0.4 | | |
| PbO | 0.36 | | |
| Na ₂ O | 0.24 | | |
| total loss in ignition | 20 | | |
| Total | 98.54 | | |

The Si content was estimated using a UV-vis spectrophotometer (Shimadzu 610) at λ_{\max} 640nm according to ¹⁶⁻²⁰ at Nuclear Materials Authority analytical laboratories. While the mineralogical composition was also performed at Nuclear Materials Authority analytical laboratories, it was found to contain different Cu, Zn, and U minerals such as zippeite, ($K_4(UO_2)_4(SO_4)_4(OH)_{10}.4H_2O$) [Card No., 8-138], atacamite ($Cu_2Cl(OH)_3$) [Card No.,23-948], paratacamite ($Cu_2(OH)_3Cl$) [card No.,23-947] rosasite ($(Cu.Zn)_2CO_3(OH)_2$, [Card No.,17-216], calcite, ($CaCO_3$) [Card No., 5-586], and dolomite, ($CaMg(CO_3)_2$. [Card No., 11-78] ³. There are no actual minerals recorded for Cd, which presented as adsorbed on Zn minerals. It is a new approach to illustrate some results in the experimental section.

2.2. Instrumentations

The elements of interest Cd, Cu, Zn, and other elements, e.g., Ni, Co...etc. The flame atomic absorption (FAAS) was determined during



2.4. Preparation of (Cu-Zn-Cd) sulfide cake and recovery of U

Copper (II), Zn (II), and Cd (II) ions in the prepared sulfate solution could be easily separated by the addition of a suitable weight of Na_2S at $pH \leq 1.2$ and stirring for 30 min at room temperature. After thickening, filtration, and washing, an appropriate weight of sulfide cake, including the elements of interest, was prepared. The sulfate solution free from Cu (II), Zn (II), and Cd (II) ions were oxidized on heating using H_2O_2 solution to convert the reduced U^{4+} to U^{6+} and adjusted to $pH 1.7$. The oxidized U

experimental procedures, Unicam 969- United Kingdom. In contrast, the relative elemental concentration of the final products was identified by (SEM- EDAX & XRD), PHILIPS - Japan. The pH values of the aqueous solutions were adjusted with a pH meter (Digimed DM-21).

2.3. Preparation of pregnant sulfate solution

The pregnant sulfate solution was prepared via leaching 500 g of the ore material using 25% H_2SO_4 solution at S/L mixed ratio of 1/3 and temperature of 80°C at the leaching time of 90min. After washing and filtration, 2L of sulfate solution ($pH 0.22$) was yielded. The resulted sulfate solution was found assaying 1.12g/L of Cu (II), 1.14 g/L of Zn (II), 0.033g/L of Cd (II), and 0.096 g/L of U (VI) with maximum leaching efficiencies of 92%, 96%, 96%, and 95%, respectively. The expected chemical reactions are illustrated in the following equilibrium equations:

sulfate solution was then passed through a column packed with 5 mL of wet settled resin (wsr) anion exchanger resin, Amberlite IRA₄₀₀ at a flow rate of 1mL / min for extracting the present uranyl sulfate anion complex, $[UO_2(SO_4)_2]^{2-}$. The loaded resin was then washed with distilled water to eliminate the adsorbed impurities and treated with 1N NaCl solution acidified with 0.2M H_2SO_4 to regenerate U. The elute solution rich in U was treated with NaOH solution to precipitate yellowcake of $Na_2U_2O_7 \cdot xH_2O$. This yellow cake is illustrated in the following equation. This yellow cake was identified with SEM, as appeared in Fig. 1.

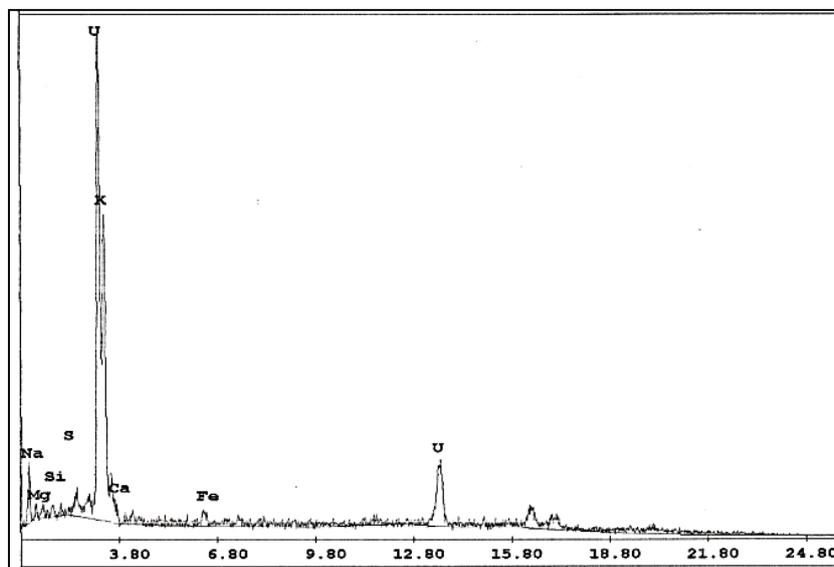


Figure 1. SEM-EDAX chart for identification of the produced yellow cake

2.5. Preparation of [Cu (II), Zn (II), Cd (II)] sulfate solution

A weight of 1.65g of the deride (Cu-Zn-Cd) sulfide cake was already treated with 100 mL of 10% H₂SO₄ solution and stirred for 30min at 50-60°C. After



The prepared sulfate solution was then directed to solvent extraction step for co-extracting of Zn(II),

washing. Filtration about 500 mL of sulfate solution was prepared and already analyzed to estimate Cu (II), Zn(II), and Cd(II) metal ions concentrations as represented in Table 2, the expected reaction equation was:

and Cu (II) ions using LIX973 in the organic solution and left behind Cd(II) ions in the aqueous solution:

Table 2. Chemical composition of sulfide cake sulfate solution.

| Metal ions | Conc., g/L |
|------------|------------|
| Cu (II) | 2.25 |
| Zn (II) | 2.28 |
| Cd (II) | 0.9 |
| Fe (III) | 0.06 |
| Pb (II) | 0.0001 |

2.6. Optimization of Solvent extraction of Cu (II) and Zn (II)

The solvent extraction process was performed using laboratory separating funnels utilizing LIX973. Several parameters such as: pH value, (0.8-2.5), organic solvent concentration (1-5%), contact time. (5-30min) and organic/aqueous mixed ratio (1/3.....1/1...3/1) were studied for optimizing the solvent co-extraction process of Cu (II) and Zn (II). On the other hand, the loaded organic solvent was directed to the stripping process using different stripping agent's solutions for regenerating the loaded Cu (II) and Zn (II) ions. This process was already optimized via investigating different effective factors such as types of different stripping agents, e.g. (0.5M of H₂SO₄, HCl, NaOH & Na₂CO₃) and concentration of stripping agent, (0.5 - 5 M), contact time (5-10min), and finally the mixed aqueous/organic ratio, (1/3.....1/1...3/1). Frankly, all the experimental procedures were done at room temperature using 10mL of the sulfate solution, where the FAAS was used for the determination of Cu (II), Zn (II), and Cd (II), which are the elements of interest. Cd (II) ions are left behind in the sulfate solution after performing the step of solvent extraction where Zn (II) and Cu (II) ions were concentrated in the organic phase. The sulfate solution rich in Cd (II) ions was then used for preparing the Cd product.

3-Results and discussions

3.1. Solvent Co-extraction of Cu & Zn and preparation of CdS

Copper (II) and Zn (II) ions in the prepared sulfate solution could be effectively co-recovered and wholly separated from Cd ions via organic solvent extraction process using the selective organic solvent, LIX97,

where the effective parameters were studied as follow:

At first, the more effective pH values factor was studied by varying the acidity of sulfate solution from pH 0.8 to 2.5 by mixing the organic solvent of 2% concentration and the aqueous solution in O/A ratio of 1/1 and shaking the mixtures for 10min. After separating in the separating funnel and analysis Cu (II), Zn (II), and Cd (II) ions, the elements of interest in the aqueous solution. The resulted data, Fig. 2, revealed that both Cu and Zn extraction efficiencies increased and attained the maximum values (73 & 68%, respectively) at pH 2.5 without any remarkable extraction of Cd (II) ions¹². So it is possible to apply the acidity of sulfate solution at pH 2.5, which already served the separation process between Cd (II) ions in the aqueous solution and both Cu (II) and Zn (II) in the organic solution. On the other hand, the other effective parameter, LIX973 concentrations, was investigated for improving the extraction efficiencies of Cu (II) and Zn (II) in the range of 1 to 5% at the fixed other parameters, which are O/A ratio of 1/1, pH 2.5, and shaking time of 10min. The obtained data (Fig. 3) showed that both Cu (II) and Zn (II) extraction efficiencies increased directly and achieved 90.8 & 81.7%, respectively, by utilizing LIX973 concentrations of 5%. The obtained data are logical due to expanding the extraction sites of the organic solvent toward the extractive species of both Cu (II) and Zn (II) ions by increasing their concentration. The effect of contact time was studied by varying the periods from 5 to 30min using 5% LIX973 at pH 2.5 and O/A ratio of 1/1. The plotted results (Fig. 4) indicated that the maximum of Cu (II), Zn (II) extraction efficiencies (95.9% & 90.8, respectively) were achieved at a contact time of 20min where there is no consideration.

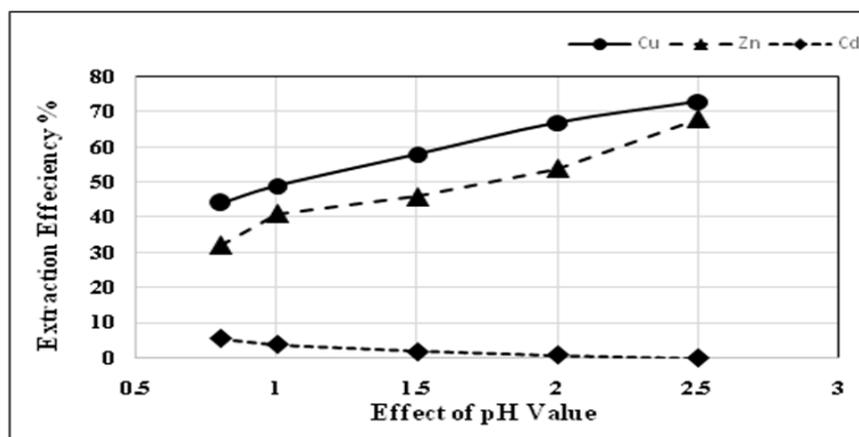


Figure 2. Effect of pH value upon Cu (II) and Zn (II) extraction efficiency, %

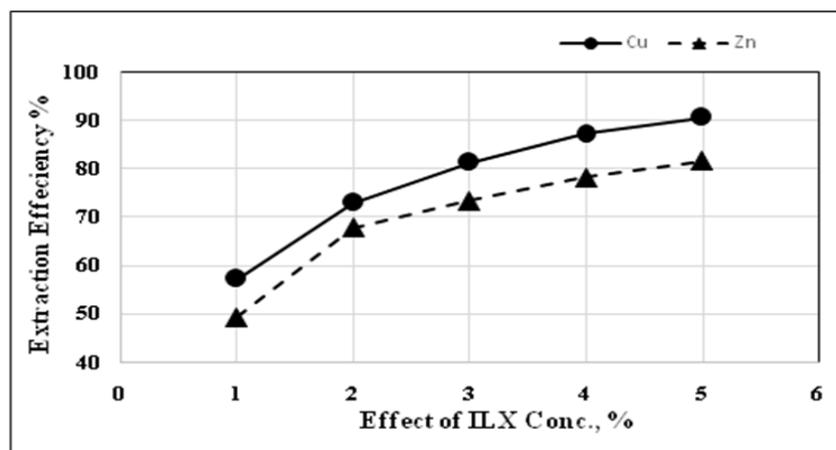


Figure 3. Effect of LIX973 concentration upon Cu (II) and Zn (II) extraction efficiency, %

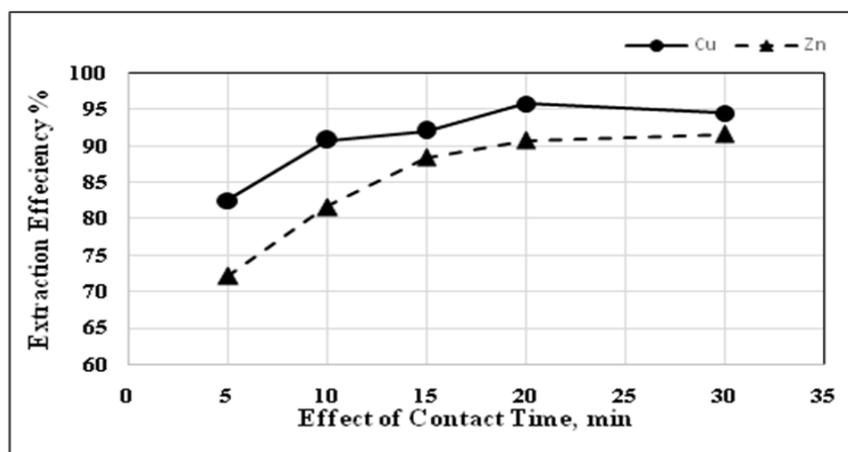


Figure 4. Effect of LIX concentration upon Cu (II) and Zn (II) extraction efficiency, %

Improvement has been occurred by increasing the contact time. Finally, the investigation of the O/A ratio effective parameter was performed by mixing 5% LIX973 with the sulfate solution (Ph 2.5) at different O/A ratios ranged between 3/1,.. 1/1...1/3 at 20 min contact. The resulting data were found in Table 3, representing the equilibrium state between organic and aqueous phases. It was observed from Table 3. However, the O/A ratios of 3/1 and 2/1 gave

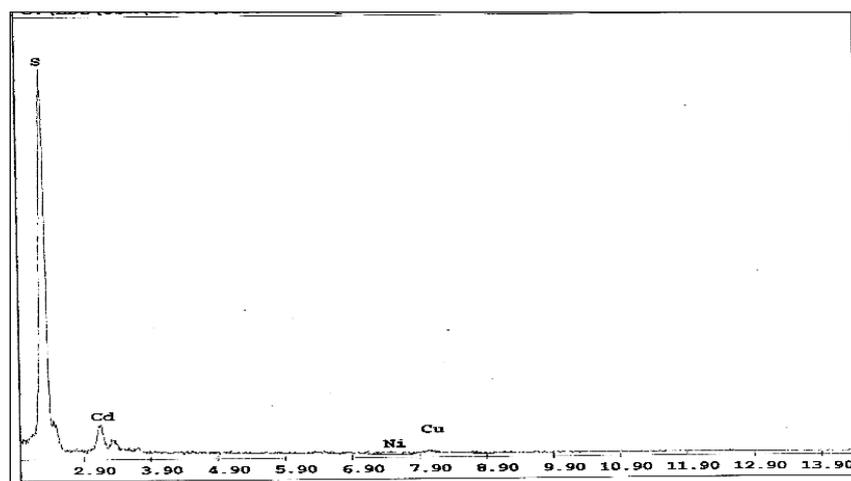
Cu (II) and Zn (II) extraction efficiencies (99.4 & 96.6 and 97.2 & 94.3, respectively) which are more than that of O/A ratio 1/1, (95.9% & 90.8, respectively) but they are not applied because they are yielded diluted Cu (II) and Zn (II) ions in the organic solution. In the meantime, O/A ratios of 1/3 and 1/2 Cu (II) and Zn (II) extraction efficiencies (66.3 & 52.6 and 88.4 & 79.4, respectively) are less than that of O/A ratio 1/1.

Table 3. Effect of O/A ratio upon Cu (II) and Zn (II) stripping efficiency, %.

| O/A ratio | Extraction efficiency, % | |
|-----------|--------------------------|---------|
| | Cu (II) | Zn (II) |
| 1/3 | 66.3 | 52.6 |
| 1/2 | 88.6 | 79.4 |
| 1/1 | 95.9 | 90.8 |
| 2/1 | 97.2 | 94.3 |
| 3/1 | 99.4 | 96.9 |

At the obtained optimum condition of all extraction parameters, about 400mL of loaded LIX973 was prepared. This organic solvent was found to contain both Cu (II) and Zn (II) ions, so it was directed to the stripping process to regenerate the loaded Cu (II) and Zn (II) ions to the aqueous solution. In the meantime, the sulfate solution free from these ions (raffinate) and concentrated with Cd (II) ions (0.88 g/L) was adjusted to pH 0.5 with few drops of concentrated H₂SO₄ and then treated with 0.25% Na₂S solution in a volume

ratio of 1/1. After stirring for 30 min at room temperature, about 99.5% of Cd (II) ions were selectively precipitated as slightly impure CdS products as equations ¹⁶⁻¹⁸. Next, the produced CdS product was carefully washed and dried to eliminate adsorbed solid salts, especially Na₂SO₄, and finally, a small amount was confirmed with SEM-EDAX, Fig. 5. On the other hand, another small amount was dissolved chemically analyzed, where it shows a purity reached 94.5% with S, Ni, and Cu impurities.

**Figure 5.** SEM-EDAX chart for confirming the prepared CdS

3.2. Investigation of the stripping parameters

Different effective parameters have been investigated to regenerate and separated between both of Cu (II) and Zn (II) ions from the loaded LIX973 through the stripping process as carried out below:

Firstly, the effective parameter, e.g., stripping reagent types, were conducted by mixing the loaded organic solvent, LIX973, and 0.5M of different reagents, e.g., H₂SO₄, HCl, NaOH, and Na₂CO₃, at A/O ratio of 1/1 and shaken for 5min at room temperature. After the separation and analysis of Cu (II) and Zn (II) and Cd (II) ions, the elements of interest in the aqueous

solution, the data obtained are presented in Table 4, highlighting that the two alkaline solutions NaOH and Na₂CO₃, were regenerated and separated between Cu (II) and Zn (II) ions by the stripping process with the best choice for the Na₂CO₃ solution. The two acidic stripping solutions H₂SO₄ and HCl, were used to extract the maximum number of two-element ions in different stripping ratios. So, it was decided to investigate the stripping process effective parameters such as Na₂CO₃ concentrations, contact time, and O/A ratio with an alkaline solution, especially Na₂CO₃ solution, because it gave Zn stripping efficiency more remarkable than that of NaOH solution.

Table 4. Effect of reagent type upon Cu (II) and Zn (II) stripping efficiency, %.

| Reagent, (0.5M) | Stripping efficiency,% | |
|---------------------------------|------------------------|---------|
| | Cu (II) | Zn (II) |
| H ₂ SO ₄ | 66.3 | 72.6 |
| HCl | 57 | 66.8 |
| NaOH | 0.68 | 46.3 |
| Na ₂ CO ₃ | 1.4 | 54.6 |

The effect of the Na₂CO₃ solution concentrations factor was studied by mixing the loaded LIX973 with Na₂CO₃ solution in different concentrations ranging between 0.5-2M at a fixed A/O ratio of 1/1 and contact time of 5min. The obtained data, Fig.6 reflected that the maximum Zn (II) stripping efficiency (82.3%) and the minimum Cu stripping efficiency (2.6%) were found at Na₂CO₃ concentrations of 2M and 1M, respectively. Thus, it was decided to utilize the concentration of 1M and try to improve Zn (II) stripping efficiency and lowering Cu (II) stripping efficiency at other stripping parameters to achieve the principal target of this work by obtaining separate pure products of these elements. On the other side, the

effect of contact time was studied in the range of periods time from 5-20 min. Data in Fig. 7 shows that the best Zn (II) stripping efficiency (92.1%) and lower Cu (II) stripping efficiency (1.41%) was given at a contact time of 10min. In addition, results in Table 5 reflect the studying data of varying different A/O ratios, (3/1.....1/1.....1/3) upon Zn (II) and Cu (II) stripping efficiencies at fixed parameters such as contact time of 10min and Na₂CO₃ concentration of 1M. This data revealed that the A/O ratio of 1/1 serves the separation process between Zn (II) (stripping efficiency 92.1%) and Cu (II) ions (stripping efficiency 2.1%) through the stripping process. It was noticed from Table 5.

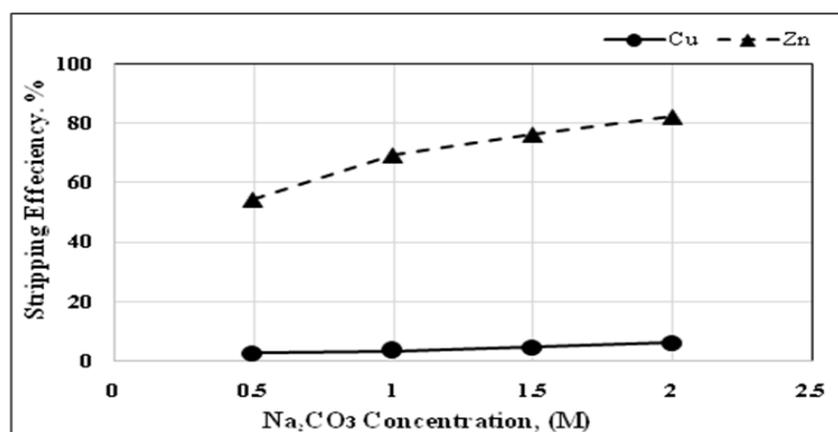
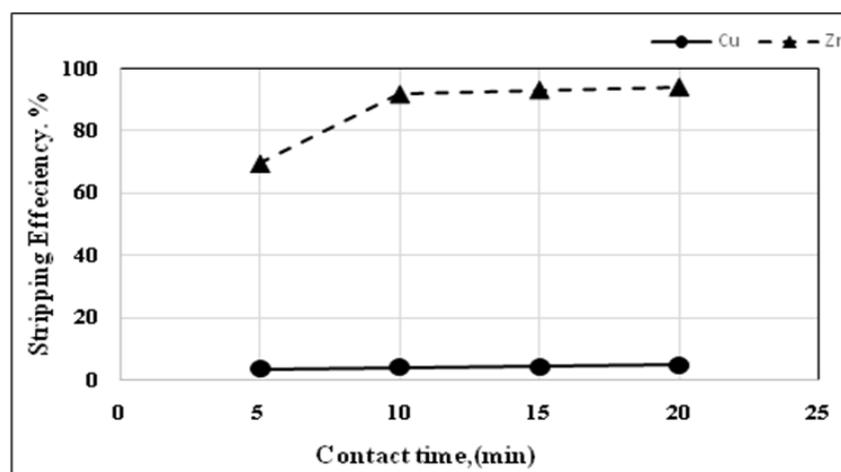
**Figure 6.** Effect of Na₂CO₃ concentration upon Cu (II) and Zn (II) stripping efficiency, %**Figure 7.** Effect of Na₂CO₃ contact time upon Cu (II) and Zn (II) stripping efficiency, %

Table 5. Effect of A/O upon Cu (II) and Zn (II) stripping efficiency, %.

| A/O ratio | Stripping efficiency, % | |
|-----------|-------------------------|---------|
| | Cu (II) | Zn (II) |
| 3/1 | 1.4 | 52.6 |
| 2/1 | 1.7 | 79.4 |
| 1/1 | 2.1 | 92.1 |
| 1/2 | 3.8 | 94.3 |
| 1/3 | 4.9 | 96.9 |

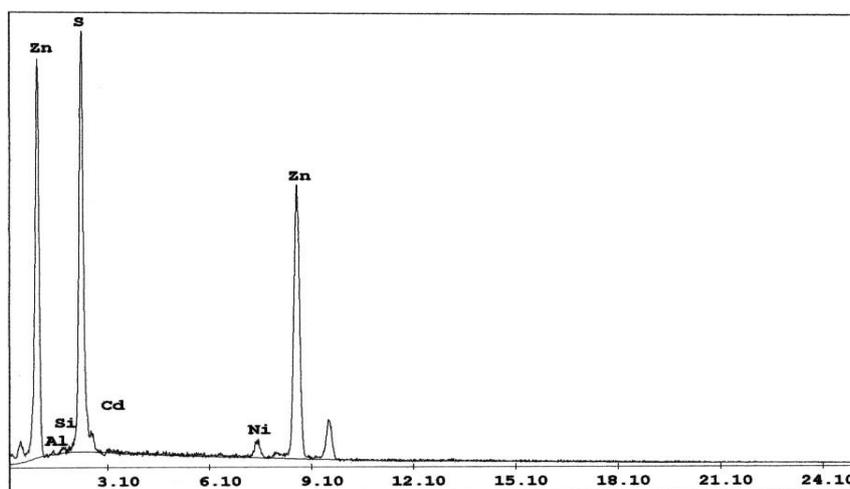
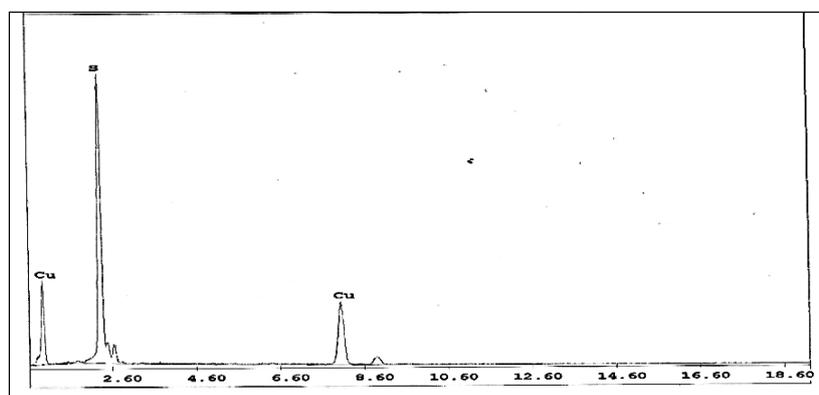
However, A/O ratios of 1/3 and 1/2 gave Zn (II) and Cu (II) stripping efficiencies (94.3 and 1.4 & 96.9 and 1.7, respectively) which are better than that of A/O ratio 1/1, (92.1% and 2.1%). Still, they are not applied because they are yielded diluted Zn (II) ions solution not favorable through the last precipitation process. In the meantime, A/O ratios of 3/1 and 2/1 represented, and Zn (II) stripping efficiencies (52.6 and 79.4, respectively) were less than those of A/O ratio 1/1.

After almost stripping of Zn (II) ions complex at the optimum stripping conditions using 1M of Na₂CO₃ solution at A/O ratio of 1/1 and contact time of 10min, the organic solvent-free of Zn (II) ions complex was treated with 1M of H₂SO₄ solution to strip the loaded

Cu (II) ions complex at A/O ratio of 1/1 and contact time of 7min. The prepared alkaline aqueous solution rich in Zn (II) ions and acidic aqueous solution rich in Cu (II) ions were directed to the precipitation process for preparing the cross ponding Zn and Cu compounds.

3.3. Preparation Zn and Cu products

The prepared carbonate aqueous solution rich in Zn (II) ions was crystallized by evaporation at 75°C and then dissolved with concentrated H₂SO₄, where the yielded Zn (II) sulfate solution (pH 0.95) was treated with 0.5% Na₂S solution in a volume ratio of 1/1 and stirred for 30min to prepare ZnS product.

**Figure 8.** SEM- EDAX chart for the identification of pure ZnS**Figure 9.** SEM- EDAX chart for the identification of pure CuS

The product was identified with SEM-EDAX (Fig. 8) and chemically analyzed, where its purity reached 94% with Cu, Na, and SO_4^{2-} impurities. On the other hand, the prepared sulfate aqueous solution rich in Cu (II) ions was treated with 0.5% Na_2S solution in a volume ratio of 1/1 and stirred for 30 min to prepare the CuS product as illustrated in equations. Finally, the product was confirmed with SEM-EDAX (Fig. 9) and chemically analyzed, where its purity reached 97.6% with Zn, Na, and SO_4^{2-} impurities.

4. Conclusions

From The Previously mentioned discussion, the agitation leaching process with 25% H_2SO_4 solution at S/L ratio of 1/3 and stirring for 90 min and temperature of 80°C was sufficient for ions Cu (II), Cd (II), Zn (II) from the representative sample of Abu Thor area West Sinai, Egypt which assaying 0.014% of Cd, 0.5% of Cu and 0.55% of Zn as the elements of interest. The resulted sulfate solution was found assaying 1.12g/L of Cu, 0.033g/L of Cd, and 1.14g/L of Zn with maximum leaching efficiencies of 92%, 96%, and 96%, respectively. This solution was used to quickly prepare a sulfide cake concentrated with almost these elements by adding a suitable weight of

Na_2S at $\text{pH} \leq 1.2$ and stirring for 30 min at room temperature.

The produced sulfide cake was dissolved entirely in 10% H_2SO_4 solution to prepare a sulfate solution assaying 2.5, 2.8, and 0.9g/L of Cu (II), Zn (II), Cd (II), respectively. This solution was adjusted to $\text{pH} 2.5$ and directed to solvent extraction step, utilizing 5% LIX973 at O/A ratio of 1/1 and contact time of 10min for separating both of Cu (II) and Zn (II) ions complexes in the organic phase and Cd (II) ions in the aqueous one. About 99.5% of Cd (II) ions were selectively precipitated as CdS using 0.25% Na_2S solution after stirring for 30 min at room temperature. Then, Cu (II) and Zn (II) ions were separated from the loaded solvent in a stripping process using 1M Na_2CO_3 solution at A/O ratio of 1/1 and contact time of 10min. Cu (II) ions were subsequently stripped using 0.5M H_2SO_4 solution at A/O ratio of 1/1 and contact time of 7min. The products, e.g., ZnS and CuS , were prepared from the prepared strip solutions using 0.5% Na_2S solution after stirring for 30 min at room temperature. A worked follow-sheet, Fig.10, was designed to process Abu Thor representative ore samples to produce Cu, Cd, Zn products, and yellowcake.

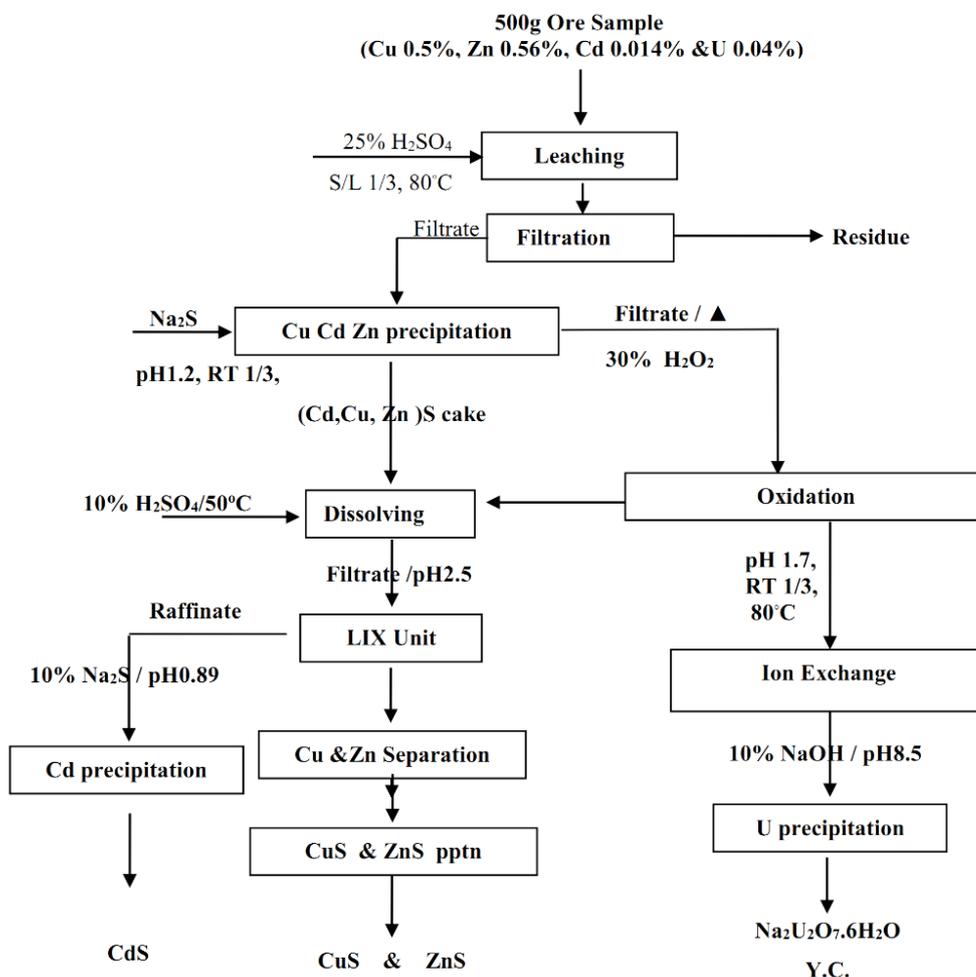


Figure 10. A worked follow-sheet for the processing of Abu Thor representative

References

- 1- M.W. El Reedy, M.A. Mahdy, I.E. El Aassy, G.A. Dabbour, Geochemistry studies of some uraniferous sedimentary rock varieties of West Central Sinai, Egypt, 4thConf. Nuc. Sci. and Appl., **1988**, 1, 224-229.
- 2- A. Abdel Monem, I.E. El Aassy, O. Hegab, I. El Fayoumy, N. El Agami, Gibbsite, uranium and copper mineralizations, Um Bogma area, Southwestern Sinai, Egypt, Sedim. of Egypt, **1997**, 5, 117-132.
- 3- H.I. Mira, S.K. Sami, Remobilization of U and Cu through karstification processes; a case study in Abu Thor locality, Um Bogma region, West Central Sinai, Egypt, Surv. Egypt, **2009**, 31, 21-42.
- 4- G.M. Abd El Wahab, M.M. Amin, S.K. Aita, Bioleaching of Uranium-bearing material from Abu Thor area, West Central Sinai, Egypt for recovering U, Arab Journal of Nuclear Sciences and Applications, **2012**, 45, 169-178.
- 5- D. Suhendra, K.P. Yeen, M.J. Haron, S. Silong, M. Basri, W.M.Z.W. and Yunus, Copper ion extraction by a mixture of hydroxamic fatty acids synthesized from commercial palm olein, solvent Extr. Ion. Exch., **2005**, 23, 713-723.
- 6- S. Feizollahi, A. Azizi, Solvent extraction of copper from an industrial sulfate liquor using Chemorex CP-150, Journal of Mining & Environment, **2018**, 4, 905-916.
- 7- A. Kumar, M. Jha, V. Kumar, L. Jae-Chun, Solvent Extraction: A Potential Tool For The Separation Of Metals From Leach Liquor Of Electronic Scraps, Proceedings of the XI International Seminar on Mineral Processing Technology, **2010**, 11, 905-912.
- 8- J. Lu, D. Dreisinger, Solvent extraction of Cu from chloride solution II: Cuprous oxidation by oxygen coupled with simultaneous cupric solvent extraction, Hydrometallurgy, **2013**, 138, 48-53.
- 9- M.C. Ruiz, I. González, V. Rodríguez alerio, R. Padilla, Solvent Extraction of Copper from Sulfate-Chloride Solutions Using LIX 84-IC and LIX 860-IC, Mineral Processing and Extractive Metallurgy Review, **2021**, 42, 1-8.
- 10- S. Keber, L. Brukner, T. Elwert, T. Kuhn, Concept of hydrometallurgical processing of a copper-cobalt nickel alloy made from manganese nodules, Chemie Ingenieur Technik, **2020**, 92, 379-386.
- 11- M.C. Ruiz, J. Risso, J. Segue, R. Padilla, Solvent extraction of copper from sulfate-chloride solutions using mixed and modified hydroxy oxime extractants, Minerals Engineering, **2020**, 146, 106-109.
- 12- U.B. Barache, A.B. Shaikh, T.N. Lokhande, G.S. Kamble, M.A. Anuse, S.H. Gaikwad, An efficient, cost-effective, sensing behavior liquid-liquid extraction and spectrophotometric determination of copper (II) incorporated with 4-(4'-chlorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole: Analysis of food samples, leafy vegetables, fertilizers, and environmental samples, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2018**, 189, 443-453.
- 13- R.A. Nalawade, A.M. Nalawade, G.S. Kamble, M.A. Anuse, Rapid, synergistic extractive spectrophotometric determination of copper(II) by using sensitive chromogenic reagent N'', N'''-bis [(E)-(4-fluorophenyl) methylidene] thiocarbonylhydrazide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2015**, 146, 297-306.
- 14- M.A. Nalawade, A.R. Nalawade, R.V. Shejwal, G.S. Kamble, Development of a reliable analytical method for the precise extractive spectrophotometric determination of cadmium(II) using chromogenic reagent: analysis of real samples, International Journal of Environmental Analytical Chemistry, **2020**, 1-20.
- 15- G. S. Kamble, S.S. Joshi, A.N. Kokare, S.B. Zanje, S.S. Kolekar, A.V. Ghule, S.H. Gaikwad, A.M. Anuse, sensing behavior synergistic liquid-liquid extraction and spectrophotometric determination of nickel(II) by using 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydro pyrimidine-2-thiol: Analysis of foundry and electroless nickel plating wastewater, Separation Science and Technology, **2017**, 52, 2238-3351.
- 16- G.M. Abd El Wahab, H.B. Zeinab, A.S. Aida, I.E. El Aassy, S.S.K. ewiseify, E.G. Awny, Sequential extraction studies of Cu, Cd and U compounds from Gibbsite-bearing shale material, Abu Thor area, Southwestern Sinai, Egypt, Journal of Scientific Research in Science, **2017**, 34, 445-461.
- 17- G. Onal, G. Bulut, A. Gul, O. Kangal, K.T. Perek, F. Arslan, Flotation of Aladag oxide Lead-Zinc ores, Minerals Engineering, **2005**, 18, 279-282.
- 18- E.M. El Sheikh, G.M. Abd El Wahab, Extraction of nickel and cadmium from scrap rechargeable Nickel-Cadmium Batteries, The 3rd international conference of inorganic chemical industries & mineral resources research division, Cairo, Egypt, **2009**.
- 19- Z. Marczenko, separation and spectrophotometric determination of elements. Second edition, Ellis Harwood, Chichester, UK. **1986**.
- 20- M.M.H. Khalil, O.M. El Hussaini, G.M. Abd El Wahab, S.K. Swafy, M.S.M. Khalafalla, Chemical Treatment of El Mossikat Fluorite-Bearing ore Material, Egypt, for Recover of pure Yttrium Oxides, Arab J. Nucl. Sci. Appl., **2018**, 89-99.