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Processing of Um-Gheig Lead-Zinc Deposits, Eastern Desert, Egypt for Separating Pure Cadmium Sulfide.

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Summary: Lead-zinc mineralization is distributed in Egypt along the Red Sea coast between El Qusier and Ras Banas. A representative sample from Um Gheig was collected and ground to -60 mesh for the mineralogical study. It contains hemimorphite ($Zn_2SiO_4.H_2O$), sphalerite (ZnS), galena (PbS), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) beside the gangue minerals gypsum ($CaSO_4.2H_2O$) and hematite (Fe_2O_3). Cadmium seems to be incorporated in the crystal structure of the zinc-lead minerals. The chemical analysis of Um-Gheig representative sample revealed that, it contains 16% zinc combined with 0.1% cadmium, 2.3% lead and 0.1% boron beside other elements.

Pug and agitation leaching were performed on samples ground to -200 mesh to achieve the maximum dissolution efficiency of cadmium with respect to other elements. Cadmium leaching efficiency reached 90% by using 40% H_2SO_4 at S/L ratio 1/2 and stirring time 2 hours at 80^o C. Cadmium was then separated as yellow precipitate of CdS from the sulfate leach liquor containing 0.9 g/l Cd, 145 g/l Zn, 0.15 g/l B and 0.01 g/l Pb. Separation of cadmium was carried out by direct precipitation using Na_2S as well as H_2S. The recovery of 94% cadmium free of zinc was achieved.

Introduction

Lead-zinc ores occur in Egypt in a few localities distributed along the Red Sea coast between El Qusier and Ras Banas. Um-Gheig Pb-Zn ore is a replacement deposit in limestone and calcareous sandstone in the basal series of the Middle Miocene rocks. The reserve of the ore deposits has been estimated by Soviet and German Experts to be about 900,000 Ton(1). As has been mentioned, zinc is a common element and cadmium is comparatively rare in almost zinc minerals. It was estimated that zinc is 200 times as abundant as cadmium. According to

Bodas[2] about 2.1% of cadmium was carried by the Zn mineral hemimorphite (15.3% Zn) in Thailand. Also, Onal et al.[3] found that 164 g/t Cd was carried by Pb–Zn ore sample containing 10.17% Pb and 10.98% Zn from Aladag in Turkey.

Cadmium metal has gained great importance due to its wide applications in civil and navy purposes as well as in nuclear field. It is characterized by its ability to absorb thermal neutrons during the chain reaction inside the nuclear reactors. It is also used in the manufacture of sheets which directed the chain reactions[4]. Moreover, cadmium alloyed with silver to be used for plating[5]. Several studies were performed upon the leaching of both Pb-Zn and Zn ores using different mineral acids[2, 6-8].

In fact, it is possible to separate Cd(II) from the acidic solutions containing Zn(II) by direct precipitation depending upon the difference in their solubility products (CdS 7.9×10^{-27} and ZnS 2.5×10^{-22})[9]. In addition, by the pH adjustment, one can achieve the complete separation between the two elements by varying the sulfide ion concentration [10]. According to Ghazy[11] the removal of Cd, Zn, Pb and Hg from drinking and sea waters was investigated using colloidal precipitate flotation with Na_2S.

Experimental

Characterization of the ore sample

A representative sample from Um-Gheig lead-zinc deposits was ground to -60 mesh and was washed completely with excess amount of tap water to get ride of slimes. The sample was allowed to dry then it was subjected to heavy liquid separation using bromoform. A small portion of the heavy fraction was ground to -200 mesh and was examined by X-ray diffraction (XRD) for the mineralogical study as shown in Figure (1) A small portion (1 g) of the ground ore sample was completely digested with mixture of acids and chemically analyzed for major and trace elements as given in Table (1).

Instruments

The elements of interest Zn, Cd, B and Pb were analyzed using flame atomic absorption spectrometry (FAAS), using Unicam 969 spectrometer at wavelengths 307.6, 228.8, 249.7 and 217 nm, respectively. The flame photometer (Sherwood Model 410) was used for the determination of Na and K at wavelengths 589 and 766 nm, respectively. In addition, the elemental relative concentration of the final products was analyzed by (EDAX-SEM), PHILIPS.

Table (1): The chemical composition of Um Gheig lead-zinc ore sample.

Major elements oxide	Concentration, (%)	Trace elements	Concentration, (ppm)
CaO	28	Ni	1200
ZnO	19.9	Cd	1000
Fe_2O_3	12	B	1000
SiO_2	2.8	P	450
MgO	4	Cu	75
PbO	2.47	Li	68
Al_2O_3	1.0	Cr	38
MnO	0.5	Ag	28
Na_2O	0.35	Ti	900
K_2O	0.15	V	15
*TLI	27	Ga	12

TLI (Total Loss on Ignition)

Processing of the representative sample

The processing of Um-Gheig Pb-Zn representative sample included leaching and the separation of the elements of interest.

Leaching

Leaching of Um-Gheig ore sample was performed using H_2SO_4 (96%) from ADWIC Company. The leaching experiments were investigated by studying the following factors; acid concentration, solid/liquid (S/L) ratio, pH value of sulfate leach liquor, stirring time and leaching temperature.

Preparation of sulfate leach liquor

In order to perform the extraction techniques of Cd from the sulfate leach liquor of Um-Gheig representative sample, it is necessary to take in consideration the economic point of view. Thus, it was decided to apply the agitation leaching technique upon 50 g of the ground ore sample for preparing the sulfate leach liquor under the optimum conditions; 40% H_2SO_4 at S/L ratio 1/2 and leaching temperature 80^{o} C for 2 hours stirring time. The prepared sulfate leach liquor was found containing 0.9 g/l Cd, 145 g/l Zn and 0.15 g/l B beside 50 g/l Fe as the major interfering element.

Separation of cadmium by sulfide anions

Separation of Cd by sulfide anions was carried out from the prepared sulfate leach liquor utilizing Na_2S solution and H_2S gas. Different factors affecting the extraction process were studied such as; pH value of sulfate leach liquor, sulfide anion concentrations and precipitation temperature.

Results and Discussion

Mineralogical study

As shown by XRD pattern represented by Figure (1), Um-Gheig Pb-Zn ore sample was found containing the following major minerals; hemimorphite ($Zn_2SiO_4.H_2O$), sphalerite (ZnS), galena (PbS), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) beside the gangue minerals gypsum ($CaSO_4.2H_2O$) and hematite (Fe_2O_3). The mineralogical study is in a good agreement with Soviet Experts results (1961)[(1)] and Atriss results (2006)[(12)]. It is worthy to mention that, Cd and B elements are not forming specified minerals but they are incorporated by substitution in the structure lattice of the Pb and Zn minerals.

Processing

Leaching

Um-Gheig ore sample was subjected to the acidic leaching using concentrated H_2SO_4 in two different techniques namely; agitation and pug leaching.

Sulfuric acid agitation leaching

Agitation leaching experiments were performed by mixing 10 g of the ground ore sample with different concentrations of H_2SO_4 with continuous stirring. Several factors influencing the agitation leaching were studied such as; sulfuric acid concentrations, solid/liquid (S/L) ratio, washing volume of the spent ore, stirring time and leaching temperature.

Effect of sulfuric acid concentration

For studying the effect of H_2SO_4 concentrations upon the leaching efficiencies of Cd, Zn and B, the ground ore sample was leached with H_2SO_4 at different concentrations ranged from 10 to 50% at S/L ratio 1/2 and 2 hours stirring time at room temperature. After washing and filtration the leach liquor was completed to 100 ml to obtain sulfate leach liquor of pH 1. The obtained data clarify that, increasing

H_2SO_4 concentration increased the leaching efficiencies of Cd from 25 to 95%, Zn from 30 to 92% and B from nil to 15%Leaching with 40% H_2SO_4 gave 95% Cd, 86% Zn and 8% B leaching efficiencies. Thus, it was thought that, these leaching efficiencies are possibly increased to levels higher than the already obtained by varying the other parameters.

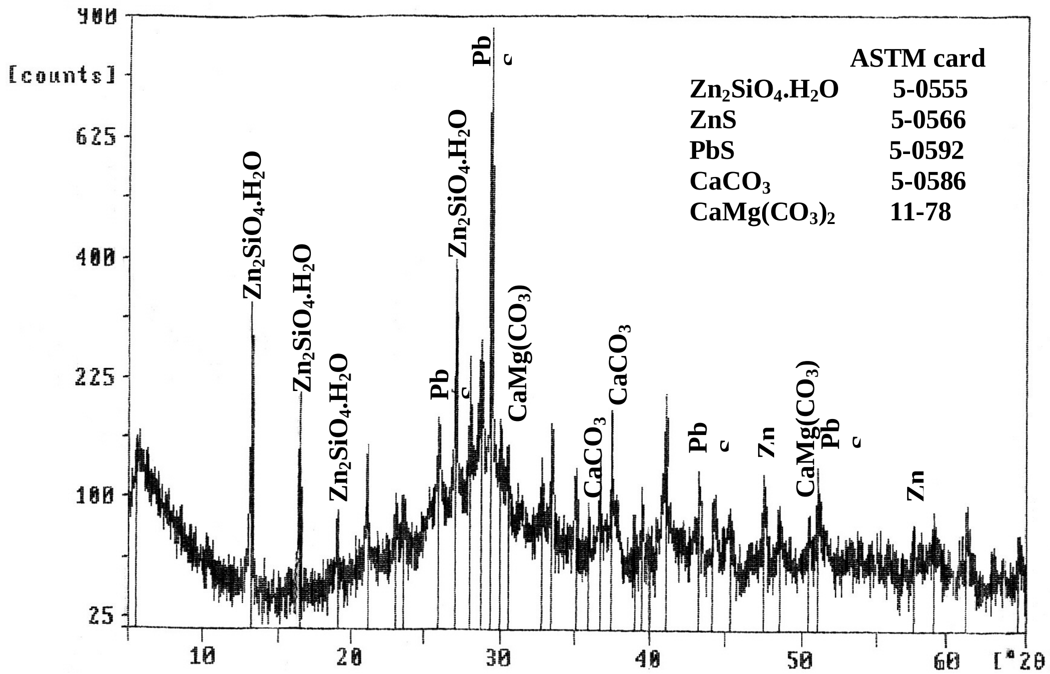


Figure (1): XRD chart for the mineralogical study of Um Gheig ore sample

Effect of solid/liquid (S/L) ratio

The effect of S/L ratio upon the leaching efficiencies of Cd, Zn and B was studied at S/L ratios ranged from 1/2 to 1/8 using 40% H_2SO_4 at room temperature and for 2 hours stirring time. The pH value of sulfate leach liquor was adjusted to be pH 1 in 100 ml volumes. It was found that increasing the S/L ratios from 1/2 to 1/8, a decrease in the leaching efficiencies occurred for Cd from 95 to 80% and Zn from 91 to 78% This may be explained by increasing the dissolution of Fe in the leach liquor (56 g/l) which affected the dissolution of both Cd and Zn as has been published by Bodas [(2)] and Bodas et al.[(13)]. On the other hand, B leaching efficiency was strongly increased from 8 to 23%.

Effect of washing volume of the spent ore

A set of leaching experiments was done by mixing 40% H_2SO_4 with the ore sample at S/L ratio 1/2 for 2 hours stirring time at room temperature. The slurries were washed with different volumes of distilled water (100, 200, 400 and 800 ml). In the mean time, the pH value of the sulfate leach liquors was varied from (1.0 to 1.8). Increasing the washing volume from (100 to 800 ml) increased the leashing efficiencies of Cd, Zn and B to 100%, 93% and 35% respectively. These results may be attributed to overcoming the interfering problems of the other elements by diluting the leach liquor.

Effect of stirring time

The effect of the stirring time upon the leaching efficiencies of Cd, Zn and B was studied under the mentioned conditions except varying of the agitation time from 1 to 8 hours. After washing the spent ore materials and filtration, the obtained sulfate leach liquors have pH 1.8. The leaching efficiencies of Cd, Zn and B raised to the maximum values; 98%, 95% and 40% at 8 hours stirring time. This indicates that increasing the contact time between the ore sample and the acid leads to increase the dissolution of the elements of interest.

Effect of leaching temperature

This factor was studied by varying the leaching temperature from 25 to 80^{o}C using 40% H_2SO_4 at S/L ratio 1/2. The pulps were stirred for 2 hours and washed with distilled water to obtain sulfate leach liquors of pH 1.8. Due to the increase in the dissolution of ore sample by heating thus the leaching efficiencies of Cd, Zn and B showed markedly improvement at 80^{o}C

Sulfuric acid pug leaching

Pug leaching was performed by thoroughly mixing 10 g of Um-Gheig representative sample with 96% H_2SO_4 and curing the slurry at slightly high temperature followed by water leaching. Many factors affecting the leaching efficiency of the elements of interest were studied namely; volumes of H_2SO_4, volumes of washing solution, curing time and curing temperature.

Effect of sulfuric acid volume

The effect of H_2SO_4 volume upon leaching efficiencies of Cd, Zn and B attained by mixing 10 g of the ore sample with different volumes of concentrated H_2SO_4; 2.5, 5, 7.5 and 10 ml. After curing the pulp at 130^{o}C for 1.5 hours, it was leached at room temperature with 100 ml distilled H_2O to have sulfate leach liquor of pH 0.8. The maximum leaching efficiencies 63% Cd, 91% Zn and 34% B were found at 5 ml of concentrated H_2SO_4. It was noticed that, the leaching efficiencies of the elements of interest decreased by increasing the acid volumes due to increase the dissolution efficiency of Fe to 70% at 7.5 ml and 85% at 10.0ml. The results are in good agreement with Fernaz, work(14).

Effect of washing solution volumes

After mixing 10 g of the ore sample with 5 ml of concentrated H_2SO_4, different volumes of distilled H_2O: 100, 250, 500 and 750 ml were used for leaching however, the pH values of the sulfate leach liquors were 0.8 ,0.9, 1 and1.2. The leaching efficiencies of Cd, Zn and B at pH 1.2 show marked improvement since they reached 98%, 92% and72%, respectively. From the obtained data, it can be inferred that, increasing the volume of washing agent turns the elements of interest to be more soluble.

Effect of curing time

Constant weights (10g) of the ground ore sample were completely mixed with 5 ml concentrated H_2SO_4 and cured at 130^{o}C from 0.5 to 2 hours. The cured samples were subjected to leaching with 500 ml distilled water at room temperature to yield sulfate leach liquors of pH 1.1. The analysis of the filtrate showed that, increasing the curing time from 0.5 to 2 hours leads to increase the leaching efficiencies of Cd, Zn and B to 91%, 97% and 74%, respectively.

Effect of curing temperature

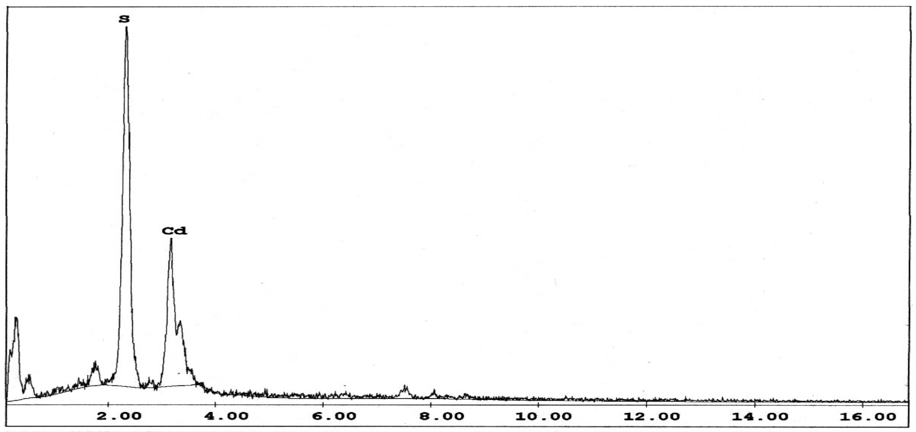
This effect was studied while keeping the other parameters of the pug leaching constant except varying the curing temperature from (80 to 160^{o}C). The obtained results emphasized that, increasing the curing temperature to 160^{o}C leads to increase the leaching efficiencies of Cd, Zn and B to be 95%, 98 % and 76%, respectively. From the economic point of view, it was necessary to use the curing temperature at 130^{o} C for saving the electrical energy.

Direct precipitation of cadmium

Cadmium was directly precipitated as CdS from Um-Gheig sulfate leach liquor containing 0.9 g/l Cd and 145 g/l Zn by using sulfide anions released from both Na_2S solution and freshly prepared H_2S gas to achieve cadmium recovery of 94% and 96%, respectively. Due to economic and environmental reasons Na_2S solution was preferred for precipitating CdS under the given optimal conditions 0.5% Na_2S solution, pH 0.82, sulfide/sulfate volume ratio1/1 at room temperature. Practically, about 200 ml of 0.5% Na_2S solution were added drop-wisely to the same volume of Um-Gheig sulfate leach liquor of pH 0.82 at room temperature. After filtration and washing the produced CdS was found to be contaminated with elemental sulfur therefore, it was washed with 20% HNO_3 to dissolve Cd ions leaving the elemental sulfur undissolved. Precipitation of Cd ions in the filtrate was performed under the previous mentioned optimal conditions. After filtration and washing with distilled H_2O about 0.11 g of CdS was recovered by decantation and analyzed semi-quantitavely using EDAX as shown in Figure (2).

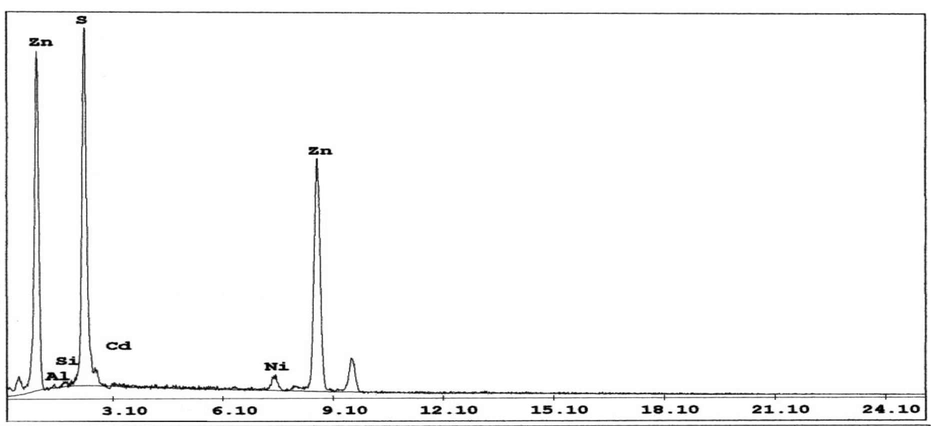
Direct precipitation of zinc

About 28 g ZnS was directly precipitated from 200 ml of sulfate leach liquor containing 145 g/l Zn and free of Cd by the addition of the same volume of 1% Na_2S solution at room temperature. However, the complete precipitation of ZnS was achieved at pH value 2.0 as has been mentioned by Eshuis et al.[(15)]. The pH value of the sulfate leach liquor was adjusted with few drops of 10% NaOH solution. After precipitation of ZnS the precipitate was washed with distilled H_2O to get rid of any impurities and recovered by filtration. The prepared ZnS was semi quantitavely analyzed using EDAX as shown in Figure (3).



Element	Wt %	At %	Z	A	F
S K	41.64	71.43	1.1049	0.7408	1.0188
CdL	58.36	28.57	0.8927	0.8216	1.0000
Total	100.00	100.00			

Figure (2): EDAX chart for identification of CdS prepared from sulfate leach liquor.



Element	Wt %	At %	Z	A	F
AlK	0.32	0.58	1.0554	0.2240	1.0040
SiK	0.45	0.79	1.0864	0.3103	1.0071
S K	30.29	46.58	1.0781	0.5249	1.0001
CdL	0.48	0.21	0.8634	0.7548	1.0000
NiK	2.36	1.98	0.9980	0.9824	1.2537
ZnK	66.11	49.87	0.9549	0.9904	1.0000
Total	100.00	100.00			

Figure (3): EDAX chart for identification of ZnS prepared from sulfate leach liquor.

Conclusions

1- Um-Gheig area is one of the highest Pb-Zn deposits distributed along Red Sea-coast in Egypt. The mineralogical study of the ground ore sample reveals that, it contains hemimorphite ($Zn_2SiO_4.H_2O$), sphalerite (ZnS), galena (PbS), calcite ($CaCO_3$), dolomite $CaMg(CO_3)_2$, gangue of gypsum ($CaSO_4.2H_2O$) and hematite (Fe_2O_3).

2- Agitation leaching with sulfuric acid was effective to dissolve Cd, Zn and B with efficiencies 100, 96 and 15% respectively. The performed optimum conditions were 40% H_2SO_4 concentration, S/L ratio 1/2, pH 1.8, 2 hours stirring time and 80^oC leaching temperature.

3- Sulfuric acid pug leaching leached 89% Cd, 97% Zn and 75% B respectively at the optimal conditions 5 ml acid volume, pH1.1, 1.5 hours curing time and 130^oC curing temperature when performed upon 10 g ore sample.

4- Obtaining higher concentrations of the leached Zn and Cd ions with fewer ions of impurities was carried out using H_2SO_4 agitation leaching.

5- Lead was remained insoluble in the residue separated from sulfate leach liquor of both agitation and pug leaching.

6- The consumption of acid by agitation leaching was 824.3 g while 892 g acid was consumed by pug leaching. The high acid consumption is mostly due to the dissolution of carbonate minerals (calcite and dolomite) as well as iron mineral (hematite).

7- Separation of cadmium as CdS was carried out from the sulfate leach liquor by direct precipitation using both Na_2S solution and H_2S gas to achieve cadmium recovery of 94% and 96% respectively. Due to economic and environmental reasons Na_2S solution was preferred for obtaining pure CdS. The performed optimal conditions were 0.5% Na_2S solution, pH 0.82, sulfide/sulfate volume ratio1/1 at room temperature.

8- Finally, a worked flowsheet was done for processing Um-Gheig ore sample to produce pure CdS and ZnS as shown in Figure(4)

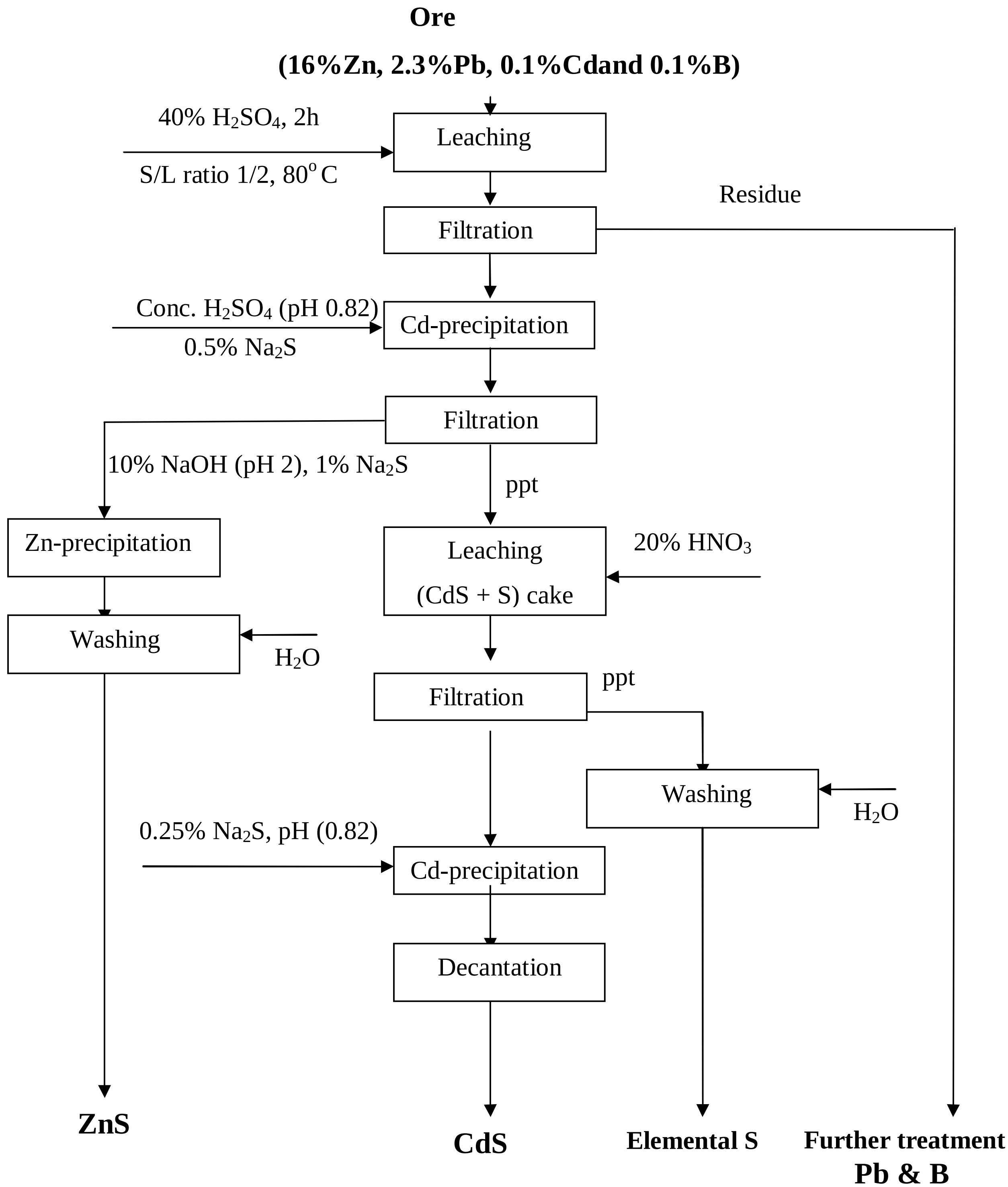


Figure (4): A worked flowsheet for separating pure CdS and ZnS from Um-Gheig ore sample

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