

Preparation and Characterization of Cadmium Oxide and some By-products from Residual Fly Ash

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Summary: The chemical analysis of residual fly ash resulted from Egyptian electrical power stations revealed the presence of some economic metals; one of the most important of them is Cd which assays 65 mg/kg as well as 45 g/kg of Zn and 48 g/kg of S. A hydrometallurgical process has been performed to prepare pure CdO together with some by-products namely; ZnS and elemental S. Leaching conditions such as: H₂SO₄ concentration, solid/liquid (S/L) ratio, leaching time and temperature were investigated to prepare suitable sulfate leach liquor. Chemical analysis of the latter shows the presence of 6.4 mg/L of Cd with achieved leaching efficiency of 99% at the applied optimum conditions.

Direct precipitation technique was conducted for the separation of (CdS + elemental S) cake from the prepared sulfate leach liquor by using 1% Na₂S at pH 0.6. The latter cake was dissolved in 10% HNO₃ solution and treated with 5% NaOH solution at pH 8.5 to precipitate Cd(OH)₂. By calcinations at 850°C for 1 h and washing, pure CdO has been prepared.

Introduction

Cadmium together with boron are the most important elements in the nuclear field industries, they are characterized by their ability to absorb thermal neutrons during the chain reactions inside nuclear reactors. Cadmium metal is utilized in the manufacturing of sheets or rods used for controlling continuous chain reaction in the nuclear reactors⁽¹⁾. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds. Generally, it is associated with zinc and copper minerals and produced as a by-product of these industries. The well-known cadmium minerals are greenockite, CdS (77.6% Cd). Other minerals are otavite, CdCO₃ (61.5% Cd), and pure CdO (87.5% Cd). Greenockite is nearly always associated with sphalerite (ZnS). Almost Cd could be produced through the mining and refining of zinc ores. The resulted Zn concentrates contain 85% ZnS, 8-10% FeS and 0.3–0.5% Cd. Cadmium can be considered as the most problematic potentially toxic element that tend to leach and accumulate in soil and plants. It enters the environment from electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides,

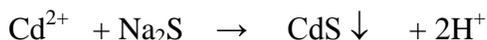
mining, pigments and dyes, textile operations and refining industries. Fly ashes contain extremely high concentrations of Cd reached 400 mg/kg ⁽²⁻⁸⁾.

Several studies were conducted concerning the processing of Cd and other valuable elements from solid wastes and some rich ores e.g. concentrated Zn ores and Pb-Zn deposits.

Boiler fly ash resulted from Egyptian electrical power stations assays 130 mg/kg of Cd beside many economic metal values e.g. V, Ni, Zn, Pb,etc. Under alkaline processing in KOH solution using KClO₃ as an oxidant up to 99% of V content was extracted with no co-extraction of Ni and Fe at the optimum conditions KOH concentration 2 mol L⁻¹ and KClO₃ concentration 2%, S/L ratio of 5/1, agitation time of 3 h, agitation temperature of 95°C and agitation speed of 600 rpm are the experimental conditions suggested ⁽⁹⁾. H₂SO₄ solution (15%) was used at the mixed S/L ratio of 1/10 and leaching time of 3 h at 50 °C to dissolve 98% of V and 96% of Ni from the carbonate matrix of the same boiler fly ash. The sulfate solution was used to prepare highly pure V₂O₅ (98.2%) and pure NiS by precipitation with H₂S solution at pH 4 and stirring for 1 h at 70 °C ⁽¹⁰⁾.

Up to 99% of the total Cd content from the Ni-Cd waste rechargeable batteries has been leached by using 6% H₂SO₄ solution at mixed S/L ratio of 1/5 and 8 h as leaching time at room temperature. The prepared sulfate solution (assaying 12.5 g/L of Cd and 60 g/L of Ni) was treated with the same volume of 0.5% Na₂S solution to precipitate pure CdS at pH 1.2 and stirring time of 1 h at room temperature ⁽¹¹⁾.

The pressure leaching of concentrated Zn-ores has been investigated by using concentrated H₂SO₄ ^(12, 13). In addition, 5 mol L⁻¹ H₂SO₄ was applied for leaching up to 95% of Zn content hosted in a ZnSiO₃ sample assaying 15.3% of Zn and 2.1% of Cd ⁽¹⁴⁾. Moreover, Cd was recovered as a yellow precipitate of CdS from sulfate leach liquor of Um-Gheig Pb-Zn deposits containing 0.9 g/L of Cd, 145 g/L of Zn, 0.15 g/L of B and 0.01 g/L of Pb ⁽¹⁵⁾.

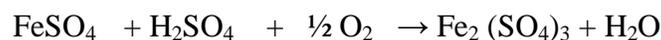
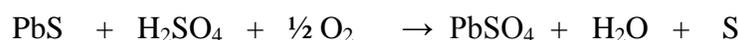


The produced CdS was then dissolved in 20% HNO₃ solution and re-precipitated to remove the co-precipitated elemental S. It is possible to separate Cd ions from sulfate solutions containing Zn or Ni ions directly by precipitation with sulfide anions depending

upon the high difference between their solubility products (K_{sp} of $\text{CdS} = 7.9 \times 10^{-27}$; K_{sp} of $\text{ZnS} = 1.6 \times 10^{-24}$); K_{sp} of $\text{NiS} = 3.2 \times 10^{-19}$)⁽¹⁶⁾.

In this context, it is worthy to mention that, excess of S^{2-} anions are always present in the sulfate solutions of Pb-Zn deposits especially that contain metal sulfides e.g. PbS and ZnS. These S^{2-} anions are oxidized in acidic solutions ($\text{pH} < 0.5$) to form elemental S. the latter is also separated through the direct pressure leaching of ZnS concentrates⁽¹²⁾.

The chemistry of this pressure leaching process is given as follow:



Finally, the present work is mainly concerned with the processing of residual fly ash that resulted from Egyptian electrical power stations for recycling of Cd and some other economic by-products e.g. ZnS and elemental S. This fly ash sample also contains considerable amounts of heavy metals such as: V, Ni, Pb and Cu.

Experimental

Materials and characterization

The working fly ash sample (2 kg) has been collected from the chimney constructed burned gases located at all the Egyptian Electric Stations. For studying its chemical composition a 1 g sample ground to a mesh size of -200 mesh was digested with the acid mixture (H_2SO_4 , HCl, HNO_3 and HF) for the complete dissociation and closed up to a volume of 100 mL and subjected to different analytical techniques to estimate its elemental chemical composition⁽¹⁷⁾.

The major oxides such as: MgO and CaO are determined via complexometric titration with standard EDTA⁽¹⁸⁾. While the major elements such as: Ni, V, Zn and Fe were determined together with the trace elements e.g. Cd, Cu, Pb, Co, ...ect by using Unicam 969 flame atomic absorption spectrophotometer, (FAAS). Elemental S was already analyzed in the solid sample by means of Energy Dispersive X-Ray Fluorescence, (EDXRF) technique.

Shemadzu 610, UV-vis spectrophotometer was used for the quantitative analysis of the total REEs using Arsenazo III at λ_{654} nm. For Si estimation, a 0.1 g of the ground sample was fused with 1 g of NaOH pellets in a nickel crucible for 20 min directly on Bunsen flame. The fused matrix was then dissolved in 1:1 HCl solution and closed up to a volume of 100 mL for Si determination at λ_{640} nm⁽¹⁹⁾. The pH values of all solutions were already adjusted with a Digimed DM-21 pH meter while the recovered products were identified by means of X-Ray Diffraction, (XRD) technique.

Optimization of agitation leaching parameters

All the agitation leaching procedures were performed by mixing 10 g of the fine ground fly ash sample (-200 mesh) with H₂SO₄ acid. Different effective leaching parameters such as: H₂SO₄ acid concentrations, solid/liquid (S/L) ratios; leaching time and the leaching temperature were investigated. The element of interest, Cd was analyzed spontaneously in all agitation leaching experiments to calculate its leaching efficiency. The pregnant sulfate leach liquor of the fly ash sample was prepared via leaching of 250 g of the latter at the obtained optimum leaching conditions. After filtration and washing with distilled H₂O, the total volume of the prepared sulfate solution was 4 liters.

Co-precipitation of (CdS + ZnS + elemental S)

The prepared sulfate solution (pH 0.34) was treated with 1% Na₂S solution with continuous stirring for 30 min at room temperature for precipitation of Cd. It was observed that Cd and Zn ions as well as elemental S were directly precipitated as a sulfide cake at pH 0.66 due to the very low concentration of Cd compared to Zn concentration. To avoid this problem the prepared sulfate solution should be treated with standard Cd solution to increase its concentration at least up to 0.093 g/L. This step helps in separation of Cd from Zn ions during the precipitation process by using Na₂S solution. However, CdS and elemental S cake was selectively separated from the prepared sulfate solution.

Separation of Cd from elemental S

CdS and elemental S cake was dissolved in 10% HNO₃ solution at room temperature, however, CdS was completely dissolved leaving behind S metal which separated by filtration. The produced Cd(NO₃)₂ solution was treated with 5% NaOH solution to precipitate Cd(OH)₂ at pH 8.5 and stirring for 1 h at room temperature. While

elemental S left behind over the filter paper was collected and washed with distilled H₂O to get rid of any adsorbed impurities to prepare pure S metal.

Direct precipitation of ZnS

The sulfate solution free from Cd was adjusted to pH 0.96 and treated with 1% Na₂S solution and stirred for 1 h at room temperature to precipitate ZnS.

Results and Discussion

Chemical composition

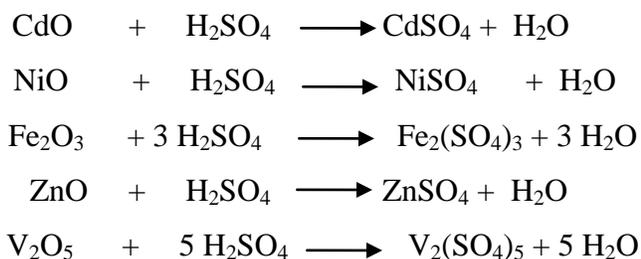
Chemical composition of the working fly ash sample, Table (1) revealed the presence of high concentrations of C, SO₃, CaO, V₂O₅, Fe₂O₃, NiO, ZnO as well as moderate concentrations of Na₂O, SiO₂ and PbO,. It also shows the presence of considerable concentrations of some valuable trace elements e.g. Cd, REEs. The obtained analysis data are most close in agreement with that obtained by ^(10, 20, 21). From the chemical composition of the studied fly ash sample, it could be concluded that it favors either acidic or alkaline leaching processes.

Table (1): Chemical composition of the studied fly ash sample.

Major oxides	Conc. %	Trace elements	Conc. ppm
SO ₃	12.00	REEs	1000
CaO	8.00	Ba	448
V ₂ O ₅	6.25	Ti	365
Fe ₂ O ₃	6.00	Co	95
ZnO	5.60	Cr	105
NiO	4.45	K	85
Na ₂ O	3.70	Cu	67
SiO ₂	3.50	Cd	65
MgO	0.90		
PbO	0.50		
*L.O.I	48		
Total	98.90		

Optimization of H₂SO₄ agitation leaching parameters

Cd as well as the other valuable metal oxides in the working fly ash sample is easily leached via agitation leaching by using H₂SO₄. Different effective leaching parameters were studied to prepare suitable leach liquor containing maximum concentration of the elements of interest. The expected chemical reactions are illustrated in the following equilibrium equations:



Effect of H₂SO₄ acid concentrations

Different concentrations of H₂SO₄ ranging from 15 to 75% were used to investigate the effect of acid concentrations on Cd leaching efficiency from the present fly ash sample. The other leaching parameters were kept constant at S/L ratio of 1/3 and agitation time of 1 h at room temperature. The obtained data, (Fig. 1), clarify that, the leaching efficiency of Cd increased from 65 to 87.5% with increasing the acid concentration from 15% to 25%. On the other hand, further increase in acid concentration resulted in decreasing Cd leaching efficiency. This may be attributed to the dissolution of some other elements such as: Ni, Fe, Zn and V.

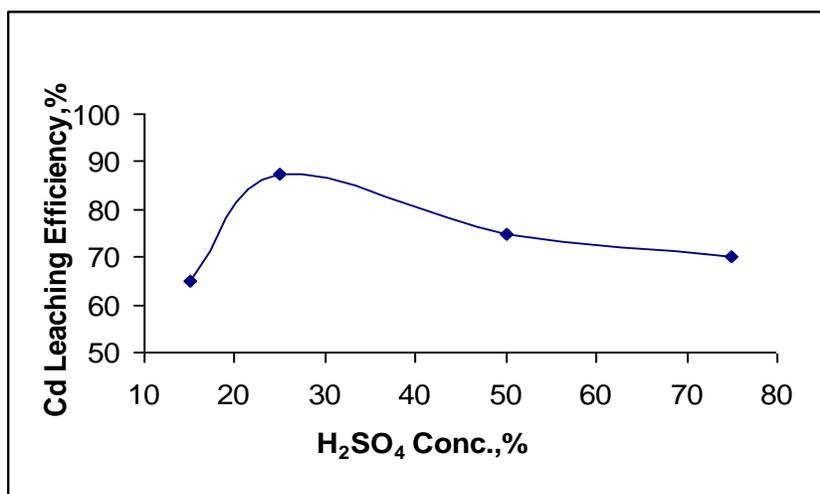


Fig. (1): Effect of H₂SO₄ concentration upon Cd leaching efficiency.

Effect of solid/liquid (S/L) ratio

This effect was studied by mixing 25% H₂SO₄ solution with the working sample at different S/L ratios ranged from 1/2 to 1/5 and stirring for 1 h at room temperature. The obtained data, (Fig. 2), indicated that, decreasing S/L ratio from 1/2 to 1/3 increased Cd leaching efficiency from 65% up to 87.5%. On the other side, further decrease in S/L

ratio more than 1/3 leads to decrease Cd leaching efficiency up to 78% due to the dissolution of some transition elements e.g. Ni, Cu, Fe, Zn.

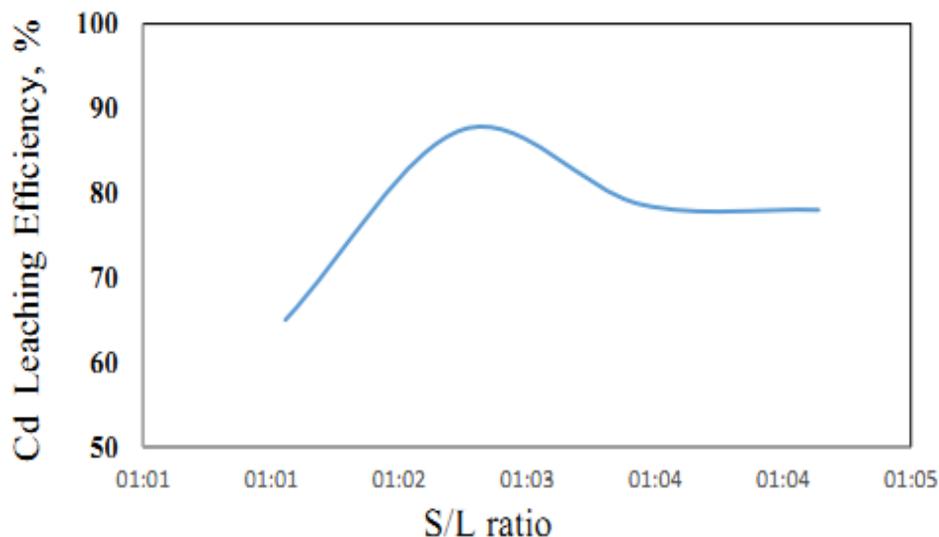


Fig. (2): Effect of S/L ratio on Cd leaching efficiency.

Effect of leaching time

This effect was studied by mixing the fly ash ore sample with 25% H_2SO_4 solution at S/L ratio of 1/3 with stirring for different time periods ranging from 60 to 180 min at room temperature. Results, (Fig. 3), revealed that, Cd leaching efficiency increased from 87.5% to 94% by increasing the leaching time from 60 to 90 min. Further increase in time to 120 and 180 min decreased Cd leaching efficiency to 90 and 88%, respectively.

Effect of leaching temperature

Fig. 4 shows the effect of changing leaching temperature from 25°C up to 100°C on Cd leaching efficiency from the working fly ash sample. The other leaching conditions were kept constant at acid concentration of 25% H_2SO_4 , S/L ratio of 1/3 and leaching time of 90 min. The obtained data shows marked increase in Cd leaching efficiency reaching 99.5% at 50°C. Further increase in leaching temperature to 75 and 100°C decreased Cd leaching efficiency to 90% due to the high dissolution of interfering elements especially Ni, V, Zn, Cu and Fe.

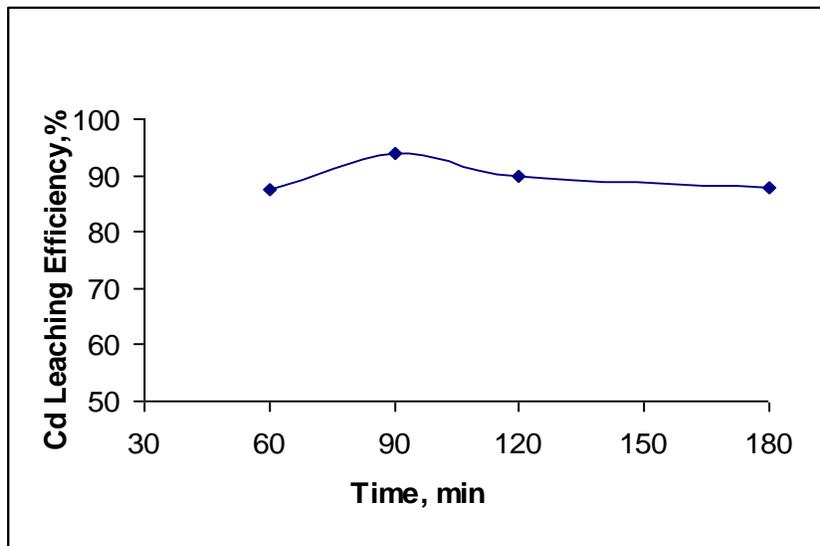


Fig. (3): Effect of leaching time on Cd leaching efficiency.

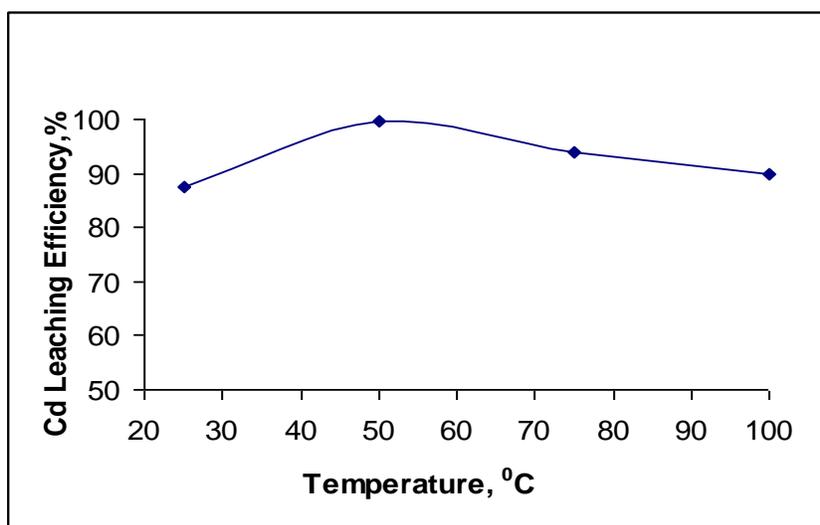


Fig. (4): Effect of leaching temperature on Cd leaching efficiency.

From the foregoing leaching study about 99.5% of total Cd content from the working fly ash sample was dissolved by using 25% H₂SO₄ solution at S/L ratio of 1/3 and stirring for 90 min at temperature of 50 °C.

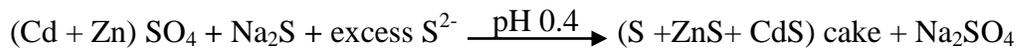
Preparation of pregnant sulfate leach liquor

Applying the above mentioned effective leaching conditions upon 250 g of the working fly ash sample, washing and then filtration yields 4 L of sulfate leach liquor (pH 0.34). The elements such as: Cd, Zn, Ni and V were already dissolved with leaching maximum efficiencies of 90, 39, 25 and 27%, respectively. The resulted sulfate solution

was found to assay 0.003 g/L of Cd, 2.38 g/L of Zn, 2.15 g/L of Ni and 2.25 g/L of V. There are also excesses of S^{2-} anions which were brought out to the sulfate solution due to the presence of some sulfide metals and elemental S in the fly ash ore sample. This solution was used to recover Cd together with the other by-products e.g. ZnS and elemental S.

Co-precipitation of CdS, ZnS and elemental S

Addition of stoichiometric amount of Na_2S solution to precipitate both of Cd^{2+} and Zn^{2+} ions in a very strong acidic media ($pH < 0.4$) was found effective to oxidize the excess amount of S^{2-} anions to elemental S^(12, 22). In the meantime, the pH value of the prepared sulfate solution increased gradually to attain pH 0.66. Thus, about 70% of Zn^{2+} ions together with 30% of Cd^{2+} ions were already co-precipitated in spite of the high difference of their solubility products, (K_{sp} of CdS = 7.9×10^{-27} and K_{sp} of ZnS = 1.6×10^{-24})⁽¹⁶⁾. This may be due to the lower concentration of Cd^{2+} ions (0.003 g/L) compared to that of Zn^{2+} ions (2.38 g/L). Indeed, that matter does not help the separation process between Cd^{2+} ions and Zn^{2+} ions as illustrated in following equation:



So, for selective precipitation of Cd, it was found necessary to increase the concentration of Cd^{2+} ions in the working sulfate solution to a suitable limit via addition of Cd^{2+} standard solution.

Selective separation of Cd & Zn via increasing Cd concentration

Fig. (5) indicates that the addition of 100 mL of standard Cd^{2+} solution, (1 g/L) would be very suitable to help in separation between Cd and Zn ions during precipitation by using Na_2S solution. Thus, the working sulfate solution which assays 0.003 g/L of Cd and 2.38 g/L of Zn at pH 0.34 was treated with 100 mL/L of Cd^{2+} standard solutions to increase its concentration to 0.093 g/L. The treated sulfate solution was adjusted to pH 0.4 followed by addition of 1% Na_2S solution in a volume ratio of 1/1.5. After stirring for 30min at room temperature, about 99.5% of Cd^{2+} ions were selectively precipitated as a mixed cake of (CdS + elemental S) leaving behind Zn^{2+} ions in the filtrate. The following equation illustrates the precipitation process.



Preparation of pure CdO and elemental S by-product

The precipitated (CdS + elemental S) cake was dissolved in 50 mL of 10% HNO₃ solution at room temperature to dissolve CdS leaving behind elemental S. The latter was recovered by filtration, washing with distilled H₂O and finally dried. The final product was confirmed by means of XRD analysis technique, (Fig. 6).

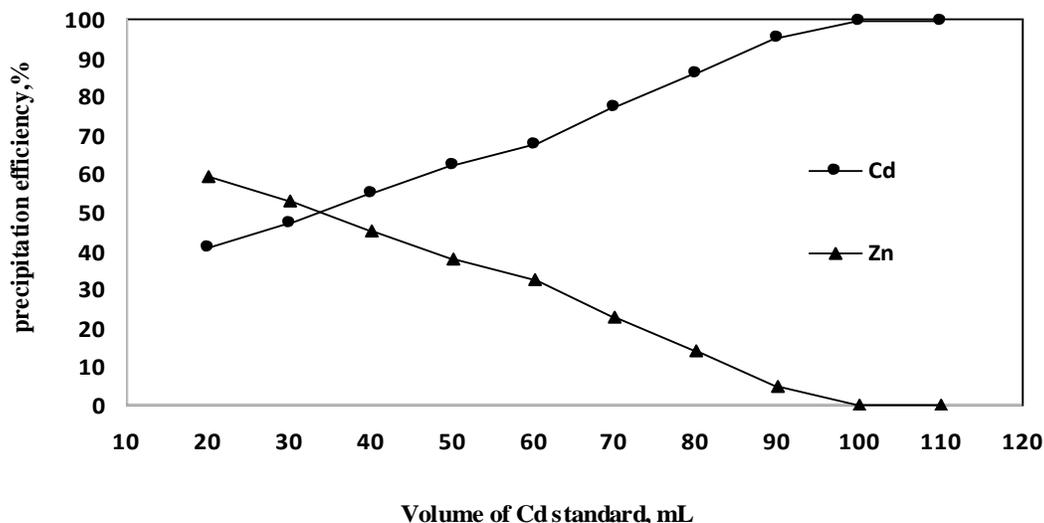
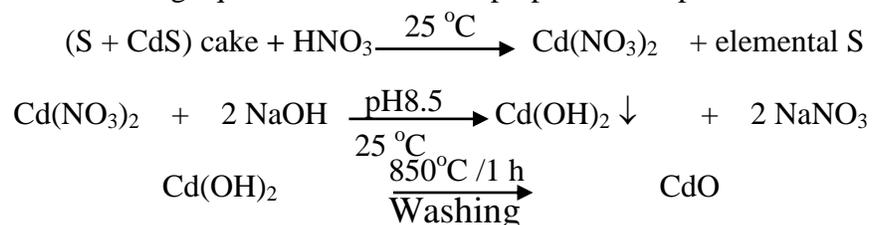


Fig. (5): Addition of Cd standard for separating Cd and Zn ions

On the other hand, the filtrate, Cd(NO₃)₂ solution was then treated with 5% NaOH solution and stirring for 1 h at room temperature till pH 8.5 to precipitate Cd⁺² ions as Cd(OH)₂. The produced Cd(OH)₂ cake was then carefully washed with distilled H₂O to get rid of any adsorbed impurities and then ignited at 850 °C for 1 h to produce pure CdO. The latter was washed, dried and then directed to XRD analysis for identification, (Fig.7). Chemical analysis of the produced CdO revealed that, it assays 85% of Cd with purity of 97.5% with some impurities e.g. 0.5% Na, 0.3% Zn, 0.015% V, 0.004% Cu and 0.05% Ni. The following equations illustrate the preparation of pure CdO.



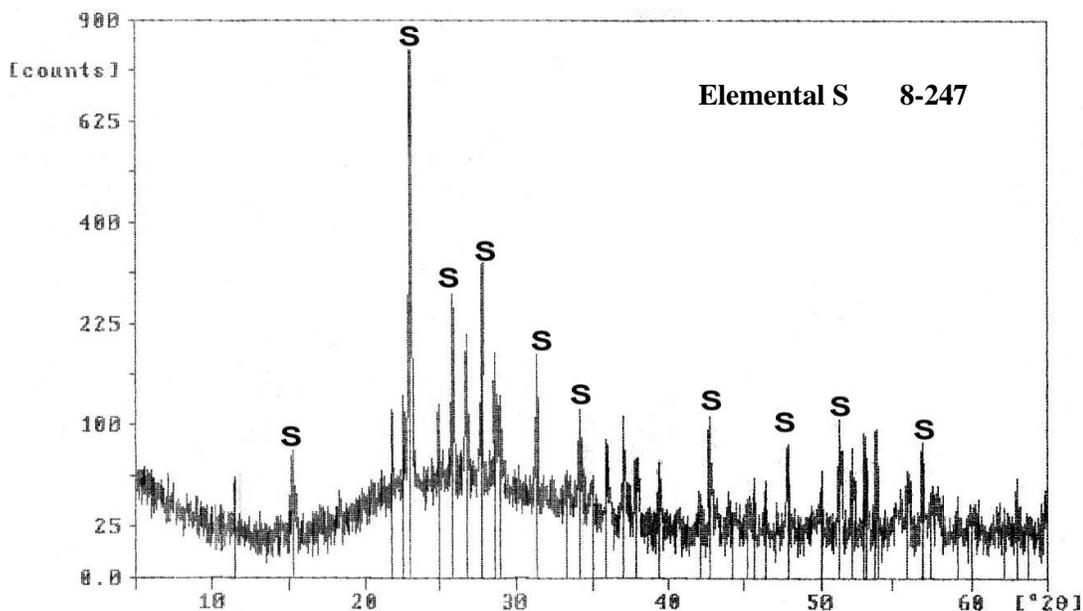


Fig. (6): XRD pattern of the prepared highly pure elemental S by-product.

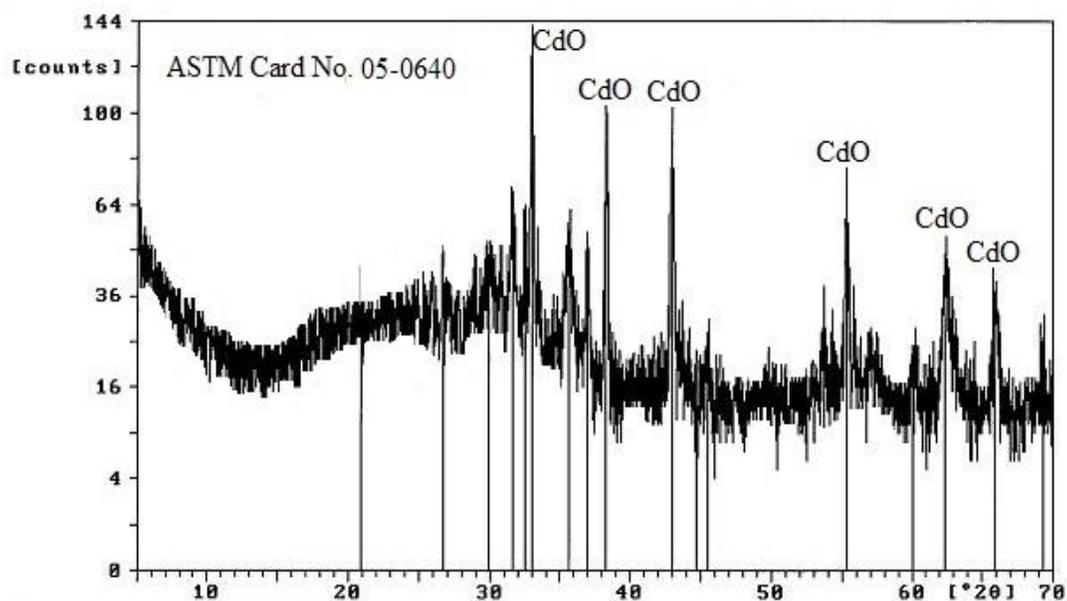


Fig. (7): XRD pattern of the prepared highly pure CdO.

Preparation of ZnS

The sulfate solution free from both of Cd and S^{2-} anions assays 0.84 g/L of Zn, 0.85 g/L of Ni and 0.9 g/L of V. This solution was adjusted to pH 0.96 and then treated with 1% Na_2S solution in the volume ratio of 1/2.5 and stirred for 1 h at room temperature. Complete precipitation of Zn^{2+} ions was achieved at pH 2⁽²³⁾. After

thickening and filtration, it was found that, a weight of 3.1 g of ZnS was precipitated realizing precipitation efficiency of 98%. After washing, filtration and drying, the product was confirmed by means of XRD analysis technique, (Fig. 8). A weight of 0.5 g of the obtained ZnS was dissolved in 50 mL of 5% HNO₃ solution to assay its purity. The obtained data emphasized the presence of 61.3% of Zn reflecting a purity of only 90% with other detected impurities include 6.3% of Ni, 0.75% of Na, 0.5% of V, 0.001% of Cd and 0.3% of Fe. The presence of Ni as the major component in ZnS precipitate is actually due to the fact that, the solubility product of NiS (alpha) ($K_{sp} 3.2 \times 10^{-26}$) is close to that of ZnS (alpha) ($K_{sp} 3.2 \times 10^{-24}$)⁽¹⁶⁾. The disappearance of NiS in the XRD pattern is due to its lower concentration.

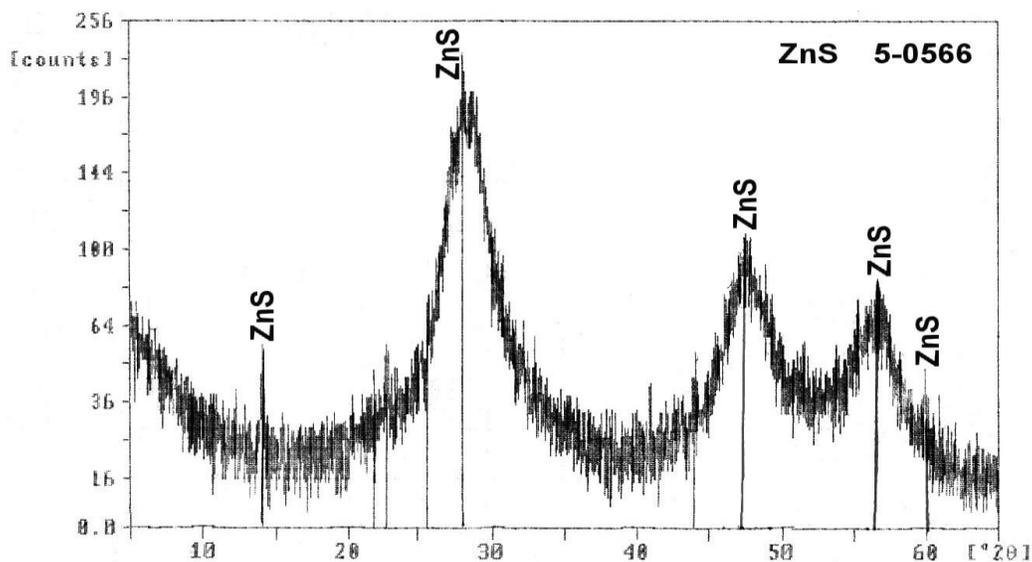


Fig. (8): XRD pattern of the prepared ZnS by-product.

Conclusion

The potentiality of preparing highly pure CdO as well as the by-products of elemental S and ZnS from the residual fly ash sample collected from Egyptian Power Stations is described. However, the acidic agitation leaching was effectively applied to dissolve Cd and Zn with achieved leaching efficiencies of 99 and 39 %, respectively. On the other hand. Direct precipitation processes were applied to recover the above mentioned metals of interest. It is very important to mention herein that, a part of the produced CdO is used to increase Cd ion concentration in the working sulfate solution to help in separating of Cd from Zn ions. Finally, the obtained data was used to design a

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flow-sheet (Fig. 9) which describes the processing of residual fly ash sample for recovering of Cd together with by-products such as: ZnS and elemental S.

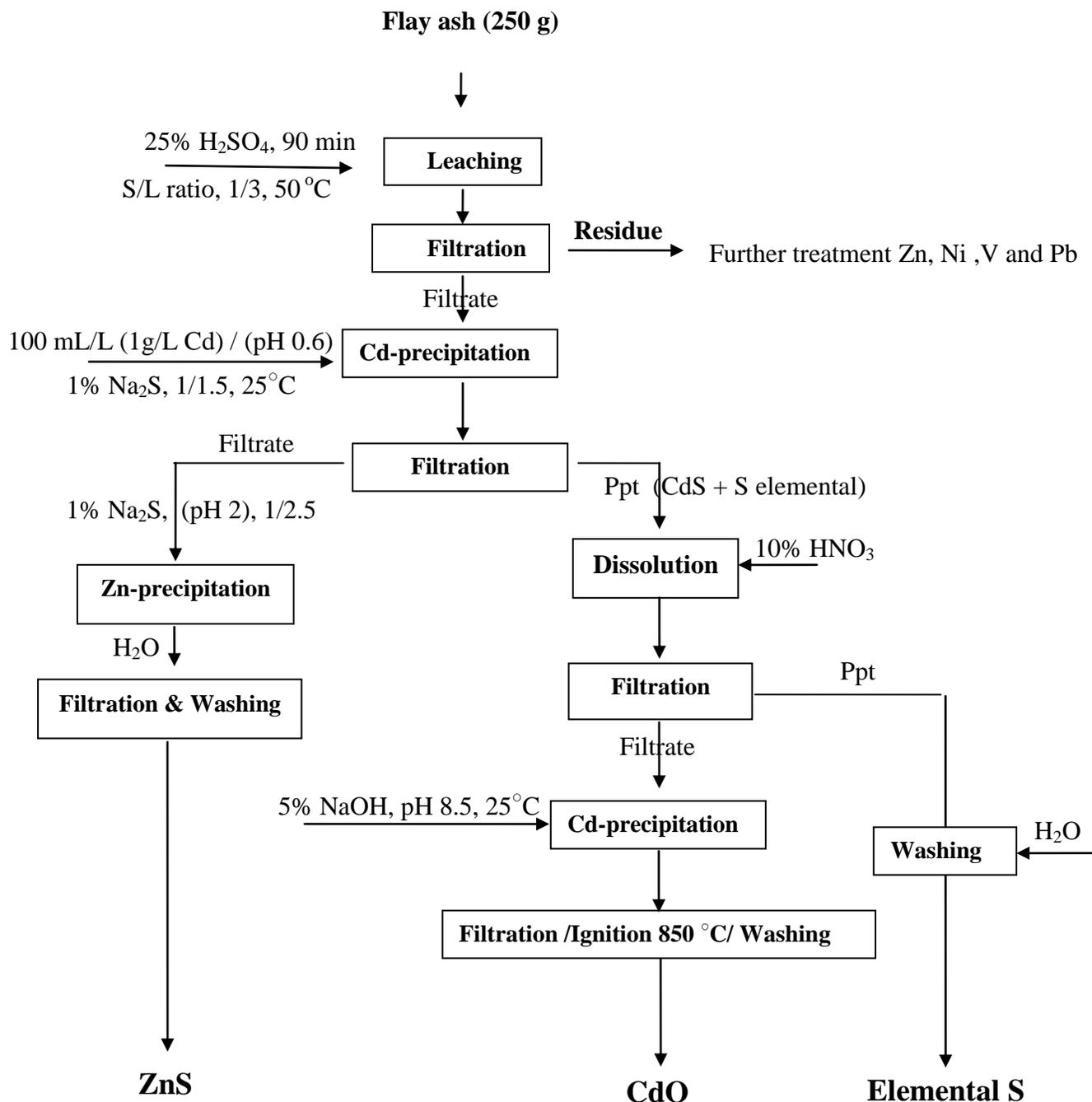


Fig. (9): A proposed flow-sheet for the recovery of CdO, elemental S and ZnS from flay ash sulfate solution.

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