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Hydrometallurgical Process for Recovery of Cadmium from the Plant Sewage Sludge

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A hydrometallurgical process has been developed for recovery of cadmium from the zinc plant sewage sludge. The residue obtained from drying of the sludge contains great quantity of zinc and cadmium and also along with lead, iron, nickel, copper and cobalt. The process consists of the following five major unit operations: (1) leaching: 2 mol L^{-1} sulfuric acid, L/S ratio of 4 : 1, 25°C and 1.5 h; (2) precipitation of iron, copper and lead: pH 5.4, 2 h, ambient temperature; (3) precipitation of nickel and cobalt: at pH 5.4, 80–85°C, 20 min by an addition of dimethylglyoxime; (4) cementation of cadmium metal: at pH 4.7–5.0, 40–50°C, 30 min by an addition of zinc metal; (5) purification of cadmium by heating the impure cadmium with sodium hydroxide in a blowing oven at temperature of 500–600°C and then washing it with hot water. The total recovery of cadmium was found to be approximately 89%.

Key Words: **Zinc sludge, Cadmium, Recovery, Sewage sludge, Zinc plant.**

INTRODUCTION

Heavy metals are omnipresent in the environment. Their presence in the environment has become a major threat to plant, animal and human life due to their bioaccumulating tendency and toxicity and therefore they must be removed from municipal and industrial effluents before discharging.

Zinc is an essential element, but cadmium is not known useful biological function in humans as well as in plants[1]. The processing cycles of zinc and cadmium are very closely interrelated because zinc minerals contain small amounts of cadmium. The mobilization of zinc and cadmium by human activities outweighs natural cycling processes. The increased quantities of cadmium mobilized are partly related to demand for cadmium itself but also to increased use of zinc and phosphate fertilizer. Cadmium is used in electroplating, in plastics, in pigments, in soldering and in nickel-cadmium batteries.

Zinc industry is growing in Iran. This industry generates a large amount of waste, which is called sludge everyday. Sludge contains high concentration of heavy metals such as cadmium, lead, etc.[2] This sludge is in an electrolytic zinc plant and generated from electrolytic production of zinc after treatment with sulfuric acid. The objective of this investigation was to determine the optimum conditions for the leaching of cadmium from zinc plant sewage sludge and also purify it to such a grade that it may be used in the laboratory and industry. To remove cadmium from the sludge, leaching and subsequent precipitation methods were selected.

EXPERIMENTAL

The sludge came from Zinc Zanjan Roeeneh (Iran) from the effluent treatment with sulfuric acid. The chemicals used were analytical/synthetic grade materials from Merck. Limewater used was prepared by addition of water to calcium carbonate and mixing it well.

Distilled water was used throughout. An atomic absorption-flame spectrometer (Varian-Spectra A-30/40) was used for the determination of the metal ion concentration. Carbon content was determined by a LECO CHN-600 elemental analyzer. A pH-meter equipped with a thermometer (Lutron pH-270) was used for determination of the pH of the solution.

Experimental work was conducted with the portion with a particle size of 500 μm. Removal of heavy metals, separation and finally purification of cadmium metal were performed in five separate steps of leaching, precipitation of iron, lead and copper, precipitation of nickel and cobalt, cementation of cadmium and purification. Before subjecting the samples of the sludge to these processes, the amounts of heavy metals were analyzed as follows: the sludge was dried in an oven (120°C) for 12 h. Then after cooling it down to room temperature a known quantity of the dried sample was treated with concentrated $HCl : HNO_3$ (40 : 15 mL) and heated (*ca.* 60°C) until dissolution was completed. Then the amount of the metals was determined by an atomic absorption spectrometer.

Leaching studies: Leaching tests were carried out using sulfuric acid solution. In each test, 100 g of residue was contacted with 500 mL of dilute sulfuric acid solution (2 M) in a 1-L beaker under stirring, except for the tests on the effect of L/S ratio. The scrubbing solution and the insoluble residue were separated by filtration, prior to a determination of the concentrations of each metal in the solution. The insoluble residue was dried under 100°C and the chemical constituent was analyzed by total dissolution with aqua regia.

Precipitation of iron, copper and lead: To 100 mL of leach solution was added 1.0 g potassium permanganate at 25°C and pH was adjusted to an appropriate value by limewater. The resulting mixture was allowed to stand for 1.5 h to complete the precipitation. In the course of reaction the pH of the solution should be maintained constant by addition of dilute limewater to make up the variation of pH value. After precipitation was completed the purified solution and precipitate were separated by filtration. The content of each metal in the filtrate was measured.

Precipitation of nickel and cobalt: To 300 mL solution of the previous step which contained nickel and cobalt were added 5 mL sulfuric acid and 0.12 g dimethyl glyoxime. The resulting mixture was heated to 80°C and then was treated with an adequate amount of limewater to adjust its pH to 5.4. To complete the precipitation the mixture was allowed to stand at 80°C for 20 min. After cooling down to room temperature the orange-red precipitate was filtered and washed with water thoroughly and the content of each metal in the filtrate was measured.

Cementation of solid cadmium: The cadmium was cemented as sponge metal from the solution by addition of an excess amount of metallic zinc. The pH of the solution was adjusted to 4.7–5.0 at 50°C for 30 min. The metallic cadmium was filtered, washed with clean water and the filtrate was taken to analyze to measure the concentration of the residual cadmium.

Purification of cadmium: Purification was carried out with mixing the sponge cadmium and sodium hydroxide and transferring the resulting mixture to an oven with temperature of 500–600°C. Air was then blown through the hot liquid cadmium. After cooling down, the residue was washed with hot water and dried in air. The metallic cadmium was analyzed to measure the content of other metals. The filtrate was recycled back to the zinc circuit to recover this value.

RESULTS AND DISCUSSION

Determination of residue: The sludge was dried at 120°C and ground (if necessary) and filtered out using a 0.5 mm screen. The chemical constituent of the residue was analyzed by total dissolution with aqua regia. The typical results (in wt. %) are: 32.60 activated carbon, 47.40 Zn, 7.79 Cd, 1.90 Pb, 1.42 Fe, 0.38 Ni, 0.24 Cu and 0.04 Co. It shows that the residue was basically composed of zinc as zinc sulfate and activated carbon, whereas other metals (cadmium, lead, iron, nickel, copper and cobalt) accounted for 18.77%, of which cadmium was only 7.79%.

Leaching studies: The effect of four variables, *viz.*, sulfuric acid concentration, liquid-to-solid ratio, temperature and reaction time were studied[3].

The relationship between the per cent metal leached and the sulfuric acid concentration is shown in Fig. 1. The leaching of cadmium and zinc nearly

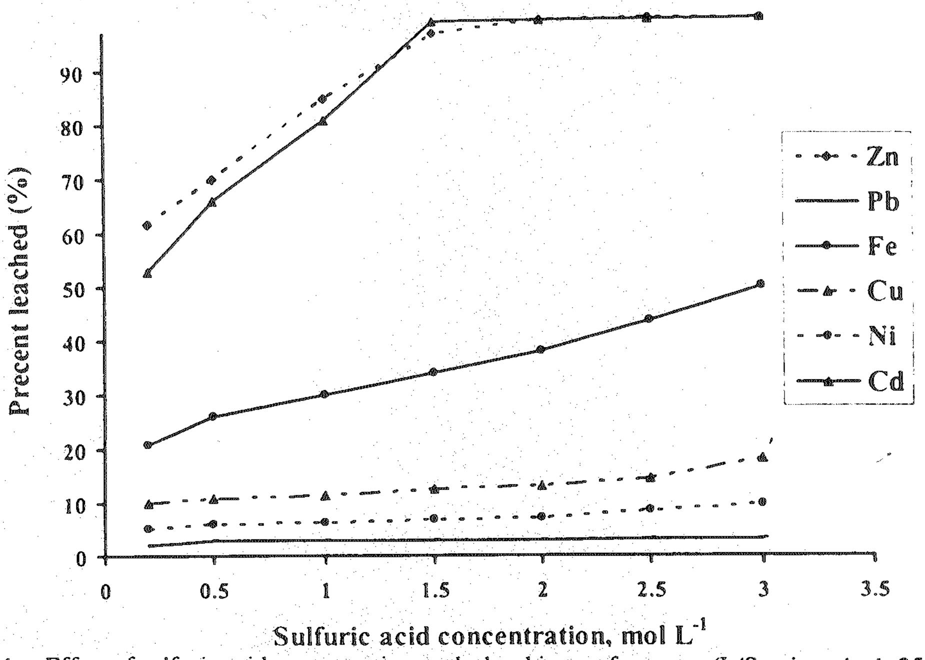

Fig. 1. Effect of sulfuric acid concentration on the leaching performance (L/S ratio = 4 : 1, 25°C, 1.5 h)

reached to completion at > 2 mol L^{-1} sulfuric acid. The leaching of nickel and lead was about 12 and 3.0%, respectively by 2 mol L^{-1} sulfuric acid and did not improve with the increase of the sulfuric acid concentration thereupon. Cobalt was very refractory under this condition with an extraction efficiency of less than 1%. On the other hand, although relatively low separated amounts of copper, nickel, lead and cobalt were observed, the leaching efficiencies of copper and iron did rise steadily with the increase of the sulfuric acid concentration within the experimental range. This phenomenon can be explained by the fact that zinc, lead and cadmium were in a sulfate form in the residue as a consequence of not reacting with the naphthol derivative. Copper, nickel and cobalt were in the naphthol complex forms, of which the cobalt complex was much more stable than the others. As to iron, some of it was in hydroxide form and some was in the naphthol complex form.

The effects of the L/S ratio and temperature on this procedure are shown in Tables 1 and 2, respectively. Overall, high L/S ratio and high temperature gave better leaching efficiency. However, the use of an excessively large volume of the leaching solution at high temperature is evidently undesirable from the point of view of high productivity and convenience. Accordingly, the leaching procedure was conducted at an L/S ratio of 4 : 1 and at a temperature of 25°C.

TABLE-1
EFFECT OF L/S RATIO ON THE LEACHING PERFORMANCE†

L/S ratio	Per cent metals leaching						
	Cd	Zn	Fe	Cu	Ni	Co	Pb
2 : 1	83.1	84.3	22.9	7.1	5.1	0.13	2.7
3 : 1	89.2	90.4	28.7	10.8	6.6	0.24	2.8
4 : 1	99.0	98.6	38.1	13.1	7.2	0.36	3.0
5 : 1	> 99.0	> 99.0	46.0	16.9	8.9	0.47	3.0
7 : 1	> 99.0	> 99.0	53.2	18.2	9.7	0.53	3.1
10 : 1	> 99.0	> 99.0	55.3	20.2	10.0	0.72	3.1

†2 mol L^{-1} H_2SO_4, 25°, 1.5 h.

TABLE-2
EFFECT OF TEMPERATURE ON THE LEACHING PERFORMANCE†

Temperature (°C)	Per cent metals leaching						
	Cd	Zn	Fe	Cu	Ni	Co	Pb
25	99.0	98.5	38.1	13.1	7.2	0.36	3.0
30	99.2	99.3	40.2	14.2	7.8	0.37	3.4
35	99.5	99.5	45.3	14.8	8.3	0.39	4.2
45	> 99.5	99.5	60.1	15.3	8.7	0.40	4.9
75	> 99.5	> 99.5	77.0	16.0	9.9	0.42	6.7

†2 mol L^{-1} H_2SO_4, L/S ratio = 4 : 1, 1.5 h.

Time dependency of the removal of metals with 2 mol L^{-1} sulfuric acid solutions at 25°C is given in Fig. 2. Apparently, 1.5 h was sufficient for leaching of metals from the residue and did not improve with raising the time contact.

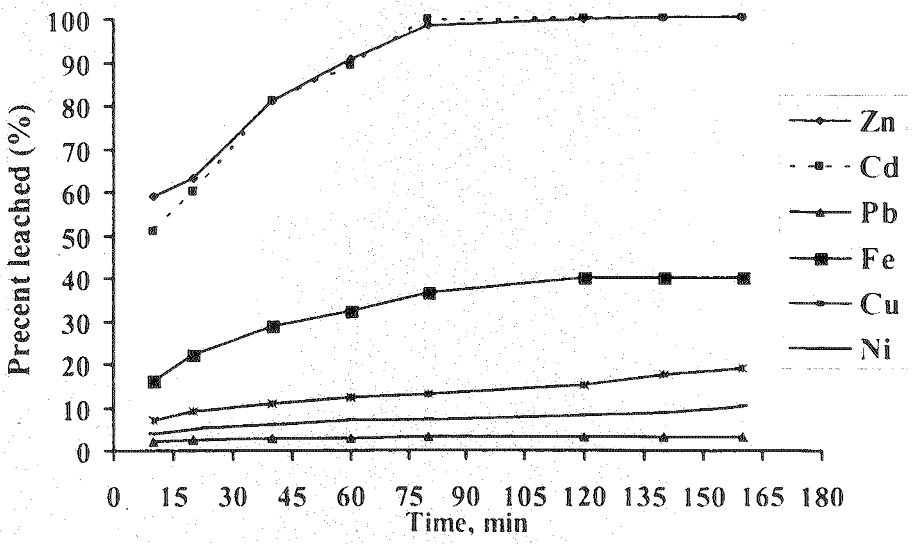

Fig. 2. Effect of the contact time on the leaching performance (2 mol L^{-1} H_2SO_4, L/S ratio = 4 : 1, 25°C)

Based on the above experimental results, the final optimum conditions for the leaching procedure were determined to be 2 mol L^{-1} sulfuric acid, L/S ratio of 4 : 1, 25°C and 1.5 h. Under these conditions, about 99.0% of Cd, 98% of Zn, 38% of Fe, 7% of Ni, 13% of Cu, 3% of Pb and less than 1% Co could be leached from the residue. At the same time, the loss of cadmium was less than 0.6%. As a result, in the leached residue, there was (in wt. %) about 0.17 Cd, 1.47 Zn, 1.96 Fe, 0.46 Cu, 0.79 Ni, 0.09 Co and 6.50 Pb. The average composition of the resulting leaching liquor was found to be approximately (in g L^{-1}) 7.71 Cd, 47.73 Zn, 0.541 Fe, 0.027 Ni, 0.0314 Cu, 0.057 Pb and 0.0004 cobalt.

Precipitation of copper, iron and lead: It is well known that iron is inclined to hydrolysis to colloidal iron hydroxide, which is difficult to filter. For the removal of iron from the leach solution, several commercial processes are available[4]. Three of these processes are named after the compounds which they precipitate: (1) Jarosite [$M{\cdot}Fe_3(SO_4)_2(OH)_6$, where $M = NH_4^+$, K^+ or Na^+]; (2) Goethite ($FeO{\cdot}OH$); and (3) Hematite (Fe_2O_3). Precipitates are easy filterable crystalline compounds. A suitable lower iron content (< 1–2 g L^{-1}) is warranted to precipitate iron as goethite. The iron in the leach solution was less than 1 g L^{-1}. As a result, its removal was conducted in goethite precipitation. It was found that high pH values facilitated the goethite precipitation of iron. At these conditions, lead and copper also co-precipitated with iron. To complete the goethite precipitation, potassium permanganate was used to precipitate iron(II) *via* oxidization[5]. It is noteworthy that the addition of potassium permanganate will cause a decrease of pH, which will affect the precipitation of copper, lead, cobalt and iron significantly[6]. Nevertheless, it can be made up by an addition of dilute limewater solution. The effect of three variables, *viz.*, pH, time and temperature on the precipitation of iron, lead and copper were studied. The pH dependency of the precipitation of iron, lead and copper is given in Fig. 3. Apparently, as the pH value increases, the precipitation increases as well. Since at the pH value of > 5.4, zinc ions in the solution started to precipitate as basic zinc sulphate and cadmium co-precipitated as well[7]; the higher pH values were not succeeded. Time dependency on the removal of the metal in pH = 5.4 and at 25°C is given in Fig. 4.

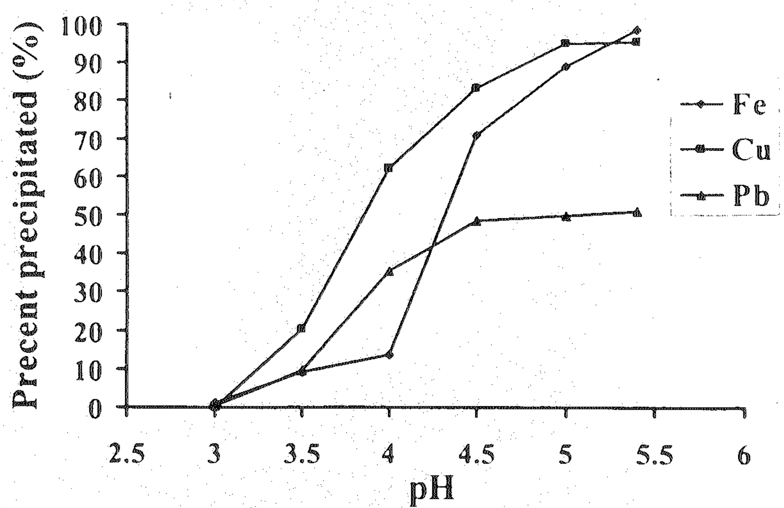

Fig. 3. Effect of pH on the precipitation of Fe, Cu and Pb (2 h, at 25°C leached solution containing (g L^{-1}): 0.5410 Fe, 0.057 Pb and 0.0314 Cu)

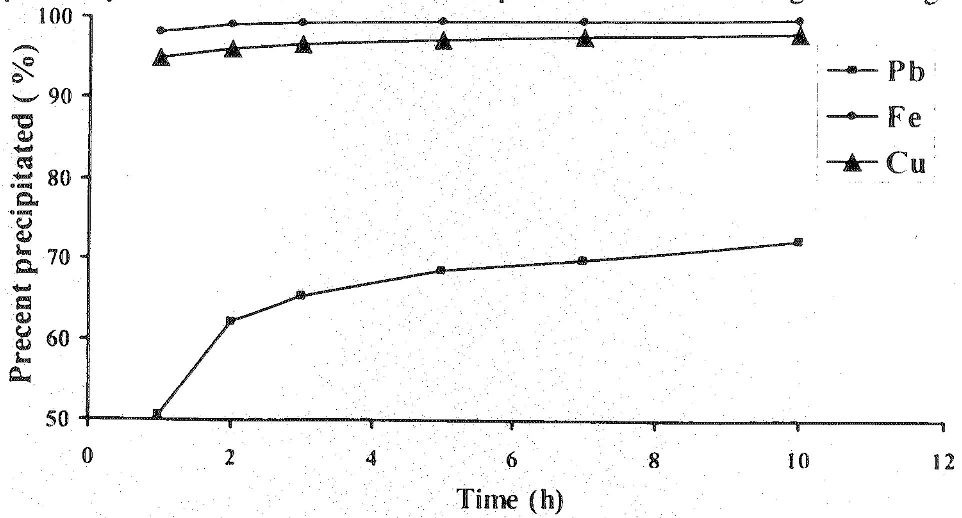

Fig. 4. Effect of time on the separation of Fe, Cu and Pb (pH = 5.4 at 25°C leached solution containing (g L^{-1}): 0.5410 Fe, 0.057 Pb and 0.0314 Cu)

These results show little increase in removal of metals at above 2 h. As a result, the precipitate was filtered after 2 h. The effect of temperature on the precipitation and further separation of iron, copper and lead is shown in Table-3. Obviously, a temperature above ambient makes the precipitation worse, specially for iron. So the precipitation was conducted under ambient temperature.

TABLE-3

EFFECT OF TEMPERATURE ON THE PRECIPITATION OF Fe, Cu AND Pb†

Temperature (°C)	Per cent metals leaching		
	Fe	Pb	Cu
25	99.3	62.1	97.9
30	98.0	60.1	98.3
40	89.0	58.5	95.0
50	80.0	55.3	92.4

†pH = 5.4, 2 h leached solution containing (g L^{-1}): 0.5410 Fe, 0.057 Pb and 0.0314 Cu.

Elimination of nickel and cobalt by precipitation

Nickel and cobalt were precipitated from the leach solution by using dimethyl glyoxime which makes insoluble complex with these metals. As pointed out in the experimental section dimethylglyoxime was added to the acid solution and the solution was taken to pH about 5 by addition of lime solution. This procedure gives a more easily filterable precipitation than does the direct precipitation from the lime solution[8]. It was found that pH affects the precipitation of nickel dimethyl glyoxime seriously, which is probably attributed to the complex formation of nickel with dimethylglyoxime. Fig. 5 shows the plot of nickel and cobalt precipitated at 25°C at the pH range 4–5.4 against the percentage of nickel and cobalt precipitated from the solution. The increment of pH to 5.4 accelerates the precipitation of nickel and cobalt from the solution. As mentioned before, the pH value higher than 5.4 was not followed due to the precipitation of cadmium from the solution. The precipitations of nickel and cobalt were investigated by increasing the time contact between dimethyl glyoxime and nickel. As shown in Fig. 6 the precipitation of nickel increased up to 20 min and then decreased till 150 min. This phenomenon is attributed to the redissolution of nickel complex[6]. As a result, the optimum time contact was selected as 20 min at pH 5.4.

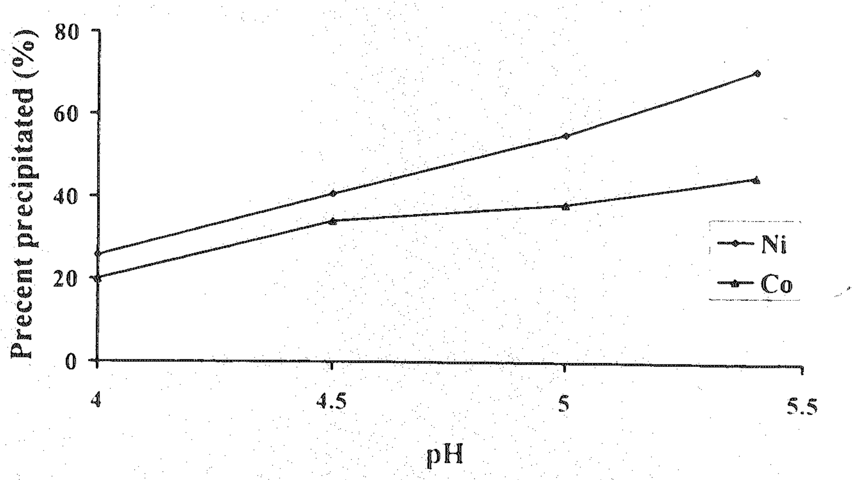

Fig. 5. Effect of pH on the precipitation of Ni and cobalt (at 25°C and 1 h contact-time leached solution containing (g L^{-1}): 0.0270 Ni and 0.0004 cobalt)

In the next step, the effect of temperature on the precipitation of nickel was studied. As shown in Table-4 at the elevated temperature the precipitation of nickel increases. The amount of cobalt was not detectable by AAS under this condition and was excluded in Fig. 6 and Table-4.

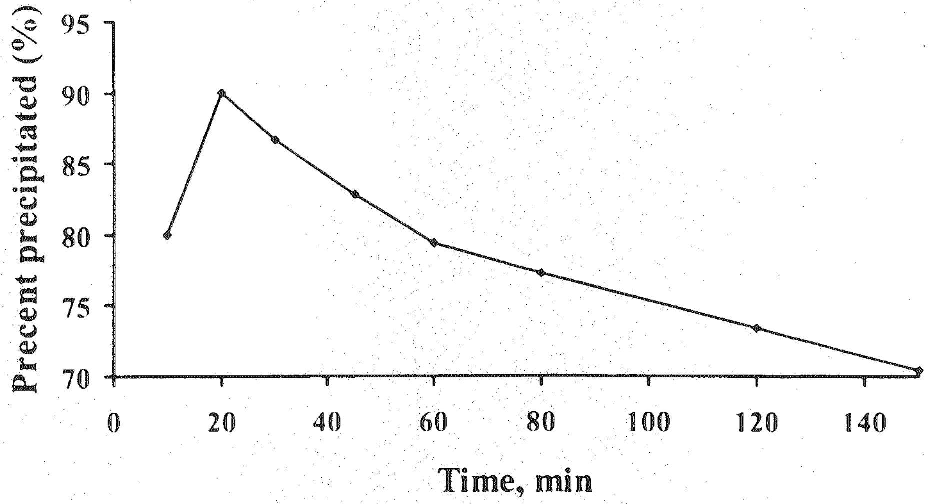

Fig. 6. Effect of time-contact on the precipitation of Ni [at pH 5.4 and 25°C leached solution containing (g L^{-1}): 0.0270 Ni and 0.0004 cobalt]

TABLE-4

EFFECT OF TEMPERATURE ON THE PRECIPITATION OF Ni†

Temperature (°C)	25	35	45	55	65	80
Per cent separated	90	92	95	97	99	> 99.5

†pH = 5.4, 20 min leaching solution containing: 0.0270 g L^{-1} Ni and 0.0004 g L^{-1} cobalt.

Based on the experimental results, the best conditions for the iron, lead, copper, nickel and cobalt elimination from the leached solution using two-stage selective precipitation are: pH 5.4 at ambient temperature for 2 h with an addition of potassium permanganate and at the same pH and temperature of 80–85°C for 20 min with an addition of dimethylglyoxime. As a result, there were only 44.2830 g L^{-1} zinc, 7.3188 g L^{-1} cadmium and 0.0213 g L^{-1} lead left in the leached solution and the loss of cadmium at these two stages was 5.1%.

Cementation of solid cadmium

Addition of zinc metal to the solution causes any cadmium ions in the solution to be displaced by zinc metal and precipitated out of the solution as sponge cadmium metallic solid and separation of metallic cadmium from the solution[9]. Cementation of cadmium as cadmium sponge from ion Cd^{2+} was based on the difference in reduction potential of zinc and cadmium. Since the standard reduction potential of zinc is more negative than that of cadmium, solid cadmium can be separated from the solution by an addition of metallic zinc. In this way an excess amount of zinc metal was added to the leached solution and solid cadmium along with the residual of zinc were filtered. It was found that acidity influenced the precipitation of cadmium significantly and this effect is shown in Table-5.

TABLE-5
EFFECT OF pH ON THE CEMENTATION OF Cd FROM THE SOLUTION UPON ADDITION OF THE METALLIC Zn†

pH	4.0	4.5	4.7	5.0	5.2	5.6
Precipitation begins to occur (h)	—	48.0	36.0	30.0	40.0	—
Filterability	—	bad	good	Very good	bad	—

†At 25°C. Leaching solution containing: 44.283 g L^{-1} Zn, 7.3188 g L^{-1} Cd and 0.0213 g L^{-1} Pb.

It is clear that at pH < 4.5 the precipitation did not occur, practically, and at pH 4.5 the precipitation was very slow and somewhat difficult to filter. The best pH was about 4.7–5.0 that was easily amenable to normal filtration. At higher pH value the precipitation and filtration got worse. Then, the effect of temperature on the precipitation of solid cadmium was investigated. As shown in Table-6, the efficiency improved as the temperature increased up to 50°C and did not rise at higher temperatures. In addition, at lower temperature the precipitate was hardly filterable. As a result, a temperature of 40–50°C was chosen for the cementation of the metal cadmium. It is noteworthy that the pH value above 5.2 causes deactivation of the metallic zinc and a pH less than 4.7 increases the metallic zinc required for the reduction process. Practically, it was found that more than the stoichiometric amount of zinc was required for the reduction of cadmium ion because some of the zinc metal is used in the reduction of hydronium ion and generation of hydrogen gas.

TABLE-6
EFFECT OF TEMPERATURE ON THE PRECIPITATION OF Cd FROM THE SOLUTION UPON ADDITION OF THE METALLIC Zn†

Temperature (°C)	25	30	40	50	60
Efficiency (%)	28	80	93	94	94

†pH = 4.7–5.0, 30 h leaching solution containing: 44.283 g L^{-1} Zn, 7.3188 g L^{-1} Cd and 0.0213 g L^{-1} Pb.

Purification

The sponge cadmium prepared in the last step is impure and is rich in zinc and zinc oxide impurities. To remove the zinc impurity the crude product was transferred to a blowing oven and heated to 500–600°C with sodium hydroxide. The sodium zincate formed was then removed by washing the residue with hot water. The resulting wash could be recycled back to the zinc production circuit to recover the value. The contents of other elements in the obtained cadmium metals were determined to be (in wt. %) 0.0010 Zn, 0.0001 Cu, 0.0050 Pb. No iron, cobalt and nickel were detected by AAS and the loss of cadmium was nearly 5%.

Conclusions

The hydrometallurgical process developed for the separation and recovery of cadmium from zinc plant residue consists of the following five major unit operations: (1) leaching with sulfuric acid; (2) precipitation of copper, iron and lead; (3) precipitation and removal of nickel and cobalt; (4) cementation of solid cadmium; (5) purification of cadmium. A conceptual total flow diagram of the process has been proposed in Fig 7.

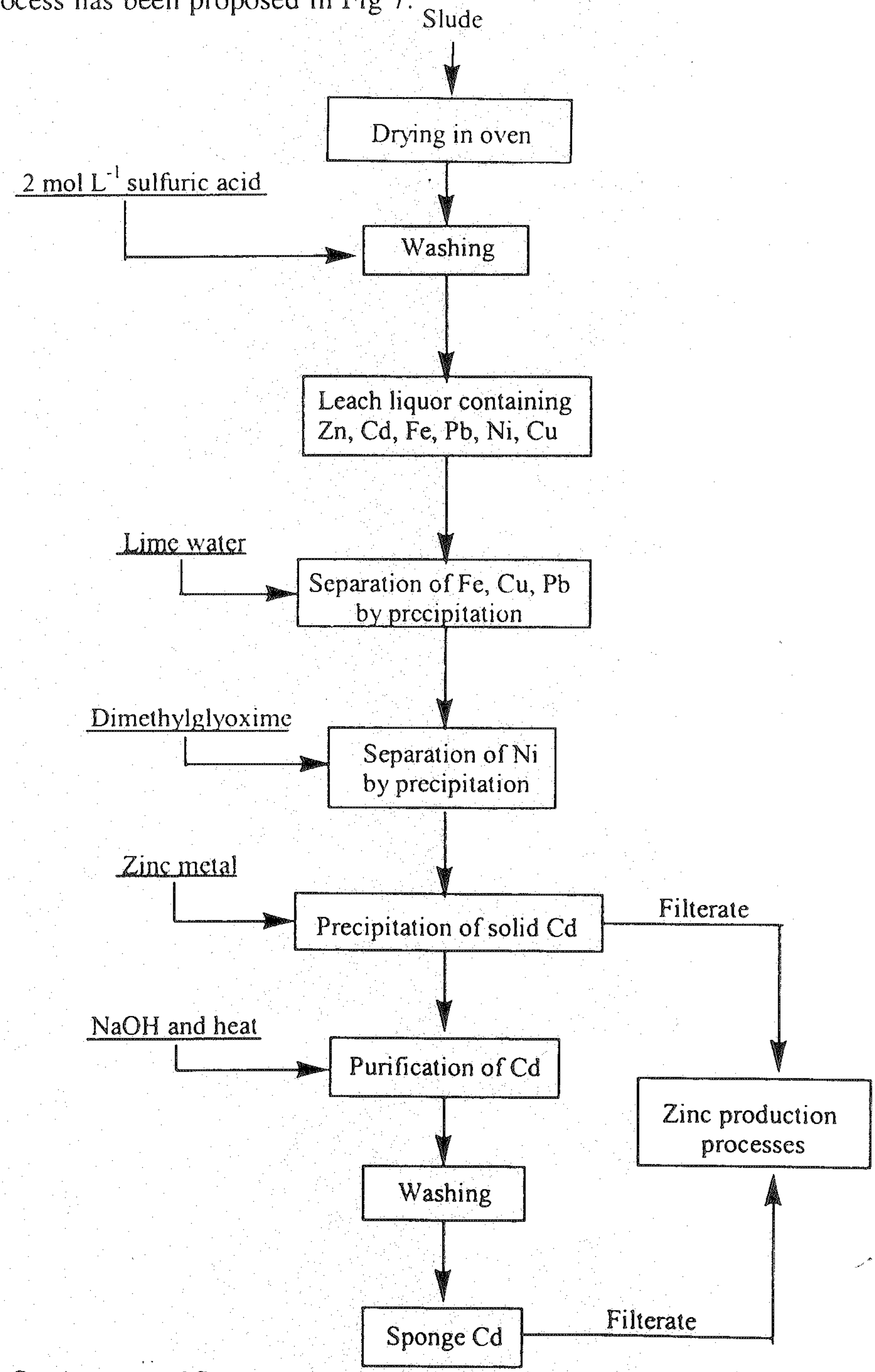

Fig. 7. A conceptual flowsheet of the hydrometallurgical process for recovery of cadmium from the zinc sewage sludge

The best condition for the leaching procedure were found to be 2 mol L^{-1} sulfuric acid at a L/S ratio of 4 : 1 and at 25°C using 1.5 h as a retention time.

Under these conditions, about 98.5% of Zn, 99% of Cd, 38% of Fe, 3% of Pb, 7% of Ni, 13% of Cu and of 1% Co could be leached from the residue and the loss of cadmium was less than 0.6%.

Iron was removed by precipitation from the leach liquor at pH 5.4 for 2 h at ambient temperature; copper and lead were co-precipitated under these conditions. As a result, 99.3% of iron, 62.1% of lead and 97.9% of copper could be separated from cadmium. The loss of cadmium was about 1.2%.

Nickel and cobalt were isolated from cadmium by using dimethyl glyoxime at pH 5.4 and temperature 80–85°C with a time of contact of 20 min. The loss of cadmium in this stage was about 3.9%.

The cadmium in the solution was cemented to the solid sponge cadmium using an addition of metal zinc at pH 4.7–5.0 for 30 min and temperature of 40–50°C. The recovery of cadmium was about 95% in this process and with some impurity of zinc.

The pure cadmium sponge was obtained by heating the impure cadmium with sodium hydroxide in a blowing oven at a temperature of 500–600°C and then washing it with hot water. The total recovery of cadmium was about 89%.

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