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Extraction of Indium from Zinc Sulphide Concentrates

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A new process for extraction of indium from zinc sulphide concentrates containing very low amount of indium was proposed. In this process, after dissolution of indium from neutral leached residue, indium precipitates from solution selectively to prepare indium concentrate solution for solvent extraction by bis(2-ethylhexyl)phosphoric acid (D2EHPA). The technologies in the processes, such as neutral leaching, leaching the neutral leached residues with high concentrated acid at high temperature and reduction of ferric ion to ferrous ion, selective precipitation of indium, solvent extraction and cementation of indium were investigated. The results show that total recovery ratio of indium from zinc sulphide concentrates containing very low amount of indium is increased from 50 % to 90 %.

Key Words: Indium, Zinc sulphide, Selective precipitation.

INTRODUCTION

Indium is an important metal extensively used in electronic industries[1]. Indium is not mined for itself, as it appears widely dispersed on the earth's surface. Rather, the metal is produced from several commercial ores[2], together with zinc (sphalerite), lead (galena), copper (polymetallic ores) and tin (stannite and cassiterite). Sphalerite present in sulphide ores is the main mineral source for the zinc and indium production[2]. The typically traditional process for extracting indium from zinc-indium concentrates involves the following steps: roasting, neutral leaching (first leaching) for recovery of zinc, second leaching to dissolution of indium, solvent extraction and cementation of indium. In this method, indium is directly extracted from leach solution by bis(2-ethylhexyl)phosphoric acid (D2EHPA)[1,3]. Generally, in this method the input to solvent extraction is leach solution containing relatively high concentrations of indium. This method is not suitable for zinc sulphide concentrates containing very low amount of indium, because indium concentration in leach solution is very low and iron concentration is relatively high. It is difficult to directly recover indium from the leach solution with solvent extraction. Therefore, an attempt has been made to develop a new process for recovering indium from zinc sulphide concentrates

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containing very low amount of indium. In new process, it was tried to first enrich indium by precipitation method and then the indium in the precipitate was further separated and purified by solvent extraction. In order to determine the optimum conditions for the selective leaching of zinc (of indium) from roasted zinc sulphide concentrate by sulfuric acid solution, the effect of pH of leach solution, reaction temperature, time reaction and liquid-to-solid ratio were studied[4]. Then in order to find out optimum conditions for the leaching of indium from neutral leaching residue, sulfuric acid concentration, reaction temperature, time reaction and amount of Na_2S (for reduction Fe^{3+} to Fe^{2+}) were investigated[3]. Then to determine the optimum conditions for the selective precipitation of indium from leach solution, the effect of pH, type of basic reagent, reaction temperature and time on the precipitation of indium, iron and zinc were studied[5].

EXPERIMENTAL

The concentrated zinc sulphide used in the experiments was provided from Bama region in Esfahan in Iran. The concentrate was sieved by using a 200 mesh ASTM standard sieve. It was determined by X-ray diffractometer that the concentrate contained mainly ZnS and FeS_2. The chemical composition of the concentrate was determined by XRF method and results are given in Table-1. Prior to the dissolution experiments[6], the concentrate was roasted in a high temperature furnace at 950 ºC for 3 h. Roasted concentrate contained mainly ZnO, $ZnFe_2O_3$ and Fe_2O_3. The chemical composition of the roasted concentrate is given in Table-2. Indium concentration in zinc concentrate and roasted concentrate were 40 and 45 ppm, respectively.

TABLE-1
CHEMICAL COMPOSITION OF ZINC SULPHIDE CONCENTRATE USED IN STUDY

Content	Mass (%)	Content	Mass (%)
Zn	54.32	MgO	1.12
SO_3	17.63	Ba	0.28
SiO_2	12.03	Pb	0.87
Fe_2O_3	7.42	Cu	0.08
CaO	1.30	P_2O_5	0.40
Al_2O_3	1.82	Na_2O	1.10
LOI	1.63	–	–

Procedure

Leach test: In the leaching experiments a hot plate with contact thermometer and a magnetic stirrer was used. The temperature of the system was controlled within ± 2 °C. The leaching was done in 250 mL glass balloons using Teflon coated magnets. At the end of each leaching experiment, the insoluble leach residue was separated from the pregnant leach solution by passing it through a filter paper. In the leaching tests the procedures followed were as follows: A measured amount of distilled water and calculated amount of pure Merck quality sulfuric acid were

TABLE-2
CHEMICAL COMPOSITION OF ROASTED ZINC SULPHIDE CONCENTRATE USED IN STUDY

Content	Mass (%)	Content	Mass (%)
Zn	68.700	MgO	1.210
SO_3	5.600	Ba	0.285
SiO_2	5.900	Pb	1.800
Fe_2O_3	6.000	Cu	0.300
CaO	0.800	P_2O_5	–
Al_2O_3	0.256	Na_2O	–
LOI	8.130	–	–

put into the glass balloon and heated to the desired temperature with constant magnetically stirring. Then, the weighed amount of roasted concentrate (neutral leaching) or neutral leached residues (reduction leaching) was added to the dilute sulfuric acid solution and the timing was initiated. At the neutral leach experiments, pH was kept constant with adding sulfuric acid solution during experiments (pH was measured by a HANNA model digital pHmeter). The stirring speed which gave sufficient mixing was kept constant in all the experiments. At the end of leaching duration, solid-liquid separation by filtration followed as explained above. The filtrate was analyzed for indium, zinc and iron.

Precipitation test: For the precipitation test, basic reagent (ammonia, sodium hydroxide and lime with Merk grades) was added dropwise to the solution using a titration burette to progressively increase pH to target level. When the effect of pH, type of basic reagent and reaction temperature on the precipitation of indium, iron and zinc were studied, the solution was mixed for 15 min to allow the reaction to reach equilibrium and then slurry sample was filtered. Indium, zinc and iron were analyzed in the filtrate. When the effect of reaction time was studied, slurry sample was withdrawn at selected time intervals and filtered.

Analysis methods: Indium, zinc and overall iron in the experimental samples were analyzed by atomic absorption model Varian AA240. Titration with potassium dichromate was used to determine Fe^{2+} concentrations. The concentration of Fe^{3+} was determined by finding the difference between overall iron and Fe^{2+} concentrations.

RESULTS AND DISCUSSION

Neutral leaching (first leaching): At this stage, the optimum conditions were determined for the dissolution of roasted zinc sulphide concentrate in sulfuric acid solutions, to minimize indium dissolution while keeping the dissolution of zinc maximum.

Effect of pH of leach solution on the leaching of zinc and indium from roasted zinc sulphide concentrate: In this stage for selective dissolution of zinc from indium was investigated at different pH of leach solution instead of initial acid concentration[7]. The effect of pH of leach solution on the leaching of zinc and indium is shown in Fig. 1. It can be seen that the pH of leach solution has a noticeable effect on the recovery of indium, also recovery of zinc and indium increase with the decrease of pH. The best result is obtained when the pH of leach solution is 3.

Effect of temperature on the leaching of zinc and indium from roasted zinc sulphide concentrate: The effect of reaction temperature on the leaching of zinc and indium from roasted zinc sulphide concentrate is shown in Fig. 2. It can be seen that in the temperature range of 50 to 70 °C does not significantly affect the leaching of indium from roasted zinc sulphide concentrate. The best result is obtained at 70 °C.

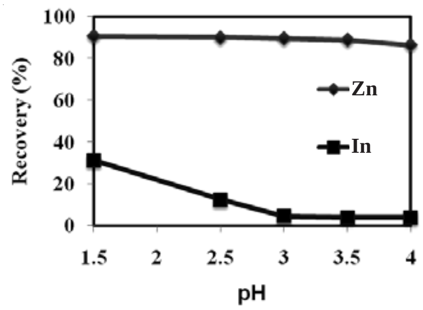

Fig. 1. Effect of pH of leach solution on the leaching of zinc and indium (temp. = 60 ºC, liquid-to-solid ratio 10:1 and time = 60 min)

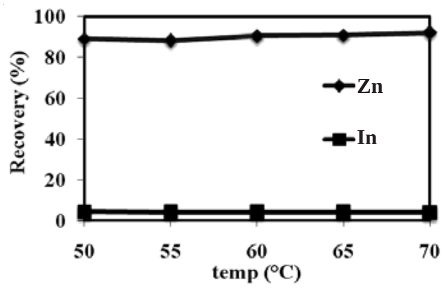

Fig. 2. Effect of temperature on the leaching of zinc and indium (pH of leaching = 3, liquid-to-solid ratio 10:1 and time = 60 min)

Effect of reaction time on the leaching of zinc and indium from roasted zinc sulphide concentrate: The effect of reaction time on the leaching of zinc and indium from roasted zinc sulphide concentrate is shown in Fig. 3. It can be seen that reaction time has not significant effect on recovery of indium in the time range of 45 to 90 min. The best result is obtained when the time of leaching is 75 min.

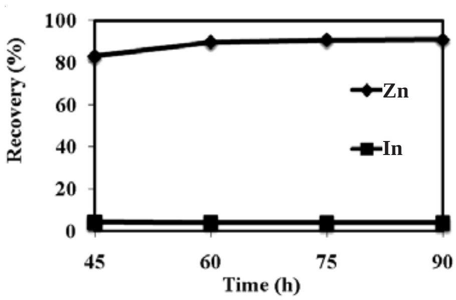

Fig. 3. Effect of reaction time on the leaching of zinc and indium (pH of leaching = 3, reaction temperature= 70 °C, liquid-to-solid ratio 10:1)

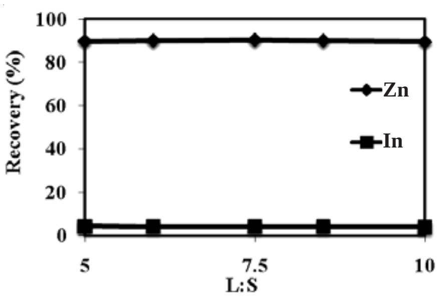

Fig. 4. Effect of liquid-to-solid ratio on recovery of zinc and indium (pH of leaching = 3, reaction temperature = 70 °C, time = 75 min)

Effect of liquid-to-solid ratio on the leaching of zinc and indium from roasted zinc sulphide concentrate: The effect of liquid-to-solid ratio on the leaching of zinc and indium from roasted zinc sulphide concentrate is shown in Fig. 4. It can be seen that liquid-to-solid ratio has not significant effect on recovery of zinc and indium in the liquid-to-solid ratio range of 10:1 to 5:1. The best result is obtained when the liquid-to-solid ratio is 7.5:1.

Under optimum conditions, the dissolution percentage of zinc and indium in sulfuric acid solutions were 92.5 and 4.2 %, respectively. The chemical composition of the neutral leached residue was determined by XRF method and result is given in Table-3. Indium concentration in neutral leached residue is 145 ppm.

TABLE-3
CHEMICAL COMPOSITION OF NEUTRAL LEACHED RESIDUE

Content	Mass (%)	Content	Mass (%)
Zn	22.5	MgO	1.4
SO_3	33.2	BaO	0.7
SiO_2	11.0	PbO	2.7
Fe_2O_3	18.6	Cu_2O	0.2
CaO	1.7	P_2O_5	–
Al_2O_3	1.4	Na_2O	–
LOI	6.3	K_2O	0.3

Reduction leaching (second leaching): In addition to determination of optimum conditions for recovery of indium from first leached residue, optimum conditions for reduction of Fe^{3+} to Fe^{2+} were investigated, in that selective precipitation of indium should be reduced from Fe^{3+} to Fe^{2+} in next stage (pH of precipitation of Fe^{3+} and Fe^{2+} are occurred before and after of pH of precipitation of In^{3+}, respectively).

Using sodium sulphide as reduction agent, effects of sulfuric acid concentration, reaction temperature, time reaction and amount of sodium sulphide on the leaching ratio are investigated.

Effect of sulfuric acid concentration on the reduction leaching: The effect of the initial acid concentration on the reduction leaching is shown in Fig. 5. It can be seen that the leaching ratios of indium, iron and zinc are increased with increasing initial acid concentration, but reduction ratio of Fe^{3+} to Fe^{2+} is decreased with increasing initial acid concentration. The best result is obtained when the initial acid concentration is 100 g/L.

Effect of temperature on the reduction leaching: The effect of the temperature on the reduction leaching is shown in Fig. 6. From Fig. 6, the leaching ratios of indium, iron and zinc are increased with increasing temperature (to 90 °C), but reduction ratio of Fe^{3+} to Fe^{2+} is decreased with increasing temperature. The best result is obtained when the temperature is 90 °C.

Effect of time on the reduction leaching: The effect of the time on the reduction leaching is shown in Fig. 7. From Fig. 7, the leaching ratios of indium, iron and zinc are increased with increasing time (to 3 h), but reduction ratio of Fe^{3+} to Fe^{2+} is decreased with increasing time. The best result is obtained when the time is 3 h.

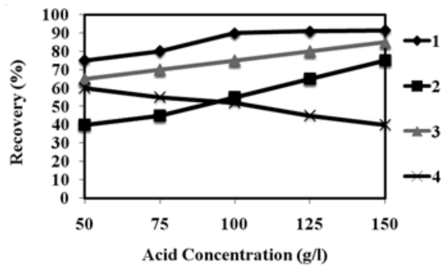

Fig. 5. Effect of the initial acid concentration on the reductive leaching: 1, 2, 3 and 4: leaching ratio of indium, iron, zinc and reduction ratio of ferric, respectively (temp. = 90 °C, time = 3 h and M_{real}/M_{theory} Na_2S = 1)

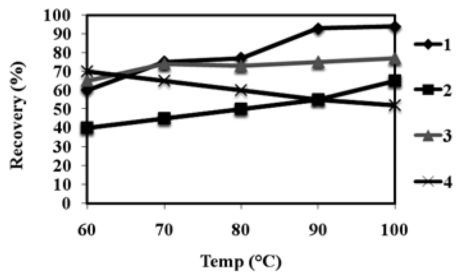

Fig. 6. Effect of the temperature on the reductive leaching: 1, 2, 3 and 4 leaching ratio of indium, iron, zinc and reduction ratio of ferric, respectively (acid concentration = 100 g/L, time = 3 h and M_{real}/M_{theory} Na_2S = 1)

Effect of reductive agent on the reduction leaching: The effect of the reductive agent addition amount on the reductive leaching is shown in Fig. 8. From Fig. 8, the leaching ratio of indium, iron and zinc is decreased, but the reduction ratio of Fe^{3+} to Fe^{2+} is increased with the addition amount of reductive agent increasing. The optimum addition amount of reductive agent is 1.5 times of theoretical amount for reducing Fe^{3+} to Fe^{2+}.

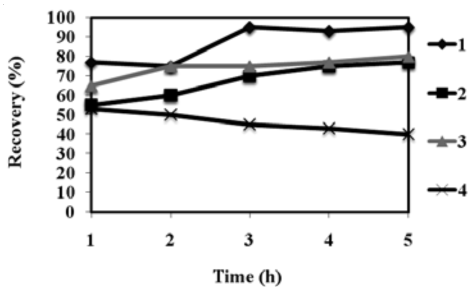

Fig. 7. Effect of the time on the reductive leaching: 1, 2, 3 and 4: leaching ratio of indium, iron and zinc and reduction ratio of ferric respectively (acid concentration = 100 g/L, temp. = 90 °C and M_{real}/M_{theory} Na_2S = 1)

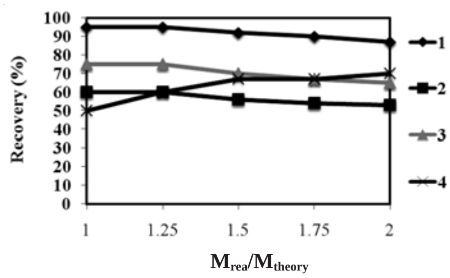

Fig. 8. Effect of the reductive agent addition amount on the reductive leaching: 1, 2, 3 and 4: leaching ratio of indium, iron and zinc and reduction ratio of ferric respectively (acid concentration = 100 g/L, temp. = 90 °C and time= 3 h)

Selective precipitation of indium from leach solution: In this stage, effects of pH, type of basic reagent, reaction temperature and reaction time on the precipitation of indium, iron and zinc from leach solution are investigated.

Effect of pH and type of basic reagent on the precipitation of indium, iron and zinc: The effect of the pH and type of basic reagent on the precipitation of indium, iron and zinc is shown in Figs. 9a-c, respectively. It can be seen that of precipitation percentage of indium, iron and zinc increase with the increase pH of solution and indium can be effectively recovered by neutralizing the leach solution to pH 6. It is also observed that when ammonia was used, precipitation percentage of iron and zinc decrease. So ammonia is selected as basic reagent.

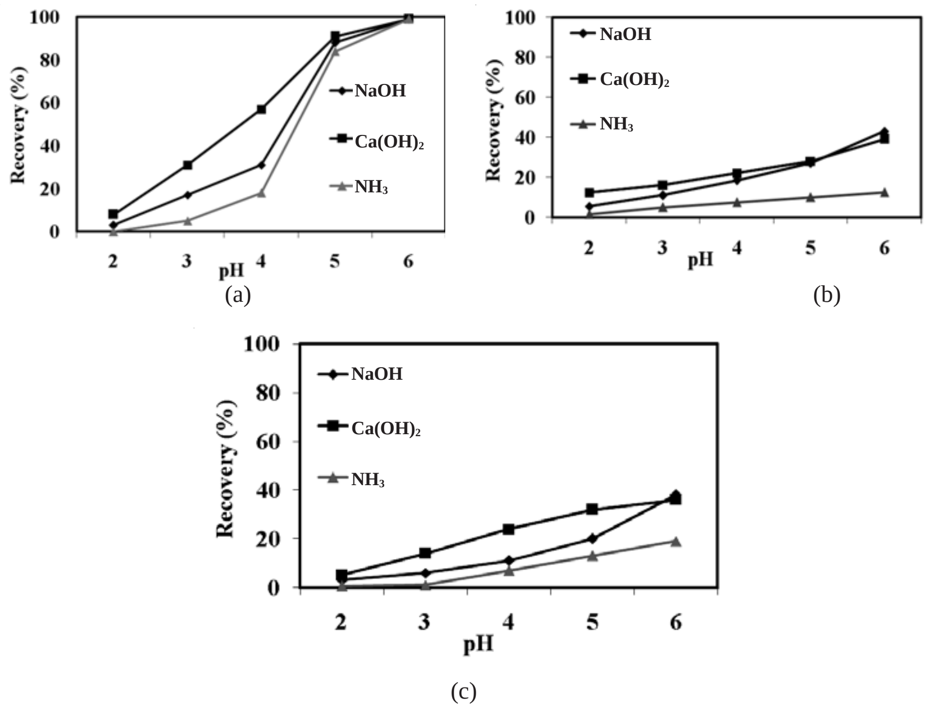

Fig. 9. Effect of the pH and type of basic reagent on the precipitation of (a) indium, (b) iron and (c) zinc (temp. = 90 °C and time = 10 min)

Effect of temperature on the precipitation of indium, iron and zinc: The effect of the reaction temperature on the precipitation of indium, iron and zinc is shown in Fig. 10. It can be seen that temperature does not significantly affect the precipitation of indium in the temperature range of 70 to 90 °C, the pH at which indium precipitates completely does not change significantly and is around 6. However, temperature has noticeable effect on the precipitation of iron and zinc. At pH 6 at 90 °C, the precipitation percentage of iron and zinc is less than 8.5 and 7 %, respectively; but at 70 °C, the precipitation percentage of iron and zinc reach 16.3 and 3.5 %, respectively. In order to minimize the precipitation of iron and zinc during the precipitation of indium, reaction should be performed at 90 °C.

Effect of time on the precipitation of indium, iron and zinc: The effect of the reaction time on the precipitation of indium, iron and zinc is shown in Fig. 11. It can be seen that the precipitation of indium complete in 10 min. But precipitation percentage of iron and zinc increase with the increase time. So the best result is obtained when the time is 10 min.

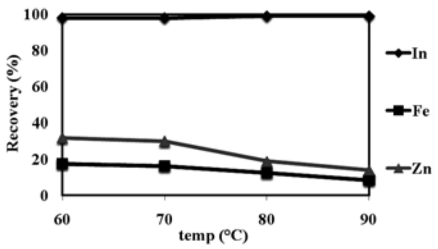

Fig. 10. Effect of the temperature on the precipitation of indium, iron and zinc (pH = 6 and time: 10 min)

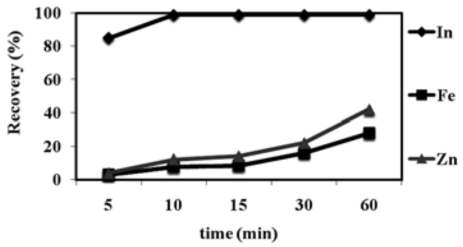

Fig. 11. Effect of the time on the precipitation of indium, iron and zinc (pH = 6 and temp. = 90 °C)

Under optimum conditions, the precipitation percentage of indium, iron and zinc were 100, 7.8 and 12 %, respectively. The chemical composition of the precipitate was determined by XRF method and result is given in Table-4. Indium concentration in the precipitate is 2650 ppm.

TABLE-4
CHEMICAL COMPOSITION OF PRECIPITATION

Content	Mass (%)	Content	Mass (%)
Zn	31.4	MgO	–
SO_3	47.4	BaO	–
SiO_2	3.7	PbO	–
Fe_2O_3	7.8	Cu_2O	–
CaO	0.5	P_2O_5	1.0
Al_2O_3	1.1	Na_2O	–
LOI	5.5	WO_3	2.1

Recovery of indium from the precipitate: The precipitate was leached with solution containing 3 mol/L sulfuric acid and at the liquid-to-solid ratio of 10:1, temperature of 90 °C and time of 3 h. The chemical composition of leach solution is listed in Table-5. The leach solution of the first leached residue contained a large amount of iron; the iron-to-indium ratio was 680:1. The leach solution was neutralized to pH 6 and reacted for 10 min at 90 °C. The precipitation percentages of indium and iron were 100 and 7.8 %, respectively. The ratio of iron to indium decreased from 680:1 in the leach solution of first leached residue to 26:1 in the leach solution of precipitate. The higher indium-to-iron ratio in the leach solution of precipitate is favourable for further separation and purification of indium. The experimental results indicate that by using precipitation method indium can be selectively recovered from solution containing large amount of iron and zinc.

Experiments of extracting indium: As reported[1,8], the optimum conditions of extracting indium by bis(2-ethylhexyl)phosphoric acid (D2EHPA) are as follows. The organic phase consists of 30 % D2EHPA and 70 % kerosene and the phase ratio is equal to 3, the time for vibration and setting are 5 and 10 min, respectively

TABLE-5
CHEMICAL COMPOSITIONS OF LEACH SOLUTION

Content	Concentration (g/L)	Content	Concentration (g/L)
Zn	21.000	Cd	0.237
Fe	6.000	Pb	0.093
In	0.252	Ni	0.017
Cu	0.219	Co	0.004
H_2SO_4	26.500	–	–

and the pH of solution is 0.8. The indium extraction is conducted at 25 °C. It can be seen that the extraction ratio of indium from solution is as high as 93 % and extraction ratio of iron is 6.9 %. The McCabe-Thiele diagram was plotted to determine the number of theoretical counter current stages required for indium extraction[9]. Fig. 12 shows the isotherm of indium extraction under the optimum experimental conditions for the maximum separation factor indium and iron. The McCabe-Thiele diagram (Figs. 12 and 13) indicates two theoretical countercurrent stages required for full indium recovery.

Experiments on indium striping: The experiments on stripping indium are carried out under the general stripping conditions as follows. The ratio of organic phase to solution is equal to 4, time for vibration and setting[3] is 5 min and a sulfuric acid solution of 3 mol/L is used as stripping agent[9] at 298 K. It can be seen that the stripping ratio of indium with sulfuric acid solution is as high as 74 % and stripping ratio of iron with sulfuric acid solution is 0 %. The McCabe-Thiele diagram was plotted to determine the number of theoretical countercurrent stages required for indium stripping. The McCabe-Thiele diagram (Figs. 12 and 13) indicates three theoretical countercurrent stages required for full indium stripping.

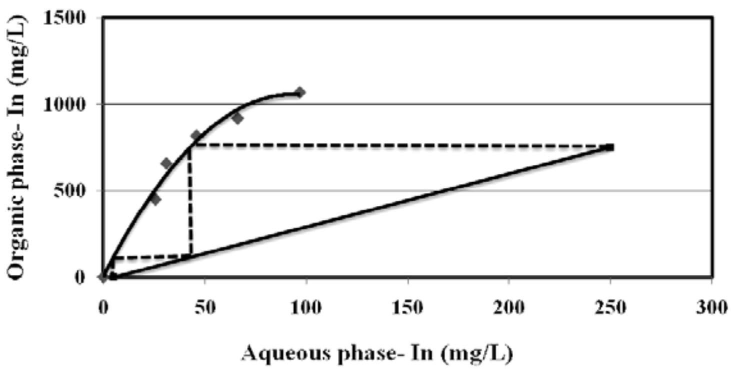

Fig. 12. Indium extraction isotherm

Experiments on cementing indium: Indium is cemented by zinc powder from the striping solution at 25 °C and pH, 3 and spongy indium is obtained. The result shows the cemented ratio of indium is more than 98% and grade of indium of cemented product is 82.5 %.

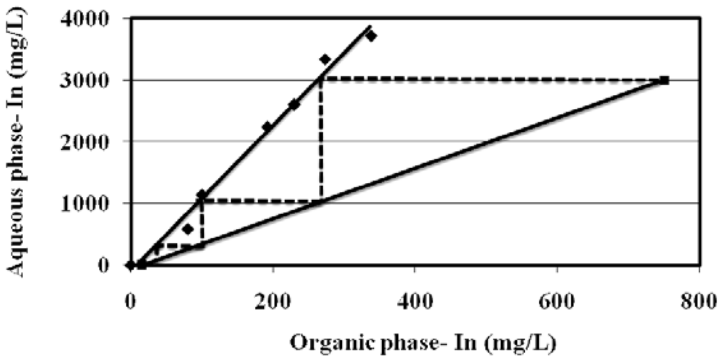

Fig. 13. Indium stripping isotherm

Conclusion

(i) Compared with traditional hydrometallurgical process of indium, the new process for extraction of indium from zinc sulphide concentrate containing very low amount of indium is suitable. (ii) Under the optimum conditions for neutral leaching, the leaching ratios of, zinc and indium are 92.5 %, 4.2 % respectively. (iii) Under the optimum conditions for reduction leaching, the leaching ratios of In, Zn and Fe are 95, 70 and 56 %, respectively and the reduction ratio of Fe^{3+} is higher than 67 % in reduction leaching with concentrated acid at high temperature. (iv) Under the optimum conditions of selective precipitation of indium the precipitation percentage of indium, iron and zinc were 100, 7.8 and 12 %, respectively. (v) Indium is extracted from leach solution of precipitation and the direct recovery ratio of indium is more than 93 %. (vi) Under the optimum conditions of cementation of indium, cementation percentage of indium by zinc powder was 98 %.

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