



Alternative solution purification in the hydrometallurgical zinc production

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Abstract

More than 80% of the world's production of zinc from its concentrate is obtained by the roast-leach-electrowin hydrometallurgical process. In the roast-leach process, very pure zinc sulphate solution must be prepared for zinc electrowinning, therefore, the purification process is one of the most important unit processes in zinc hydrometallurgy.

The conventional methods for the zinc solution purification are the „hot-cold“ and the „reversed“ purification processes. In both methods the liquor is purified by cementation of harmful elements with zinc dust and activators in a continuous, multistage process. The disadvantages of these procedures are the high zinc dust consumption and even more the complex composition of the residues.

Experimental work was carried out in laboratory scale to separate the metallic impurities, principally copper, cobalt and nickel from the leach solution by solvent extraction with hydroxyoximes. The separation of copper was excellent, with a final concentration in the raffinate of < 1 ppm. The extraction of cobalt and nickel wasn't favorable because of the possible coextraction of zinc.

Purification processes including copper solvent extraction and cementation of the other impurities for the hot-cold and the reversed solution purification methods are proposed.



1 Conventional zinc solution processing

In the conventional electrolytic process for recovery of zinc from sulphide concentrates (see flow diagram in Fig. 1) the concentrate is first calcined by roasting to convert zinc sulphide to zinc oxide, which is readily solubilized in dilute sulfuric acid solutions. The calcinated material also contains iron and other elements, such as copper, cobalt, nickel, cadmium and antimony, which if allowed to remain with the zinc would interfere with the succeeding electrolytic process.

Leaching the calcinated material in spent electrolyte produces an impure zinc sulphate solution, which, after the removal of iron, still includes as major impurities copper, cadmium, cobalt and nickel. These metal impurities must be substantially removed through succeeding solution purification. Apart from the necessity of such purification, the recovery of these metals, in particular copper and cadmium, is economically beneficial [1].

The zinc electrowinning process is unusual from a thermodynamic point of view because zinc metal has a more negative reduction potential than hydrogen:



One would therefore expect hydrogen gas to evolve at the expense of zinc deposition. However, zinc metal is electrowon economically from acidic zinc sulfate solution because hydrogen evolution has a high overpotential on zinc metal. In order to maintain this large overpotential, almost all impurities in the leach solution must be completely removed [2]. Any remaining impurities act as catalysts for hydrogen evolution causing large drops in current efficiency.

Primary impurity removal in the roast-leach-electrowinning process takes place towards the end of the neutral leach stage by the neutralization-precipitation of a ferric hydroxide phase that acts as a scavenger for impurities like arsenic, antimony, germanium and tin [3]. Remaining traces of impurities in the zinc electrolyte are subsequently removed in the main purification section of the process by cementation with zinc dust [4].

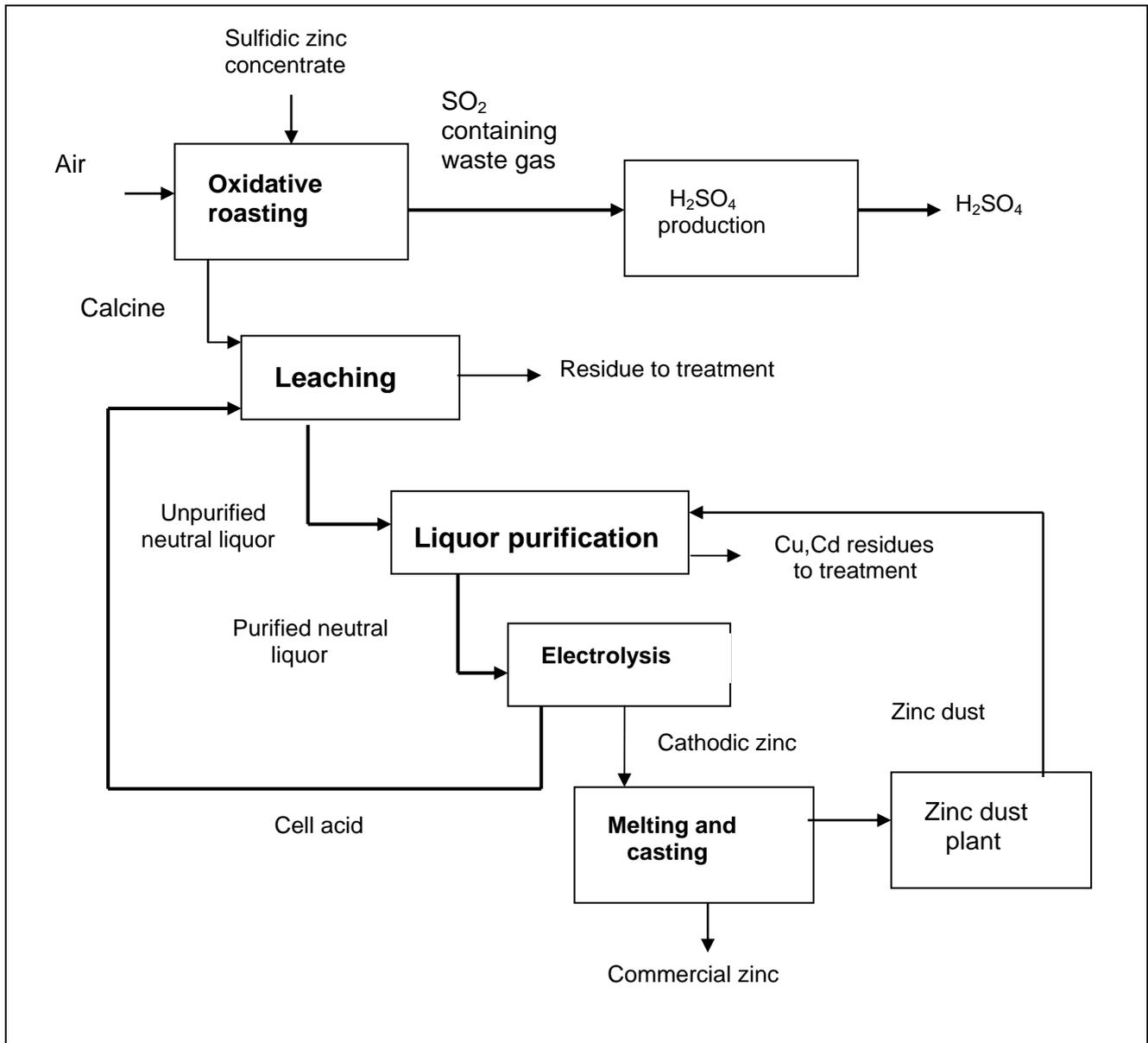


Figure 1: Flow diagram of the electrolytic zinc production process

1.1 Solution purification

Zinc solution purification is accomplished on a large scale by cementation of the impurities with zinc dust, in accordance with the reaction:



With Me = Cu, Co, Ni, Cd, etc. and n=valence. Cementation takes place because zinc has a more positive oxidation potential than the impurities.



Modern solution purification processes using zinc dust require several purification stages and are accomplished in agitator tanks at varying operating conditions. In the „arsenic hot-cold process“ (Fig. 2) [5,6], copper, cobalt and nickel are precipitated at high temperatures during the first stage by adding zinc dust and arsenic trioxide. Cadmium is separated at low temperatures in a second stage, using zinc dust and copper sulphate as activator.

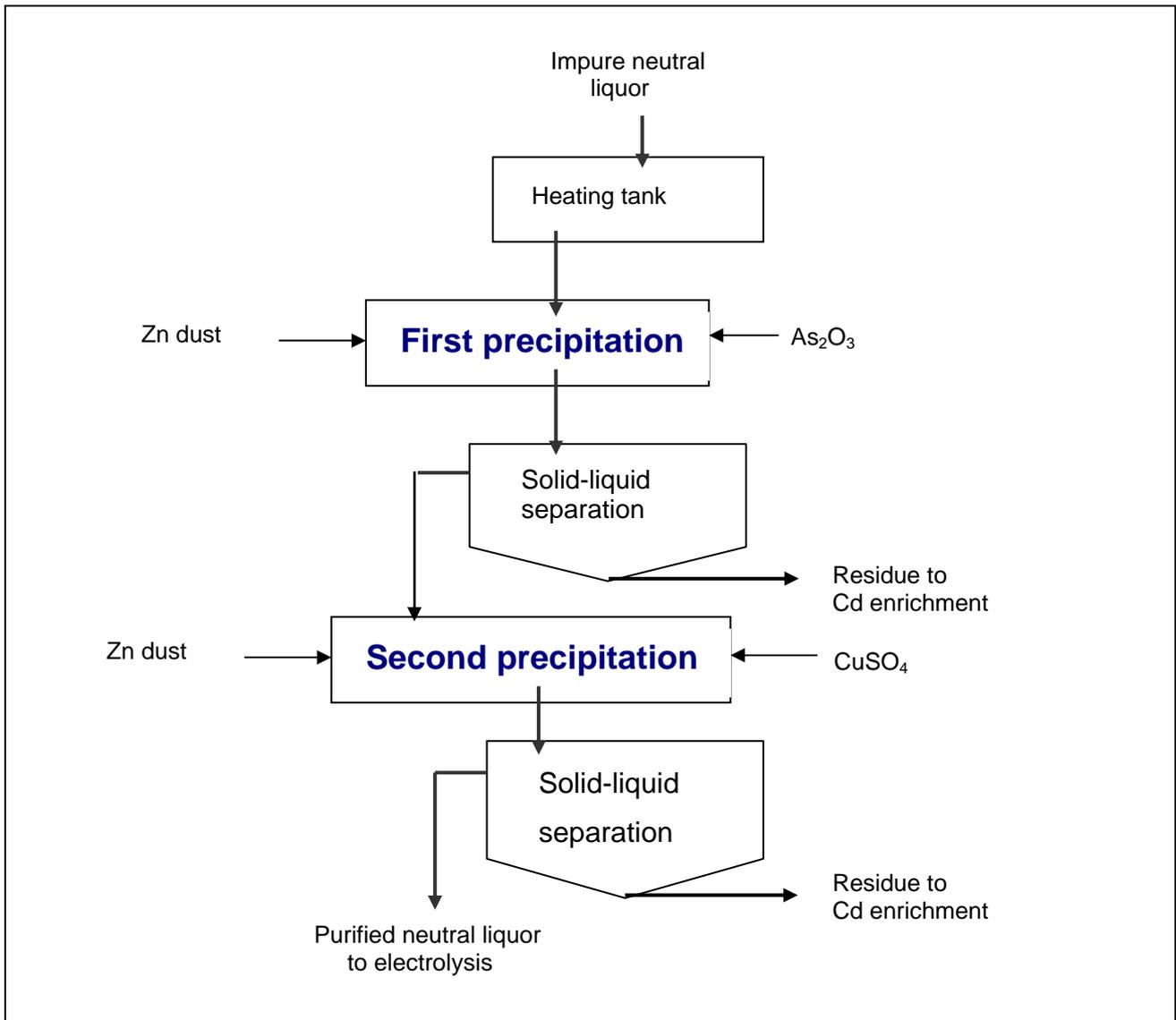


Figure 2: Arsenic “Hot-cold” purification process

The „reverse antimony process“ (Fig. 3) [7], also known as the Vielle Montagne method, provides for cementation of copper, cadmium and part of the nickel during the first stage at low temperatures



by adding zinc dust. In the second stage, cobalt and the remaining nickel are precipitated at high temperatures by adding zinc dust, antimony trioxide and copper sulphate if necessary.

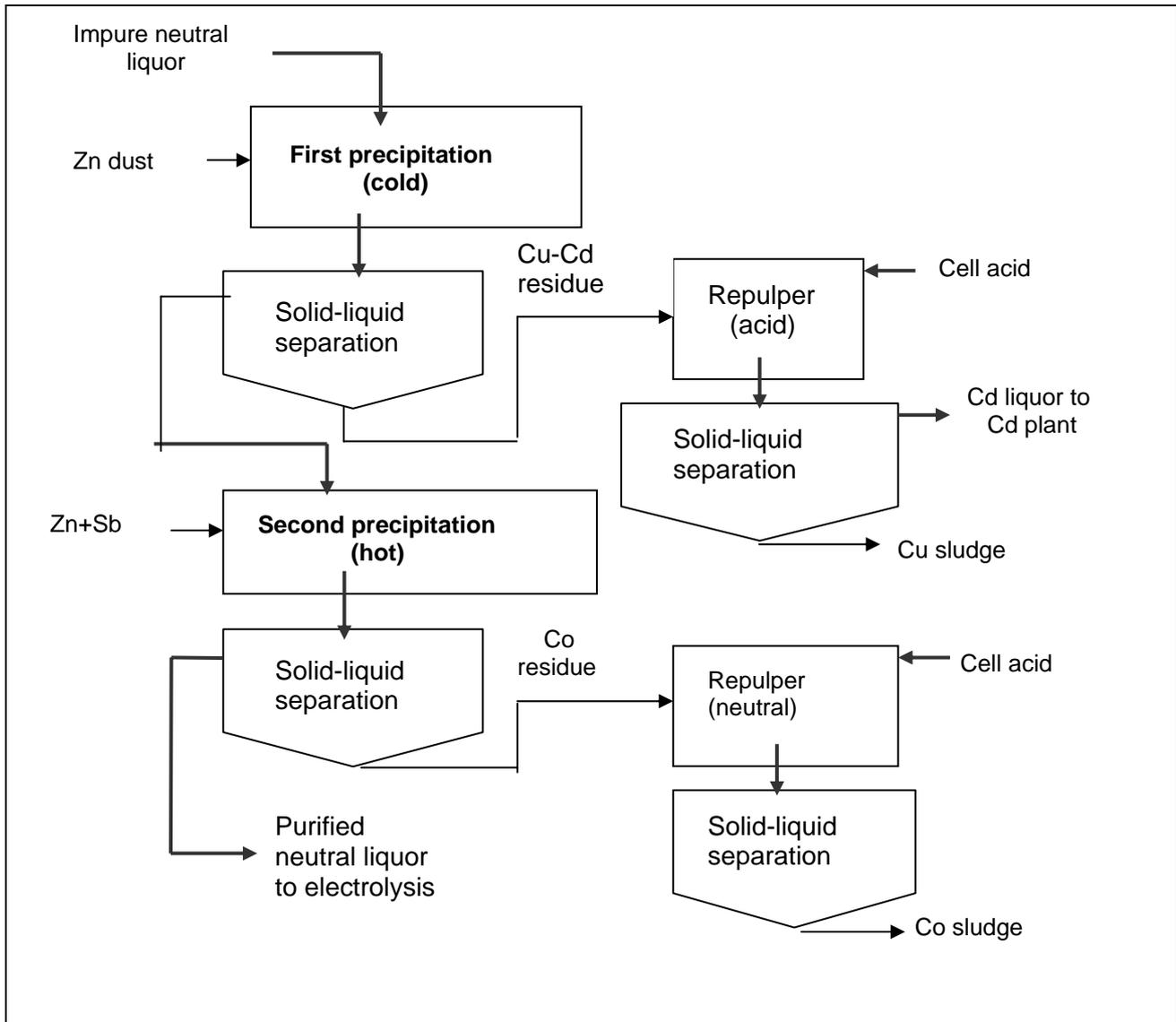


Figure 3: Reverse solution purification

A number of plants [8,9] use three or more purification steps, with, for example, additional decoppering or polishing stages.

Another process was developed in the Kokkola zinc plant of Outokumpu Oy [10,11]. The solution purification comprises three stages. In the first stage, the copper is removed with zinc dust in a continuous process. The copper residue is separated in thickeners and the solution continues to the cobalt and nickel removal. These metals are removed with zinc dust and arsenic trioxide in an automatic batch process. The solution is filtered on filter presses and the clear solution goes to the



third stage in which the cadmium is removed in fluidized bed reactors using a zinc dust bed. After this, the solution is ready to be fed to the cell house. Originally normal hot arsenic-zinc dust purification was used for the removal of copper, cobalt and nickel, and zinc powder purification for the removal of cadmium, but all the Cu in the solution came out of the process as a precipitate containing 7-10% of arsenic, which in Kokkola made the value of Cu close to zero. Studies were started to get better understanding of the mechanism of the Co and Ni precipitation because if the amount of Cu in this step could be lowered, it would be possible to precipitate at least some of the Cu contained in the raw solution in a preceding step, and thus a pure copper product without arsenic could be obtained. The findings were that Co could be successfully precipitated with no Cu at all in the solution. Later results showed, however, that small amounts of Cu (50-80 ppm) in the solution are beneficial.

Some authors have intended to elucidate if Cu is necessary for the Co precipitation. Yamashita [12,13] propose that a galvanic cell is formed between zinc dust and copper particles, which are precipitated first by zinc dust, and cobalt is deposited on copper particles by this galvanic current and arsenious oxide in a solution accelerated the rate of precipitation of cobalt by co-deposition of As and copper

At the Pasminco Metals –EZ refinery in Hobart, Tasmania [14], the solution purification process is based on a 2-stage zinc dust cementation with precipitation of Cu (<0.5 mg Cu/l in product solution) in the primary purification stage at 80°C and Co, Cd and Ni in the secondary purification stage at 75°C with Sb₂O₃ and PbSO₄ as activators for Co removal. In this case Cu was not necessary for the Co precipitation with antimony.

The drawbacks of the currently used zinc solution purification processes are:

- High zinc dust consumption (16-152 Kg/t electrolytic zinc)
- Addition of activators (As₂O₃, Sb₂O₃, CuSO₄, etc.)
- Possible formation of high toxic AsH₃
- Contamination of copper cementates with As
- The process sometimes fails to meet the target level of impurities in the electrolyte
- Re-dissolution of impurities when the retention time is long
- The complex composition of the cementates make their processing uneconomical and difficult



These drawbacks are a technical and economic incentive to investigate ways to improve the performance of the solution purification systems. In this work was the possible use of the solvent extraction techniques for the zinc solution purification examined.

2 Solution purification by solvent extraction

In the hydrometallurgical copper recovery by leaching-solvent extraction-electrolysis the currently used extraction reagents are hydroxy oximes. These substances, like most of used extraction reagents, have the characteristic to extract various metals depending on the pH field where the extraction takes place. Fig. 4 shows extraction isotherms of LIX 84-I for several metals depending on pH. Another hydroxy oximes of LIX-group show similar behavior [15,16].

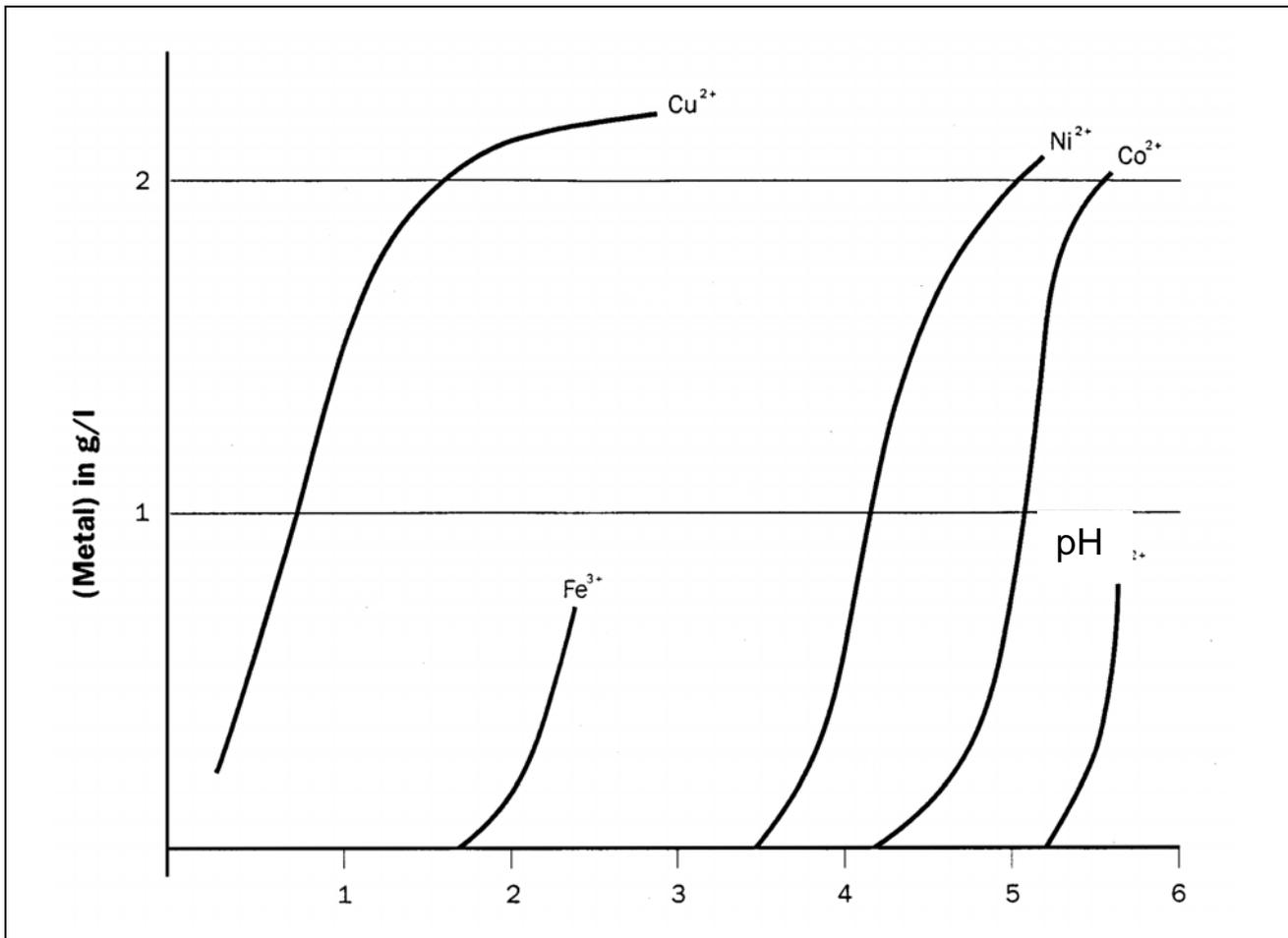


Figure 4 Extraction isotherms of LIX 84-I depending on pH



At low pH values the copper extraction is not favourable, but at high pH values is not selective over other metals like iron, cobalt and nickel.

In the case of zinc solution purification, the impure neutral solution has a pH between 4.5 and 5.5 because of partially neutralization for iron removal. According to Fig. 4 it is possible to remove the most important impurities of the zinc neutral solution (Cu, Co and Ni) with LIX 84-I at suitable pH (Table 1 shows the average composition of impure solution). It is expected that copper extraction takes place without problems and on the other hand that the extraction of Co and Ni would require an exact pH control.

Table 1: Composition of the neutral impure solution

Component	Concentration
Zinc	160 g/l
Copper	93 mg/l
Cobalt	2,8 mg/l
Nickel	2,3 mg/l
Cadmium	206 mg/l

2.1 Experimental

All experiments were carried out with the industrial neutral solution, which composition is shown in Tab. 1. The organic reagents LIX 984 and LIX 84-I were used as received and diluted with kerosene (Shellsol D70 and Exxsol D80). The strip solutions were prepared with sulfuric acid of analytical grade. The experiments were carried out on stirred (300 rpm) glass containers at room temperature. For pH control were used NaOH 0.1N and H₂SO₄ 0.1N solutions. The analysis of the solutions were realized by atomic absorption spectrometry.

2.2 Results and discussion

2.2.1 Copper extraction with LIX 984

First experiments to determine the efficiency of copper extraction with LIX 984 at normal concentrations used for the hydrometallurgical copper recovery at industrial scale have shown an optimal copper removal (100%) from zinc neutral solution. Subsequent analysis was to determine



the highest capacity of very diluted LIX 984 solutions for copper extraction. The loaded organic solution was put in contact with fresh neutral solution until the loading capacity was exhaust. Number of contacts in Figs. 5 and 6 mean the times that already loaded organic solution was put in contact with new neutral solution. Table 2 shows the analyzed variables and Figs. 5 and 6 show the best results.

Table 2: Variables for the optimization of copper extraction with LIX 984

Organic/aqueous ratio	1/3, 1/5
LIX 984 concentration (vol.%)	1, 3, 5
Number of contacts	1, 2, 3, 4, 5, 6, 7, 8

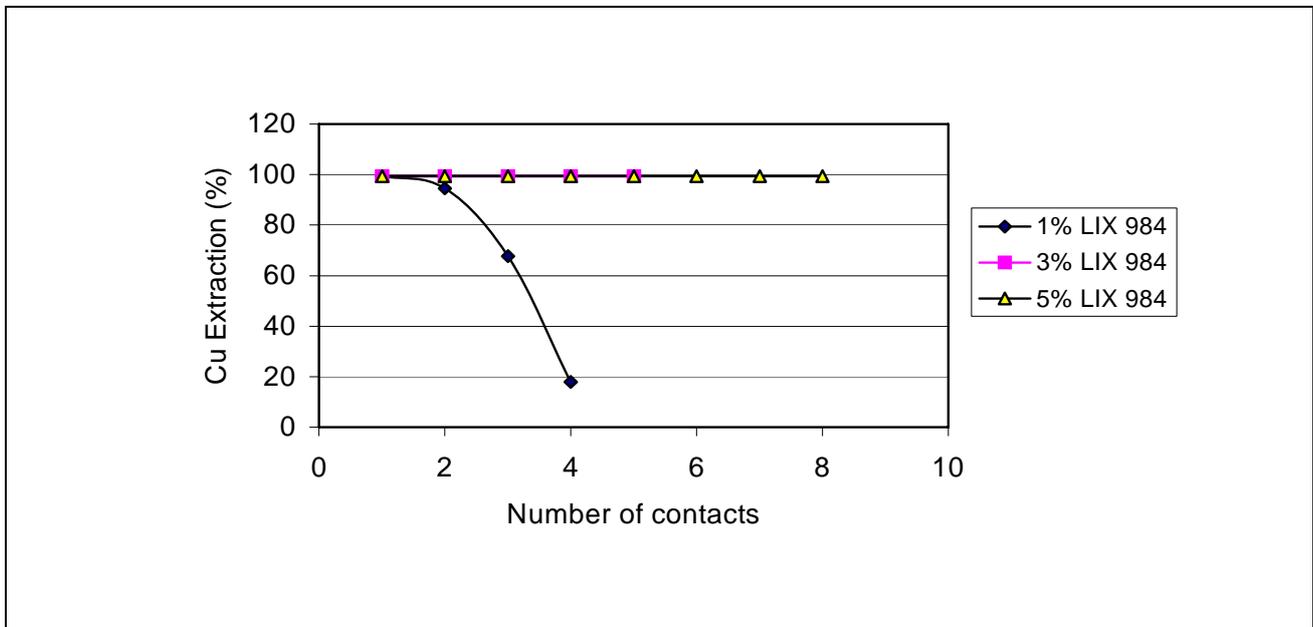


Figure 5: Effect of LIX 984 concentration and number of contacts on copper extraction.

A/O:3/1

The copper extraction was optimal for the concentrations 3 and 5 vol%. Only for the lowest concentration, that is 1 vol.% was observed a diminution of the loading capacity and therefore of the copper extraction: ~20% was extracted in the fourth contact. Fig. 6 shows the final concentration of copper in the neutral zinc solution. This concentration was below 1 mg/l copper for five contacts with LIX 984 3 vol.% and eight contacts with LIX 984 5 vol.%. For the LIX concentration of 1 vol.% the copper final concentration was 62 mg/l after four contacts.

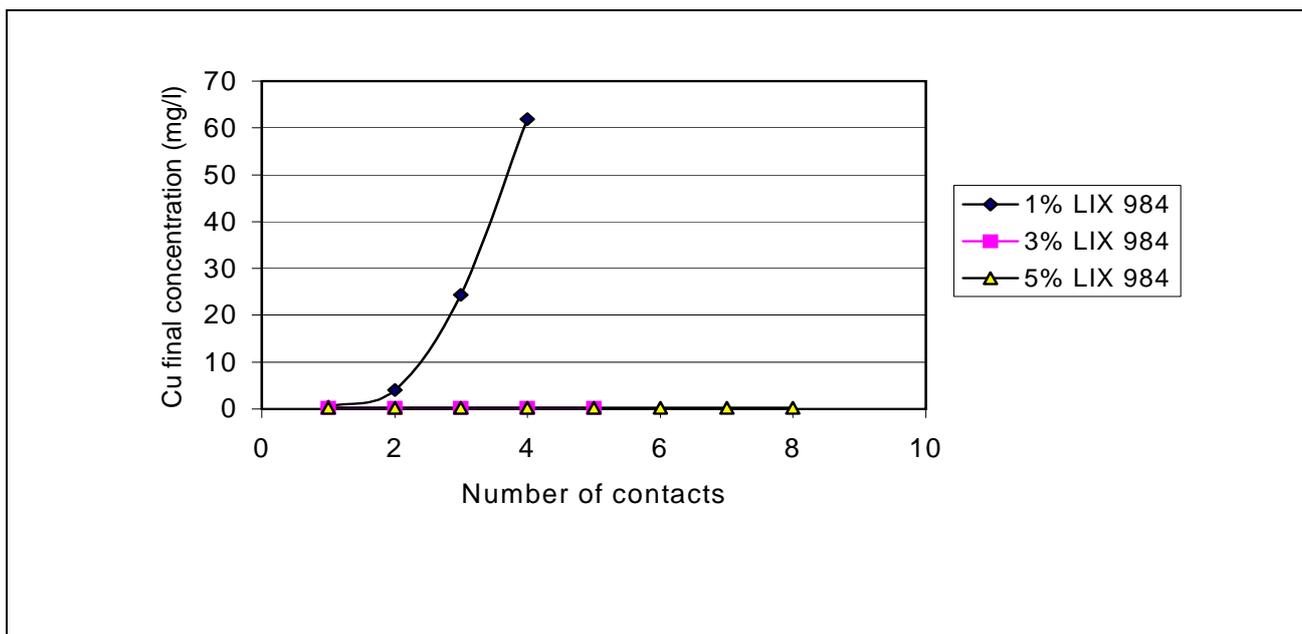


Figure 6: Effect of LIX 984 concentration and number of contacts on copper final concentration. A/O:3/1

2.2.2 Copper stripping from LIX 984

The use of strong extraction reagents like hydroxy oximes makes necessary high concentrated acid strip solutions to remove loaded copper, but for the following step of copper recovery by electrolysis the acid concentration should not be very high in order to avoid anode corrosion, in this case, the highest acid concentration was 160 g H₂SO₄/l. Table 3 shows the examined variables for copper stripping from LIX 984 organic solutions and the results are presented in figures 7 and 8. An organic/aqueous ratio of 5/1 was used.

Table 3: Variables for the optimization of copper stripping

LIX 984 conc. (vol.%)	3, 5
H ₂ SO ₄ conc. (g/l)	100, 130, 160
Number of contacts	1, 2, 3

Even for the highest acid concentration the stripping of copper is only around 40%. This makes necessary to perform repeated contacts with fresh organic LIX solution. In order to improve the stripping efficacy was decided to use a less strong extraction reagent, in this case LIX 84-I.

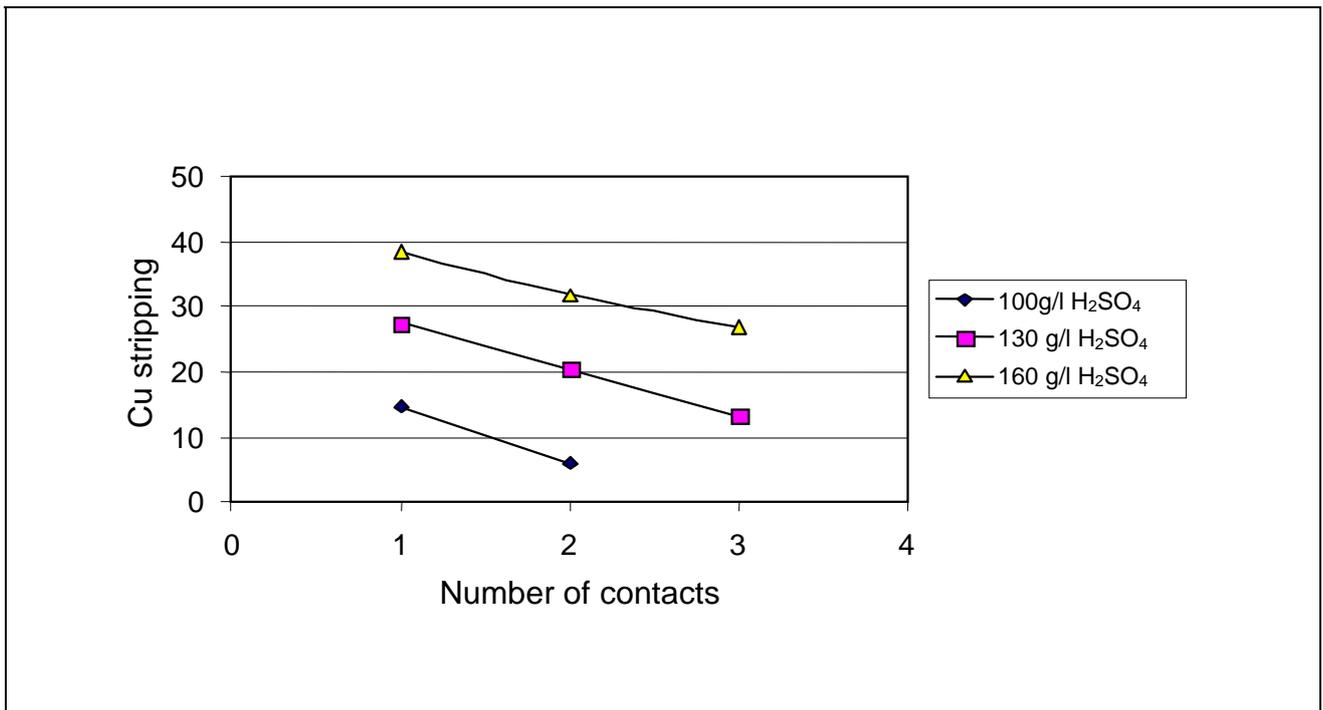


Figure 7: Effect of H₂SO₄ concentration and number of contacts on copper stripping from LIX 984. LIX concentration: 3 Vol.%

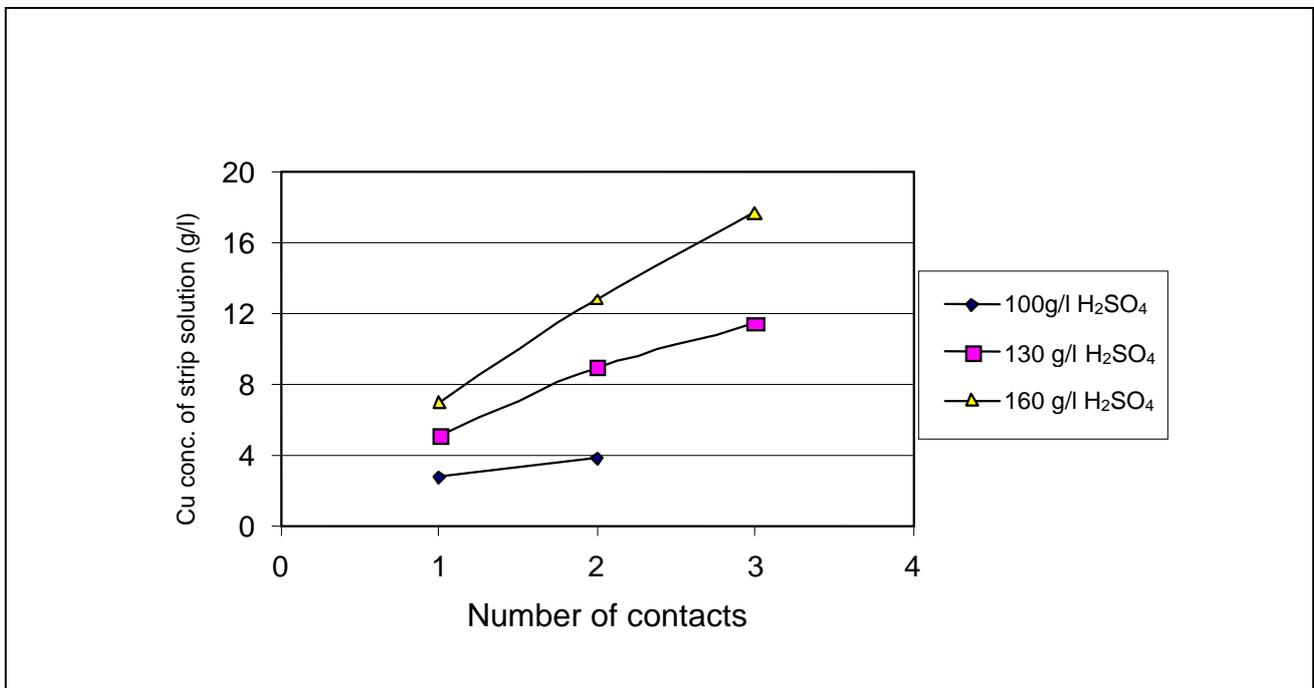


Figure 8: Dependence of copper final concentration in the strip solution on number of contacts for various H₂SO₄ concentrations. O/A:5/1, LIX conc. 3 Vol.%



2.2.3 Copper extraction with LIX 84-I

Similar experiments like for LIX 984 were carried out to determine the copper extraction characteristics of LIX 84-I from the neutral zinc solution. Figures 9 and 10 present the optimal results and Table 4 shows the experimental conditions. For a LIX 84-I concentration of 3 vol.% the extraction was optimal until the fifth contact, like for LIX 984, but for the concentration of 1 vol.% a light extraction improvement of LIX 84-I over LIX 984 was observed, although LIX 84-I is described as weaker extraction reagent.

Table 4: Variables for the optimization of copper extraction with LIX 84-I

Organic/aqueous ratio	1/3, 1/5
LIX 984 concentration (vol.%)	1,3
Number of contacts	1, 2, 3, 4, 5

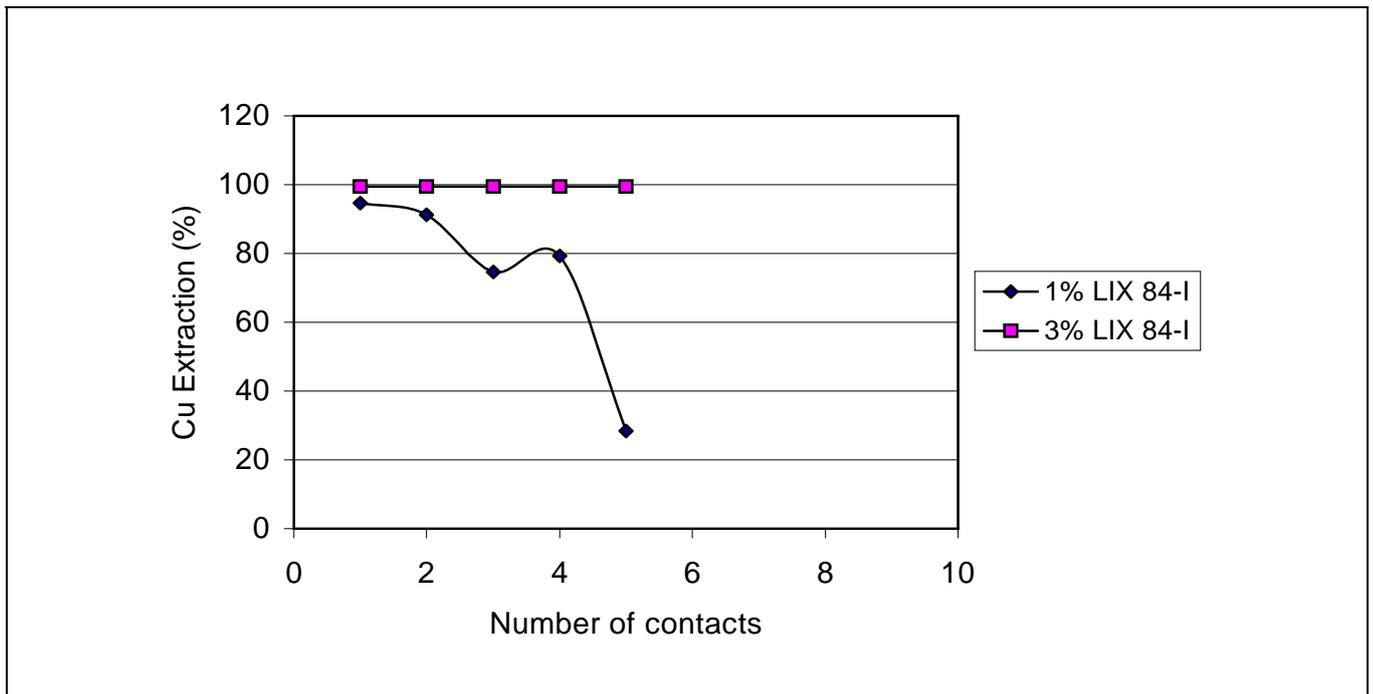


Figure 9: Dependence of copper extraction on number of contacts for various LIX 84-I concentrations. A/O:3/1

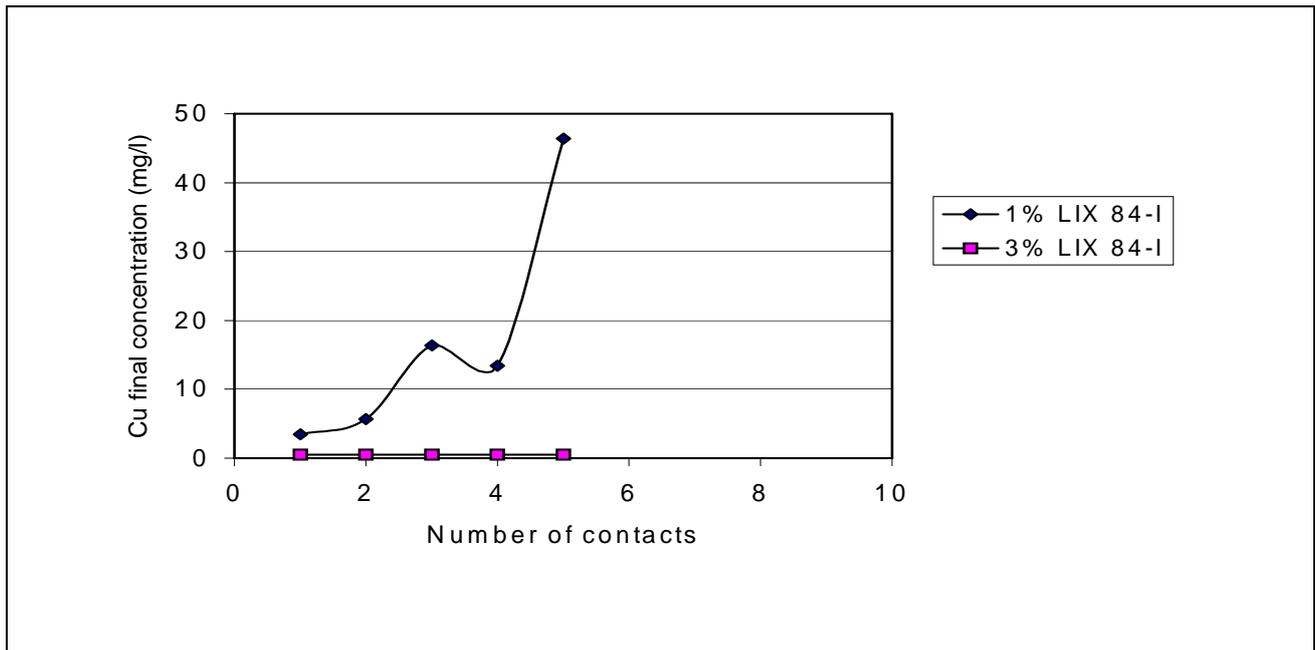


Figure 10: Effect of number of contacts on copper final concentration for various LIX 84-I concentrations. A/O:3/1

2.2.3 Copper stripping from LIX 84-I

Table 5 shows the examined variables for the optimization of copper stripping from organic solutions of LIX 84-I and figures 11, 12 and 13 present the results. An unusual behavior of the strip solutions was observed. The best result was not at the highest acid concentration but with 130 g H_2SO_4/l . At low concentration (100 g/l) a decrease and then an increase of the stripping percentage was observed, while at higher concentrations a typical decrease of the loading capacity of the organic solution was determined.

The efficacy of the copper stripping from LIX 84-I was better as from LIX 984. A stripping percentage of more than 60% was reached for the acid concentration of 130 g H_2SO_4/l and an organic/aqueous ratio of 5/1. To optimize the stripping step an organic/aqueous ratio of 1/1 was examined. Fig. 13 shows the optimal results with this ratio after five contacts.

Table 5: Variables for the optimization of copper stripping from LIX 84-I

LIX 84-I conc. (vol.%)	3, 5
H_2SO_4 conc. (g/l)	100, 130, 160
Organic/aqueous ratio O/A	5/1, 1/1
Number of contacts	1, 2, 3

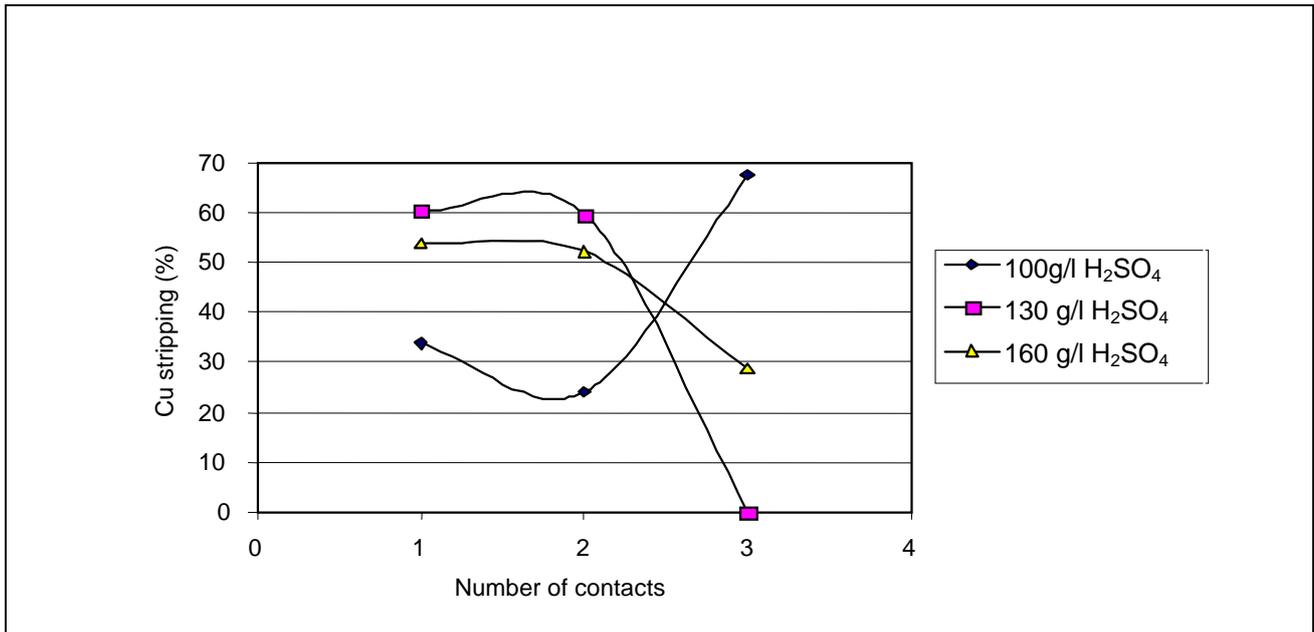


Figure 11: Dependence of copper stripping on number of contacts for various H₂SO₄ concentrations. O/A: 5/1, LIX conc. 3 vol.%

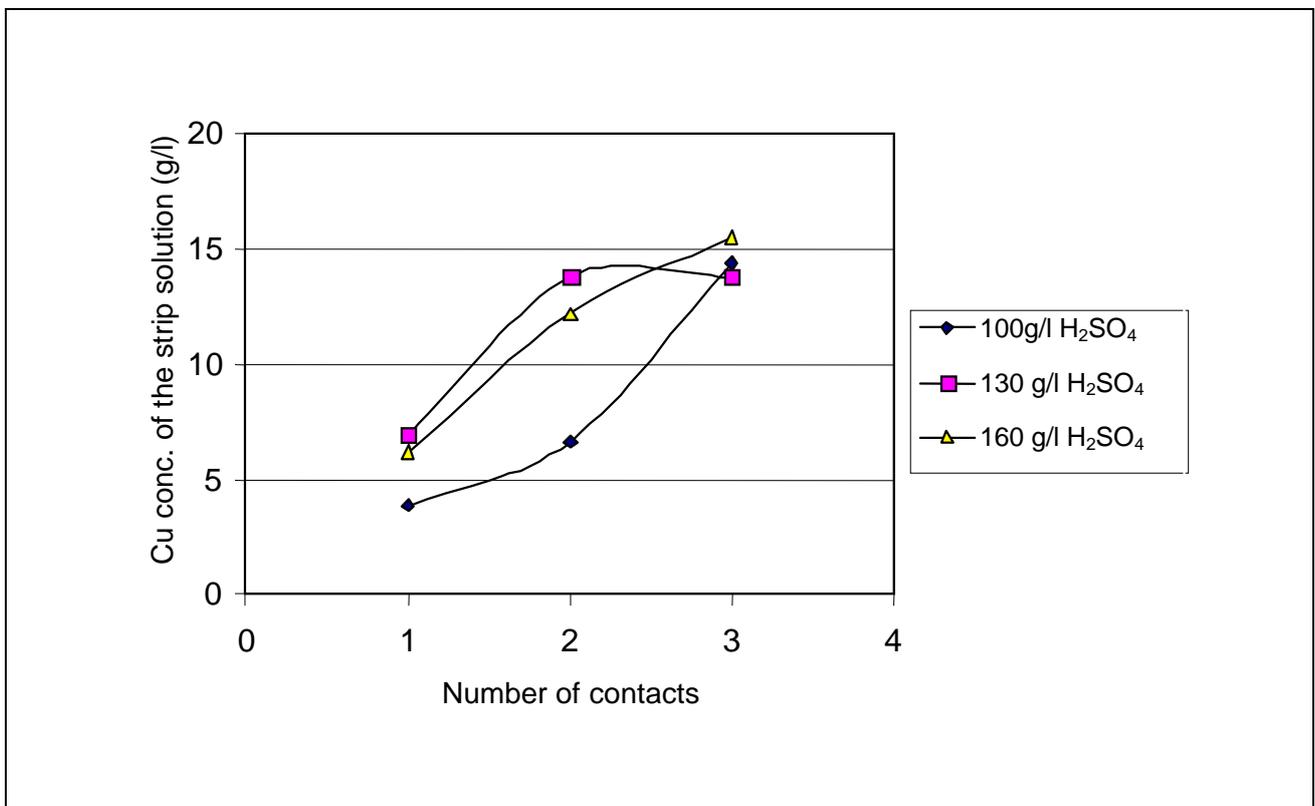


Figure 12: Dependence of copper final concentration of strip solution on number of contacts for Various H₂SO₄ concentrations. O/A:5/1, LIX conc. 3 vol.%

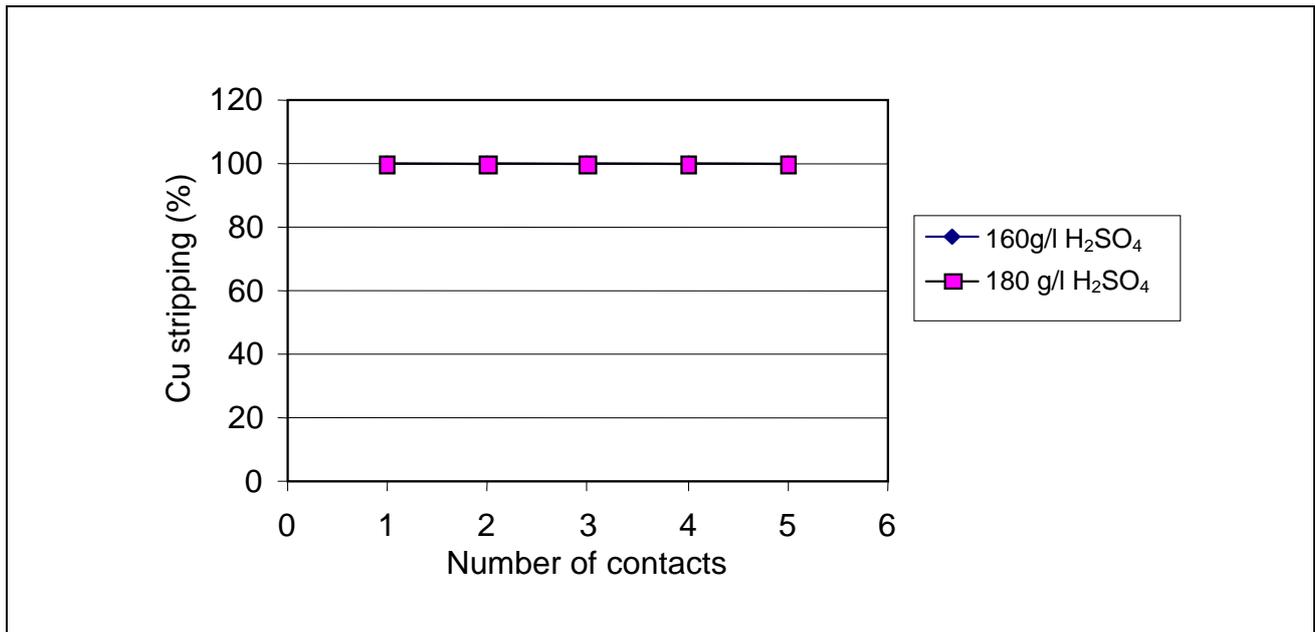


Figure 13: Effect of number of contacts on copper stripping for various H₂SO₄ concentrations. O/W:1/1. LIX conc. 5 vol.%

2.2.5 Cobalt and nickel extraction

The cobalt and nickel extraction experiments were carried out only with LIX 984. First step was to determine the pH field of extraction. In this case pure cobalt and nickel solutions were used to avoid interferences due to the high zinc concentration of the neutral zinc solution. It was worked with an organic/aqueous ratio of 1/5 and a LIX 984 concentration of 4 vol.% at room temperature. Figures 14 and 15 show the results. The best cobalt extraction (~80%) was observed at a pH of 4.65 and of nickel at 5,4 (~90%). This results were an incentive to further examination of extraction at pH values of 5.0.

Next step was the determination of cobalt and nickel extraction efficacy of LIX 984 with solutions which contain both metals. The results (Fig. 16) showed lower extraction percentages for both metals. The mix has apparently a negative influence on extraction.

Finally the cobalt and nickel extraction of the zinc neutral solution for various pH values was examined, but due to the very high zinc concentration and the closeness of the zinc hydrolysis pH zinc precipitation was readily observed. At lower pH the extraction was not satisfactory. For this reason it was decided to stop the examination of cobalt and nickel extraction for this solution.

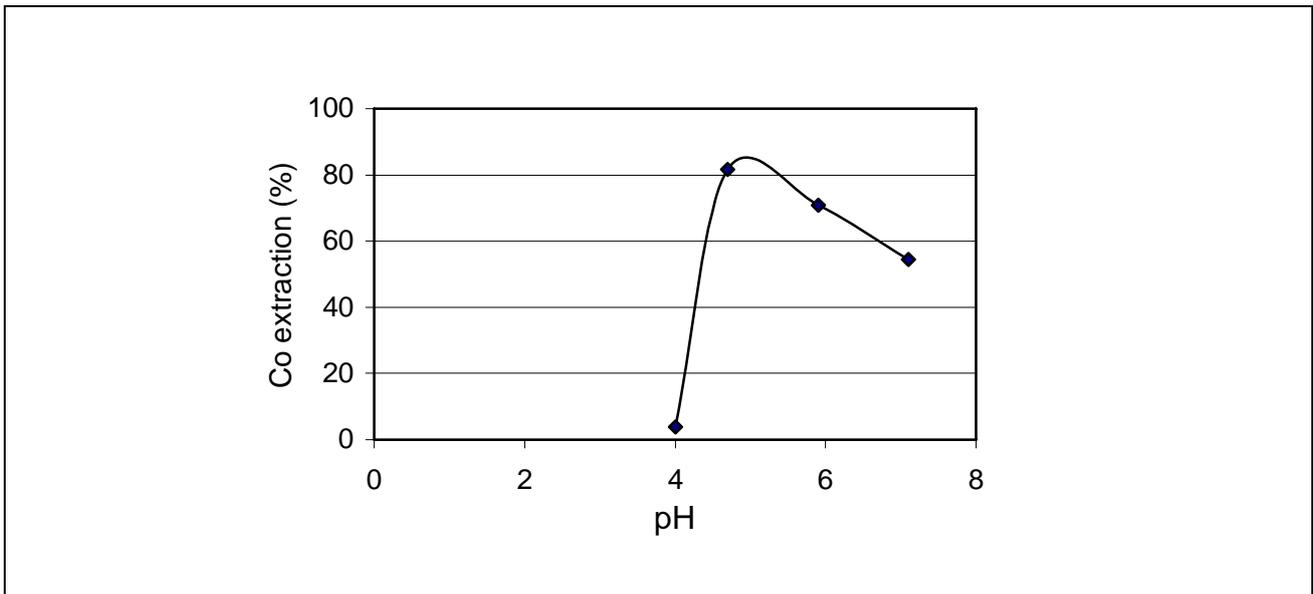


Figure 14: Dependence of cobalt extraction on pH. LIX 984 conc. 4 vol.%, O/A:1/5

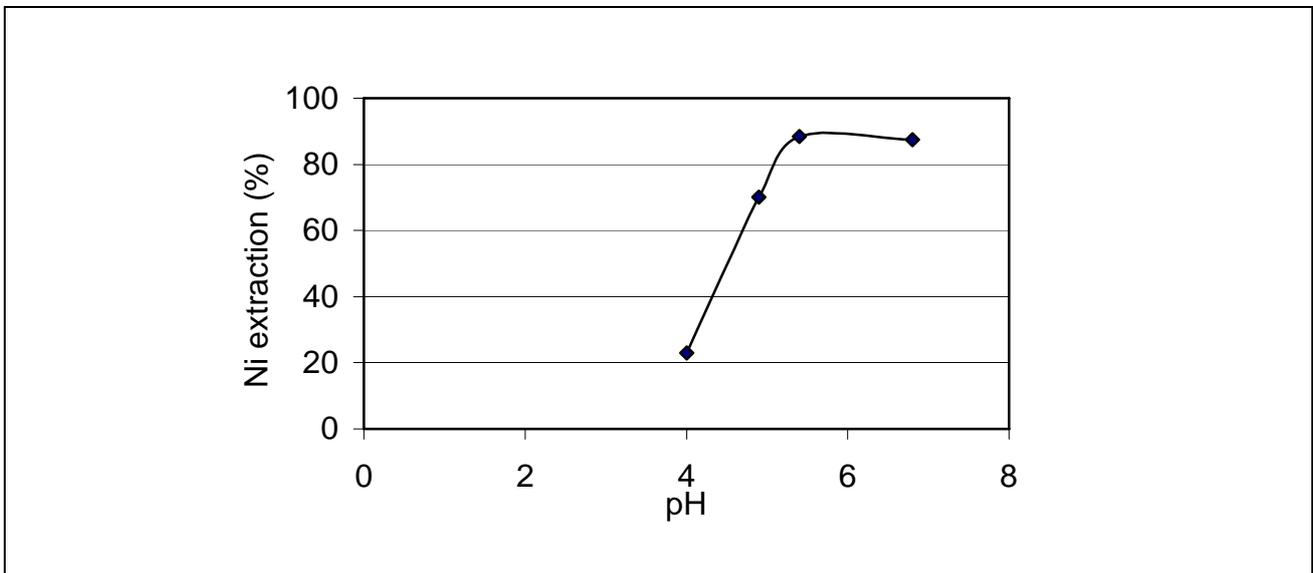


Figure 15: Dependence of nickel extraction on pH. LIX 984 conc. 4 vol.%, O/A:1/5

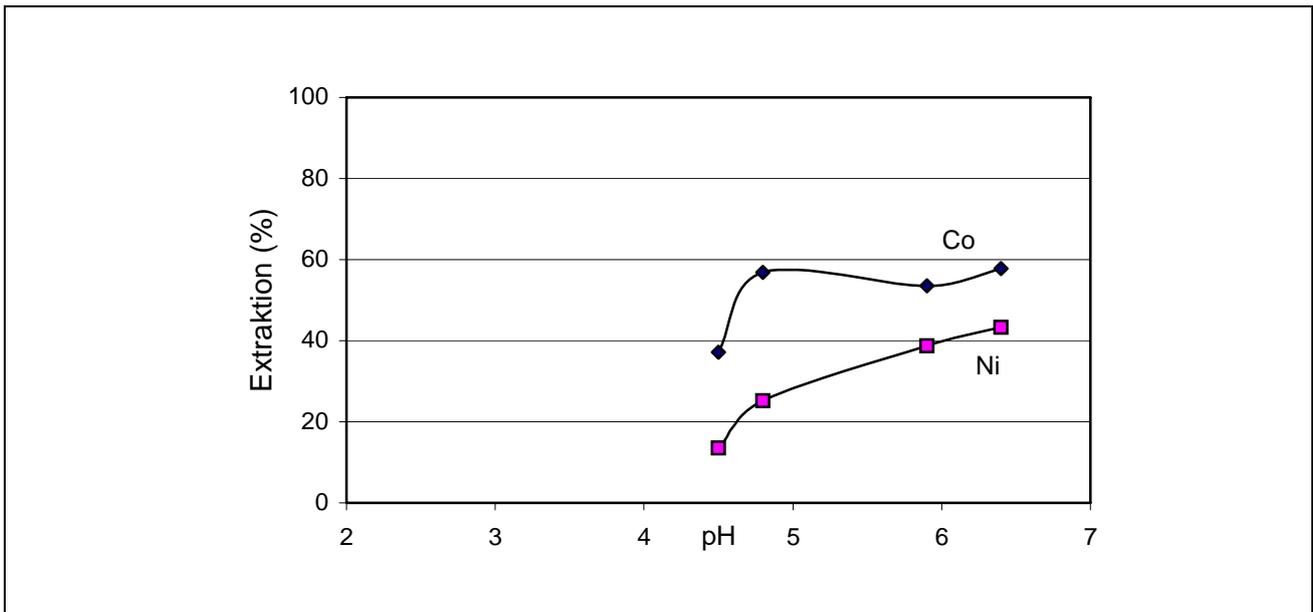


Figure 16: Dependence of cobalt-nickel extraction on pH. LIX 984 conc. 4 vol.%, O/A:1/5

2.2.6 Cementation of cobalt and nickel

Some authors [10,13] affirm that the presence of copper is necessary for the cobalt and nickel cementation with zinc dust and activators. For this reason it was decided to examine the cobalt and nickel cementation after removal of copper by solvent extraction from the neutral zinc solution. Figures 17 and 18 show the cobalt and nickel cementation for various copper initial concentrations. It was observed that a little copper concentration in the solution has a positive influence on the cobalt and nickel cementation.

In order to avoid an addition of copper after its complete removal by solvent extraction for cobalt elimination by cementation, it was examined the possibility that also a low cadmium concentration would improve the cobalt cementation. Figure 19 shows the positive results also with cadmium, which in any case will be removed also by cementation. Removal of copper by solvent extraction followed by cadmium removal until a concentration of 30-50 mg/l and finally cobalt and nickel cementation with activators is recommended as conclusion.

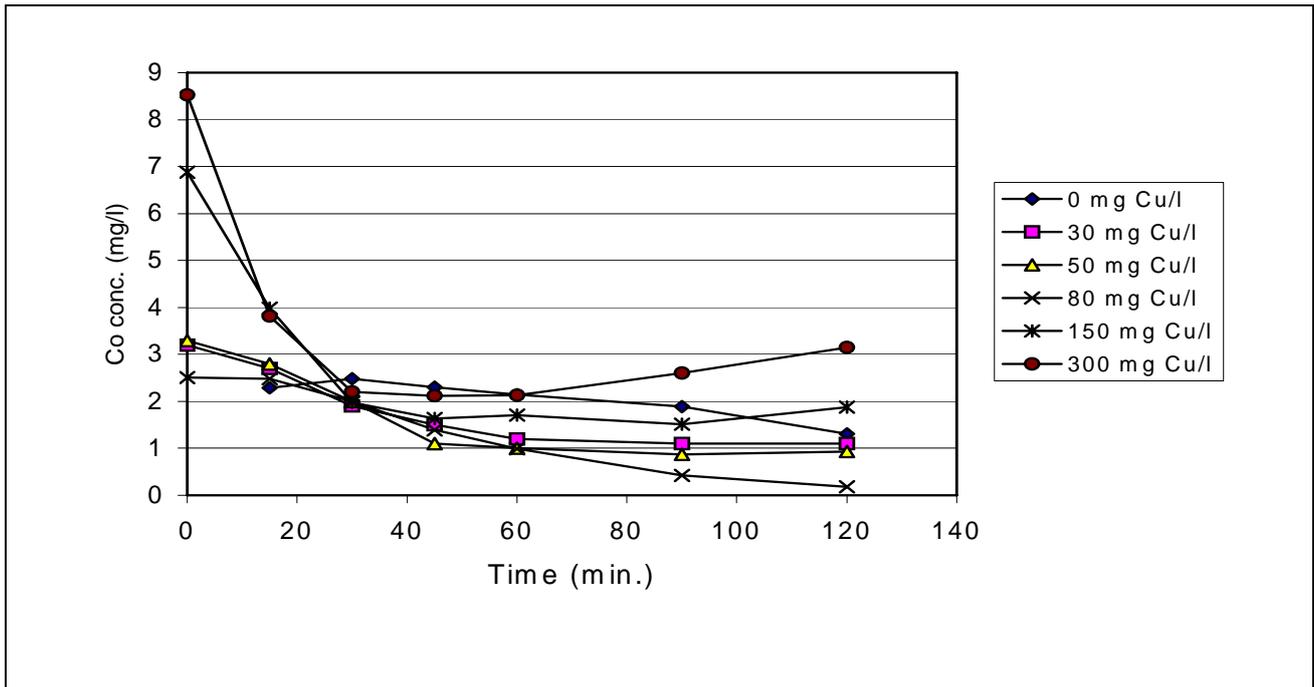


Figure 17: Dependence of cobalt cementation on time for various copper concentrations.
 2 g/l zinc dust, 60 mg/l As_2O_3

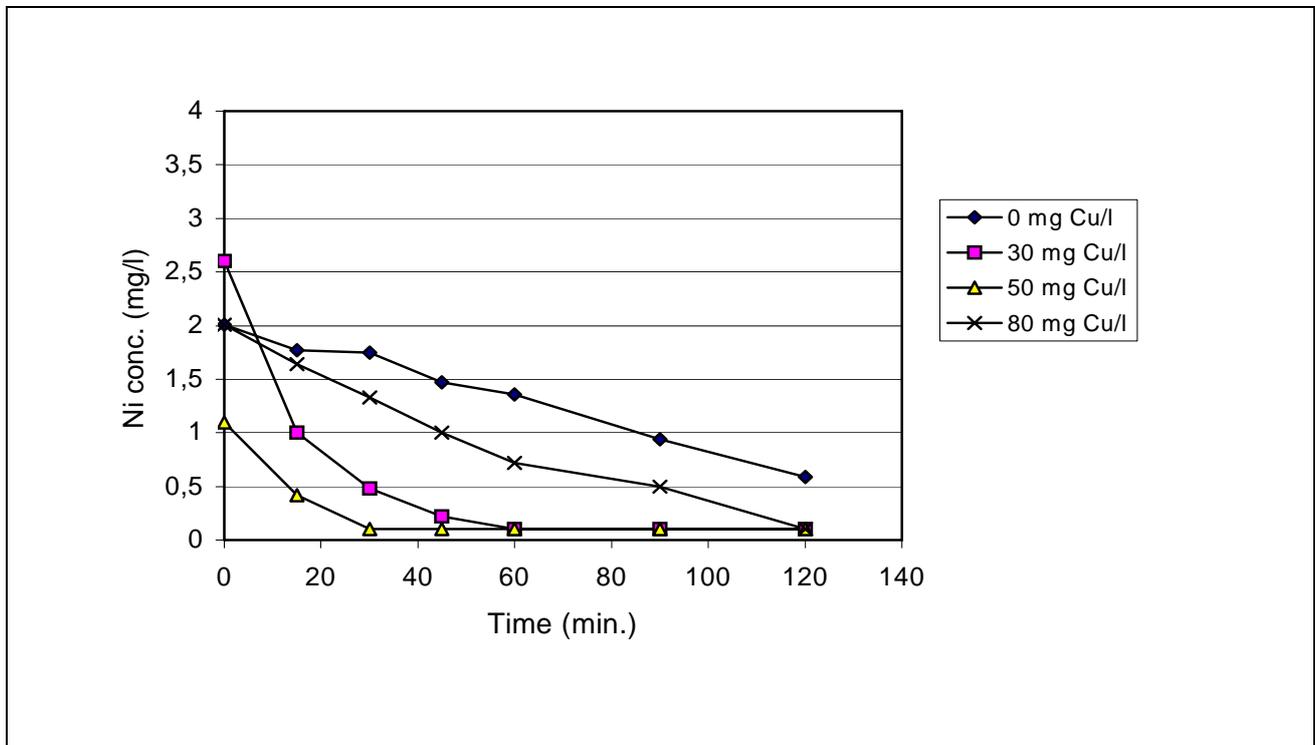


Figure 18: Dependence of nickel cementation on time for various copper concentrations.
 2 g/l zinc dust, 60 mg/l As_2O_3

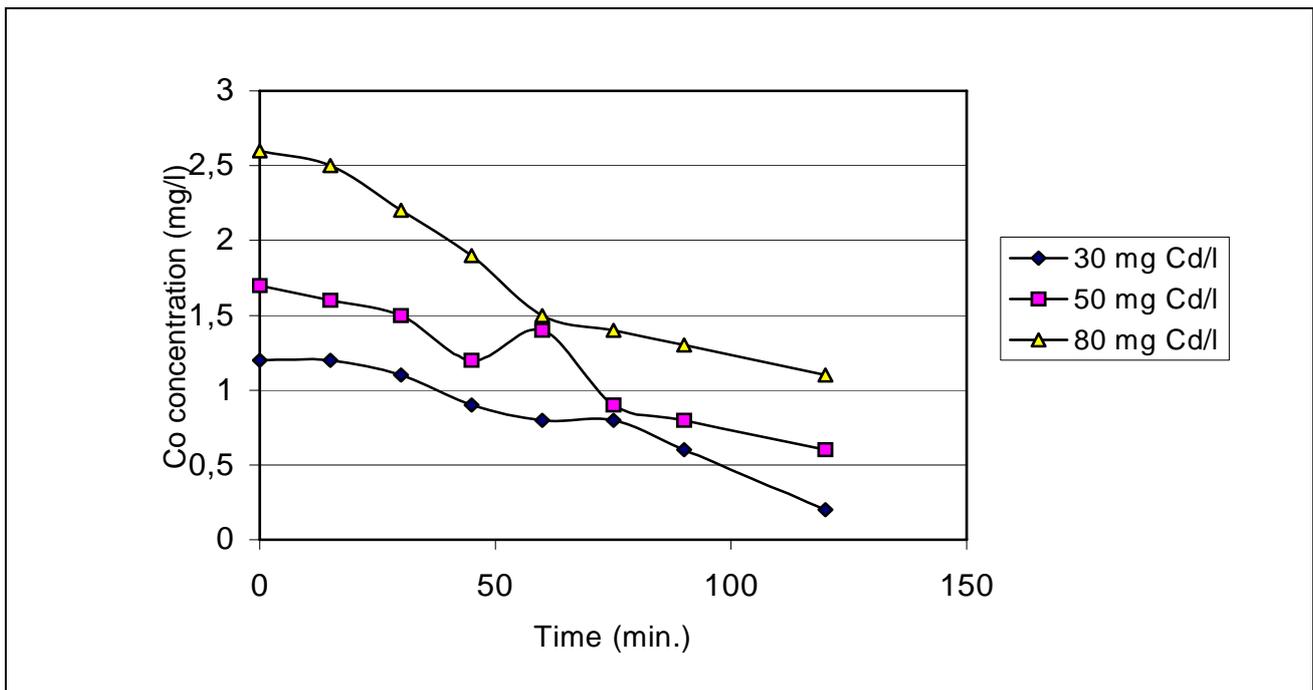


Figure 19: Dependence of cobalt cementation on time for various cadmium initial concentrations. 2 g/l zinc dust, 60 mg/l As_2O_3

3 Proposed alternative solution purification processes

According to the experimental results is clear, that the copper removal from zinc solutions by SX is effective and selective. The use of the SX technique in the zinc solution purification makes also possible the hydrometallurgical processing of zinc materials with high copper content.

The possible introduction of the SX technique in the conventional practice of the zinc solution purification is showed in Figs. 20 and 21. In the case of the hot-cold purification process the copper extraction is carried out until the required copper concentration for the further cobalt removal in the second purification step is reached. For the cadmium removal is recommended to use fluidized bed reactors in order to minimize the zinc dust consumption.

For the introduction of copper solvent extraction in the reverse purification process is also a copper extraction as first step recommended and then cadmium removal by cementation with zinc dust. In this case the separation of copper and cadmium of the cementate is not necessary. For the Co and Ni cementation is recommended the addition of a little volume of copper free solution from the first



purification step in order to accelerate the Co removal with antimony as activator in the presence of a low cadmium concentration (see cap. 2.2.6).

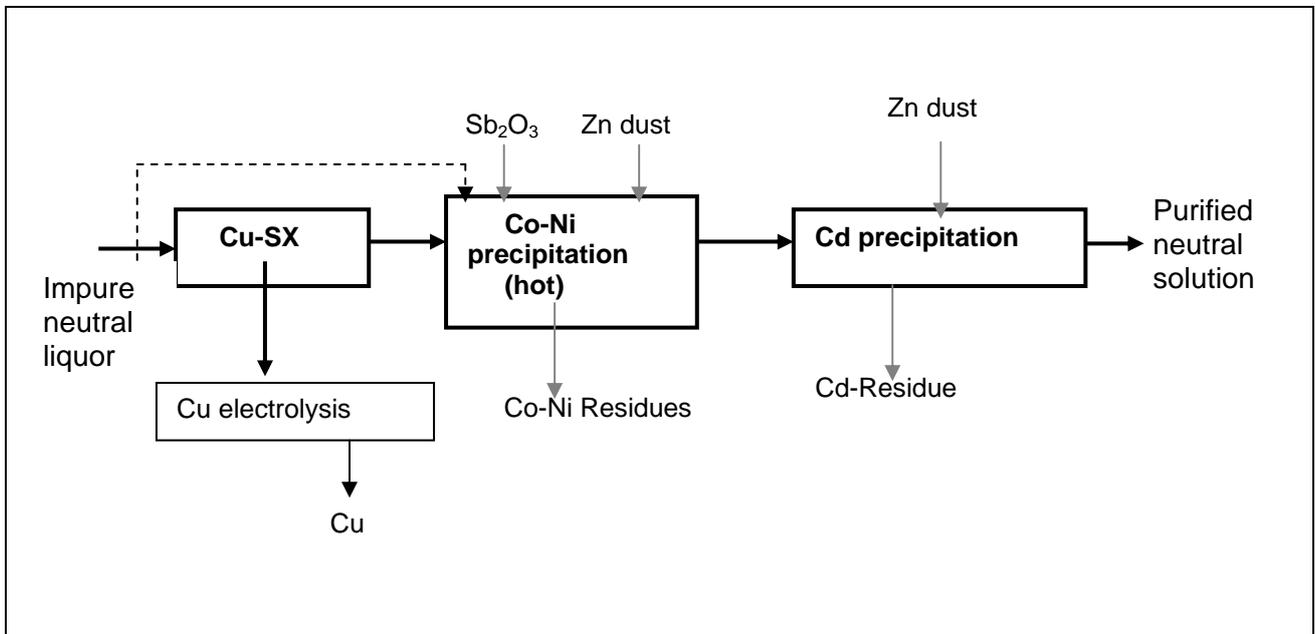


Figure 20: Alternative solution purification by the hot-cold process

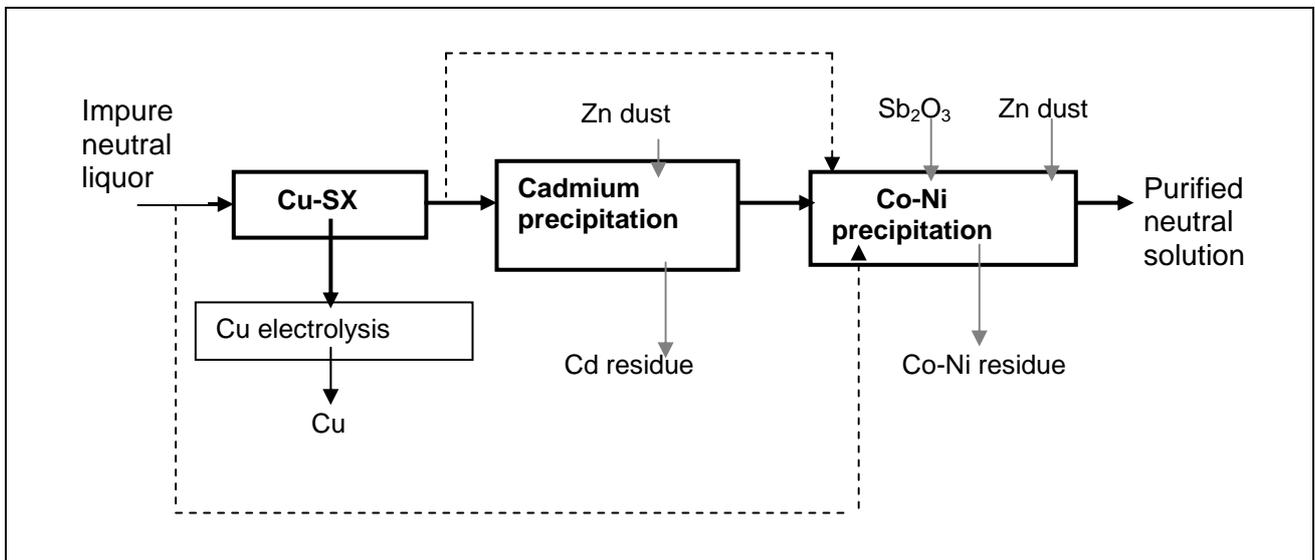


Figure 21: Alternative solution purification by the reverse process



4 Conclusions

The drawbacks of the conventional zinc solution purification process are an economical and technical incentive to search for ways to improve the performance of the purification systems. In this work the possible use of the solvent extraction technique to eliminate the most important impurities as copper, cobalt and nickel from the neutral zinc solution after leaching process was examined.

Optimal results were reached for the extraction of copper using two modern organic extractants (LIX 984 and LIX 84-I) which are currently in use in hydrometallurgical copper winning plants. The reached final copper concentration was lower than 1 mg/l. The stripping of copper with high concentrated sulfuric acid solutions is also optimal. From the enriched copper solutions can be copper electrolytically readily recovered.

The cobalt and nickel extraction was only partially reached and since the pH field of extraction for these metals is very near to the zinc extraction field, is the co-extraction and the precipitation of zinc hydroxides very probable.

The examination of the possibilities to complete the elimination of impurities of the zinc solution gave as best result the removal of copper by solvent extraction, followed by the cadmium removal by cementation with zinc dust and finally the cobalt removal by cementation with activators (preferably Sb_2O_3) in presence of Cd at low concentration. The use of the solvent extraction process is more convenient in the reverse than in the hot-cold purification process.

5 References

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