

METALS RECOVERY FROM INDUSTRIAL EFFLUENTS BY SOLVENT EXTRACTION PROCESS

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ABSTRACT

This work presents the results of three experimental researches developed at CDTN – Centro de Desenvolvimento da Tecnologia Nuclear, using the solvent extraction technique, applied to industrial residues recovery. The main goal of these projects is to define a technically feasible process, to solve the environmental problem. The first one presents a study of indium and iron recovery from sulfuric liquor generated during the hydrometallurgical processing of zinc. A study of the main parameters of the process was conducted by the following steps: iron and indium extraction, indium stripping, iron stripping and solvent regeneration. It was obtained high purity products of these metals. If it applied industrially can solve the environmental problem generated by the jarosite waste.

In Brazil, the neutralization/precipitation method is applied for the treatment of the waste from the pickling process generating a large quantity of nitric nitrogen. Another work developed describes a study of nitric and hydrofluoric acids mixture recovery, as well as iron, nickel and chromium, present in industrial waste from stainless steel pickling process.

The hydrometallurgical processing of zinc concentrate, generates a solid waste with a high concentration of soluble zinc that contaminate the aquiferous. The last project investigates the solvent extraction technique applied to zinc recovery in order to solve the aquiferous contamination. Besides that the loss of this metal and water processing could be reduced.

Key words: acid recovery, industrial effluent treatment, metals recovery.

INTRODUCTION

Minas Gerais, a state of Brazil, presents a prominence mineral and metallurgical profile and a high number of industries in this area with a variety of minerals and metals products. The liquid effluents of these processes usually contain acids and distinct kinds of metals according to the industrial activity.

One example of that occurs in the siderurgical area, on the pickling of stainless steel step. In that process is generated a high volume of acid effluent with a high level of metals. The hydrometallurgical processing of ores generates effluents that contain other value metals besides the basis metals that usually are precipitate. This precipitation gives origin to big tailing deposits.

The iron is the most abundant metal in those effluents. Besides that we meet nickel, zinc, Chromium, indium, Gallium and others. These effluents are considered a environmental preoccupation because of their chemical characteristics. So the treatment of these effluents is a fundamental step to minimize the environmental impact caused by the development of these industrial activities.

The traditional methodology to treat these effluents involves one step of neutralization in order to precipitate the metals and discard the water. The Disposal of these residues constitutes high cost of implantation and maintenance and can take to polluting emission.

At present the recovery of the industrial wastes from the hydrometallurgical process has been showed as a main challenge of the technological development. This development aims the application of new technologies and to evaluate the existent process and take to a rational utilization of the natural resources and the byproducts recovery. The final product is the minimization of the environmental impact with increasing of the profit.

The most used process for this propose involves the solvent Extraction technique as the main step associated to the precipitation step. The solvent extraction is an equilibrium process between two immiscible phases, aqueous and organic, where occurs a selective transference of one or more species from one phase to the other. By this process, can be obtained a purified product of the required metal or specie.

In the first step (extraction stages) the metal is transferred from the aqueous phase to an organic phase. The second step is reverse of the first, the metal is transferred from the organic phase to the aqueous phase (Stripping stage). The conditions are adjusted to became the metal separation as selective as possible.

STUDY OF CASES

In this section is showing three researches that were developed at CDTN. These studies were made in order to solve a environmental aspect caused by the industry disposal.

Iron and Indium Recovery from Industrial Zinc Residues

The industrial solution of the hydrometallurgical processing of zinc was taken from a sulfuric liquor with 90 to 100 g/L of zinc and other metals ions such as iron, indium, gallium and copper. Iron is present in significant amounts (25 g/L) and its removal and disposal constitutes a major operational problem. At present iron removal is accomplished with precipitation techniques as used in the zinc industry, which, despite their effectiveness, are associated with high consumption of neutralizing agents, and large accumulations of complex iron residues which might lead to environmental problems (Demopoulos, 1984).

It is known that most of indium in the feed to the jarosite circuit collects in the jarosite residue. In³⁺ replaces Fe³⁺ in the jarosite structure to form a nearly ideal solid solution series.

The consequence is that it is virtually impossible to avoid indium losses in jarosite, while at the same time it is difficult to concentrate indium in the jarosite precipitate (Dutrillac and Mingmin, 1993).

Because of the leach solutions are extremely complicated and have low concentrations of scarce

metals, the ultimately employed method should be extremely selective and active, and the concentration should be very high to obtain the proper liquors and eventually produce the metals. Most desirable would be a solvent extraction process for direct recovery of metals from sulfuric acid liquors (Zhou et al., 1989).

This work presents the study of iron and indium recovery from the industrial liquor of zinc processing using an amine as extractant, the PRIMENE JMT. The main products of the industry would not be affected by the introduction of this step, since that the conditions are adjusted for selective extraction of the iron and indium.

Experimental

The sample used in this investigation was collected from the sulfuric liquor flowing off the acid leach step of the industrial zinc process. The concentrations of the iron and indium present in the sulfuric liquor are 25.7g/L and 80 µg/mL respectively.

It was investigated the main parameters of the solvent extraction process of iron and indium in bath scale. These were: kind and concentration of extractant reagent , the pH of the extraction equilibrium, phases relation and kinetics of the extraction . This parameters were studied for the stripping step too. After defined the optimized conditions of the process, they were tested in a pilot plant of mixer-settler (Benedetto, et al, 1999).

Results and Discussions

The final flowsheet of the process consisted of five main steps. They are:

- iron and Indium Extraction;
- indium stripping;
- iron Stripping;
- solvent scrubbing;
- solvent regeneration.

It was possible to reach a selective separation of the metals iron and indium from the original liquor using amine extractant 20% dissolved in Exxol D100 . This elements can be selectively recovered on the stripping step by adjustment of the aqueous solution acidity.

The table I presents de concentrations of the main elements in the feed and in the extraction effluent liquor (raffinate).

Table I- Characterization of the main species in the feed and extraction raffinate.

Species	Concentration	
	Feed	Raffinate
In	80 µg/mL	8.0 µg/mL
Ga	20 µg/mL	<10µg/mL
Fe	25.7 g/L	0.5 g/L
Zn	95.0 g/L	95.0 g/L
Cu	4.30 g/L	4.30 g/L
Acidity	0.5 mol/L	0.3 mol/L

The aqueous effluent with zinc, copper and others metals, without this contaminants can be fed on the conventional industrial circuit to be recovered.

Recovery of Metals and Acids from Pickling Bath

Over 2 million tons of stainless steel are produced annually in the world, 10% of which comes from Brazil. Stainless steel is pickled in the final steps of the production line in acid bath to remove the oxides layer that is formed on the its surface. The pickling solution is a mixture of nitric and hydrofluoric acids. Due to this pollution potential and corrosiveness this waste is considered hazardous from the environmental legislation viewpoint (Rydberg, et al, 1973).

In general, neutralization is carried out before the discharge of this pickling bath, resulting in the precipitation of the metals and anions present in the solution. The reutilization of both acids and metals, which represents large savings potential, is thus made impossible. In other countries process development studies for the recovery of valuable acids and metals present in these industrial waste have been devised, leading to commercial applications aiming at the reduction of the environmental impact, while keeping a favorable economic balance (Rydberg, et al, 1973; Negro, et al, 1994; Saracco and Onofrio, 1993).

The technique of solvent extraction, by its selectivity, has been broadly applied to the recovery of elements present in aqueous solutions with a high degree of purity (Ritcey and Asbrook, 1984).

Experimental

A study of acids and metals recovery that are presents in the industrial pickling waste liquor, was made through two process routes. In the first, the acids are recovered by solvent extraction in a pulsed column, followed by metals precipitation. The second and more complex route, includes the separate recovery of the metals. Iron and nickel are recovered by solvent extraction using a mixer-settler cascade, while chromium is recovered by precipitation.

The aqueous phase used in this work is a waste liquor from stainless steel pickling processes. The composition of the waste is shown in table 2. Tributylphosphate-TBP diluted in isoparaffin was used as extractant for the acids extraction and water as stripping agent. Di-2-ethylhexyl phosphoric acid-D2EHPA was used for the recovery of iron and nickel in the extraction step, and hydrochloric acid in the stripping step.

Table II – Chemical characterization of the waste solution

Species	H ⁺	NO ₃ ⁻	F ⁻	Fe	Ni	Cr
Content (g/L)	1.80	110	45.3	30.2	5.9	3.5

Preliminarily studies in laboratory scale permitted the definition of two different process routes, which are shown in figure 1. The first idea for the process (route 1) encompasses the recovery of nitric and hydrofluoric acids after preconditioning of the waste solution with sulfuric acid, followed by joint precipitation of the metals, through neutralization of the leached liquors. In route 2, initially the iron is extracted with D2EHPA. The sulfuric acid addition promotes the dislocation of the NO₃⁻ and F⁻ species for subsequent extraction. The high acidity of the liquor allows a selective extraction of the iron in relation to other metals present, what gives an additional advantage to this process. The acid extraction occurs after the iron recovery stage, with the liquor conditioning being accomplished by hydrochloric acid. The aqueous effluent, almost without any acid (nitric and hydrofluoric acids) and iron, feeds a solvent extraction step where the separation of the nickel and chromium metals are carried out.

Results and Discussion

It was possible to obtain an aqueous solution of high purity containing nitric and hydrofluoric acids that may return to the steel pickling process after adjusting for the required concentration. The yield of

the extraction of these acids was 97% and 81% for nitric acid and hydrofluoric acid respectively.

The extraction of iron with D2EHPA in chloride medium was highly selective, considering that no other metals were identified in the iron concentrate. This selectivity is due to the acidity level in that step. The iron can be extract in a higher acidity than the other elements. The yield of the separation of this element was of approximately 99%. The metals

can be recovery together or isolated depending the purpose. Together they can return to the furnace for the steel production and isolated they can have other applications.

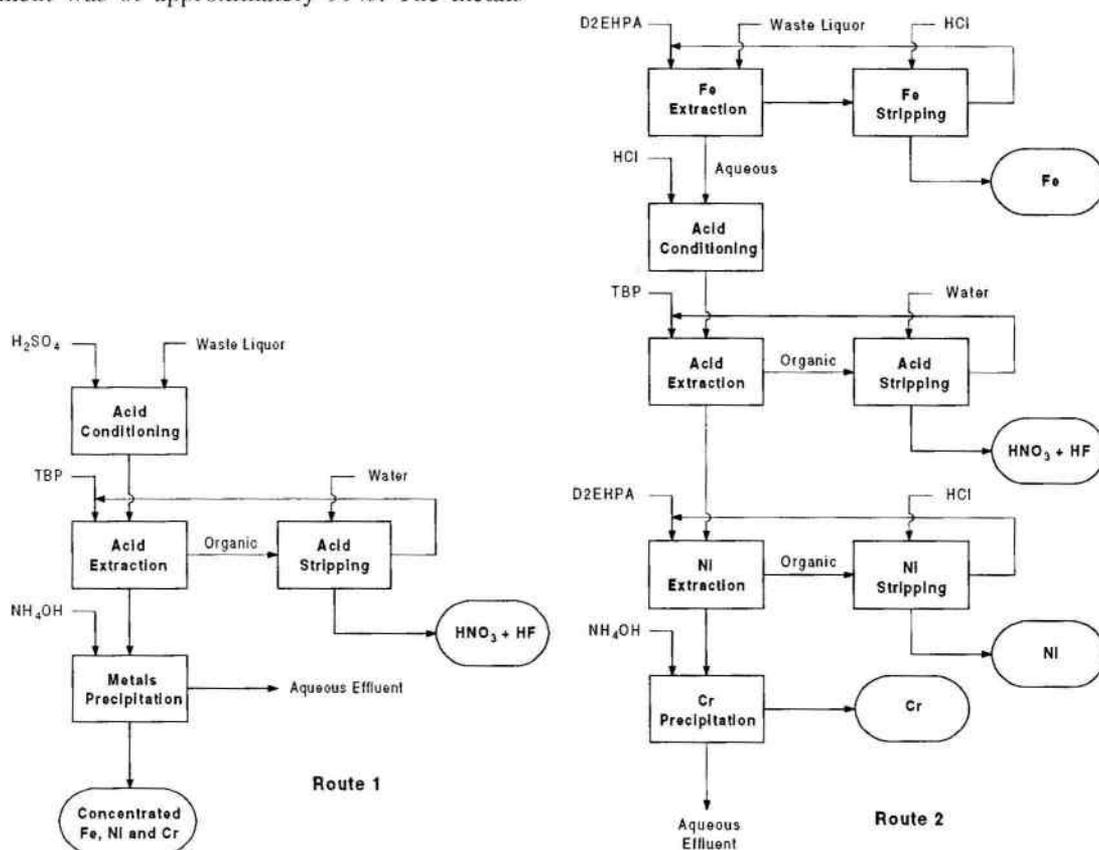


Figure 1: Route 1 and route 2 flowsheet

Zinc Recovery from Industrial Effluent

The aquiferous contamination by industrial effluents is a frequent problem that is always questioned by environmental departments. The solutions to minimize these impacts are searched by the industries but the process cost is a fundamental factor for the implementation. To the liberation of industrial effluent of the hydrometallurgical processing of zinc, this element has to be present in concentration less than 0.1 g/L.

The recovery of zinc from this effluents by solvent extraction technique is carried out by others countries with success. The application of this process can give a significant financial return, and reduce this metal concentration in the effluent that has to be discarded, in admitted level by the environmental departments.

The main goal of this research was to define the operational conditions for the soluble zinc recovery originating from the slime resulted of the zinc processing by the solvent extraction technique. The zinc extraction can be carried out by a

organophosphoric acid, like di (2-ethylhexyl) phosphoric acid (D2EHPA) (Ritcey and Asbrook, 1984) or by a neutral organophosphorus compounds, like cyanex 925 (Preston and du Preez, 1996).

Experimental

The zinc recovery studies were carried out with a feed solution containing 10.1 g/L Zn using D2EHPA as extractant. The stripping study was carried out with a pure H₂SO₄ solution and then with a sulfuric solution effluent of the zinc electrolysis process (H₂SO₄ 2.0 mol/L with 43.1 g/L Zn). The main constituents of the sample are presented in table 3.

Table III: Chemical composition of the feed solution

Species	Zn	SO ₄ ²⁻	Ca	Si	Fe	Mn
Content (g/L)	10.1	22.4	1.78	0.52	0.08	0.05

pH = 5.3

A detailed study of the variables of the process was conducted for the extraction, stripping and solvent regeneration stages. The main parameters investigated were: pH of the feed solution, concentration of the extractant agent (D2EHPA), concentration of the stripping agent (H₂SO₄), contactation time and organic and aqueous phases relation. The research was made in laboratory scale and lately confirmed the process flowsheet in a continuous mixer-settler unit with 2.6 L/h capacity.

Results and Discussions

The experimental conditions for the extraction step were set at: pH feed solution 2.5, D2EHPA concentration 40% V/V, contactation time 5 min. and aqueous/organic relation (A/O) equal 3. For the stripping were: H₂SO₄ concentration 2.0 mol/L, contactation time 5 min. and phases relation (O/A) equal 5. The continuous assay results are presented in mass balance form in figure 2.

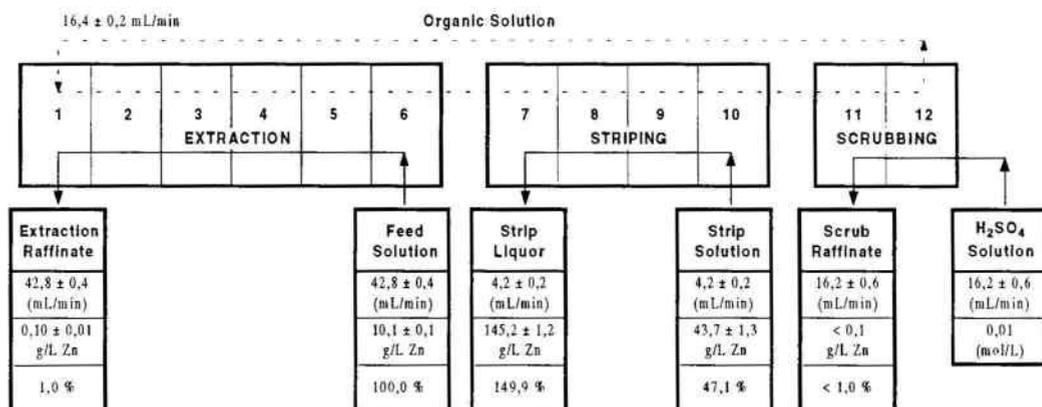


Figure 2: Mass balance of zinc recovery – continuous assays.

In this developed process, the extraction raffinate with 0.1 g/L Zn was obtained and in the stripping liquor the Zn concentration reached 145 g/L Zn. Its means that the effluent of the extraction stage can be discarded without problem and the stripping liquor can be recycled in the electrolysis process. These results indicate the technical feasible to the process with very significant environmental impact reduction

CONCLUSIONS

The three research presented here showed a common results:

- It was possible to define a process to recovery heavy metals and other compounds presents in industrial effluents. This recovery can mean an economical return if applied to the industrial process.
- The solvent extraction technique was applied with success in these three process studied, generating high purity products since that it is very selective technique.

- The levels of the contaminates on the aqueous effluent from each process were according the required established conditions without solid residues generation.

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