IMPROVEMENTS OF HYDROMETALURGICAL PROCESSES BY APPLICATION OF THE ACID RETARDATION PROCEDURE - ACTUAL SITUATION AND DEVELOPMENTS

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ZDOKONALENIE HYDROMETALURGICKÝCH PROCESOV POMOCOU POSTUPU "ACID RETARDATION" - AKTUÁLNA SITUÁCIA A BUDÚCI VÝVOJ

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Abstrakt

Katióny kovov môžu byť oddelené z roztokov voľných kyselín prostredníctvom difúzneho procesu ktorý sa realizuje tak, že použitý roztok sa naleje do reaktora obsahujúceho vrstvu špeciálneho iónomeniča. Katióny kovov prechádzajú cez vrstvu okamžite, zatiaľ čo voľná kyselina je s vysokým stupňom účinnosti následne z iónomeniča eluovaná pomocou vody. Preto je tento proces nazývaný ako "acid retardation".

Vzhľadom na skutočnosť, že týmto spôsobom môžu byť regenerované cenné kyseliny, počas niekoľko minulých rokov boli zariadenia na regeneráciu kyseliny úspešne aplikované v priemysle povrchovej úpravy kovov, najmä pre regeneráciu roztokov z odstraňovania okovín, morenia, anodického pokovovania, chemického opracovania a pod.

Za účelom aplikácie takejto procedúry v hydrometalurgii sa začína overovanie odstraňovania Mg a Mn z elektrolytov pre elektrolytické získavanie zinku ako aj odstraňovanie As z vyčerpaných elektrolytov z elektrolytickej rafinácie medi. Výsledky týchto výskumných projektov budú publikované neskôr s dôrazom na technické a ekonomické aspekty.

Abstract

Metal cations can be separated from free acids by a diffusion process which is carried out by feeding the spent solution into a particle bed of a special ion exchange resin. The metal cations are passing the resin bed immediately while the free acid to a high degree is eluated from the resin afterwards just by use of water. Therefore, this procedure has been termed acid retardation.

Due to the fact, that valuable acids can be recovered in this way, equipments for acid retardation have been applied successfully during the past few years in the metal finishing industry, mainly for the regeneration of solutions for scale removal, pickling, acid dipping, bright dipping, anodizing, chemical machining, etc.

For the application of this procedure in hydrometallurgy, investigations have been started for the separation of Mg and Mn from electrolytes in zinc winning plants as well as for the removal of As from spent electrolytes in copper refineries. Results of these research projects will be reported under technical and economical aspects.

Key words: hydrometallurgy, acid retardation procedure, pickling solution, acid waste solutions, ecological aspects, economical aspects

Introduction

In the European Community, metals like cadmium, chromium, copper, lead, mercury, nickel, zinc etc. are regarded as "hazardous materials", and effluents resulting from their production or processing have to be treated in the near future by use of the best available technology. As well, process solutions have to be regenerated and, as a rule, can no longer be discarded. The volumes of solid waste have to be decreased by preventing losses of materials (e.g. recycling, closed-loop operation, recovery of water and materials contained in effluents), or by reuse of materials, and only if there is no chance for a further utilization of water, chemicals or metals, waste water can be drained and solid waste can be disposed of.

Under these aspects, in the metal finishing industry new procedures for environmental protection have been developed to meet these new regulations and to comply with considerably reduced residual concentrations of the constituents in the effluents to be drained into the sewer.

Spent acid solutions in most cases contain free acids to a high extent, which in the conventional route have been neutralized for precipitation of heavy metals. But recovery of free acids can save part of the acid consumption, alkali for neutralization, and smaller amounts of neutral salts will pollute the sewer.

In hydrometallurgy, similar problems have to be solved in connection with bleeding solutions for the limitation of impurity build-up. Therefore, investigations have been started with this promising procedure and the results have indicated that acid retardation can bring about many advantages compared with the conventional mode of operation.

Experimental procedure in laboratory-scale

Hatch and Dillon [1] have alternately passed an acidified metal salt solution and water through a column filled with an anion exchange resin and found out that the eluation of the free acid is clearly retarded, whereas the metal salt is passing the resin bed immediately.

The concentrations of the liquids resulting from the elution process have been presented in Fig.1.

Fig.1 Acid retardation effect

There is a marked separating effect, and after collecting the eluate solutions alternately in two different tanks, these storage bins contain a weak acid solution with a high metal concentration and a strong acid with a decreased metal content.

It has been confirmed that this effect greatly depends on the type of resin applied and that the reason for the process of acid retardation is the different rate of diffusion of metal ions, dissociated acids and acid molecules, respectively.

Strongly basic anion exchange resins are most suitable for this application. The ratio of the height of the column and the diameter, as Hartinger [2] has found out, is very important for the retardation effect, as can be seen from Fig.2.

Fig.2 Influence of the geometry of the column on the separation of copper and sulfuric acid by acid retardation (example: $CuSO_4 + H_2SO_4$)

The degree of separation also depends on the initial concentration of the free acid. In very dilute solutions, retardation becomes less distinct (Fig. 3), whereas acid retardation can be applied for acid solutions with a low metal content as well as for higher metal concentrations (Fig.4).

Acid retardation has a wide range of application, because strong acids like hydrochloric acid, sulfuric acid, nitric acid and acid mixtures have been tested quite successfully.

Fig.3 $CuSO_4$-H_2SO_4 -solutions with 20 g/l Cu^{2+} and different concentrations of free acid

For phosphoric acid and hydrofluoric acid, the applicability has to be checked individually. The formation of metal complexes can have a detrimental effect on acid retardation, but in some cases the separation can even be improved due to the very steep shape of the elution curves.

Fig.4 Separation of a solution containing 42 g/l Ni^{2+}, 3 g/l Cu^{2+}, 15 g/l Zn^{2+}, 7 g/l Fe^{3+} and 95 g/l free sulfuric acid

Outline of technical equipments

The main part of an industrially used equipment for acid retardation is the column containing the special ion exchange resin. For alternating feeding the column with the metal containing acid and water as the eluant, dosing pumps as well as apportioning vessels can be used. The volumes of the liquids leaving the resin bed can be separately adjusted by independently operated valves to meet the requirements resulting from the eluation curves. In this way, different types of solutions can be treated individually to attain optimum results with regard to the concentration ratios of the materials to be separated.

An equipment with a capacity of about 300 liters per hour of acid metal salt solution is presented in Fig.5.

Fig.5 Equipment for regeneration of electrolytes for Al anodizing (GOEMAPUR Al100) -photo by courtesy of GOEMA

This appliance is operated automatically, and this type of column is a proven system, used in many metal finishing plants for different processes.

Industrial applications

In the metal finishing industry, one main application of the acid retardation process is the regeneration of electrolytes for anodizing of aluminum. These solutions mostly consist of 150 to 275 g of sulfuric acid per liter but should not contain more than 10 g/l of aluminum, to maintain a high specific conductivity and to guarantee oxide layers of optimum quality. As aluminum concentration of more than 2 g/l markedly decreases the conductivity, for an optimum current density a higher cell voltage and a growing energy demand for cooling are necessary. Therefore, a continuous regeneration of electrolytes for anodizing of aluminum is an important process step for environmental protection. Moreover, savings for high purity sulfuric acid, alkali for neutralization, sludge disposal and energy have been attained. That's why acid retardation is a very profitable procedure for every anodizing shop [3].

Acid retardation has also been applied under technical conditions for the regeneration of etchants, bright dips and pickling solutions. In all these cases, large amounts of free acids have been saved, and the conditions for metal recovery, by which metal containing sludge can be avoided, have been improved.

In order to make use of acid retardation in hydrometallurgy, investigations have been started to find out optimum conditions for the removal of impurities and for acid recovery in zinc electrowinning as well as in copper refining plants. In every zinc tank house, large volumes of electrolytes have to be discarded for a constant concentration level of Mg and Mn. Many tests have been run to confirm that Mg and Mn can be easily removed from the electrolytes, thus returning the major part of the sulfuric acid directly into the electrolyte conduit system (Fig.6). Zinc can be simply recovered from the Mg and Mn eluate by precipitation with a controlled pH (Fig.7).

For the removal of As und Mi from electrolytes in copper refineries, laboratory-scale tests have indicated that several different portions of eluates can be collected separately to concentrate the impurities under such conditions that they can be eliminated at the lowest possible expense (Fig.8).

Economy

In the Rear future, companies processing "hazardous materials" such as As, Cd, Cr, Cu, Ni, Pb, Zn etc., have to comply with new legislative rules for environmental protection, demanding the use of a new low-waste technology. Under these aspects, acid retardation can effectively contribute to the application of improved procedures, combined with low expenditure. Modest costs for investments, energy and labor, small floor space requirements and big savings for fresh acids, neutralization chemicals, sludge disposal and lower metal losses guarantee that such an investment pays for itself within a short period of time.

Fig.6 Separation of H_2SO_4 and the sulfates of Mg, Mn and Zn by acid retardation.

201 g/l H_2SO_4; 46.9 g/l Zn; 9.4 g/l Mn; 7.9 g/l Mg

Therefore in zinc electrowinning plants, bleeding off impurities in a conventional way requires the treatment of several ten m^3 of electrolyte per day, leading to large volumes of sludge and everlasting environmental problems. Therefore, a rapid repay of the investment is obvious.

The removal of As and Ni in copper refining can be performed in quite different ways. But a pre-separation of As and Ni, returning part of the liquid directly into the tank house, and the treatment of smaller volumes of bleeding electrolytes will certainly contribute to cost savings and will make it easier to meet the environmental requirements.

Fig.7 Precipitation of Zn^{2+} as a hydroxide in the presence of Mg^{2+} and Mn^{2+} from fractions 6-15

Fig.8 Separation of Cu^{2+}, Ni^{2+} and As^{5+} from sulfuric acid by acid retardation

Feeding solution: 9.5 g/l Cu^{2+}, 30 g/l Ni^{2+}, 21 g/l As^{5+} and 430 g/l free H_2SO_4

Summary

Acid retardation is a proven procedure for the recovery of free acids from spent metal bearing solutions. The process is based on different diffusion rates of metal ions and acids into a special ion exchange resin. For acid recovery, no chemicals are necessary. Therefore, this recovery technique can contribute to meet the environmental requirements. The procedure has been made use of in metal finishing already, but there are good chances for other applications, e.g. in hydrometallurgy.

Literature

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