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# Application of Solvent Extraction to the Treatment of Industrial Wastes

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There are several steps such as slicing, lapping, chemical etching and mechanical polishing in the silicon wafer production process. The chemical etching step is necessary to remove damaged layer caused in the slicing and lapping steps. The typical etching liquor is the acid mixture comprising nitric acid, acetic acid and hydrofluoric acid. At present, the waste acid is treated by a neutralization method with a high alkali cost and balky solid residue. A solvent extraction method is applicable to separate and recover each acid. Acetic acid is first separated from the waste liquor using 2-ethlyhexyl alcohols as an extractant. Then, nitric acid is recovered using TBP(Tri-butyl phosphate) as an extractant. Finally hydrofluoric acid is separated with the TBP solvent extraction. The expected recovered acids in this process are 2mol/l acetic acid, 6mol/l nitric acid and 6mol/l hydrofluoric acid. The yields of this process are almost 100% for acetic acid and nitric acid.

On the other hand, it is important to recover and reuse the metal values contained in various industrial wastes in a viewpoint of environmental preservation. Most of industrial products are made through the processes to separate impurities in raw materials, solid and liquid wastes being necessarily discharged as industrial wastes. Chemical methods such as solvent extraction, ion exchange and membrane, and physical methods such as heavy media separation, magnetic separation and electrostatic separation are considered as the methods for separation and recovery of the metal values from the wastes. Some examples of the application of solvent extraction to the treatment of wastes such as Ni-Co alloy scrap, Sm-Co alloy scrap, fly ash and flue dust, and liquid wastes such as plating solution, the rinse solution, etching solution and pickling solution are introduced.

Keywords: Solvent Extraction, Recovery, Industrial Waste, Recycling

## Introduction

Historically, a solvent extraction method was established for the purpose of pretreatment of calorimetric analysis. From 1940, solvent extraction has been applied for separation and refining of U and other radioactive substances. After 1980, solvent extraction of copper was investigated for hydrometallurgy, where a series of processes, leaching of copper oxide ores with sulfuric acid -solvent extraction- electrowinning, was developed. At present there are about fifteen copper hydrometallurgy plants using solvent extraction in the world. Solvent extraction is considered to be one of the solution purification methods and it is possible to use it for recovery of valuable metals from industrial wastes and for a recycling process of wastes. Many processes for which the solvent extraction method is applied are used practically or under investigations for the treatment of wastes. Solvent extraction is a technique of separation and recovery of substances by use of distribution between two liquid phases. Extraction characteristics of many extractants are studied for various metal ions and the suitable extractants are almost fixed for the metal ion. The complex between metal ions and extractants is formed, which is extracted and separated to the organic phase. Metal ions in the organic phase are stripped with stripping agent such as inorganic acid and then metal ions are reduced by an electrowinning. Solvent extraction method makes it possible for metal ions and mineral acids to be separated and recovered in large quantity, low cost and easy operation. Therefore, it is desirable to use solvent extraction for recovery of

valuable materials from industrial wastes which contain metal ions and mineral acids at considerably high concentration. In this paper, we introduce some examples of the solvent extraction process to show how the method is applied to recover valuable materials from industrial wastes.

## Acid mixture from silicon wafer production

There are several steps such as slicing, lapping, chemical etching and mechanical polishing in the silicon wafer production process. The chemical etching step is necessary to remove damaged layer caused in the slicing and lapping steps. The typical composition of etching liquor is the acid mixture comprising 10mol/l nitric acid, 2mol/l acetic acid and 6.5mol/l hydrofluoric acid. At present, the waste acid is treated by a neutralization method with a high alkali cost and balky solid residue.

The solvation type extractants are used for mineral acid separation from wasted acids mixture. These extractants are alcohols with long alkyl chain, TBP(Tri-butyl phosphate) , TOP(Tri-octyl phosphate) and so on. The extraction mechanism of mineral acids is based on the physical distribution between the organic phase and aqueous phase. Generally speaking, therefore, the extraction percent at one stage operation is not so high and also the separation factor between mineral acids is inferior to that in metal ion separations. This is a serious and important thing in mineral acid separation.

When the solvent extraction is applied to wasted acid mixture comprising nitric acid, acetic acid and hydrofluoric acid, first acetic acid is separated from the mixture, secondly nitric acid is recovered and finally hydrofluoric acid is removed from the mixture by using a solvent extraction. In the case of acetic acid extraction, 2-ethylhexyl alcohol (abbreviated as EHA) is used, where the 3-stage countercurrent extraction operation is adopted with the phase ratio (O/A) of 1.7 and the 10-stage countercurrent scrubbing operation with the phase ratio (O/A) of 10 is applied. After the extraction and scrubbing operations, the organic phase contains only acetic acid and then the organic phase goes to a stripping operation, where acetic acid is stripped by water in 4-stage countercurrent stripping with the phase ratio (O/A) of 2. The concentration of final recovered acetic acid is 2mol/l. Then, the TBP extraction is applied to extract nitric acid in the condition of 3-stage countercurrent extraction with the phase ratio (O/A) of 2. The organic phase goes to the scrubbing step, where impurities like hydrofluoric acid and silicon are removed by the operation of 10-stage scrubbing with the phase ratio (O/A) of 10. The stripping of nitric acid is accomplished by water in 5-stage stripping with the phase ratio (O/A) of 2.3 to obtain 6mol/l nitric acid. Hydrofluoric acid is captured by the 4-stage TBP extraction with the phase ratio (O/A) of 2.7 and then stripped by water in the condition of 4-stage stripping with the phase ratio (O/A) of 4 with the concentration of 6 mol/l hydrofluoric acid[1-3].The flow sheet for mineral acid recovery from wasted acid mixture is proposed in **Figure 1**

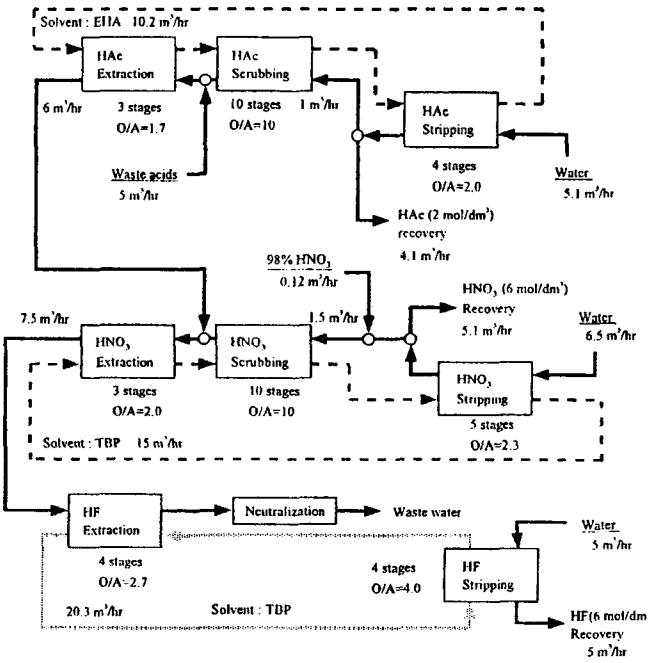


**Figure 1 Flowsheet of the acid recovery process from waste liquor**

## Pickling waste

METSEP process, namely a recovery process of Zn from pickling waste, is designed by National Institute of Metallurgy (NIM) in South Africa[4)-6)]. It is the process for the separation of Zn from hydrochloric acid solution containing Fe with strong basic anion exchange resin.

Hydrochloric acid and iron oxide are produced by atomized roasting of the solution after the removal of Zn. After eluting Zn from the resin with water, Zn is extracted with D2EHPA. Then, the organic phase is back extracted with sulphuric acid in order to divert sulphuric acid solution from hydrochloric acid solution, which is suitable for electrolysis. The raffinate solution after the extraction of Zn is used for the production of hydrochloric acid. MX-Processer AB developed the MeS process in order to recover Zn from pickling waste[4]. Zn is extracted and separated from Fe with TBP, but it is important that in this process Fe has to be Fe(Ⅱ) because Fe(Ⅲ) can be extracted with TBP. Zinc is stripped with water or dilute sulfuric acid and the stripped solution is mixed with sulfuric acid. Finally, hydrochloric acid is removed from the mixed solution by evaporation, and at the same time $ZnSO_4$ is produced. Evaporated hydrochloric acid is sent back to the process of pickling treatment after fractional distillation to 6M of its concentration.

## Recovery of acid from pickling waste

$HNO_3$ and HF are recovered from the pickling waste of stainless steel withTBP. The Kawatetsu process, which is developed by Kawasaki Steel Co.,Ltd. is as follows; Fe(Ⅲ) in pickling waste is extracted with the mixed solution of 30% D2EHPA and 70% n-paraffin diluent, Fe(Ⅲ) in the organic phase is back extracted with $NH_4HF_2$ solution and crystallized as $(NH_4)_3Fe_3F_6$. $(NH_4)_3Fe_3F_6$ is converted into $\alpha$ -$Fe_2O_3$ by roasting decomposition in air or in air containing steam. Hydrochloric acid is added to the raffinate solution from an extraction step of Fe(Ⅲ) to make free $HNO_3$. The mixed acid of nitric acid and hydrofluoric acid is extracted with 70% TBP diluted in n-paraffin diluent and back extracted with water in order to reuse in acid rinse process.

## Ni-Co alloy scrap

The process for separation and recovery of Fe, Ni and Co from Ni-Co alloy scrap was developed by Gullspang Electrochemical Company in Sweden[7)-9)]. **Figure 2** represents the flow sheet of their treatment process. This process consists of four steps; dry treatment, electrolytic dissolution in the chloride solution, separation by solvent extraction and electrowinning. As an organic phase, 25% Alamine 336 diluted in kerosene, which contains 15% dodecanol as a modifier, is used. The flow of the extraction process is as follows; Fe(Ⅲ), which is obtained in the diaphragm electrolytic cell, is extracted by mixer-settler of three stages at 50～100g/l $Cl^-$ concentration. Extracted Fe(Ⅲ) is stripped with water by mixer-settler of eight stages and is reduced to Fe(Ⅱ) in the diaphram electrolytic cell again. The raffinate solution from the extraction of Fe(Ⅲ) is evaporated to make $Cl^-$ concentration 200g/l and Co is extracted by mixer-settler of six stages at over 200g/l $Cl^-$ concentration. Extracted Co is stripped with weak acid(pH 2～3) by three stage mixer-settler. The residual solution containing Ni after the removal of Co is put back to the diaphragm electrolytic cell, where we can get Ni by electrowinning.

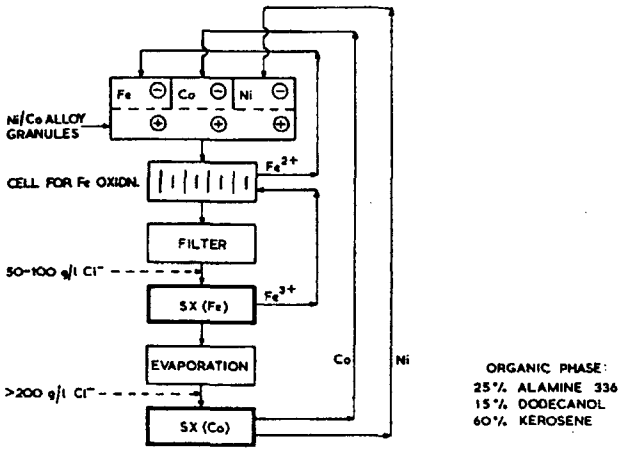


**Figure 2 Nickel-cobalt alloy scrap process (Gullspang Electrochemical Co., Sweden)**

Metallurgie Hoboken Method, which was established in Belgium, is known as an industrial recovery process of Ni and Co from scraps and solid wastes[7)-9)]. The flow sheet is shown in **Figure 3**. After leaching of Ni-Co alloy scrap with chloride solution, Fe and Cr are precipitated with air oxidation and lime. Copper is recovered by a cementation process with Co. Paradium can be separated from Mn with Cr oxide and Co oxide. Solvent extraction using Alamine 336 has two steps; in the first step the

separation of Zn is carried out when the concentration of HCl is low (5～10g/l),and in the second step Co is separated from Ni at high concentration of HCl (110g/l). Zinc can be recovered by precipitation and filtration from the organic phase as $Zn(OH)_2$ when NaOH is added.

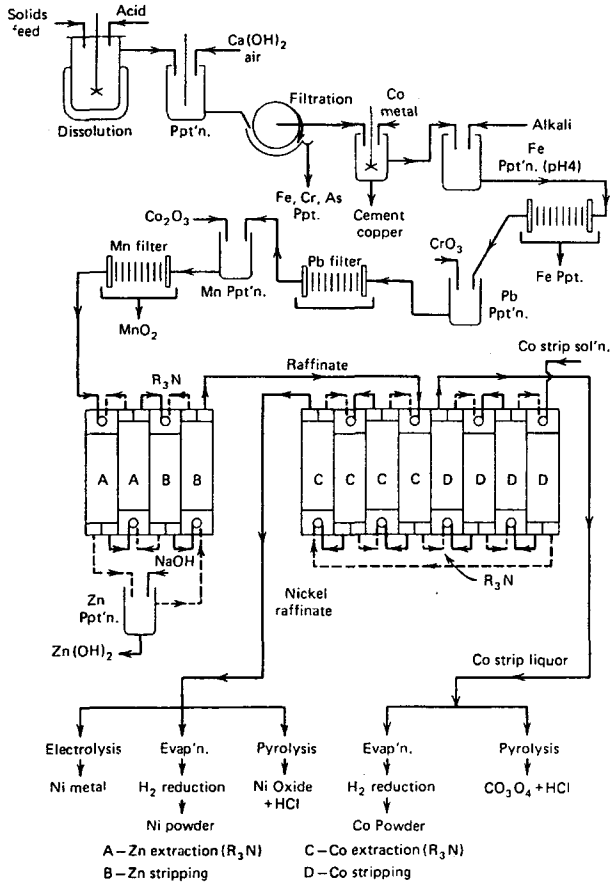


**Figure 3 Nickel/Cobalt recovery process at Metallurgie Hoboken (Belbium)**

## Sm-Co alloy scrap

The application of solvent extraction for recycling of Sm-Co alloy scrap, which appears during the production step of Sm-Co alloy magnets, is under investigation. The treatment process has two steps; the first step is to leach Sm-Co scrap with HCl and the second step is to extract Sm with D2EHPA. By this method, we can get almost perfect selective separation of Sm if Fe(Ⅲ), which co-exists in the solution, has reduced to Fe(Ⅱ). A recent increase in scraps containing Pd and Nd makes it necessary to separate Sm from them by solvent extraction. Mitsui Mining & Smelting Co.,Ltd. established the following separation process by solvent extraction; firstly rare earth is extracted and separated from Co, which has a large separation factor in the extraction, and then Sm is separated from Pr and Nd, using acidic organo-phosphorous extractant in both separation steps.

## Flue dust

MX-Processer AB in Sweden proposes the treatment process of Cu-Zn flue dust from steel or brass factories. The recovery of Cu consists of several steps; leaching of flue dust containing Cu with sulfuric acid, extraction of Cu with LIX64, stripping with spent electrolyte and electrolysis. In the case of Zn recovery, the process has also some steps; leaching of flue dust containing Zn with the aqueous phase after extraction of Cu, and extraction of Zn with 50% D2EHPA diluted in kerosene. The aqueous phase(pH0.7) after extraction of Zn is reused for leaching of flue dust of Cu-Zn and flue dust of Zn.

## Fly ash

MX-Processer AB developed the process of recovery of V and Ni from fly ash discharged from petroleum thermal power plant[10]. This is so-called SOTEX process; after leaching of fly ash with sulfuric acid, V is extracted with the mixed extractant of 20% D2EHPA and 15% TBP diluted in kerosene. During the leaching, V(V) is reduced to V(IV) by $SO_2$ for the purpose of the next step, namely solvent extraction. Ferrous ion is precipitated and removed as jarosite. The extracted V is stripped by three stages with 1.5M $H_2SO_4$ and recovered as precipitates by sodium carbonate or ammonia.

## Recovery of Zn from plating rise water

Electroplating of Zn is done in alkaline Zn cyanide solution. It is necessary to remove cyanide from the plating rinse water before draining. Zinc cyanide is extracted efficiently from alkaline solution with the mixed organic phase containing 0.05M Adogen 464 (tri-alkyl (C8-C10)methyl ammonium chloride) and 20% tri-decyl alcohol diluted with Amsco 125-82(Union Oil

Co.). Union carbide Co. developed an extraction process using the above extraction property[11]. **Figure 4** represents the flow sheet, where Zn is extracted as cyanic complex. Raffinate solution after the extraction of two stages is reused as plating rinse water. Extracted Zn cyanic complex is stripped with 6N NaOH by two stages, and the aqueous solution is returned to electroplating. The typical plating rinse water contains 0.07M NaOH, 40ppm CN and 23.2ppm Zn after solvent extraction. The raffinate solution has composition of dissolved amine of 30~50ppm, NaOH of 0.006M, CN of 0.4ppm, and Zn of 0.07ppm. The concentration of amine, CN and Zn is still more decreased with activated carbon. Stripping is carried out at phase ratio of 162(A/O).The stripped solution contains Zn of 1.83g/l and CN of 2.89g/l.

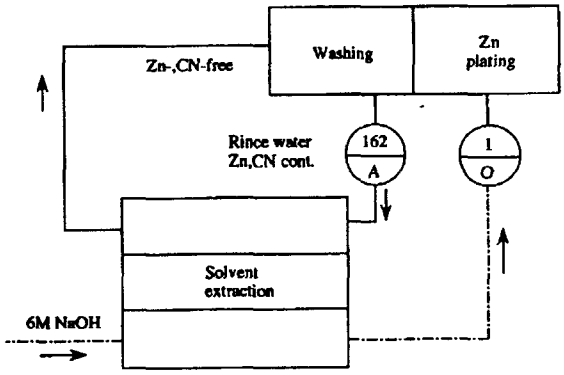


**Figure 4 Zinc recovery process from plating rinse water (Union Carbide Co.)**

## Recovery of Cu from etching solution

As the etching process proceeds, its efficiency decreases because of the increase in the concentration of Cu in the etching solution. Criterion Co. in USA suggests the process for recycling of the etching solution; extraction of Cu with LIX64 from spent etching solution and electrolysis of Cu[4]. MECER process in Sweden is made up of two solvent extraction steps; the first step is to extract Cu with LIX54 from spent etching solution and to put back the solution to the etching process after decreasing in the concentration of Cu[4]. In the second step, Cu which is contained in the rinse water of the etching process is removed by solvent extraction. The extracted Cu into the organic phase in both processes is stripped with spent electrolyte and put back to the electrolysis process.

## Conclusions

We reported some examples of application of solvent extraction for the treatment of industrial wastes in this paper. Except for the examples mentioned here, solvent extraction methods are applied for the recovery of precious metals from electronic parts, the recycling of valuable metals from waste catalysts and the separation of Zn and Cu from waste solution discharged from rayon factories. Considering from some merits of the solvent extraction method such as an operation at normal temperature and pressure, high selectivity and easiness of a continuous operation, the method is suitable for recycling of industrial wastes for which we need low cost. We will be able to find various applications of solvent extraction for recovery of valuable materials.

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