Journal of Environmental Sciences Vol. 11, No. 3, pp. 381—384, 1999
ISSN 1001—0742
CN 11—2629/X

Recovery of heavy metals from electroplating sludge and stainless steel pickle waste liquid by ammonia leaching method

Zhang Yi, Wang Zhi-kuan, Xu Xia, Chen Yong-qi, Qi Tao

Institute of Chemical Metallurgy, Chinese Academy of Sciences, P. O. Box 353, Beijing 100080, China

Abstract—A coordinative disposal process for treatment of electroplating sludge and stainless steel pickle waste liquid containing Cu, Ni, Zn, Cr and Fe etc., has been developed to recover valuable metals and to eliminate pollution. The recovery of Cu, Ni, Zn and Cr is 94%, 91%, 90% and 95%, respectively. The ammonia was recycled by the simplified process of CaO caustic distillation. The precipitated product of Cu, Ni and Zn obtained from caustic distillation of ammonia was separated by extraction or high-pressure hydrogen reduction in an autoclave. The qualified metal salt products were obtained through extraction. The rich chromium residue from coordinative dispcsal was subjected to recover Cr by hydrothermal oxidation in NaOH medium and Fe_3O_4 was synthesized by wet methods from the residue produced by extracting Cr. Cr was a stable chemical fixed in Fe_3O_4 and harmless. The recovery process has been used in a pilot plant with sludge production capacity of 2000 t/a.
Keywords: coordinative disposal, recovery, valuable metals, electroplating sludge, stainless steel pickle waste liquid.

1 Introduction

Electroplating sludge, containing Cu, Ni, Zn, Cr, Fe, etc., is harmful waste material produced by galvanization industry. There is still no effective method to recover resource and control pollution both at home and abroad. The metals discarded by galvanization industry amount up to 100 thousand tons per annum, which not only pollute environment seriously but also waste valuable resources. Stainless steel pickle waste liquid is another typical heavy metal pollution source, and difficult to be dealt with.

With the aggravation of resource deficiency and environmental pollution, the new technology of recovering heavy metals from electroplating sludge has attracted more attention from industrialized countries since the 1970's. Many processes(Mueller, 1980; Gelimov, 1977) have been developed, but there is no comprehensive method for recovering valuable metals from the electroplating sludge. The ammonia leaching method for treatment of heavy metal sludge was developed by Baffele-Columbus Laboratory of American State Environmental Protection Agency (Lallowell, 1977). In this process, Cr was not well separated and recovery of Cu and Ni was low. Am-MAR process for the treatment of electroplating sludge developed by the Chalmers University of Technology, Sweden(Andersson, 1979) had completed the industrial experiment. The recovery rate of Cu, Ni and Zn is 80%, 70% and 70% respectively. German Patent 2726783(Reinhardt, 1979) reported the similar ammonia leaching method, the recovering rate of Cu, Ni and Zn is 83%, 45% and 73% respectively. But it has not been put into industrial application. So far there are no available comprehensive methods for recovering valuable metals from electroplating sludge and stainless steel pickle waste liquid.

This paper focuses on the research of a new coordinative disposal process and auxiliary technology for recovery of valuable metals from electroplating sludge and stainless steel pickle waste liquid.

2 Process diagram

The process diagram for recovery of heavy metals from electroplanting sludge and stainless steel pickling waste liquor is shown in Fig. 1.

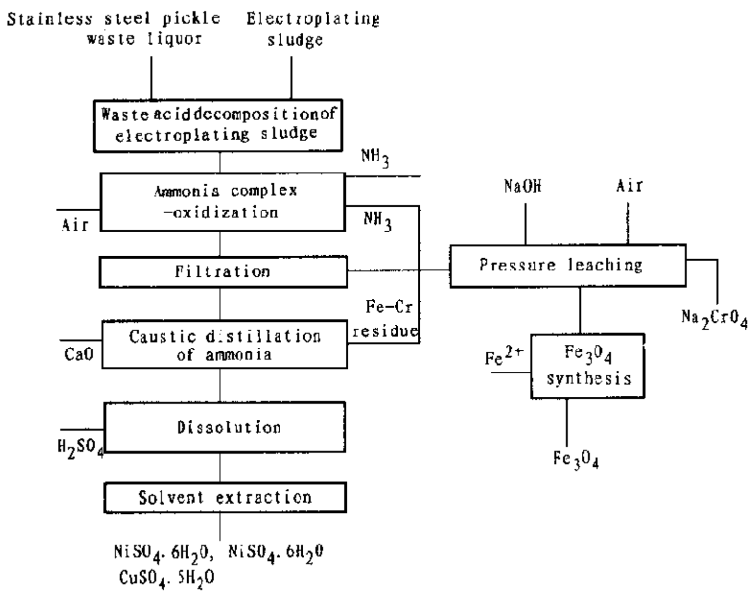

Fig.1 Process diagram for recovery of heavy metals from electroplating sludge and stainless steel pickling waste liquid

The chemical composition of the electroplating sludge and stainless steel pickling waste liquid tested is listed in Table 1.

Table 1 Chemical composition of tested electroplating sludge and stainless steel pickling waste liquid

Sample	Ni	Cu	Zn	Cr	Fe	SO_4^{2}
Electroplating sludge, %	4.0	3.0	3.0	6.0	13.0	
Stainless steel pickling waste liquor, g/L	7.8	3.0	3.0	14.6	25.0	383

The process diagram given in Fig.1 consists of five principal operation steps: (1) Waste acid decomposition of electroplating sludge; (2) ammonia complex transformation and ferrite synthesis method to separate Cr-Fe; (3) recycle use of ammonia; (4) separation of Cu-Ni-Zn; (5) recovery of chromium by liquid phase oxidization method and synthesize Fe_3O_4 by wet method.

3 Process results

3.1 Waste acid decomposition of electroplating sludge

Free acid in stainless pickling waste liquid reacted equivalently with liquid Cu, Ni, Zn, Cr, Fe (II) and Fe(III) metal oxides in electroplating sludge at normal room temperature, the ratio of waste liquid to waste sludge was 4:1 and made them enter solution:

$$Me(OH)_n + n/2H_2SO_4 \rightarrow Me(SO_4)_{n/2} + nH_2O. \quad (1)$$

The leaching yield of Ni, Cu, Zn and Cr was 99%, 98%, 98% and 99%, respectively. Under acid condition, polyacrylamide was decomposed. PAA and acid inert impurity which were disadvantageous in the later separation process were filtered.

$$nPAA + mH_2SO_4 + nH_2O \rightarrow (PAA)_n(SO_4)_m + nNH_4^+. \quad (2)$$

3.2 Ammonia complex transformation and ferrite synthesis method to separate Cr-Fe from Cu-Ni-Zn acid solution

Because of serious absorption and coprecipitation, it is difficult to completely separate Cr-Fe by adopting the conventional precipitation method. With ammonia complex transformation and ferrite synthesis method, Cu-Ni-Zn-Cr-Fe acid system was rapidly changed into NH_3-$(NH_4)_2SO_4$ system by adding ammonia under weak oxidation condition. Cu, Ni and Zn were transfered into ammonia complex by undergoing interim activated hydroxide and became stable in liquid phase. Simultaneously the system produced CrO(OH) (inactivated state) and Fe_3O_4 precipitation which could be effectively separated with Cu-Ni-Zn. The complex reactions are as follows:

$$Cu(OH)_2 + 2NH_3 + (NH_4)_2SO_4 \rightarrow Cu(NH_3)_4{}^{2+}SO_4{}^{2-} + 2H_2O. \quad (3)$$

$$Ni(OH)_2 + 4NH_3 + (NH_4)_2SO_4 \rightarrow Ni(NH_3)_6{}^{2+}SO_4{}^{2-} + 2H_2O. \quad (4)$$

$$Zn(OH)_2 + 2NH_3 + (NH_4)_2SO_4 \rightarrow Zn(NH_3)_4{}^{2+}SO_4{}^{2-} + 2H_2O. \quad (5)$$

The probability of complex is ranked at $Cu^{2+} > Zn^{2+} > Ni^{2+} > Cr^{2+} > Fe^{2+} > Mn^{2+}$.

Ammonia complex transformation was completed with the concentration of 2.5mol/L NH_3 and 1.75mol/L $(NH_4)_2SO_4$ at oxide partial pressure of 0.03 mPa and room temperature. The recovery yield of Ni, Cu and Zn is 98%, 99% and 99% respectively.

The behavior of Cr(Ⅲ) was fairly complicated. In ammonia medium the active $Cr(OH)_3$ reached at weak complex equilibrium. But the transfer of active $Cr(OH)_3$ were proceeded in the presence of a highly dispersed metal basic salt and turned into the passive CrO(OH).

The hydrolysis mechanism of Cr(Ⅲ) is:

$$2Cr(OH)_3\text{active} + 6NH_3 + 3(NH_4)_2SO_4 \rightarrow 2[Cr(NH_3)_6{}^{3+}]_2(SO_4)_3{}^{2-} + 6H_2O. \quad (6)$$

$$Cr(NH_3)_6{}^{3+} + 2H_2O \rightarrow CrO(OH)\downarrow \text{passive} + 3NH_4{}^{+} + 3NH_3. \quad (7)$$

Fe(Ⅱ) was oxidized slowly by blowing air in NH_3-$(NH_4)_2SO_4$ medium. Fe_3O_4 was synthesized by controlling the process condition to decrease the adsorption and coprecipitation of Cu, Ni and Zn.

3.3 Caustic distillation of ammonia

The caustic distillation of ammonia was carried out at 95—100℃ and low negative pressure. The satisfied result was obtained when the ratio of CaO practical quantity to theoretical quantity was 1.2 and the ratio of solution to steam was 2.0. The simplified process of CaO caustic distillation of ammonia-fractional condense-tail gas absorption was adopted to recycle ammonia. The recovery yield of ammonia is 98% and metal recovery yield of metals is 99%. The process of CaO caustic distillation of ammonia is the process of chemical distillation accompanying the chemical reaction and solid precipitation.

$$(NH)_2SO_4 + Ca(OH)_2 \rightarrow 2NH_3 \cdot H_2O\uparrow + CaSO_4\downarrow. \quad (8)$$

$$Ni(NH_3)_6SO_4 + Ca(OH)_2 \rightarrow 6NH_3\uparrow + Ni(OH)_2\downarrow. \quad (9)$$

The caustic distillation of ammonia was no-stable intermittence operation. The distillation rate of ammonia depends on the concentration, operation pressure and temperature.

3.4 Separation of Cu-Ni-Zn

3.4.1 Extraction separation of Cu-Ni-Zn

The product obtained from caustic distillation of ammonia was dissolved under weak acid condition. Then it proceeded into the solvent extraction step after a little of Fe was removed by adjusting pH. Cu^{2+} and Zn^{2+} were extracted by using N-510 and P-204 extractants, respectively. The pure metal salt products were obtained by evaporating and crystalling the re-extraction sulphate solution.

3.4.2 High pressure hydrogen reduction separation of Cu-Ni-Zn

The high pressure hydrogen reduction experiments were carried out in an autoclave with mechanical stirring by magnetic driving. The product obtained from caustic distillation of ammonia was dissolved under weak acid condition. The first step was the reduction of Cu, the pH was adjusted by NH_4OH and H_2SO_4, dispersant and buffering agent were added. At a temperature of 160—170℃, the metallic Cu powders were obtained. In the second step the metallic Ni powders were separated. Hydrogen reduction of Cu is a self-catalyzed reaction. An ammonium polyacylate (PAA) was added as additive to improve the physical property of the Cu metallic powders and prevent the sinter. The main reactions are:

$$2Cu^{2+} + H_2 \rightarrow 2Cu^{+} + 2H^{+}. \qquad (10)$$

$$2Cu^{2+} \rightarrow Cu^{0} + Cu^{2+}. \qquad (11)$$

Hydrogen reduction of Ni in the presence of catalyst are:

$$H_2{}^{+} \rightarrow H + H. \qquad (12)$$

$$Ni^{2+} + H \rightarrow Ni^{+} + H^{+}. \qquad (13)$$

$$Ni^{+} + H \rightarrow Ni^{0} + H^{+}. \qquad (14)$$

3.5 Extract chromium by liquid phase oxidization method and synthesize Fe_3O_4 by wet method

The Cr-Fe residues produced in the process was treated by liquid phase oxidation method in NaOH medium to extract Cr.

$$FeO \cdot Cr_2O_3 + 4NaOH + 7/4O_2 \rightarrow 2Na_2CrO_4 + 1/2Fe_2O_3 + 2H_2O. \qquad (15)$$

The work showed that the high extraction rate of chromium was obtained at 140℃, the concentrations of NaOH 50—100 g/L and an oxygen partial pressure of 0.1—0.2 mPa. The yield of Cr was 95%. The content of Cr in residue was 0.9%.

When the ratio of heavy metals to Fe_3O_4 is less than 5% and the ratio of Cr to Fe_3O_4 is less than 1% in the residues produced in the process, Fe_3O_4 was synthesized by adding Fe^{2+} at pH 7—9. Two steps of control reaction are:

$$Fe^{2+} + 2FeO(OH) \rightarrow Fe_3O_4 + 2H^{+}. \qquad (16)$$

$$Me^{2+} + 2FeO(OH) \rightarrow Fe_2O_3MeO + 2H^{+}. \qquad (17)$$

(Me: heavy metals)

4 Conclusions

The work results showed that the high recovery yield of the valuable heavy metals from various types of heavy metal sludges and stainless steel pickling waste was achieved. The recovery yield of Cu, Ni, Zn and Cr is 94%, 91%, 90% and 95% respectively. The quality of recoverable metal salts and metal powder products all reaches up to the standards. Cr less than 1% in the residues produced by extracting Cr was stably chemically fixed in Fe_3O_4 and harmless. In this process there is no secondary pollution. A demonstration pilot, which can dispose of 2000 tons electroplating sludges per year, has been set up in Tianjin, China. The process is a clean technology which has no harmful waste discarded.

References

Andersson S O S, 1979. Proceeding of the international solvent extraction conference, ISEC(1977), (2): 798—804

Galimov M D, 1977. Non-Ferrous Metals (USSR), (3):54—56

Hallowell J B, 1977. Ammonium-carbonate leaching of metal values from water treatment sludges. PB Reports, USA. PB—271014

Mueller W, 1980. Treatment of non-ferrous metal hydroxide sludges residues. Ger. Offen 2841271

Reinhardt M, 1979. Extraction of metal from a mixture of metal hydroxide. Ger. Offen 2726783