绿色过程工程与清洁生产技术

——张懿院士论文集精选

《绿色过程工程与清洁生产技术》编写组　编

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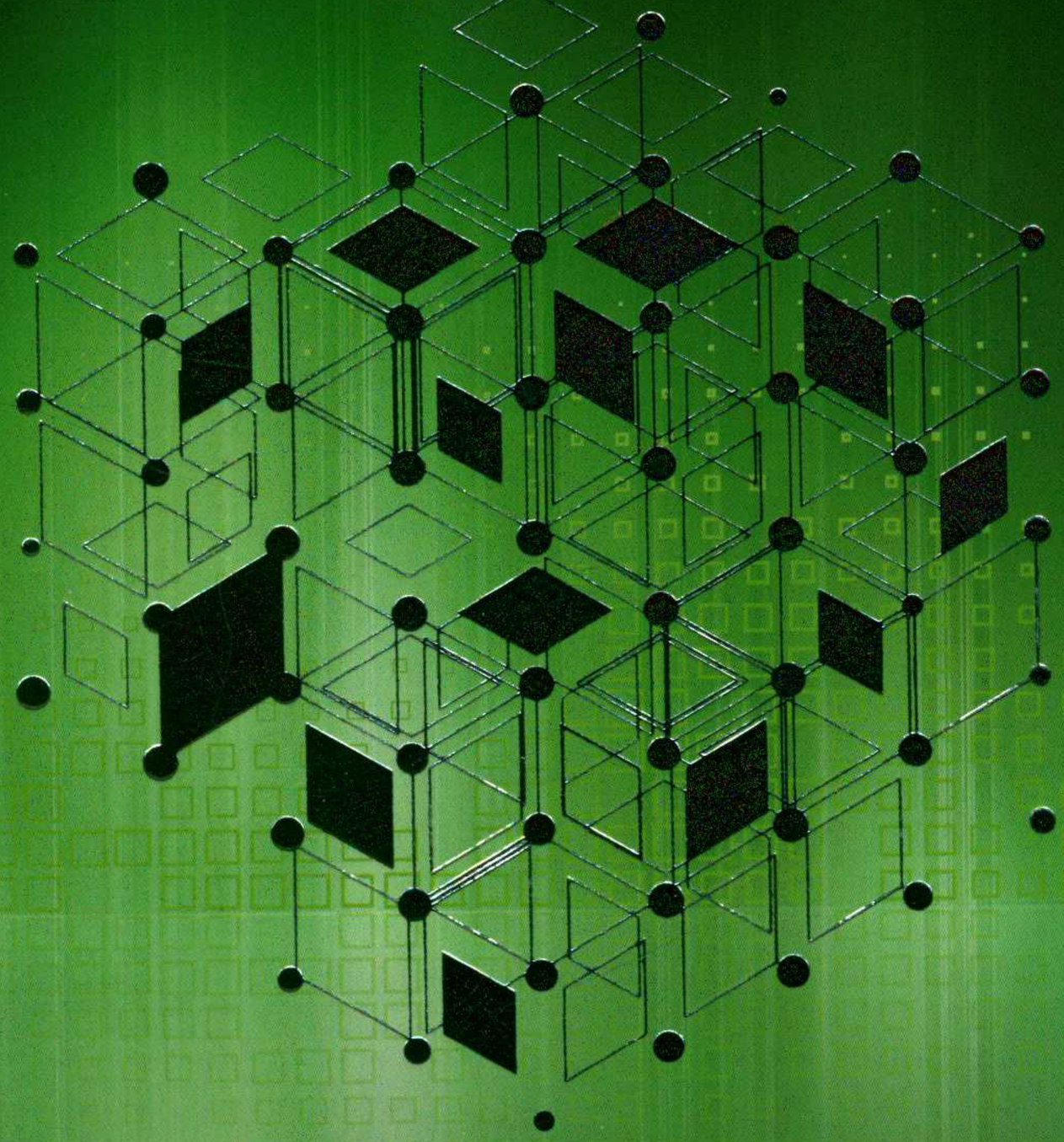

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本书选登了中国科学院过程工程研究所张懿院士的130余篇学术论文，内容分为总论、亚熔盐绿色化工冶金平台技术、重化工业环境污染治理技术与工程、热点与前沿领域四大主题。本书还附有张懿院士的照片资料、学术成长经历及学术成就、承担的主要科研项目、主要获得奖励和社会兼职等内容，展示了张懿院士科学研究、学术交流及培育人才的经历与成就。

本书充分反映了张懿院士在绿色过程工程方面做出的学术贡献，可供从事绿色化工的科研人员、技术人员参考，也可供高等学校化学工程与工艺、环境科学与工程及相关专业师生参阅。

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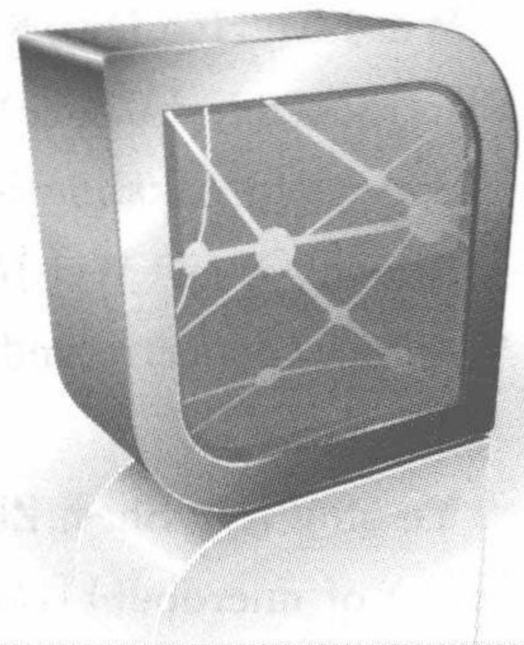

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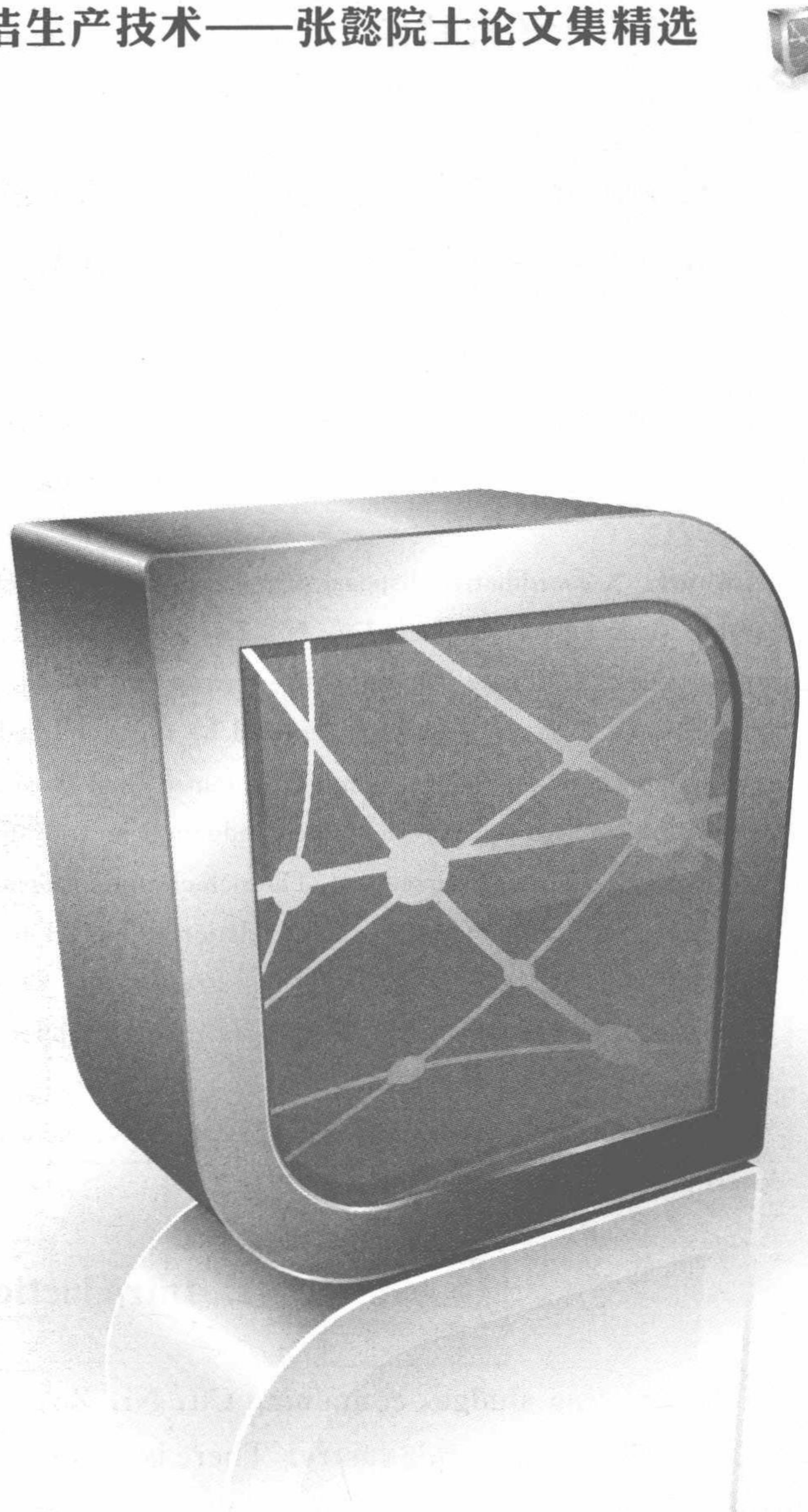

第3章 重化工业环境污染治理技术与工程

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

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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 disposal was subjected to recover Cr by hydrot hermal 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 2000t/a.

Key Words 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. Stainles 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 1970s. 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 st ainless 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 electroplating sludge and stainless steel pickling waste liquor is shown in Fig. 1.

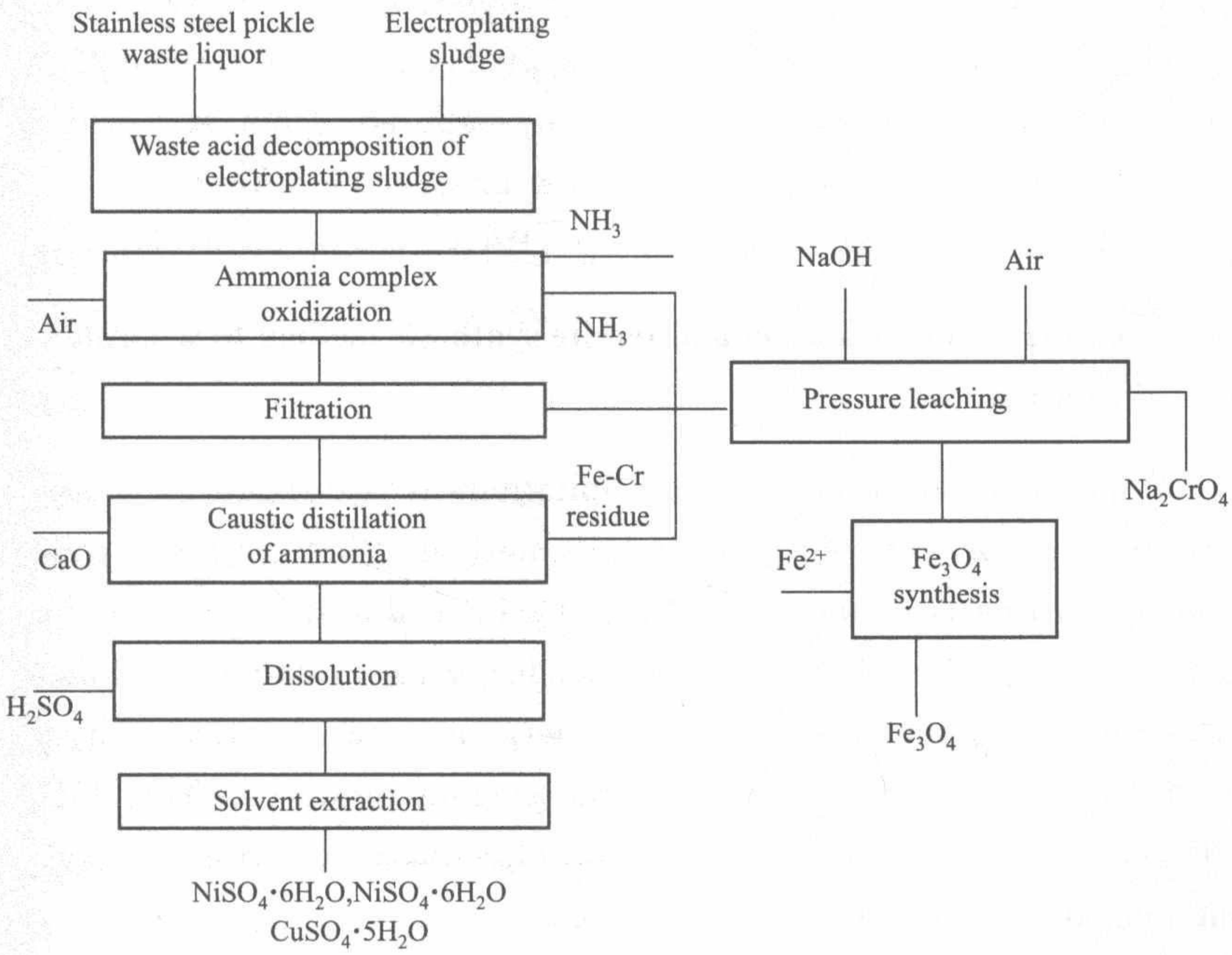

Fig. 1 Process diagram for recovery of heavy metals from electroplating sludge and stainless steel pickling waste liquid

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

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.

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

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:

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

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.

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

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:

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

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

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

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 0.03mPa 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