The Recovery of Precious Metals from Copper Refinery Anode Slime(銅精製陽極泥中の貴金属の回収)

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論　文　内　容　要　旨

SUMMARY AND CONCLUSIONS

A new hydrometallurgical procrss for recovering precious metals copper refining anode slimes has been developed and tested successfully. The process comprises three major unit operations: (1) leaching unit, where the precious metals are introduces to the aqueous environment from solid state, (2) solvent extraction unit, where the metals are separated and purified, and (3) reduction unit, where the metallic ions are reduced and precipitated from the solutions.

The anode slime is first leached with sulfuric acid to obtain copper-containing solution and then copper is recovered from the leached solution by solvent extraction technique. The sulfuric acid-leached residue is then leached with ammonium acetate solution to remove lead and copper. The lead and copper in the acetate leach solution are separated by a solvent extraction technique. The acetate-leached residue is then leached with nitric acid to obtain a leached solution which contains silver, selenium, tellurium, copper and some other impurities. Silver in the nitric acid-leached solution is recovered in the from of silver chloride. Subsequent to the recovery of silver, the selenium, tellurium, copper and other impurities-containing solution is then denitrated and chlorinated by a solvent extraction telhnique to change from nitric from into chloride form. This chloride solution is treated to separate tellurium form selenium, copper and other impurities by a solvent extraction technique. Selenium is then reduced and recovered by passing sulfur dioxide gas through the selenium-containing solution.

The nitric acid leached residue is then treated with mixed acid to leach gold. The gold-containing solution is sent to separate gold from other impurities by a solvent extraction technique. High purity of gold is then recovered by introducing the oxalic acid solution into the gold-loaded organic extractant. After the sulfuric acid, ammonium acetate, nitric acid and mixed acid leach steps, the tin concentration in the residue is increased. The tin concentrate is subjected to high temperature roasting by using calcium oxide, carbon and iron powder as fluxes and high purity of tin is obtained. The overall process based on selective leaching and solvent extraction techniques is showen as in Fig. 1.1.

Two kinds of slimes were used in the process study. One from the refining of copper concentrate (ores) designared as primary anode slime has a relatively high gold, silver and selenium content supplied by Taiwan Metal Mining Corporation. The other from the recycled scrap copper designated as secondary anode slime has higher lead and tin content supplied Company, Carrollton, Georgia, U.S.A. Composition is shownin Table 1.2. This process is applicable to both primary secondary anode slimes. As precious metal content can be different by a large percentage with different anode slimes, the process has been so designed that units used can be facilitatingly altered or spared depending on content of the slime.

To cope with the process studies, the process equipment design, manufacturing, equipment material testing and treatment of waste produced from the process are also conducted both in laboratory and pilot opration.

There are six chapters in this paper. The topics for each chapter are given in the table of contents attached.

The following conclusions may draw for the previously described hydrometallurgical process:

(1) The overall process consists of four selective leaching steps, the sulfuric acid leaching for copper, the acetate leaching for lead, the nitric acid leaching for silver, selenium and tellurium, and the mixed acid leaching for gold.

(2) Generally speaking, the leaching rates for the objective metal(s) increases with incresing concentration of leaching reagents, reaction time, liquid to solid ratio and temperature in the four leaching steps.

(3) The copper sulfate soluation from sulfuic acid leaching can be purified by hydroxyoxime or hydroxybenzophenone solvent extraction system and very high quality of copper sulfate solution can be obtained. The extraction of lead from acetate leaching solution by hydroxybenzophenone is very effective at pH in the neighborhood of 9.5.

(4) The silver in the nitric acid leaching solution can be recovered as AgCl by hydrochloric acid

precipitation method, and the nitric acid can be recovered by tributyl phosphate solvent extraction system.

(5) The extraction of tellurium from Se- and Te-containing solution by tributyl phosphate system is very effective and the separation efficiency between selenium and tellurium is excellent.

(6) The rate of reduction of selenious ion to elemental Se increased with increasing solution acidity, gas flow rate, and temperature and decreased with increasing selenious ion concentration.

(7) The gold in the mixed acid leaching solution can be recovered by solvent extraction with diethylene glycol dibutyl ether, followed by reduction with oxalic acid.

This novel, developed process is pollution-free, energy-saving and economic to compare with the conventional pyrometallurgical process in that:

(1) The energy consumption for the present process is much lower then that for the pyrometallurgical art.

(2) The treatment of the waste from the developed process is much easier than from the pyrometallurgical art.

(3) The recovery rate of selenium by the developed process is greater then 95 per cent whereas for the pyrometallurgical process, it seldom exceeds 80 per cent.

(4) In the present process, gold and silver can be recovered directly without going through a gold-silver alloy (Dor′e metal) stage.

(5) The solvent extraction technique is suitable for recovering metals from low concentration mother liquors. This technique is easy to operate and is also suitable for the continuous operation.

(6) In this process, all of the organic extractants and most of the mineral acids are recovered and reused along with the low energy consumptions, making the process more economical and more attractive.

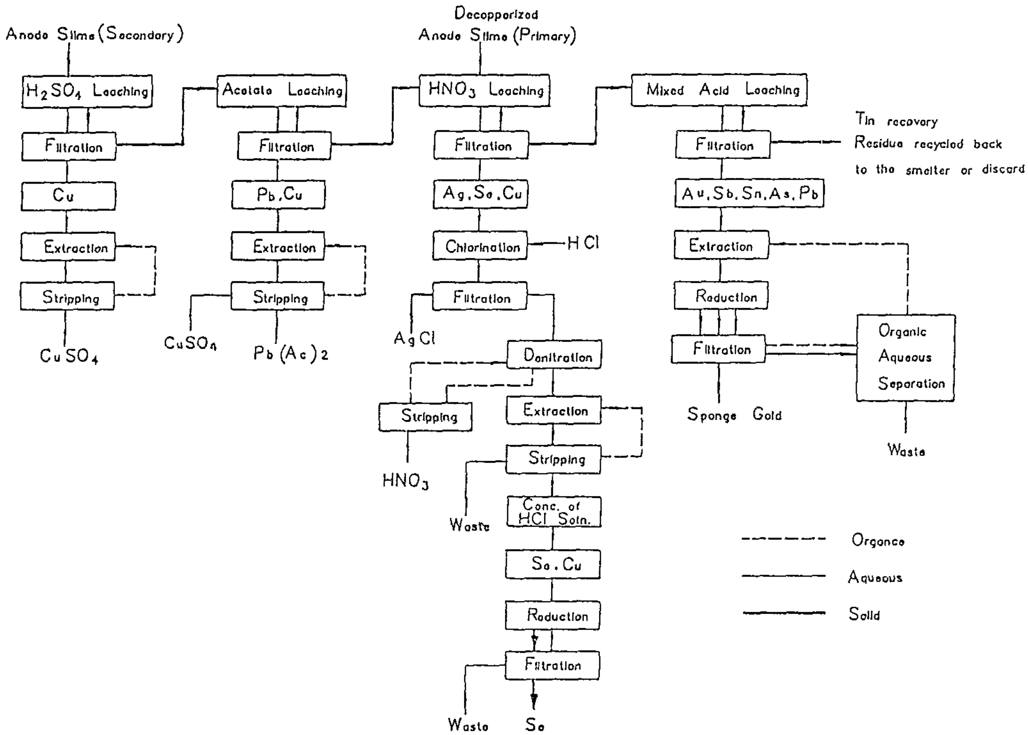

Fig.1.1 Blockdiagram for the recovery of precious metals from copper refinery anode slime.

Table 1.2 Slimes Compositions For Experimental Tasts

Element	Primary Slime A (From Copper Concentrate) wt. %	Secondary Slime B (From Recycle Scrap Copper) wt. %
Copper	2.0	0.188 - 3.96
Gold	1.44	0.056 - 0.067
Silver	18.9	5.38 - 6.33
Selenium	14.8	1.8 - 2.16
Tellurium	0.93	-
Lead	18.5	22.2 - 26.0
Tin	-	11.2 - 13.27
Arsenic	2.0	1.1
Bismuth	1.5	-
Moisture	4.17	1.2 - 3.2

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審査結果の要旨

大量の資源やエネルギーを扱う金属製錬工業に関しては，高度利用や省エネルギーの観点から現行製錬プロセスの一層の見直しが必要となっている。

本論文は，銅の電解精製工程で副生する陽極泥から金，銀等の貴金属を高純度，高収率で回収するに際し，従来の高湿乾式方と異なり，種々の浸出および溶媒抽出を組み合わせた新しい湿式プロセスの基礎研究とその成果に基づく試験研究の成果を纏めたもので，全編6章からなる。

第1章は序論であり，本研究の目的およびその意義について述べている。

第2章は，陽極泥の脱銅・脱鉛の研究結果を述べている。銅を硫酸で浸出除去した後，40℃，6M酢酸アンモニウム溶液で2段浸出し，95%以上の収率で鉛を浸出する。浸出液中の鉛は，LIX64Nで銅と共抽出し，2%酢酸で鉛のみを逆抽出した後濃縮し，高純度酢酸鉛として回収する。

第3章は，脱銅・脱鉛残渣の硝酸抽出による銀，セレン等の回収の研究結果を述べている。100℃，7M硝酸により，銀とセレンをそれぞれ96.1%，98.9%浸出した後，10M塩酸により高純度(>99%）塩化銀を回収する。トリブチルリン酸（ＴＢＰ）で2.2M硝酸を抽出回収した後，セレンとテテルを分離するため塩酸濃度4.7Mまで濃縮する。ＴＢＰでテテルを抽出分離した溶液に二酸化硫黄を吹き込み，純度99.5%以上のセレン粉末を90%以上の収率で回収している。この方法では従来法と比較すると，セレン純度と回収率は著しく向上する。

第4章は湿式法による金の回収の研究結果を述べている。硝酸浸出残渣を硝酸対塩酸1：10の混酸で浸出し，スズ等の不純物の浸出を抑制しつつ金を99%以上選択的に浸出している。浸出液からジチルカルビトール（ＤＢＣ）で金を抽出（>99.95%）する。抽出物及びスズの分離工程の温度に関しては金の純度と回収率が二律背反の関係にあり，溶媒抽出の温度抽出の温度管理が重要であることを明らかにしている。金を含む有機層を80℃シュウ酸水溶液と2時間接触させると純度99.9%のスポンジ状金を定量的に取得できることを示している。

第5章は，以上の基礎研究の成果に基づいた日産30kgの試験装置による約2年間の研究成果を述べている。金，銀及びセレン（純度）収率はそれぞれスポンジ状金（(>99.5%）として99%以上，銀は塩化銀（>99%）として95%以上，粉末セレン（>99%）として90%に達する。また硝酸や塩酸は大部分循環使用し，抽出試薬のＴＢＰやＤＢＣの損失はそれぞれ4.7及び21kg／t陽極泥で済むことを明らかにしている。この研究結果に基づいて，年間300tの陽極泥処理プラントが設計されている。

第6章は結論である。

以上要するに本論文は，今後の金属製錬工学の重要な分野である複雑な組成の原料の循環・省エネルギー型の新しい処理プロセスに関して，各工程の基礎研究の成果をパイロット試験で実証したもので湿式製錬工学の発展に寄与するところが少なくない。

よって，本論文は工学博士の学位論文として合格と認める。