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Separation and Recovery of Gold, Copper and Silver from Waste Acid Residues by Novel Alkaline Dechlorization-Acid Leaching Process

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A new process involving alkaline dechlorination and acidic leaching is developed for separation and recovery of valuable metals (such as copper, gold and silver) from waste acid residues containing 20.5 % sulfur and 3.198 % chlorine. It is shown that under the conditions of the liquid/solid ratio of 6:1 mL/g, leaching time of 1.5 h, pH 7-14, alkaline washing can effectively remove copper chloride from waste acid residues, favoring the subsequent operations for leaching and recovery of metals. The leaching rate of copper reaches 91.54 % and more than 99.8 % of gold and silver are enriched in the slag for further recovery when the alkaline washed waste acid residues are subjected to the following leaching conditions: L/S ratio of 6:1 mL/g, concentration of the mixed acid consisting of reagent A of 1.24 mol/L and reagent B of 0.3 mol/L, temperature of 85 °C and leaching time of 1.5 h. The process is thus very promising for efficient separation and high recovery of copper, gold and silver from waste acid residues.

Keywords: Waste acid residues, Mixed acid leaching, Dechlorination by alkaline washing, Copper, Gold, Recovery.

INTRODUCTION

With the rapid development of the economy and increasing demand of mineral resources, the amount of industry wastewater discharged during the exploration and utilization of the mineral resources keeps rising. The wastewater produced from the mining industry poses a great threat to the environment and human health due to its high contents of heavy metals and high acidity[1]. Therefore, wastewater treatment has always been one of the major issues obstructing the development of metallurgical industry[2].

In order to effectively recycle valuable metals and reduce the amount of the pollutants discharged, the residues treatment technologies, which includes active and passive systems[3], keep improving and can be categorized into three distinct subsets: physical, chemical and biological approaches[4-7].

Currently, it is fairly common for domestic metallurgical enterprises adopting the anode slime technique to treat the acid drainage produced during the manufacture with additional technique[8]. This technique involves the use of a precipitation-neutralization process with the additions of sodium sulfide and flake caustic soda[9]. Being generated from the precipitation-neutralization process, the residues could be precious secondary resources in which contain valuable metals, such as copper, gold, silver, tellurium, platinum, palladium, *etc*. Now

due to the lack of suitable treatment techniques, most of the residues were cheaply sold or simply disposed, squandering the resources. To improve resource utilization, it is important to separate and recycle metals from the waste residues efficiently.

In this study, a considerable amount of experiments were conducted after investigation of the physical and chemical characteristics of the waste acid residues. A new procedure including caustic washing-acid leaching-basic cupric carbonate precipitation was developed. Furthermore, it was discovered that the mixed acid direct leaching combined with caustic washing technique could effectively extract the copper and recycle it in the form of cupric sulfate. Meanwhile most of the valuable metals, for instance, gold, silver, tellurium, platinum, palladium entered into the leaching residue which could be recirculated to the anode slime processing system[10]. In this way, a desirable outcome could be achieved because of the increased recycling rates of gold, silver, tellurium, platinum and palladium. The research also contributes to better economic benefits. Because this technology can attain efficient leaching after caustic washing without roasting, it is one of the best new procedures presently for processing copper sulfide materials. The procedure displays the following advantages: high copper extraction yield, simplified process flow, environmental friendliness and cost-benefit effectiveness.

EXPERIMENTAL

The raw materials used for experiments are residues obtained from a production line of a metallurgical factory. The residues were crushed, screened and their chemical compositions were determined by X-ray fluorescence spectrometry, as shown in Table-1. It is seen that the residues have a high sulfur content (20.5 %), indicating a great amount of metal sulfides.

Apparatus: Electronic constant speed blender, mode JHS-1; electronic continuous adjustable temperature heating jacket, mode KDM; digital pH meter, mode PHS-25; electrothermal drying oven, mode GW-03; X-Ray Diffractometer, mode TTRIII, Rigaku, mode D/max-rA; Atomic absorption spectrophotometer, mode WXY-402C; XRF spectrometer, mode XRF-1800; Two-meter raster spectrometer, mode WSP-1.

Reagents: Reagent A; Reagent B, SAA; sodium hydroxide; anhydrous sodium carbonate.

Experimental procedures: Certain amount of waste acid residues was pulped under the condition of L/S = 1:1 mL/g for 2 h. Then the waste acid residues were added to 2 L beaker to undertake dechlorination by alkaline washing with a controlled stirring speed, temperature and reaction time. When the reaction is complete, under certain temperature and time the residues acquired from dechlorination by alkaline washing were leached with mixed acids, followed by filtration before cooling. Valuable metals like gold, silver were enriched into the leached residues. Copper was efficiently recycled in the form of basic cupric carbonate from the leach solution after a series of steps including silver precipitation with sodium chloride, purification, copper precipitation with sodium carbonate. The experimental procedures are shown in Fig. 1.
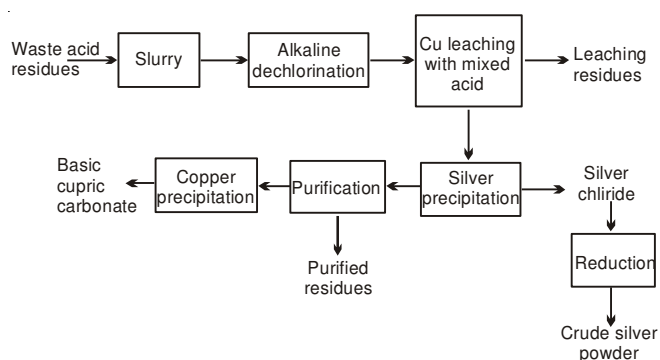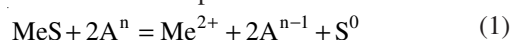

Fig. 1. Flowsheet of comprehensive utilization of waste acid residues

RESULTS AND DISCUSSION

Direct acid leaching of waste acid residue

Fundamental principles of direct acid leaching: Metal sulfides can be easily decomposed into metal ions and elemental sulfur in acid medium with the presence of oxidant A

$$MeS + 2A^n = Me^{2+} + 2A^{n-1} + S^0 \qquad (1)$$

The relation of free enthalpy (ΔG) and solution potential (ε) can be expressed as $\Delta G = -nF\varepsilon$, because reaction (1) belongs to multiphase redox reaction and electrochemical reaction mechanism of hydrometallurgy can be applied[11]. Therefore, solution potential ε can be used as an indicator showing the redox reaction trends of sulfides in the solution.

According to Nernst formula (2) when the leaching pulp's oxidation potential is lower than the equilibrium potential ε^0 of metal sulfides in solution, the reaction (1) will go reversely during the process of oxidative decomposition leaching of metal sulfides. That is to say, the metal sulfides can't be oxidatively decomposed. The oxidative decomposition of metal sulfides can be implemented only if the leaching pulp's oxidation potential is higher than the equilibrium potential ε^0 of metal sulfides. The Nernst formula is given by

$$\varepsilon = \varepsilon^0 - (RT / nF) \ln K \qquad (2)$$

where R is the molar gas constant, T is the absolute temperature, n is the is the number of electrons transferred, F is the Faraday constant and K is the reaction quotient.

Based on the metallurgical theory[12], it can be recognized from Fig. 2 that potential ranges of various metal sulfides like CuS, Au_2S and Ag_2S are different. In that case, copper sulfide can be selectively leached by controlling the leaching potential and pH value so as to inhibit the leaching of precious metals like Au and Ag and thus the separation and leaching of valuable metals can be realized[13].
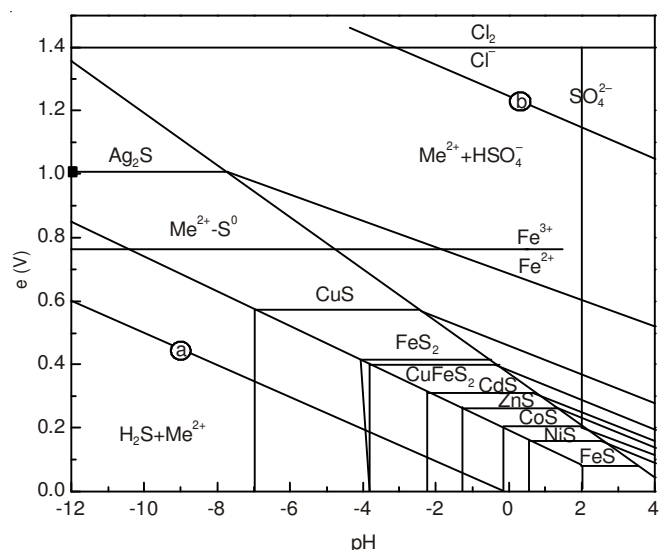

Fig. 2. Potential-pH diagram of MeS-H_2O([HSO_4^-] + [SO_4^{2-}] = 1 mol/L; [Me^{n+}] = 1 mol/L; [H_2S] = 0.1 mol/L) ref.[14]

Oxidant selection: Table-1 shows Cu exists as copper sulfide in acid waste acid residues. In order to find suitable oxidants for direct acid leaching of copper sulfide, the effects of oxidants on the solution potentials were measured by calomel and platinum electrodes combined with a digital voltmeter. The results are presented in Table-2, in which ε_1, ε_0

TABLE-1 MAIN CHEMICAL COMPOSITIONS OF WASTE ACID RESIDUES (MASS FRACTION, %)								
Components (%)	Cu	Au	Ag	S	Pb	Pt	Bi	Zn	Te
	40.38	0.009701	0.155	20.5	0.01781	0.005	0.4592	1.31	3.114
Components (%)	SiO_2	Pb	As	Fe	Na	Cl	Ni	Ca	O
	0.3	0.34	2.64	0.71	3.8	3.198	0.123	0.139	24

TABLE-2				
INFLUENCE OF OXIDIZING AGENTS ON SOLUTION POTENTIAL (mV)				
Oxidizing agent name	$HClO_4$	Reagent A	$K_2Cr_2O_7$	$NaClO_3$	H_2O_2
$\Delta\varepsilon = \varepsilon_0 - \varepsilon_1$	529	342	237	126	119

and $\Delta\varepsilon$ represent the potential measured when only 300 mL of H_2O was used as the base solution and the potential measured after 10 mL liquid oxidant or 10 g solid oxidant (dissolved in sodium chlorate solution) added and the raised potential value caused by the oxidant, respectively.

Table-2 indicates that reagent A cause the second highest potential increase next to perchloric acid. However, compared to perchloric acid, reagent A is much cheaper and won't dissolve gold. Hence, reagent A was chosen as the oxidant for leaching waste acid residues.

Effect of leaching time on leaching rates of Cu, Au and Te

Leaching conditions: The influence of leaching time on the leaching rates of copper, gold and tellurium are displayed in Fig. 3. The leaching experiments were conducted under the following conditions: mass of waste acid residues of 100 g, concentration of reagent A of 1.24 mol/L, leaching temperature of 85 °C and liquid/solid ratio (L/S) of 6:1 mL/g.

As shown in Fig. 3, the leaching rate of Cu increases from 98.46 to 99.95 % when the leaching time increases from 1 to 1.5 h. It then declines as the leaching time is extended. The oxidative leaching of Cu from the waste acid residues can be divided into two stages[15]:

$$Cu_2S + 4H^+ + 2A^- = CuS + Cu^{2+} + 2B + 2H_2O \qquad (3)$$

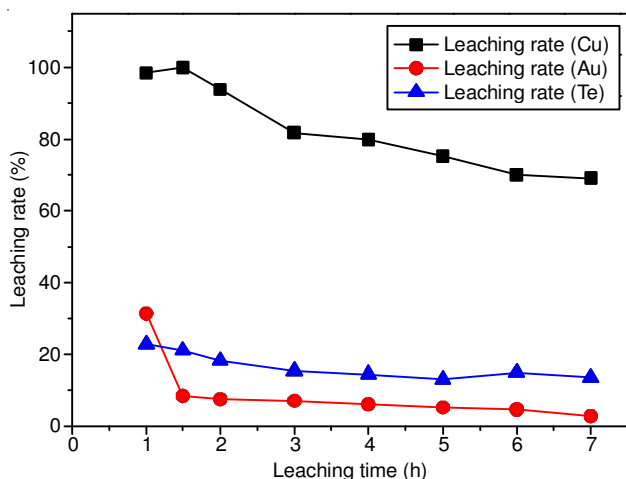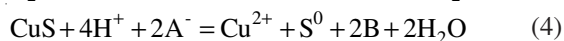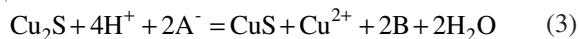$$CuS + 4H^+ + 2A^- = Cu^{2+} + S^0 + 2B + 2H_2O \qquad (4)$$

Fig. 3. Effect of leaching time on leaching rates of Cu, Au and Te

When leaching time reaches 1.5 h, copper in the waste acid residues is completely leached into the solution in the form of Cu^{2+} ions, leading to a high leaching rate (99.95 %). However, as the leaching time is further prolonged, continuous consumption of oxidant A gives rise to a reduction in the oxidation potential of the solution. When the potential is lower than the equilibrium potential ε^0 of metal sulfides the reverse reaction of (1) takes place and CuS is precipitated from the solution, resulting in a decreased leaching rate of Cu.

Likewise, the leaching rates of Te and Au show descending trends as the leaching time is increased. Due to the instability of reagent A^-, the dissolved Te and Au in the solution decompose and enter into the slag, which leads to the decrease of leaching rate.

Therefore, to achieve the separation of copper and gold, relatively higher leaching rate of copper and lower leaching rate of gold are essential. The best leaching time for the experiments is 1.5 h.

Effect of reagent B on leaching rates of Cu and Au: The effect of the concentration of reagent B on the leaching rates of copper and gold is illustrated in Fig. 4. The leaching experiments were conducted under the following conditions: mass of waste acid residues of 100 g, concentration of reagent A of 1.24 mol/L, leaching temperature of 85 °C, liquid/solid ratio (L/S) of 6:1 mL/g and leaching time of 1.5 h.
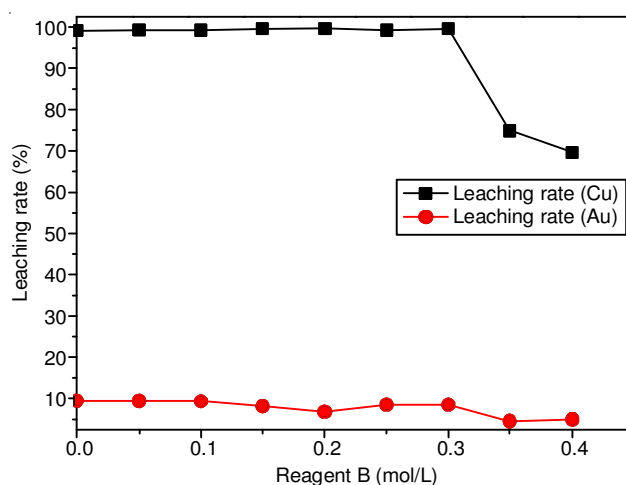

Fig. 4. Effect of concentration of reagent B on leaching rates of Cu, Au

The curve represents the leaching rate of Au is almost straight which indicates that the effects of reagent B dose is quite small. The potential of reagent B is very low and Au can't be dissolved, so the dosage of reagent B won't change the leaching rate of Au with a certain amount of reagent A. Moreover, the fluctuation of the leaching rate of Au is associated with the existence of Cl^- ions in the system. With regard to the influence of reagent B on the leaching rate of Cu, when the concentration is less than 0.3 mol/L, reagent B has very little impact on the leaching rate of Cu. The rate decreases dramatically when the concentration of reagent B exceeds 0.3 mol/L[16]. The variation in the leaching rate of Cu can be attributed to the supersaturation of reagent B and the generation of silica gel. The supersaturation accelerates the crystallization and precipitation of copper compounds, causing significant loss of copper. The silica gel is formed due to the reaction between the reagent B and quartz contained in the waste acid residues. As it has a good absorptivity, a certain amount of copper ions will be adsorbed onto the surface. As a result, the leaching rate of copper decreases. These results demonstrate that the optimal concentration of reagent B is 0.3 mol/L. From above all, it can be concluded that the best dose of reagent B should be 0.3 mol/L.

Effect of liquid solid ratio on leaching rates of Cu and Au: The influence of liquid solid ratio on the leaching rate of

Cu and Au is shown in Fig. 5. The leaching experiments were performed under the following conditions: mass of waste acid residues of 100 g, concentration of reagent A of 1.24 mol/L, concentration of reagent B 0.3 mol/L, leaching temperature of 85 °C and leaching time of 1.5 h.
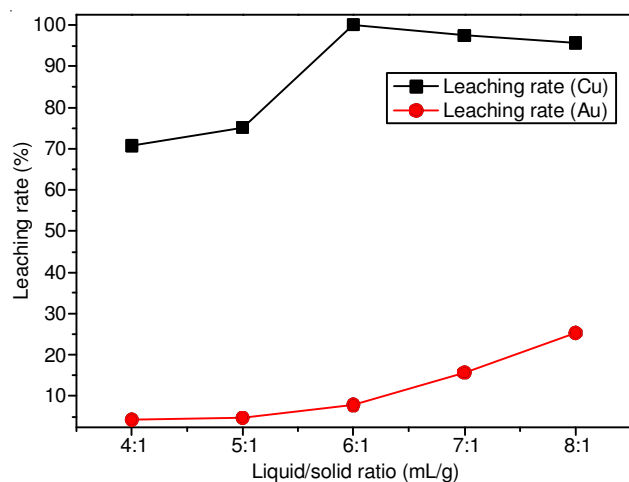

Fig. 5. Effects of liquid-soild ratio on leaching rates of Cu and Au

According to Fig. 5, the leaching rates of Cu and Au are proportional to the liquid/solid ratio when the value of L/S is lower than 6:1 mL/g. When L/S is higher than 6:1 mL/g, the leaching rates first experience a little decrease and then approach a steady state. This is because at given concentration of mixed acids consisting of oxidants A and B, more acids will be involved in leaching of Au and Cu at higher liquid/solid ratios. When the L/S ratio is low, there is not enough acid for leaching and the high viscosity of the solution formed impedes the stirring effect, causing the leaching rates of copper and gold remaining at a relatively low level. Nevertheless, the leaching rate of Cu reaches 99.95 % when L/S is 6:1 mL/g, which indicates Cu is almost completely leached. Continuous increase in the L/S ratio has little impact on the Cu leaching rate but promotes leaching rate of Au, resulting in more difficult separation of copper and gold. Thus, the suitable liquid/solid ratio is 6:1 mL/g.

Effect of temperature on leaching rates of Cu and Au: The influence of temperature on the leaching rates of Cu and Au is shown in Fig. 6. The experiments were carried out under the following leaching conditions: mass of waste acid residues of 100 g, concentration of reagent A of 1.24 mol/L, concentration of reagent B of 0.3 mol/L, leaching time of 1.5 h and liquid/solid ratio (L/S) of 6:1 mL/g.

As shown in Fig. 6, high temperatures benefit the leaching of Cu and Au. However, after the temperature exceeds 85 °C the leaching rate of Cu keeps nearly stable while the leaching rate of Au increases rapidly until 90 °C. This is because thermal activation leads to an accelerated reaction. Under normal circumstances, the diffusion velocity speeds up 20 % and the chemical reaction rate is doubled for each 10 °C step. When the temperature is above 85 °C, the leaching rate of Cu reaches approximately 99.95 %. Further increase in temperature have weak effects on the leaching rate of Cu, but leads to a rapid increase in the leaching rate of Au, which is unfavorable for separating copper and gold from the solution. Additionally,
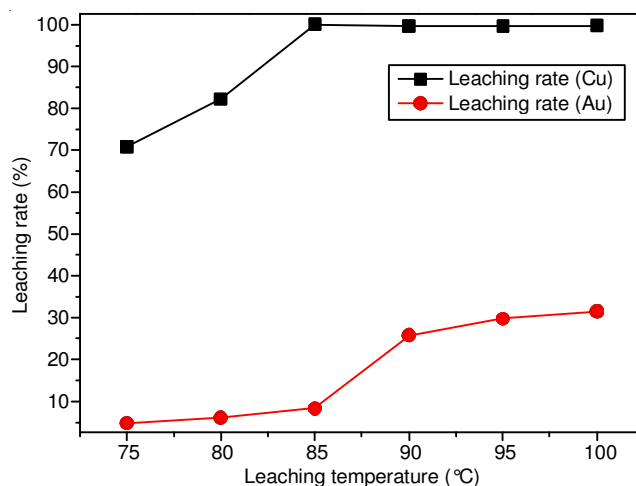

Fig. 6. Effects of temperature on leaching rates of Cu and Au

high temperatures could increase the energy cost and bring about unstable factors during the production, so the suitable leaching temperature is 85 °C.

Dechlorination through alkaline washing followed by acid leaching of waste acid residues

Alkaline washing of waste acid residues: From above results, the optimum process conditions for direct acid leaching can be determined as follows: reagent A 1.24 mol/L, reagent B 0.3 mol/L, leaching time 1.5 h, leaching temperature 85 °C, liquid solid ratio 6:1 mL/g. Under these conditions, although the leaching rate of Cu reaches 99.95 %, the leaching rate of Au would also approach 7.26 %. The relatively high leaching rate of Au is adverse to the separation of copper and gold.

In order to make leached gold enter the slag instead of solution, dechlorination of the residues is necessary. This is because the waste acid resides has a high content of chlorine (about 3.198 %), which will form gold complex under the condition of acid leaching and the potential of gold would decline from 1.53 V to approximately 1 V, resulting in higher dissolution of gold. The removal of chlorine can be achieved by washing the residues with aqueous sodium hydroxide solutions. The reaction is:

$$CuCl_2 + 2NaOH = 2NaCl + Cu(OH)_{2(s)} \qquad (5)$$
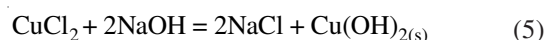
It can be seen that the sodium chloride generated will enter into the effluent and copper will precipitate in the form of copper hydroxide. The experiments results are shown in Table-3. Table-3 demonstrates that alkaline washing is effective for dechlorination of waste acid residues as the dechlorination rates are over 99 %.

Acid leaching after alkaline washing: Duplicate tests were conducted with 100 g waste acid residues treated with dechlorination by alkaline washing under the optimum conditions obtained from previous sections. The results are summarized in Table-4. As shown in Table-4, the leaching rates of gold and silver are less than 0.195 and 0.187 %, respectively. It indicates that 99.805 % of gold and 99.815 % of silver are enriched in the residues. Also, a comparison between the results of experiments A and B reveals that the mixed acid consisting of reagents A and B shows a higher leaching rate than individual acid which contains only reagent A. With the optimal

TABLE-3
DECHLORINATION OF WASTE ACID RESIDUES BY ALKALINE WASHING

No.	Alkaline washing				Water washing		Dechlorination rate (%)
	L/S (mL/g)	Temp. (°C)	Time (h)	pH	Temp. (°C)	Time (h)	
1	6:1	90	1.5	7~14	80	1	99.33
2	6:1	90	1.5	7~14	80	1	99.04
3	6:1	90	1.5	7~14	80	1	99.52
4	6:1	90	1.5	7~14	80	1	99.13
5	6:1	90	1.5	7~14	80	1	99.39

TABLE-4
RECOVERY OF VALUABLE METALS BY ACIDIC LEACHING OF ALKALINE WASHED WASTE ACID RESIDUES

No.	Oxidants (mol/L)	L/S (mL/g)	Temp. (°C)	Leaching time (h)	Leaching rate (%)		
					Cu	Au	Ag
A	Reagent A 1.24	6:1	85	1.5	59.7	0	0
B	Reagent A 1.24 Reagent B 0.3	6:1	85	1.5	91.21	0.195	0.0005
C	Reagent A 1.24 Reagent B 0.3	6:1	85	1.5	91.33	0	0.187
D	Reagent A 1.24 Reagent B 0.3	6:1	85	1.5	91.54	0	0

leaching conditions, the leaching rate of copper reaches 91.54 %, while the rates of gold and silver remain very low.

Conclusions

A new process involving alkaline dechlorization and acidic leaching is developed for separation and recovery of valuable metals from waste acid residues with 20.5 % sulfur and 3.198 % chlorine. The following general conclusions can be drawn from the experiments:

(1) Under the conditions of L/S = 6:1 mL/g, leaching time = 1.5 h, pH = 7-14, alkaline washing can effectively remove the chlorine from waste acid residues, favoring the recovery of gold.

(2) When the alkaline washed waste acid residues are subjected to the experimental conditions as follows: the L/S ratio of 6:1 mL/g, mixed acid consisting of 1.24 mol/L reagent A and 0.3 mol/L reagent B, temperature of 85 °C and leaching time of 1.5 h, the leaching rate of copper reaches 91.54 % with little gold and silver being leached. The effective separation of copper, gold and silver are achieved.

(3) After purification and precipitation, a main product, basic cupric carbonate with copper grade of 50.4 %, Te content of 0.344 %, Ni content of 0.5013 % and a valuable metal rich leaching slag as by-product with Cu, Te, Si content of 16.36, 9.265 and 0.477 %, respectively were obtained. In general, with this process, the recovery rates of gold, silver reaches 99.8 % and the rate of copper are beyond 90 %. The study thus provides a promising method for selectively separate and recover valuable metals from the waste acid residues.

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