Experimental Research on Enrichment of Precious Metals from Lead Matte by Nitric Acid Leaching

Xingxiang Fan[a,*], Kunbin Yang[b], Chunmei Tan[b]

[a] Faculty of Metallurgical Material, Kunming Metallurgy College, Kunming,Yunnan, 650033, China
[b] Yunnan Copper Co., Ltd, Kunming,Yunnan,650102, China

Corresponding author: +86 13888355042; fax:086 0871 66050935.

E-mail address: fanxingxiang@tom.com(Xingxiang Fan).

Abstract: Based on the phase and element composition of lead matte, this paper presents an enrichment process of precious metals by selective leaching of base metals of Pb and Cu from lead matte with nitric acid. The effects of nitric acid dosage, leaching time, leaching temperature, liquid-solid ratio on the leaching rate of lead and copper were also discussed in detail. Through the experiments, the optimal process data were obtained as follows: nitric acid dosage 1.54 times the weight of lead matte, leaching time 3h, leaching temperature 75℃, and liquid-solid ratio 4:1. Under this condition, the slag rate was 33.20%, Pb/Cu leaching rates were 91.14% and 89.99%, Au and Ag contents in the leaching residue were 10.54 g/t, Ag 2693.95 g/t, respectively; and the enrichment ratio of precious metals up to 3.01 times. The effect of milling of lead matte on Pb/Cu leaching rate was also investigated while keeping the leaching condition constant. Experiments show Pb/Cu leaching rates were up to 97.46% and 96.73% and the slag rate was 30.16%, Pb/Cu content in residues were 4.58% and 1.29%, respectively, when ball milling time was 30 min. Compared with direct leaching, Pb/Cu leaching rate increased by 6.32% and 6.74%, the enrichment ratio increased by 0.31 times. It was proved that ball milling of lead matte was helpful to improve Pb/Cu leaching rate.

1. Introduction

Lead matte is a by-product from pyrometallurgical process for Pb/Cu smelting, which can be produced from complex Pb/Cu materials treatment in blast furnace in some companies, such as Yunnan Chihong Zn & Ge Co., Ltd., Yunnan Copper Co., Ltd. (YCC), local private enterprises in Yongxing County in Hunan Province and etc. With quite high metal values, Lead matte, besides Pb and Cu, also contains some rare metals (such as In and Ge)[1], precious metals (such as Au and Ag), PGM (such as Pt and Pd) and so on. Recovery of rare metals can bring significant economic benefits. At present, some available treatment processes for the Lead matte include pressure acid leaching [2-6], pressure plkaline leaching[7], chlorination leaching[8], converting process[9-10] and etc. Among them, pressacid leaching process has been studied systematically in YCC, and industrialization design remains to be done. Pyrometallurgical process has been applied in Yunnan Chihong Zn & Ge Co., Ltd. Based on the lead matte materials supplied by an enterprise, the authors proposed a hydrometallurgical process of lead matte leaching with nitric acid. The aim of the thesis is to provide a reference for the precious metals production enterprises to provide a simple, efficient and less expensive process of precious metal enrichment.

2. Experiment

2.1. Reagent & Equipment

Main reagent for experiments: nitric acid, AR, purity of 65.0%, supplied by Chongqing Chuandong Chemical Industry (Group) Co., Ltd.

Experiment equipment: Sealed Sampling Crusher (Type: GJ400-4m, Power: 1.5kw, Supplier: Nanchang General Sample Test & Preparation Machine Plant); Resistance Furnace (Type: KSY-12-16A, Power: 12kw, Voltage: 380V, Supplier: Tianjin Zhonghuan Experimental Resistance Furnace Co., Ltd.); Multi-function Digital Signal Electric Mixer (Type: DW-3, Supplier: Gongyi Yuhua General Instrument Co., Ltd.); Intelligent Digital Display Thermostatic Water Bath (Type: HH-WO-5L, Supplier: Gongyi Yuhua General Instrument Co., Ltd.); Vacuum Pump with Circulated Water System (Type: SHZ-95B, Power: 370W, Voltage: 220V, Rotational Speed: 2800rpm, Supplier: Gongyi Yuhua General Instrument Co., Ltd.); Filter Paper; Wash Bottle; Glass Rod; pH Indicator Strips； 50mL Volumetric Flask; Thermometer Beaker; Volumetric Cylinder.

Analytical instruments: D/max-2200 X-Ray Diffraction (XRD), Rigaku, Japan; S-3400N Scanning Electron Microscopy (SEM), Hitachi High-Technologies (Shanghai) Co., Ltd.; Optima 5300 DV Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, PerkinElmer); X-Ray Fluorescence (XRF), Thermo Fisher Scientific, Type: ARL3460.

2.2. Materials

After sample preparation for experiment materials, sample particle sizes are -53~74μm accounted for 81.57%, particle sizes of less than -53μm accounted for 18.43%. The element analysis results are shown in Table 1. XRD analysis shows that Pb and Cu exist in the form of sulfide.

Table 1 chemical composition of lead matte materials (%)

Element	Pb	Cu	Bi	Sb	As	S	Au	Ag
Content	54.30	11.91	0.19	0.79	0.08	14.46	3.5	895

* Unit for precious metals: g/t

2.3.Experimental Process

The experiment was carried out in a 1000ml round bottomed flask. The flask was placed in a constant temperature water bath and a variable frequency agitator was installed. Weighing a certain amount of lead matte is placed in a closed flask, and adding dilute nitric acid according to the ratio of liquid to solid, started to stirring and controlled the temperature, leaching time; filtered and washed after completion of leaching. The content of lead and copper in leaching solution was analyzed, and the leaching rate of copper and lead was calculated. The nitrogen oxides in the leaching process are absorbed by sodium hydroxide, and the absorption series is three.

2.4. Experiment Principle

As the reaction happened in nitric acid system, Pb and Cu in lead containing copper matte were produced in form of sulfide. The reaction was quite complex. The Reaction could be classified as adequate or excessive amount of nitric acid.

Reactions with adequate amount of nitric acid:

$$3CuS+8HNO_3=3Cu(NO_3)_2+2NO+3S+4H_2O \quad (1)$$

$$3PbS+8HNO_3=3Pb(NO_3)_2+2NO+3S+4H_2O \quad (2)$$

Reactions with excessive amount of nitric acid:

$$CuS+8HNO_3=8NO_2+CuSO_4+4H_2O \quad (3)$$

$$PbS+4HNO_3=8NO_2+PbSO_4+4H_2O \quad (4)$$

3. Results & Discussions

3.1. Effect of nitric acid dosage

Leaching was carried out under the conditions of liquid-solid ratio 4:1, leaching temperature 75°C, leaching time 3h and mixing speed 250 rpm. After completion of leaching, small amount of copper powder was added to displace precious metals in leaching solution, and then filtered and washed leaching residue. Experimental results of nitric acid dosage are given in Table 2.

Table 2 Experimental results of the different nitric acid dosages

HNO_3 dosage to weight of Lead matte (times)	slag rate(%)	Pb/Cu content of leaching slag(%)
0.70	60.90	14.68/13.69
1.12	37.70	10.25/13.30
1.54	33.20	14.49/3.59
1.96	39.20	9.62/2.25

As can be seen from Table 2, addition of nitric acid is 0.70 to 1.54 times the weight of lead matte. Cu/Pb leaching rates increase gradually with the increasing of nitric acid consumption. Increasing of Pb leaching rate was not as obvious as that of Cu leaching rate while nitric acid consumption was 1.96 times the weight of lead matte. Due to the excessive amount of nitric acid, elemental sulfur produced was oxidized into sulfuric acid by nitric acid during reaction, and sulfuric acid reacted with lead nitrate to form precipitate of lead sulphate. The reaction equation was as follows.

$$S+2HNO_3=H_2SO_4+2NO\uparrow \quad (5)$$

$$Pb(NO_3)_2+H_2SO_4=PbSO_4\downarrow+2HNO_3 \quad (6)$$

It was not beneficial to improving leaching rate of Pb and enrichment ratio of precious metals. The leaching residue, which was obtained from the dosage of nitric acid was 1.96 times the weight of lead containing copper matte, was characterized by scanning electron microscopy. The results are shown in Fig 1. As can be seen from Fig 1, needle-shaped particles were lead sulfate and the remaining particles are elemental sulfur and so on. With overall consideration, it was recommended that dosage of nitric acid was 1.54 times the weight of lead matte, which more than 90% of Pb and Cu have entered into the leaching liquor, and cost would greatly increase if dosage of nitric acid further would be increased.

Fig. 1 SEM images of leaching residue

3.2. Effect of temperature

To study the effect of temperature, the experiments were carried out at 35℃, 45℃, 55℃, 65℃, 75℃ and

85℃, keeping all other conditions constant. After completion of leaching, adding small amount of copper powder was used to displace precious metals in leaching solution, and then filtered and washed leaching residue. Experimental results of leaching temperature are given in Table 3.

Table 3 Experimental results of the different leaching temperatures

leaching temperature (℃)	sla g rate(%)	Pb/Cu content of leaching slag(%)	Pb/Cu leaching rate (%)
35	39.90	11.05/17.51	92.08/42.81
45	38.00	11.12/13.43	92.03/56.13
55	35.90	10.18/12.01	93.27/63.80
75	33.20	14.49/3.59	91.14/89.99
85	36.30	14.48/0.28	90.32/99.15

It can be seen from table 3 that the leaching temperature has little influence on the leaching rate of lead, but has obvious influence on the leaching rate of copper, and then the leaching of copper increased obviously with the increase of leaching temperature. It was also found that the increase of slag rate during leaching was unfavorable to the enrichment of precious metals. Therefore, the leaching temperature was determined to be 75℃. Under this temperature, Cu/Pb leaching rate was up to 90%.

3.3. Effect of time

Leaching was carried out under the conditions of liquid-solid ratio 4:1, the dosage of nitric acid for 1.54 times the weight of lead matte, leaching temperature 75℃ and mixing speed 250 rpm. After completion of leaching, small amount of copper powder was added to displacing precious metals in the leaching solution, and then filtered and washed leaching residue. Experimental results of leaching time were given in Table 4.

Table 4 Experimental results of the different leaching time

leaching time (h)	slag rate(%)	Pb/Cu content of leaching slag(%)	Pb/Cu leaching rate (%)
2	35.80	15.92/5.37	89.50/83.86
3	33.20	14.49/3.59	91.14/89.99
4	37.60	10.39/0.60	92.80/98.10

Table 4 showed that the leaching time had little influence on the leaching rate of lead, but had obvious influence on the leaching rate of copper, and the leaching rate of Cu increases obviously with the increase of leaching time. However, it was found that the leaching time was too long, the slag rate increased with the increase of the leaching time. The main reason was that the elemental sulfur produced during leaching reacted with the residual nitric acid to produce sulfuric acid and nitric oxide, and sulfuric acid reacted with lead nitrate to form precipitate of lead sulphate, which the enrichment ratio of precious metals decreased. Therefore, the leaching time was determined to be 3 h.

3.4. Effect of liquid-to-solid ratio

liquid-to-solid ratio was varied from 3:1 to 5:1 while keeping nitric acid dosage, leaching temperature, leaching time and mixing speed. After completion of leaching, adding small amount of copper powder was aim to displace the precious metals in leaching solution, and then filtered and washed leaching residue. Experimental results of the different liquid-to-solid ratio were given in Table 5.

Table 5 Experimental results of the different liquid-to-solid ratio

liquid-to-solid ratio	slag rate(%)	Pb/Cu content of leaching slag(%)	Pb/Cu leaching rate (%)
3:1	36.60	12.14/1.58	91.82/95.14
4:1	33.20	14.49/3.59	91.14/89.99
5:1	34.30	12.35/7.24	90.67/77.75

Table 5 shows that the effect of the liquid-solid ratio on the leaching rate of lead was small, but the effect of the liquid-solid ratio on the leaching rate of copper was significant, which the leaching rate of copper obviously decreased with the liquid-solid ratio increasing. Therefore, the ratio of liquid to solid was determined as 4:1.

The influence of the amount of nitric acid, leaching temperature, leaching time and liquid solid ratio on the leaching rate of lead / copper has been investigated. The leaching process parameters were obtained as follows: nitric acid dosage 1.54 times the weight of lead matte, leaching time 3h, leaching temperature 75℃, and liquid-solid ratio 4:1. Under this condition, the slag rate was 33.20%, Pb/Cu leaching rates were 91.14% and 89.99%, respectively; the other metal contents in the leaching residues were as follows: Au 10.54 g/t, Ag 2693.95 g/t, Pb 14.49%, Cu 3.59%; and then the enrichment ratio of precious metals was up to 3.01 times. However, higher content of Pb/Cu in leaching residue affected the subsequent extraction of precious metals. The experiments of prolonging leaching time and increasing leaching temperature had been conducted, the results showed the leaching rate of copper increased but the leaching rate of lead decreased and the slag rate increased instead, which has been confirmed by the conditions experiments of leaching time and leaching temperature. It was necessary to research the effects of grain size of lead matte on Pb/Cu leaching rate.

3.5. Ball Milling Experiments

The materials of lead matte was milled with roller ball milling for 30min. After ball milling, the lead matte particle sizes of 20~53μm accounted for 8.18% and less than 20μm accounted for 91.82%, which the size of lead matte was finer than before grinding. Leaching experiments were carried out using the same leaching conditions. The slag rate was 30.16%, lead and copper content of in residues were 4.58% and 1.29%, lead and copper leaching rate were 97.46% and 96.73%, respectively, and the enrichment ratio of precious metals was 3.32 times. Compared with results of direct leaching, lead and copper leaching rates were increased by 6.32% and 6.74%, respectively. This main reason was that the ball milling could increase specific surface area and surface energy of lead matte, which was helpful to improve reaction rate of leaching, and then the leaching rates of lead and copper were further increased

4. Conclusions

It was practical to adopt direct leaching method to leach lead matte with nitric acid for the purpose of enrichment of precious metals. Through the experiments of single factor condition, the optimal process data were obtained as follows: nitric acid dosage 1.54 times the weight of lead containing copper matte, leaching time 3h, leaching temperature 75℃, and liquid-solid ratio 4:1. Under this condition, the enrichment ratio of precious metals was up to 3.01 times.

Ball milling experiment results show that the particle sizes of 20~53μm accounted for 8.18%, particle sizes of less than 20μm accounted for 91.82% after ball milling 30 min. Leaching experiments were carried out under the same leaching conditions. The results showed that the leaching rates of lead and copper were obviously higher than that without ball milling and ball milling was helpful to improve the leaching rate of lead and copper and reduce the slag rate.

Acknowledgment
We are thankful for the financial support provided by talent introduction and research support of Kunming College of Metallurgy (No.2015RC001), and would like to thank professor Chunmei Tan for translating the manuscript.

References
[1] Zhang Hou-wen, Fan Xing-xiang, Wu Hong-lin, Zou Li-ming. Experimental research on pressure leaching of copper using sulfuric acid[J]. Hydrometallurgy of China, 2013, 32 (5): 305-308.
[2] Kyung-Ho Park, Debasish Mohapatra, B. Ramachandra Reddy, Chul-woo Nam. A study on the oxidative ammonia/ammonium sulphate leaching of a complex (Cu-Ni-Co-Fe) matte [J]. Hydrometallurgy, 2007, 86(3-4): 164-171.
[3] J.A.M. Rademan, L. Lorenzen, J.S. J. Van Deventer. The leaching charateristics of Ni-Cu matter in the acid-oxygen pressure lea process at Impala Platinum [J]. Hydrometallurgy, 1999, 52(3): 231-252
[4]J.L. Provis, J.S.J. Van Deventer, J.A.M. Rademan, L. Lorenzen. A kinetic model for the acid-oxygen pressure leaching of Ni-Cu matte [J]. Hydrometallurgy, 2003, 70(1-3): 83-99
[5] S. Anand, R.P. Das, P. k. Jena. Sulphuric acid pressure leaching of Cu-Ni-Co matte obtained from copper converter slag-optimisation through factorial design [J]. Hydrometallurgy, 1991, 26(3): 379-388
[6] Bingjie Jin, Xianwan Yang, Qingfeng Shen. Pressure oxidative leaching of lead containing copper matte [J]. Hydrometallurgy, 2009, 96(3): 57-61.
[7]Xiao Feng, Yang Tian-zu. Studies on the behavior of copper in the process of pressure alkali treating lead copper matte[J]. Metal materials and metallurgy engineering, 2011, 39 (2)： 7-10.
[8] Wen Jian-feng, Yang Tian-zu, Wang An, Xiao Feng, et al. Chlorination-leaching of lead-matter at controlled potential [J]. Hunan nonferrous metals, 2011, 27(1): 27-29.
[9] Ding Wei-an, Niu Hui-xian, Guo Xian-jian. Melting behavior of silica flux in converting process of high grade copper matte [J]. Chinese journal rare metals, 1999, 23(6)： 417-420.
[10] Bao Chong-jun, Jia Zh-hong, Wu Hong-lin, Ren Zhan-yu, et al. Industrial test for treating copper dross with converter [J]. Chinese nonferrous metals, 2009, (3): 27-28.