

Extraction of arsenic from arsenic-containing cobalt and nickel slag and preparation of arsenic-bearing compounds

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Abstract: The arsenic extraction from the arsenic-containing cobalt and nickel slag, which came from the purification process of zinc sulfate solution in a zinc smelting factory, was investigated. The alkaline leaching method was proposed according to the mode of occurrence of arsenic in the slag and its amphoteric characteristic. The leaching experiments were conducted in the alkaline aqueous medium, with bubbling of oxygen into the solution, and the optimal conditions for leaching arsenic were determined. The results showed that the extraction rate of arsenic was maximized at 99.10% under the optimal conditions of temperature 140 °C, NaOH concentration 150 g/L, oxygen partial pressure 0.5 MPa, and a liquid-to-solid ratio 5:1. Based on the solubilities of As₂O₅, ZnO and PbO in NaOH solution at 25 °C, a method for the separation of As in the form of sodium arsenate salt from the arsenic-rich leachate via cooling crystallization was established, and the reaction medium could be fully recycled. The crystallization rate was confirmed to reach 88.9% (calculated on the basis of Na₃AsO₄) upon a direct cooling of the hot leachate down to room temperature. On the basis of redox potentials, the sodium arsenate solution could be further reduced by sulfur dioxide (SO₂) gas to arsenite, at a reduction yield of 92% under the suitable conditions. Arsenic trioxide with regular octahedron shape could be prepared successfully from the reduced solution, and further recycled to the purification process to purify the zinc sulfate solution. Also, sodium arsenite solution obtained after the reduction of arsenate could be directly used to purify the zinc sulfate solution. Therefore, the technical scheme of alkaline leaching with pressured oxygen, cooling crystallization, arsenate reduction by SO₂ gas, and arsenic trioxide preparation, provides an attractive approach to realize the resource utilization of arsenic-containing cobalt and nickel slag.

Key words: arsenic-containing cobalt and nickel slag; alkaline leaching; cooling crystallization; sodium arsenate; arsenic trioxide

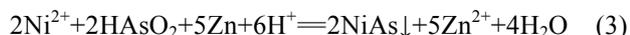
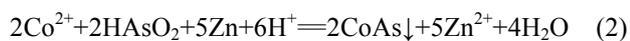
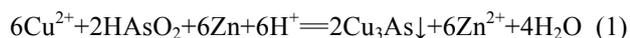
1 Introduction

Arsenic, is carcinogenic to the human beings [1]. The amount of the arsenic-containing wastes is increasing gradually upon the mining activities, combustion of fossil fuels and smelting of nonferrous metals, posing great threat to the environment. Therefore, the innocuous treatment of the wastes has drawn much attention worldwide [2].

The arsenic-containing cobalt and nickel slag containing more than 11% arsenic is produced from the zinc hydrometallurgical process [3]. In the zinc hydrometallurgical process, zinc sulfate solution is obtained by the acid leaching of zinc-bearing materials.

The zinc sulfate solution mainly contains metallic cations including Cu, Cd, Co, Ni and other trace metal cations, which have to be removed to avoid their influence on subsequent zinc electrolysis. Theoretically, according to the comparison of standard electrode potentials, these cations are expected to be reduced with zinc powder to form corresponding metals and be removed from the solution. However, in practice, it is extremely difficult to control the Co and Ni concentration to the level that meets the downstream electrolysis requirements, even with the addition of excess amount of zinc powders. To solve this problem, trivalent arsenic or antimony salts have usually been added into the zinc sulfate solution as the activators. When trivalent arsenic salts are utilized, the arsenic-containing cobalt and nickel slag will be

produced. The main reactions during the generation of the slag can be described as follows:



At present, this kind of slag is used practically to extract Cu by pyrometallurgical process. It will generate high arsenic-bearing ash which is sold out to other plant, which may cause serious arsenic pollution dispersion and transfer.

It is worth noting that large amounts of arsenic, copper, zinc, cobalt, nickel and other metals co-exist in the arsenic-containing cobalt and nickel slag, exhibiting substantial value for resource utilization. For this goal, relevant hydrometallurgical method had been studied and reported by LIN et al [4]. The slag was first selectively leached with sulfuric acid to produce zinc sulfate solution and the leaching residue, which was calcined and leached again with sulfuric acid. Then the leachate was neutralized with NaOH to obtain arsenic and copper precipitate, which was processed by copper recovery system. The filtrate without arsenic and copper was used to deposit cobalt and nickel with Na_2CO_3 . This method could achieve the separation and recovery of valuable metals including zinc, copper, cobalt, and nickel, but failed to extract arsenic. Further, the highly toxic arsine gas might be produced during the sulfuric acid leaching.

But there are some studies on treating other arsenic-bearing slags by calcination or acid leaching methods. Direct calcination [5] was used in the early stage, which could transform the arsenic-bearing phase, such as As_2S_3 , into As_2O_3 , but it was very difficult to control the contamination from As_2O_3 dust and arsenic-containing steam. Gradually, this process was replaced by alkaline roasting by adding NaOH or Na_2CO_3 [6–8]. Due to the addition of alkali, sodium arsenate could be generated in the roasting residue instead of As_2O_3 , and it could be leached out into the liquid phase later. This process has the advantages of easy operation and high arsenic extraction efficiency, but suffers from high energy consumption originated from high temperature calcination at 700–800 °C and the secondary As pollution due to volatilization. As to the acid leaching process, sulfuric acid was the main leaching medium [9]. The arsenic-bearing compounds could be transformed into As_2O_3 after leaching at high temperature of 140–210 °C. This process takes the advantage of wide material serviceability, and high arsenic extraction efficiency under the optimized conditions, but has to bear the danger of generation of strong poisonous arsine.

In view of the foregoing, an effective and

environmental method to realize the comprehensive utilization of the arsenic-containing cobalt and nickel slag is yet to be established. Arsenic is an amphoteric metal, which can form water soluble alkali arsenate salt under oxidative environment. The other major valuable metals including copper, cobalt and nickel are not expected to react with the alkali medium. Therefore, it is possible to separate arsenic with other metals via alkaline treatments. Based on this analysis, alkali medium leaching of arsenic-containing cobalt and nickel slag by NaOH solution with oxygen was carried out preliminarily, and the results showed that oxygen was a crucial factor for guaranteeing the nearly 100% leaching rate of arsenic. In light of this, the factorial investigation had been carried out in this study to clarify the influence of the parameters including temperature, alkali concentration, oxygen partial pressure, and liquid-to-solid ratio. Furthermore, in order to realize the recycle of the arsenic salt activator used in the zinc sulfate solution purification process, measures with respect to the separation of the arsenic compounds from the leachate and preparation of trivalent arsenic salts were studied. Other metals, including copper, nickel and cobalt, can be extracted from the leaching residue, which were not mentioned in this study.

2 Experimental

2.1 Materials and reagents

Reagents used in this work included analytical-grade reagent NaOH, deionized water with a resistivity larger than 18.2 MΩ·cm, oxygen with a purity of about 99%, Na, Cu, Zn, As, Co, Pb standard solutions with the concentration of 1000 μg/mL.

The arsenic-containing cobalt and nickel slag used in this work was provided by a zinc smelter. The chemical composition and phase composition analyses are shown in Table 1 and Fig. 1, respectively. The morphology for the outer surface and the cross section is shown in Fig. 2, and the distribution of major elements is shown in Fig. 3. According to the data in Table 1, measured by ICP-OES, it is known that the major elements in the slag are Cu, As and Zn, and the content of toxic arsenic reaches 10.92%. The particles are superfine, with an average size of 11.27 μm and 98.7% of them smaller than 74 μm. Thus, the slag was used directly for the experimental research without further grinding. The X-ray diffraction (XRD) analysis result

Table 1 Chemical composition of arsenic-containing cobalt and nickel slag (mass fraction, %)

Cu	As	Zn	Pb	Co	Ni	Si	Cd
47.61	10.92	5.01	2.33	2.27	1.3	0.41	0.52

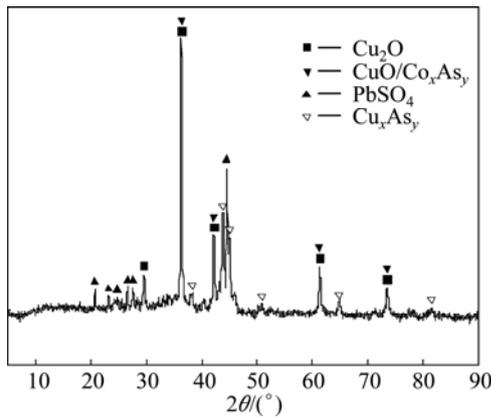


Fig. 1 XRD pattern of arsenic-containing cobalt and nickel slag

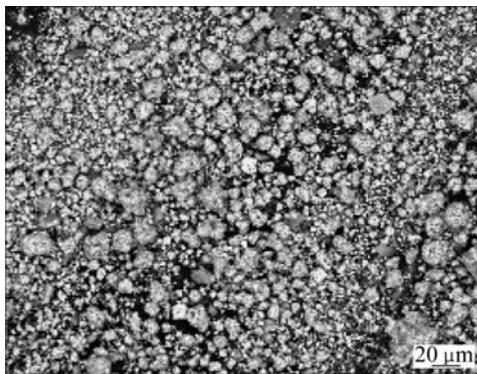


Fig. 2 SEM image of outer surface of arsenic-containing cobalt and nickel slag

shows that the main phases in the slag are CuO , Cu_2O , PbSO_4 , Cu-As alloy and Co-As alloy. The morphologies in Fig. 2 and Fig. 3 reveal that the particles are highly dispersed, and the major elements including Cu, As, Zn and Co are encapsulated tightly in the Cu-bearing matrix.

2.2 Apparatus and analytical instruments

All the leaching experiments were carried out in a stainless steel nickel-lined autoclave with mechanically stirring (volume 500 mL, manufactured by Dalian Automatic Control Equipment Factory, China). A CKW-III temperature controller with controlling accuracy of 1 °C was used to manipulate the electrical heating system (manufactured by Chaoyang Automation Factory, China). The schematic diagram of the apparatus is shown in Fig. 4.

The main analytical instruments used in the research are as follows. The particle size distribution was measured by a LS13320 laser particle size analyzer (Beckman Coulter). The morphology was tested by a JEOL 5800SV scanning electron microscope (JEOL Ltd.). The chemical composition was analyzed by an inductively coupled Optima 5300DV plasma atomic emission spectrometer (ICP-OES, Perkin-Elmer Corporation). The phase composition was determined by X-ray powder diffraction using X'Pert PRO MPD, and the patterns were collected between 2θ angles of 5°–90° (at $\text{Cu K}\alpha$ radiation of 40 kV, 40 mA; Holland Panalytical Company). The concentration of trivalent arsenic was determined by ceric sulfate–potassium bromate titration.

2.3 Experimental methods

After mixing the arsenic-containing cobalt and nickel slag with sodium hydroxide solution under a certain liquid-to-solid ratio, the obtained slurry was poured into the autoclave. When the slurry temperature reached the pre-set value, oxygen was bubbled into the autoclave, and the reaction was maintained for a pre-determined time. After finishing the reaction, the slurry was cooled to about 85 °C, followed by solid/

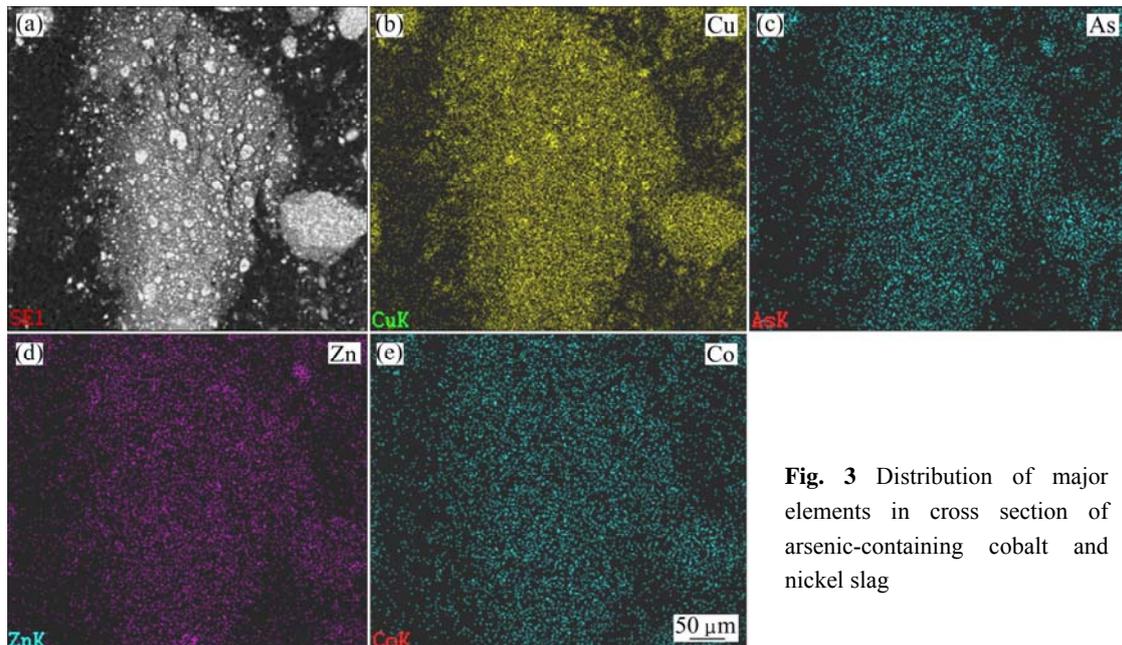


Fig. 3 Distribution of major elements in cross section of arsenic-containing cobalt and nickel slag

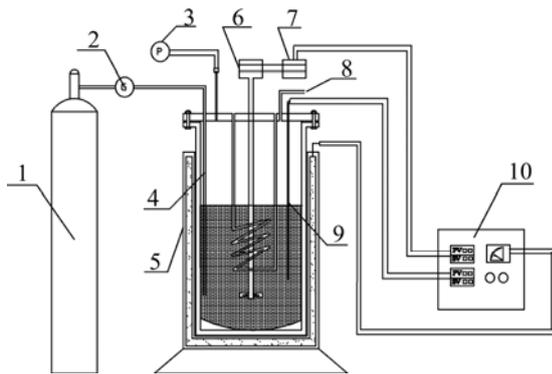


Fig. 4 Schematic diagram of experimental apparatus: 1—Oxygen cylinder; 2—Oxygen pressure reducing valve; 3—Pressure gauge; 4—Gas introduction pipe; 5—Heating mantle; 6—Magnetic agitator; 7—Electric motor; 8—Exit pipe; 9—Thermocouple; 10—Controller

liquid separation to obtain the arsenic-rich leachate. The solid residue was washed, dried, and analyzed to determine the leaching rate of arsenic. The sodium arsenate crystals were obtained by cooling crystallization of the arsenic-rich leachate, and then they were reduced with SO_2 gas to prepare trivalent arsenic salts.

Due to the high content of copper and its low solubility in alkaline solutions, copper was chosen as the reference substance to calculate the leaching rate of arsenic, η .

$$\eta = \left(1 - \frac{m_{R,Cu}}{m_{T,Cu}} \times \frac{m_{T,As}}{m_{R,As}} \right) \times 100\% \quad (4)$$

where m_R represents the element content in the original slag, and m_T represents the element content in the leached residue.

3 Results and discussion

3.1 Effect of reaction time on arsenic leaching rate

The effect of reaction time on arsenic leaching rate from the arsenic-containing cobalt and nickel slag was investigated and the experiment results are presented in Fig. 5. It is obvious that the increase of reaction time results in increased arsenic extraction, and near 100% of arsenic leaching rate could be achieved if the reaction time is longer than 2 h. Even though the reaction went smooth 1 h later, in order to make the poisonous arsenic leaching rate as high as possible to avoid contamination dispersion, reaction time of 2 h was chosen for the following studies.

3.2 Effect of temperature on arsenic leaching rate

The influence of temperature on the leaching rate of arsenic with oxygen was examined and the results are shown in Fig. 6. It is evident that a rise in temperature

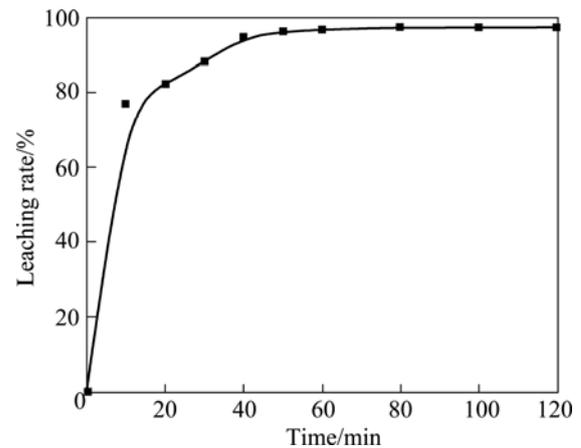


Fig. 5 Effect of reaction time on arsenic leaching rate (leaching temperature 140 °C, oxygen partial pressure 0.5 MPa, NaOH concentration 200 g/L, liquid-to-solid ratio 5:1)

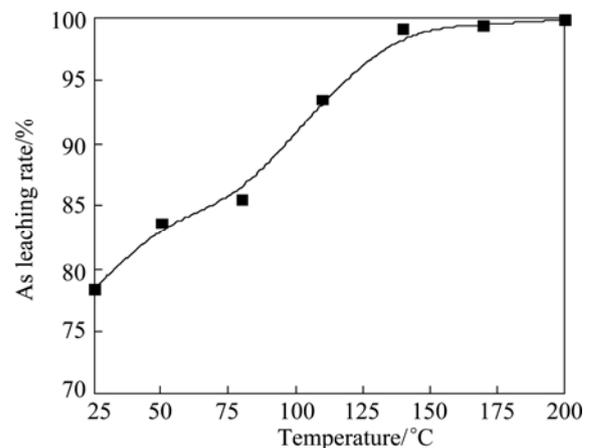


Fig. 6 Effect of temperature on arsenic leaching rate (oxygen partial pressure 0.5 MPa, NaOH concentration 200 g/L, reaction time 2 h, liquid-to-solid ratio 5:1)

facilitates the leaching of arsenic. The leaching rate increases from 78.37% to 99.14% when the temperature gradually increases from room temperature to 140 °C. Further increasing the temperature to 200 °C yields a negligible increase in arsenic leaching rate. Based on the obtained results, reaction temperature in the following research was chosen at 140 °C.

3.3 Effect of oxygen partial pressure on arsenic leaching rate

The effect of oxygen partial pressure on the arsenic leaching rate is shown in Fig. 7. The result reveals that the existence of oxygen could improve the leaching performance obviously. And even very low oxygen partial pressure can greatly promote the leaching of arsenic. With the oxygen partial pressure changing from zero to 0.3 MPa, the leaching rate was improved remarkably from 43.03% to 98.53%. A further increase in the oxygen partial pressure causes negligible change.

In order to obtain steady and high arsenic leaching results, the oxygen partial pressure of 0.5 MPa was chosen in the following research.

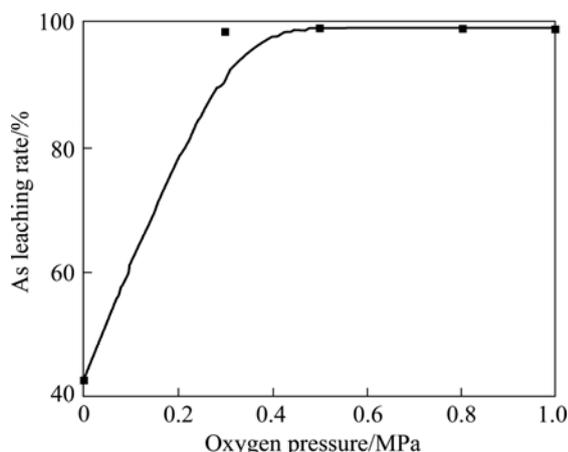


Fig. 7 Effect of oxygen pressure on arsenic leaching (NaOH concentration 200 g/L, leaching temperature 140 °C, reaction time 2 h, liquid-to-solid ratio 5:1)

3.4 Effect of NaOH concentration on arsenic leaching rate

The influence of NaOH concentration on the arsenic leaching rate was studied and the results are shown in Fig. 8. The arsenic leaching rate is only about 70% in 50 g/L NaOH system, but increases rapidly to 96.65% with NaOH concentration increasing to 100 g/L. The leaching rate continues to improve with solution alkalinity and can reach 99.14% in 200 g/L NaOH solution. However, the solution alkalinity does not show significant effect on the arsenic leaching rate when the solution concentration is higher than 150 g/L NaOH. In order to reduce the zinc co-leaching rate with arsenic and avoid the crystallization of the arsenic compounds during the filtration caused by temperature decreasing, the optimum alkaline concentration was fixed at 150 g/L.

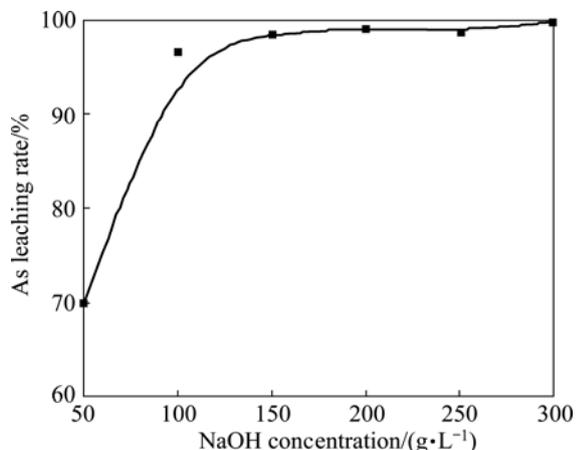


Fig. 8 Effect of NaOH concentration on arsenic leaching rate (leaching temperature 140 °C, oxygen partial pressure 0.5 MPa, reaction time 2 h, liquid-to-solid ratio 5:1)

3.5 Effect of liquid-to-solid ratio on arsenic leaching rate

The effect of liquid-to-solid ratio on the arsenic leaching rate is shown in Fig. 9. It can be seen that with the liquid-to-solid ratio increasing from 3:1 to 9:1, the leaching extent remained almost constant at 99%. The liquid-to-solid ratio does not show significant influence on the leaching of arsenic. To guarantee a sufficient arsenic dissolution capacity, and to avoid arsenic cooling crystallization during the solid/liquid separation, the liquid-to-solid ratio of 5:1 was chosen.

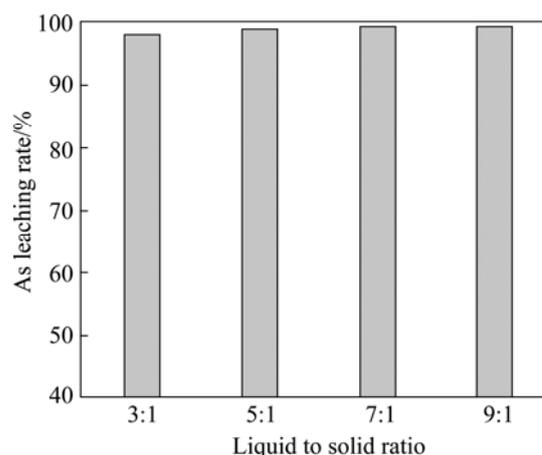


Fig. 9 Effect of liquid-to-solid ratio on arsenic leaching rate (leaching temperature 140 °C, NaOH concentration 150 g/L, oxygen partial pressure 0.5 MPa, reaction time 2 h)

3.6 Comprehensive leaching results under optimal conditions

Based on the above research results, the optimal conditions for arsenic leaching are determined: alkali NaOH concentration 150 g/L, leaching temperature 140 °C, liquid-to-solid ratio 5:1, oxygen partial pressure 0.5 MPa, and reaction time 2 h. Under these optimized conditions, the arsenic leaching rate was 99.10%. The chemical composition, phase analysis, particle size distribution, and morphology of residue obtained after leaching are shown in Table 2, Figs. 10, 11 and 12, respectively. The main chemical component in leaching residue is copper existing in the form of Cu_2O , and the copper content is as high as 63.5%, exhibiting substantial value for further extraction. After leaching, the solid particle size becomes small and highly porous, which is totally different from the original slag shown in Fig. 3. Besides that, the chemical compositions of the leachate are shown in Table 3, which indicates that some other alkali-soluble metals, such as zinc, lead, cobalt and

Table 2 Chemical composition of leaching residue under optimal conditions (mass fraction, %)

Cu	As	Zn	Pb	Co	Ni	Si	Cd
63.5	0.13	1.90	0.99	2.86	1.72	0.13	0.70

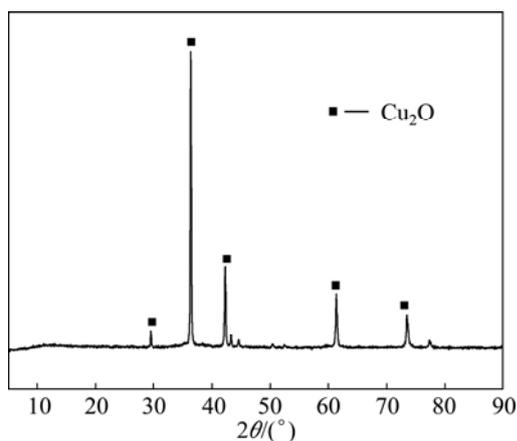


Fig. 10 XRD pattern of leaching residue

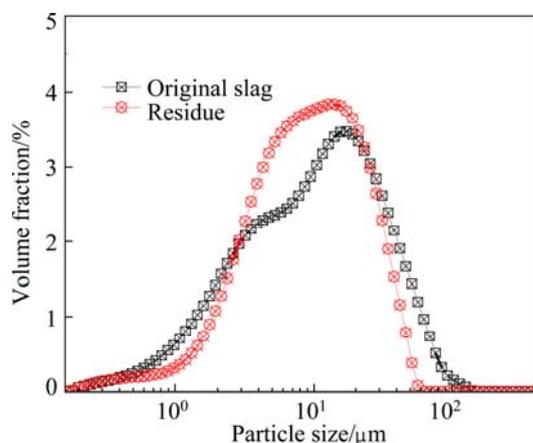


Fig. 11 Comparison of particle size distribution between original slag and final residue

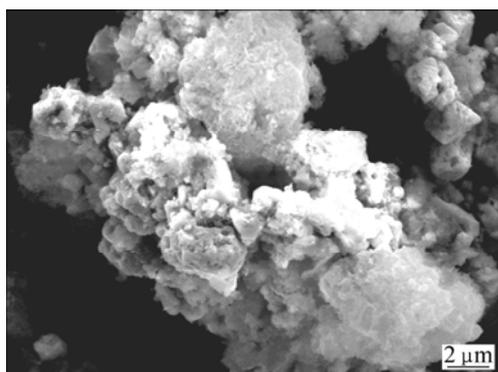


Fig. 12 SEM image of final residue

Table 3 Chemical composition of leachate under optimal conditions (g/L)

As	Zn	Pb	Co	Si
24.50	8.12	3.59	0.28	0.71

silicon, can be partially dissolved into the alkali medium, and their corresponding leaching rates are shown in Table 4. The leaching rate of valuable metal Co is 5.54%,

which mainly comes from the free cobalt ions remaining in the original slag and is due to the low solubility of cobalt in alkali medium. Even though the zinc, lead and silicon have the abilities of obvious dissolution in alkali medium, the results indicate that these metals will not accumulate in the circulating medium during the circulating leaching process due to the inhibitory effects, which means that the existing zinc, lead and silicon in circulating medium will inhibit their further dissolution in the next batch. Consequently, the dissolution of these metals has no negative impacts on the leaching unit.

Table 4 Leaching rates of main elements under optimal conditions (mass fraction, %)

As	Zn	Pb	Co	Si
99.10	71.56	68.14	5.54	76.23

3.7 Separation and reduction of arsenic from leachate

3.7.1 Separation of arsenic from leachate

After the oxygen oxidation leaching of the arsenic-containing cobalt and nickel slag in the alkaline medium, the arsenic-rich alkaline solution was obtained. Following works were further carried out to separate arsenic from the leachate and to simultaneously achieve the recirculation of the alkali medium for its use in a closed loop.

In order to design a rational separation strategy, the solubilities of sodium arsenate in alkaline solutions at different temperatures were studied, and the results are summarized in Fig. 13. As can be seen from Fig. 13, the solubility of As_2O_5 decreases with the increase of Na_2O concentration in general, and there are two break points at 23.25% and 28.47%, corresponding to the variation of the crystallization water number from 7 to 3.5. According to the difference in As_2O_5 solubilities in NaOH solution at 25 °C [10] and 75 °C [11], it can be concluded that the solubility of sodium arsenate (counted as As_2O_5) at 75 °C is much higher than that at 25 °C with alkali concentration (counted as Na_2O) in the range of 5% to 27%, so the sodium arsenate solids can be separated from the leachate directly by cooling crystallization from the leaching solution. Based on the comparative analysis of the ternary phase equilibriums at 25 °C for $Na_2O-As_2O_5-H_2O$ [10], $Na_2O-ZnO-H_2O$ [12] and $Na_2O-PbO-H_2O$ [13] systems shown in Fig. 14, the alkaline soluble impurities, such as Zn and Pb, exhibit comparatively high solubilities in NaOH solution within the alkali concentration range mentioned above. Thus, sodium arsenate crystals with few Zn and Pb impurities could be obtained via cooling crystallization under the conditions that the alkali concentration is well controlled.

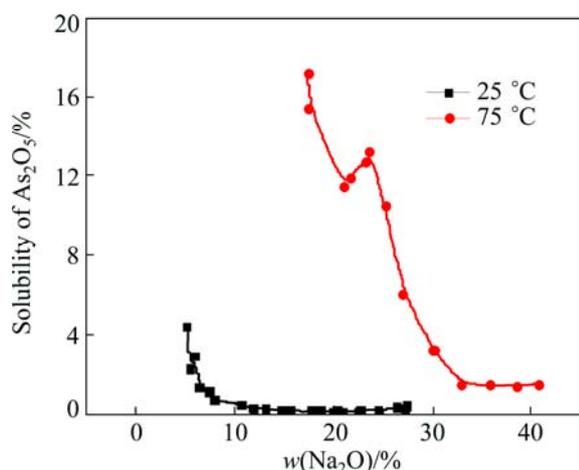


Fig. 13 Solubility of As_2O_5 in NaOH solution at 25 °C and 75 °C

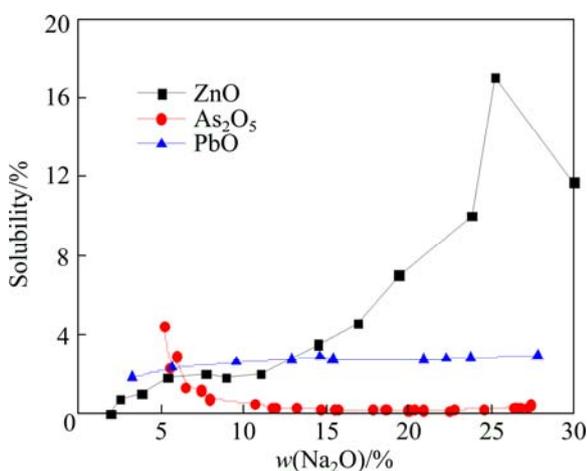


Fig. 14 Solubilities of As_2O_5 [10], ZnO [12] and PbO [13] in NaOH solution at 25 °C

In order to examine the designed sodium arsenate separation methods, the leachate containing 115.3 g/L free NaOH (89.4 g/L Na_2O) and 40.5 g/L As_2O_5 , obtained from previous leaching reaction operation, was used for crystallization study. The leachate was placed in a water bath at 25 °C for cooling and crystallization. After stirring for 0.5 h, a large number of needle-like sodium arsenate crystals appeared, as shown in Figs. 15 and 16. The solution after crystallization contained 101.5 g/L free NaOH (78.7 g/L Na_2O) and 4.49 g/L As_2O_5 , and accordingly the crystallization extent for arsenic was calculated to be 88.9% on the basis of Na_3AsO_4 . The solution after sodium arsenate crystallization can be recycled for further leaching reaction after supplementing fresh alkali.

3.7.2 Reduction of sodium arsenate

Trivalent arsenic salts are usually used in the zinc sulfate purification process, and the arsenic in the sodium arsenate is pentavalent. In order to reuse the obtained

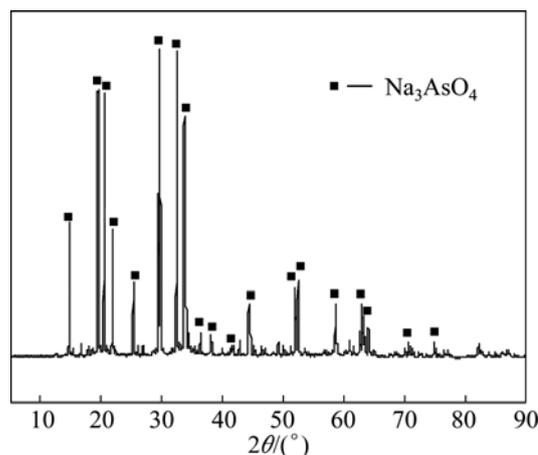


Fig. 15 XRD pattern of sodium arsenate crystal

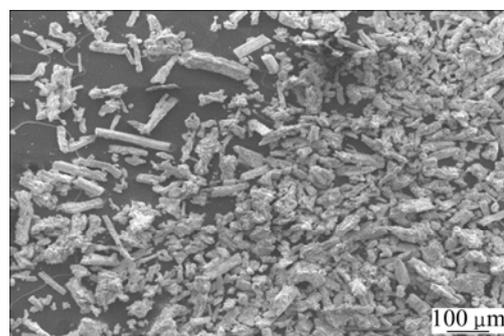


Fig. 16 SEM image of sodium arsenate

sodium arsenate, it is necessary to convert sodium arsenate to arsenite.

Theoretically, all the substances with the redox potential more negative than $\text{AsO}_4^{3-}/\text{AsO}_2^-$, such as zinc and aluminum, can be used to realize the reduction of As(V). However, instead of forming trivalent arsenic salt, As(V) will be reduced to As(III) by zinc, aluminum and other strong reducing agents [14]. According to Ref. [15], sulfur dioxide shows a quick reaction with H_3AsO_4 following reaction (5). It was reported by LI and LAWSON [14] and PALMER et al [16] that sodium arsenate could be reduced by sulfur dioxide, and catalysis mechanism in the presence of iodide ions was proposed [17]. This method was also used by other researchers [18,19] to deal with the As(V) reduction problem.



Furthermore, the solubility of arsenic pentoxide in 100 g water is greater than that of arsenic trioxide, as shown in Fig. 17 [20]. Therefore, it is expected that with the reduction reaction proceeding, As_2O_3 crystals will precipitate from the solution spontaneously when the newly formed arsenious acid exceeds its solubility in water. In this regard, SO_2 gas was used as reducing agent to reduce the sodium arsenate directly. According to the solubility data [21], the solubility of sodium arsenate in

water at 27 °C (calculated as As_2O_5) is 106.8 g/L, so sodium arsenate stock solution containing 55 g/L As_2O_5 was used in this work. Considering the low SO_2 dissolving rate and low gas utilization at high flow rate, a flow rate of 80 mL/min was selected in the experiments. Further, because the solubility of SO_2 gas decreases with increasing temperature, the reaction temperature was set to be 25 °C. Under these conditions, the reduction extent of sodium arsenate could reach 92% after 2 h, and the As_2O_3 crystals (Fig. 18) with the octahedral shape (Fig. 19) were obtained. The obtained As_2O_3 could be used in the zinc sulfate purification process, and the solution after reduction could be returned to the purification system directly.

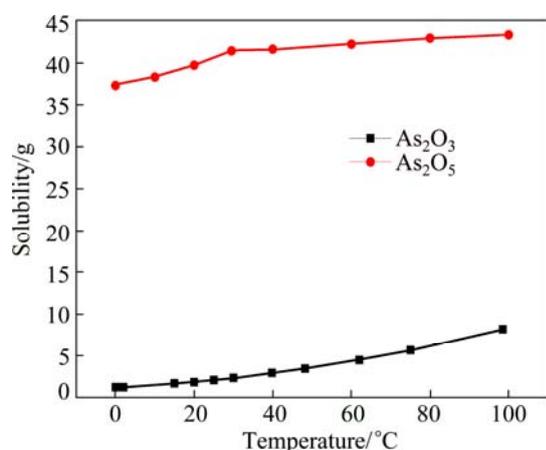


Fig. 17 Solubility of As_2O_5 and As_2O_3 in water at different temperatures [20]

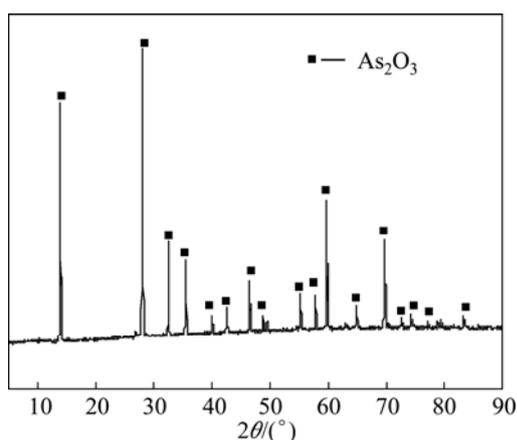


Fig. 18 XRD pattern of As_2O_3 crystal obtained from reduction of sodium arsenate using SO_2 gas

3.8 A novel circulating process for arsenic extraction and recycling from arsenic-containing cobalt and nickel slag

Based on the systematic results discussed above, a technical scheme for the processing of the arsenic-containing cobalt and nickel slag is proposed and the flow sheet is shown in Fig. 20. The flow sheet is

basically composed of three independent units, namely, alkaline leaching with pressured oxygen, sodium arsenate separation from the leachate, and the preparation of trivalent arsenic salts.

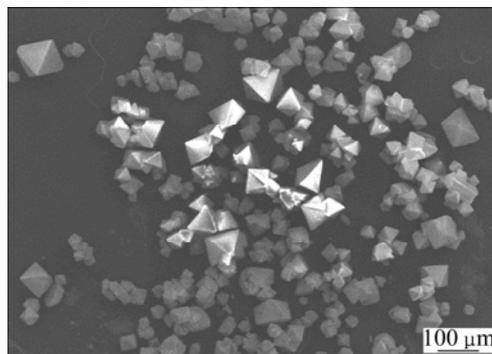


Fig. 19 SEM image of arsenic trioxide

When alkaline medium was mixed with the slag in the autoclave in an oxygen-rich environment, the slag decomposition reaction would occur, producing water soluble Na_3AsO_4 . Based on the Na_3AsO_4 solubility variation in NaOH solutions at different temperatures, sodium arsenate crystals could be obtained via cooling crystallization from the solution with NaOH concentration varying from 5% to 27%. The alkaline medium could be recycled to the leaching stage. The obtained sodium arsenate crystals, after dissolving into the water, could be reduced by SO_2 to form arsenite, which could be precipitated out, and be reused as the activator in zinc sulfate solution purification unit.

The proposed technical scheme could successfully realize the cyclic utilization of the arsenic in the zinc sulfate solution purification process with the advantages of alkali recycle, mild reaction conditions and no wastes. Thus, this novel process not only provides an environment-benign strategy for the arsenic utilization of the arsenic-containing cobalt and nickel slag, but also provides an approach for the circular utilization of arsenic in zinc sulfate solution purification process.

4 Conclusions

1) The arsenic content in the arsenic-containing cobalt and nickel slag is 14.4% (calculated on the basis of As_2O_3), existing in the form of Cu–As alloys and Co–As alloys. Taking advantage of the amphoteric characteristic of arsenic under oxidative circumstance, alkali leaching has been presented in this research. Upon the use of pressurized oxygen, the leaching rate of arsenic reached nearly 100% under a rather mild conditions of NaOH 150 g/L, leaching temperature 140 °C, liquid-to-solid ratio 5:1, oxygen partial pressure 0.5 MPa, and reaction time 2 h. The leaching residue with porous structure is mainly composed of Cu_2O .

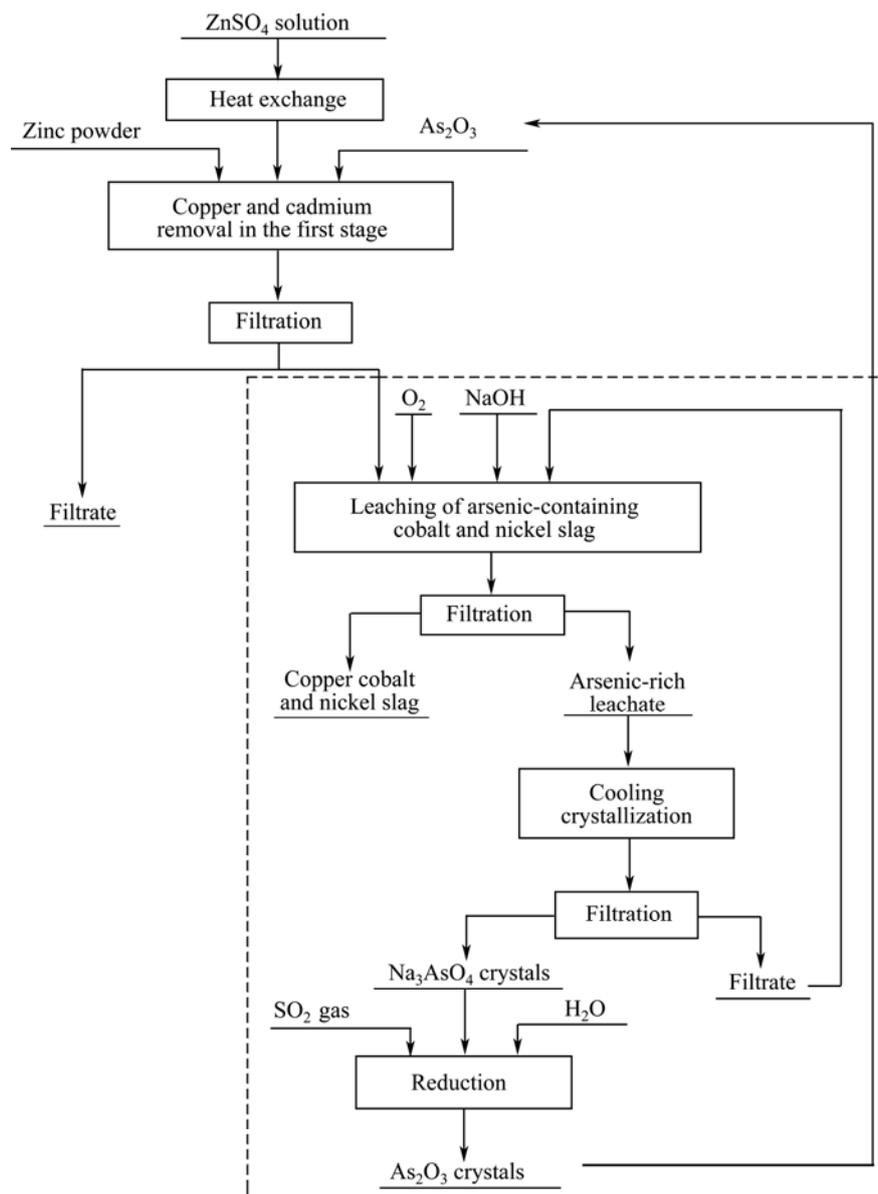


Fig. 20 Proposed technical scheme

2) Based on the solubilities of As_2O_5 , ZnO and PbO in NaOH solution, cooling crystallization method was used to separate arsenic from arsenic-rich leachate. When cooling to $25\text{ }^\circ\text{C}$, the purified needle-like sodium arsenate crystals were obtained and the crystallization extent was 88.9% (calculated on the basis of Na_3AsO_4). According to the redox potential, sodium arsenate was reduced into trivalent arsenic salt by SO_2 gas. The reduction extent for sodium arsenate solution with As_2O_5 55 g/L reached 92% under the conditions of SO_2 gas flow rate 80 mL/min, temperature $25\text{ }^\circ\text{C}$ for 2 h. Further, octahedral shaped As_2O_3 was prepared from the reduction solution, which could be reused in the zinc sulfate solution purification system.

3) The technical scheme of alkaline leaching with pressured oxidation, cooling crystallization, arsenate

reduction by SO_2 gas and arsenic trioxide preparation, can realize the clean extraction of arsenic and preparation of arsenic salts for the arsenic-containing cobalt nickel slag.

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含砷钴镍渣中砷提取与砷盐制备的资源化利用

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摘要: 对某厂硫酸锌溶液砷盐净化工艺产生的含砷钴镍渣进行砷提取与资源化利用研究。基于含砷钴镍渣中砷的存在形态并利用砷的两性特性, 考察碱介质氧压浸出砷的方法, 确定并优化氧气气氛下碱介质浸出砷的最佳条件。结果表明, 在溶出温度 140 °C、碱介质 NaOH 浓度 150 g/L、氧压 0.5 MPa、液固比 5:1 的条件下, 砷的浸出率达到 99.14%。根据 As_2O_5 、ZnO 和 PbO 在 NaOH 溶液中的溶解特性, 提出采用富砷浸出液直接冷却结晶分离获得砷酸钠晶体的砷分离–碱介质循环的方法, 且富砷浸出液直接在 25 °C 下的结晶率达 88.9%; 根据氧化还原电位, 将砷酸钠晶体溶解获得的溶液直接采用 SO_2 气体进行还原来制备三价砷盐, 在一定条件下砷的还原率达 92%, 从还原液可制得正八面体结构的 As_2O_3 晶体循环或将还原液直接循环回用于硫酸锌溶液砷盐的净化系统。利用含砷钴镍渣中砷的氧压碱介质浸出–浸出液冷却结晶–砷酸钠溶液 SO_2 气体还原– As_2O_3 晶体制备的技术路线可实现含砷钴镍渣中砷的提取与资源化利用。

关键词: 含砷钴镍渣; 碱介质浸出; 冷却结晶; 砷酸钠; 三氧化二砷