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Microwave-assisted and regular leaching of germanium from the germanium-rich lignite ash

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Abstract: Demand for germanium (Ge) is rapidly growing in recent years in various fields including semiconductors, aerospace, and solar cells. However, the Ge resources are very limited in the world. Hence, in this work, microwave-assisted leaching and conventional leaching methods are employed for the leaching of Ge from the Ge-rich lignite ash (GA). The effects of leaching temperature, leaching time, initial acid concentration, oxidizing agent amount, and stirring speed on leaching of Ge were investigated and microwave-assisted and conventional methods of leaching were compared. Here, HCl solution is used as a leaching agent, and MnO_2 is used as an oxidizing agent. From the results, the leaching rate of Ge was found to be 89.49% in the microwave-assisted method, and 83.62% in the conventional leaching method. The optimal conditions for microwave-assisted method include a leaching temperature of 65°C, a leaching time of 90 min, an oxidizing agent amount of 10 g/l, an initial acid concentration of 10 mol/l, and a stirring speed of 250 rpm. The leaching rate of Ge significantly improved in the microwave-assisted method as compared to the conventional method. Therefore, the microwave-assisted method is a suitable method for the leaching of Ge from the GA and is a novel way for the efficient utilization of Ge concentrate.

Keywords: germanium (Ge); leaching; microwave.

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1 Introduction

Germanium (Ge) is another most important semiconductor material other than silicon [1]. In addition to its use in the semiconductor industry, this rare bulk metal being a promising industrial material, is also widely used in the fields of aerospace technology, high-frequency electronics, optical fiber communication, infrared optics, thermal solar cell, chemical catalyst, biomedical sciences, etc. [2–9]. At present, the average growth rate of Ge worldwide remains at 2%–4% per annum [10]. With the gradual increase in the applications of Ge, the current Ge production is far from meeting the demand; thus, research needs to be urgently carried out to enhance the leaching rate of Ge.

At present, hydrometallurgy has become an effective way for recycling secondary resources [11], and the main processes of traditional technology method of recovering Ge from the Ge-rich lignite ash (GA) are as follows: (1) sulfuric acid leaching of GA, (2) precipitate Ge by tannin, (3) chloridizing roasting, (4) chlorination distillation, and (5) hydrolysis. The chlorination distillation is the most important step [12]. The chlorination distillation method is mainly divided into three parts as follows: firstly, Ge and other mineral elements generated chlorides. Secondly, Ge chloride is separated from other chlorides based on the different boiling points. Finally, the Ge chloride is hydrolyzed to generate the purified GeO_2 . Nevertheless, there are many issues in the cross of chloride distillation, such as low leaching rate of Ge, difficulty in gathering the steam of Ge chloride, and some safety problems.

In recent years, microwave is used as an ancillary equipment in hydrometallurgy during the mineral leaching process. Apparently, this application is becoming increasingly prevalent [13–16]. The microwave is an electromagnetic wave that features 0.3–300 GHz frequency and 0.1–100 cm wavelength. Microwave can separate and extract the valuable elements from the mineral efficiently by transmitting energy what the chemical reaction requires to molecule/atom directly by dielectric loss in mineral internally; on account of the microwave-absorbing characteristic, the valuable mineral and gangue are so different that the temperature of multiphase complex mineral stone system is inhomogeneous in the

distribution on microcosmic, intensifying the dissociation of valuable mineral and gangue, forming a nonequilibrium reaction and conditions and promotes interface chemical reaction [15–17]. This technology exhibits the characteristics of homogeneous heating and selective heating, which lead to many exceptional advantages over conventional processing methods including both energy and cost saving, improved thermal diffusivity and mass diffusivity, faster processing and greater eco-friendliness, making microwave heating appropriate for applications in hydrometallurgy [18–22].

In this study, leaching of Ge from the GA using microwave-assisted leaching is presented. The effects of leaching temperature, leaching time, initial acid concentration, oxidizing agent amount, and stirring speed on leaching of Ge are studied and microwave-assisted and conventional leaching methods are compared.

2 Materials and methods

2.1 Materials

The GA sample used in this work was obtained from Yunnan Province in PR China. The element composition of GA detected using X-ray fluorescence (XRF) technique is shown in Table 1; it can be seen that the main elements in the GA include Si, Al, S, Ca, Fe, K and Ge, and the accurate content of Ge in GA analyzed with chemical methods is 9263.2 g/t. The phase compositions that were analyzed with X-ray diffraction (XRD) are displayed in Figure 1, and it can be observed that GA consists of Al_2O_3 , SiO_2 , CaSO_4 , $\text{Ca}(\text{PO}_3)_2$, KPO_3 , and GeO_2 . The microstructure and element distribution of GA were observed using scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) technique, as shown in Figure 2. It can be found that GA consisted of relatively smooth white particles with a size between 3 μm and 150 μm and amorphous powders with a size <20 μm . Specially, the EDS analysis results of point A and point B indicate that the Ge exists in two different types of phases. The oxidizing agent used in this research was MnO_2 (Tianjin Fengchuan Chemical Reagent technologies Co., Ltd.) in view of its industrial application in the future.

2.2 Apparatus and procedure

Microwave-assisted leaching experiments are carried out using the micro-assisted leaching equipment. The equipment assembled in the Key Laboratory of Unconventional Metallurgy in Kunming University

of Science and Technology consisted of high-pressure toughened glass reactor, NJL2-8 microwave oven (supplied by Nanjing Jiequan Microwave Development Co., Ltd), DSX-120 digital stirring (supplied by Hangzhou instrument electric co., Ltd.), thermoelement (supplied by Dongtai Xinrui Instruments Co., Ltd.), Erlenmeyer flask, and SHB-III circulating water vacuum pump (supplied by Zhengzhou Great Wall instrument co., Ltd.). The output power of the microwave was automatically controlled by the temperature. The schematic diagram of the micro-assisted leaching experimental setup is shown in Figure 3.

2.00 kW was chosen as the microwave power output in this work. The solution temperature was measured by a thermoelement, which is plugged inside the reaction vessel in the 0°C–120°C range. A lid covered the vessel to ensure a tight seal and was connected with the stirrer, thermoelement and breather pipe, which was used to guide Ge tetrachloride vapor to the condenser pipe. The output power of the microwave oven can be continuously adjusted from 0 to 2.5 kW. When the solution temperature reaches the target temperature, the microwave-assisted leaching experiment begins. The SHB-III circulating water vacuum pump was opened to guide Ge tetrachloride vapor into condenser pipe and collect in conical flask after the leaching experiment was completed.

2.3 Exploratory experiment

Firstly, the glass reactor was loaded with 100 g of GA mixed with HCl and MnO_2 ; then placed in the microwave oven and heated to a certain temperature. Secondly, the solution was heated to 95°C after the leaching reaction. Thirdly, the circulating water vacuum pump was started and Ge tetrachloride vapor was collected in an Erlenmeyer flask through a condenser pipe. Finally, on completion of the experiment, the lixivium and the leaching residue were separated and the concentration of Ge was estimated by chemical analysis.

Figure 1: XRD pattern of Ge-rich lignite ash (GA).

Table 1: Major chemical composition of raw material (%).

Element	Si	Al	S	Ca	Fe	K	Ge	Zn	Mg	Na	As	Pb	W	P
Content	51.76	12.79	10.99	8.25	6.36	3.48	1.73	0.92	0.88	0.71	0.66	0.42	0.23	0.20

Figure 2: SEM-EDS analysis of GA. (A) EDS spectrum of point A, and (B) EDS spectrum of point B.

Figure 3: Microwave-assisted leaching equipment diagram: (1) high pressure toughened glass reactor, (2) NJL2-8 microwave oven, (3) DSX-120 digital stirrer, (4) thermoelement, (5) conical flask, and (6) SHB-III circulating water vacuum pump.

2.4 Calculation method of leaching rate of Ge

The leaching rate is calculated by following equation:

$$X = \frac{m_0 \cdot C_0 - m_1 \cdot C_1}{m_0 \cdot C_0} \times 100\% \quad (1)$$

where X is the leaching rate of Ge, %; m_0 is the initial mass of GA in leaching experiment, g; C_0 is the content of Ge in raw material, g/t; m_1 is the mass of leached residue, g; and C_1 is the content of Ge in the leached residue, g/t.

3 Results and discussion

Ge is the target element of this research. In order to explore the best conditions for leaching Ge from GA and to discuss the effect of the present method by using a microwave, the optimum leaching conditions are obtained by investigating the effect of leaching time, leaching temperature, concentration of HCl, and stirring speed. After some grouping experiments, 4:1 is set as the liquid-solid ratio in all experiments and 2 kW microwave power was adopted in this research.

3.1 Effect of leaching temperature on leaching rate of Ge

GeO_2 is reduced to metallic Ge in the process of microwave leaching of GA, and then Ge tetrachloride is evaporated into a gaseous phase and condensed on the low-temperature zone. The reaction between GeO_2 and HCl, and the standard Gibbs free energy (ΔG°) are listed in Eq. (2) [23]:

The experiments were conducted in the temperature range from 40°C to 70°C; the concentration of HCl was 10 mol/l, the leaching time was 90 min while the stirring speed was 250 rpm. The relationship between the recovery of Ge and the reaction temperature is shown in Figure 4. The leaching rate increases with a temperature between 40°C and 65°C by the microwave-assisted method and it is similar from 40°C to 55°C by the regular method. The microwave treatment presented a higher leaching rate of Ge than that of the regular method (89.01% and 84.35%, respectively) when the temperature was 65°C.

However, if the temperature is higher than 65°C, the leaching rate decreases, which may be due to the increased hydrolysis. When the system temperature is higher than

Figure 4: Effect of leaching temperature on leaching rate of Ge.

65°C, the HCl will decrease rapidly; parts of the HCl will evaporate and parts of the HCl will involve in fast reaction with other element at high temperature. The hydrolysis reaction is listed in Eq. (3):

The generated GeO_2 belongs to the residue, which will decrease the leaching rate of Ge. Similarly, the heating time of the regular method is longer than that of the microwave method; the higher the target temperature, the longer it takes. As a result, the hydrochloric acid concentrations are reduced, and Ge tetrachloride hydrolysis is reduced seriously.

3.2 Effect of leaching time on leaching rate of Ge

The effect of time on Ge leaching with microwave treatment and regular method was investigated from 30 to 150 min. These experiments were conducted at 65°C–55°C microwave-assisted/regular, and the stirring speed was 250 rpm and the concentration of HCl was 10 mol/l. The relationship between recovery ratio of Ge and time is shown in Figure 5. The leaching quality increases significantly from 30 to 90 min due to the crystal structure destroyed by microwave selectivity heating and emerges with more pores that increased the contact rate between Ge and HCl, and the similar phenomenon appears from 30 to 90 min when operated with regular method. However, in both methods, the leaching quality decreases greatly after 90 min.

During the leaching process, some component including GeO_2 will react with HCl; moreover, HCl will volatilize at a relatively high temperature. As a result, the

Figure 5: Effect of leaching time on leaching rate of Ge.

Figure 6: Effect of initial acid concentration on leaching rate of Ge.

concentration of HCl will decrease. With the increase of chlorides and the decrease of the concentration of HCl, GeCl_4 is hydrolyzed to GeO_2 , which will precipitate in the final slag.

Figure 5 shows that the optimal leaching rate of Ge with 90 min of microwave treatment is 88.59%, whereas the optimal leaching rate with 90 min of regular leaching is 83.62%. Water bath heating from 25°C to 55°C is needed for 20 min, and 2 kW microwave heating for only 2–3 min. It indicates that the heating time is reduced by as much as 90% and the leaching rate of Ge is enhanced by microwave leaching. The experimental result shows that leaching rate of Ge is enhanced and the experimental period distinctly shortened with the microwave method. It may be mainly attributed to the microwave selective heating and polarization effect, which destroy the crystal structure and emerge porously or react with additives to update the response interface, thus inducing increase in the contact rate between Ge and HCl [24–26], and the microwave absorption of water is extremely strong; the polar vibration of water molecules enhances the mass transfer, improves the kinetics of leaching, reduces the mass transfer resistance of HCl and products to enhance the effect [27, 28].

3.3 Effect of initial acid concentration on leaching rate of Ge

As the HCl solution is adopted as the leaching system, so the initial acidity is a vital factor in the process of Ge leaching. Figure 6 shows that the optimal concentration of HCl is 10 mol/l, and the leaching rate of Ge with microwave treatment is 4.33% higher than that with regular method (86.75% and 82.42%, respectively).

The leaching rate of Ge (84.24%) in 9 mol/l HCl with microwave treatment is even higher than that (82.42%) in the optimum 10 mol/l HCl with the conventional method. Some analyses conducted are as follows: firstly, the higher the acidity of the reactants the more favorable the leaching response balance moves to the resultant. In addition, an increase in the concentration of chloride ion as a coordination agent is beneficial to produce the coordination compound with chloride ion, which increases the leaching rate of Ge. In fact, the GeCl_4 is soluble in dilute HCl; with the increase in HCl concentration, its solubility increases. When the concentration of hydrochloric acid is up to 6–7 mol/l, GeCl_4 has the greatest solubility. If the initial concentration of HCl is too low, it will cause an incomplete reaction of Ge in the raw material; the resulting GeCl_4 is easily hydrolyzed to produce the GeO_2 precipitation [23], thereby reducing the leaching rate of Ge.

3.4 Effect of oxidizing agent amount on leaching rate of Ge

Due to some elements of the raw material existing in an elementary substance, there is a strong reducibility, making the oxidation-reduction potential of Ge higher, so the leaching process must have enough oxidants to oxidize these elementary substances [29].

Cl_2 gas is usually adopted as the oxidizing agent in the industries, but there are some potential safety hazards while using Cl_2 during the operation. In the experiments, the solid-state MnO_2 is chosen to replace Cl_2 gas. The amount of oxidizing agent is very important to oxide metals, which are in a state of incomplete oxidation during the leaching stage.

Figure 7: Effect of oxidizing agent amount on leaching rate of Ge.

The effects of the amount of oxidizing agent on the leaching behavior of Ge are shown in Figure 7. It can be found that Ge leaching can be enhanced when the addition of oxidizing agent reaches 4 g. At the optimal leaching condition of this section, the leaching rate of Ge by microwave treatment is 6.12% higher than the regular method (88.36% and 82.24%, respectively). The leaching rate of Ge reduces with excessive oxidant due to the concentration of HCl changing with the adding of MnO₂. The chemical reaction given as follows will occur:

It can be observed that Cl₂ produced in this reaction, works as an oxidant, which influences the GeCl₄ solubility.

3.5 Effect of stirring speed on leaching rate of Ge

To observe the effect of stirring speed on the leaching rate, experiments were carried out using five different stirring speeds in the range of 200–400 rpm. These experiments were conducted at 65°C/55°C (microwave-assist/regular), leaching time was 90 min and the concentration of HCl was 10 mol/l. The experimental results that are given in Figure 8, show that both methods of the leaching quality increase inconspicuously from 200 rpm to 250 rpm, and leaching rate has slight fluctuation from 250 to 400 rpm; the leaching rate is nearly independent of the stirring speed. The 250 rpm chosen in this experiment is to prevent solid and liquid-state admixture to the container wall due to high stirring speed.

The experimental parameters are gradually optimized, and the optimal conditions of microwave-assisted

Figure 8: Effect of stirring speed on leaching rate of Ge.

Figure 9: XRD pattern of the residual slag after microwave-assist leaching process.

leaching were as follows: leaching temperature of 65°C, leaching time of 90 min, oxidizing agent amount of 10 g/l, initial acid concentration of 10 mol/l, and stirring speed of 250 rpm. The maximum leaching ratio is 89.49%, which is significantly higher than that of conventional leaching method.

3.6 Characteristics of the residual slag after leaching process

The phase composition of leaching residue (leaching conditions: temperature 65°C, leaching time 90 min, HCl concentration 10 mol/l, stirring speed 250 rpm) is shown in Figure 9, and it can be found that the residual slag consists of SiO₂, Al₆Si₂O₁₃, and Al₂O₃. The other phases have reacted with HCl during leaching process. The residual GeO₂ in the reaching residue cannot be detected by XRD due to its very low content.

Figure 10: SEM-EDS analysis of the residual slag after microwave-assisted leaching process. (A) EDS spectrum of point A, and (B) EDS spectrum of point B.

The microstructure and element distribution of leaching residue were observed with SEM-EDS, as shown in Figure 10, and it can be found that the microstructure of leaching residue is different from that of GA. The leaching residue mainly consists of amorphous powders with the size $<30\ \mu\text{m}$. The peak strength of Ge is weak, which indicates that the content of Ge in the leaching residue is low, as shown in the EDS spectra of point A and point B. The microwave absorbing ability and thermal conductivity coefficient of various crystalline phases in the GA are different, and the temperature differences between different phases generated in the microwave-assisted leaching process will result in the local crushing stress and tension stress [30]. The formation of internal tiny

cracks of slag particles increases the effective reaction interface area and therefore promotes the rate of leaching reaction [31].

3.7 Leaching behavior of the impurity ions from the GA

The leaching behaviors of the impurity ions such as Al^{3+} , Ca^{2+} , Fe^{3+} , K^{+} , etc. in the microwave-assisted leaching process were analyzed with XRF, and the element composition of the leaching residue (leaching conditions: temperature 65°C , leaching time 90 min, HCl concentration 10 mol/l, stirring speed 250 rpm) is shown in Table 2. It

Table 2: Element composition of the leaching residue (%).

Element	Si	Al	S	Ca	Fe	K	Ge	Zn	Mg	Na	As	Pb	W	P
Content	76.90	10.89	0.92	1.46	2.66	3.09	0.59	0.17	0.60	0.25	0.05	0.05	0.17	0.05

can be deduced that the S, Ca, Fe, Zn and Pb-containing phases are extensively dissolved. In contrast, the Si, Al and K-containing phases are not soluble in HCl system.

4 Conclusions

In this study, the recovery of Ge from GA using microwave-assisted leaching was investigated. Some conclusions are arrived at as follows:

1. Comparison of the leaching rate of normal leaching method with that of the microwave-assisted leaching is significantly improved. The leaching ratio is 89.49% under the optimized technological parameters as follows: leaching temperature of 65°C, leaching time of 90 min, oxidizing agent amount of 10 g/l, initial acid concentration of 10 mol/l and stirring speed of 250 rpm.
2. The main reason for the low leaching rate of Ge is the hydrolysis of GeCl_4 . The main factors that affect hydrolysis are the concentration of HCl and leaching time, GeCl_4 hydrolysis seriously under the condition that the concentration of HCl is lower than 7 mol/l and leaching time is too long, resulting in low Ge leaching rate.
3. The microwave-assisted method is a suitable method for the leaching of Ge from the Ge-rich lignite ash due to the extremely strong microwave absorption of water and the microwave internal heating and rapid heating.

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