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Comparison of ultrasonic-assisted and regular leaching of germanium from by-product of zinc metallurgy

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ABSTRACT

A major source of germanium recovery and also the source of this research is the by-product of lead and zinc metallurgical process. The primary purpose of the research is to investigate the effects of ultrasonic assisted and regular methods on the leaching yield of germanium from roasted slag containing germanium. In the study, the $HCl–CaCl_2$ mixed solution is adopted as the reacting system and the $Ca(ClO)_2$ used as the oxidant. Through six single factor (leaching time, temperature, amount of $Ca(ClO)_2$, acid concentration, concentration of $CaCl_2$ solution, ultrasonic power) experiments and the comparison of the two methods, it is found the optimum collective of germanium for ultrasonic-assisted method is obtained at temperature 80 °C for a leaching duration of 40 min. The optimum concentration for hydrochloric acid, $CaCl_2$ and oxidizing agent are identified to be 3.5 mol/L, 150 g/L and 58.33 g/L, respectively. In addition, 700 W is the best ultrasonic power and an over-high power is adverse in the leaching process. Under the optimum condition, the recovery of germanium could reach up to 92.7%. While, the optimum leaching condition for regular leaching method is same to ultrasonic-assisted method, except regular method consume 100 min and the leaching rate of Ge 88.35% is lower about 4.35%. All in all, the experiment manifests that the leaching time can be reduced by as much as 60% and the leaching rate of Ge can be increased by 3–5% with the application of ultrasonic tool, which is mainly thanks to the mechanical action of ultrasonic.

1. Introduction

Germanium is a critical element mainly produced as a by-product of zinc mining. Scarce metal germanium, a kind of high-tech material, is used more and more widely in many fields including optical fiber communication, national defense science and technology, aerospace technology, health care, geological exploration, chemical and semiconductor fields, etc. Especially when the knowledge and economy are developing explosively nowadays, the research on high and new sci-tech becoming more and more widespread and profound, the application of germanium material is also greatly expanding.

In recent decades, the application of ultrasound as auxiliary means in hydrometallurgy during the ore leaching process is more and more popular [1–4]. Ultrasonic consists of a series of longitudinal wave with differences density, and spread around through the medium. Ultrasonic energy irradiating solution causes bubble formation and subsequent implosion, which is the important "acoustic cavitation" [5]. Microscopic turbulence is created and boundary layer becomes thinner around the particles with much bubbles collapsing, due to the generation of extremely high local temperature and pressure gradients [6]. The use of ultrasonic energy brings the effects of optical, electrical, mechanical, thermal, chemical, biological, etc. [7,8]. Such advantages can be attributed to the mechanical action, the acoustic cavitation and the heat effect finally. Many ultrasonic leaching and extraction processes have been studied [9–12]. Şayan et al. [9] found that there is a 20% increase in TiO_2 by ultrasonic leaching than regular method under the same conditions. And they point out ultrasound energy induces some mechanical and chemical effects, indicating that ultrasonic energy is a very effective tool for enhancing reaction rates. Li et al. [10] studied the process of ultrasonic-assisted leaching valuable metals from spent lithium-ion batteries; then they received that ultrasonic wave improved the convective motion and provide

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energy facilitating the dissolution of the material. With 2 M citric acid mixed, 0.55 M H_2O_2, an S/L ratio of 25 g/L, 60 °C, and an ultrasonic power of 90 W for 5 h, the leaching rate of Co is more than 96% and the leaching rate of Li is nearly 100%.

At present, the main technological process of recovering Ge from the by-product of zinc metallurgy usually is as follows, (1) the neutral leaching of hard zinc slag, (2) the oxidizing roasting, (3) the chlorination distillation and (4) the hydrolysis. Thereinto the chloride distillation is an essential and crucial step. First, Ge and other metals generate chlorides, and then germanium chloride is separated with other chlorides according to the different boiling points. At last, the germanium chloride is hydrolyzed to generate the purified GeO_2 and which is a semi-finished products. However, there are many problems during chloride distillation, such as the high acidity, low leaching rate of Ge, equipment corrosion and some security issues. In order to increase the resources utilization, reduce cost, improve operational conditions and alleviate environment pollution, the HCl–$CaCl_2$ solution system and ultrasonic energy are employed to intensively extract Ge. Besides, the differences on the ultrasonic and conventional leaching are studied in detail.

2. Experimental

2.1. Materials

Raw material used in the study is a kind of roasted residue containing Ge, which comes from the hard zinc residues first went through dezincification of neutral leaching to enrich Ge and then passed oxidizing roasting to produce a high metal state. It is obtained from a local plant in Yunnan of China. The X-ray fluorescence (XRF) analysis of raw material revealed the complex nature of the roasted residue which mainly includes Pb, Fe, Zn, Cu, etc. The specific compositions and content detected by XRF as follows Table 1.

2.2. Leaching equipment and procedure

Leaching experiments are carried out in a 500 mL glass beakers (diameter 9 cm, flat bottomed), in which filled reaction solution heated and solution stirred by the PF-101S collector thermostat heating magnetic stirrer. A lid is used on the vessel to ensure the seal. Solution temperature is measured by a thermometer plugged inside of the leaching vessel in the range 0–100 °C. For the ultrasonic-assisted experiment, ultrasonic energy produced by a domestic SKTC-500 ultrasonic device. 20.21 kHz is chosen as the ultrasonic work frequency. Ultrasonic power is continuously adjustable from 0 to 1000 W. The amplitude-change pole is made of zirconium and the probe diameter is about 2 cm. When the ultrasonic treatment and magnetic stirring are initiated simultaneously, the ultrasonic-assisted leaching experiment begins (see Fig. 1).

Firstly, put HCl (2.5–4.5 mol/L) and $CaCl_2$ (100–250 g/L) solution into the reaction vessel with the L/S ratio as 8/1 (mL/g). When the solution is heated to the specified temperature (30–90 °C), add the solid raw materials 30 g and the oxidizing agent (4–16 g). Lastly, when the experiment is over, the lixivium and leached residue should be separated and analyzed respectively by spectrophotometer and to get their content of Ge.

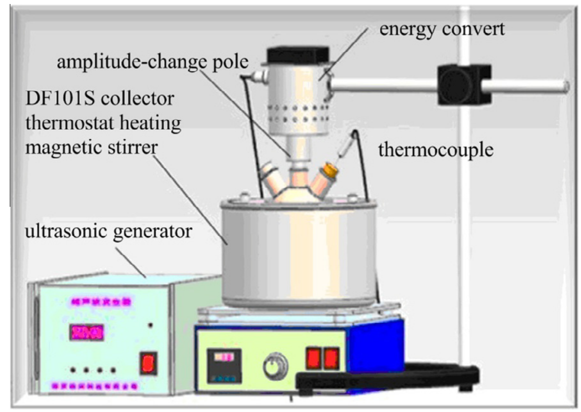

Fig. 1. Ultrasonic-assisted leaching equipment drawing.

2.3. Calculation method of leaching rate of Ge

The leaching rate is calculated by following equations:

$$x = \frac{x_1 \times V}{x_1 \times V + x_2 \times M} \times 100\%$$

where x is the leaching rate of Ge, %. x_1 is the content of Ge in the filtrate, g/L. V is the constant volume of filtrate, L. x_2 is the content of Ge in the dried final filter residue, %. M is the mass of dried final filter residue, g.

3. Results and discussion

The aim of the research is to explore the best condition of leaching Ge from roasted residue and to discuss the effect of the present method using an ultrasonic. The optimal leaching conditions are obtained with univariate method by investigating the effects of leaching time, reaction temperature, the amount of $Ca(ClO)_2$, the concentration of HCl and $CaCl_2$ and ultrasonic power. Besides, after some groping experiment, raw material particles 100–125 μm is adopted in the paper, and 8:1 is set as the liquid–solid ratio of all experiments in the article.

3.1. Effect of leaching time on leaching rate of Ge

The effects of time on germanium leaching with ultrasonic treatment and regular method are investigated. The outcomes reveal the leaching quantity increase significantly from 10 to 40 min with an ultrasonic appliance and it is similar from 40 to 100 min by regular method (Fig. 2). However, both methods the leaching quantity decreases greatly respectively after 40 min of ultrasonic treatment and 100 min of regular leaching. It is because most of metals including Ge have become chloride, such as $GeCl_4$ and the hydrochloric acid concentration decrease for the consuming by other reactions and the slight volatilization by itself at a high temperature even with a tightly sealed reaction vessel. With the increasing of the chlorides and the decreasing of the concentra-

Table 1
Major chemical composition of raw material.

Element	Pb	Fe	Zn	S	Cu	Sn	Si
Content, %	65.6057	10.6510	5.3507	4.5656	3.9495	3.1396	2.7041
Element	As	Ca	Bi	In	Al	Sb	Ge
Content, %	1.3948	1.1201	0.5766	0.4850	0.4584	0.2893	0.2205