

Process Improvement of Regeneration of Germanium from Germanium Dioxide Washing Water with Composite Germanium Precipitant

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Abstract

In this study, magnesium chloride and ferric chloride were used to replace the single magnesium salt or ferric salt as a new composite germanium precipitant, and the process improvement of germanium regeneration and enrichment in high purity germanium dioxide washing water was studied. The results show that: under the condition of adjusting the pH value of the solution about 8.5, the total amount of compound germanium precipitator is 4 times of germanium in the solution, and the weight ratio of ferric chloride and magnesium chloride is 7:3, a better germanium precipitation rate and grade of regenerated germanium concentrate can be obtained. The technology of composite germanium precipitator is simple, low cost and high efficiency, which is significantly better than that of germanium precipitator with single magnesium salt or iron salt in economic and technical indexes.

Keywords

Composite Germanium Precipitant; Germanium Dioxide Washing Water; Germanium Precipitation Rate; Germanium Concentrate.

1. Introduction

Germanium is one of the important rare and dispersed metals, which has very unique and excellent physical and chemical properties, and is widely used in high-end fields such as electronics, optoelectronics, semiconductors, medicine, new energy, aerospace and national defense industry [1-2]; Germanium is one of the important resources for the development of strategic emerging industries. At present, many countries have listed germanium as a strategic metal and made national reserves [3-4].

Germanium has the characteristics of rarity, dispersion and high value. Because of its complex extraction and purification process, germanium metal is easily dispersed in the three wastes produced in the production process. Therefore, the limited resource regeneration of germanium metal in the whole production process is an essential core link [5]. High purity germanium dioxide is prepared from germanium concentrate by chlorination distillation, re distillation, distillation and hydrolysis process. A large amount of chloride ions remain in the high purity germanium dioxide generated in the hydrolysis process, which needs to be removed by multi-stage washing with high purity water [6]. Therefore, a certain amount of germanium is dissolved in the washing water in this link, and the solution must be recycled.

The most widely used methods for recovering germanium from solution in industry are extraction method, tannin precipitation method, displacement method and coprecipitation method of germanium precipitant, each of which has its own advantages and disadvantages [7-10]. After several rounds of industrial technological progress and improvement, the commonly

used germanium precipitation process in germanium containing solution is magnesium salt or iron salt germanium precipitation process, which has the advantages of simple process and environment-friendly compared with tannic germanium [11]; However, due to the high addition of germanium precipitant, the germanium content of the produced germanium concentrate is generally below 10%. In order to further limit the cost reduction and improve the enrichment ratio of germanium, it is particularly important to explore or improve the more sufficient and low cost germanium precipitant and its process conditions. In order to further reduce the cost and increase the efficiency, based on the fact that the hydroxides produced by the hydrolysis of magnesium chloride and ferric chloride can adsorb and co precipitate germanium, the technology of germanium resource utilization with composite germanium precipitant was designed, and the comprehensive experimental verification and data comparison were carried out. The results show that the recovery of germanium is over 99.4% and the germanium content of germanium concentrate is over 15%.

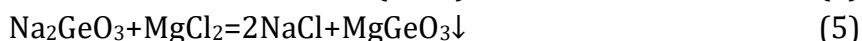
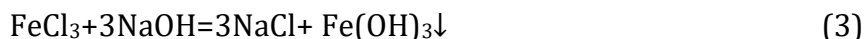
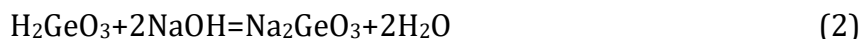
2. The principle of germanium precipitation in iron and magnesium salts

The GeO_2 formed by hydrolysis of high-purity germanium tetrachloride is a small particle aggregate, and its structure is similar to that of SiO_2 quartz, belonging to hexagonal crystal type; The hexagonal GeO_2 is soluble in water and alkali to form germanate. Alkali metal germanate is soluble in water, heavy metal and alkaline earth metal germanate is difficult to dissolve in water, but easy to be decomposed by acid. The germanium in the washing water of hydrolyzed high-purity germanium dioxide exists in the form of GeO_2 or weakly dissociated H_2GeO_3 . Adding NaOH to adjust the pH value of the solution, the reaction of GeO_2 and NaOH in the solution is transformed into Na_2GeO_3 . Na_2GeO_3 is easily soluble in water and generates GeO_3^{2-} , as shown in the reaction equations (1) and (2) [12].

When FeCl_3 is added to the alkaline solution, FeCl_3 is dissolved in the solution. The Fe^{3+} generated after dissolution will be hydrolyzed to $\text{Fe}(\text{OH})_3$ precipitate when pH value is greater than 1.6, and completely hydrolyzed when pH value is greater than 5.2. The hydrolysis reaction is shown in the reaction equation (3). $\text{Fe}(\text{OH})_3$ precipitation has strong adsorption for Ge, and then the co precipitation process is completed by gravity.

In addition, the insoluble $\text{Fe}_2(\text{GeO}_3)_3$ precipitate can be obtained by the reaction of Fe^{3+} with GeO_3^{2-} , so that germanium in the solution can be precipitated and enriched in the form of ferric germanate, as shown in equation (4).

After the addition of MgCl_2 to the alkaline solution, Mg^{2+} reacts with GeO_3^{2-} to obtain insoluble MgGeO_3 precipitation, so as to precipitate and enrich germanium in the washing water containing germanium in the form of magnesium germanate. See equation (5) for details.



3. Test part

3.1. Test materials

High purity germanium dioxide [13] was produced under the condition that the interlayer cooling temperature of hydrolysis kettle was controlled from -5°C to -10°C and the volume ratio of high purity germanium tetrachloride and high purity water was 1:7. After solid-liquid separation, a large amount of chloride ions remained in the product, which could be completely

removed after multistage washing with high purity water. The solution collected after washing high-purity germanium dioxide and solid-liquid separation is called washing water, which is the raw material of this improvement test. The main components are shown in Table 1.

Table 1. Main components of washing water containing germanium

Ge	As	Pb	Cu	Zn	HCl
520mg/L	0.01mg/L	Not detected	Not detected	Not detected	0.18mol/L

It can be seen from table 1 that the main characteristics of washing water are low germanium concentration and low acidity, which can not be returned to germanium distillation process. Therefore, it is necessary to precipitate germanium to concentrate and produce germanium concentrate before returning to chlorination distillation process.

Main chemical reagents:

Caustic soda: industrial grade;

Magnesium chloride: industrial grade;

Ferric chloride: industrial grade.

Main experimental apparatus:

2L glass beaker: 2000ml * 10 pieces;

Top mounted electric mixer 60W * 2 sets;

Laboratory vacuum filtration device: hp-01 * 2 sets;

Vacuum oven: 200 °C * 1 set.

3.2. Test procedure

Take 1000ml of germanium containing washing water each time and put it into 2000ml beaker. Referring to the relevant research results and production practice experience, at room temperature, adjust the pH value of the solution to 8.5 with caustic soda, add a certain amount of ferric chloride, magnesium chloride or composite germanium precipitant (ferric chloride + magnesium chloride), fully stir for 20min, stand for 10h, then solid-liquid separation, and dry the precipitate at 120 °C for 24h.

The experiment was divided into four groups: in the first group, the optimal amount of germanium precipitated by ferric chloride alone was investigated; In the second group, the optimum amount of germanium precipitated by magnesium chloride alone was investigated; In the third group, the optimum amount of compound germanium precipitant with ferric chloride: magnesium chloride (weight ratio) of 1:1 was investigated; In the fourth group, under the condition of determining the total amount of composite germanium precipitant, the effects of different proportions of composite germanium precipitant were investigated.

The germanium precipitation rate (germanium metal yield) of different germanium precipitation agents and different amounts were investigated by detecting the content of Ge in the residue of germanium precipitation after solid-liquid separation; The enrichment effect was investigated by detecting the grade of germanium concentrate after filtration and drying.

3.3. Test method

Impurity elements in germanium containing washing water were determined by ICP-OES [14]; The content of germanium in washing water and solution after germanium precipitation was determined by spectrophotometry [15]; The molar concentration of HCl in the solution was determined by acid-base titration.

4. Results and discussion

The washing water mainly contains Ge and HCl, and the other metal ions are trace; The purpose of the experiment is to separate Ge in the form of precipitate as much as possible. The lower the concentration of Ge in the solution after germanium precipitation, the higher the germanium grade of the product after drying, the better the experimental effect.

The concentration of germanium in the solution containing germanium before germanium precipitation is 520mg / L. the concentration of solution after germanium precipitation and the germanium grade of the precipitated germanium concentrate can pass the detection and verification.

4.1. Determination of the amount of ferric chloride as germanium precipitant

Referring to the relevant research conclusions and production practice experience of germanium precipitation with ferric salt [16], at room temperature, adjust the pH value of the solution to 8.5, directly add ferric chloride in the form of small solid particles to the germanium containing solution at one time, stir for 20 minutes, and then conduct solid-liquid separation after aging for 10 hours. The produced germanium concentrate is dried at 120 °C for 24 hours under the above fixed conditions.

The theoretical amount of germanium precipitated by ferric chloride can be calculated according to the chemical equation (3). About 1g germanium needs at least 1.5g ferric chloride. Referring to the relevant experimental research of germanium precipitation with polyferric sulfate, when the dosage of polyferric sulfate is about 16 times of germanium content, the ideal effect of germanium precipitation is achieved. According to this data and effective component conversion, the addition amount of ferric chloride is set as 3-7 times of germanium content in the solution, and the interval is 1 time. The five groups of data are compared and analyzed, The test results are shown in Table 2.

Table 2. Effect of germanium precipitation with different amount of ferric chloride

Serial number	Adding times of ferric chloride	Dosage of ferric chloride (g)	Germanium content in residual solution of germanium precipitation (mg/L)	Germanium precipitation rate	Germanium content of germanium concentrate
A-1	3	1.56	18.6	96.4%	16.58%
A-2	4	2.08	6.2	98.8%	14.83%
A-3	5	2.60	6.1	98.8%	14.20%
A-4	6	3.12	5.9	98.9%	12.36%
A-5	7	3.64	6.0	98.8%	10.34%

It can be seen from table 2 that there is a positive correlation between the rate of germanium precipitation and the amount of ferric chloride, which is that increasing the concentration of ferric chloride is conducive to the right of reaction (4) and makes germanium precipitation more thorough; However, the grade of germanium concentrate is negatively correlated with the addition of ferric chloride, because excessive ferric chloride will also produce ferric hydroxide precipitation, which increases the total amount of reaction precipitation and reduces the grade of germanium concentrate.

Comprehensive consideration, the serial number A-2 test is relatively better. Under the condition of adding 4 times of ferric chloride, the germanium precipitation rate is as high as 98.8%, and the germanium content in the solution after germanium precipitation is 6.2mg/l, which reaches the production emission index; And the grade of germanium concentrate reaches 14.83%, which can also meet the feed demand of germanium purification production.

4.2. Determination of the amount of magnesium chloride used in germanium precipitation

Referring to the relevant research conclusions and production practice experience of germanium precipitation with magnesium salt [17], at room temperature, after adjusting the pH value of solution to 8.5, magnesium chloride is directly added to germanium containing solution in solid form at one time, stirred for 20min, and aged for 10h before solid-liquid separation. The produced germanium concentrate is dried for 24h at 120 °C.

The theoretical amount of magnesium chloride to precipitate germanium can be calculated according to the chemical equation (5), about 1g germanium needs at least 1.31g magnesium chloride. The experimental study on germanium precipitation of magnesium chloride hexahydrate shows that the amount of magnesium chloride hexahydrate reaches the ideal effect when it is about 7 times the amount of germanium. Refer to this data and make prediction, set the amount of magnesium chloride as 3-7 times the amount of germanium, and increase it by 1 time. Compare and analyze the five groups of data. The test results are shown in Table 3.

Table 3. Effect of germanium precipitation with different magnesium chloride addition

Serial number	Adding multiple of magnesium chloride	Magnesium chloride dosage (g)	Germanium content in residual solution of germanium precipitation (mg/L)	Germanium precipitation rate	Germanium content of germanium concentrate
B-1	3	1.56	22.3	95.7%	18.11%
B-2	4	2.08	10.6	98.0%	15.44%
B-3	5	2.60	7.3	98.6%	14.37%
B-4	6	3.12	7.1	98.6%	12.93%
B-5	7	3.64	6.9	98.7%	11.52%

It can be seen from table 3 that there is a positive correlation between the rate of germanium precipitation and the amount of magnesium chloride, which is because increasing the concentration of magnesium chloride is conducive to the right of reaction (5), making germanium precipitation more thorough; However, the grade of germanium concentrate is negatively correlated with the addition of magnesium chloride, because excessive magnesium chloride will also produce magnesium hydroxide precipitation, which increases the total amount of precipitates and reduces the grade of germanium concentrate.

Based on comprehensive consideration, the No. B-3 test is relatively optimal. Under the condition that the addition amount of magnesium chloride is 5 times, the germanium precipitation rate is as high as 98.6%, and the germanium content in the solution after germanium precipitation is 7.3mg/l, meeting the production emission index; The grade of germanium concentrate reaches 14.37%, which can also meet the feed demand of germanium purification production.

4.3. Determination of the amount of compound germanium precipitant

Based on 4.1 and 4.2, the pH value, stirring time and aging time were fixed; The ratio of ferric chloride and magnesium chloride in the composite germanium precipitant is 1:1 (weight ratio); Referring to the optimal multiple of ferric chloride and magnesium chloride (4 times and 5 times), the amount of compound germanium precipitant is set at 3-7 times of the germanium content in the solution, and it is increased by 1 time. The five groups of data are compared and analyzed. The test results are shown in Table 4.

It can be seen from table 4 that there is a positive correlation between the rate of germanium precipitation and the amount of compound germanium precipitation agent. This is because increasing the concentration of ferric chloride and magnesium chloride is conducive to the right of reaction formula (4) (5), which makes the precipitation of germanium more thorough; However, the grade of germanium concentrate is negatively correlated with the addition

amount of germanium precipitant. This is because excessive germanium precipitant will also generate hydroxide precipitation, which increases the total amount of precipitate and reduces the grade of germanium concentrate.

Table 4. Effect of germanium precipitation with different magnesium chloride addition

Serial number	Adding multiple of composite germanium precipitator	Ferric chloride: magnesium chloride	Amount of compound germanium precipitator (g)	Germanium content in residual solution of germanium precipitation (mg/L)	Germanium precipitation rate	Germanium content of germanium concentrate
C-1	3	1:1	1.56	12.3	97.6%	18.35%
C-2	4	1:1	2.08	5.2	99.0%	16.72%
C-3	5	1:1	2.60	5.2	99.0%	13.12%
C-4	6	1:1	3.12	4.9	99.1%	12.79%
C-5	7	1:1	3.64	5.0	99.0%	10.76%

Comprehensive consideration, the serial number C-2 test is relatively optimal. Under the condition that the amount of compound germanium precipitant is 4 times, the germanium precipitation rate is as high as 99.0%, and the germanium content in the liquid after germanium precipitation is 5.2mg/l, which reaches the production emission index; The grade of germanium concentrate reaches 16.72%, which can also meet the feed demand of germanium purification production.

4.4. Determination of the ratio of composite germanium precipitant

On the basis of 4.3 test, the pH value, stirring time and aging time remained unchanged; The amount of composite germanium precipitant is 4 times of that of germanium; Set the weight ratio of ferric chloride and magnesium chloride in the composite germanium precipitation agent between 2:8 And 8:2 to investigate whether there are better test results. Compare and analyze the seven groups of data obtained. The test results are shown in Table 5.

Table 5. Effect of germanium precipitation with different magnesium chloride addition

Serial number	Adding multiple of composite germanium precipitator	Ferric chloride: magnesium chloride	Amount of compound germanium precipitator (g)	Germanium content in residual solution of germanium precipitation (mg/L)	Germanium precipitation rate	Germanium content of germanium concentrate
D-1	4	2:8	2.08	5.7	98.9%	16.32%
D-2	4	3:7	2.08	6.1	98.8%	16.49%
D-3	4	4:6	2.08	5.8	98.9%	16.65%
D-4	4	5:5	2.08	5.2	99.0%	16.72%
D-5	4	6:4	2.08	4.9	99.1%	16.63%
D-6	4	7:3	2.08	3.1	99.4%	16.57%
D-7	4	8:2	2.08	3.5	99.3%	16.62%

It can be seen from table 4 that adjusting the ratio of ferric chloride and magnesium chloride has little effect on the germanium precipitation rate and germanium grade of germanium concentrate under the condition that the total amount of germanium precipitation agent remains unchanged.

Comprehensive consideration, the test result of serial number D-6 is relatively optimal. Under the condition of adding 4 times of compound germanium precipitating agent, the ratio of ferric chloride and magnesium chloride is 7:3, the germanium precipitation rate is as high as 99.4%, and the germanium content in the solution after germanium precipitation is 3.1mg/l, which reaches the emission index of production; The grade of germanium concentrate is as high as 16.57%, which can also meet the feed demand of germanium purification production.

Compared with the test data in 4.1, 4.2, 4.3 and 4.4, the composite precipitant method has a certain relative advantage over the single precipitant method. See Table 6 for details.

Table 6. Comparison of optimal test results under four test ideas

Test serial number	Germanium precipitant	Germanium precipitant and its ratio	Adding multiple of germanium precipitant	Concentration of liquid germanium after germanium precipitation (ug/mL)	Germanium precipitation rate (%)	Germanium grade of germanium concentrate (%)
A-2	Ferric chloride	Ferric chloride 100%	4	6.2	98.8%	14.83%
B-3	Magnesium chloride	Magnesium chloride 100%	5	7.3	98.6%	14.37%
C-2	Composite germanium precipitator	Ferric chloride 50%+ Magnesium chloride 50%	4	5.2	99.0%	16.72%
D-6	Composite germanium precipitator	Ferric chloride 70%+ Magnesium chloride 30%	4	3.1	99.4%	16.57%

It can be seen from table 5 that the three germanium precipitation methods (four groups of tests) can basically meet the economic index requirements for production. Compared with A-2 and B-3 tests, C-2 and D-6 tests, i.e. composite germanium precipitant method, have slightly higher germanium precipitation rate and germanium content of regenerated germanium concentrate, and the continuous improvement effect is more remarkable. Compared with C-2, the grade of germanium in test D-6 decreases by 0.15%, but the rate of germanium precipitation increases by 0.4%. Therefore, the test result of D-6 is the best.

5. Conclusion

In this experiment, the germanium precipitation process of composite germanium precipitant (ferric chloride and magnesium chloride) was studied, and the more suitable process parameters were determined. The pH value of germanium containing washing water was adjusted to 8.5 by adding alkali; The weight ratio of ferric chloride and magnesium chloride is 7:3; After adding germanium precipitant into the solution, stirring for 20 minutes and aging for 10 hours, solid-liquid separation and drying can be carried out. By using this method, the recovery rate of germanium is as high as 99.4%, and the germanium content in germanium concentrate is more than 15%, which meets the quality requirements of jge-3 specified in the industrial standard YS / T 300-2015 germanium concentrate.

Compared with single FeCl₂ or MgCl₂ germanium precipitation method, the germanium precipitation rate and germanium content of regenerated germanium concentrate are improved, and the relative advantages are obvious.

Based on iron salt and magnesium salt, the experiment of germanium precipitation with binary composite germanium precipitant was carried out. The addition of aluminum salt and other precipitants was not considered. In the future, ternary or more composite germanium precipitant can be considered for continuous improvement of the process.

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