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Study on the Process of Enriching Germanium from Germanium Hydrolysis Residue based on "Step Method"

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Abstract

In this paper, the advantages and disadvantages of germanium precipitation by PFS and tannic acid were compared, and the process idea of "distribution method" for efficient recovery of germanium from germanium hydrolysis residue was established. By adjusting different pH values, the step-by-step sedimentation method can make the iron ions in PFS hydrolyze sufficiently, and then effectively adsorb germanium in liquid phase and form coprecipitation. After solid-liquid separation of the precipitate, germanium concentrate can be obtained. The results show that the recovery of germanium is about 99.5% and the grade of germanium concentrate is over 7%. Through the test verification, the optimal economic and technical indexes can be achieved by adjusting the pH value to be about 9.5 and 7.5 respectively, adding polyferric sulfate in two steps, the weight ratio of adding amount to germanium in solution is 12:1, and aging in two steps for 6 hours respectively; the germanium residue can be returned to supplement the waste gas leaching system, so as to realize the closed cycle of the whole system.

Keywords

Germanium; Step by Step Method; Polyferric Sulfate; Recovery.

1. Introduction

Germanium is a high-value scattered metal with extremely rare earth content, an important semiconductor material, with a global possession of about 8,600 tons. At present, many countries have listed germanium as a strategic metal [1]. Germanium is mainly used in the production of infrared materials, photovoltaic industry, optical fiber industry, PET catalysis industry, food and pharmaceutical production and other fields. Germanium is widely used in high-tech fields such as new energy, infrared optics, optical fiber, catalyst, electronics and solar energy, and is an important resource for the development of strategic emerging industries [2-3].

Because of the complex process of germanium, the direct metal yield in the production process is not high; and because of its high value and scarcity, the systematic and comprehensive recovery of germanium in the production process is indispensable and significant [4-6]. The production process of high-purity germanium oxide is that high-purity germanium tetrachloride and high-purity water undergo a hydrolysis reaction at a volume ratio of 1:7 to generate GeO2 precipitation and hydrochloric acid solution. After solid-liquid separation, germanium oxide needs to be washed to remove chlorine in the residual liquid. Root [7], the content of germanium in the mixed hydrolysis residue and washing water is about 612ug/mL.

The traditional recovery process of germanium-containing solution is the tannic acid adsorption precipitation method, which has the advantages of simple process; but the high cost and incomplete recovery are its significant shortcomings, and the precipitated germanium tannin needs to be roasted

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and decomposed. The secondary loss of germanium has increased the environmental burden [8]. Therefore, it is particularly important to find a new method for recovering germanium from germanium-containing solution fully, thoroughly and at low cost. In order to further reduce costs and increase efficiency, this study designed a polymerized ferric sulfate step-by-step germanium precipitation process based on the characteristics of ferric hydroxide that can adsorb and co-precipitate germanium, and carried out systematic experimental verification. The results show that the recovery rate of germanium by this method is more than 98.5%, and the content of germanium is more than 5%, and the cost of recovering germanium is only about 10% of tannin precipitation, and the germanium precipitation residue contains no organic matter. It can be returned to supplement the eluent of the exhaust gas system, so as to realize the closed loop of the whole system.

2. Test principle

The mechanism of tannic acid precipitation of germanium: the use of the adsorption and complexation of germanium by polymer compounds, it is generally believed that the full precipitation of germanium can be basically achieved with tannic acid 16 to 40 times the amount of germanium in the solution [9]. In production and research, a large number of experiments have been carried out on the relationship between the amount of tannic acid added and the germanium concentration in the initial solution. The recommended amount of tannic acid is shown in Table 1. The acidity in the solution, Fe3+, Zn2+ plasma concentration, operating temperature, stirring conditions, and germanium concentration all have a certain impact on the amount of tannin extract [10-11]. The tedious conditions increase the difficulty of tannin precipitation of germanium. And cost.

Tab. 1 Experimental

Germanium concentration(ug/mL)	>500	250-500	100-250	50-100	20-50
Adding tannic acid is a multiple of the amount of germanium	16-20	20-25	26-33	34-40	40—60

Polymeric ferric sulfate precipitation of germanium: The Fe3+ formed after the dissolution of polymeric ferric sulfate will be hydrolyzed to Fe(OH)3 precipitation when the pH value is greater than 1.6, and the hydrolysis is complete when the pH value is greater than 5.2. The hydrolysis reaction is:

$$Fe^{3+}+3OH^{-}= Fe(OH)_3\downarrow$$

The resulting Fe(OH)3 precipitate has adsorption properties for Ge, and then the co-precipitation process is completed by gravity.

Studies have shown that when Fe:Ge≥5:1, the adsorption of Fe on Ge is relatively saturated, which provides a reference for the amount of polymeric ferric sulfate.

3. Test part

3.1 Test material

Germanium-containing solution: the germanium-containing hydrochloric acid solution after mixing the residue from the hydrolysis process of high-purity germanium tetrachloride and washing water. The components are shown in Tab. 2.

Tab. 2 Concentrations of main substances in solutions containing germanium

name	Ge	HCl
content	612ug/mL	2.1mol/L

Tannic acid: industrial grade, tannic acid content is greater than 80%.

Polymeric ferric sulfate: industrial grade, the content of ferric sulfate is greater than 21%.

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3.2 Experiment procedure

3.2.1 Germanium precipitation test with tannin

In each test, 1000 mL of germanium-containing solution was put into a 2000 mL glass beaker, heated to a temperature above 80°C in an electric furnace, and a certain amount of tannic acid was added and stirred. The stirring time was 15 m, and then stood for 12 hours before solid-liquid separation. In this round, other conditions were fixed, and different tannic acid additions were controlled to carry out a gradient test, and finally the optimal tannic acid addition for the ideal tannin precipitation of germanium was determined and the germanium yield (germanium precipitation rate) and other indicators were calculated.

3.2.2 One-step germanium precipitation test of polymeric ferric sulfate

For each test, 1000 mL of germanium-containing solution was put into a 2000 mL glass beaker, and then a certain amount of polyferric sulfate was added at one time and stirred. The stirring time was 15 m, and the solid-liquid separation was carried out after standing for 12 hours. In this round, other conditions are fixed, and different amounts of polymeric iron oxides are controlled to conduct gradient tests, and finally the optimal amount of polymeric iron oxides for one-step germanium precipitation is determined and the germanium yield and other indicators are calculated.

3.2.3 Stepwise germanium precipitation test

In each test, 1000 mL of germanium-containing solution was put into a 2000 mL glass beaker, a certain amount of polyferric sulfate was added in two rounds and stirred, and the stirring time was 15 m each time. The last germanium precipitation can be carried out after 6 hours of aging for the first germanium precipitation, and the solid-liquid separation can be carried out after standing for 6 hours after the last germanium precipitation. Fix other conditions in this round, control the total amount of polymerized iron oxide added in two different rounds to conduct gradient tests, and finally determine the optimal amount of polymerized iron oxide for stepwise precipitation of germanium and calculate the germanium yield and other indicators. The flow chart of the distribution of germanium is shown in Figure 1.

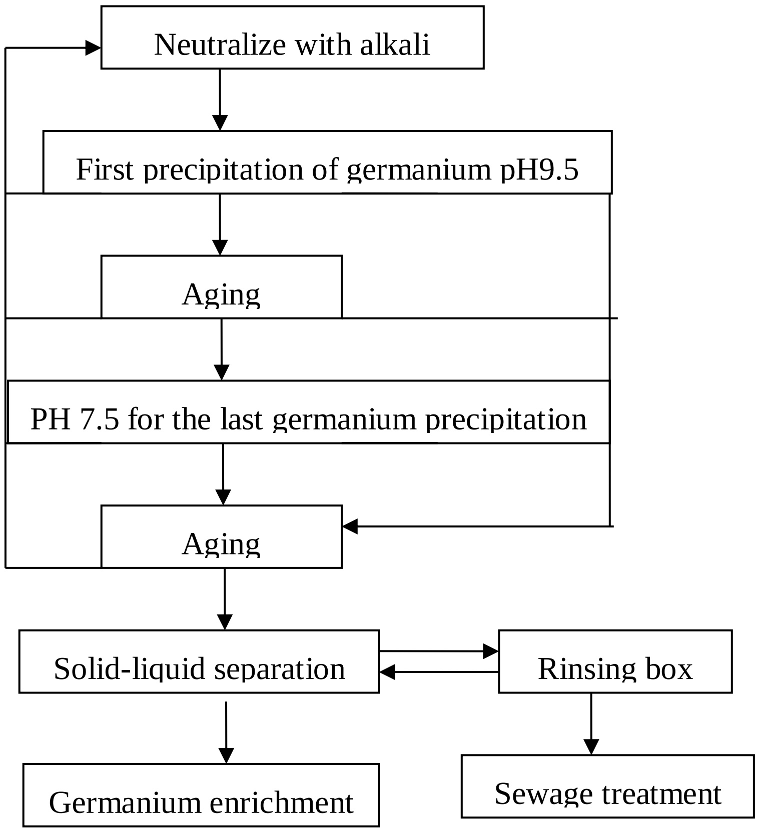

Figure 1. Flow chart of the step-by-step germanium precipitation test

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4. Results and discussion

The concentration of germanium in the germanium-containing solution before the sample was analyzed was 612ug/mL, and the concentration of the residual solution of the germanium precipitation and the germanium grade of the precipitated germanium enrichment were determined by analysis and detection[12].

4.1 Experimental analysis of tannin precipitation of germanium

According to the traditional production experience of germanium precipitation with tannic acid, the pH value of the solution is adjusted to about 2.5 by adding alkali, the temperature of precipitation of germanium is selected to be greater than 80 ℃, the stirring time of adding tannic acid is 15m, and the aging time is 12h as the fixed conditions. With reference to the recommended dosage of germanium tannin at different germanium concentrations, set the dosage of tannic acid at 15-25 times the amount of germanium, and increase the dosage at an interval of 2 times, to obtain 6 different groups The test results under the added amount of tannin were compared, and the test results are shown in Table 3. The calculation method of the germanium direct yield in the table is to quantify the germanium precipitation residue to 1000mL, analyze the germanium concentration and compare it with the germanium content in the original solution; the grade of the germanium enrichment is the solid-liquid separation and the oven drying at 120℃ After 24h, the results are obtained for inspection and analysis.

Tab. 3 Experimental

Test number	Tannin addition multiple	Addition of tannic acid (g)	Concentration of liquid germanium after germanium precipitation (ug/mL)	Yield of germanium/rate of precipitation (%)	Germanium grade of germanium enrichment (%)
1-1	15	9.18	32.2	94.7%	5.53%
1-2	17	10.40	12.3	98.0%	5.17%
1-3	19	11.63	9.9	98.4%	4.61%
1-4	21	12.85	8.3	98.6%	4.27%
1-5	23	14.08	7.2	98.8%	3.89%
1-6	25	15.30	7.3	98.8%	3.61%

It can be seen from Table 3 that increasing the amount of tannic acid can significantly increase the direct yield of germanium, but due to the increase in the amount of tannic acid, the grade of the germanium enrichment also decreases with the increase in the amount of tannic acid, and Tannic acid is expensive, and the increase in the cost of germanium precipitation is also excessive. At a lower tannin addition ratio of 15 times, the germanium grade of the germanium enrichment material reached 5.53%, but the germanium precipitation rate was only 94.7%, and the germanium content of the germanium precipitation solution was as high as 32.2 ug/mL, which was unacceptable in production. Such a loss of germanium (the germanium in the general solution in production needs to be less than 10 ug/mL to be considered for emissions). At 23 and 25 times the addition of tannin, the germanium precipitation rate is about 98.8%, indicating that the germanium precipitation limit has been reached under this process, and increasing the amount of tannin will not increase the yield of germanium, and at this multiple Under this range, the consumption of tannic acid is large and uneconomical, and the germanium grade in the germanium enrichment is reduced to 3.61%-3.89%, which increases the subsequent germanium extraction cost. In the serial number 1-3 and 1-4 experiments, the amount of tannic acid added was 19 to 21 times, the germanium precipitation rate reached 98.4%-98.6%, the germanium content in the germanium precipitation liquid reached the level of discharge acceptable for production, and the germanium was rich The collection also reached 4.27%-4.61%, which reached the range of the corresponding technical indicators acceptable in production.

Comprehensive analysis of the above data, adding alkali to adjust the pH of the solution to about 2.5, the germanium precipitation temperature is greater than 80 ℃, adding tannic acid stirring time is 15m,

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aging time is 12h, adding tannic acid multiples of 19 times the comprehensive index of germanium precipitation The most ideal.

4.2 Experimental Analysis on Precipitation of Germanium by Polymeric Ferric Sulfate

According to the production experience, the normal temperature condition was selected, the pH was adjusted to about 7.5, the polyferric acid was added at one time, the stirring time was 15m, and the aging time was 12h as the fixed conditions. With reference to production experience, the amount of polyferric sulfate added was set at 8-18 times the amount of germanium, and the dosage was increased at an interval of 2 times. The results of 6 groups of different amounts of polyferric sulfate were compared and tested. The results are shown in Table 4. The calculation method of the germanium direct yield in the table is to quantify the germanium precipitation residue to 1000mL, analyze the germanium concentration and compare it with the germanium content in the original solution; the grade of the germanium enrichment is the solid-liquid separation and the oven drying at 120℃ After 24h, the results are obtained for inspection and analysis.

Tab. 4 Test results of germanium sinking with different polyferric sulfate addition multiples (one-time addition)

Test number	Polyferric sulfate addition multiple	Addition of polyferric sulfate (g)	Concentration of liquid germanium after germanium precipitation (ug/mL)	Germanium deposition rate (%)	Germanium grade of germanium enrichment (%)
2-1	8	4.90	54.3	91.1%	9.61%
2-2	10	6.12	15.3	97.5%	8.32%
2-3	12	7.34	13.1	97.9%	7.19%
2-4	14	8.57	10.6	98.3%	6.12%
2-5	16	9.79	8.7	98.6%	5.31%
2-6	18	11.02	7.9	98.7%	4.94%

It can be seen from Table 4 that increasing the amount of polymerized ferric sulfate can significantly increase the direct yield of germanium, but due to the increase of the amount of polymerized sulfuric acid added, the grade of the germanium-enriched material also decreases with the increase of the amount of polymerized ferric sulfate added. In the serial number 2-1, 2-2 and 2-3 tests, the germanium grade of the germanium enrichment material reached the highest value of 7.19%-9.62% under the lower polyferric sulfate addition multiple (8-12 times), but the germanium precipitation rate was only It is 91.1%-97.5%, and the germanium in the solution needs to be recovered twice in production. In the serial number 2-6 test, the germanium precipitation rate was as high as 98.7%, but the germanium grade in the germanium enrichment dropped to 4.94%-5.31%, which increased the subsequent germanium purification cost. In the test of No. 2-5, the amount of polyferric sulfate added was 16 times, the germanium precipitation rate reached 98.6%, the germanium content in the germanium precipitation solution reached the discharge level acceptable for production, and the germanium enrichment also reached 5.31%. Corresponding technical index range acceptable in production.

Comprehensive analysis of the above data, adding alkali to adjust the pH of the solution to about 7.5, at room temperature, adding polyferric sulfate, stirring time is 15m, aging time is 12h, and the comprehensive index of germanium precipitation is 16 times when polyferric sulfate is added at a time.

4.3 Experimental analysis of the stepwise polymerization of ferric sulfate for germanium precipitation

Refer to the test data in 4.2, choose normal temperature conditions, adjust the pH to 9.5 and 7.5 respectively, add the same amount of polyferric sulfate in two steps, and the stirring time is 15m, the two aging time is 6h each, and the total aging time is 12h. Fixed conditions. With reference to production experience, set the cumulative amount of two polymerized ferric sulfate to 8 to 18 times the amount of germanium, and increase the amount at an interval of 2 times. The results of 6 groups

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of different amounts of polymerized ferric sulfate are obtained. For comparison, the test results are shown in Table 5. The calculation method of the germanium direct yield in the table is to quantify the germanium precipitation residue to 1000mL, analyze the germanium concentration and compare it with the germanium content in the original solution; the grade of the germanium enrichment is the solid-liquid separation and the oven drying at 120°C Analyzed after 24h.

Tab. 5 Test results of germanium sinking with different polyferric sulfate addition multiples (two-step addition)

Test number	Polyferric sulfate addition multiple	Addition of polyferric sulfate (g)	Concentration of liquid germanium after germanium precipitation (ug/mL)	Germanium deposition rate (%)	Germanium grade of germanium enrichment (%)
3-1	8	4.90	26.3	95.7%	10.10%
3-2	10	6.12	10.3	98.3%	8.49%
3-3	12	7.34	3.2	99.5%	7.27%
3-4	14	8.57	3	99.5%	6.30%
3-5	16	9.79	2.8	99.5%	5.56%
3-6	18	11.02	2.9	99.5%	4.98%

It can be seen from Table 5 that increasing the amount of polyferric sulfate can significantly increase the direct yield of germanium, but due to the increase in the amount of polysulfuric acid, the grade of the germanium enrichment also decreases with the increase of the amount of polyferric sulfate. In the serial number 3-1 test, at a lower polyferric sulfate addition multiple (8 times), the germanium grade of the germanium enrichment material reached the highest value of 10.10%, but the germanium precipitation rate was only 95.7%, which was not feasible in production. In the serial number 3-2 test, the germanium deposition rate reached 98.3%, and the germanium-enriched article position was 8.49%, which basically met the standard; but compared with the 3-3 test, the addition factor was 12 times, and the germanium deposition rate reached the highest value of 99.5%. The germanium grade has also reached 7.27%. Obviously, the comprehensive index of 3-3 is even better. The addition times of No. 3-4 to 3-5 are 14-18 times, and the germanium precipitation rate is around 99.5% and there is no significant difference from the 12 times of the 3-3 test. Obviously, the germanium precipitation rate under this condition has basically reached the limit.

Comprehensive analysis of the above data, adding alkali to adjust the pH value of the solution to about 9.5 and 7.5, normal temperature, adding polyferric sulfate, stirring time is 15m, aging time is 12h, two steps average equal amount of polyferric sulfate is added when the cumulative total is 12 times of germanium precipitation The comprehensive index is the most ideal.

4.4 Test data comparison

According to the test data of 4.1, 4.2 and 4.3, the step-by-step polymerization ferric sulfate germanium precipitation method has significant advantages, as shown in the table below for details.

Tab. 6 Comparison of optimal test results under three different test ideas

Test number	Add substances	How to join	Polyferric sulfate addition multiple	Concentration of liquid germanium after germanium precipitation (ug/mL)	Germanium deposition rate (%)	Germanium grade of germanium enrichment (%)
1-3	Tannin	Join at once	19	9.9	98.4%	4.61%
2-5	Polyferric sulfate	Join at once	16	8.7	98.6%	5.31%
3-3	Polyferric sulfate	Join in two steps	12	3.2	99.5%	7.27%

It can be seen from Table 6 that all the three methods of germanium precipitation can basically meet the requirements of economic indicators required for production. The serial number 2-5 test is relative to the 1-3 test, that is, the one-time polymerization ferric sulfate germanium precipitation method has a slightly higher germanium precipitation rate than the traditional tannin precipitation method, and the germanium enrichment material has a slightly higher germanium grade, and the process advantage

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is not particularly significant. The serial number 3-3 test, that is, the improved polymerized ferric sulfate step-by-step germanium precipitation method has significant advantages over the first two processes, the germanium precipitation rate (99.55%) and the germanium grade (7.27%) of the germanium enrichment material. And the added amount of auxiliary materials is lower, the cost is lower, and the advantages are obvious.

5. Conclusion

Polymeric ferric sulfate was used to carry out the stepwise precipitation test of germanium. The relatively ideal process conditions of the stepwise precipitation method were verified by the experiment as follows: adjust the pH value to about 9.5 and 7.5 respectively at room temperature, and add the same amount of polymerized ferric sulfate in two steps. The weight ratio of the total amount to the amount of germanium in the solution is 12:1, and the two steps require 6 hours of aging; the recovery rate of germanium under this process condition is as high as about 99.5%, and the concentration of germanium is as high as 7% or more.

Compared with the tannic acid precipitation and the one-step polymerization iron sulfate germanium precipitation process, the step-based polymer ferric sulfate precipitation germanium process has absolute advantages in terms of the germanium precipitation rate and the germanium concentration of the germanium enrichment. The amount of auxiliary materials added is lower, the cost is lower, and the superiority is significant.

The step-by-step polymerization ferric sulfate germanium precipitation method is used to recover germanium from the germanium hydrolysis residue, which has the advantages of high efficiency, resource saving, simple operation and so on. Because the germanium precipitation supernatant contains trace amounts of germanium and contains no organic matter, it can be introduced into the exhaust gas leaching system. After being formulated as a leaching solution, the volatiles such as germanium tetrachloride will be leached and absorbed to remove the water and Germanium resources carry out an infinite closed loop.

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