

1

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## PROCESS FOR THE EXTRACTION OF GERMANIUM

Charles Francis Allen, Stamford, Francis Mario Aimone, Greenwich, and Robert Ben Booth, Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to improved processes of recovering germanium.

Germanium occurs normally in small amounts in conjunction with much larger amounts of other minerals, for example, germanium sulfides may occur with sulfides of arsenic, copper, lead, cadmium, tin, iron, zinc, etc. Another source of germanium is the fly ash from certain coals.

When germanium occurs as a sulfide and the ore is beneficiated by froth flotation as ores of these types usually are, the sulfides of germanium report in the sulfide concentrate, and it is with materials of this type that the present invention is particularly concerned. When germanium is to be recovered from the coal ash, it is ordinarily present in an oxidized form and for the present invention to be effective must first be transformed into the sulfide.

One of the processes which has been proposed in the past involves sublimation of germanous sulfide, usually after first removing arsenic sulfides. A very serious problem is presented by reason of the fact that the germanium content of sulfide concentrates is normally very much smaller and sometimes only a minute fraction of the other metal sulfides. Yet it is necessary to obtain high recoveries of germanium and at the same time to prevent contamination of the germanium sublimate with undue amounts of other metals. It has been proposed to subject a mixture of sulfides of germanium, lead, cadmium to sublimation in a reducing atmosphere formed by a hydrocarbon, propane, at temperatures of 1000° C. and higher. The sublimation of the germanium is very complete, but the resulting sublimate is of no practical value because some 95% of the lead and cadmium is also volatilized, producing a product in which there has been no substantial separation of germanium from such other metals as lead and cadmium.

It has been found according to the present invention that if lower temperatures are used, it is possible to obtain a high recovery of germanium, and arsenic if present, without excessive volatilization of lead sulfide. In general, the temperature has to be below 1000° C. and will vary somewhat with different reducing atmospheres. The reducing atmosphere is essential, but different reducing atmospheres produce different results. For example, in the case of ammonia, there is excessive lead volatilization at 900° C.; whereas, excellent results are obtained from slightly below 800 to somewhat below 900° C. In the case of the highly active hydrogen atmosphere it is not feasible to obtain satisfactory yields of germanium sulfide at any temperature without excessive volatilization of lead. Thus, for example, it is necessary to go down to not more than 600° C. in order to keep the lead volatilization within bounds, but at this temperature only about 1/2 of the germanium is recovered. We have found that hydrocarbon atmospheres may be used below 1000° C., preferably from 800 to slightly over 900; carbon monoxide atmospheres may be used from temperatures of slightly over 700 to

2

just below 1000 and various reducing atmospheres containing carbon monoxide such as water gas, producer gas and the like give excellent results at temperatures from 800 to slightly over 900° C. Another reducing atmosphere which can be used is hydrogen sulfide which gives excellent results at around 900° C., but is less desirable by reason of its toxicity. However, to the extent that the hydrogen sulfide can be used as a sulfidizing agent to transform oxidized germanium compounds into germanous sulfide, it presents some advantages.

In addition to the use of lower temperatures of volatilization in reducing atmospheres having a lower reduction potential than hydrogen, the present invention includes in a more specific aspect a two-step process for the recovery of germanium from concentrates which contain germanium and arsenic as well as the other metal sulfides. In the case of these concentrates, the first step, that is, volatilization in a reducing atmosphere below 1000° C. and preferably from about 700 to slightly over 900° C., serves to remove a very high percentage of the germanium and arsenic in the form of germanous and arsenious sulfides leaving the other metal sulfides in a form in which they are more valuable for further processing as the arsenic which is often a drawback has been almost completely removed. The sublimate of germanous and arsenious sulfides is then subjected to a roasting operation in an oxidizing atmosphere at temperatures below 1000° C. and preferably at temperatures considerably lower; down to 500° C. or even lower. The roasting operation oxidizes both the arsenious and germanous sulfides to their oxides and volatilizes the more volatile arsenious oxide leaving behind a residue containing substantially all of the germanium. However, in this second step there is an extremely critical factor. The roasting must take place in equipment in which the germanium and arsenic does not come in contact with a metal capable of reacting therewith, such as nickel, iron and even platinum. This part of the process was tried in metallic equipment and no useful recovery of germanium from the residue occurred. It was evidently not previously realized that the nature of the equipment is vital, and it therefore forms a critical limitation in the process of the present invention in its more specific aspect which involves the oxidizing roast. While it is merely necessary to keep the arsenious and germanous sulfides out of contact with metals capable of reacting or alloying therewith, as a practical matter we find that the preferred equipment surfaces which are to be in contact with the sulfides are various ceramic surfaces and similar types of refractories. Such surfaces are therefore preferred.

This invention will be described in greater detail in conjunction with the following specific examples which are typical.

### EXAMPLE 1

A copper concentrate was prepared by froth flotation from a copper-lead ore from South West Africa containing arsenic and germanium. It assayed 38.9% copper, 8.5% lead, 10.2% arsenic and .086% germanium, all as the sulfides, the germanium being present with some of the copper as germanite and renierite. The concentrate was sublimed at 900° C. in an atmosphere of ammonia. A copper sinter was obtained and a sublimate or fume containing the sulfides of germanium and arsenic. This sublimate was then roasted with air, the temperature being between 300° C. and 500° C., to obtain a fume containing most of the arsenic and a residue containing most of the germanium. The following metallurgical table shows the results:

3  
Table I

|                   | Wt.,<br>Parts | Assays |       |       |       | Distribution |      |
|-------------------|---------------|--------|-------|-------|-------|--------------|------|
|                   |               | Ge     | As    | Pb    | Cu    | Ge           | As   |
| Raw Copper Conc.  | 100.0         | .086   | 10.2  | 8.5   | 38.9  | 100.0        | 10.0 |
| Cu Sinter         | 73.3          | .0056  | .25   | 7.2   | ----- | 4.6          | 1.6  |
| Sulfide Sublimate | 22.1          | .38    | 50.2  | ----- | ----- | 95.4         | 98.4 |
| Do                | 22.1          | -----  | ----- | ----- | ----- | 95.4         | 98.4 |
| White Arsenic     | 14.1          | .013   | 68.6  | ----- | ----- | 1.9          | 94.3 |
| Ge Conc.          | 9.1           | .96    | 4.15  | ----- | ----- | 93.5         | 4.1  |

It will be seen that almost 94% of the germanium was recovered in a concentrate assaying nearly 1% germanium. This concentrate contains some of the lead which was volatile but was quite low in arsenic, and an arsenic fume was obtained containing very little of the germanium.

In the roasting procedure described above, the sublimate containing germanium and arsenic sulfides was roasted in equipment where it was in contact only with ceramic surfaces and was kept from contact with metals reacting with either the germanium or the arsenic.

EXAMPLE 2

The first step of Example 1 was repeated with various atmospheres and at different temperatures. There was included by way of comparison with the reducing atmospheres a nitrogen atmosphere which has been proposed in the past. The results are shown in the following table:

Table II

| AMMONIA ATMOSPHERE                          |           |      |       |               |     |      |                             |    |    |
|---------------------------------------------|-----------|------|-------|---------------|-----|------|-----------------------------|----|----|
| Temp.,<br>°C.                               | Sublimate |      |       | Copper Sinter |     |      | Volitization,<br>Percentage |    |    |
|                                             | Ge        | As   | Pb    | Ge            | As  | Pb   | Ge                          | As | Pb |
|                                             | Ge        | As   | Pb    | Ge            | As  | Pb   | Ge                          | As | Pb |
| 1,000                                       | .29       | 36.3 | 18.4  | .0038         | .25 | 4.3  | 97                          | 98 | 73 |
| 900                                         | .63       | 67.1 | 8.5   | .0083         | .54 | 8.5  | 93                          | 96 | 29 |
| 800                                         | .44       | 72.8 | 1.5   | .015          | .13 | 7.6  | 83                          | 98 | 8  |
| 700                                         | .22       | 66.8 | 1.4   | .032          | 1.0 | 7.4  | 50                          | 90 | 2  |
| NITROGEN ATMOSPHERE                         |           |      |       |               |     |      |                             |    |    |
| 1,000                                       | .30       | 49.2 | 5.9   | .0035         | .06 | 8.5  | 96                          | 99 | 21 |
| 900                                         | .28       | 39.3 | 4.6   | .022          | .18 | 6.4  | 71                          | 98 | 15 |
| 800                                         | .097      | 58.3 | 1.9   | .080          | 1.9 | 10.3 | 20                          | 84 | 6  |
| HYDROGEN ATMOSPHERE                         |           |      |       |               |     |      |                             |    |    |
| 1,000                                       | .39       | 44.4 | 16.1  | .0046         | .16 | 7.0  | 96                          | 99 | 45 |
| 900                                         | .60       | 38.7 | 17.8  | .0028         | .13 | 7.4  | 97                          | 99 | 40 |
| 800                                         | .38       | 50.7 | 16.4  | .008          | .16 | 10.1 | 93                          | 98 | 25 |
| 700                                         | .35       | 60.2 | ----- | .045          | 3.5 | 6.4  | 54                          | 70 | 36 |
| 600                                         | .35       | 80.9 | .31   | .059          | .70 | 10.2 | 44                          | 94 | 4  |
| 500                                         | .12       | 85.2 | .30   | .081          | 2.7 | 9.5  | 19                          | 87 | 4  |
| CARBON MONOXIDE ATMOSPHERE                  |           |      |       |               |     |      |                             |    |    |
| 1,000                                       | .56       | 64.3 | 14.6  | .0045         | .07 | 8.3  | 95                          | 99 | 18 |
| 900                                         | .44       | 77.4 | 3.3   | .0090         | .24 | 10.0 | 92                          | 98 | 7  |
| 800                                         | .50       | 89.1 | 6.0   | .011          | .07 | 10.2 | 90                          | 99 | 5  |
| 700                                         | .37       | 84.1 | 7.0   | .033          | .06 | 10.0 | 70                          | 99 | 7  |
| NATURAL GAS ATMOSPHER (PRINCIPALLY METHANE) |           |      |       |               |     |      |                             |    |    |
| 900                                         | .49       | 70.3 | 1.1   | .0066         | .12 | 9.9  | 93                          | 99 | 7  |
| HYDROGEN SULFIDE ATMOSPHERE                 |           |      |       |               |     |      |                             |    |    |
| 900                                         | .19       | 23.8 | 1.1   | .011          | .73 | 9.7  | 90                          | 94 | 7  |
| WATER GAS 50% CO, 50% H <sub>2</sub>        |           |      |       |               |     |      |                             |    |    |
| 900                                         | .64       | 79.0 | 2.9   | .0062         | .37 | 10.0 | 94                          | 97 | 7  |
| PRODUCER GAS                                |           |      |       |               |     |      |                             |    |    |
| 900                                         | .64       | 72.9 | 4.4   | .014          | .16 | 9.3  | 87                          | 98 | 10 |
| 900                                         | .68       | 76.8 | 3.7   | .0083         | .52 | 9.3  | 92                          | 95 | 9  |
| 900                                         | .67       | 78.4 | 3.1   | .0069         | .54 | 10.0 | 94                          | 95 | 5  |

It will be seen that no temperature gave satisfactory results with nitrogen. For purposes of this test it is considered that more than 10% of lead volatilized gives an unsatisfactory product. At a temperature of 1000° C. the germanium and arsenic were volatilized but so was 21% of the lead; whereas, at temperatures at which the lead content was satisfactory, that is, temperatures below 900° C., the germanium recovery was insufficient.

It will be noted that with hydrogen there is evidently too great reduction of lead sulfide to metallic lead for even at 700° C. lead volatilization was still excessive and at 600° C. there was unsatisfactory germanium recoveries.

Ammonia which has a fairly high reduction potential was only usable below 900° C. and at 800° C. while practical results were obtained, the germanium recovery is not as high as is desirable. At 700° C. it is completely unsatisfactory. Ammonia is included broadly in the present invention but is not a preferred reducing atmosphere.

It will be noted that carbon monoxide, natural gas, hydrogen sulfide, water gas, and producer gas all give good results around 800 to 900° C. The three tests on producer gas were with different compositions, all of them having 50% nitrogen: the first test 50% CO, the second test, 25% CO, 25% H<sub>2</sub>, the third, 38% CO and 12% H<sub>2</sub>.

EXAMPLE 3

The oxidation step of the two-step process of Example 1 was carried out at various temperatures. The results are shown in the following table:

Table III

| Temp.,<br>°C. | As <sub>2</sub> O <sub>3</sub> Fume |      |              |      | Ge Residue |      |      |              |
|---------------|-------------------------------------|------|--------------|------|------------|------|------|--------------|
|               | Assays                              |      | Distribution |      | Assays     |      |      | Distribution |
|               | Ge                                  | As   | Ge           | As   | Ge         | As   | S    | Ge As        |
| 400           | .012                                | 65.8 | 2.3          | 97.6 | 4.75       | 14.9 | 11.3 | 97.7 2.4     |
| 500           | .009                                | 70.2 | 1.7          | 98.7 | 5.30       | 9.3  | 8.3  | 98.3 1.3     |
| 600           | .0059                               | 67.9 | 1.1          | 99.1 | 5.41       | 6.2  | 6.9  | 98.9 0.9     |
| 700           | .0097                               | 67.7 | 1.8          | 99.1 | 5.44       | 6.8  | 5.7  | 98.2 0.9     |
| 800           | .0083                               | 69.3 | 1.7          | 99.4 | 6.75       | 5.6  | 4.1  | 98.3 0.6     |

It will be noted that in each case satisfactory recoveries of germanium were obtained, the best temperatures being nearer the higher part of the range. Somewhat higher temperatures may be used but at 1000° C. the residue tends to fuse to ceramic material and this temperature is therefore too high for practical use. All tests were made entirely with equipment presenting a ceramic face to the sulfides being roasted.

The procedure of this example was repeated with test equipment presenting nickel, iron and platinum surfaces to the mixture of germanium and arsenic sulfides. Entirely unsatisfactory results were obtained, the metal being strongly corroded by reaction with the arsenic and germanium and no satisfactory germanium recoveries obtainable.

EXAMPLE 4

The procedure of Example 1 was carried out using a copper concentrate from a Belgian Congo ore instead of South West Africa ore. The arsenic content was lower but the germanium recovery was substantially the same.

EXAMPLE 5

The zinc sulfide concentrate from a lead-zinc ore containing in addition germanium and cadmium was subjected to volatilization in various atmospheres. The zinc concentrate had the following analysis:

HEAD SAMPLE OF ZINC CONCENTRATE

46.4% Zn  
3.3% Pb  
.47% Cu  
.027% Ge  
1.01% Cd  
.067% As  
24.1% S

The results of the sublimation are given in the following table:

temperature of from about 700 to about 900° C. in an atmosphere of a reducing gas having a reduction poten-

Table IV

## CARBON MONOXIDE ATMOSPHERE

| Temp.,<br>°C. | Sublimate |      |      |      | Zinc Residue |    |     |      | Volatilization, Percent |     |    |    |
|---------------|-----------|------|------|------|--------------|----|-----|------|-------------------------|-----|----|----|
|               | Ge        | Cd   | Pb   | Zn   | Ge           | Cd | Pb  | Zn   | Ge                      | Cd  | Pb | Zn |
| 900-----      | .17       | 22.9 | 16.4 | 51.5 | .0052        | Tr | 3.4 | 50.4 | 83                      | 100 | 11 | 5  |

## HYDROGEN ATMOSPHERE

|          |     |      |      |      |       |    |     |      |    |     |    |   |
|----------|-----|------|------|------|-------|----|-----|------|----|-----|----|---|
| 900----- | .15 | 11.0 | 24.0 | 46.4 | .0089 | Tr | 2.6 | 49.8 | 73 | 100 | 36 | 8 |
|----------|-----|------|------|------|-------|----|-----|------|----|-----|----|---|

## NITROGEN ATMOSPHERE

|          |     |      |      |      |      |      |     |      |    |    |    |   |
|----------|-----|------|------|------|------|------|-----|------|----|----|----|---|
| 900----- | .19 | 13.9 | 17.1 | 26.0 | .026 | .056 | 2.5 | 51.5 | 13 | 94 | 32 | 2 |
|----------|-----|------|------|------|------|------|-----|------|----|----|----|---|

PRODUCER GAS ATMOSPHERE, 50% N<sub>2</sub>, 25% CO, 25% H<sub>2</sub>

|          |     |      |      |      |       |    |     |      |    |     |   |   |
|----------|-----|------|------|------|-------|----|-----|------|----|-----|---|---|
| 900----- | .09 | 30.9 | 12.8 | 48.7 | .0038 | Tr | 3.5 | 49.8 | 87 | 100 | 8 | 3 |
|----------|-----|------|------|------|-------|----|-----|------|----|-----|---|---|

It will be noted that satisfactory recoveries of germanium were obtained without excessive volatilization of lead, except in the case of hydrogen and nitrogen atmospheres, the behavior in this respect being very similar to that shown in Table II. Cadmium, of course, was volatilized with the germanium which is not objectionable as the present invention is not designed to separate germanium from cadmium in the first, or sublimation step.

## EXAMPLE 6

A lead concentrate from a lead-zinc ore containing 73.7% Pb, 0.044% Ge and 1.1% As was volatilized in a reducing atmosphere as described in Example 1, using four different reducing atmospheres, ammonia, carbon monoxide, water gas and producer gas. The results are shown in the following table:

## AMMONIA ATMOSPHERE

| Temp.,<br>°C. | Sublimate |     |      | Lead Residue |     |      | Percent Volatilized |    |    |
|---------------|-----------|-----|------|--------------|-----|------|---------------------|----|----|
|               | Ge        | As  | Pb   | Ge           | As  | Pb   | Ge                  | As | Pb |
| 900-----      | .13       | 2.9 | 64.3 | .0038        | .29 | 55.9 | 92                  | 78 | 26 |

## CARBON MONOXIDE ATMOSPHERE

|          |     |      |      |       |     |      |    |    |   |
|----------|-----|------|------|-------|-----|------|----|----|---|
| 900----- | .94 | 30.4 | 51.9 | .0083 | .14 | 73.2 | 82 | 88 | 5 |
|----------|-----|------|------|-------|-----|------|----|----|---|

WATER GAS, 50% CO, 50% H<sub>2</sub>

|          |     |      |      |       |     |      |    |    |   |
|----------|-----|------|------|-------|-----|------|----|----|---|
| 900----- | .74 | 22.9 | 62.7 | .0052 | .10 | 74.9 | 89 | 91 | 6 |
|----------|-----|------|------|-------|-----|------|----|----|---|

PRODUCER GAS, 50% N<sub>2</sub>, 25% CO, 25% H<sub>2</sub>

|          |     |      |      |       |      |      |    |    |   |
|----------|-----|------|------|-------|------|------|----|----|---|
| 900----- | .63 | 19.9 | 64.3 | .0010 | .067 | 74.1 | 97 | 94 | 6 |
|----------|-----|------|------|-------|------|------|----|----|---|

It will be noted that as in the case of Example 1, 900 C. is too high when using ammonia. Excellent results, however, are obtained with carbon monoxide and other reducing gases containing carbon monoxide.

We claim:

1. The process of separating germanium sulfide from a material containing a minor amount of germanium sulfide associated with major amounts of other sulfides comprising a sulfide of at least one of the metals copper, zinc and lead which comprises heating the material at a

25 tial lower than that of pure hydrogen, so as to volatilize germanous sulfide preferentially and continuing the heating until substantially all of the volatilizable germanium sulfides have been sublimed.

2. A process according to claim 1 in which the reducing gas contains carbon monoxide.

3. A process according to claim 1 in which the reducing gas is water gas.

4. A process according to claim 1 in which the reducing gas is producer gas.

5. A process according to claim 1 in which the reducing gas is ammonia.

6. A process according to claim 1 in which the reducing gas is a low paraffin hydrocarbon.

7. A process according to claim 1 in which the reducing gas is hydrogen sulfide.

8. A process according to claim 1 in which the material contains substantial amounts of arsenic sulfides which are volatilized with the germanous sulfide and the sublimate is roasted in an oxidizing atmosphere out of contact with metals capable of reacting or alloying with germanium sulfides at a temperature above the volatilization point of arsenious oxide and below that at which germanium oxide is volatile.

9. A process according to claim 8 in which the temperature of the oxidizing roast is from 400 to 900° C.

10. A process according to claim 8 in which the sublimation step is effected in the presence of a reducing atmosphere containing carbon monoxide.

11. A process according to claim 10 in which the atmosphere is water gas.

12. A process according to claim 8 in which the reducing gas in the sublimation step is hydrogen sulfide.

13. A process according to claim 8 in which the reducing gas in the sublimation step is producer gas.

14. A process according to claim 8 in which the reducing gas in the first sublimation step is a lower paraffin hydrocarbon.

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