Recovering Germanium from waste Optical fiber cable

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The Formosa Association of Resource Recycling—Secretary-general
Outline

- Circumstances of Germanium around the world
- Application of Germanium
- Recovery of germanium from fiber-optic cables
- Summaries
Germanium (Ge) is a rare metal (Scattered Metals).

- Melting Point: 937.4 °C
- Boiling Point: 2830 °C
- Density: 5.35 g/cm³
- Hardness: 6～6.5

Germanium has a great semiconductor property and is an important material of the semiconductor.

Arrangement of atoms in crystals of germanium is same as diamond, its chemical characteristic is stable.

- Insoluble in: dilute acids and alkalis
- Dissolves slowly in: concentrated sulfuric acid and reacts violently with molten alkalis to produce germanates ([GeO₃]²⁻)
Reserves and Distribution

- The reserves of Germanium: **8,600 tons**
- The average annual demand of growth rate is about **33.89 %**.
- Current world’s reserves of germanium is only enough for **40 years**.

![Bar Chart](chart.png)

- Fiber demand for germanium (ton)

  - World
  - China
The largest country in production: **China**

72 percent of global production of germanium

The production of germanium in USA is subject to the production of lead and zinc.

US annual production of germanium: **4.6 tons**, (Global production: **3%**).
Early in 1984, the United States made **germanium** as a defense germanium reserves of **strategic resources** protection.

**U.S Annual consumption**: 60 tons, **Imports accounted for**: 86.67%.

**Imported Source:**
- China: 51%
- Belgium: 24%
- Russia: 16%
- Germany: 6%, other 3%.

### U.S. germanium production, imports and demand statistics

- **Production**
- **Imports**
- **Demand**

<table>
<thead>
<tr>
<th>Year</th>
<th>Production</th>
<th>Imports</th>
<th>Demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>4400</td>
<td>10000</td>
<td>25000</td>
</tr>
<tr>
<td>2005</td>
<td>4500</td>
<td>13400</td>
<td>27000</td>
</tr>
<tr>
<td>2006</td>
<td>4600</td>
<td>37600</td>
<td>55000</td>
</tr>
<tr>
<td>2007</td>
<td>4600</td>
<td>40700</td>
<td>60000</td>
</tr>
<tr>
<td>2008</td>
<td>4600</td>
<td>49700</td>
<td>54000</td>
</tr>
<tr>
<td>2009</td>
<td>4600</td>
<td>39000</td>
<td>44000</td>
</tr>
<tr>
<td>2010</td>
<td>3000</td>
<td>36700</td>
<td>40000</td>
</tr>
<tr>
<td>2011</td>
<td>3000</td>
<td>39000</td>
<td>36000</td>
</tr>
<tr>
<td>2012</td>
<td>0</td>
<td>32600</td>
<td>33200</td>
</tr>
</tbody>
</table>

**Source**: USGS year statistics
## Market of Germanium

<table>
<thead>
<tr>
<th>Year</th>
<th>RMB/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014e</td>
<td>12,000</td>
</tr>
<tr>
<td>2013</td>
<td>11,625</td>
</tr>
<tr>
<td>2012</td>
<td>11,250</td>
</tr>
<tr>
<td>2011</td>
<td>10,875</td>
</tr>
<tr>
<td>2010</td>
<td>10,500</td>
</tr>
<tr>
<td>2009</td>
<td>10,125</td>
</tr>
<tr>
<td>2008</td>
<td>9,750</td>
</tr>
<tr>
<td>2007</td>
<td>9,375</td>
</tr>
</tbody>
</table>

- **Germanium dioxide 99.99%** $1,435 / kg
# Market of Germanium

## Tables: import and export statistics germanium Taiwan

<table>
<thead>
<tr>
<th>Ge</th>
<th>Import</th>
<th></th>
<th>Export</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kg</td>
<td>Total price</td>
<td>Unit price (kg/dollae)</td>
</tr>
<tr>
<td>98</td>
<td>782</td>
<td>40,170,000</td>
<td>51,368</td>
</tr>
<tr>
<td>99</td>
<td>4,011</td>
<td>133,723,000</td>
<td>33,339</td>
</tr>
<tr>
<td>100</td>
<td>8,503</td>
<td>234,817,000</td>
<td>27,616</td>
</tr>
<tr>
<td>101</td>
<td>10,672</td>
<td>304,193,000</td>
<td>28,504</td>
</tr>
<tr>
<td>102</td>
<td>10,625</td>
<td>371,781,000</td>
<td>34,991</td>
</tr>
</tbody>
</table>

Source: 財政部關稅總局統計資料
The Source Of Germanium-Mine

- Germanium content in the crust: **0.0007%** (Seven millionths)
- Dispersed exist in other minerals:
  - 鍺石 Germanium stone (including germanium 10%),
  - 硫鍺鐵銅礦 Copper iron sulfide germanium (Ge containing 7.7%),
  - 硫銀鍺礦 Argyrodite (germanium-containing 6.7%),
  - 黑硫銀錫礦 Black silver tin sulfide (germanium-containing 1.8%),
- mainly in industry recycled or recovered as a byproduct from coking Dust while processing sulfide ore.

- Germanium ore containing **more than 20ppm** has recovery value.
Germanium World Consumption Structure in 2013

- Fiber Optics (39%)
- Polymerization Catalysts (25%)
- Infrared Optics (25%)
- Other (Electronic, Solar power, Fluorescent powder, Chemotherapy, Metallurgy)
Optical fiber cable

MDPE outer jacket
(Medium-density polyethylene 中密度聚乙烯)
Strength steel wire

Optical fiber
Filling compound
Filler
Steel-polythene compound belt

Optical fiber
# Optical fiber cable

## Proportion by Weight

<table>
<thead>
<tr>
<th>Outer Jacket (MDPE)</th>
<th>Optical Fiber</th>
<th>Steel wire</th>
<th>Filling compound (Thin plastic wire, fiber ointment, etc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60%</td>
<td>10~15%</td>
<td>10~15%</td>
<td>10~15%</td>
</tr>
</tbody>
</table>

## Germanium optical fiber element content analysis

<table>
<thead>
<tr>
<th>Si</th>
<th>Ge</th>
<th>GeCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.17%</td>
<td>3%</td>
<td>10%</td>
</tr>
</tbody>
</table>
Recycling Process of Optical Fiber

1. Waste Germanium-containing Fiber
2. Multifunction Cable Stripping Machine
3. Remove the plastic casing
4. Removing fiber ointment
5. Gas cited grinder
6. Milling (grinder)
7. Roasting
8. LiBO2
9. Leaching
10. Filtering
11. Extraction
12. Germanium precipitation
13. Chloride Distillation
14. Sulfuric acid, oxidant (hydrogen peroxide)
15. Tertiary amine extractant
16. NH3[aq]
17. Hydrochloric acid
Remove the plastic casing - Multifunction Cable Stripping Machine

**Voltage power:**
220V / 2.2KW (Motor: 3HP)

**Cutting capacity:** 1mm ~ 40mm, a total of 20 stringing holes

**Scope:** computer line to 325 square feet of wire (cable) line

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**Milling (grinder) - Gas cited grinder**

Milling to at least 200 mesh
(1) Weighed Germanium-containing fiber abrasive in platinum crucibles (graphite crucible), add toner and flux (Lithium metaborate LiBO$_2$) mixed. (Fiber abrasive / flux = 1/5 ~ 1/10)

(2) Placed in a furnace heated to 800 ~ 1000 °C.

(3) heating from 10 to 20 minutes, removed and quickly placed into cold water to cool down, then condensed as a solid balls.
Leaching

- 0.1 ~ 1M sulfuric acid was added ($S / L = 1 / 1.5 \sim 2$), adding hydrogen peroxide as the oxidant ($S / L = 1 / 0.2 \sim 1$).

- The reaction at a temperature of **2 to 2.5 hours** at **80 ~ 100 °C** condition.
Solvent extraction

- (1) Selection of **Alamine 308** Triocetylamine (R3N): extraction agent 30%, 15% modifier (TBP), diluent (kerosene) 55% as the organic extraction system.
- (2) The aqueous phase acidity **pH: 2.0 ~ 2.5.**
- (3) The volume of the aqueous phase and an organic phase ratio **O / A = 1/3 ~ 4**
- (4) Extraction of the reaction time from 5 to 10 minutes.
- (5) Ambient temperature.
- (6) Germanium extraction rate was more than **97%**
(1) Adding **Ammonium hydroxide** (NH₃(aq)) for **Germanium precipitation**.

(2) Add 9 mol/l **hydrochloric acid** to dissolve, S/L 1: 1 ~ 3, the reaction at 100-110 °C, 2-4 hours to obtain steam at a temperature of 50-70 °C is condensed, collecting the liquid and will get Germanium tetrachloride (GeCl₄).

(3) Ge(OH)₄ + 4HCl → GeCl₄ + 2H₂O.

(4) germanium recovery rate was above 98%.
THANKS FOR YOUR ATTENTION