Physicochemical characteristics of rhenium

Rhenium is bound with molybdenum in porphyry deposits of copper and molybdenum ores

\[
\text{75} \quad \text{Re} \\
\text{186} \\
\text{melting point: 3180 °C} \\
\text{density: 21.0 g/cm}^3
\]
Content

1. Primary production of rhenium
2. Rhenium-containing products and market
3. Secondary rhenium production
# Global Rhenium production in 2012-2015

<table>
<thead>
<tr>
<th>Country</th>
<th>Rhenium production, Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2012</td>
</tr>
<tr>
<td>Chile</td>
<td>27</td>
</tr>
<tr>
<td>USA</td>
<td>7.9</td>
</tr>
<tr>
<td>Poland</td>
<td>6.0</td>
</tr>
<tr>
<td>Armenia</td>
<td>0.6</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>3.0</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>5.4</td>
</tr>
<tr>
<td>Russia</td>
<td>1.5</td>
</tr>
<tr>
<td>Others</td>
<td>1.2</td>
</tr>
<tr>
<td>Global production</td>
<td>52.6</td>
</tr>
</tbody>
</table>
# World Mine Production and Reserves

<table>
<thead>
<tr>
<th>Mine production</th>
<th>2015</th>
<th>2016</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>7,900</td>
<td>7,600</td>
<td>390,000</td>
</tr>
<tr>
<td>Armenia</td>
<td>350</td>
<td>350</td>
<td>95,000</td>
</tr>
<tr>
<td>Canada</td>
<td>—</td>
<td>—</td>
<td>32,000</td>
</tr>
<tr>
<td>Chile</td>
<td>26,000</td>
<td>26,000</td>
<td>1,300,000</td>
</tr>
<tr>
<td>China</td>
<td>2,400</td>
<td>2,400</td>
<td>NA</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>1,000</td>
<td>1,000</td>
<td>190,000</td>
</tr>
<tr>
<td>Peru</td>
<td>—</td>
<td>—</td>
<td>45,000</td>
</tr>
<tr>
<td>Poland</td>
<td>8,900</td>
<td>7,000</td>
<td>NA</td>
</tr>
<tr>
<td>Russia</td>
<td>NA</td>
<td>NA</td>
<td>310,000</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>1,000</td>
<td>1,000</td>
<td>NA</td>
</tr>
<tr>
<td>Other countries</td>
<td>1,800</td>
<td>1,800</td>
<td>91,000</td>
</tr>
</tbody>
</table>

World total (rounded) 49,400 47,200 2,500,000
Over 50% of rhenium global output comes from Chile where a world leader Molibdenosy Metales - Molymet (almost all of production is metallic rhenium that is imported mainly by American aerospace industry) is operating. The biggest rhenium recovery plants from molybdenite concentrates. In addition to installation in Chile Molymet owns:

- **Roasting plant Molymex** in Mexico (based on concentrates from La Caridad mine managed by Grupo Mexico),
- **Roasting plants and ferromolybdenum smelters** in Belgium (Sadaci) and
- **Metallurgical plants Chemiemetall** in Germany and
- **Luoyang High-tech Molybdenum & Tungsten Material** in China.

Besides, it is processing copper-molybdenite concentrates in form of service, coming from other Chilean roasting plants, mainly Codelco and Xstrata companies but also imported from Peru, Canada and USA.[1-5]

**USA** is the second rhenium producer that acquires rhenium as a by-product of molybdenite concentrate roasting from porphyry-type of Cu-Mo deposits. Sierrita, Freeport McMoRan Copper&Gold in Arizona is the only roasting plant for rhenium recovery in the USA.
In **Kazakhstan** rhenium raw materials are bought by national Redmet Company from rhenium-bearing wastes during metallurgical processing of copper ores in a Copper Factory Dżezkazgan managed by Kazachmysi Samsung.

Other important rhenium producers are:

- **Russia** (Uralelektromed),
- **Uzbekistan** (Navoi — Cu-Mo concentrate processing plant in Metallurgical Factory Almalyk, enables rhenium and osmium recovery),
- **Armenia** (Ironworks Yerevan equipped with plant for rhenium and molybdenum production by a German Cronimet Holding) and
- **Poland** (KGHM).

In Poland rhenium exists in domestic copper concentrates. These concentrates are processed by KGHM Polska Miedź S.A. in three smelters, i.e., Huta Miedzi “Głogów I”, Huta Miedzi “Głogów II” and Huta Miedzi “Legnica”.

* In some countries, such as: **Iran, Mongolia** and **Chile**, only a part of rhenium from molybdenite concentrates is recovered. This is due to the lack of appropriate processing plants (roasting plants equipped with wet dust collectors).
Rhenium in Poland

In Poland rhenium can be found in copper concentrates at the level of 5 to 15 ppm

<table>
<thead>
<tr>
<th>Mine</th>
<th>Rhenium content in the ore, g/Mg</th>
<th>Rhenium content in concentrate, g/Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZG „Lubin“</td>
<td>1.22</td>
<td>8.2</td>
</tr>
<tr>
<td>ZG „Rudna“</td>
<td>1.41</td>
<td>12.1</td>
</tr>
<tr>
<td>ZG „Polkowice“</td>
<td>1.68</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Rhenium recovery by Kennecott process
Flowsheet of NH$_4$ReO$_4$ Production at KGHM S.A.
Flowsheet of metallic rhenium production

1. Preparation of $\text{NH}_4\text{ReO}_4$
2. Reduction
3. Mixing of rhenium powder
4. Pressing of rhenium powder
5. Sintering of rhenium pellets
6. Packing of rhenium pellets

$\text{NH}_4\text{ReO}_4 \rightarrow \text{H}_2 \rightarrow \text{H}_2, \text{N}_2, \text{H}_2\text{O} \rightarrow \text{waste H}_2$
Application of rhenium

- Catalysts: 83.3%
- Other: 7.4%
- Alloys and superalloys: 9.3%

http://www.mmta.co.uk/rhenium-market-overview
Application of rhenium

in production of **heat-resisting alloys and superalloys**, mechanically and thermally resistant alloys used in manufacture of rocket propulsion nozzles and rotating parts of aircraft engines as well as in power engineering equipment in manufacture of **Pt-Re catalysts** for production of lead-free high-octane petrol

**others**: as a component of catalytic systems for processes of hydrodesulphurisation, production of thermocouples, heating elements, electrodes, electrical connectors, electromagnets; as well as in organic synthesis and catalysis and medicine
The main rhenium products

- ammonium perrhenate
- perrhenic acid
- rhenium
### Application of rhenium products

<table>
<thead>
<tr>
<th>Product</th>
<th>Typical application</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonium perrhenate</td>
<td>production of rhenium metal and perrhenic acid, manufacture of Pt-Re reforming catalysts,</td>
</tr>
<tr>
<td>perrhenic acid</td>
<td>manufacture of Pt-Re reforming catalysts</td>
</tr>
<tr>
<td>rhenium metal powder</td>
<td>addition to superalloys, production of sheet, foil, strip and wire</td>
</tr>
<tr>
<td>rhenium metal briquettes</td>
<td>addition to superalloys</td>
</tr>
</tbody>
</table>
### Composition of Ni based superalloys

<table>
<thead>
<tr>
<th>Superalloy</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>Re</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX4</td>
<td>5.7</td>
<td>11.0</td>
<td>0.4</td>
<td>5.2</td>
<td>5.6</td>
<td>-</td>
<td>5.2</td>
<td>0.7</td>
<td>3.0</td>
<td>0.10</td>
</tr>
<tr>
<td>CMSX10</td>
<td>2.0</td>
<td>3.0</td>
<td>0.4</td>
<td>5.0</td>
<td>8.0</td>
<td>0.1</td>
<td>5.7</td>
<td>0.2</td>
<td>6.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Rene N5</td>
<td>7.0</td>
<td>8.0</td>
<td>2.0</td>
<td>5.0</td>
<td>7.0</td>
<td>-</td>
<td>6.2</td>
<td>-</td>
<td>3.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Rene N6</td>
<td>4.2</td>
<td>12.5</td>
<td>1.4</td>
<td>6.0</td>
<td>7.2</td>
<td>-</td>
<td>5.7</td>
<td>-</td>
<td>5.0</td>
<td>0.15</td>
</tr>
<tr>
<td>RR3000</td>
<td>2.3</td>
<td>3.3</td>
<td>0.4</td>
<td>5.5</td>
<td>8.4</td>
<td>-</td>
<td>5.8</td>
<td>0.2</td>
<td>6.3</td>
<td>0.03</td>
</tr>
<tr>
<td>UCSX8</td>
<td>2.3</td>
<td>6.0</td>
<td>3.0</td>
<td>6.0</td>
<td>8.4</td>
<td>-</td>
<td>5.8</td>
<td>0.2</td>
<td>6.3</td>
<td>0.03</td>
</tr>
<tr>
<td>TMS75</td>
<td>3.0</td>
<td>12.0</td>
<td>2.0</td>
<td>6.0</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
<td>0.10</td>
</tr>
<tr>
<td>TMS162</td>
<td>2.3</td>
<td>3.3</td>
<td>0.4</td>
<td>5.5</td>
<td>8.4</td>
<td>-</td>
<td>5.8</td>
<td>0.2</td>
<td>6.3</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Rhenium prices

Excess production based on early over expectation

Introduction of lead-free petrol

First aerospace applications

End of USSR and de-stocking

Dispute in Kazakhstan and expected demand from GTL (Gas to Liquids)

Global recession and signs of slowdown in aerospace industry

Growth of use of rhenium in single crystal blades for aerospace and industrial gas turbines

After Millensifer, Sinclair, Jonasson, Lipmann
Current price

Engelhard Industrial Bullion (EIB) Prices.

<table>
<thead>
<tr>
<th>Metal Name</th>
<th>Symbol</th>
<th>Price(USD)</th>
<th>Unit of Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>18.390</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>1262.79</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt</td>
<td>1029.00</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd</td>
<td>790.00</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Rh</td>
<td>915.00</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir</td>
<td>750.00</td>
<td>troy ounce</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Ru</td>
<td>42.00</td>
<td>troy ounce</td>
</tr>
<tr>
<td><strong>Rhenium</strong></td>
<td><strong>Re</strong></td>
<td><strong>1050.00</strong></td>
<td><strong>pound</strong></td>
</tr>
<tr>
<td>Osmium</td>
<td>Os</td>
<td>400.00</td>
<td>troy ounce</td>
</tr>
</tbody>
</table>
## Leading processors and consumers of rhenium in EU

<table>
<thead>
<tr>
<th>Country</th>
<th>Company</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>Plansee</td>
<td>powder alloy maker</td>
</tr>
<tr>
<td>France</td>
<td>Axens</td>
<td>producer of reforming catalysts</td>
</tr>
<tr>
<td></td>
<td>Alsthom Power</td>
<td>powder systems maker</td>
</tr>
<tr>
<td>Germany</td>
<td>H.C. Starck</td>
<td>producer of rhenium pellets</td>
</tr>
<tr>
<td></td>
<td>W.C. Heraeus</td>
<td>producer of rhenium pellets and powder</td>
</tr>
<tr>
<td>UK</td>
<td>Criterion Catalysts</td>
<td>producer of reforming catalysts</td>
</tr>
<tr>
<td></td>
<td>Doncasters</td>
<td>superalloy manufacturer</td>
</tr>
<tr>
<td></td>
<td>Siemens</td>
<td>consumer of rhenium alloys</td>
</tr>
<tr>
<td></td>
<td>Rolls-Royce</td>
<td>consumer of rhenium alloys</td>
</tr>
</tbody>
</table>
## Leading processors and consumers of rhenium in USA

<table>
<thead>
<tr>
<th>Company</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cannon Muskegon</td>
<td>superalloy manufacturer</td>
</tr>
<tr>
<td>BASF</td>
<td>rhenim refiner and trader</td>
</tr>
<tr>
<td>Lipmann Walton</td>
<td>supplier of rhenium pellets and APR</td>
</tr>
<tr>
<td>UOP</td>
<td>producer of reforming catalysts</td>
</tr>
<tr>
<td>GE Aircraft Engines</td>
<td>consumer of rhenium alloys</td>
</tr>
<tr>
<td>GE Medical Systems</td>
<td>consumer of rhenium alloys</td>
</tr>
<tr>
<td>GE Power System</td>
<td>producer of reforming catalysts</td>
</tr>
</tbody>
</table>
Recycling situation

Recycling of rhenium from waste materials covers mainly:

- spent bi-metallic catalysts,
- scrap from metallic rhenium production – mill scrap
- waste formed during mechanical processing of superalloy products.
- engine revert – end-of-life gas turbine scrap

Only rhenium contained in catalysts is systematically recovered, but rhenium from this source is fully used up in preparation of new catalysts (catalyst regeneration loop) and data covering production volume and recovery methods are not published.
Rhenium recycling from metallic scrap represents over 10% of the total global rhenium output (ca. 10t) that is estimated on 50-60 Mg/year.
Recycling of catalysts

- Closed loop system
- Catalysts are regenerated several times
- Afterwards they are recycled
- Recycling with very low losses
- Heraeus Precious Metals is the leading company
- About 15 t of Re recycled in that way
Spent platinum-rhenium reformer catalysts

Technologies available for recycling of the spent platinum-rhenium catalysts.
The document discusses the dissolution of alumina catalysts and the recovery of rhenium and platinum. It outlines two methods:

**I method**
- Complete dissolution of the alumina substrate:
  - During complete dissolution of the alumina substrate, sulfuric acid may be used for dissolution of alumina, rhenium, and, to some extent, platinum. As an alternative to sulfuric acid, sodium bicarbonate may also be used as a lixiviant.
  - Rhenium-rich solution is separated from the platinum-containing residue and aqueous aluminum using ion exchange.
  - Rhenium is eluted from the organic amine resin by way of hydrochloric acid addition. After elution, the rhenium-rich eluate is neutralized using ammonium hydroxide.
  - Solution is then evaporated to form a supersaturated solution, and cooled to allow for crystallization of ammonium perrhenate.
  - After continued redissolution and recrystallization, a high-purity ammonium perrhenate precipitate is produced.

**II method**
- Selective dissolution and recovery of rhenium and platinum:
  - By calcination of the catalyst at temperatures up to 1,150°C, the γ-Al2O3 undergoes a phase transition to the chemically stable α-Al2O3 phase, lowering the dissolution of the alumina catalyst.
  - The rhenium can then be selectively leached in concentrated (5 mol/L) sulfuric acid solutions containing sodium chloride and a potassium persulfate oxidant.
  - Rhenium solution is separated from the platinum by using ion exchange.
  - Solution is then evaporated to form a supersaturated solution, and cooled to allow for crystallization of ammonium perrhenate.
Recycling of mill scrap

- Material from production
- Grindings, turnings etc.
- Re content above 1%
- Closed loop
- Recovery of 5-10t Re per year
Recycling of engine revert

- End of life gas turbine parts
- Growing with growing use of superalloys
- Melting after removal of coatings and bonding agent
- High quality superalloy meltstock
- Rolls-Royce, GE – major players
- Recovery of about 6t Re per year
SUPERALLOYS AND ALLOY SCRAPS RECYCLING
**W-Re scrap**

W-Re scrap may be recycled via an oxidative pyrometallurgical roasting technique, the scrap is roasted at 1,000°C, under an oxidizing atmosphere to produce rhenium heptoxide, which is subsequently condensed in the cooler part of the tube furnace, material is then sent for digestion in water, aqueous rhenium is subsequently precipitated as potassium perrhenate upon the addition of potassium chloride - potassium perrhenate is filtered and further purified via continued dissolution and recrystallization, the salt is dried and sent for reduction under a hydrogen atmosphere at approximately 350°C.
Rhenium recovery in Poland from superalloy scrap IMN

superalloy scraps

Segregation

waste < 30mm

Chemical dissolution

Electrodisolution

waste ≤30mm

Filtration

residue (Ta, W, Mo and/or Zr)

Recovery of rhenium by IX

ammonium perrhenate

solution
Superalloys scrap – H.C. Starck

Superalloys are digested in a molten salt melt containing NaOH, Na$_2$CO$_3$, and Na$_2$SO$_4$ at temperatures of 850-1100°C in a directly fired rotary kiln, in addition to this, oxidizing agents such as nitrates and peroxides of the alkali metals are added, the melt from this process is then cooled and sent to a comminution process for size reduction, the material is then leached using water as the lixiviant to dissolve the 6 and 7th group elements present in the superalloy, this slurry is then filtered to separate the insoluble Co, Ni, Fe, Mn and Cr from the leach liquor, magnetic separation is then applied to the insoluble components for further separation and concentration, the pregnant leach solution is sent to an ion exchange step.
the baskets containing the superalloy scrap are fed to a polypropylene electrolysis cell containing a 18% HCl solution, the electrolytic dissolution is carried out for 25 hours at a frequency of 0.5 Hz, current of 50 amps, voltage of 3-4 V and a temperature of 70° C, the remaining scrap is then filtered from the pregnant solution and sent for further dissolution in sodium hydroxide/peroxide solution. After completion, this filtrate is sent to ion exchange for the recovery of rhenium and molybdenum, rhenium is recovered using the ion exchange processes.
**SOURCES of Re outside EU to EU**

**Primary concentrate**
- Chile (26.0 t)
- USA (8.5 t)
- Other (3.7 t)

**Recycling**
- Reforming catalysts (USA) (4.0 t)
- Aircraft engine scrap (USA) (6.0 t)
- Recyclers (USA, Russia, Canada) (5.0 t)

**Balanced 0.7-23.9 t**

**PROCESSING PLANTS**

**INTERMEDIATE PRODUCTS**
- Rhenium metal
- Perrhenic acid
- Ammonium perrheneate

**END-USE PRODUCTS**
- Superalloys (83%)
- Catalysts (9.2%)
- Other (7.8%): thermocouples, heating elements, electrodes, electrical connectors, electromagnets

**AIRCRAFT ENGINE SCRAP**

**Extractive metallurgy**

**Recycling**
- Collecting & sorting
- Processing

**SOURCES of Re inside EU**

**Ore mining & concentrating**
- Poland

**Primary concentrate**
- Poland (7.8 t)

**Recycling**
- Industrial waste (Germany, Estonia) (6.0 t)
- Reforming catalysts (Germany) (6.0 t)

**Balanced 0.7-23.9 t**

**PROCESSING PLANTS**

**INTERMEDIATE PRODUCTS**
- Rhenium metal
- Perrhenic acid
- Ammonium perrheneate

**END-USE PRODUCTS**
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**AIRCRAFT ENGINE SCRAP**

**Extractive metallurgy**

**Recycling**
- Collecting & sorting
- Processing

**Legend**

Available resources in EU
Flows of Re used in EU

**Export 1,483 t products (Re t)**

**Current demand 65 t**

**END-USE BY INDUSTRIES**

- Aerospace (59%)
- Gas turbines (12%)
- Automotive (5%)
- Tools
- Oil/gas
- Chemical
- Medical
- Pharmaceutical industry
- Other
Final comments

- Currently the supply exceeds the demand
- There is already some spare production capacity in Re recycling from metallic scrap as confirmed by fluctuation in the level of secondary production of Re in recent years (12 – 10 t).
- Some material stockpiled
Thank you very much for your attention!