MSP-REFRAM Final Conference
Rhenium

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1. Overview of Rhenium market

Global Rhenium production from ore from 1970 to 2012
## 1. Overview of Rhenium market

### Global Rhenium production in 2012-2016

<table>
<thead>
<tr>
<th>Country</th>
<th>Rhenium production, tonnes</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>China</td>
<td>-</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>
Consumption of Rhenium

Rhenium Consumption

- Aerospace 78%
- IGT 6%
- Catalyst 9%
- Others 7%

*Others: heating elements, electrical contacts, electrodes, electromagnets, vacuum and X-ray tubes
1. Overview of Rhenium market
1. Overview of Rhenium market

Rhenium market price

[Graph showing the price of Rhenium from 2003 to 2017 with a peak around 2008 and a decline afterwards.]
Overview of Rhenium Production

- **Molymet – Molycorp, Chile, 1975:** controlling the 50% of rhenium primary production.
  - Molymex S.A., 1994, Sonora, Mexico
  - Chemiemetall GMBH, 2001, Biterfield, Sajonia-Anhalt, Germany
  - Sadaci N. V., 2003, Ghent, Belgium
  - Luoyang High-Tech – 50% Joint Venture, ChinaMoly, 2010

- **Freeport McMoRan Inc., Arizona, USA**

- **KGHM, Poland, 1949:** Glogow I and Glogow II smelters, 1968.

- **Redmet, Kazakhstan, 1973**

- **Navoi Mining&Metallurgy Combinat, Uzbekistan**

- **Uralelectromed is the core enterprise of Ural Mining and Metallurgical Company, Rusia, 1934.**

- **Pure Ironworks, Yerevan - German Cronimet Holding, Armenia.**
2. Innovation on Rhenium metallurgy

- Hydrometallurgical extraction of Rhenium from secondary resources: e.g. KENNECOTT Process; KGHM Process and many other experimental (laboratory or pilot) hydrometallurgical processes (e.g. rhenium recovery from copper concentrates or molybdenite roasting).

- Pyro-metallurgical extraction of Rhenium from secondary resources (many pyro-processes using the volatility of certain rhenium compounds, e.g. rhenium present in the molybdenum concentrate is oxidized to rhenium heptoxide).
Rhenium recovery during copper production

Chalcopyrite ore

Crushing and grinding

Bulk flotation → Tailings
Concentrate: 25–35% Cu, 0.02–2% MoS₂, 700 ppm Re

Steaming

Selective flotation

Chalcopyrite concentrate

Purification, e.g., leaching → Cu²⁺

MoS₂

Roasting → MoO₃

Dust collector → Re₂O₇

SO₂
Rhenium recovery by Kennecott process
Rhenium recovery by KGHM process, Glogow, Poland
Solvent – Extraction
An alternative process

- Electrosmelting of copper concentrate
- Volatalization of rhenium heptoxide (Re₂O₇)
- Scrubbed with sulfuric acid
Alternative Methods: Pressure oxidation

US Patent 0263490A1

pH = 7
T = 80 – 110°C
Alternative Methods: MoRe leach process

MoS$_2$ + 9NaClO + 3H$_2$O = MoO$_4^{2-}$(aq) + 9NaCl + 2SO$_4^{2-}$(aq) + 6H$^+$

ReS$_2$ + 9.5NaClO + 2.5H$_2$O = ReO$_4^-$ (aq) + 9.5NaCl + 2SO$_4^{2-}$(aq) + 5H$^+$
Alternative resources

✓ In situ leaching solution of uranium ores; 0.28 – 0.5 mg/dm³ Re.
✓ Uranium sorption filtrates; 840 g/t
✓ Anionite after uranium elution; 2.5 – 3 mg/dm³
✓ Mother liquors from uranium precipitation; 2 – 7.6 mg/dm³

➢ The rhenium content varies:
✓ in the wash sulfuric acid from 100 to 250 mg/L,
✓ in the electrostatic dust: from 140 to 320 g/t,
✓ in the slime from 400 to 900 g/t.
3. Secondary sources of Rhenium

* Treatment scheme selection and preparation method for rhenium recovery from particular industrial residue materials depends primarily on the physical and chemical form in which the residue exists.

**Industrial residues for possible Re recovery.**

<table>
<thead>
<tr>
<th>Name of residue source</th>
<th>Main industry</th>
<th>Estimated content of Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhenium containing titania spent catalyst</td>
<td>Hydrogenation reactions (reforming of naphtha). Preparation of hydrocarbons from synthesis gas via the Fischer-Tropsch process</td>
<td>1.20%</td>
</tr>
<tr>
<td>Spent platinum-rhenium reformer catalysts</td>
<td>Petroleum industry</td>
<td>-</td>
</tr>
<tr>
<td>Dust from exhaust gas</td>
<td>Mo concentrate roasting process</td>
<td>-</td>
</tr>
<tr>
<td>Residue materials</td>
<td>Residue materials from the old sulphur abandoned mine</td>
<td>1.34 – 3.40 ppm</td>
</tr>
<tr>
<td>Super-alloys</td>
<td>Jet engines and gas turbines of power plants</td>
<td>≥ 3.0%</td>
</tr>
</tbody>
</table>
Life cycle of Rhenium

Mining of copper-molibdenite

Reprocessing from primary source

Ammenium Perrhanate (APR)

Catalyst

Collection

Recycling

50 – 60 tonnes Re

5 – 7 tonnes

40 – 50 tonnes

Others

Super-Alloys

5% 10%

Recycling

Collection

Date: 20/03/2017
4. Mineral/waste processing of Rhenium

- **Rhenium containing titania spent catalysts**: e.g. ExxonMobil Research and Engineering Company developed and patented the method for recovering rhenium from a titania-supported, rhenium-containing catalyst by treating the catalyst in the reduced form with an acid in an amount and for a time sufficient to dissolve the rhenium without dissolving the support.

- **Spent platinum-rhenium reformer catalysts**: e.g technologies available for recycling of the spent platinum-rhenium catalysts can be roughly divided into two groups: one incorporating decomposition of catalyst aluminum oxide base, the other – selective extraction of rhenium without the base decomposition. In the former, the catalyst is decomposed by chemical (acid or base leaching) and thermochemical methods (sintering with base)
4. Mineral/waste processing of Rhenium

- **Residues from old abandoned sulphur mine:** e.g. Rhenium can be found in residues resulting from a long-term mining, particularly of sulphide ore deposits. For example the waste materials from the old sulphur factory at the abandoned mine of São Domingos (Iberian Pyrite Belt, Southeast Portugal).

- **Dust from exhaust gases:** e.g. Significant amounts of rhenium compounds evaporate during molybdenum roasting process. The dust in exhaust gases can be collected with scrubbers and then be processed for recovery of rhenium.

- **Super-alloys:** Main amount of rhenium is used in the aerospace and industrial gas turbine applications. These alloys consist of nearly 3w% rhenium. Thus super-alloys are the significant secondary source, and suitable collection and pretreatment methods should be developed.
Recycling of rhenium catalysts

Technologies available for recycling of the spent platinum-rhenium catalysts.
Super alloys (Re containing alloys) recovery

1. Re containing alloy waste
   - Sintering with embrittment agent
   - Crashing and milling
   - Selective Re recovery

   - Remelting of the waste

   - Oxidation-thermal methods
   - Hydrometallurgical methods

   - High temperature oxidative distillation Re$_2$O$_7$
   - Thermochemical Separation

   - Electrochemical leaching
   - Chemical leaching
5. Future Trends

- **Alternative sources, processes and products**

  - The Russians have noticed that in the volcano on Iturup island rhenium can be found and it leaves the inside of the Earth together with the gases.

  - Volcano exhaust gases, ReCl₅ and ReF₅

  - It was found that they contain a considerable amount of Re (0.5 – 2.5 g/t)

  - The resource estimation is around 20 t/yr.

  - A method was developed to catch the Re by sublimate formaton on natural zeolite Kudriavy Volcano

Rheniite, ReS₂
5. Future Trends

- Alternative sources, processes and products

Rhenium diboride, ReB₂
Superhard material

- Several Re (I) organometallic compounds have been shown to be toxic to various cancer cell lines.

- Rhenium-188-HEDP, radiopharmaceutical applications.
5. Future EU Market

- Demand for rhenium is showing growth at the present because of demand for engines in both commercial and military jets.
- This is forecast to continue to rise over the next twenty-five years.
- The use of rhenium catalysts in reforming is also growing but at a lower rate.
- The rhenium annual EU demand for advanced fossil fuel power generation forecasted by 2020 and 2030 is 0.6 tonnes/year, which represents one of the greatest material requirement.

- Recycling of the metal has grown considerably over the past several years.
- Rhenium secondary production takes place in Germany (Buss & Buss Spezialmetalle, H.C. Starck and Heraeus Precious Metals).
- Secondary rhenium is also recovered in Estonia (Toma Group).
- It is considered that, despite some worries within the industry as to future supply, "primary and secondary resources are sufficient to allow producers and potential producers to keep pace with demand"
<table>
<thead>
<tr>
<th>Topic</th>
<th>Barrier</th>
<th>Potential Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary source – Policy</td>
<td>Lack of information/investigation of existing and/or new deposits in the EU</td>
<td>Promote exploration at EU level</td>
</tr>
<tr>
<td>Secondary source – Policy</td>
<td>Tailings recovery from existing/old mines: even more difficult than new mines if they have been already restored as in new mines tailings are nowadays minimized</td>
<td><em>Environmental studies. The activity should solve instead of create an environmental problem to demonstrate its feasibility.</em></td>
</tr>
<tr>
<td>Market</td>
<td>Lack of effective logistic system of Re containing spent materials. They are not segregated, which hampers their further processing.</td>
<td><em>More efficient collection, sorting logistics and cleaning infrastructure for EoL products, establishing a stable supply source</em></td>
</tr>
<tr>
<td>Technology</td>
<td>Limited technology to recover the Re from super-alloys</td>
<td>R&amp;D, pilot scale trials and feasibilities</td>
</tr>
</tbody>
</table>
6. Conclusion

- Demand can increase in the next decade due to the increasing need to the super-alloys.
- It is expected that supply and demand relation will be balanced.
- Potential mines and developing more effective processes.
- Innovative recovery solutions to attract industrial interest.
- Basis of the rhenium management:
  - Establish long-term cooperation.
  - Encourage internal sources.
  - Promote recycling.
  - Support R&D and education.
Thank you very much for listening!