Recovery of metals from low grade primary and secondary resources – IMN experience.

Andrzej Chmielarz, Witold Kurylak
Instytut Metali Nieżelaznych (Institute of Non-Ferrous Metals, IMN)

- state-owned Institute established in 1952
- one of the largest research institutes in Poland (≈450 employees)
- the main research centre of the Polish non-ferrous industry
Instytut Metali Nieżelaznych (Institute of Non-Ferrous Metals, IMN)

Complex research works conducted in 14 research departments.
From laboratory, through piloting and industrial tests to implementation, experimental production, technical services and consulting.
Studies into all non-ferrous metals, especially Cu, Al, Zn, Pb and by-product ones.
Areas of expertise:

- processing of non-ferrous ores and other mineral resources
- pyrometallurgy
- hydrometallurgy
- analytical chemistry
- processing of metals and alloys
- materials engineering – new materials
- processing of scrap and waste
- environmental protection
- chemical power sources
Agenda

- **IMN’s activities within H2020 projects:**
  - Biomore
  - ADIR
  - Metgrow+
  - Intmet
  - Rigat
- **Other technologies for recovery of metal value from low grade resources.**
  - Zn/Pb concentrate from flotation tailings
  - Li-ion batteries treatment process
  - W recovery
New Mining Concept for Extracting Metals from Deep Ore Deposits using Biotechnology
acronim: **Biomore**

The BioMOre design concept:
indirect bioleaching process, whereby acidic ferric iron-rich leach liquors are injected through boreholes into a fractured ore deposit and – after metals stripping - regenerated in surface bioreactors.
View of the final reactor after drilling and blasting.
The completed pilot plant - solution bio-regeneration and circulation system.
### IMN Activities

#### WP4 - Hydrometallurgical aspects

<table>
<thead>
<tr>
<th>Select cost effective flowsheet</th>
<th>State-of-the-art analysis of existing techniques for metals recovery – draft flowsheets preparation</th>
</tr>
</thead>
</table>
| Preparation of leachate solutions, sulphide/hydroxide precipitation (Cu, Ni, Zn, Co), removal of Fe, As, Mg, Re recovery | • Preparation of laboratory solutions by leaching of the ore  
• Determination of relations between leaching conditions, raw material composition and composition of the solution.  
• Develop techniques and parameters for sequential precipitation of metals (Cu, Ni+Co, Zn) with H$_2$S or other suitable precipitation agents.  
• Preliminary evaluation of potential for recovery of other by-product metals (including magnesium). |
H$_2$SO$_4$ & Fe(III) dependent leaching - summary graphs
Next generation urban mining - Automated disassembly, separation and recovery of valuable materials from electronic equipment

acronim: ADIR

A machine is worked out being capable to selectively disassemble printed circuit boards and mobile phones with short cycle times to gain sorting fractions containing high amounts of valuable materials. The concept is based on image processing, robotic handling, pulsed power technology, 3D laser measurement, real-time laser material identification (to detect materials), laser processing (to access components, to selectively unsolder these; to cut off parts of a printed circuit board) and automatic separation into different sorting fractions.
<table>
<thead>
<tr>
<th>Requirement analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical analysis</strong></td>
</tr>
</tbody>
</table>

**Process development**

| Metallurgical treatment of selected components with valuable materials | Metallurgical proces routes are studied which allow the recovery of high-value materials from the sorting fractions. Draft flowsheets preparation. |

**Set-up of modules**

| Metallurgical characterisation of pre-treated components | Pyro- and hydrometallurgical tests on lab scale to be carried out to evaluate the processing routes for recovering the high-value components from the expected fractions. |

**Field tests**

| Recovery of valuable materials based on the sorted fractions | The fractions obtained in the field tests will be treated chemically and metallurgically to demonstrate the processing route worked out to recover the high-value materials. The test will be conducted in the demo-scale furnaces and reactors. |
I. Leaching
II. Filtration
III. Pb precipitation
IV. Filtration
V. Au extraction
VI. Au reduction from org. phase
VII. Pd sorption
VIII. Cu, Ni precipitation
Non-precious metals concentrate

Precious metals recovery from scrap of electronic parts

- HCl, oxidizer
- Plastic, AgCl, Sn
- H₂SO₄
- PbSO₄
- C₂H₂O₄
- Na₂CO₃, NaOH
- Au 4N powder
- Pd concentrate
IX. Ag reduction

Leaching residue from electronic scrap

NaOH, N₂H₄·H₂O

XI. Ag dissolution

HNO₃

XII. Filtration

Residue for Pb, Sn recovery

XIII. Ag cementation

Cu_{met}

XIV. Raw Ag filtration

H₂SO₄

XV. Pb precipitation

effluent

Raw silver for refining

Silver recovery
Neodymium recovery

Nd-containing raw material

I. Material preparation

II. Leaching

III. Nd salt precipitation

IV. Desulfurisation

V. Calcination

Nd oxide concentrate

Remaining metals recovery

Acid

NaOH

NaOH
**Metal Recovery from Low Grade Ores and Wastes Plus**

Acronym: **METGROW PLUS**

METGROW+ will address and solve bottlenecks in the European raw materials supply by developing innovative metallurgical technologies for unlocking the use of potential domestic raw materials.

*The remaining anticipated economic resources of ’Szklary’ deposit were estimated at 14.64 million tones of ore.*

**Polish laterite ore composition, % (IMN analysis)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Zn</th>
<th>P</th>
<th>Ga</th>
<th>Ge</th>
<th>Al</th>
<th>In</th>
<th>Co</th>
<th>Si</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0001</td>
<td>0.0007</td>
<td>0.41</td>
<td>&lt;0.01</td>
<td>0.0040</td>
<td>0.0015</td>
<td>&lt;0.001</td>
<td>0.81</td>
<td>&lt;0.0001</td>
<td>0.015</td>
<td>17.89</td>
<td>10.6</td>
</tr>
<tr>
<td>Mn</td>
<td>0.14</td>
<td>&lt;0.01</td>
<td>1.22</td>
<td>0.011</td>
<td>0.070</td>
<td>0.0014</td>
<td>0.50</td>
<td>0.097</td>
<td>8.6</td>
<td>0.038</td>
<td>0.0001</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>
Feed preparation (grinding)

Acid leaching

Neutralization

Precipitation of metal hydroxides

Mixed hydroxides concentrate Ni-Fe-Co

H₂SO₄

MgO

Fe residue for disposal

Iron removal

Solvent extraction

Crystallization

Electrowinning

Ni ore

water
### IMN Activities

<table>
<thead>
<tr>
<th></th>
<th>Lab scale</th>
<th>Up-scaling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pre-treatment</strong></td>
<td>√ Tests of: grinding, sulphidation, flotation</td>
<td>√ Grinding</td>
</tr>
<tr>
<td>**Atmospheric acid</td>
<td>√ Tests of: acid leaching ($\text{H}_2\text{SO}_4$, $\text{HCl}$ solutions), filtration, precipitation (eg hydroxides/carbonates)</td>
<td>√ Leaching upscaling (1-3m³ reactor, chamber-membrane filtration press)</td>
</tr>
<tr>
<td>leaching and PLS</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Heap leaching</strong></td>
<td>√ Heap leaching tests in column</td>
<td>X</td>
</tr>
<tr>
<td><strong>Solvent extraction</strong></td>
<td>√ Best extractant and SX process conditions selections (SX isotherms, pH, temperature) (Ni, Co, Mn, Cr)</td>
<td>√ pilot-scale, continues flow tests (combination of 2dm³ - mixers-settlers instalation)</td>
</tr>
<tr>
<td><strong>Metal electrodeposition</strong></td>
<td>√ Best electrodeposition process conditions selections (Ni)</td>
<td>X</td>
</tr>
<tr>
<td><strong>Flowsheet validation</strong></td>
<td>X</td>
<td>√ Validations tests</td>
</tr>
</tbody>
</table>
Integrated innovative metallurgical system to benefit efficiently polymetallic, complex and low grade ores and concentrates

acronym: INTMET

The INTMET approach represents a unique technological breakthrough to overcome the limitations related to difficult low grade and complex ores to achieve high efficient recovery of valuable metals (Cu, Zn, Pb, Ag) and CRM (Co, In, Sb).
Main objective of INTMET is applying on-site mine-to-metal hydroprocessing of the produced concentrates enhancing substantially raw materials efficiency thanks to increase Cu+Zn+Pb recovery vs. existing selective flotation.
### Valorisation of tailings, wastes and effluents

<table>
<thead>
<tr>
<th>Tailings and wastes pre-concentration:</th>
<th>Flotation focused on production of collective non-ferrous metals concentrate from tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravitational method for pyrite concentrate separation</td>
<td></td>
</tr>
<tr>
<td>Gypsum purification and making by-products:</td>
<td>Crystallization of calcium sulphate from the mixture of spent acids (from Polish copper &amp; zinc smelters and INTMET partners plants)</td>
</tr>
</tbody>
</table>

### Development of integrative pressure leaching process

| Ag & Pb and other metals recovery | Close-looped and completely effluent free process of Pb recovery from solid residue produced in pressure leaching using thriethylenetetramine |
Cu ore

**Leaching** (bio, atmospheric, pressure)
- Acidic effluents
- Neutralization
  - CaSO₄·2H₂O crystallization

**Solid waste** (from pressure leaching)
- Amine leaching
- Pb recovery

**Wastes**
- Flotation
  - Collective concentrate Cu, Zn, Pb
- Gravitational method
  - Pyrite concentrate

**Flotation**

**CaCO₃**
Lead recovery from PbSO₄ containing feed.
Technology for recovery of In, Ge & Sn from lead bearing alloys generated in zinc refinement for direct implementation in industrial practice.

**Acronym:** RIGAT

**Project objective:** To develop technology for recovery of tin, indium and germanium from polymetallic alloys formed in production of zinc and lead by ISP method.
<table>
<thead>
<tr>
<th>Alloys</th>
<th>Mass</th>
<th>Composition [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[tpa]</td>
<td>In</td>
</tr>
<tr>
<td>PbInSn</td>
<td>250</td>
<td>0.25</td>
</tr>
<tr>
<td>PbSnCuGeIn</td>
<td>30</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**RIGAT**

[Image of alloy bars]
Up-scaling of technologies for recovery of In and Ge from the alloys:

**PbSnIn alloy**

- Zinc removal in the presence of NaOH and NaNO3
- Thermal oxidising with air leading to formation of crude lead and drosses
- Screening of drosses, to separate droplets of lead
- Leaching of drosses in HCl solution, leaving Pb in the residue
- Collective precipitation of metals hydroxides with NaOH
- Reverse leaching (H2SO4) of the concentrate, to produce indium enriched solution and tin based residue
- Precipitation of In with NaOH and its smelting to In61Sn37 alloy
- Smelting of tin concentrate to Sn85In12Pb3 alloy
Up-scalling of technologies for recovery of In and Ge from the alloys:

**PbSnCuInGe alloy**
- thermal oxidising with air producing PbSnAg alloy for further treatment in lead refinery and polymetallic oxidised phase (drosses),
- leaching the drosses in sulphuric acid; after solid/liquid separation Cu, Zn, In, Ge are found in the liquid phase, while Pb, Sn and Ag in the residue
- precipitation or electroprecipitation of copper
- precipitation of indium concentrate (e.g. via cementation on Zn)
- Ge precipitation in a form of tannin concentrate (tannin, oxalate solution)
Technology for production of Zn/Pb bulk concentrate from flotation tailings at ZGH BOLESŁAW

Composition of tailings: **1,37 % Zn, 0,96 % Pb**
Bulk concentrate: **48,0 % Zn, 8,0 % Pb**
Other developments of the IMN

Plant capacity: 2 mln Mg/y
Other developments of the IMN

Technology and pilot plant (100kg/h) for mechanical processing of Li-ion and NiMH batteries at Inneco.

Freezing  Grinding  Roasting  Separation
Other developments of the IMN

Technology and plant for tungsten recovery from scrap of Cu-W alloys (W concentration 50 – 70%)

Technology consists of:
1. Roasting (600°C), milling and sieving
2. Alkaline leaching of roasted fraction (<100µm)
3. Evaporation and crystallization of Na$_2$WO$_4$
4. Conversion into H$_2$WO$_4$
5. Cu recovery from the leach residue
Other developments of the IMN

Technology and plant for tungsten recovery from scrap of Cu-W alloys

<table>
<thead>
<tr>
<th>H₂WO₄</th>
<th>W, %</th>
<th>Cu, %</th>
<th>Na₂WO₄</th>
<th>W, %</th>
<th>Cu, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57,95</td>
<td>0,21</td>
<td>A</td>
<td>55,30</td>
<td>0,089</td>
</tr>
<tr>
<td>B</td>
<td>57,35</td>
<td>0,067</td>
<td>B</td>
<td>59,60</td>
<td>0,017</td>
</tr>
<tr>
<td>C</td>
<td>60,60</td>
<td>0,095</td>
<td>C</td>
<td>55,40</td>
<td>0,120</td>
</tr>
<tr>
<td>D</td>
<td>56,00</td>
<td>0,083</td>
<td>D</td>
<td>56,20</td>
<td>0,360</td>
</tr>
<tr>
<td>E</td>
<td>50,40</td>
<td>0,074</td>
<td>E</td>
<td>60,20</td>
<td>0,041</td>
</tr>
<tr>
<td>F</td>
<td>59,00</td>
<td>0,073</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Thank you for your attention!

Instytut Metali Nieżelaznych
ul. Sowińskiego 5
44-100 Gliwice

tel. + 48 32 238 02 00
fax + 48 32 231 69 33
e-mail: imn@imn.gliwice.pl
www.imn.gliwice.pl