Development of Mitsubishi Continuous Process for Copper Extraction

Moto Goto
President Director
PT. Smelting
History of Copper

- Copper is one of the oldest metal
- 6,000-8,000 years ago in the East Europe and the Middle East
- 4,000 years ago in China
- 2,000 years ago in Japan
“DOTAKU” Unearthed
“DOTAKU” Has a BABY
“DOTAKU”
“WADO-KAICHIN”
Buddha in NARA
Smelting Process in 15th Century in Japan
Copper History in 16th Century

- Mining and smelting was improved in Germany and Japan
  - High grade copper ore
  - Good quality of wood as fuel
  - Good quality clay for hearth making
  - Blasting technology like hand bellows and piping
Copper History in 17\textsuperscript{th}-19\textsuperscript{th} Century

- Leading countries of copper production are Germany, United Kingdom, Russia and Japan
- A few thousand tons of copper was produced in Japan at the end of 17th century
Rapid Increase of Copper Consumption

• Copper consumption in the world
  – Year 1,800: 10,000 tons
  – Year 1,900: 500,000 tons
  – Year 2,000: 15,000,000 tons

• UK was a leading producer
Copper History in 19th-20th Century

• Big copper deposits were found
  – In North America, South America, and Africa. <1% Cu in deposit
  – 4-5% required to extract copper economically

• New technology
  – Open pit & Flotation
Copper History in 20th Century

- New copper mines were found in Asia
  - Indonesia, Philippines, Malaysia, Papua New Guinea
Comparison between Steel and Copper Industry

<table>
<thead>
<tr>
<th></th>
<th>Steel</th>
<th>Copper</th>
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<tbody>
<tr>
<td>Production in Japan</td>
<td>80M tons</td>
<td>1.3M tons</td>
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<tr>
<td>Metal content in Ore</td>
<td>60%</td>
<td>1%</td>
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<tr>
<td>Gangue</td>
<td>2.2 times</td>
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New Technology

• Blast furnace
  – At middle of 19th century

• Electrolytic refining
  – In 1877 in USA

• Reverberatory furnace
  – In 1920’s in USA

• Outokumpu Flash furnace
  – In 1949 in Finland
# Grasberg Concentrate

## Conc. Com position

**2000 Avg.**

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<tr>
<th>Element</th>
<th>Concentration</th>
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<tr>
<td>Au</td>
<td>g/T</td>
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<tr>
<td>Ag</td>
<td>g/T</td>
</tr>
<tr>
<td>Cu</td>
<td>%</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
</tr>
<tr>
<td>S</td>
<td>%</td>
</tr>
<tr>
<td>Pb</td>
<td>%</td>
</tr>
<tr>
<td>Zn</td>
<td>%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
</tr>
<tr>
<td>As</td>
<td>%</td>
</tr>
<tr>
<td>Sb</td>
<td>%</td>
</tr>
<tr>
<td>Bi</td>
<td>%</td>
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Reverberatory Furnace
Outokumpu Flash Furnace
Conventional Process
Now in Use

• Smelting furnace
  – Electric furnace, Outokumpu flash furnace, Inco flash furnace, Noranda reactor

• with batch-wise converters
  – Peirce-Smith converter
Inco Flash Furnace
Peirce-Smith Converter

- Off-gas
- 'Gaspé' tuyere puncher
- Blast
- Blast (Air or O₂ enriched Air)
Peirce-Smith Converter

Charging

Matte

Blowing

Off-Gas

Skimming

Copper or Slag

Hood
Hood for PS Converter
Gas Condition

Batchwise

Continuous
Continuous Converting

• In 1959 (Pioneer)
  – at Balhashi in Kazakhstan then in Szekoslovakia

• In 1960’s
  – Worcra process in Australia
  – Noranda process in Canada
  – Mitsubishi process in Japan
Worcra Process
Noranda Process
Mitsubishi Process

• Pilot plant of Mitsubishi process by 72T/D in 1968
• Basic idea
  – Smelting and converting in separate furnace (Two steps)
  – Transportation through launders
  – Top blow lances blowing and feeding
Furnace Arrangement of Mitsubishi Process

- S-Furnace
- C-Furnace
- CL-Furnace
- Lances for Concentrate
- C-Slag
- Blister
- Electrodes
- Matte
- Launder
- Anode Furnaces
- Hazelett Caster
- Mannesmen Shear
- Anodes
- Lances
Cu-Fe-S Phase Diagram
<table>
<thead>
<tr>
<th></th>
<th>Onahama</th>
<th>Gresik</th>
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<td>15</td>
<td>66</td>
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<tr>
<td>Ag</td>
<td>105</td>
<td>134</td>
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<tr>
<td>Cu</td>
<td>43.4</td>
<td>68.58</td>
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<tr>
<td>Pb</td>
<td>0.53</td>
<td>0.14</td>
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<tr>
<td>Zn</td>
<td>1.08</td>
<td>0.13</td>
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<tr>
<td>Fe</td>
<td>26.4</td>
<td>8.47</td>
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<tr>
<td>S</td>
<td>26.1</td>
<td>22.15</td>
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Semi-Quantitative Representation
Alternatives for Continuous Process

- **Single reactor**
  - counter-current plug flow is approximated
- **At least two reactor**
  - one to produce discard slag and one to produce blister
- **Single reactor**
  - Attempt to produce discard slag is abandoned
Difficulties of Direct Extraction

- Insufficient copper recovery from slag
- Poor minor element elimination
## Minor Element Recovery

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<th>Two Steps</th>
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<tr>
<td><strong>Dust Treatment</strong></td>
<td>Separate</td>
<td>Separate</td>
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<tr>
<td><strong>C-Slag Treatment</strong></td>
<td>Separate</td>
<td>Separate</td>
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</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>One Step</th>
<th>Two Steps</th>
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<tbody>
<tr>
<td>Pb</td>
<td>13%</td>
<td>11%</td>
</tr>
<tr>
<td>Zn</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>As</td>
<td>15%</td>
<td>3%</td>
</tr>
<tr>
<td>Sb</td>
<td>31%</td>
<td>14%</td>
</tr>
<tr>
<td>Bi</td>
<td>14%</td>
<td>7%</td>
</tr>
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</table>
Advantage of Injection Smelting

• Rapid melting and chemical reaction
• Small mechanical dust generation
• Low copper content in slag
• High oxygen utilization
Advantage of Top Blow Lance

- Possible to replace during operation
- Reduce damage of refractory
- Campaign life of Mitsubishi Converting furnace is longer than that of PS converter
PS Converter Operation

- Two different stage operation
  - Slag blow stage: oxidation of matte to produce white metal, iron silicate slag and off gas
  - Copper blow stage: oxidation of white metal to produce blister copper and off gas
Reactions in the Slag Blow Stage

- \(2\text{FeS} + 3\text{O}_2 = 2\text{FeO} + 2\text{SO}_2\)
- \(2\text{FeO} + \text{SiO}_2 = 2\text{FeOSiO}_2\)
- \(3\text{FeS} + 5\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{SO}_2\)
Reactions in the Copper Blow Stage

- $\text{Cu}_2\text{S} + \text{O}_2 = 2\text{Cu} + \text{SO}_2$

- $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6\text{Cu} + \text{SO}_2$
Reaction at C Furnace

- $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6\text{Cu} + \text{SO}_2$
- $7\text{Cu}_2\text{O} + 2\text{FeS} = 14\text{Cu} + \text{Fe}_2\text{O}_3 + 2\text{SO}_2$
- $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$
- $4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O}$
- $10\text{Cu}_2\text{O} + 3\text{FeS} = 20\text{Cu} + \text{Fe}_3\text{O}_4 + 3\text{SO}_2$
### Blister and Slag Composition

<table>
<thead>
<tr>
<th></th>
<th>Blister Copper</th>
<th>Slag</th>
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<tr>
<td></td>
<td>C-furnace</td>
<td>PS converter</td>
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<tr>
<td>Cu</td>
<td>98.24%</td>
<td>98.60%</td>
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<tr>
<td>Pb</td>
<td>0.292</td>
<td>0.244</td>
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<tr>
<td>Zn</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Fe</td>
<td>0.002</td>
<td>0.039</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.29</td>
<td>0.17</td>
</tr>
<tr>
<td>CaO</td>
<td>17.33</td>
<td>0.59</td>
</tr>
<tr>
<td>MgO</td>
<td>0.31</td>
<td>0.38</td>
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<tr>
<td>S</td>
<td>0.84</td>
<td>0.025</td>
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<tr>
<td>As</td>
<td>0.089</td>
<td>0.08</td>
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<tr>
<td>SiO₂</td>
<td>0.39</td>
<td>26.86</td>
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<tr>
<td>Se</td>
<td>0.013</td>
<td>0.043</td>
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<tr>
<td>Bi</td>
<td>0.011</td>
<td>0.013</td>
</tr>
<tr>
<td>Sb</td>
<td>0.025</td>
<td>0.009</td>
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<td>Te</td>
<td>0.007</td>
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<tr>
<td>Ni</td>
<td>0.184</td>
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<tr>
<td>Sn</td>
<td>0.003</td>
<td>0.004</td>
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<tr>
<td>Oxygen</td>
<td>0.1</td>
<td>0.3</td>
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<tr>
<td>Insol</td>
<td>0.026</td>
<td>0.07</td>
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Cu-S Phase Diagram
Relation between CaO/SiO2 and Po2
Features of the Mitsubishi Process

- Continuous operation with multi-furnace constitution
- Injection smelting using top blow lances
- Calcium-ferrite slag for converting furnace
Furnace Arrangement of Mitsubishi Process

- C-Furnace
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- Cl-Slag
- Blister
- Matte
- Launder
- Anode Furnaces
- Mannesmen Shear
- Hazelett Caster
- Anodes
Cavity and Deep Penetration
Behavior of gas/solid jet in Smelting Furnace

- Velocity (m/s) 200
- Lance tip: +50, 0
- Melt Surface: 0, 3.5
- Chalcopyrite: -8, 4.5
- Matte flow: -150, 36.0
Furnace Arrangement of Mitsubishi Process

C-Furnace
CL-Furnace
S-Furnace

Electrodes
Lances
CL-Slag
C-Slag
Blister
Matte
Launder

Anode Furnaces
Hazelett Caster

Mannesmen Shear
Anodes
Lances for Concentrate
## Typical Assay of CL Slag

<table>
<thead>
<tr>
<th></th>
<th>Gresik</th>
<th>Naoshima</th>
<th>Kidd Creek</th>
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<tbody>
<tr>
<td>Cu</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>0.4</td>
<td>0.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe</td>
<td>38.6</td>
<td>35.8</td>
<td>39.4</td>
</tr>
<tr>
<td>SiO2</td>
<td>34.3</td>
<td>34.5</td>
<td>32.0</td>
</tr>
<tr>
<td>Al2O3</td>
<td>4.8</td>
<td>4.9</td>
<td>4.8</td>
</tr>
<tr>
<td>CaO</td>
<td>5.7</td>
<td>5.7</td>
<td>3.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0.8</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe/SiO2</td>
<td>1.12</td>
<td>1.04</td>
<td>1.23</td>
</tr>
<tr>
<td>CaO/Al2O3</td>
<td>1.16</td>
<td>1.16</td>
<td>0.71</td>
</tr>
<tr>
<td>Matte Grade</td>
<td>68.1</td>
<td>68.6</td>
<td>68.1</td>
</tr>
</tbody>
</table>
FeO-SiO$_2$ Phase Diagram

- Fe$_2$SiO$_4$
- Liq.
- Cristobalite + L
- Tridymite + L
- Wüstite + L
- Fayalite + L
- Fayalite + Wüstite
- Tridymite + Fayalite
Dissolved Cu in FeO$_x$-SiO$_2$ Slag
Stokes’ Law

\[ u = \frac{2g ( \rho_m - \rho_s ) \gamma^2}{9 \eta} \]

- \( u \): settling velocity
- \( g \): acceleration of gravity
- \( \rho_m \): density of matte
- \( \rho_s \): density of slag
- \( \gamma \): radius of matte grain
- \( \eta \): viscosity of slag
Actual Copper Loss
Several Pattern of copper loss in slag

- Clear bottom
- Unclear bottom
- Clear bottom
- Jumping
- Occasional peak
- Independent high

- 27 hr
- 15 hr
- 8 hr
Furnace Arrangement of Mitsubishi Process

Anode F'ce

Lances

Hazelett Caster

Mannesmen Shear

C-Slag

CL-Slag

Electrodes

Blister

Matte

Lances for Concentrate

Launder

Anode Furnaces

S-Furnace

C-Furnace

CL-Furnace

Furnace Arrangement of Mitsubishi Process
Main Reaction at C furnace

Zone B Reactions
\[ 3\text{FeS} + 10\text{Cu}_2\text{O} = 20\text{Cu} + \text{Fe}_3\text{O}_4 + 3\text{SO}_2 \]
\[ \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2 \]

Zone A Reactions
\[ 4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O} \]
\[ \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \]
Phase Diagram of Cu$_2$O - CaO System
Kennecott-Outokumpu Flash Converter

- Operation started in 1995 in USA
- Matte is granulated by water, piled, reclaimed, ground, dried and charged to converter
- Independent operation of both furnaces
- Additional equipment, additional energy and high dust generation
Process Control of Mitsubishi Continuous Process at Gresik Smelter

M. Goto, R.Kojima, T.Muto and T. Matsutani
Gresik Smelter & Refinery, PT. Smelting
Design Capacity

Copper Concentrate
660,000 mtpy

Water Granulated Slag
400,000 mtpy

Copper Cathode
200,000 mtpy

Sulfuric Acid
600,000 mtpy
Major Process

Smelter : Mitsubishi Process
Acid Plant : Lurgi-Mitsubishi
Double Contact / Absorption
Anode Casting : Hazelett Caster & Travelling Shear
Refinery : ISA Stainless Steel
Cathode
Map of Gresik
Unloader
Expert System
For Mitsubishi Process
CL slag granulation
Copper Anode
Treated Concentrate and Anode Production

Concentrate and Anode (K)

<table>
<thead>
<tr>
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<th>Concentrate</th>
<th>Anode</th>
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<tr>
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<td>T11</td>
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<tr>
<td>T12</td>
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0 50 100 150 200 250
Conclusion

- The designed yearly capacity will be confirmed
- All the strict environmental standards are cleared
- Plant have been operated 100% by Indonesian staffs