Dongying Fangyuan Nonferrous Metals Co., Ltd

Treatment of Arsenic in copper smelting
Overview of Fangyuan
Overview

Founded in 1998;
Products: Copper Cathode, sulfuric acid and various valuable metals;
Technical support and service supplier.

3 Key-Points

The forth largest Copper producer in China
In 2017:
Cathode: 680,000 tons
Gold: 26 tons
Silver: 410 tons
Total revenue: 12.6 billion USD

Co-developed Bottom Blowing Smelting process with other two Co. in 2008;
Independently developed Two-Step process in 2015.
Overview

Technical Strength & International technical cooperation

- 492 technology standards
- 311 patents & proprietary technologies
- 4 pilot test lines
- R&D
- 4 national research platforms
- 311 patents & proprietary technologies
- 5 pilot test lines
- 4 national research platforms
- 9 national major research projects

- Long-term cooperative relationship with Central South University and Northeastern University, etc.
- Co-built metallurgical engineering laboratory with Purdue University, USA.
- Co-built Research Center with University of Queensland, Australia.
- Mutual training plan for talents with UdeC, Chile.
- Co-built engineering and technology center with Codelco, Chile.
Overview

Innovations

- BBF in 2008
- Purification of electrolyte in 2010
- Unitary furnace granted Chinese patent in 2013
- Recovery of contaminated acidic water in 2013
- Slag clean technology in 2012
- Poly-metal recovery from dust in 2014
- Two step smelting process in 2015

2005

2010

2015

2020
02

Arsenic in China
2017, 8.89 million tonnes of cathode copper were produced in China, while 22 billion tonnes of copper concentrate were consumed. As a result, around 50,000 tonnes of arsenic were left to be treated.

As is highly toxic and carcinogenic element and currently still considered as a surplus element in the world, meaning that arsenic recovered by smelting is far beyond the application; Re-solidification and storage after low-toxicity disposal is the safest measures in China, but how to solve this problem still has a long way to go.

As is mainly present as sulfides in concentrates, and is dispersed in dust, slag, anode mud and sulfuric acid with distribution closely related to the smelting process. Finally, it is enriched in by-products of various metallurgical processes, including white ash, anode slime, arsenic sulfide residue, contaminated acid and so on, or cyclically accumulated in the system.

**Chinese Standard of Arsenic for Copper Industry GB25467--2010**

<table>
<thead>
<tr>
<th>Category</th>
<th>Limit</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total As in drainage of smelting building</td>
<td>&lt;0.5mg/L</td>
<td>(existing smelter, non urban area)</td>
</tr>
<tr>
<td></td>
<td>&lt;0.1mg/L</td>
<td>(high population density area)</td>
</tr>
<tr>
<td>Total As in emission</td>
<td>&lt;0.4mg/m³</td>
<td>(discharge point)</td>
</tr>
<tr>
<td>As in air</td>
<td>&lt;0.01mg/m³</td>
<td>(corporate fence border)</td>
</tr>
</tbody>
</table>
Arsenic in White Ash

White ash is one of the major by-product during copper smelting. 70-100 kg white ash will be generated with each ton of copper is made. Arsenic content ranges from 10% to 15% in white ash, other including lead, copper and zinc.

<table>
<thead>
<tr>
<th>Typical element content from a Chinese copper smelter</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
</tr>
<tr>
<td>wt%</td>
</tr>
<tr>
<td>14.14</td>
</tr>
</tbody>
</table>

As to Bottom Oxygen-rich Blowing Smelting (BBS) process, most Cu/Pb/Zn exist as the form of their sulfates in white ash, while As shows its forms as trioxide and arsenate \([\text{Pb}_3(\text{AsO}_4)_2]\).

Over 80% Cu/As and 90% Zn can be extracted from white ash using acid leaching.
Arsenic in China

Typical copper pyrometallurgical process in China

- White ash
- Waste acid
- Slag
- Slime

As to be treated or disposal
Classic method for treating White Ash

white ash, ~15%As

leaching

Pb/Bi residue, ~5%As

leachate

Crystallization

CaFeAsO$_x$, ~5%As

CuAsO$_x$

Caustic leaching

Cu residue

Na$_x$AsO$_x$ soln

Zn recovery

Filtrate

Purification

Sodium sulfate

Lime adding

regenerated alkali

Crystallization

CaAsO$_x$, ~20%As
Arsenic in China

Classic method for treating White Ash

1. **Sulfation Roasting**
   - White ash/coal
   - Waste acid
   - Sulfation roasting
   - As recovery
   - Leaching Bi
   - Leaching Au/Ag
   - Residue
   - Leachate
   - Cu/Zn leachate
   - Acid plant
   - As$_2$O$_3$ ~93%wt
   - Reduction
   - Metal As
   - Cathode Cu
   - ZnSO$_4$·(H$_2$O)$_x$
   - Electrowinning
   - Au/Ag recovery
   - Residue for sale
Strategy of treating As at Fangyuan
Fangyuan's two-step copper smelting process:

The 1st production line of two-step process has been operating at the 3rd Industrial Park of Fangyuan since 2015.
Core of Fangyuan two-step process:

Submerged lance smelting + Submerged lance converting & refining

Mixed feeding (0.2% ~ 0.25% As)
Sealed conduit

Submerged lance smelting furnace (SLS)
Submerged lance converting & refining furnace (SLCR)

Casting wheels
Cathode copper (Cu≥99%)
Arsenic speciation in copper smelting process

**Slag**
- \( \text{As}_2\text{O}_5 \)

**Copper concentrate**
- \( 3\text{Cu}_3\text{S} \cdot \text{As}_2\text{S}_3 \) (Tennantite)
- \( \text{Cu}_3\text{AsS}_4 \) (Enargite)

**Matte**
- \( \text{Cu}_3\text{As} \)
- Simple substance \( \text{As} \) (small amount)

**Refining**
- **Anode plate**
  - \( \text{Cu}_3\text{As} \), \( \text{As}_2\text{O}_3 \), \( \text{As}_2\text{O}_5 \) (Little)

**Electrolysis**
- **Anode slime**
  - \( \text{As}_2\text{O}_3 \), \( \text{Cu}_3\text{As} \)
- **Electrolyte**
  - \( \text{H}_3\text{AsO}_4 \)

**Purification**
- **Contaminated acid** (3-10g As/L)
  - As (III) (most), As (V)
  - \( \text{H}_3\text{AsO}_3 \), \( \text{H}_3\text{AsO}_4 \), \( \text{HAsO}_2 \) (small amount)

**Dust**
- \( \text{As}_2\text{O}_3 \)

**Off-gas**
- \( \text{As}_2\text{O}_3 \)
Proportion of arsenic distribution in Fangyuan smelter

- **Concentrate**
  - Total As: 100%
  - Slag, ~20% As
  - Off-gas, ~70% As
  - Anode plate, ~8%

- **Sulfide wastewater**
- **Arsenic sulfide**
  - ~35% As

- **Dust**
  - ~45% As
  - (Hazardous wastes)

- **Recovery of copper anode slime and crude nickel sulfate**
- **Contaminated acid**
  - ~27% As

Arsenic mainly enters smelting dust (~45%) and arsenic sulfide residues (~35%). Both of them belong to the hazardous wastes containing As. The rest (~20%) goes to slag.
Analysis of hazardous wastes containing As at Fangyuan

- Hazardous wastes contain valuable elements such as Cu, Zn, Pb, As, etc.
- Improper handling of hazardous wastes can lead to serious environment disasters;
- Recovery of valuable elements from hazardous wastes can improve the economic benefits of copper smelting

Major elements in smelting dust and arsenic sulfide residues

<table>
<thead>
<tr>
<th>element, wt%</th>
<th>As</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>5~10</td>
<td>7~15</td>
<td>2~6</td>
<td>12~24</td>
<td>1~3.5</td>
</tr>
<tr>
<td>Arsenic sulfide residues</td>
<td>10~30</td>
<td>2~12</td>
<td>0.1~1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>
Strategy of treating As at Fangyuan

Conventional treatment method

**Arsenic sulfide residues and smelting dust**

**Recovery of valuable elements**

Metallic products Cu, Zn, Pb

**Solidification of As**

As

As$_2$O$_3$

**Harmless landfill**

Scorodite

Calcium arsenate

Other solidified residues

Metallic arsenic (arsenic alloy)

Arsenic hydride (raw material for semiconductors)

Materials for pharmaceutical products

Additives for glass and ceramics

Raw materials for preservative and pesticide
Treatment of As-wastes at Fangyuan
Treatment of As-wastes at Fangyuan

Treatment of As-containing wastes at Fangyuan

As-containing wastes → As-containing leachate

As settlement

CuSO₄ soln

As: 10 ~ 25g/l
Cu: 20 ~ 60g/l
H₂SO₄: ≤ 50g/l

Copper arsenite

As dissolution

NaOH

Sodium arsenite soln

Calcium arsenite

Lime

As solidification

As: 20 ~ 30%
H₂O: ≤ 25%

Cu(OH)₂

NaOH
Feature of calcium arsenite process

1. Arsenic is converted into solid calcium arsenite with lower toxicity;
2. Arsenic and copper are separated without introducing other impurities;
3. NaOH and Cu(OH)₂ employed in the process can be recycled repeatedly.

Treatment of As-wastes at Fangyuan
Recovery of As at Fangyuan

Fangyuan is able to treat more than 2 million tons of polymetallic concentrates per year and produces about 30,000 t/a copper smelting dust with average content of 7.5% As. It also produces about 8000 t/a arsenic sulfide residues (dry basis, 22% As). The recovery of the two kinds of arsenic hazardous wastes is of great significance to Fangyuan.
Treatment of As-wastes at Fangyuan

Process flow of As product at Fangyuan

Dust containing As

Leaching with sulfuric acid

Filter cake

Filtrate

As$_2$O$_3$

Arsenic sulfide residues

Cu-As replacement

Filtrate containing As

Copper sulphide
Treatment of As-wastes at Fangyuan

Arsenic trioxide

Composition: $\text{As}_2\text{O}_3$ above 99.5%

Cu under 30ppm
Zn under 20ppm
Fe under 20ppm
$\text{H}_2\text{O}$ under 0.5%
Features of As treatment at Fangyuan

1. Use the hazardous wastes generated from copper smelting process to produce arsenic trioxide which is the basic raw materials for arsenic chemicals;

2. Use the hazardous wastes containing As to produce arsenic trioxide while other valuable elements such as Cu, Zn and Pb, etc are recovered;

3. Reduce the stockpiling and discharge of As-containing residues such as calcium arsenate residues and scorodite and maximize environmental safety.
Thank you