ENVIRONMENTAL PROTECTION TECHNOLOGY AT SMELTER

Japan Oil, Gas and Metals National Corporation
# Table of Contents

1. Preface ................................................................. 1

2. Role of the Non-Ferrous Metals Industry .......................... 1

3. Environmental Standards for Prevention of Air Pollution and Emission Standards .................................................. 2
   3.1 Environmental Standards ........................................ 3
   3.2 Emission Standards ................................................ 3
   3.3 Total Emission Regulation Standards .......................... 3

4. Present Conditions of Air Pollution in Japan ..................... 3

5. Air Pollution Prevention Technology ............................... 4
   5.1 The Copper Smelting and Refining Process .................... 4
   5.2 The Sulfuric Acid Manufacturing Process ..................... 6
   5.3 The Flue Gas Desulfurization Process ......................... 9
   5.4 Applications for Sulfuric Acid and Gypsum .................. 11

6. Postscript ............................................................. 11
1. Preface

The problem of industrial pollution in Japan is said to have begun in the late 1800's when the industrial modernization started. At that time, mine water and smoke pollution give rise to agricultural damage in certain regions, sometimes with serious consequences. Also, following Japan's rapid postwar industrialization, health problems among populations living near industrial centers began to appear in the 1950s. Some of these developed into significant national problems.

To address these issues, in 1967 the national government proclaimed the Anti Pollution Basic Measures Law, establishing the world's most stringent environmental standards and clarifying the responsibilities of enterprises for them, setting a clear course toward a lasting solution.

Despite the considerable costs involved, Japan's business community greeted this law by upgrading equipments, strengthening controls and introducing new technology. Today, those standards have been met or exceeded throughout the country.

The purpose of this video and text is to introduce the air pollution prevention technology used for sulfur oxides in Japan's non-ferrous metals smelter.

2. Role of the Non-Ferrous Metals Industry

Japan's non-ferrous metals smelting industry carefully and thoroughly extracts a wide variety of valuable natural resources from the earth. These range from base metals such as copper, lead and zinc, and by-products such as the precious metals gold and silver, through rare metals such as selenium, indium and cadmium, and finally to such chemicals as sulfuric acid and gypsum. In so doing, the industry delivers and makes effective use of the resources that are indispensable in the lives of modern people.

The earth's supply of these resources is extremely limited. The average estimated proportions of the elements included in the earth's crust, excluding seas and oceans, is shown in a table below for some of them. Copper, for example, the 26th most common element, is estimated to represent only 0.0055% of the crust.

<table>
<thead>
<tr>
<th>EFelements</th>
<th>Order of Quantity</th>
<th>Proportions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1</td>
<td>46.6</td>
</tr>
<tr>
<td>Si</td>
<td>2</td>
<td>27.72</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>8.13</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>5.00</td>
</tr>
<tr>
<td>Zn</td>
<td>24</td>
<td>0.0070</td>
</tr>
<tr>
<td>Cu</td>
<td>26</td>
<td>0.0055</td>
</tr>
<tr>
<td>Pb</td>
<td>36</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
As this table shows, copper, lead and zinc are extremely rare. When smelting these metals, companies seek to establish mines where the metal is accumulated in concentrations of around 10% or more (for copper, that figure is usually around 1% or less). The ore must be further concentrated up to 30-50% by floatation prior to smelting.

Japan has boasted its share of rich mines. Until the end of former century, Japan was one of the world's largest producers of copper, but today, it is obliged to import most of the concentrates along with oil.

The following graphs indicate the volumes of copper, lead and zinc supplied in Japan in 1995 and their applications. As 15-20% of domestic demand was supplied from imports as metals, 80-85% of supply may be considered domestic production volume from concentrates and scraps.

Copper is used in such applications as the electric cable and piping of air conditioning and heating systems for its high electrical and thermal conductivity and excellent workability. Copper alloy products which are alloyed with zinc and other metals to improve their properties, are used in a wide variety of electric home ware applications such as electrical contacts and springs as well as substrates for semiconductors.

Lead is used in car batteries and, due to its superior resistance to acid, as a component in acid-resistant equipment used in chemical plants.

Lead-Tin alloy has long been useful as solder because of its low melting point.

Great quantities of zinc are used in galvanized steel to prevent corrosion. When bridges and other steel structures exposed to corrosive environments are plated with zinc, they can be protected from corrosion for decades without painting.

Galvanized steel sheets are used in construction materials, and more recently in automobile bodies. In die casting as well, zinc is widely used in mechanical parts for its precision and aptitude for mass production. Also, zinc-based inorganic chemicals mainly as zinc oxides in white pigments and as a vulcanization accelerator for rubber.

In short, while non-ferrous metals comprise only a vanishingly small proportion of the volume of the earth's crust, they are a precious resource that is indispensable in supporting the prosperous life we take for granted. Providing a secure and reliable supply of this resource is the responsibility of the non-ferrous metals industry.

3. Environmental Standards for Prevention of Air Pollution and Emission Standards

Japan's environmental standards are established by the Ministry of the Environment in the spirit of the Anti Pollution Basic Measures Law, which calls for "standards that are desirable to uphold the protection of human health and the preservation of the living environment." In recognition of the effects of pollution on people and agricultural products, this law sets environmental standards that are desirable wherever people live and work, then specifies standards for gas emission and wastewater to satisfy those requirements.
3.1 Environmental Standards

Air pollution standards target five phenomena:
(1) Sulfur dioxide (SO\textsubscript{2}), (2) carbon monoxide (CO), (3) suspended particulate matter, (4) nitrogen oxide (NO\textsubscript{x}), and (5) photo-chemical oxidants.

Environmental standards in Japan for SO\textsubscript{2} are:
- Daily average of hourly value; less than 0.04 ppm
- Hourly value; less than 0.1 ppm

As the following graph of environmental standards of key countries illustrates, these values are the strictest in the world.

SO\textsubscript{2} ENVIRONMENTAL STANDARDS in KEY COUNTRIES

3.2 Emission Standards

Emission standards must be observed by the companies which cause the emissions in order to satisfy environmental standards. Violations of these standards are subject to penalties and improvement orders.

Representing the emission limit for sulfur dioxide as \(q\) (m\textsuperscript{3}/h) and the maximum ground concentration as \(C_{\text{max}}\) (ppm), the relation between these two can be expressed as:

\[ q = 0.584 \times C_{\text{max}} \times H_e^2 \]

Here, \(H_e\) is the effective height of stack (m). The effective height of stack is derived by theoretically correcting the actual height of stack for exhaust gas speed and temperature. This number increases as the speed and/or temperature rises.

As the above equation shows, plants with large emission volumes (large \(q\)) must increase \(H_e\) to reduce \(C_{\text{max}}\) to the set value or lower.

Sulfur dioxide emission standards in Japan are set so that, in the equation \(0.584\times C_{\text{max}}\times 10^3 = K\), \(C_{\text{max}}\) is 0.03 ppm, which is stricter than the environmental standard of 0.04 ppm. This determines \(K\) as 17.5.

However, in areas where numerous plants are concentrated, companies must satisfy more than their individual emission standards. If the area as a whole is estimated to be unable to satisfy its environmental standards, a smaller \(K\) value must be applied to that area to make each company's emission standard stricter.

Each region is therefore divided into 16 levels, with the \(K\) value for the strictest areas—large metropolitan areas and industrial belts—determined as 3.0 (for \(C_{\text{max}}\) of 0.005 ppm) instead of 17.5.

3.3 Total Emission Regulation Standards

By regulating the value of \(K\), we seek to achieve the environmental standards for each region by regulating \(C_{\text{max}}\), that is, maximum ground concentrations of sulfur dioxide, for each facility. This means that plants with high emission volumes can meet standards simply by increasing the height of their stacks.

To deal with such character of \(K\) value regulation system, total emission regulation is set for certain areas of high concentration of factories. Total emission regulation standards are standards imposed to regulate absolute emission volumes of sulfur dioxide, especially.

4. Present Conditions of Air Pollution in Japan

Japan's environmental standards for sulfur dioxide are some of the toughest in the world. Yet they are now almost completely attained. The graph below left shows Japan's unprecedented achievement: by 1987, the emissions in Japan had been reduced to only one fifth of their 1970 level.

In the graph below right, annual emission levels for major industrialized nations are listed in 1990.
In Europe, North America and parts of East Asia, however, concerns are mounting over the damage to forests and soil caused by acid rain containing airborne sulfur dioxide and nitrogen dioxide. These pollutants are chiefly generated by combustion of fossil fuels such as petroleum and coal. Once emitted, however, these substances cross regional and national borders, spreading their effects across a wide area. As the above graphs indicate, although sulfur dioxide emission levels in the industrialized countries are declining, global emission levels are on the rise due to increasing emissions in the developing world, redoubling fears that the damage from this pollution is growing.

5. Air Pollution Prevention Technology

Because sulfide concentrate is a feedstock used by the non-ferrous metals smelter, large volumes of sulfur dioxide gas are evolved in the smelting process. In Japan's smelting plants, this sulfur dioxide is recovered as sulfuric acid and gypsum. In this section we provide an overview of the technology used in the recovery process, taking copper smelting and refining as an example.

5.1 The Copper Smelting and Refining Process

Copper concentrate is used as the copper feedstock. Because copper ore obtained from a mine generally has a low grade of about 1%, the copper content is concentrated, taking advantage of the fine copper sulfide particles' propensity to adhere to soap bubbles. The main component of the copper concentrate is chalcopyrite (CuFeS₂) which contains approximately 25% of copper.

To produce metallic copper from the concentrate, sulfur and iron must be separated.

At the modern copper smelter, the flash smelting furnace or the Mitsubishi furnace is used. In the following discussion the flash smelting furnace method is explained, in which gas treating process, however, is almost identical.

Dried copper concentrate, along with hot air (sometime with a 50% oxygen concentration to improve the equipment's efficiency) and heavy oil blown through concentrate burners at the top of the furnace. At this point, the concentrate is instantaneously melted by an oxidation reaction with oxygen, generating copper-bearing matte and slag as well as SO₂ gas. During the reaction, heat is generated, raising the temperature in the furnace to approximately 1,300 °C while using very little of fuel.

\[
2\text{CuFeS}_2 + 13/4\text{O}_2 \rightarrow \text{Cu}_2\text{S} \cdot 1/2\text{FeS} + 3/2\text{FeO} + 5/2\text{SO}_2
\]

(Copper concentrate) (Oxygen) (Matte) (Slag) (Sulfur dioxide)

Having a high specific gravity, the melted matte collects at the bottom of the settler. The slag floats above the matte, allowing it to be separated naturally. The matte is transferred in its melted state to a converter, while the slag is quenched by water and pulverized, usually to be
sold as a cement feedstock. The SO\textsubscript{2}-bearing off-gas is conducted to an acid plant.

In the converter, the matte is re-oxidized by air (or oxygen-enriched air) blown in from a tuyeres to yield blister copper of approximately 98% grade.

(1) \[ \text{FeS} + \frac{2}{3}\text{O}_2 = \text{FeO} + \text{SO}_2 \]  
\text{(Slag making stage)} 
\text{(Slag) (Sulfur dioxide)}

(2) \[ \text{Cu}_2\text{S} + \text{O}_2 = 2\text{Cu} + \text{SO}_2 \]  
\text{(Copper concentrate period reaction)} 
\text{(Blister copper) (Sulfur dioxide)}

In the converter as well, the heat generated in oxidation reaction of the sulfur and iron is used, so no fuel is required at all. The remaining heat is also used for melting copper scraps recovered from the city.

The blister copper contains many inclusions and impurities such as gold and silver. Electrolytic refining is further applied to refine the copper. To produce anodes of high quality, the blister copper is charged into an anode furnace which mainly removes the oxygen from it, then anodes approximately 1m x 1m x 4cm in its shape (320-380Kg) is cast for use as a feedstock for electrolytic refining.

In the electrolytic refining process, the electrorefined copper with a final purity of 99.99% and the gold and silver bearing anode slime are obtained. The anode slime is further processed to yield gold, silver, platinum and other precious metals.

Figure of Flash smelting furnace and converter are as follows;
5.2 The Sulfuric Acid Manufacturing Process

As expressed the off-gas emitted from the flash furnace and converter is rich in SO$_2$ (approximately 15%), and also extremely hot (approximately 1000°C) and contains dust composed of reaction products. Before manufacturing sulfuric acid, therefore, it must be cooled and thoroughly refined.

The following is a flow chart of a copper smelting and refining plant, including an acid plant;

![Copper Smelter Flow Chart]

The following is a simple explanation for each step in the sulfur manufacturing process;

**Waste heat boiler;**

First, SO$_2$ gas from the flash furnace and converter is conducted to the waste heat boiler, where heat and dust are recovered. The heat is recovered as steam used efficiently for power generation and for heating where necessary in the plant.

When SO$_2$ in the gas is oxidized it becomes sulfur trioxide (SO$_3$), which corrodes equipment and causes deterioration of the catalysts of the SO$_2$ converter to be described later. Therefore the gas must be quickly cooled to 500°C or lower.

Because the recovered dust contains copper, it is returned to the flash furnace.

To refine the dust further, it is conducted to an electrostatic precipitator.

**Electrostatic precipitator;**

As shown in the figure to the left, the electrostatic precipitator has a number of electrodes arrayed vertically in the chamber.
A high DC Voltage of several 10,000 of kv is applied between the discharge electrodes and the collecting electrodes to generate a corona discharge. This discharge creates a negative electric charge on the surface of the dust suspending in the gas, so that the dust deposits on the positive collecting electrode.

The collected dust then loses its electric charge and falls into the hopper, from which it is returned to the flash furnace for repeated smelting.

Humidifying tower;

The gas left from the electrostatic precipitator still carries a certain amount of dust, and it is still fairly hot at about 300 °C. Sulfur trioxide (SO₃) must also be thoroughly eliminated before the gas can be sent to the SO₂ converter.

In the humidifying tower, the gas is sprayed with water or dilute acid to lower its temperature and to humidify the gas to improve the effectiveness of the wet electrostatic precipitator.

Humidification causes the SO₃ to be absorbed by the water, turning it into fine water droplets (sulfuric acid mist) which suspend in the gas.

$$\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4$$

Wet electrostatic precipitator (mist Cottrell);

The purpose of the wet electrostatic precipitator is to thoroughly eliminate the sulfuric acid mist and remaining dust from the gas. The principle is the same as in the electrostatic precipitator but, since contact with the acidic mist is involved, the electrodes and casing are made with lead or lead lining.
Drying tower;
The gas is dried, because the moisture in the gas to be sent to the SO\(_2\) converter causes deterioration of the catalysts and corrosion of the equipment.

To do this, approximately 95% sulfuric acid is sprayed from the top and placed in contact with the wet gas.

This process uses sulfuric acid's property of excellent water absorption.

Heat exchanger (gas heater);
The gas is heated to the optimum temperature for the next conversion reaction. Depending on the concentration of SO\(_2\), this temperature is about 400\(\degree\)C.

SO\(_2\) converter;
The dried gas is placed in contact with catalyst to oxidize sulfur dioxide into sulfur trioxide;
\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3
\]
The SO\(_2\) converter holds several catalyst columns. As it passes through the successive catalyst columns, it is oxidized to SO\(_3\). Heat is generated at each stage, so after each stage the gas is cooled by the heat exchanger to the optimum temperature (approximately 400\(\degree\)C).

The catalyst is consisted of vanadium pentoxide (V\(_2\)O\(_5\)) with a carrier such as aluminum silicate, forming a tablet or ring with a radius of about 10mm and length of 15mm.

Absorption tower;
The gas emitted from the catalytic converter is cooled to approximately 50-80\(\degree\)C in the heat exchanger and transferred to the absorption tower.

Acid with a concentration of about 98.5% is sprayed from the top of the tower. As the gas flows upward from the bottom of the tower, the SO\(_3\) contacts the acid by the counter-current manner and is absorbed by the acid.

Part of the acid flowing out of this tower is extracted as product-grade concentrated sulfuric acid. The remaining acid is supplemented with an equivalent volume of water or dilute acid and absorption is continued.

The concentrated sulfuric acid is 99% H\(_2\)SO\(_4\).
The reaction used in manufacturing sulfuric acid from the SO₂ gas is as follows:

In the SO₂ converter; \( \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \)

In the absorption tower; \( \text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \)

The gas emitted from the absorption tower still contains about 0.2% SO₂, so there are double contact acid plant in which exit gas from absorption tower is passed once more through another SO₂ converter and absorption tower to reduce the SO₂ content to around 0.03%. Generally, absorption tower exhaust gas is conducted to the flue-gas desulfurization process along with the exhaust gas from the anode furnace for further elimination of SO₂.

5.3 The Flue Gas Desulfurization Process

(1) The lime-gypsum method

Water is mixed with calcium carbonate (limestone, CaCO₃), calcium oxide (lime, CaO), or calcium hydroxide (Ca(OH)₂) to form a slurry. When this slurry is placed in contact with SO₂ in the absorption tower, calcium sulfate and carbon dioxide gas are produced (when calcium carbonate is used).

\[
\text{CaCO}_3 + \text{SO}_2 + \frac{1}{2}\text{H}_2\text{O} = \text{CaSO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4 + \text{CO}_2 \quad (\text{absorption reaction})
\]

\[
\text{CaCO}_3 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} = \text{CaSO}_4 + 2\text{H}_2\text{O} \quad (\text{oxidation reaction})
\]

Next, this liquid is conducted to an oxidation tower. The gypsum sulfite is oxidized by air to form calcium sulfate (gypsum). In the oxidation tower, sulfuric acid is added to neutralize the minute quantities of unreacted CaCO₃.

\[
\text{CaCO}_3 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{SO}_2 + \frac{3}{2}\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (\text{gypsum})
\]

The gypsum slurry out from the oxidation tower is treated with a thickener to concentrate the gypsum and dehydrated in a centrifuge to obtain product gypsum.
(2) Basic aluminum sulfate-gypsum method

Basic aluminum sulfate is used as the absorption liquid. Because $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2\text{O}_3$ dissolves easily in water and the absorption liquid does not become a slurry like CaCO$_3$, it provides efficient sulfur dioxide absorption and prevents clogging of the piping system.

Basic aluminum sulfate is regenerated in the neutralization reaction, so it can be reused in the absorption reaction. The reactions proceed as follows:

\[
\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2\text{O}_3 + 3\text{SO}_2 = \text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \tag{absorption reaction}
\]

\[
\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 + 3/2\text{O}_2 = \text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \tag{oxidation reaction}
\]

\[
\text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 + 3\text{CaCO}_3 + 6\text{H}_2\text{O} = \text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 3\text{CO}_2 \tag{Gypsum (neutralization reaction)}
\]

(3) Ammonia-ammonium sulfate method

The $\text{SO}_2$ is absorbed by aqueous ammonia to manufacture ammonium sulfate $(\text{(NH}_4\text{)}_2\text{SO}_4)$, which is used as chemical fertilizer.

The reaction proceeds as follows:

\[
2\text{NH}_3\text{OH} + \text{SO}_2 = (\text{NH}_4\text{)}_2\text{SO}_3 + \text{H}_2\text{O}
\]

\[
(\text{NH}_4\text{)}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} = 2\text{NH}_4\text{HSO}_3 \tag{absorption reaction}
\]

The absorption reaction proceeds in two stages as above. If only one stage is used, the high partial pressure of NH$_3$ causes inclusion in the exhaust gas, resulting in significant loss of NH$_3$.

\[
\text{NH}_4\text{HSO}_3 + \text{NH}_3\text{OH} = (\text{NH}_4\text{)}_2\text{SO}_3 + \text{H}_2\text{O} \tag{neutralization reaction}
\]

Momentarily, a surplus of $\text{SO}_2$ is absorbed to NH$_4$HSO$_3$ and reverts to $(\text{NH}_4\text{)}_2\text{SO}_3$. 

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**Diagram:**

- **Basic Aluminum Sulfate-Gypsum Method**
  - Gas Emission
  - Absorber
  - Oxidation Tower
  - Thickener
  - Centrifuge
  - Product Gypsum

- **Ammonia-Ammonium Sulfate Method**
  - Gas Emission
  - Absorber
  - Oxidation Tower
  - Crystallizer
  - Centrifuge
  - Product Ammonium Sulfate
\[(\text{NH}_4)_2\text{SO}_3 + \frac{1}{2}\text{O}_2 = (\text{NH}_4)_2\text{SO}_4\] (oxidation reaction) (ammonium sulfate)

The ammonium sulfate solution left from the oxidation tower is transferred to the vacuum crystallize, to crystallize ammonium sulfate.

A flow chart of the main aspects of this process is given below.

Although numerous other methods exist, only the above three are described for information.

5.4 Applications for Sulfuric Acid and Gypsum

In Japan's non-ferrous metals industry, almost all rich SO$_2$ gas is recovered as sulfuric acid and dilute SO$_2$ gas is recovered as gypsum. This is due to a combination of Japan's relatively abundant lime reserves and the demand for sulfuric acid and gypsum.

6. Postscript

The principal source of SO$_2$ is the combustion of fossil fuels as an exhaust from factories and cars. Previously, as Japan's industry developed, her use of these fuels grew as well. Japan's ability to achieve the world's strictest environmental standards is the result not only of the exhaust gas desulfurization technology described here, but of desulfurization of heavy oil and the development of efficient combustion technologies as well.

Because many of the efforts to develop these technologies were based on national government assistance, this success can be fairly called a tangible result of cooperation between the government and private sectors.

The critical importance of protecting the environment is universally recognized. Yet the cost to industry of installing and operating the necessary equipment is often prohibitively expensive. A clean environment cannot be given for free.

Today, concern is mounting over the environmental destruction, not on a regional but on a global scale, accompanying the rapid economic progress of many developing nations. In the months and years to come, Japan is committed to effecting a valuable contribution to the protection of the earth's environment through guidance and assistance to these countries.

At the same time, problems arising from vehicle exhaust gas, garbage and domestic waste water should be concerned more deeply as a citizen's standpoint.