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Sulfur Dioxide Emission Control in Japanese Copper Smelters

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SULFUR DIOXIDE EMISSION CONTROL IN JAPANESE COPPER SMELTERS

by

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ABSTRACT

Most Japanese copper smelters are located in areas of concentrated industrial activity and high levels of atmospheric pollution. A review of unofficial sulfur dioxide emission control data from major Japanese smelters shows capture of 91 to 99.7 percent of the sulfur in the smelter feed. The bulk of Japanese smelting capacity was constructed in the last 10 years. Six of the major smelters use flash furnaces, and two use reverberatory furnaces. A prototype three-furnace continuous system is in use as a parallel train with reverberatory furnaces at one smelter. Most of the sulfur dioxide is manufactured into sulfuric acid. The remainder is captured by gas scrubbers that yield gypsum and sodium salts. Ready markets exist in Japan for the acid and other sulfur byproducts.

INTRODUCTION

The copper smelting industry of Japan is second in size only to that of the United States. While U.S. smelters mainly process copper concentrate produced from U.S. mines, most Japanese smelting is done on imported concentrates. U.S. copper smelters are generally located in sparsely inhabited areas contiguous to the mines, whereas Japanese smelters are generally located in coastal ports in areas of high population density and intense industrial activity. Thus, residential areas and fisheries may be near the Japanese smelters.

A smelter location in a seaport industrial complex offers advantages in ready accessibility to supplies and markets. Liquid and gaseous fuels and chemicals may be available from an adjoining petrochemical plant that, in turn, is a user of sulfuric acid. Adjoining fertilizer and pigment plants also may be ready customers for acid, and nearby wallboard and cement plants may be customers for gypsum and smelter slag. A disadvantage of locating a copper smelter in an industrial complex or near residential areas, farms, and fisheries is the severe restraints that such locations impose on emission of pollutants.

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Sulfur dioxide (SO_2) is the pollutant most frequently identified with copper smelters. Restrictions on SO_2 emissions from copper smelters in Japan vary in severity with smelter location. All major smelters are required to capture at least 90 percent of the sulfur in the smelter feed, and several are required to capture 99 percent of the sulfur. These high rates of SO_2 control have been obtained by utilizing advanced smelting technology in conjunction with sulfuric acid manufacture for most of the SO_2; also, gas scrubbers yield salable gypsum and sodium salt byproducts from part of the SO_2.

The bulk of Japanese copper smelting capacity was constructed in the last 10 years. In addition to their being largely new, the smelters have a ready market for the sulfuric acid, gypsum, and sodium salts that are byproducts of SO_2 capture systems. For these reasons, and because the pollution is more acute in Japan, the smelter situation with regard to SO_2 emission controls is different from that in the United States. Yet a perspective of current Japanese smelting and emission control practice is of interest here.

This Bureau of Mines publication provides a summary of smelting and SO_2 emission control practices in 8 of the 10 large Japanese copper smelters. Information was obtained from scattered reports on Japanese copper smelting practice published in the last few years. Supplemental information was obtained during a visit to four of the main Japanese smelters in November 1974 by two Bureau of Mines metallurgists under joint sponsorship of the Bureau and the U.S. Environmental Protection Agency. The SO_2 emission control data reported herein were furnished by the staff of the smelters and are not necessarily accepted as official by the Japanese Government.

The 85,000-ton smelter of the Mitsui Mining Co. at Hibi and Sumitomo's copper smelter at Shisakajima are not described because a suitable report was not available and the smelter was not visited.

SULFUR DIOXIDE AMBIENT AIR AND VOLUME EMISSION STANDARDS IN JAPAN

National Ambient Air Quality Standards for Japan require that the daily average of hourly values shall not exceed 0.04 part per million (ppm). The hourly value shall not exceed 0.1 ppm. By comparison, the U.S. SO_2 Primary Ambient Air Quality Standard is 0.03-ppm annual arithmetic mean, and 0.13-ppm maximum 24-hour concentration not to be exceeded more than once per year. The more stringent U.S. Secondary Ambient Air Standard for SO_2 is 0.02-ppm annual arithmetic mean, 0.09-ppm maximum 24-hour concentration not to be exceeded more than once a year, and 0.45-ppm maximum 3-hour concentration not to be exceeded more than once a year.

The National SO_2 Emission Standard for each SO_2-emitting facility in Japan is determined by applying the formula $q = K \times 10^{-3} He^2$ in which q is the hourly volume of sulfur oxides emitted in units of normal cubic meters (Nm^3), He is the smoke ascent height in meters (height of stack plus plume rise above stack), and K is a constant established by Government order for each of the eight air control regions in Japan. The required degree of emission control increases as K decreases. K ranges from 22.2 in outlying areas to 6.42 in

central Tokyo, Osaka, Yokohama, and other industrial centers. Special standards applicable to new construction in the heavily industrialized areas have K values ranging from 5.26 to 2.92.

As an example, a smelter in an area where a K value of 11.7 applies and that has a smoke ascent height of 150 meters would have a q of 262 $\underline{Nm}^3$, equivalent to emission of 1,680 pounds SO_2 per hour. If the smelter produced 100,000 metric tons of copper annually from concentrate containing 25 percent Cu and 27 percent S, the equivalent of 56,700 pounds SO_2 would enter the smelter hourly, and only 3 percent of the SO_2 could be emitted to the atmosphere. A smelter with a lower stack in an area with a lower K value could be required to capture over 99 percent of the sulfur.

HISTORY OF COPPER SMELTING IN JAPAN

This abbreviated history of copper smelting in Japan was mainly extracted from a 1972 paper by Mitsuo Kamedo (3).[4] The recorded history of copper discovery and production in Japan dates from 698 A.D. Smelting of sulfides or partly roasted sulfides in hearth furnaces started in the early 1500's. Separation of part of the gold and sulfur that occurred with the copper by liquation with lead was initiated in the 1600's using technology from China or Europe. Copper production in Japan for the year 1697 reached 6,000 tons using the labor of 20,000 miners and 10,000 smeltermen. This production level was not attained again until the introduction of European mining and smelting technology late in the 1800's.

Blast furnace smelting to matte on charges of lump ore, pellets, sinter, and plasticized wet concentrates was commonly used until the 1960's, and it still is used at two large installations (Hibi and Shisakajima) and at several small smelters. Reverberatory furnace smelting of calcine from hearth roasters started at Naoshima in 1918, and of green concentrates at Onahama in 1965. A flash furnace of Outokumpu design replaced the blast furnace at Ashio in 1956. Subsequently, flash furnace smelting was adopted at five other smelters.

Rotatable converters replaced hearth converters at Ashio in 1892, and were in general use by the 1920's. The last of the hearth converters was retired in 1962. Smelting of concentrate in converters with oxygen-enriched blast was established at Hitachi in 1956, and continued until a flash furnace was built in 1972. A three-furnace continuous smelter linking fixed hearth melting, slag cleaning, and smelting furnace was added at Naoshima in 1974.

Serious pollution damage from smelter stack gas was first recorded in 1893 when farmers near a new smelter at Niihama complained of crop damage. To avoid payment of reparation for crop damage, the smelter was relocated in 1905 to the uninhabited island of Shisakajima, 12 miles from Niihama. However, adverse winds carried the smelter plume over the mainland with continued crop damage and reparation payments. An acid plant was installed in 1929 to treat

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

the converter gas, and this alleviated, but did not eliminate, the pollution problem. Satisfactory pollution control was obtained by ammonia scrubbing of the blast furnace offgas from 1939 to 1953, but ammonia scrubbing proved to be expensive. The ammonia scrubber was replaced in 1954 by an acid plant when a new technique for blast furnace operation (Momoda) was developed that yielded gas rich enough for acid manufacture. Copper smelting at Shisakajima was curtailed starting in 1971 when the parent Sumitomo Co. constructed the Toyo flash furnace smelter near Niihama. Sulfur dioxide capture of 99 percent is attained at Toyo by use of hoods, ducts, and scrubber to capture and treat fugitive emissions, by manufacture of acid from the flash furnace and converter gases, and by caustic scrubbing of acid plant tail gas.

FIGURE 1. - Location map of 10 largest copper smelters in Japan.

SUMMARIES OF PRACTICE AT THE MAIN COPPER SMELTERS IN JAPAN

Japan has 14 copper smelters. Ten have capacities of 40,000 or more metric tons[5] of copper per year; four are rated at 10,000 to 25,000 metric tons of copper per year. The locations of the 10 largest smelters are shown in figure 1. The processes used for smelting and SO_2 capture at eight of the smelters are listed in table 1. The smelters at Hibi and Shisakajima use blast furnaces, but are not otherwise described. Individual summaries of practice follow for the eight other large smelters. The four small smelters generally use blast furnaces for smelting sulfide concentrates, scrap, and various residues. They are located at Kunitomi (Sumitomo Metal Mining Co.), Miyako (Rasa Industries), Okayama (Dowa Mining Co.), and Onahama (Toho Zinc Co.).

[5]Capacity and production quantities in this report are metric tons of 2,205 avoirdupois pounds.

TABLE 1. - Smelting and SO_2 emission control practice

Smelter	Copper capacity, 1,000 metric tons per year	Smelting process	Offgas SO_2, pct	Furance gas treatment	Acid plant tail gas scrubber	Sulfur capture, pct
Ashio: Furukawa Mining Co.	40	Flash furnace	-	ST acid plant	-	91
		P-S converters	(1)	-	-	
Hitachi: Nippon Smelting Co.	150	Flash furnace, O_2 enriched.	10-12	DT acid plant	None	97
		P-S converters	4- 6	ST acid plant	do	
Kosaka: Dowa Mining Co.	60	Flash furnace	8-10	do	CaO slurry	99
		P-S converters	4- 6	do	do	
Naoshima: Mitsubishi Smelter Co. (2 systems).	150	Fluid-bed roaster	11	DT acid plant	None	98
		Reverberatory furnace	(2)	-	-	
		P-S converters	(3)	-	-	
	50	3-furnace continuous	10	ST acid plant	CaO slurry	
Onahama: Onahama Smelting & Refining Co.	240	Reverberatory furnace	2-2.5	1/2 to MgO scrubber, then strong SO_2 to DT acid plant, 1/2 to CaO scrubber.	NaOH solution	99
		P-S converters	7- 9	ST acid plant	CaO slurry	
Saganoseki: Nippon Mining Co.	150	Flash furnace O_2 enriched.	10-12	DT acid plant	None	97
		P-S converters	4- 6	ST acid plant	NaOH solution	
Tamano: Hibi Kyodo Smelting Co.	80	Flash furnace	7- 8	DT acid plant	None	99
		P-S converters	(1)	-	-	
Toyo: Sumitomo Metal Mining Co.	120	Flash furnace	7- 8	ST acid plant	NaOH solution	99
		P-S converters	(1)	-	-	

DT--Double train. P-S--Pierce-Smith. ST--Single train.

[1] Combined with flash furnace gas.

[2] Combined with continuous furnace gas.

[3] Combined with roaster gas.

Ashio

The Ashio mine and smelter were described in a Mining and Metallurgical Institute of Japan-American Institute of Mining, Metallurgical, and Petroleum Engineers (MMIJ-AIME) paper in 1972 (1). Both Japanese and imported concentrates are processed. Blast furnaces were used from the startup in 1877 until replaced by an Outokumpu-type flash furnace (the first flash furnace in Japan) in 1956. After 5 years of troublesome and inefficient operation, the initial flash furnace was rebuilt and the new furnace started up in 1962. About 400 tons per day of concentrates are mixed with flux, dried to 0.2 percent moisture in a rotary dryer and cage mill, and injected with fuel into the flash furnace by air preheated to about 430° C. Slag, after settling in an electric furnace to separate entrained matte, is granulated and sold. The granulated slag contains, in percent, 0.5 Cu, 38 Fe, and 33 SiO_2. Matte of about 47-percent-copper grade from the flash and electric furnaces is converted to blister copper in rotary furnaces. Converter slag is slowly cooled, and then ground and floated to recover both a copper concentrate for recycle to the flash furnace and tailings high in iron for sale.

Offgas from the flash furnace is cooled from 1,290° to 360° C, in a waste heat boiler, cleaned in cyclones and electrostatic precipitators, and then fed along with the converter gas to a single-train sulfuric acid plant. Dust from the electrostatic precipitator on the converter gas is sent to a lead smelter for treatment. The 1972 report shows 91 percent of the feed sulfur to the smelter was converted to 98-percent grade sulfuric acid, at the rate of about 300 tons H_2SO_4 per day.

Hitachi

The Hitachi smelter was described in an AIME paper in February 1974 (6). Domestic and imported concentrates are blended for smelter feed. Blast furnaces in use from 1908 gave way to converter smelting of concentrate with an oxygen-enriched blast in 1956. In 1971 converter smelting was replaced by flash furnace smelting using hot, slightly enriched air.

Concentrates from the blending plant are mixed with flux, dried to 0.2 percent moisture in a rotary dryer and cage mill, and along with fuel oil and recycled dust, are injected into the flash furnace with 900° to 950° C oxygen-enriched air. The air is preheated using checker-type hot stoves that are heated by burning fuel oil. The air is only slightly enriched to between 21 and 23 percent O_2 to avoid excessive formation of magnetite concretions in the flash furnace. Use of a high-temperature blast is preferred to burning of extra fuel oil in the furnace because the latter increases the furnace gas volume and the dust load and dilutes the SO_2 content of the offgas.

Slag from the flash furnace is settled in an electric furnace with pyrite added to reduce copper losses and then granulated. The granulated slag contains 0.5 percent copper. Matte of about 50-percent-copper grade from the flash and electric furnaces is converted to blister copper in rotary converters using blast air enriched to 22 or 23 percent oxygen. Converter slag is cooled on a conveyer and then ground and floated to recover copper concentrate

for recycle to the flash furnace and a residue high in iron for sale to cement manufacturing plants. Heavy oil injected through the tuyeres is used as the reductant for refining the blister in the anode furnace. Typically, anodes contain, in percent, 99.3 Cu, 0.15 O_2, 0.07 Pb, 0.047 As, 0.02 Sb, and 0.005 S.

Offgas from the flash furnace after cooling in a waste heat boiler and cleansing in cyclones and electrostatic precipitators is fed to a double-train acid plant. The acid plant feed gas contains 10 to 12 percent SO_2. Offgas from the electric furnace settler and converters is cleaned and then processed in a single-train acid plant. Fugitive gas is collected by hoods and ducts at tap and transfer points, and is discharged along with acid plant tail gas up a 156-meter stack atop a 200-meter hill.

Total production of H_2SO_4 as 98-percent-grade acid is about 900 tons per day, and overall sulfur capture in acid, slag, and dust is about 97 percent.

Kosaka

The Kosaka smelter was described in two papers presented in May (9) and October 1972 (12). It was visited by Bureau of Mines metallurgists in November 1974. Domestic concentrates of unusually fine grind, and relatively high in lead, zinc, cadmium, and bismuth, are the principal copper feed. Blast furnaces were used from startup in about 1900 until replaced by a flash furnace (the second in Japan) in 1967.

Concentrates are wet and difficult to dry because of the unusually fine grind required for selective flotation of Japanese complex copper-lead-zinc ores. Two stages of drying--first in a rotary dryer, then in a flash dryer--reduce the moisture content from about 14 percent to 0.2 percent. Dried concentrate, flux, and fuel oil are injected into the flash furnace with air preheated to 450° C. Flash furnace slag containing 1 to 1.5 percent Cu is settled in an electric furnace to a copper content of about 0.6 percent, and then granulated and used for mine fill.

Matte of about 45 percent Cu grade, containing 3 percent Pb and 4 percent Zn, is converted to blister copper in rotary converters using blast air enriched to 24 percent O_2. The metal is overblown at the end of the metal stage to further remove lead from the blister copper. Converter slag, containing about 5 percent Cu, is slowly cooled on a sandbed, crushed and ground, and then floated to make a concentrate for recycle to the flash furnace and a tailing for disposal.

Ammonia, injected through tuyeres, is the reductant in the rotary refining furnaces. The composition of smelter feed and products in 1972 is shown in table 2. In November 1974, the feed concentrate composition was stated as, in percent, 22 Cu, 26 Fe, 29 S, 12 SiO_2, and 8 combined Pb and Zn.

Offgas from the flash furnace is at a temperature of 1,300° C and contains 8 to 10 percent SO_2. It is heavily laden with dust and fume. The gas is cooled in a waste heat boiler to 350° C, and the dust density drops from 120 grams per cubic meter to 70 grams per cubic meter. Lead sulfide that

volatilizes from the charge tends to condense and stick on the water tube walls, necessitating frequent soot blowing and hand lancing for dust and scale removal. En route to a single-train acid plant, the gas goes through cyclones and an electrostatic precipitator that drops the dust load to about 1 gram per cubic meter. Converter gas containing 4 to 6 percent SO_2 goes through an electrostatic precipitator to a single-train acid plant. Tail gas from the acid plants containing 0.15 to 0.18 percent SO_2 is scrubbed with a lime slurry to make gypsum of wallboard grade, and scrubbed gas containing 0.02 to 0.03 percent SO_2 for discard. About 700 tons of H_2SO_4 is made daily in the form of 98-percent-grade acid. Less than 1 percent of the feed sulfur is discharged to the atmosphere. About 2.8 percent is fixed in the slag, 5.2 percent in gypsum, and 91 percent in sulfuric acid.

TABLE 2. - Typical analysis of products at Kosaka smelter, Dowa Mining Co., 1972

	Grams per metric ton		Percent									
	Au	Ag	Cu	Pb	Zn	Fe	S	SiO_2	As	Bi	Cd	Sb
Smelting charge.	2.5	309	17.9	2.7	4.9	26.4	31.9	12.8	0.17	0.04	0.03	0.11
Matte.....	5.9	698	40.1	2.9	4.4	24.9	24.9	ND	.03	.02	.02	.12
Slag.....	.14	22	.7	.5	6.8	40.5	ND	29.0	.05	ND	ND	.12
Boiler dust.....	2.3	329	18.9	7.4	8.6	28.3	7.9	2.6	.43	.05	.09	.20
Cyclone dust....	2.7	276	14.4	11.9	9.4	21.2	8.7	1.9	.77	.16	.17	.31
Cottrell dust...	1.6	264	10.9	19.7	9.1	11.3	10.0	1.0	2.04	.50	.38	.47
Converter Cottrell dust..	ND	ND	.7	40.1	14.7	1.1	10.7	ND	2.18	.65	.23	.21
Converter slag..	.3	40	2.8	2.9	7.7	46.8	ND	18.6	.07	ND	ND	.15
Copper concentrate from converter slag.	2.7	468	28.4	5.8	4.9	28.8	8.0	10.0	ND	ND	ND	ND
Tailing of slag flotation.....	.17	8.9	.5	1.2	5.8	49.4	.2	17.5	ND	ND	ND	ND
Copper anode....	16.3	2,023	99.1	.20	.01	.01	.01	ND	.04	.01	[1].02	.04

ND--Not determined.
[1]Selenium.

Dust collected in the boiler and cyclones is returned to the flash furnace. Dusts recovered in the electrostatic precipitators have a high lead content, and these are separately processed to recover lead bullion and copper matte.

Naoshima

The continuous-smelting process at Naoshima was described in an MMIJ-AIME paper in 1972 (11). The smelter complex was visited by Bureau of Mines metallurgists in November 1974, at a time when the continuous furnace was not operating. Both domestic and foreign concentrates are processed at Naoshima. Reverberatory furnace smelting of calcine from hearth roasting of copper concentrate started at Naoshima in 1918. A smelter addition of slightly greater capacity than the original smelter and using a fluidized-bed roaster was constructed in 1969. The original smelter was closed in 1973, and a prototype continuous smelter (Mitsubishi three-furnace process) with a capacity of about 50,000 tons of copper per year started operation in 1974.

In the conventional smelter constructed in 1969, concentrates are roasted at bed and freeboard temperatures of 630° and 560° C, respectively. A bed is

maintained by feeding minus 3-mesh flux with the concentrate. About 80 to 90 percent of the calcine, with about 45 percent of the sulfur removed, exits with the offgas and is collected in cyclones. Calcine is fed to the reverberatory furnace using a Wagstaff gun. The furnace is fired with fuel oil and preheated air. Reverberatory furnace slag containing 0.5 percent Cu is granulated in seawater and sold to cement manufacturers.

Matte containing about 40 percent copper is processed to blister in rotary converters. Oxygen enrichment of the blast may be used when cement or scrap copper is part of the converter charge. Converter slag is slow-cooled and then ground and floated to recover copper concentrate for recycle to the roaster, and an iron-rich tailing containing 0.3 percent Cu is sold.

Only the pilot plant and semicommercial stages of the three-furnace continuous smelter have been described. In the semicommercial stage, dried concentrate flux and oxygen-enriched air were injected through top-blown lances into the smelting furnace. From there, slag and matte flowed to an electric slag-cleaning furnace. Cleaned slag was granulated and the matte flowed to a top-blown converting furnace. Blister of about 98-percent grade was made in the converter. Converter slag was granulated and recycled to the smelting furnace.

Offgas from the roaster is cleaned and cooled by passing through primary and secondary cyclones, a waste heat boiler, tertiary cyclones, and an electrostatic precipitator. The gas, containing about 11 percent SO_2, is mixed with cleaned converter gas to obtain a blend containing about 5 percent SO_2 that is fed to a double-train acid plant and then discharged to the atmosphere. Cleaned and mixed gases from the continuous and reverberatory furnaces are treated in a single-train acid plant; the tail gas goes to a lime slurry scrubber that makes wallboard-grade gypsum. A part of the manufactured acid at about 50 percent strength is bled from the drying tower and reacted with lime to make gypsum. Total gypsum manufacture is 10,000 tons per month. Total production of 98 percent acid is 40,000 tons per month, and about 2,000 tons per month of fuming-grade acid also is produced. About 98 percent of the feed sulfur is fixed in the slag or captured in gypsum and acid.

On May 25, 1975, the Texas Gulf office in New York City announced that its copper smelter to be built at Timmins, Ontario, Canada, would incorporate the continuous-smelting process developed by Mitsubishi at Naoshima.

Onahama

The Onahama smelter was described in an MMIJ-AIME paper in May 1972 (5), and in an AIME paper in February 1974 (2). This is a seaport smelter that started operations in 1965 on a custom basis, mostly on foreign concentrates. A residential area adjoins the smelter, and rice paddies are nearby. The original smelter had one green-charge reverberatory furnace and three Pierce-Smith converters. Reverberatory gas was discharged to the atmosphere through a 170-meter stack, and converter gas was treated in a single-train acid plant for capture of about 65 percent of the feed sulfur. In 1971, the single-train acid plant was modified, fortified with a refrigeration system, and switched

to processing of 2.5-percent-SO_2 gas from the reverberatory furnace. The reverberatory furnace was tightened, and oxygen-enriched air was used for firing to achieve the 2.5-percent-SO_2 grade. A new double-train acid plant was provided for the converter gas. Sulfur capture was raised to 99 percent. In 1973, the smelter was expanded by adding another green-charge reverberatory furnace and two converters. An MgO scrubber and magnesium-salt calciners were installed to treat half of the reverberatory gas, and a lime scrubber was installed to treat the other half with production of gypsum. Strong SO_2 from the calciner is fed to a double-train acid plant, and the tail gas is scrubbed with dilute NaOH solution. Converter gas is fed to the single-train acid plant, and the tail gas is scrubbed with lime solution to make gypsum. Overall sulfur capture was raised to 99.7 percent.

Concentrates containing about 7 percent moisture are fed to the reverberatory furnaces through fettling chutes along the side walls. Two of the eight fuel oil burners in each furnace use oxygen for atomization and combustion. Reverberatory furnace slag is granulated in seawater and sold to cement mills. Matte grade averages 33 percent Cu. Lump copper silicate and other oxide ores are added to the converter during the slag blow with a blast enriched to 23 percent O_2. Converter slag is recycled to the reverberatory furnace. Commercial scrap, anode scrap, and cold blister are added during the copper-blowing stage. A butane-enriched mixture of CO and H_2 from a neighboring fertilizer plant is used as the reductant in the rotary anode furnace.

Reverberatory furnace gas at about 2.5 percent SO_2 and 6 percent O_2 goes through waste heat boilers and electrostatic precipitators en route to the MgO or CaO scrubbers. Dust removed by the electrostatic precipitator is pelletized and charged to the converters. The MgO scrubber and calciner produce 10 to 13 percent SO_2 gas, which is fed to the double-train acid plant where over 99-percent conversion to acid is obtained. The mixture of $CaSO_3$ and $CaSO_4$ made in the lime absorption tower is oxidized to sulfate with air in a second tower, then thickened, centrifuged, and used in a captive gypsum wallboard plant. Tail gas from the MgO and CaO scrubber systems containing less than 100 ppm SO_2 is passed through wet electrostatic precipitators and then discharged up a 75-meter stack. Tail gas from the double-contact acid plant is scrubbed with dilute NaOH solution to fix the residual SO_2 as sodium bisulfate or sodium sulfate. In turn, tail gas from the caustic scrubber goes through a wet electrostatic precipitator and is discharged up the 75-meter stack.

Converter gas is rapidly cooled in heat boilers and then passed through an electrostatic precipitator en route to the single-train acid plant. Rapid cooling of the gas appears to minimize SO_3 formation and facilitates dust collection. Dust from the precipitator is sent to a lead-zinc plant for processing. The single-train acid plant recovers about 97 percent of the SO_2 as sulfuric acid. Acid plant tail gas is scrubbed with lime slurry to convert most of the residual SO_2 to gypsum. Gas from the lime scrubber at about 100 ppm SO_2 is passed through an electrostatic mist precipitator and discharged to the atmosphere through the 75-meter stack.

Hoods and ducts are used to collect fugitive emissions at tap and transfer points throughout the smelter. Additionally, the converter building is

sealed and ventilation air is collected and filtered before discharge through the 170-meter stack. Gas collected at the hoods is scrubbed with water, passed through an electrostatic mist precipitator, and discharged through the 75-meter stack. Acidic solution from the gas washing in the acid plants is neutralized with lime. Sludge is removed by filtration and blended with the concentrate feed. About 1,200 tons of 98 percent H_2SO_4 is made daily. A typical sulfur balance of the smelter is shown in table 3.

TABLE 3. - Typical monthly sulfur balance in Onahama smelter

Input	Tons	Pct	Output	Tons	Pct
Concentrate and ore....	15,554	93.9	Acid.....	12,562	75.8
Fuel oil.....	243	1.5	Gypsum.....	2,721	16.4
Reclaimed scale and spills.....	793	4.6	Slag.....	308	1.9
			Converter dust.....	51	.3
			Reclaimed scale and spills.....	793	4.6
			Disposed water.....	108	.7
			To atmosphere.....	47	.3
Total.....	16,590	100	Total.....	16,590	100

Saganoseki

The Saganoseki installation was described in an MMIJ-AIME paper in May 1972 (7). It is a custom smelter at a dockside location and processes mainly foreign concentrate. Blast furnaces were used from establishment of the smelter in 1915 until they were replaced in 1970 by a flash furnace using high-temperature, oxygen-enriched air.

Concentrate containing about 25 percent Cu and 28 percent S is blended with flux and dried to 0.1 percent moisture in a combination rotary and flash dryer. The dried feed is injected into the flash furnace by about 900° C air enriched to as much as 23 percent oxygen. The air is preheated in checker-type hot stoves by burning blast furnace gas from a nearby iron-nickel blast furnace. Slag from the flash furnace is settled in a 3,000-kva electric furnace and then granulated for disposal. The granulated slag contains about 0.6 percent Cu. Matte containing 52 percent Cu and 24 percent S is converted to blister in rotary converters using oxygen-enriched air. Converter slag analyzing 3.2 percent Cu is slow-cooled, and then crushed, ground, and floated to recover a 33-percent copper concentrate for recycle to the flash furnace and slag containing about 0.3 percent Cu and 48 percent Fe for disposal. About 10,000 tons of converter slag is floated monthly. The blister copper is refined to 99.3 percent Cu for anodes in a rotary furnace by blowing first with air and then with ammonia.

Gas from the flash furnace at 1,280° C is cooled in waste heat boilers to 380° C, cleaned in cyclones and electrostatic precipitators, and delivered to a double-train acid plant. Despite gas dilution, which occurs when blowing soot and lancing boiler tubes, the feed to the acid plant gas-cleaning system contains 10 to 12 percent SO_2. Over 99 percent of the SO_2 in the flash furnace gas is converted to acid. Tail gas from the acid plant is discharged to

the atmosphere through a tall stack. About 600 tons H_2SO_4 per day is made by treating 1,070 Nm^3 gas/min (38,000 ft^3/min) of flash furnace gas.

Converter gas is cleaned in an electrostatic precipitator en route to a single-train acid plant. Tail gas is scrubbed with caustic solution and sodium hyposulfite is recovered for sale. About 450 tons of H_2SO_4 per day is made by treating 960 Nm^3 gas/min (34,000 ft^3/min) of converter gas.

Recapitulation of overall sulfur balance shows 93 percent as sulfuric acid, 1.4 percent as sodium hyposulfite, 1.7 percent in slag, 0.6 percent in dusts and solutions, and about 3 percent discharged into the atmosphere.

Tamano

The Tamano smelter was described in an AIME paper in February 1973 (4). It was visited by Bureau of Mines metallurgists in November 1974. The smelter has a dockside location and is near the Seto Inland Sea National Park. It started operation in 1972 and processes mainly foreign concentrates by flash smelting.

About 35,000 tons per month of blended concentrates and flux is dried to 0.2 percent moisture, ground in a cage mill, and then injected with fuel oil and recycled dust into the flash furnace by air preheated to 450° C. The concentrates contain about 24 percent Cu and 28 percent S. Electrodes are provided for heating the slag in the settler part of the furnace, thus eliminating the need for a separate electrically heated furnace for slag settling. Consumption of the Soderberg-type electrodes in this service is somewhat higher than in separate electric furnace settlers. Slag from the flash furnace containing about 0.5 percent Cu, 37 percent Fe, and 35 percent SiO_2 is granulated in seawater for disposal. Matte of 47-percent grade is converted to blister in rotary converters. Slag from the converters is slow-cooled, and then crushed, ground, and floated to make copper concentrate which is recycled to smelter feed and tailings for disposal. Liquid petroleum gas is used as the reductant in the anode furnace.

The temperature of the offgas from the flash furnace is dropped about 200° C in a water-jacketed uptake leading to the waste heat boiler. Dust and fume deposits form in the uptake and must be periodically removed, but problems with scale formation of the boiler tubes are largely suppressed. From the waste heat boiler the gas passes through cyclones and electrostatic precipitators en route to the acid plant. Gas from the converters also goes through a waste heat boiler and electrostatic precipitator and then joins the flash furnace gas to a double-train acid plant. The combined gas feed to the acid plant contains 7 to 8 percent SO_2. Tail gas from the acid plant contains 200 ppm SO_2. About 900 tons of H_2SO_4 as 98 percent acid is produced daily. Overall capture of sulfur in acid and slag is about 99 percent.

Toyo

The Toyo copper smelter at Niihama City was described in an MMIJ-AIME paper in May 1972 (10), and in an AIME paper in February 1974 (8). It was

visited by Bureau of Mines metallurgists in November 1974. This is a custom smelter with a dockside location processing mainly foreign concentrates. The first Sumitomo Co. copper smelter at Niihama City was built in 1893. Because of air pollution damage to crops near the smelter, the smelter was moved in 1905 to Shisakajima Island, about 12 miles away. By using flash smelting and rigorous emission control technology, it became possible to reestablish the smelter at Niihama in 1971.

About 1,000 tons of concentrate per day is blended with silica flux dried to 0.2 percent moisture and, along with fuel oil and recycled dust, injected into the flash furnace. Slag is settled in an electric furnace, and then granulated for disposal. Matte containing about 50 percent copper is converted to blister in rotary furnaces. Converter slag is slow-cooled, crushed, ground, and floated to recover a copper concentrate that is sent to the Shisakajima smelter and tailings for disposal. Ammonia is used as the reductant for refining the blister in the anode furnace.

X-ray analyzers and a computer are used to obtain stable integrated operation of the flash furnace, converters, and acid plant. Specifically, computer control is exercised over the flash furnace slag composition, matte grade and temperature in the slag furnace, scheduling of converting operation and blowing rate, and converter slag composition.

Offgas from the flash furnace is cooled in a water-jacketed uptake and then passed through waste heat boilers and an electrostatic precipitator en route to the acid plant. Converter gas also goes through a waste heat boiler and electrostatic precipitator, and then is mixed with the flash furnace gas to the single-train acid plant. The combined feed gas to the acid plant contains 7 to 8 percent SO_2. About 900 tons of 98 percent acid is produced daily.

Tail gas containing 0.2 to 0.3 percent SO_2 is scrubbed with NaOH solution to prepare Na_2SO_3 for market. Two countercurrent scrubbing stages are used. In the first scrubber tail gas is contacted with Na_2SO_3 solution to react with SO_2 and form $NaHSO_3$. In the second scrubber, SO_2 in the tail gas reacts with NaOH solution to form Na_2SO_3 solution that is used in the first scrubber. The $NaHSO_3$ from the first scrubber is reacted with NaOH to form Na_2SO_3, which is crystallized from solution and marketed. Offgas from the scrubbers contains less than 10 ppm SO_2.

About 29 hoods are used to collect fugitive gases at tap and transfer points. The collected gas is scrubbed with water and then passed through an electrostatic mist precipitator before discharge to the atmosphere. Acid solutions formed in scrubbing the smelter gases are neutralized with lime. Overall sulfur capture is 99 percent or more. The sulfur distribution is shown in table 4, typical monthly operating data are shown in table 5, and a typical analysis of charge, products, and waste water is shown in table 6.

TABLE 4. - Sulfur distribution of Toyo smelter

	Distribution, pct
Sulfuric acid	91.9
Sodium sulfite	2.8
Dilute acid	1.6
Converter slag	1.4
Flash smelting slag	1.3
Converter electrostatic precipitator	.1
Emission at Na_2SO_3 plant	.0
Emission of sulfur	.3
Balance	.6
Total	100.0

TABLE 5. - Typical monthly operating data for Toyo smelter

Flash smelting furnace:		
Smelted:		
Concentrates	dry tons	28,903
Siliceous flux	do	1,310
Copper residue	do	281
Recycled dust	do	2,263
Total smelted	do	30,642
Produced:		
Matte	do	16,206
Slag	do	8,331
Oil used (per ton concentrate):		
At shaft	liters	36.8
At settler	do	18.2
Converter furnace:		
Charged:		
Matte	dry tons	16,484
Scrap and blister	do	792
Produced: Crude copper (98.5 pct Cu)	do	11,168
Anode furnace: Anodes produced (99.6 pct Cu)	tons	10,308
Acid plant: H_2SO_4 produced	do	25,709

TABLE 6. - Typical analysis of charge, products, and waste water for Toyo smelter

	SiO_2	Cu	S	Fe
Concentrate charged, pct	8.0	28.2	27.7	23.0
Matte produced, pct	-	49.2	23.1	22.5
Slag after cleaning, pct	33.0	.55	-	39.6
	H_2SO_4	Cu	Zn	Pb
Waste water:				
Before treating, mg/l	3,000	600	250	19
After treating, pH 7.0, mg/l	-	0.2	0.2	0.05

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