Introduction

Introduction

Non-ferrous smelter is the most versatile heavy metal processing facility which can be used for recycling purpose, without high investment of dedicated facility. In Japan, many non-ferrous smelting facilities accept hazardous industrial waste to recover heavy metal, on economical basis. This practice can provide the most extensive recycling mechanism of heavy metal waste. On the other hand, non-ferrous metal smelting facility normally has negative image as pollution industry. In Romania, Copsa Mica and Baia Mare were known to be the most polluted town in the country. The facilities itself has to improve waste minimization and internal recycling practice.

In order to promote recycling of heavy metal containing wastes in Romania, pilot project No.1 has conducted. Target non-ferrous smelters are S.C. ROMPLUMB S.A., R.B.G. PHOENIX S.A. and S.C. SOMETRA S.A. A Japanese engineer, who has well experiences on recycling of heavy metal containing waste, has conducted reconnaissance survey to above three smelters. Then, the engineer made recommendations regarding the management and 3 R (Reduce, Reuse and Recycle) of their internal wastes.

On the other hand, location of generator, amount, physical and chemical component of the external wastes that generate out of the non-ferrous smelters has investigated. The results of above investigation are utilized for the study of heavy metal containing waste recycling. In order to promote recycling of internal and external wastes in the non-ferrous smelters, test briquette machine was procured in the SOMETRA ISP smelter. By using this test equipment, above internal and external wastes can be made briquette and fed easily to Imperial Smelting Process furnace. The briquette test of heavy metal containing wastes has conducted in the SOMETRA smelter. Produced test briquettes were analyzed, evaluated and measured the hardness. After evaluating all the results of these investigation and test, the possibility of heavy metal containing wastes by using existing non-ferrous metal smelter in Romania was studied.

Part 1

Technical Improvement Recommendation for Target Smelters in terms of 3 R activities

1. Technical Improvement Recommendation of Target Smelters in Terms of 3 R Activities

The reconnaissance was conducted two times by well experienced non-ferrous metal smelting engineer. Total duration of site survey is approximately one month. No.1 Site survey $2002/12/7 \sim 2002/12/22$

S.C. ROMPLUMB S.A., R.B.G. PHOENIX S.A. and S.C. SOMETRA S.A. No.2 Site survey 2003/1/4~2002/12/24

S.C. SOMETRA S.A.

Objectives are as follows.

- To review the current smelting facility and operation in the smelter.
- To provide improvement plan for internal 3R and treatment of external waste materials.

1.1 S.C. ROMPLUMB S.A.

1.1.1 Outline of the Smelter

This smelter is a toll smelter, which receives lead concentrate from a company in Poland and returns metal lead. Please refer to $IMNR^1$ Research Report 1 for the outline of the process, capacity, etc.

1.1.2 Problems and Request of the Smelter

Slag produced from the blast furnace is kept in the smelter and there is no space to store it. The request of the smelter is to have it treated out of the smelter to stop accumulation of the slag in the smelter plant area. Amount of annual production is approx. 30,000 tons/year and average composition is as follows.

Chemical composition of slag

Pb	2 to 3%
Fe	39 to 42%
CaO	9 to 10%
Cu	0.5 to 1%
SiO2	29 to 33%
S	1 to 2%

Slag is stock piled in the smelter plant area. Rain water falling on the slag is sent together with rain water in the plant to two pits of $25m \times 7m \times 2,5m$ depth alternately where solids are settled and then, water is analyzed to confirm its quality. Then water is discharged out of the plant. Lead has not been observed by this analysis.

1.1.3 Recommendation

Do the elution test of slag to confirm that it meets the EU Standards. When EU regulations are adopted, there should be some standard for elution from the wastes. In such case, the analysis method should also be specified in the regulation. (See Annex 1, Japanese standard and measuring method)

¹ Institute for nonferrous and rare metals

Rain water normally is neutral but the regulation is made taking into consideration the possibility of elution depending on how the wastes are stored so it is necessary to confirm that there is no elution even under such regulation. For your reference, relationship between pH value of water and dissolution of hazardous elements is shown in Figure 1.1.1.

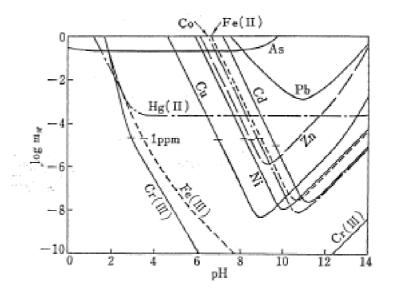


Figure 1.1.1 Dissolution of Hazardous Elements and pH

Slag is a kind of glass and heavy metals in slag cannot be dissolved in water.

The substances other than glass, as shown in Figure 1.1.1, the hazardous elements tend to dissolve easily at low pH.

1.1.4 Slag Treatment Method in Japan

• Raw material for cement

Most of slag generating from non-ferrous metal smelters in Japan are used as raw material for cement. Average composition of raw material for cement is approximately 78% limestone, 16% clay, 4% silica and 2% iron material. Slag contains iron, silica and calcium and therefore, it can be used as raw material for cement. Clinker production capacity in Rumania is 11 million tons per year, which is sufficient to accept slag as raw material. However, it is necessary for cement producers to positively accept the hazardous wastes. Even if there is a little lead content, there will be no elution after it becomes concrete cement and therefore, it can be well used as raw material. Main raw materials of cement are limestone and clay and industrial wastes including slag are used as sub-materials. In 2001, total of 335 kg industrial wastes were used per ton of cement by the cement producers in Japan. Slag cleared the elution regulation is able to use the following usages.

• Use as substitute material for sand in sand blasting

In shipbuilding yards, sand blasting is done before painting to remove rust. Non-ferrous metal slag as a substitute material for sand. However, we cannot expect to treat much quantity of slag by this method.

• Use for the roads

In Poland and Germany, slag is used for a material of road such as paving stone.

• Other usages

Fill a caisson with slag and use it as a weight.

Raw material for steel manufacturing.

Tests to remove hazardous S, Cu, etc. to be used as raw material for steel manufacturing were once done but it was not adopted due to high cost.

1.2 R.G.B. PHOENIX S.A.

1.2.1 Outline of the Smelter

The smelting process can be roughly classified into smelting and refining and in this plant. Smelting process has been stopped since June 2000. It is considered just as a temporary stoppage and there is a possibility of resuming operation in the future. The sludge, which is the subject of the project, is from the smelting and there is no generation at present. Please refer to IMNR Research Report 1 for the outline of the process, capacity, etc.

1.2.2 Problems and Requests of the Smelter

The subject sludge contains arsenic. At present, it is stored in a concrete pit but if there is a leak from the pit, there is a possibility of contaminating the surrounding environment. The roof covers the pit, but the roof is broken. Amount of stored sludge is approx. 4,000 tons and average composition is as follows. Now it is not generating, it is historical waste.

Averag	e Composition
Cd	0.01 %
Bi	0.01-0.025 %
MgO	0.21-0.24 %
MnO	0.006 %
Al	0.47-0.78 %
S	10.2-11.71 %
SiO ₂	8.15-11.55 %
As	1.5-2.06 %
Fe	4.9-7.93 %
CaO	29.4-34.43 %
Cu	1.86-3.1 %
Pb	0.53-0.58 %
Zn	3.65-3.9 %
Sb	0.46-0.55 %
Au	1.0-2.0 g/t
Ag	39-114.6g/t

Survey team measured the pH value of water pooled on top to sludge and it was pH 6. This sludge was generated when heavy metals were removed from water discharged from the gas washing process of sulphuric acid production process by neutralization with lime and turning the pH value to 11 or 12. The present process is shown in Figure 1.2.1

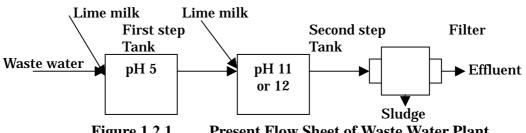


Figure 1.2.1 **Present Flow Sheet of Waste Water Plant**

When rain water is pooled in the pit, this water is treated in the waste water treatment plant, where water from the entire plant is treated, and then discharged. Therefore, there is no problem. Concern of the plant is when there is a leak from the pit bottom, there is a possibility of contaminating the surrounding environment. As a countermeasure, they are considering the repair of roof and making a monitoring well around the pit to detect if there are any leaks from the pit.

1.2.3 Recommendation

- In addition to repair of the roof, walls may be made around the pit so that there will be no penetration of rain water. Then, there will be no more concern about leak from the pit after evaporation of water in the pit.
- We propose to carry out the following tests to confirm the minimum elution of heavy metals from the sludge.

Verify the PH value that keeps to minimum the elution of arsenic from the sludge. Prevent re-elution of arsenic by adding iron to water and let iron absorb arsenic. Add cement to sludge and see if arsenic elutes from the solidified material (or if it will solidify or not).

Reduce the quantity of sludge. When the smelting operation is resumed in the future, maintain the first stage to around pH 3. In this stage, there will be no deposition of heavy metals but only gypsum is produced. After separating this gypsum from water, raise the pH value to 11 or 12 to deposit heavy metals. By this measure, the quantity of sludge is decreased equivalent to the quantity of gypsum. This flow sheet is shown in Figure. 1.2.2.

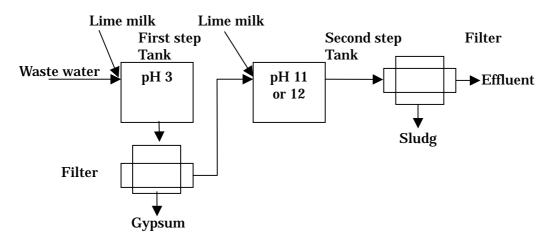


Figure 1.2.2 Improved Process Flow Sheet

• Method to prevent elution of arsenic from sludge (Reference)

Annex 2 shows the test report stating that there will be no elution of arsenic when sludge is incinerated at 900 degree C.

1.3 S.C. SOMETRA S.A.

1.3.1 Outline of the Smelter

S.C. SOMETRA S.A. is the largest refinery, which has a simultaneous lead and zinc smelting (Imperial Smelting Process, ISP) and refining processes, in Romania. The No.1 line has converted to the ISP process "Imperial Smelting Process" and begun operation in 1966. The No. 2 line was originally designed and was put into operation in 1985. The line was stopped in 1992 because of its low productivity and serious pollution. Lead and zinc are refined by electrolysis and rectification, respectively, after the ISP smelting process. The sulphuric acid plant is superannuated and is now out of operation. Construction of a new sulphuric acid plant is being planned. Please refer to IMNR Research Report 1 for the outline of the process, capacity, etc.

1.3.2 Problems and Requests of the Smelter

SOMETRA itself thinks that following items are the problems regarding HW management and 3 R. Therefore, Japanese engineer made recommendations to these problems.

- Improvement of SO₂ emission (Study of H₂SO₄ Production)
- Reduction and process improvement of Pb-Zn dross
- Reduction of blue powder
- Reduction of Cu-Pb dross
- Improvement of internal powder products
- Utilization of slag

1.3.3 SO₂ Emission and H₂SO₄ Production

(1) SO₂ Emission from the Smelter

The emission source of SO_2 gas is the sintering plant. This plant is the preparation process for the Imperial Smelting Furnace (ISF) where raw zinc concentrate and lead concentrate, which are raw materials, are sintered, to be ready for feeding to ISF. The regulation is ground concentration limitation. There is no limitation to the concentration and quantity of SO_2 emission

Regulation limits (ground level)

30 minutes	$0.75 \text{ mg/m}^3 \text{ max.}$
24 hours	$0.25 \text{ mg/m}^3 \text{ max}.$

In the year 2001, the maximum value for 24 hours was 0.391 mg/m³ and the

minimum was 0.0025 mg/m^3 , and it often exceeds the regulation limits.

Both zinc concentrate and lead concentrate are sulphides and they are burned in this sintering plant where sulphur is turned to SO_2 gas.

Material balance of the sintering plant in the year 2000 is shown in Table 1.3.1.

		Gross	Pb			Zn		Cu	S	
			%	t	%	t	%	t	%	t
Feed	Pb conc.	19,690	63.6	12,524	7.8	1,532	0.4	80	19.1	3,762
	Zn conc.	50,909	2.3	1,153	51.3	26,117	0.5	233	29.7	15,112
	Bulk conc.	73,441	14.1	10,391	42.4	31,174	1.0	771	28.6	21,013
	Blue powder	5,385	29.6	1,593	26.8	1,442	1.0	55	3.7	200
	Secondaries	11,881	34.3	4,070	29.5	3,504	1.2	141	0.0	0
	Flue dust	9,851	61.7	6,074	7.0	690	0.5	52	9.2	910
	Others	2,428	7.0	171	54.8	1,330				
	Return sinter	661,662	17.9	118,563	40.9	270,339	0.7	4,896	2.3	15,217
	Lime stome	9,618								
	Silica snad	0								
	Iron oxide	10,448								
	Total	855,312	18.1	154,538	39.3	336,127	0.7	6,228	6.6	56,215
Product	Sinter	812,975	17.9	145,686	40.9	332,184	0.7	6,017	2.0	15,944
	Flue dust	12,895	60.6	7,819	8.5	1,096	0.4	57	9.2	1,186
	Burnt S									39,085

 Table 1.3.1
 Material Balance for Sintering Machine in SOMETRA(2000)

Quantity of SO₂ gas volume calculated from the above table is $3,565 \text{ Nm}^3/\text{hr}$. Meanwhile, concentration of SO₂ gas emitted from the sintering plant is 2.8% to 3.7%. This gas is cooled, de-dusted and then discharged through 250m stack. One of the methods to remove this SO₂ gas is to recover sulphuric acid using SO₂ gas as a raw material and before, there was a sulphuric acid plant at SOMETRA but it did not work well and is left untouched without any operation.

(2) Outline of Sulphuric Acid Plant

SO₂ gas concentration required for recovery of sulphuric acid.

SO₂ over 6%; Double contact process can be applied. Sulphur recovery rate is higher than 99.5%.

 SO_2 over 4%; Single contact process can be applied. Sulphur recovery rate is higher than 95%.

(With the single contact process, Sulphur recovery rate is low and therefore, there are cases wherein de-sulphurization plant is installed after the sulphuric acid plant.)

SO₂ lower than 1%.

De-sulphurization is applied.

(There is a process called Topso process that can recover sulphuric acid from 2.4% SO₂ or higher gas but the plant is expensive and the application is limited. This process is used to produce sulphuric acid is from lead sintering machine exhaust gas at Metaleurop, Nayelles-Godaut, France.)

Process reaction of sulphuric acid is as follows

 $SO_2 + 1/2O_2 = SO_3 + heat generation$ $SO_3 + H_2O = H_2SO_4 + heat generation$ The reaction $SO_2 + 1/2O_2$ is promoted at the temperature higher than 420 degrees C with the existence of catalyst. The temperature is elevated to 420 degrees C utilizing the heat from reaction but when the SO_2 concentration is low, the heat generated by exothermic reaction becomes insufficient. It is possible to make up this heat using an auxiliary fuel but it will raise the fuel cost and it is therefore, not practiced.

Further, the facilities are mainly made of normal steel and therefore, it is necessary to maintain sulphuric acid concentration to over 93% H₂SO₄. Otherwise, it will become necessary to use very expensive materials. In the above formula, H₂O is carried in from the gas. Its quantity is determined by the saturation temperature. In an ordinary facility, the sulphuric acid concentration goes down if there is no 4%SO₂ or higher.

This is the reason why the sulphuric acid plant of SOMETRA was not used and left untouched. The SO₂ content in the exhaust gas from sintering machine of SOMETRA is lower than 4% and both heat balance and water balance do not satisfy the conditions for sulphuric acid plant. Increasing the concentration of SO₂ in the exhaust gas from sintering machine of SOMETRA can be achieved by recycling the sinter gas. By this method, SO₂ gas concentration can be raise to somewhere around 7%. With this means, sulphuric acid plant can be installed and it is possible to produce sulphuric acid.

(3) Improvement of Sintering Plant

ISF (Imperial Smelting Furnace) is just like the blast furnace for iron, the oxide ore is reduced. Hot air is blown into the furnace from its bottom to generate heat and do reduction by coke. In order to maintain good gas flow in the furnace, raw materials are fed in a form of lumps. Zinc and lead ores which are raw materials, are mainly sulfide ores in a powder form. Prior to feeding into IFS, they are oxidized and sintered to form lumps by the reaction heat of oxidation. This function is done by the sintering machine. Sintering process is illustrated in Figure 1.3.1.

First, the ores are spread in a thin layer and ignited by heating from the top. Then ores are fed over this layer at a fixed thickness. Air is fed from the bottom for ore combustion. While ores are moving to right as illustrated in Figure 1.3.1, they are dried, pre-heated, reacted and cooled to form lumps of oxidized state. Because they are sulfide ores, they produce SO_2 gas by this reaction.

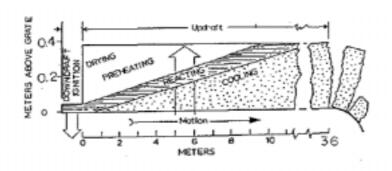


Figure 1.3.1 Sintering Machine

Gas flow at present SOMETRA Plant is shown in Figure 1.3.2.

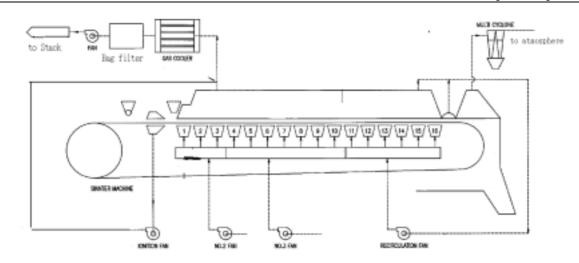


Figure 1.3.2 Gas Flow (Present)

A modification plan is shown in Figure 1.3.3.

The major function of the end part is cooled the sintered ores and almost no sulphur is burned at this place. In other words, almost no oxygen is consumed and the gas is returned to the front part of the sintering machine where combustion mainly takes place so as to minimize the quantity of gas generated in the sintering machine. The quantity of burned sulphur remains the same which means that SO_2 concentration can be raised up to the gas concentration suitable for treatment in the sulphuric acid plant.

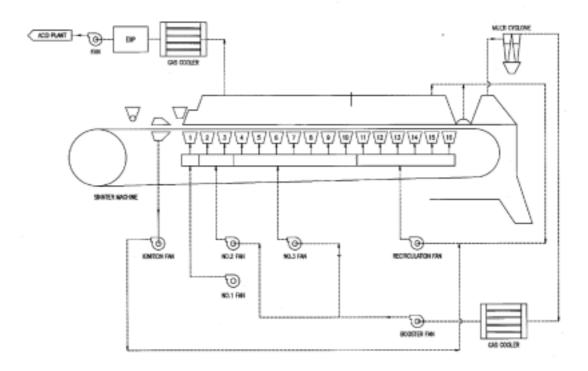


Figure 1.3.3 Gas Flow (Improvement)

A change in sulphur in sintering machine after the improvement is shown in Figure 1.3.4.

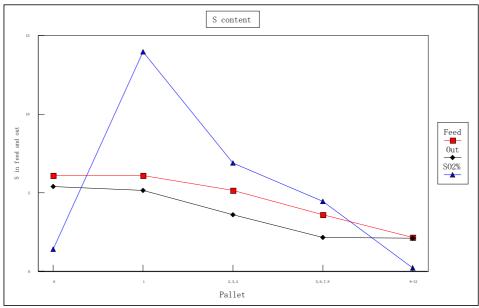


Figure 1.3.4 Sulphur content in Ore and Sinter and SO₂ in Gas

Gas with high SO_2 concentration can be obtained from the front area of sintering machine and gas is drawn out mainly from this part to become the raw material for acid plant. Changes in temperature inside the sintering machine are shown in Figure 1.3.5. The temperature of exhaust gas from the sintering machine reaches 350 to 450 degrees C.

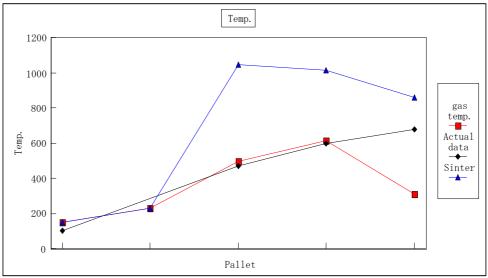


Figure 1.3.5 Temperature of Sintered Ore and Gas

When gas with high SO_2 concentration is fed to the sulphuric acid plant, the gas temperature rises and therefore, the bag filter that is presently used can no longer be used and an electrostatic precipitator will be used for dust removal. Further, the existing sintering machine has a problem of dust leak from the end of the machine. By recycling a large amount of gas from the end of the machine, it will prevent scattering of dust to outside of the machine.

(4) Sulphuric Acid Plant

Quantity of sulphuric acid production $(98\%H_2SO_4, possible to produce 95\%H_2SO_4)$ is 120,000 t/y. Flow sheet for gas purification process is shown in Figure 1.3.6.

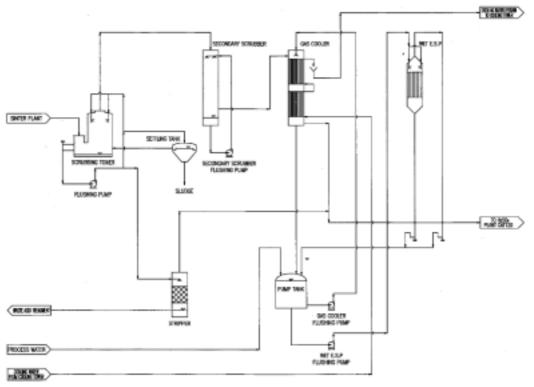


Figure 1.3.6 Gas Purification Process in Acid Plant

Dust cannot be completely removed by the electrostatic precipitators installed at the outlet of the sintering machine. Further, contents like Cl_2 exists in a form of gas. Some of these components like Cl_2 and As shorten the life of catalysts and therefore, it is necessary to remove them by washing the gas with water. Further, when sulphuric acid is produced by the reaction $SO_3 + H_2O = H_2SO_4$. The moisture content required to produce 98% sulphuric acid differs depending on SO_2 concentration but the gas is sent to the converting process after dropping the temperature to lower than the design operating condition and therefore, a gas cooling facility is equipped. At the end of this process, there is a wet type electrostatic precipitator, which collects and removes water drops and mist coming together with the gas.

(5) Converting Process

Converting process of SO_2 gas and absorption process of SO_3 gas are shown in Figure 1.3.7.

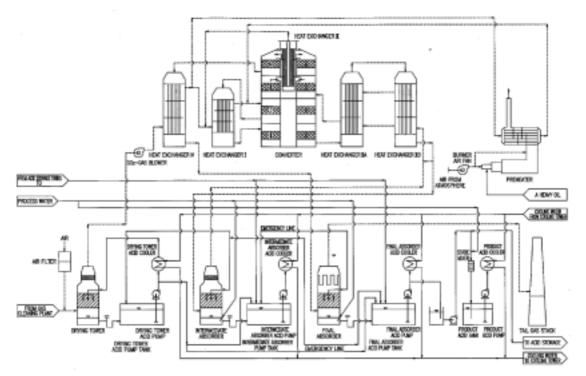


Figure 1.3.7 SO₂ Gas Conversion and SO₃ Gas Absorption Process

For SO_2 to react to make SO_3 under existence of catalyst in converter, temperature above 420 degrees C is required. Heat is generated by this reaction and this reaction heat is used in the heat exchanger to heat the raw material gas to the reaction temperature. At start up of the plant, a pre-heater is used to heat up to the specified temperature but after reaction starts, the operation can be done with only reaction heat. The generated SO_3 is absorbed in circulation sulphuric acid at the absorbing towers.

• Double contact

In the reaction $SO_2 + 1/2 O_2 = SO_3$, SO_2/SO_3 will balance at a certain point and the reaction will not proceed further. However, when SO_3 is removed, the reaction will proceed from left to right and SO_2 decreases. Installing two stages in the absorption tower for absorption of SO_3 is called a double contact process.

• Moisture in feed gas and absorption of SO₃

It consists of a drying tower and a double stage absorption tower. Wet gas from the purification process is first dried in the drying tower. This drying tower is operated by 95% H₂SO₄. The concentration drops by absorbing moisture but the concentration is kept constant by receiving 98% sulphuric acid form the absorption tower and sending residual 95% sulphuric acid to the absorption tower.

In the absorption tower, 98% sulphuric acid is circulated. SO_3 is absorbed in the remaining 2% water. Water is further added to keep constant the 98% of concentration. The volume increases by this addition and this excess is extracted to become a product sulphuric acid. The sulphuric acid produced from the gas of sintering machine is black and hydrogen peroxide is added to erase this color. The coagulation temperature of 98% sulphuric acid is high so during wintertime, the product is diluted to 95%. These reactions are exothermic so a cooler for sulphuric acid is installed.

(6) Waste water Treatment Plant

Flow sheet of the waste acid neutralization plant is shown in Figure 1.3.8 and Figure 1.3.9.

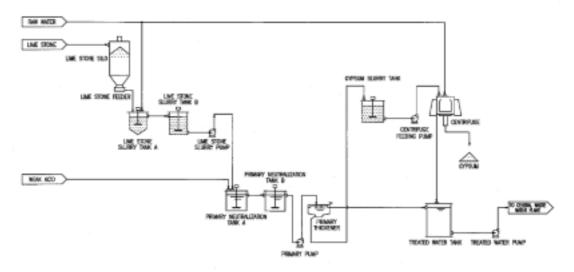


Figure 1.3.8 Waste Acid Treatment Process-1

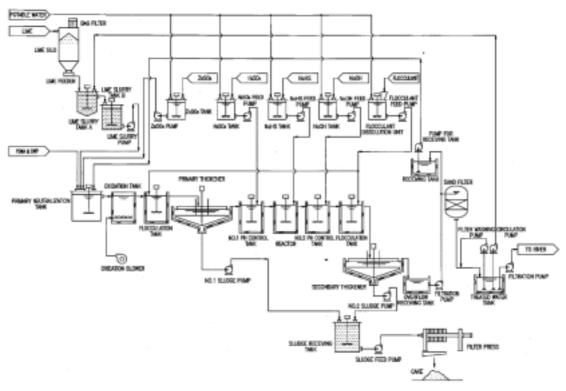


Figure 1.3.9 Waste Acid Treatment Process-2

This facility is for the treatment of waste solution coming out of the gas purification process of sulphuric acid plant. Dilute sulphuric acid and heavy metals are contained in the solution. The dilute sulphuric acid is removed as gypsum at the first stage (Figure 1.3.8) and then heavy metals are removed (Figure 1.3.9).

(7) Rough Estimate of Construction Cost

Modification of sintering machine (modification of blow system, improvement of end dust) is estimated 1.5 million US\$.

Dry electrostatic precipitator, gas cooler is 3.5 million US\$, sulphuric acid plant main (Specification: 420t/d as 100%, 6,600Nm³/h x 6%SO₂) is 24 million US\$, cooling water facility is 1 million US\$ and waste acid treatment plant is 2 million US\$. Total cost would be 32 million US\$.

1.3.4 Decreasing the Quantity of Zinc-Lead Dross

Outline of top part of ISF (Imperial Smelting Furnace) is shown in Figure 1.3.10.

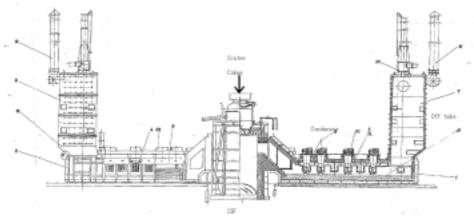


Figure 1.3.10 General Structure of ISP Furnace

Zinc gas generated by ISF is cooled in the condenser with lead spraying and absorbed in liquid lead. Zinc absorbed in lead is separated by taking out this lead and cooling it. A facility that conveys lead from condenser to cooling launder is called a sump tank. Lead and zinc dross floats on the surface of this sump tank. This dross is taken out from the sump tank by an automatic skimming device.

Dross is sieved and over sieve is fed directly to ISF. Under sieve is returned to the sintering machine. The quantity of dross generation at the plant is greater than other ISF plants causing the rise in smelting cost. Table 1.3.2 shows a comparison of dross generation among SOMETRA and other plants.

Table 1.3.2	Dross Generation	(Unit; kg/ton of zinc)
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Sometra	В	С	D	Ε	F	G	Н		J	K	L
242	190	143	217	100	103	95	202	141			169

1) Zinc-Lead Dross

Quantity generated in 2001 was around 12,200 tons. Example of chemical analysis is as follows.

	An	alysis	
Pb	35 - 45%	Cu	0.5 – 1%
Zn	23 - 33%	CaO	1.5 - 2.5%
S	0.1 – 1%	SiO ₂	2.5 - 3.2%
Fe	2.0 - 4.5%	С	9%

2) Presumption of the Causes

This dross is mainly composed of sintered and coke powder scattered from ISF. Components such as Fe, SiO₂ and CaO are normally to become slag and should not come into the condenser and indicate scattering from ISF. There are many causes of scattering. One of the main reasons is a forming of blow hole inside the ISF where air flow is concentrated and comes into the condenser together with powders. One of the probable reasons for the blow hole is the uneven dispersion of sintered lumps and coke in the furnace at charging. Strength of sintered lumps and coke can also be the reason. The strength of coke is unknown but it is apparent that a part of coke has been scattered from the fact that there is 9% C. Further, charging height in the furnace can also be the cause. If the charging height is too low, falling distance of sintered lumps and coke will be long and they are crushed by the impact of falling to become fine particles and scatter. A proper size of sintered lump is also required and there should be no powders mixed in the feed.

3) Proposal for Remedy

It is expected that the generated quantity can be minimized by operating procedures. The team recommend to have a supervision of the operation specialists.

1.3.5 Reduction of Blue Powder

(1) Blue Powder

Zinc gas generated by ISF is cooled in the condenser with lead spraying and absorbed in liquid lead. Exhaust gas from the condenser is washed in a scrubber and zinc and scattered lead that were not collected in the condenser are collected in this scrubber. This collected material is called a blue powder. This blue powder is returned to the sintering machine after recovery at the Oliver filter.

Generation of blue powder at SOMETRA is 223kg/ton of zinc, which is high compared to other ISF plants resulting in higher smelting cost. Comparison with other ISF smelters is shown in Table 1.3.3.

Sometra	В	С	D	E	F	G	Н		J	Κ	L
223	165	190	146	158	208	174	138	163	106	117	150

 Table 1.3.3
 Blue Powder Generation (kg/ton of .zinc)

Amount generated in 2001 was 11,343 tons and chemical composition is as follows.

Pb	30 - 38%
Zn	20 - 35%
Fe	0.3 – 7%
Sb	0.02 - 0.1%

(2) Estimation of Cause

It is assumed that zinc steam coming from ISF is not well collected at the condenser.

(3) **Proposal for Remedial Measure**

In order to collect Zn steam, it becomes a question whether gas velocity, gas flow direction, quantity of dispersed lead, which is the collecting material, and area of dispersion in the condenser are proper or not.

• Dispersion of lead

Rotor of SOMETRA is no well immersed in the lead bath and because of this, there is a high possibility that quantity of dispersed lead is becoming insufficient. A rotor level drawing is shown in Figure 1.3.11. At present, the blades of rotor are not completely immersed in the lead bath. It is necessary to do a modification to have the blades completely immersed in lead.

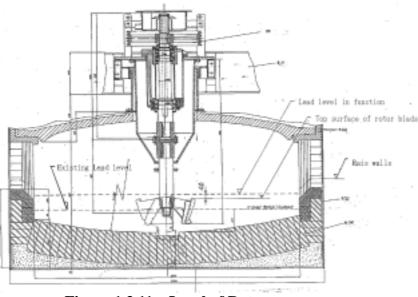


Figure 1.3.11 Level of Rotor

• Flow of gas

There are buffer plates in the condenser to change the direction of gas flow but they are coming out from only one side and there is a possibility that they are pushing the gas to wall side. Buffer plates should be coming out from both sides to collect the gas to the center of condenser. (Refer to Figure 1.3.12.)

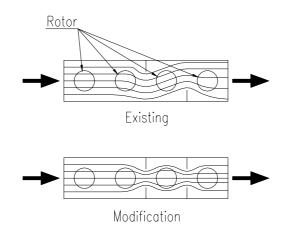


Figure 1.3.12 Gas Flow in the Condenser

In order to decrease the generation of blue powder, first of all, a modification to have proper depth of rotor is necessary.

(4) Rough Estimate of Modification Cost

First of all, priority should be given to changing the level of lead bath. Rough estimate of modification cost is US\$0.4 million. Modification of buffer plates should be reviewed after observing the results of modification of lead bath level and decided whether to modify them or not.

1.3.6 Reduction of Lead-Copper Dross

(1) **De-Copper Dross**

In the ISF, lead oxide in the sintered ore is reduced and turns to metal lead. Iron oxide is combined with silica and lime and turns to slag. They are collected at the bottom of ISF and extracted to fore-hearth. In the fore-hearth, they are separated into lead and slag by the difference of specific gravity. When arsenic is contained in the sintered ore, a layer called speiss that is mainly composed of arsenic, copper and iron is formed.

In the lead, there are metals such as copper melted in it. Lead is sent to electrolytic refining but as anode for electrolytic refining, this copper is a harmful element and therefore, de-copper is done by a dry process before casting the anodes. Copper in lead is separated from lead as dross and floats when the temperature of lead is dropped. An example of de-copper process at SOMETRA is shown in Figure 1.3.13.

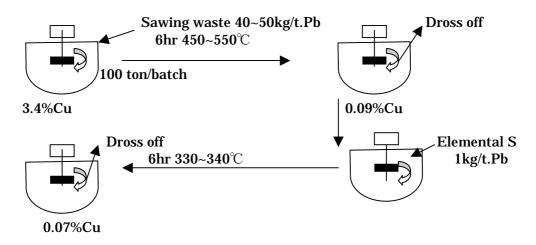


Figure 1.3.13 De-Copper Operation Flow

At SOMETRA, a speiss layer is found in the fore-hearth. Generated quantity in 2000 was 6,100 tons.

Co	mposition
Pb	40 – 75%
Cu	10 – 18%
Fe	3 – 7%
Sb	1.5 - 3.25%
Zn	2 - 6.5%
Bi	0.1 - 0.2%
CaO	2.3 - 4.5%
SiO ₂	0.75 - 3.25%
As	1 - 2%
S	0.8 – 1.5%

(2) Estimation of Probable Cause and Proposal for Remedial Measures

Copper dross generation at SOMETRA is 6,100t/y and the ratio to 20,000t/y lead production is 0.3. This ratio at other smelters is 0.12 to 0.14 and SOMETRA is very

high. To decrease the copper dross generation, the following measures is proposed.

• Shortening the de-copper time

Dross is generated by deposit of Cu and oxide Pb separated from metal Pb. The longer the operating time is, the more oxidation of Pb is promoted. Final content of Cu is determined by the temperature of Pb bath so it is necessary to think of some measure to shorten the time required for cooling to a specified temperature. For example the de-copper ladle is equipped with a heater to maintain the temperature and utilizing this, a method of forced cooling by sending only air without burning fuel can be taken during cooling time.

Meanwhile, in other smelters, de-copper operation is done at a temperature of 390 to 400 degrees C. The copper content will be smaller when the temperature is lowered.

• Elemental sulphur de-copper

In other smelters, de-copper by elemental sulphur is not done but electrolytic refining is done at about Cu 0.08 to 0.1%. If there is no influence to electrolytic refining, de-copper by elemental sulphur may be unnecessary. If this is possible, then the dross generated at this process can be decreased. Normally, elemental sulphur de-copper is a process applied not for electrolytic refining but for pyrometallurgical refining.

• Treatment of speiss

Speiss generated in the fore-hearth of ISF exists as a separate layer over lead and under slag because of its specific gravity. This speiss is not removed at SOMETRA and therefore, it is discharged together with lead or slag. When speiss is mixed with lead, the de-copper time will become longer and therefore, it is necessary to remove speiss beforehand at the fore-hearth. Further, speiss is soluble in water so when it is mixed with slag, heavy metals will be dissolved from slag. Removal of speiss at fore-hearth is necessary also from this point.

(3) Speiss Removal Equipment

An outline drawing of speiss removal equipment is shown in Figure 1.3.14.

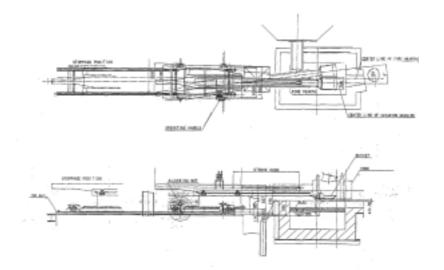


Figure 1.3.14 Speiss Removal Equipment

(4) Rough Estimation of Equipment Cost

Rough estimation of equipment cost is 0.1 million US\$.

1.3.7 Improvement of Treatment Process of Interim Powder Products

At SOMETRA, there are so many interim powder materials produced at various places and in various forms. For example, blue powder is generated as mixed in water. This blue powder is filtered by a filtering machine and returned to sintering machine but when it is directly charged into a raw material bin, it solidifies inside the bin and does not come out. In order to prevent this phenomenon, cakes filtered by the filtering machine is first dried in an open air and then charged into the bin. However, when it is dried too much, it turns to dust and scatters, and when there is a rain, it becomes muddy.

Further, powder form dross and dust from sintering machine that is collected in the bag filter are very dry and becoming a source of dust. SOMETRA is planning to mix them together to make them to non-dust generating form. The procedure is shown in Figure 1.3.15 where wet materials and dry materials are piled up alternately but high dust generation during piling process is foreseen.

Shuttle conveyor

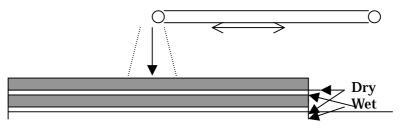
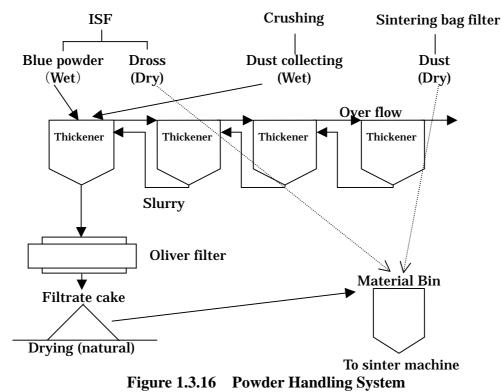
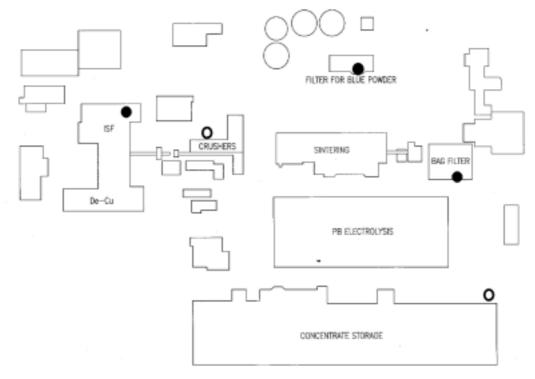


Figure 1.3.15 Mixing Method

1) Present Powder Handling System



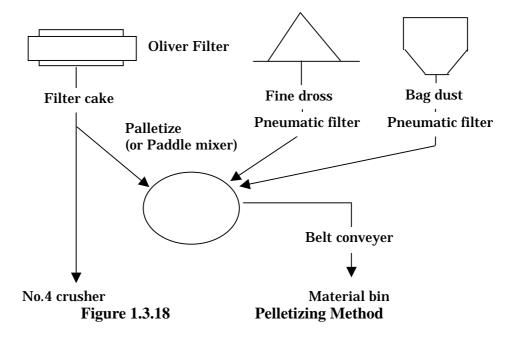
The locations where these powders are generated are shown in Figure 1.3.17.



Black round; Powder generation. White round; Material bin and crusher Figure 1.3.17 Location of Powder Generation

2) Method to Adjust Moisture Content

Turn the materials into pellets. (or mixed by Paddle mixer)



Quantity of blue powder is very big compared with dross and dust and it is expected that there will be excess blue powder when forming pellets. The excess will be sent to No. 4 crusher and dried by the heat of sintered lumps before returning to the sintering machine.

3) Cost for Facility Improvement Cost for facility improvement is 1.5 million US\$.

1.3.8 Slag Treatment Method

At SOMETRSA, there is approximately 50,000 tons of slag generated per year. A part of it is sold to outside consumers as a substitute material for sand blasting but the quantity is very small and a large amount is piled up in the plant area.

(1) **Recommendation**

Carry out the elution test of slag to confirm that it satisfies the EU standard. When EU standards are adopted, there should be a standard limiting the elution from waste materials. If so, the analysis method to measure the elution must also be included in the standard. (Reference: Annex 1 Standards in Japan and its measuring method) Rain water is normally neutral but the standards are made taking into consideration the possibility of elution depending on the environment at the place where the wastes are stored and therefore, it is necessary to confirm that there will be no elution even under such standard. For reference, relationship between the pH value of water and the elution of hazardous materials is shown in Figure 1.1.1. lag is a kind of glass and heavy metals contained in it should not elute.

As shown in Figure 1.1.1, those that are not glass has easy dissolution of hazardous materials at low pH value. At SOMETRA, there is a speiss at the fore-hearth of ISF. Speiss is soluble in water so when speiss is mixed with slag, heavy metals elute

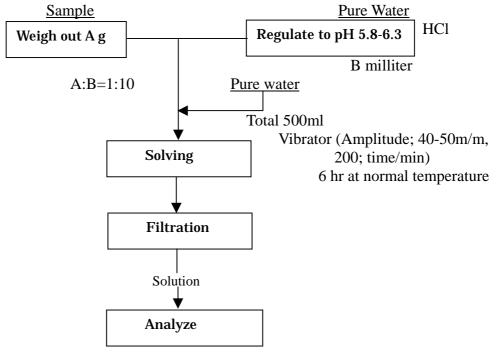
from speiss even if they do not elute from slag itself. It may be necessary to install a facility to extract speiss from the fore-hearth as proposed in the chapter 1.3.6.

Annex Annex 1 Japanese Standard and Measuring Method

Regulation

Cd	0.01mg/liter or less
Pb	0.01mg/liter or less
Cr(VI)	0.05 mg/liter or less
As	0.01 mg/liter or less
Total Hg	0.0005 mg/liter or less
Se	0.01mg/liter or less

Measuring method



Annex 2 Roasting of Arsenic Containing Sludge Test Report

The Characteristics of in-solubilization is varied depending on the characteristics of sludge, and test will be conducted considering this report.

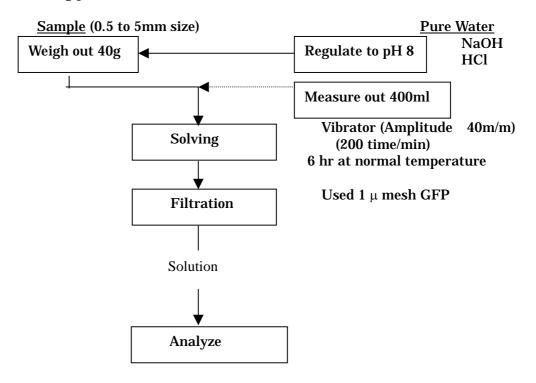
1. <u>Testing Procedure</u>

1) Roasting

Sludge in an unglazed melting pot or on an unglazed plate is roasted in the Electric Muffle Furnace.

2) Solution Test

The testing procedure is as follows.



Divide Element	SEA DUMPING*	LANDFILL
ARSENIC (As)	< 0.5 mg/l	< 1.5 mg/l

Table 1DECISION STANDARD

*Prohibited at present.

1. Result of Test

1) Solution Test of the Roasted Cake and Un-roasted Cake

The results of solution test of the un-roasted cake and 1 hour roasted cake in Electric

Muffle Furnace at the temperature 900°C, are shown in the Table 2.

The test proves the insolubilization of Arsenic by roasting.

Table 2RESULTS OF SOLUBILITY TEST(ROASTED CAKE : UNROASTED CAKE)

ROASTED CAKE COMPOSITION				ANALYSIS (As mg/l)	
As	CaO	SO ₂	H ₂ O	ROASTED at 900°C	UNROASTED
1.6	19.4	2.6	65	0.00	3.1
3.4	13.0	4.6	60	0.03	3.9
2.3	13.6	9.0	61	0.01	3.2
0.5	13.3	6.2	65	0.00	2.8
1.9	11.4	5.8	62	0.02	3
1.3	11.3	7.4	62	0.00	3.3

2) Insolubilization and Roasting Temperature and Roasting Time

The relation between insolubilization and roasting temperature and time is shown in Figure.1 and 2. As shown in Figures, roasting temperature is more effective than roasting time for insolubilization.

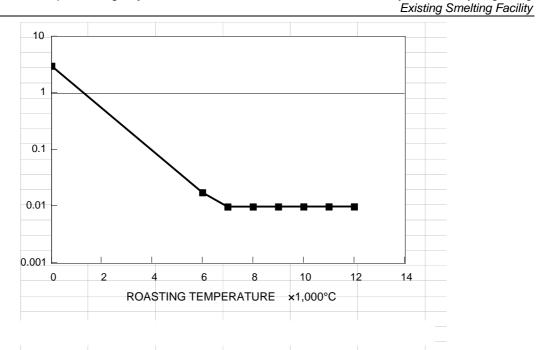


Fig. 1 Relation Between Cake Roasting Temperature and as Solubility

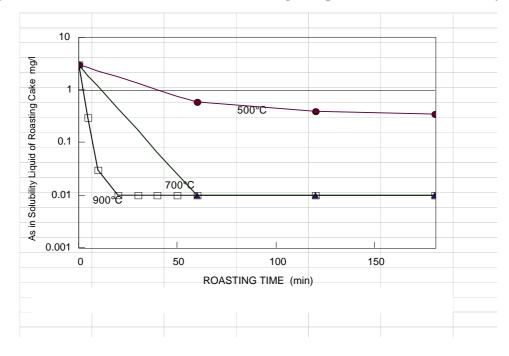
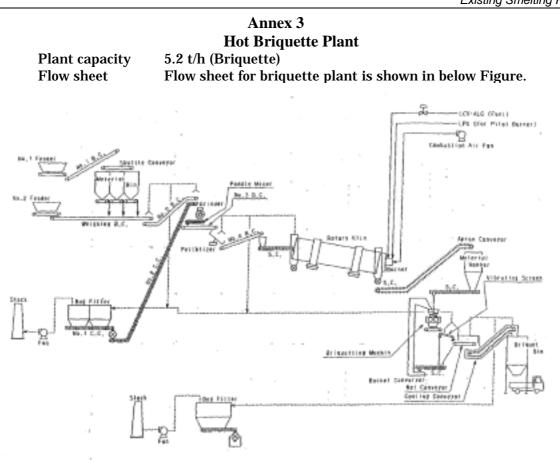


Fig. 2 Relation Between Cake Roasting Time and as Solubility



Briquette plant flow sheet

Raw materials are stored separately in bins depending on their type. Raw materials are cut out are a specified rate and sent to a grinder. At grinder, the lumps are crushed and turn into powders. Then they are formed into pellets, fed to a kiln where they are heated at 450 degrees C. Fuel used for heating is LVC. Heated pellets are formed by a briquette machine. Briquettes are sieved and the under sieves are returned to the briquette machine. Over sieves are directly sent to ISF where they are fed to ISF while they are still hot. (Pellet preparation: When raw materials are heated in a powder form, the powders go together with gas and they are scattered. By turning them to pellets before heating, scattering of dust can be minimized.)