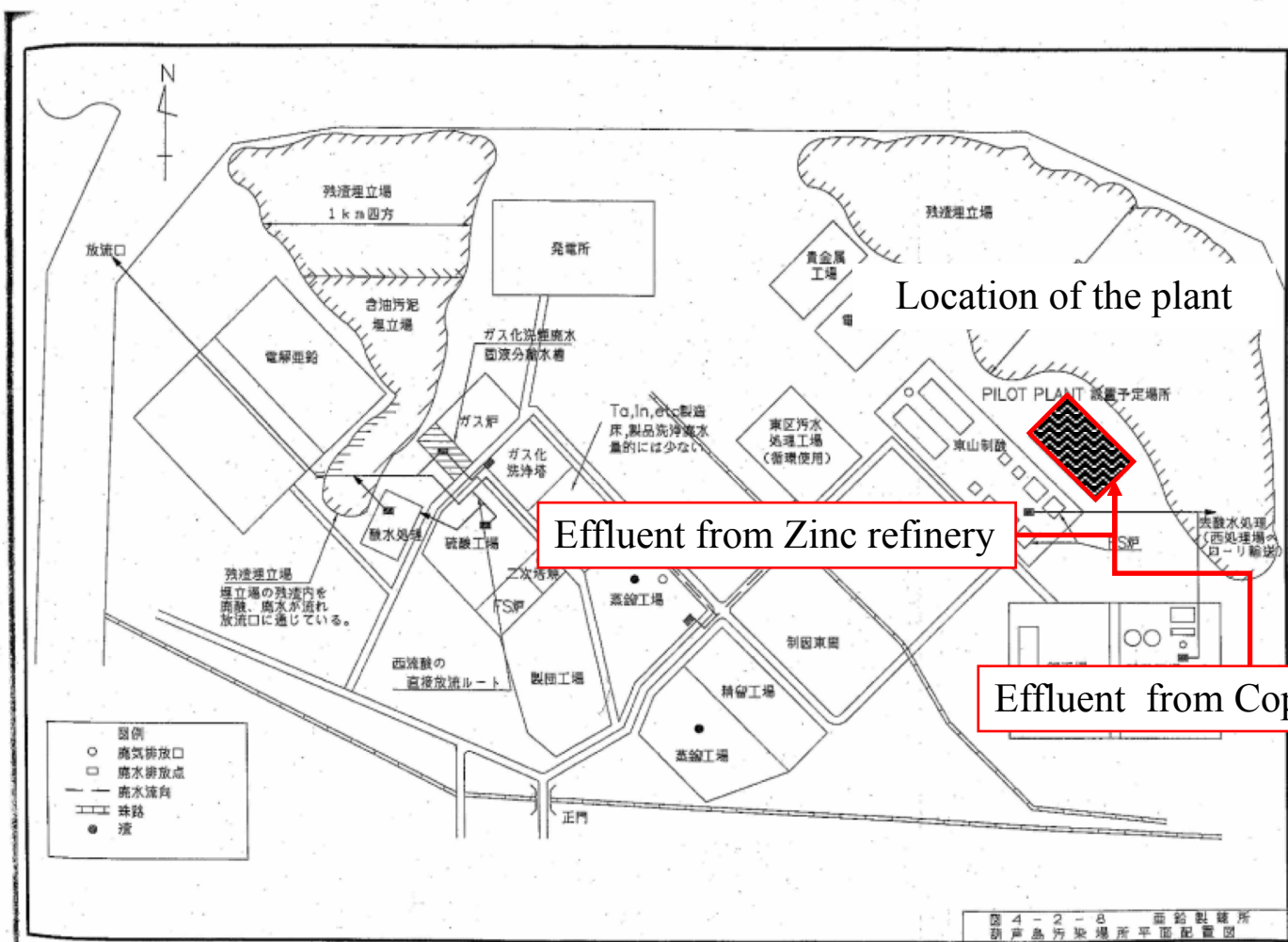


Huludao Zinc Refinery Effluent Treatment Plant

JOINT VENTURE
Of
MITSUI MINING & SMELTING CO.,LTD
MITSUBISHI MATERIAL CORPORATION

**Process Technology and Plant Engineering
by MESCO Inc.**

Location of Effluent Treatment Plant (Huludao Zinc Refinery)



Main elements of the Effluent

1999 Survey

	Flw (m ³ /d)	H ₂ SO ₄ (m g/l)	Zn (m g/l)	Cd (m g/l)
Effluent from Zinc refinery	600	20000	1600	400
Effluent from Copper refinery	600	20000	4800	1200

Pb (m g/l)	As (m g/l)	F (m g/l)	Cu (m g/l)	Hg (m g/l)
420	1460	1700	1.6	10.0
110	8400	1600	167	8.0
270	4930	1650	84.3	9.0

Treatment methods of materials

H_2SO_4	:	Removal method of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
Zn, Cd, Pb, Cu	:	<ul style="list-style-type: none">▪ Flocculation Sedimentation Method with insoluble salt▪ Ion exchange process▪ Magnetic separation with ferrite
As	:	<ul style="list-style-type: none">▪ Coprecipitation method▪ Flocculation Sedimentation Method with sulfide
F	:	Calcium fluoride method
Hg	:	<ul style="list-style-type: none">▪ Flocculation Sedimentation Method with sulfide▪ Absorption Method

The process of our Effluent Plant

(Specializing and combining the disposing method of various heavy metals respectively)

1st Neutralization Treatment

*Removing SO₄



2nd Neutralization Treatment



*Removing various heavy metals using the Method by Flocculation Sedimentation with insoluble salt

3rd Final Treatment



*Removing heavy metals which not enough to be removed by 2nd neutralization treatment by using the method of Flocculation Sedimentation with sulfide

Sand Filtration Treatment

* Removing suspended solids remained after Solid-liquid separator

First Neutralization Treatment (Precipitation method of Calcium sulfate)

<Processing Object>



<Treating Method>

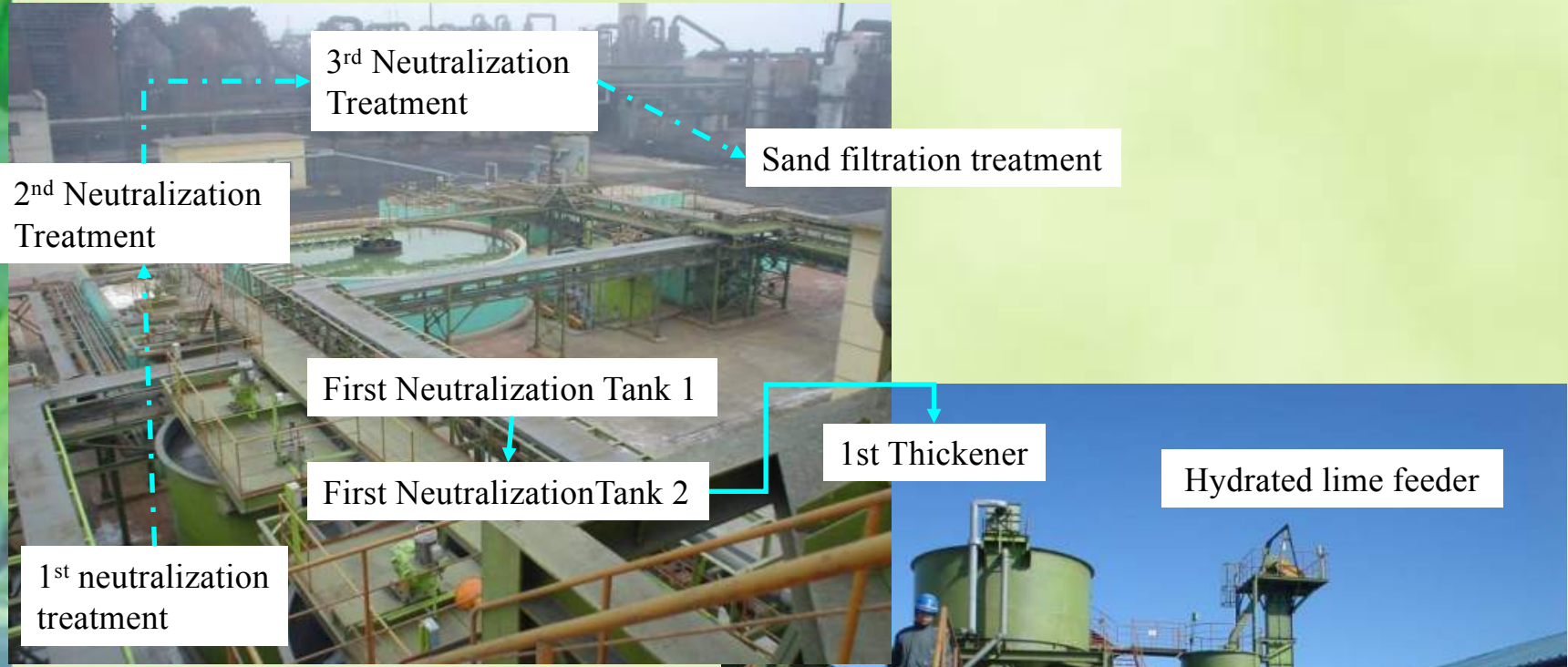
To neutralize with hydrated lime ($\text{Ca}(\text{OH})_2$) upto approximately pH 2.5.

<Reaction>

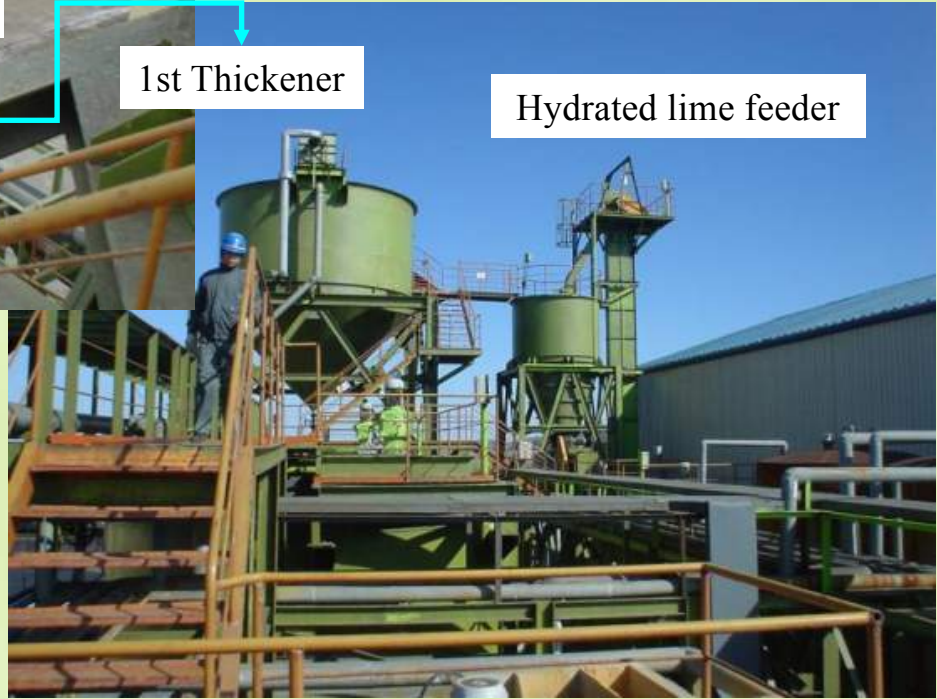
Calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is produced reacting SO_4^{2-} and Ca^{2+}



1st neutralization treatment



The panoramic of equipment.



2nd Neutralization Treatment

< Treatment Materials >

Zn、Cd、Pb、Cu、As、F (Fe)

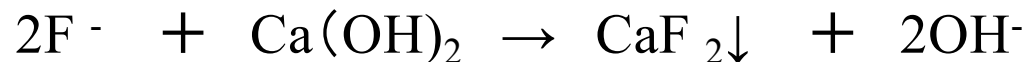
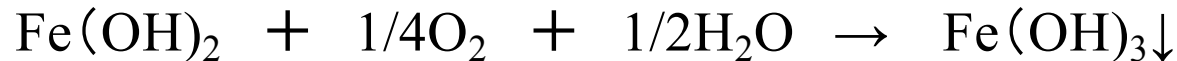
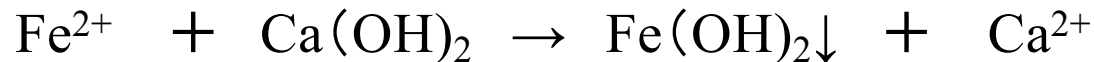
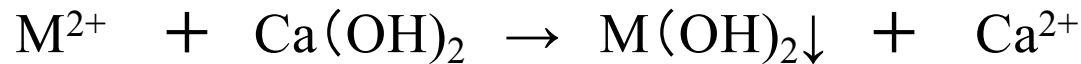
< Treatment Method >

*To add $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to the Effluent to remove Arsenic with precipitation method.

*To neutralize the Effluent with hydrated lime ($\text{Ca}(\text{OH})_2$) upto pH 11 approximately.

*To promote the oxidation of $\text{Fe}(\text{OH})_2$.

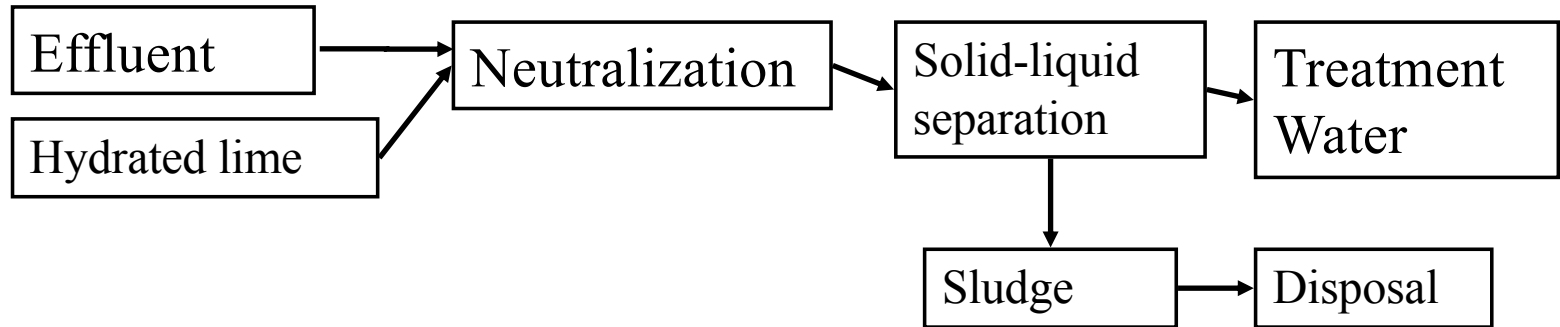
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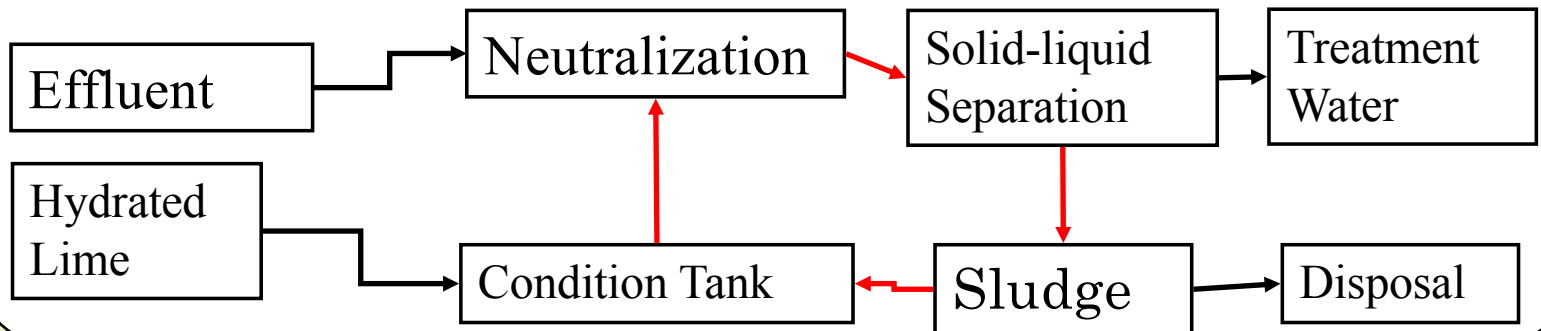
Returned Sludge method

(Sedimentation method with insoluble salt)

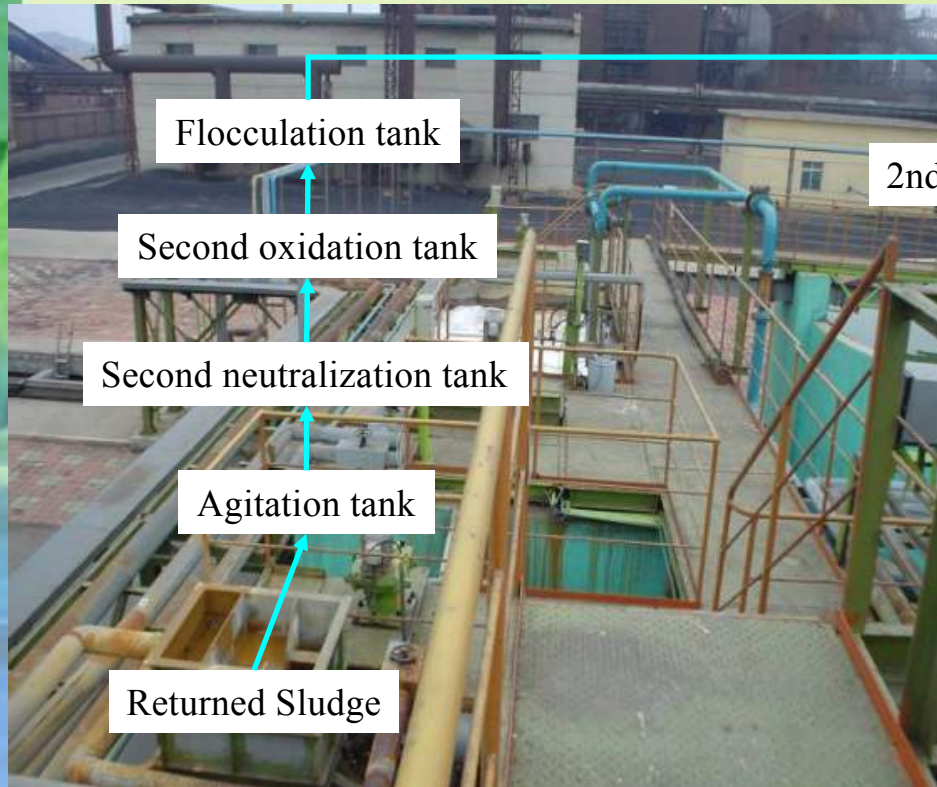
○Conventional method (Plain neutralization method)



- Reaching a high concentration of Sludge
- Improving dehydration of Sludge.
- Longer life-cycle of dumping yard



2nd Neutralization Treatment



3rd Treatment

< Treatment Materials >

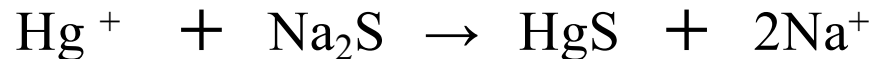
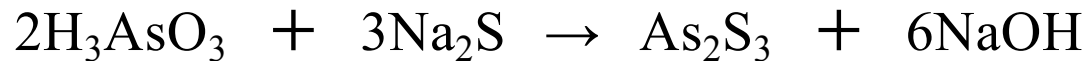
As, Hg

< Treatment Method >

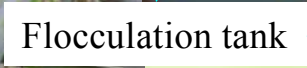
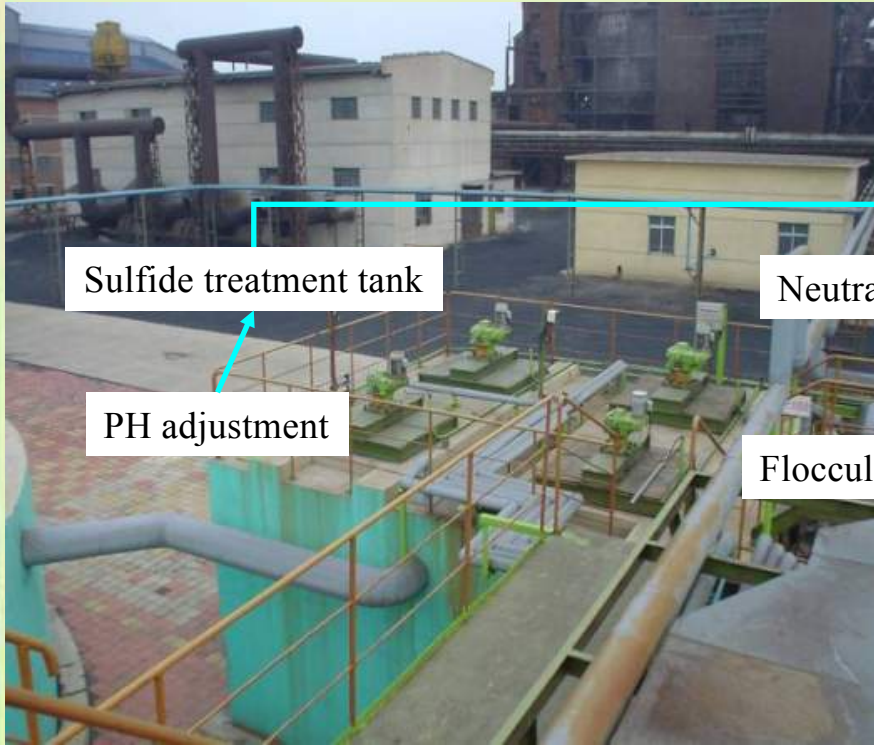
- * After neutralization of secondary effluent with H_2SO_4 upto pH 5-6 approximately, Na_2S to be added.
- * To add $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and flocculent to collect sludge.
- * To re-neutralize with NaOH upto pH 8.

< Reaction >

*To form insoluble As_2S_3 , HgS reacting of As and Hg with S



3rd Treatment

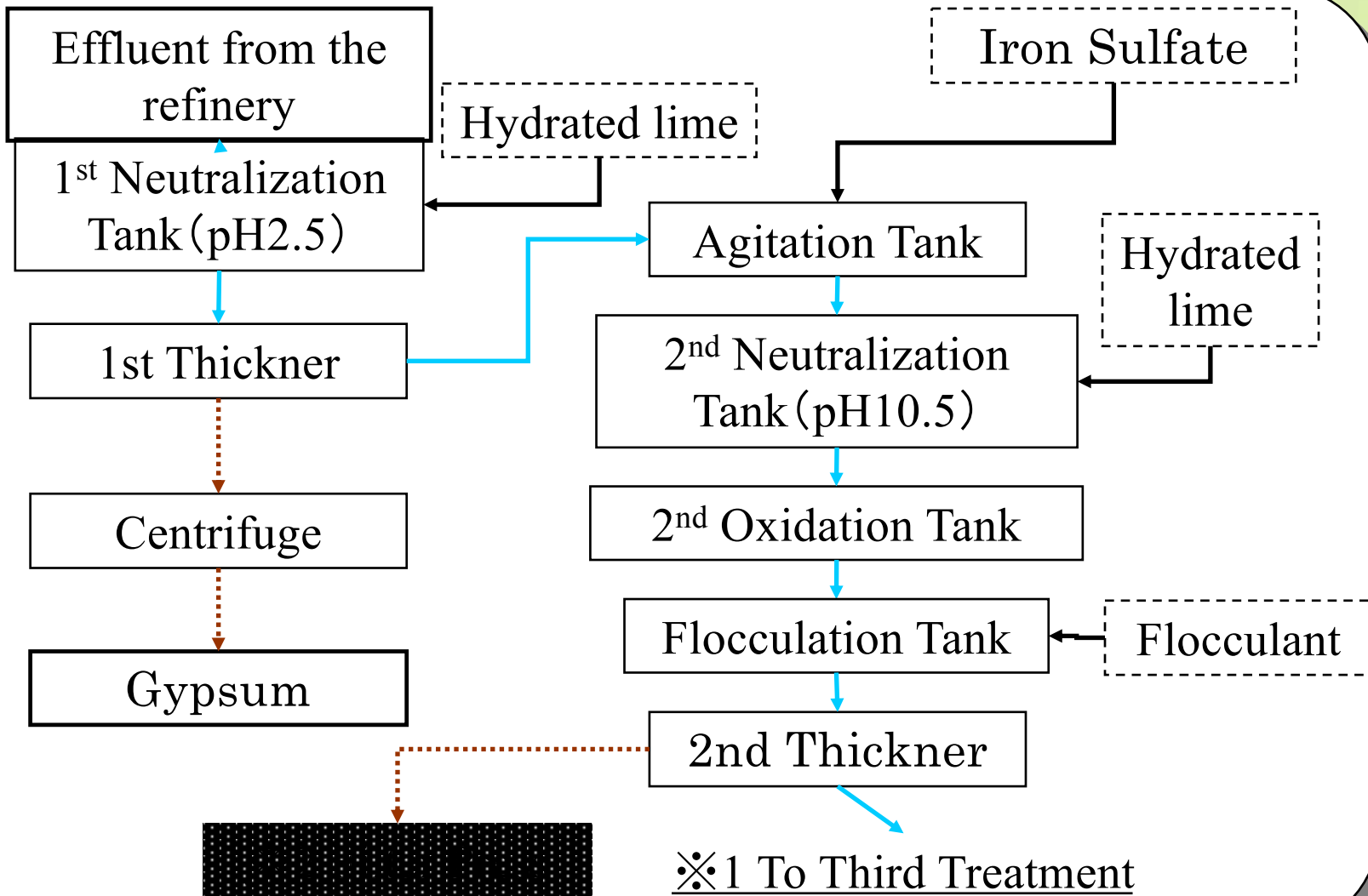


Third treatment

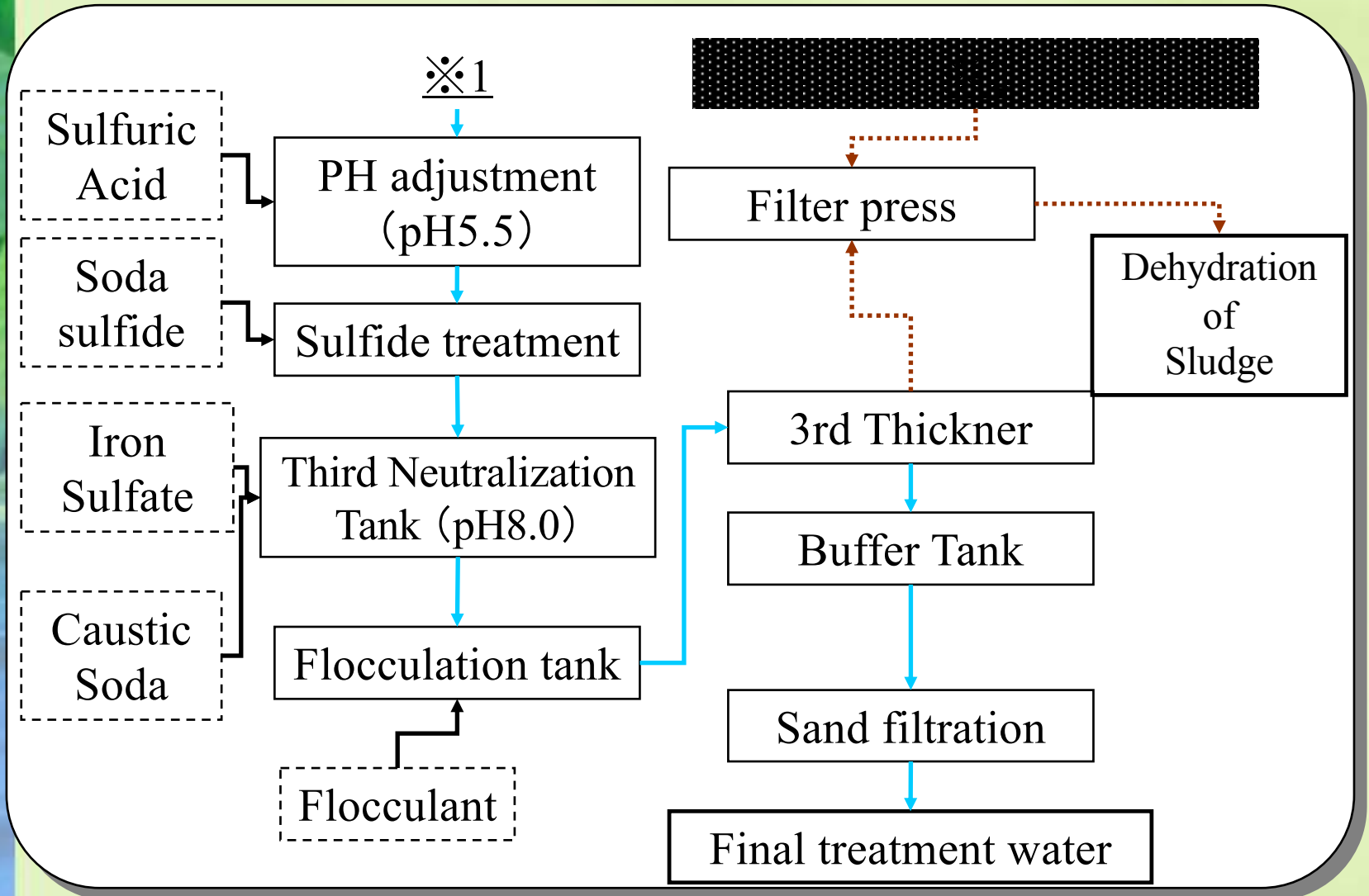


Sand filtration treatment

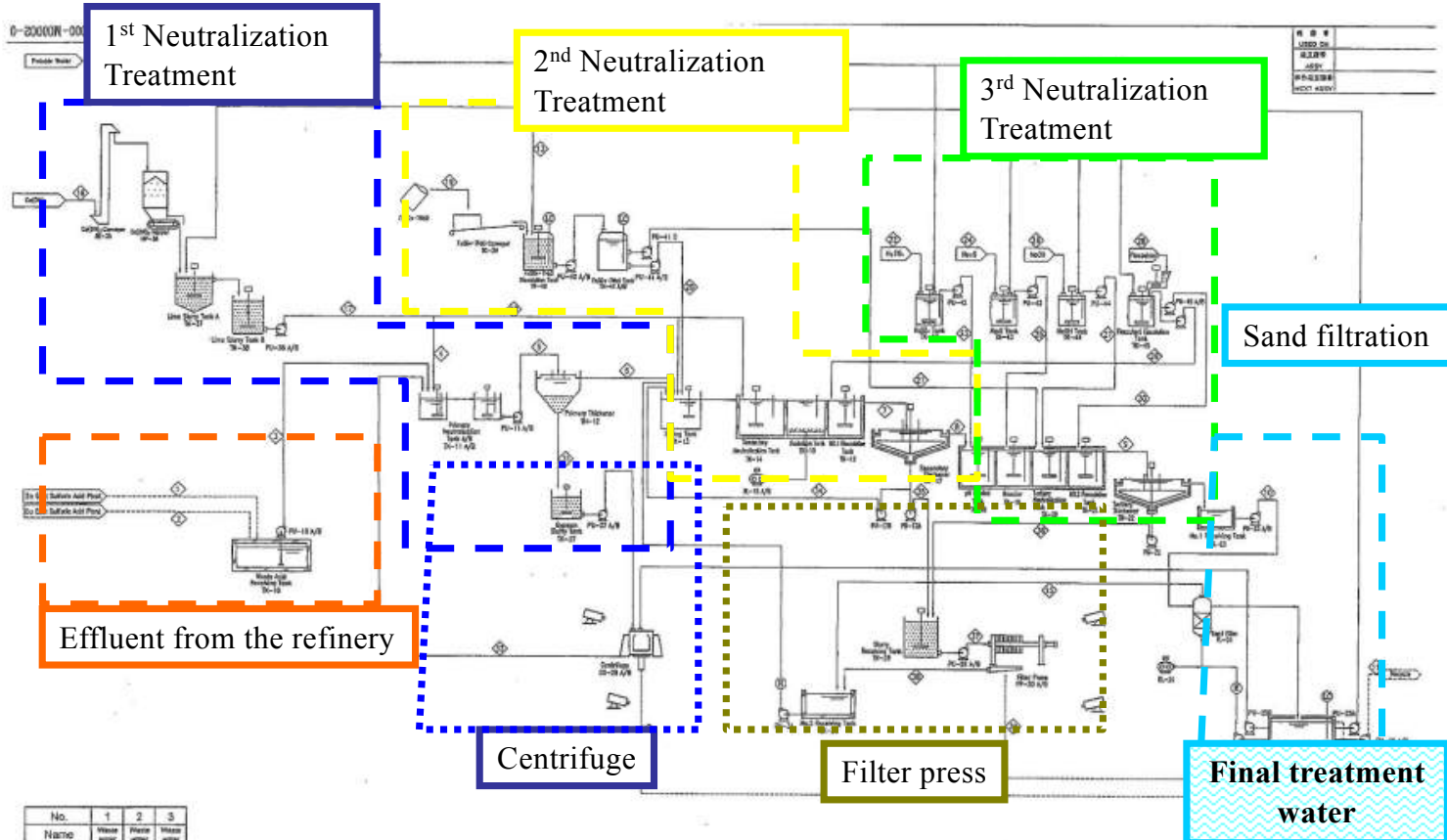
Flowchart of plant (First and second neutralization treatment)



Flowchart of plant (Third treatment and Sand filtration treatment)



Cross-section diagram of pilot plant



Effluent from the refinery

1st Neutralization Treatment

2nd Neutralization Treatment

3rd Neutralization Treatment

Sand filtration

Centrifuge

Filter press

Final treatment water

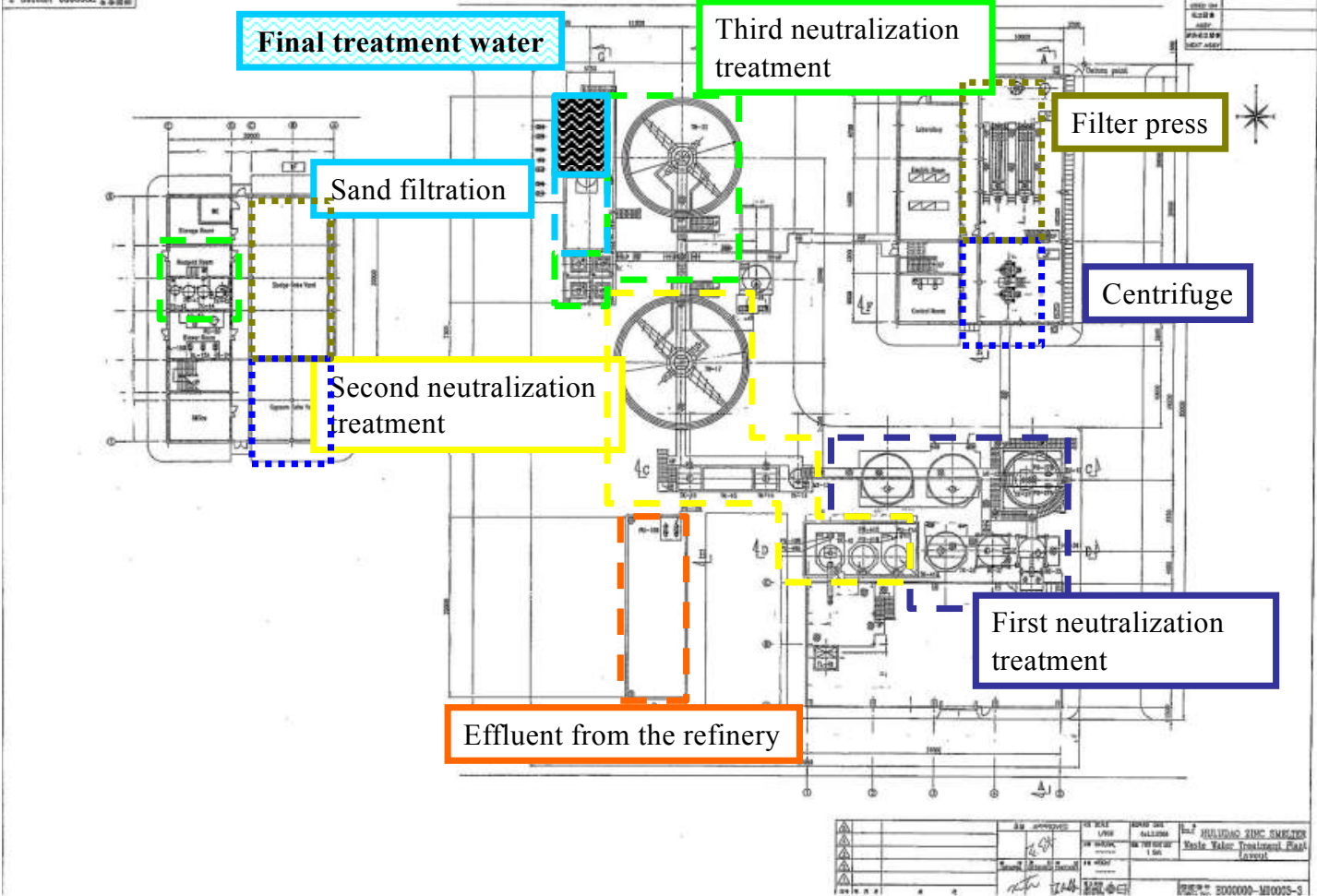
No.	1	2	3
Name	Waste water	Plumbe water	Waste water
Mass (m3/d)	900	900	1200
H2SO4 (g/L)	20.0	20.0	20.0
Zn (g/L)	1.6	4.8	3.2
Oil (mg/L)	3.4	1.2	9.8
Pb (g/L)	0.42	0.11	0.27
As (g/L)	1.46	8.4	4.93
F (g/L)	1.7	1.6	1.05
Cu (mg/L)	1.8	187	84.3
Hg (mg/L)	10.0	8.0	8.0

#	APPROVED	DATE	DATE	DATE
1				
2				
3				
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Scale: 1:100
Date: 10/10/10

BAS.F.W. B000010-M00002-0

Planform of pilot plant



Centrifuge



Centrifuge

Gypsum



Filterpress



Filterpress

Dehydration Sludge



Operation management of treatment plant



- * Monitoring system
 - Function management of equipments
 - Start, Stop, state of trouble
 - Indication of instantaneous value of pH
 - Indication of treating water quantity
 - State of each progression
 - Output of monthly and daily report
 - Maximum, minimum, and average of pH and
 - Quantities of treatment water
- * Monitoring system
 - Camera
 - Filter press
 - Centrifuge
 - Paging system
 - Filter press
 - Centrifuge
 - Reagent room

Control System of Treatment plant



Main Control room

- * Main control panel
 - Automatic controll
 - Select of operating condition of each equipment (Automatic, Manual, and Stop)
 - Set the level of pH
 - Indication of quantities of treating water
 - Indication of several alarm
- * Local control panel
 - Manual operation
 - Maintenance of equipments

Target treatment water and Actual treated water

< Properties of Inlet Water >

	pH	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)	As (mg/l)	F (mg/l)	Cu (mg/l)	Hg (mg/l)
Target	0.4	3200	800	270	4930	1650	84.3	9.0
Actual Max.	0.44	4343	379	153	1037	548	343	1.1
Actual Average	1.8	269	38	121	44	35	2.6	4.0

< Properties of Treated Water >

	pH	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)	As (mg/l)	F (mg/l)	Cu (mg/l)	Hg (mg/l)	SS (mg/l)
Target	6~9	4.0	0.1	1.0	0.5	15	1.0	0.1	150.0
Actual	6.9-8.5	0.5-2.0	0.05-0.15	0.5-2.0	0.2-0.4	10-15	0.08-0.15	0.003-0.008	30-72

< Quantities of Treatment Water >

	(m ³ /Day)
Target	1200
Actual	500-1080

Target and Actual Sludge

< Sediments >

Gypsum :

Target :39.7t-Dry/d (45.2t-Wet/d)
Moisture content 12%

Actual :1.5t-Dry/d (1.7t-Wet/d) Average amount
Moisture content 12% Actual performance

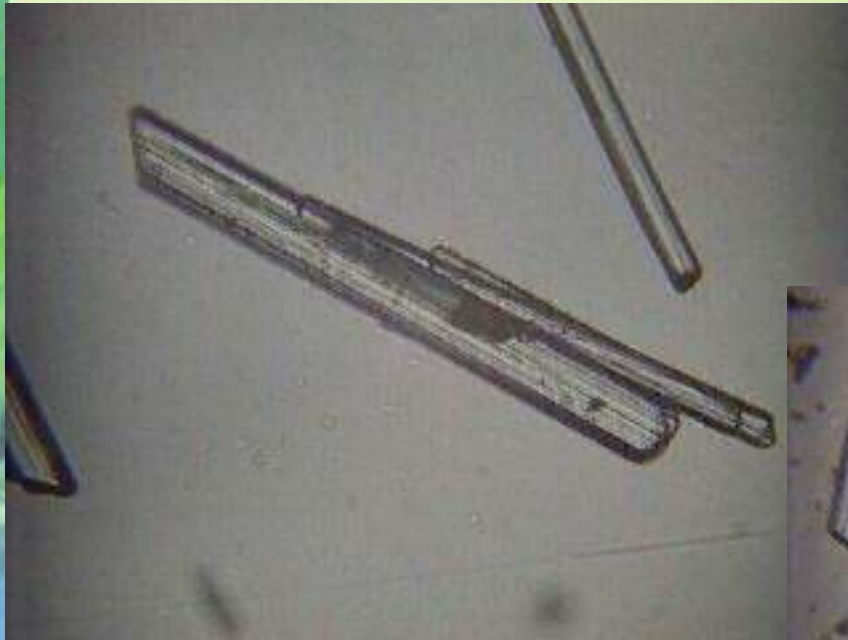
Sludge :

Target: 37.1t-Dry/d (106.1t-Wet/d)
Moisture content 65%

Actual: 4 t-Dry/d (11.4t-Wet/d) Average amount
Moisture content 60% Actual performance

Target and Actual Sludge

< Crystal picture of Gypsum >



Good Crystal Figure

