

# REPORT ON CONCENTRATED LIQUID CYANIDE WASTE TREATMENT TECHNOLOGY

March 1972



Japan Environment Corporation (JEC)

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### **NOTE**

- Method of Measuring COD  
The COD values given in the text, unless specified otherwise, are obtained by the manganese measuring method.
- Currency used in this report is all Japanese Yen (JPY or yen).

## **I Necessity of Establishing Concentrated Liquid Cyanide Waste Treatment Technology**

There are many sources that discharge cyanide such as the electroplating (including "in-house plating"; the same applies wherever the electroplating industry is mentioned hereafter), metal heat treatment, coke manufacturing, acrylonitrile manufacturing, photo-developing and other industries. For the treatment of weak liquid cyanide waste with a cyanide concentration of about 50 to 300 ppm, the hypochlorination method of decomposing the cyanide has taken root, and their industrial wastes are currently treated by this process either independently or jointly.

However, when the cyanide concentration is in the 30,000 to 50,000 ppm range, the form of concentration is not simply cyanide but contains large quantities of various complex heavy metal-cyanides. Since such waste liquids cannot be completely treated even with the highly expensive hypochlorination process, at present they are either being treated by mixing small quantities in weak liquid cyanide waste or by diluting them with large volumes of water and discharging them into public water areas. However, these processes are costly and onerous for the electroplating and other industries of which are mostly composed small business entities, and therefore are sometimes not fully carried out, resulting in accidents from time to time.

Accordingly, JEC decided to make investigation and study of this subject. There was an urgent need to identify an economical method of treating the concentrated liquid cyanide waste discharged by the electroplating process, since it occupied a considerable amount of such wastes with the most difficult composition to treat.

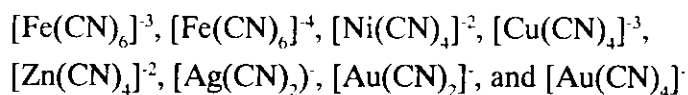
## **II Properties of Concentrated Liquid Cyanide Waste Discharged from Electroplating Process**

### **1. Composition of Concentrated Liquid Cyanide Waste**

The types of electroplating that use cyanide are copper plating, zinc plating, alloy plating, gold and silver plating and cadmium plating, etc. The cyanide compounds used are sodium cyanide [NaCN], potassium cyanide [KCN], zinc cyanide [Zn(CN)<sub>2</sub>], copper cyanide [CuCN], potassium silver cyanide [KAu(CN)<sub>2</sub>], cadmium cyanide [Cd(CN)<sub>2</sub>], and others.

Sources of discharge of concentrated liquid cyanide waste from the plating processes that use these cyanide compounds are aged liquids from the above-mentioned various types of plating, electrolytic degreasing liquid (discharge ratio 30 - 40%), sodium cyanide neutralizing liquid (immersing solution) (discharge ratio 30 - 40%), copper strike liquid (discharge ratio 20 - 30%), material stock liquid, copper and nickel plating remover, tumbling liquid, etc. As some of these

waste liquids are the following sort of complex metal-cyanide ions, they make the waste liquid all the more difficult to treat.



Note: As aged liquids of gold and silver plating are almost never discharged, there is no need to make the complex gold- and silver-cyanide ions mentioned above the subject for treatment.

As a considerable variation in volume and composition can be seen in these concentrated liquid cyanide wastes depending on the plating technique of each company, quantitative standardization of the composition of mixed concentrated liquid cyanide wastes is difficult, but nevertheless some sort of quantitative guide is required. For that purpose, we assumed the following composition for the mixed concentrated liquid cyanide waste as a result of studies made based on fact-finding surveys conducted by the Tokyo Metropolitan Government.

Total cyanide	50,000 ppm
Free cyanide	25,000 ppm
Copper	2,700 ppm
Iron	2,700 ppm
Nickel	3,100 ppm
Zinc	4,700 ppm
Others	1,000 ppm

- Note: 1) The above list indicates ratios, and as total cyanide varies between 30,000 - 50,000 ppm, the other components also vary by that ratio.
- 2) The 'Others' in the above list consist of EDTA, chelating agents such as gluconic acid soda, etc., organic acids, surfactant, potassium rhodanite, Rochelle salt (potassium sodium tartrate), potassium pyrophosphate, triethanolamine, etc.
- 3) There are traces of lead, chromium, cadmium, and other metals contained in actual aged electroplating liquids.

## 2. Quantities Discharged of Concentrated Liquid Cyanide Waste

Nowadays, with pollution problems in the limelight, there are some enterprises who deny producing any concentrated liquid cyanide waste at all when questioned about the quantity they discharge of what is regarded as one of the foremost sources of pollution, concentrated liquid cyanide waste. For this reason, grasping the actual state of discharge is difficult. It is hard to believe such waste is permanently left undischarged although the frequency may be low.

According to a Tokyo Metropolitan Government survey, the quantity of concentrated liquid cyanide waste discharged by 861 factories in the electroplating business (average number of employees: 12.9), is 473.6 m<sup>3</sup>/month, making it 0.55 m<sup>3</sup>/month per plant (or 43 l/month per employee). However, according to a survey of leading enterprises, there are plants who discharge as much as 250 l/month per employee. It therefore seems that the actual quantity of liquid waste being discharged is considerably in excess of 43 l/month per employee.

### **3. Problems in Treatment as Seen from the Composition and Discharge Quantity of Concentrated Liquid Cyanide Waste**

As there are large quantities of complex iron-, nickel- and other metal-cyanides contained in concentrated liquid cyanide wastes, and in view of the following and other facts:

- 1) That it is practically impossible to remove cyanide compounds completely from the waste liquid by the normal hypochlorination process,
- 2) That, in company with the recent intensifying of restrictions on heavy metals, the treatment of which the electroplating industry had hitherto tended to view lightly, the discharging party is now held responsible for treating the waste liquid,
- 3) That the COD load of waste liquids has increased due to recent increases in the use of various chelating agents. The electroplating industry comprised of the mostly small business entities would be impossible to treat properly the small quantity of concentrated liquid cyanide waste, amounting to less than 1 m<sup>3</sup>/month per enterprise, even from the aspect of the cost of individual facilities and treatment. Therefore the joint treatment system should be adopted although there are considerable problems in collection and other factors.

### **III Comparative Study of Various Treatment Methods**

The study was made in the various treatment methods being currently advocated to lower concentrated liquid cyanide waste to below the regulatory standard of the Water Pollution Control Law and that would moreover produce only a small quantity of sludge and would not cause any risk of secondary pollution by cyanide gas and other factors.

The results are as follows:

## **1. Electrolytic Oxidation Process**

This method has the merits of low sludge generation, treatment costs of about 1/7 to 1/10 that of the hypochlorination method, and its electrolytic operation being familiar to, and thus easy to adopt by, the electroplating industry. However, as its economical processing limit for cyanide concentration is about 1,000 ppm, the hypochlorination method must be jointly used as a secondary treatment process. Yet when there are large quantities of complex iron- and nickel-cyanides in the waste, another treatment process requires to be found as these complex cyanide ions cannot be decomposed by electrolytic oxidation.

## **2. Electrolytic Oxidation Process Adding Common Salt**

This method requires countermeasures to be considered against secondary pollution caused by residual chlorine after treatment. The rest is the same as for the electrolytic process.

## **3. Heated and Pressurized Air Oxidation Process**

This method does not use any chemicals that could cause secondary pollution and increase the quantity of sludge. It is considered to be promising by using only air and heat to decompose cyanide compounds. However, as for its generation of ammonia gas is causing concern, further research is needed and hoped for in the development of a method to restrict this and on the possibility of decomposing complex copper-, zinc-, iron- and nickel-cyanides.

## **4. Boiling Down Process**

As many of the cyanide compounds remain as evaporation residue in their original but more concentrated form after being treated by this method, secondary processing of this sludge is required at a nonferrous metal smelting plant or some such place, so joint treatment with a smelting plant is desirable. Also, a method is required safely to remove the ammonia and cyanide gases that are generated in the evaporation process.

## **5. Impulse Process**

This method is viewed as an effective process for a single waste liquid of relatively low cyanide concentration and, moreover, with a large amount of free cyanide, but in recovering the large quantity of cyanide gas with caustic soda there are such issues such as measures against leaking cyanide gas and the purity of the recovered sodium cyanide. Also, with mixed waste liquids, a secondary process must be developed for treating complex iron- and nickel-cyanides which decompose poorly.

## **6. Venting Process**

Same as impulse process.

## **7. Hypochlorination Process**

Although this method is well-established for treating low cyanide concentrations, for processing concentrated liquid cyanide waste, it is extremely costly and, moreover, it cannot completely remove complex iron-cyanides.

## **8. Chlorine Gas Process**

This method is suitable for treating low cyanide concentrations containing no complex iron-cyanides, but it is not suitable for concentrated cyanides and, furthermore, maximum care is required in handling the chlorine gas.

## **9. Ozone Oxidation Process**

A high output ozone generator is expensive and moreover has the demerit of a strong possibility of the reaction stopping with sodium cyanate.

## **10. Complex Iron-Cyanides Forming Process**

Since this method creates much sludge mainly composed of ferrocyanide blue in the process of treating waste liquid which is a problem from the standpoint of toxicity, a secondary processing of the sludge is necessary. Also, it is impossible to reduce the cyanide concentration to 1 ppm or less by this sole treatment, so that a secondary process for the sludge is required.

## **11. Eade Cyan\* Additive Process**

The processing cost of this method is expensive and due to the Eade Cyan, the BOD and COD of the waste water that is treated become high, so the activated sludge method or some such process is required as post treatment.

\* Main ingredients of "Eade Cyan": Organic carbonyl compound and addition compound of sulfite.

## **12. Ion-Exchange Process**

Although it is required for this method to be developed further for the treatment of waste liquids with cyanide concentrations of about 100 ppm, it is not suitable for treating concentrated liquid cyanide waste.

## **13. Heated, Pressurized, Hydrolysis Process**

This method has the same merit as the heated and pressurized air oxidation process of not using any chemicals. It however requires further research with respect to measures against the ammonia gas that is created by hydrolysis and to the possibility of decomposing complex zinc-cyanides, etc.

#### **14. Combustion Process**

With this method, as with the impulse and venting processes, the decomposing of complex iron- and nickel-cyanides is difficult so secondary treatment is necessary. With regard to the combustion of the cyanide gas generated during the processing of waste liquids, it is necessary to develop a perfect combustion method and measures against gas leakage.

#### **15. Activated Sludge Process**

This method cannot be adopted for concentrated liquid cyanide waste containing large quantities of copper and other heavy metals as the micro-organisms perish.

### **IV. Necessity and Contents of Investigation and Study**

As summarized in III above, each of the various treatments has its merits and demerits with regard to the processing of concentrated liquid cyanide waste containing complex iron-cyanides, but the optimum method is yet to be found and it is clear that further research and development are required.

Accordingly, the study came to the conclusion that the following processes need further research and development as a result of carefully making comparative studies of the various methods described above.

1. Electrolytic oxidation process
2. Electrolytic oxidation process adding common salt
3. Combustion process
4. Impulse process
5. Heated and pressurized air oxidation process
6. Heated, pressurized, hydrolysis process

However, due to the budgetary restrictions of JEC (the former name: the Environmental Pollution Control Service Corporation), this investigation and study based on the judgment that (1) the electrolytic oxidation process including (2) the process of adding common salt, (3) the combustion process because although its free cyanide removing system was very similar to (4) the impulse and venting processes, its basic post treatment research was one step ahead of the others, and (5) the heated and pressurized air oxidation process incorporating air oxidation in (6) the heated, pressurized, hydrolysis process, were the most suitable, and worked up an interim report (refer to the Annex) recommending that research on these processes be carried out.

Note: With regard to the boiling down process, since there was no suitable method of processing the great amount of cyanide-containing sludge that was generated at



the time of when this study prepared its interim report, this process was omitted from the research. However, subsequently, a method of processing the sludge by transporting it to a non-ferrous smelting plant, feeding the sludge into a blast furnace and making the cyanide harmless was developed. The Tokyo Metal Plating Industry Association has adopted this process and is currently constructing a new facility using this process that is scheduled to begin operating in early June 1972.

## V Results of Investigation and Study

This investigation and study bore considerable fruit as is summarized below, although restricted by time and budgetary limitations, and all the processes were found to be able to meet the discharge standards of the Water Control Pollution Law. However, as described later, there are certain issues remaining that require further study when building actual plants.

### A Electrolytic Oxidation Process

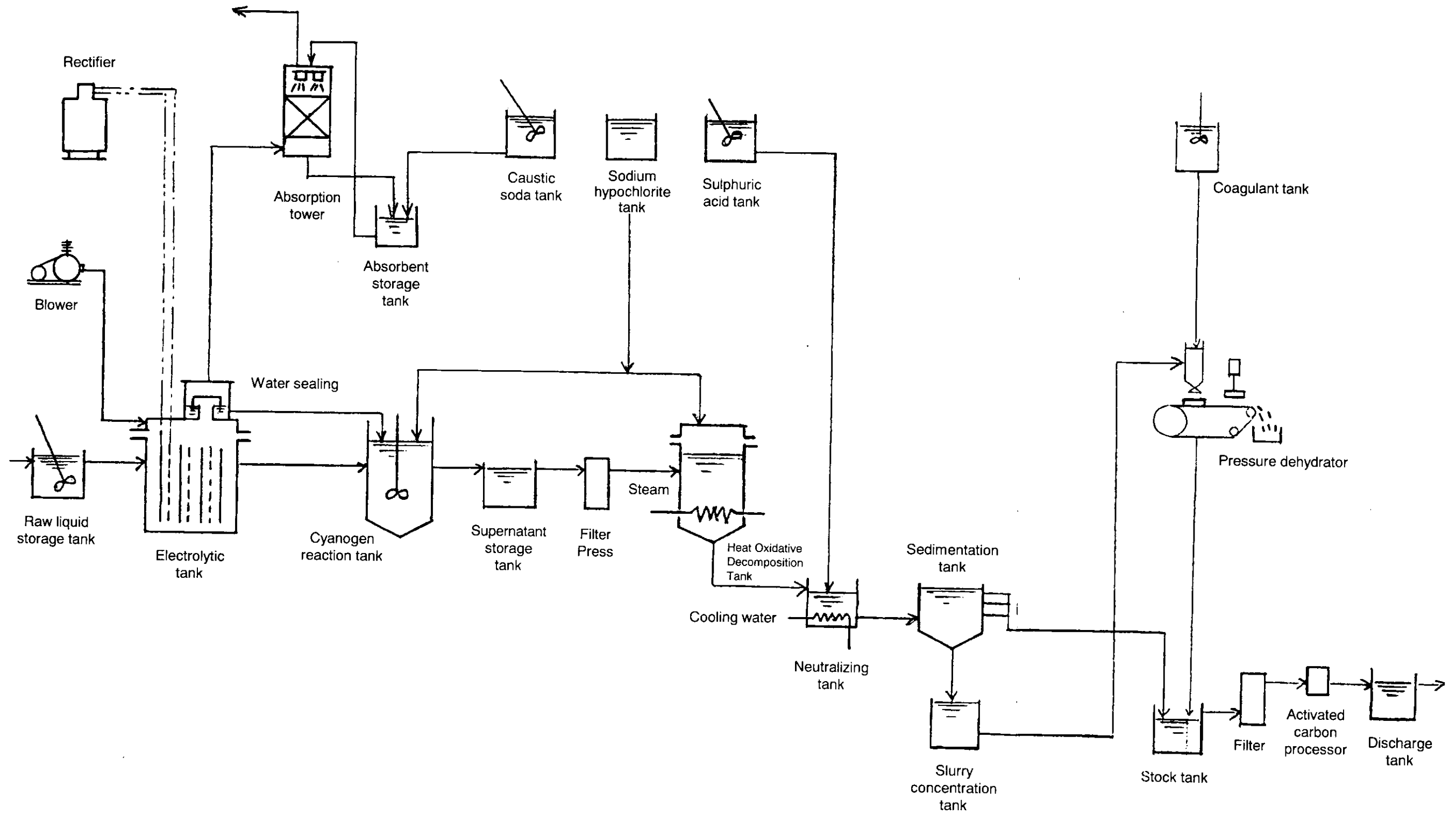
#### 1. Composition of Raw liquid

	Chemical	JEC's Instructions	Quantity Actually Used
Quantities of Chemicals Dissolved in 1 m <sup>3</sup>	NaOH	61.8 kg	61.8 kg
	NaCN	60.0	60.0
	CuCN	3.8	3.8
	Zn(CN) <sub>2</sub>	8.5	8.5
	Na <sub>2</sub> [Ni(CN) <sub>4</sub> ]	10.7	-
	Ni(CN) <sub>2</sub>	-	6.6
	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	7.8	7.8
	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ]	7.4	-
	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ] · 10H <sub>2</sub> O	-	7.4
	EDTA	0.5	0.5
	Gluconic Acid Soda	0.5	0.5

	Dissolved Component	Calculated Value of JEC's Instructions	Actual Test Liquid		Remarks
			Calculated Value	Measured Value	
Concentration of Components in Waste Liquid	Fe	ppm 2,683	ppm 2,177	ppm 1,811	<p>① The values in parentheses ( ) were calculated on the assumption that the complex metal-cyanide ions were in the form shown in brackets [ ].</p> <p>② The differences between the calculated values and the measured values are presumed to be due to the degree of purity of the chemicals, measuring errors and other factors.</p>
	Ni	3,009	3,500	2,515	
	Cu	2,696	2,696	2,612	
	Zn	4,734	4,734	3,610	
	Fe-CN[Fe(CN) <sub>6</sub> ]	7,494	6,081	(5,058)	
	Ni-CN[Ni(CN) <sub>4</sub> ]	5,330	6,200	(4,455)	
	Cu-CN[Cu(CN) <sub>4</sub> ]	4,413	4,413	(4,275)	
	Zn-CN[Zn(CN) <sub>4</sub> ]	7,531	7,531	(5,743)	
	Na-CN	24,761	24,761	(20,160)	
	T-CN	49,529	48,986	39,691	
	F-CN	24,761	24,761	27,106	

## 2 Flow Chart

Flow Chart for Electrolytic Oxidation Process



### 3. Research Results

#### 1) Electrolytic Treatment

- a) If graphite is used as the anode material and SUS 27 as the cathode material, and, holding the distance between electrodes at 30 mm, the waste liquid is treated at a current density of 5 Amp/dm<sup>2</sup>, the total cyanide concentration and the free cyanide concentration (initial concentration of total cyanide 40,000 ppm, and free cyanide, 27,000 ppm) can be lowered respectively to 8,500 ppm and 1,000 ppm in about 20 minutes with a current efficiency of 80 to 85%.

Electrolysis to reduce cyanide concentrations to even lower values than these causes the current efficiency to drop abruptly and so is not advisable.

- b) The temperature of the liquid during electrolysis was maintained at 30 to 40°C by cooling with tap water but if cooling was not carried out, it is expected to rise to 60 to 70°C. However, a rise in temperature of the liquid does not have a particularly adverse effect on current efficiency and operation.
- c) If a Ti-Pt electrode was used as the anode, the problem of wear of the electrode is solved but as the current efficiency becomes a poor 60 to 70% and the electrode itself is extremely costly, the idea is not practical.
- d) Adding common salt, while making current efficiency not much different than when salt is not added, causes severe damage to the graphite electrode and has a bad effect on subsequent processes, and so is meaningless.
- e) Replacement of the cathode and anode is required about every 15 days and 6 months respectively.

#### 2) Elimination of Mist Generated During Electrolytic Oxidation

Cyanide and other mists tend to be generated in large quantities the more the current density and blown air volume become, but if the following measures are taken with the current density at 5 Amp/dm<sup>2</sup> and air volume at 0.66m<sup>3</sup>/min., there are no problems with respect to explosion of hydrogen and clogging of pipes due to sodium carbonate and elimination of cyanide gas.

- i) Providing a water seal midway between the electrolytic bath and the absorption tower and using a 3% hypochlorous acid solution as the seal water, will keep the total cyanide concentration of the seal water at about 50 ppm.
- ii) Therefore, the load on the absorption tower which uses a 1% caustic soda solution is very much lightened and only a small-scale tower is required.

#### 3) Processing of Complex Nickel-Cyanides by Hypochlorination

- a) If the waste liquid after being processed by electrolytic oxidation (to a total cyanide concentration of about 8,500 ppm and a free cyanide concentration of about 1,000 ppm) is treated for two hours with a 12% available chlorine

hypochlorous acid solution, of about pH 12, a reaction temperature at ordinary temperature (15 - 25°C), and with oxidation-reduction potential of 200 mV, total cyanide can be reduced to 3,500 ppm, iron to 1,500 ppm, nickel to 50 ppm, copper to 1 ppm, and zinc to 1 ppm, or less. In this case, the quantity of hypochlorous acid required is about 1.36 times against the theoretical quantity of the primary reaction.

- b) If the sludge that is generated in this process (3.85 g/l), after being thickened by standing sedimentation (to 19.2 g/l), is subjected to pressure filtration of 0.5kg/cm<sup>2</sup>, it can be dehydrated to sludge with a water content of 74%.

The quantity of sludge per one m<sup>3</sup> of raw liquid is 16.9 kg with a water content of 74%, or 4.4 kg in the dry state. It is made up of hydroxides mainly consisting of nickel with slight amounts of copper, zinc and iron.

#### 4) Processing of Complex Iron-Cyanides by Heat Oxidative Decomposition Process

- a) If the waste liquid after being processed by hypochlorination is diluted with water to lower the total cyanide concentration to about 2,000 ppm, and is then treated for about 2.5 hours with a 12% available chlorine hypochlorous acid solution, of pH 11 or less, and a reacting temperature of 95°C, the concentrations of total cyanide, nickel and iron can be lowered to approximately the discharge standard. There are however the problems of pH and COD which make neutralization and activated carbon filtration necessary as post treatment.

- b) The quantity of hypochlorous acid required for the above reaction is quite a large amount being about 3.4 times against the theoretical quantity of the primary reaction. This is assumed to have been consumed by the vaporization of the available chlorine due to the high temperature, the oxidation of the chelating agent, the progress of the secondary reaction, and other factors.

- c) If the sludge that is generated in this process (2.3 g/l), is neutralized with sulfuric acid, and, after being thickened by standing sedimentation (to 30 g/l), is subjected to pressure filtration at 0.3 kg/cm<sup>2</sup>, it is dehydrated to sludge with a water content of 79.7%.

The quantity of sludge per one m<sup>3</sup> of raw liquid is 27.3 kg with a water content of 79.7%, or 5.5 kg in the dry state. It is made up of hydroxides mainly consisting of iron with a slight amount of nickel.

- d) With respect to the material of the reaction chamber, experiments were carried out on the corrosion resistance of titanium, from which it was learned that the reduction of weight by corrosion was 0.08% in 90 days, so titanium is quite suitable for use as the material of the chamber.

5) Filtration with Activated Carbon

- a) As waste water after heat oxidative decomposition treatment and neutralization has a high COD and chromaticity due to the chelating agent, it requires to be subjected to activated carbon filtration. The quantity of activated carbon required is 17.75 g per one m<sup>3</sup> of raw liquid.

Note that the table below is one example of the composition of the finally treated water, from which it can be see that although it fully satisfies the discharge standards, its available chlorine is a high 2,100 ppm.

pH	T-CN	Cu	Zn	Ni	Fe	COD	Chromaticity	Available Chlorine
8.0	0.3 ppm	0.1 ppm or less	0.05 ppm or less	0.1 ppm or less	0.1 ppm or less	100 ppm	5 degrees	2,100 ppm

6) Automatic Detection of End Point of Electrolytic Oxidation Process

Since, in electrolytic oxidation, the metals of complex metal-cyanides are deposited primarily on the cathode and create free cyanide, it is necessary to measure the free cyanide concentration continuously in order to ascertain the end point of the electrolytic oxidation process (free cyanide concentration 1,000 ppm).

For measuring cyanide concentrations, there is the ions electrode but since this is primarily for measuring low concentrations and, moreover, has the problems of being costly and short-lived, the development of an ion electrode for measuring high concentrations is desirable. Therefore, from the practical point of view, the duration of electrolysis needs to be determined by measuring the initial concentration of free cyanide.

7) Automatic Control of Complex Nickel-Cyanides in Hypochlorination Process

In the case of the test sample liquid that was used, automatic control was possible by setting the oxidation-reduction potential at 200 mV, but if the waste liquid to be treated is different, the oxidation-reduction potential will vary. Therefore the waste liquid actually needs to have the potential setting at a suitable rate.

#### 4. Construction Cost

Size of Facility	50 m <sup>3</sup> /month	200 m <sup>3</sup> /month
Total Construction Cost	JPY 83,700,000	JPY 157,400,000
Machinery Work	JPY 39,500,000	JPY 86,700,000
Electrical Work	JPY 5,000,000	JPY 10,500,000
Instrumentation Work	JPY 4,900,000	JPY 6,700,000
Civil Engineering Work	JPY 17,500,000	JPY 23,000,000
Construction Site Expenses	JPY 12,800,000	JPY 22,700,000
Overhead Expenses	JPY 4,000,000	JPY 7,800,000

Note 1: Analysis apparatus not included.

2: Land for temporary work and working area is presumed to be able to be borrowed free of charge.

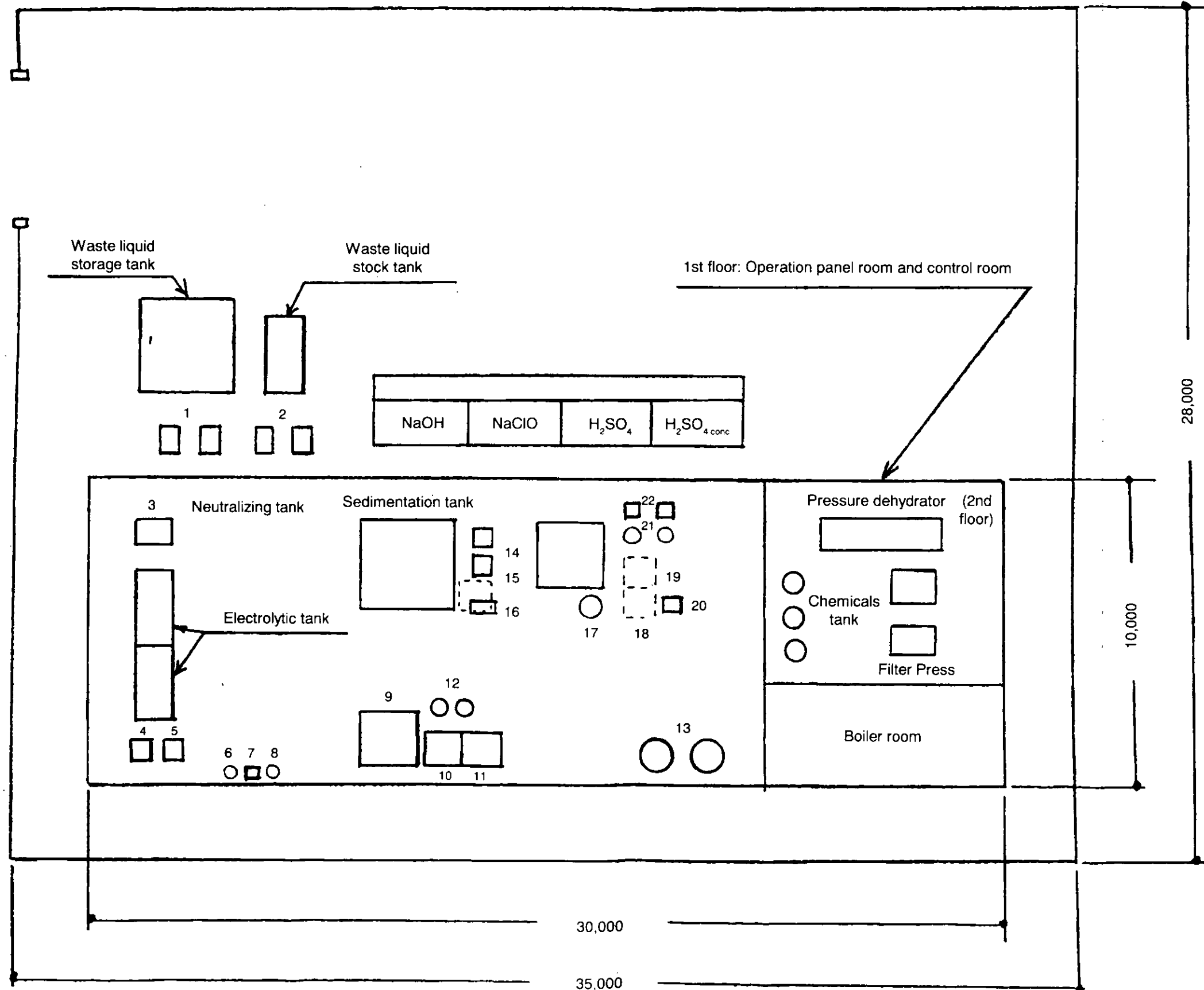
#### 5. Running Cost

	50 m <sup>3</sup> /month			200 m <sup>3</sup> /month	
	Unit Cost	Consumption/day	Cost	Consumption/day	Cost
Electricity	6 yen/kWh	1,333 kWh	7,998 yen	4,607 kWh	27,642 yen
Sodium hypochlorite	15 yen/kg	2,100 kg	31,500 yen	8,400 kg	126,000 yen
Sulfuric acid (98%)	12 yen/kg	130 kg	1,560 yen	520 kg	6,240 yen
Coagulant	1,000 yen/kg	0.068 kg	68 yen	0.27 kg	270 yen
Filter aid	120 yen/kg	0.4 kg	48 yen	1.6 kg	192 yen
Activated carbon	800 yen/kg	35.5 kg	28,400 yen	142 kg	113,600 yen
Heavy oil A	12 yen/l	75 liter	900 yen	300 liter	3,600 yen
Filter medium			890 yen		2,050 yen
Tap water	50 yen/m <sup>3</sup>	40 m <sup>3</sup>	2,000 yen	158 m <sup>3</sup>	7,900 yen
Electrodes			13,600 yen		54,400 yen
Total			86,964 yen		341,894 yen
Running cost per m <sup>3</sup>			43,482 yen		42,737 yen

## 6. Construction Area

1) For 50 m<sup>3</sup>/month (980 m<sup>2</sup>)

Layout of Electrolytic Oxidation Process

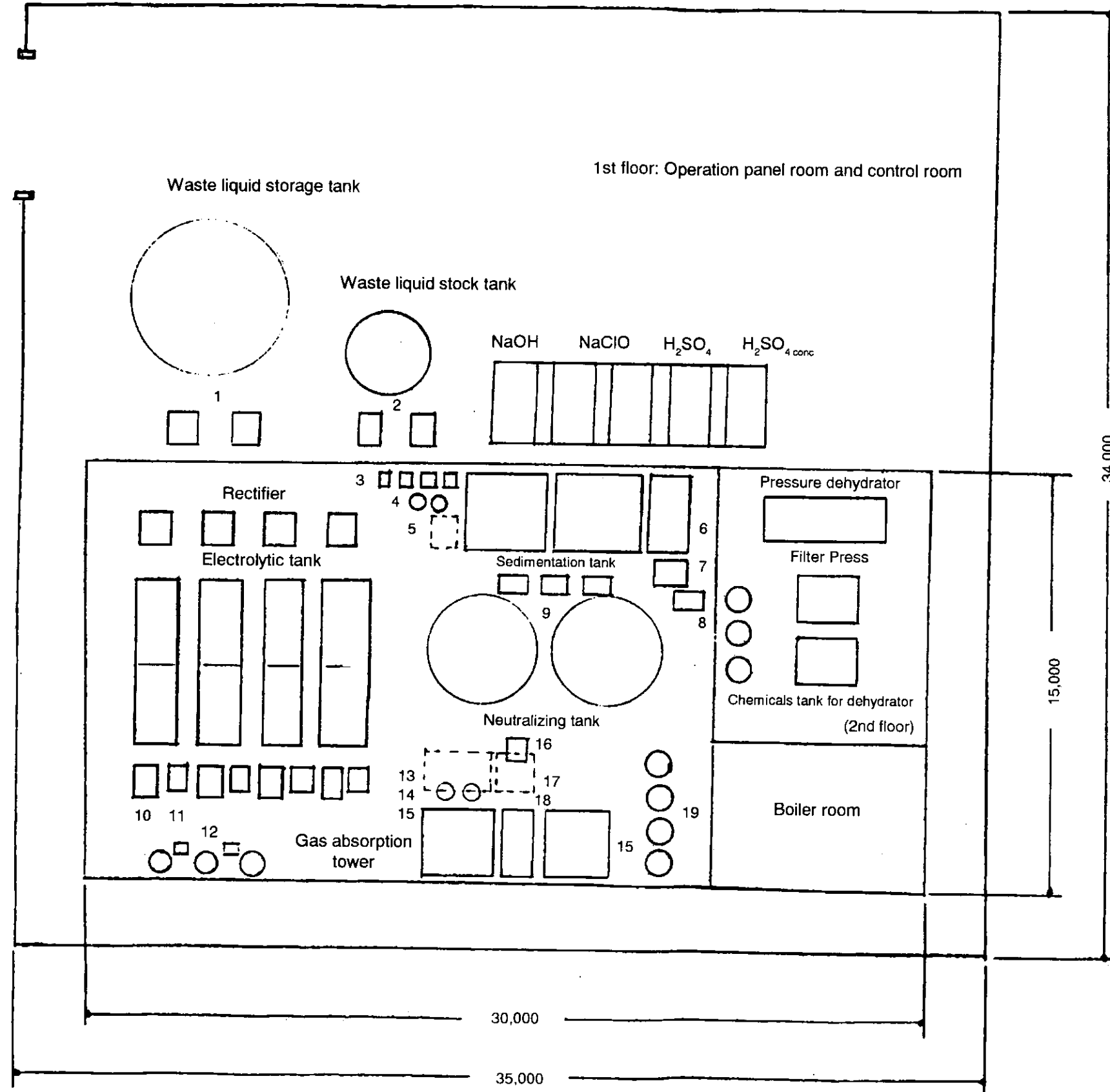


No.	Name
1	Waste liquid feeding pump
2	Waste liquid feeding pump
3	Rectifier
4	Electrolytic tank circulating pump
5	Blower
6	Gas absorption tower
7	Gas absorption pump
8	NaOH tank
9	Nickel-cyanogen reaction tower
10	Supernatant storage tank
11	Slurry receiving tank
12	Filter
13	Heating oxidation tank
14	Neutralizing tank feeding pump
15	Cooling water storage tank
16	Neutralizing tank cooling water feeding pump
17	Slurry concentration tank
18	Sludge tank
19	Stock tank
20	Sludge feeding pump
21	Filter
22	Activated carbon processor



2) For 200 m<sup>3</sup>/month (1190 m<sup>2</sup>)

Layout of Electrolytic Oxidation Process



- | No. | Name   |
|-----|--|
| 1   | Waste liquid feeding pump                    |
| 2   | Waste liquid feeding pump                    |
| 3   | Activated carbon filter                      |
| 4   | Filter                                       |
| 5   | Stock tank                                   |
| 6   | Slurry concentration tank                    |
| 7   | Sludge tank                                  |
| 8   | Sludge feeding pump                          |
| 9   | Neutralizing tank                            |
| 10  | Blower                                       |
| 11  | Electrolytic tank circulating pump           |
| 12  | Gas absorption pump                          |
| 13  | Supernatant storage tank                     |
| 14  | Filter                                       |
| 15  | Nickel-cyanogen reaction tower               |
| 16  | Neutralizing tank cooling water feeding pump |
| 17  | Cooling water storage tank                   |
| 18  | Slurry receiving tank                        |
| 19  | Heating oxidation tank                       |

## 7. Operating Personnel

Duty \ Personnel		Size of Facility	
		50 m <sup>3</sup> /month	200 m <sup>3</sup> /month
Day	Operating Personnel	4	4
	Analyzing Personnel	1	1
Night	Operating Personnel	2	2
Total		7 persons	7 persons

Note: Only the electrolysis process operates 24 hours a day; others are 8-hour operations.

## B Combustion Process

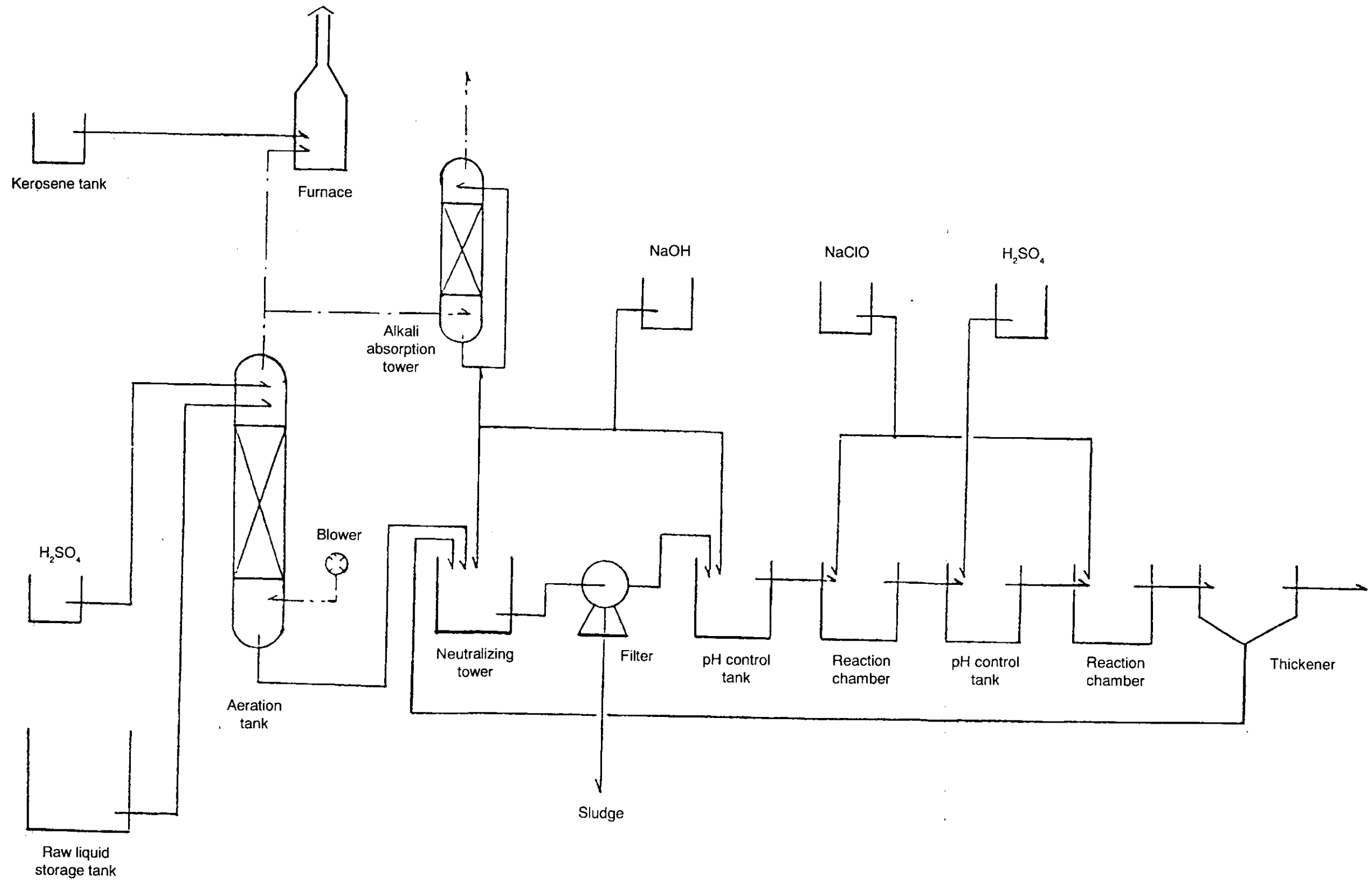
### 1. Composition of Raw liquid

	Chemical	JEC's Instructions	Quantity Actually Used
Quantities of Chemicals Dissolved in 1 m <sup>3</sup>	NaOH	61.8 kg	61.8 kg
	NaCH	60.0	65.0
	CuCN	3.8	3.8
	Zn(CN) <sub>2</sub>	8.5	8.5
	Na <sub>2</sub> [Ni(CN) <sub>4</sub> ]	10.7	-
	Ni(CN) <sub>2</sub> · 4H <sub>2</sub> O	-	9.4
	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	7.8	7.8
	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ]	7.4	-
	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ] · 10H <sub>2</sub> O	-	11.8
	EDTA	0.5	0.5
	Gluconic Acid Soda	0.5	0.5

	Dissolved Component	Calculated Value of JEC's Instructions	Actual Test Liquid		Remarks
			Calculated Value	Measured Value	
Concentration of Components in Waste Liquid	Fe	ppm 2,683	ppm 2,685	ppm 2,424	① The values in parentheses ( ) were calculated on the assumption that the complex metal-cyanide ions were in the form shown in brackets [ ]. ② The differences between the calculated values and the measured values are presumed to be due to the degree of purity of the chemicals, measuring errors and other factors.
	Ni	3,009	3,020	2,912	
	Cu	2,696	2,696	2,512	
	Zn	4,734	4,734	4,616	
	Fe-CN[Fe(CN) <sub>6</sub> ]	7,494	7,500	(6,771)	
	Ni-CN[Ni(CN) <sub>4</sub> ]	5,330	5,350	(5,158)	
	Cu-CN[Cu(CN) <sub>4</sub> ]	4,413	4,413	(4,112)	
	Zn-CN[Zn(CN) <sub>4</sub> ]	7,531	7,531	(7,344)	
	Na-CN	24,761	27,414	(24,215)	
	T-CN	49,529	52,208	47,600	
	F-CN	24,761	27,414	33,300	

## 2. Flow Chart

Flow Chart for Combustion Method (Cyanogen Decomposition Process)



### 3. Research Results

#### 1) Improvement of Aeration Efficiency

- a) If 60% sulfuric acid (about 20% of raw liquid) was added to the raw liquid and the pH made to be 1 or less, and then aerated at the rate of approximately 300 liter of air per one l of raw liquid, it is possible to lower the total cyanide concentration to 7,000 - 7,500 ppm.

Note: As there was practically no further drop in total cyanide concentration in re-aeration tests, 6,000 - 7,500 ppm is considered to be limit of aeration.

- b) Between aeration temperatures of 20 to 45°C there was practically no difference in aeration efficiency, but at 60°C or above there was some tendency for it to rise.
- c) By using 98% concentrated sulfuric acid, there is a possibility of raising the aeration efficiency.
- d) Varying the aeration air volume from 209 to 686 liter per one liter of a mixture of raw liquid and sulfuric acid was tried, but there was practically no difference in efficiency.

- 2) When aerated gas (cyanide gas concentration 3.4 - 14%) was burnt in an incinerator at a temperature of 800 to 1,000°C, the cyanide gas concentration in the waste gas was less than 1 ppm to 5 ppm. From these results, it was found that in order to make the cyanide gas concentration in the waste gas 1 ppm or less, the cyanide gas concentration in the aerated gas would have to be 9% or less and the temperature of the incinerator at 900°C or more.

#### 3) Neutralizing Process

- a) After adjusting the post-aeration waste liquid to a pH of 7 to 9, and then filtering the liquid, the concentration of total cyanide, free cyanide and heavy metals in the filtered liquid can be greatly reduced.

This is believed to be because, by adjusting the pH, the complex iron- cyanide compounds become resistant to dissolving and settle in the liquid. The following shows an example of treatment of aerated liquid (total cyanide concentration 6,500 ppm, and free cyanide concentration 240 ppm).

Filtered liquid	pH	T-CN	F-CN	Zn	Cu	Ni	Fe	COD
	7	ppm 41	ppm 30	ppm 1,030	ppm 32	ppm 1,280	ppm 3	ppm 870
	9	106	81	95	45	7	5	803
Sludge	pH	T-CN	Zn	Cu	Ni	Fe	Moisture content	Quantity produced g/l of aerated liquid
	7	6.0%	4.0%	2.7%	1.6%	3.1%	67%	94
	9	5.2	4.0	2.5	3.0	2.7	71	104

- b) By pre-coating the sediment with diatomaceous earth (#800) and vacuum filtrating the sediment, sludge with a moisture content of 69.4% was obtained. This quantity is 180.3 kg per 1 m<sup>3</sup> of raw liquid or a dry weight of 55.2 kg. Of this, as 29.2 kg of diatomaceous earth is included, the net dry weight of sludge is 26.0 kg.

Note that the filtration rate is 209 l/m<sup>2</sup>.hr.

- c) When the filtration described above was carried out, a cyanide content of approximately 4% as total cyanide concentration was contained in the sludge, there was the danger of cyanide gas being generated. The concentration of the cyanide gas was measured by the venting method. It was found to be 0.1 ppm and less than 0.1 ppm respectively generated from aerated liquid pH-adjusted to 7 and 9. As the result, cyanide gas seems to be no problem in the actual filtration operation.

#### 4) Treatment of Filtered Liquid by Hypochlorination Method

- a) If the filtered liquid mentioned above is treated by the hypochlorination method and then filtered, the water quality of the waste liquid fully meets the discharge standards, except for pH and COD, as in the example shown in the table below.

pH	T-CN	Zn	Cu	Ni	Fe	COD
8.6	ppm 0.7	ppm 1.2	ppm 0.8	ppm 1.1	ppm 0.9	ppm 317

- b) The hypochlorination treatment conditions, as a result of various studies, are as follows.

Item	Reaction	Primary Reaction	Secondary Reaction
Added quantity of NaClO, ml/Raw liquid, ml		4.4 - 5.0	12.5
ORP		300 - 400 mV	650 - 800 mV
pH		10.5 - 11	8.5 - 9.0
Temperature		25°C and higher	25°C and higher
Duration		30 minutes and longer	120 minutes and longer

5) Special Treatment

As the COD of the waste liquid, after hypochlorination, exceeded the discharge standards because of the chelating agent and other organic matter, and also, in order to remove heavy metals even more, the waste liquid described in (4)-(a) above was filtered through activated carbon and treated with organic sulfur compound, with the following results.

pH	T-CN	Zn	Cu	Ni	Fe	COD
7.8	ppm 0.7	ppm 0.5	ppm 0.6	ppm 0.6	ppm 1.2	ppm 78

6) Explosion Limit

The explosion limit of cyanide gas is a concentration of 6.7% in air. This is higher than the documented value of 5.6% but is believed to be due to the moisture contained in the aerated gas. Therefore, the concentration of cyanide gas during the aeration process needs to be maintained at less than 6.7%.

7) Safety Measures

a) Measure against Explosion

Measure the cyanide gas concentration with an infrared gas analyzer and control it to less than 6.7% by adjusting the aeration air volume.

b) Emergency Stop Measures

i) Inject caustic soda into the aeration tower and suppress the generation of cyanide gas by making the contents alkaline.

ii) Seal off the system instantaneously, purge the cyanide gas with nitrogen and absorb it with the caustic soda absorption column.

#### 4. Construction Cost

Size of Facility	50 m <sup>3</sup> /month		200 m <sup>3</sup> /month	
	Cyanide Removal	Heavy Metals Removal	Cyanide Removal	Heavy Metals Removal
Total Construction Cost	JPY 40,500,000		JPY 77,000,000	
Construction Cost	JPY 33,000,000	JPY 7,500,000	JPY 65,000,000	JPY 12,000,000
Machinery Work	JPY 13,000,000	JPY 4,000,000	JPY 34,000,000	JPY 7,200,000
Electrical Work	JPY 4,000,000	JPY 800,000	JPY 6,000,000	JPY 1,000,000
Instrumentation Work	JPY 7,000,000	JPY 800,000	JPY 8,000,000	JPY 800,000
Civil Engineering Work	JPY 3,000,000	JPY 700,000	JPY 7,000,000	JPY 1,000,000
Construction Site Expenses	JPY 2,000,000	JPY 400,000	JPY 3,000,000	JPY 600,000
Overhead Expenses	JPY 3,000,000	JPY 600,000	JPY 5,000,000	JPY 1,000,000
Designing Work	JPY 1,000,000	JPY 200,000	JPY 2,000,000	JPY 400,000

Note 1: Analysis apparatus, and office and auxiliary facility work not included.

2: Estimating Presumptions

- (a) Electricity and water for construction and air for instrumentation are presumed to be supplied free of charge.
- (b) Land for temporary work and working area is presumed to be able to be borrowed free of charge.
- (c) Spares are not included in the estimate.



## 5. Running Cost

### 1) Cyanide Removal Running Cost

	Unit Cost	50 m <sup>3</sup> /month		200 m <sup>3</sup> /month	
		Consumption/day	Cost	Consumption/day	Cost
Electricity	6 yen/kWh	260 kWh	1,560 yen	640 kWh	3,840 yen
Sodium hypochlorite	15 yen/kg	80 kg	1,200 yen	320 kg	4,800 yen
Sulfuric acid (98%)	12 yen/kg	440 kg	5,280 yen	1,760 kg	21,120 yen
Caustic soda (97%)	27 yen/kg	200 kg	5,400 yen	800 kg	21,600 yen
Kerosene	14 yen/l	60 liter	840 yen	240 liter	3,360 yen
Diatomaceous earth	45 yen/kg	26 kg	1,170 yen	104 kg	4,680 yen
Tap water	50 yen/m <sup>3</sup>	24 m <sup>3</sup>	1200 yen	80 m <sup>3</sup>	4,000 yen
Lubricating oil and others			630 yen		760 yen
Total			17,280 yen		64,160 yen
Running cost per m <sup>3</sup>			8,640 yen		8,020 yen

### 2) Special Removal (Heavy Metal Removal) Running Cost

	Amount per m <sup>3</sup>
Special treatment running cost	3,500 yen
Metal insoluble agent	600 yen
Coagulant	150 yen
Coagulant aid	10 yen
Electricity	100 yen
Water	100 yen
Diatomaceous earth	250 yen
Activated carbon	2,000 yen
Others	290 yen

## 7. Operating Personnel

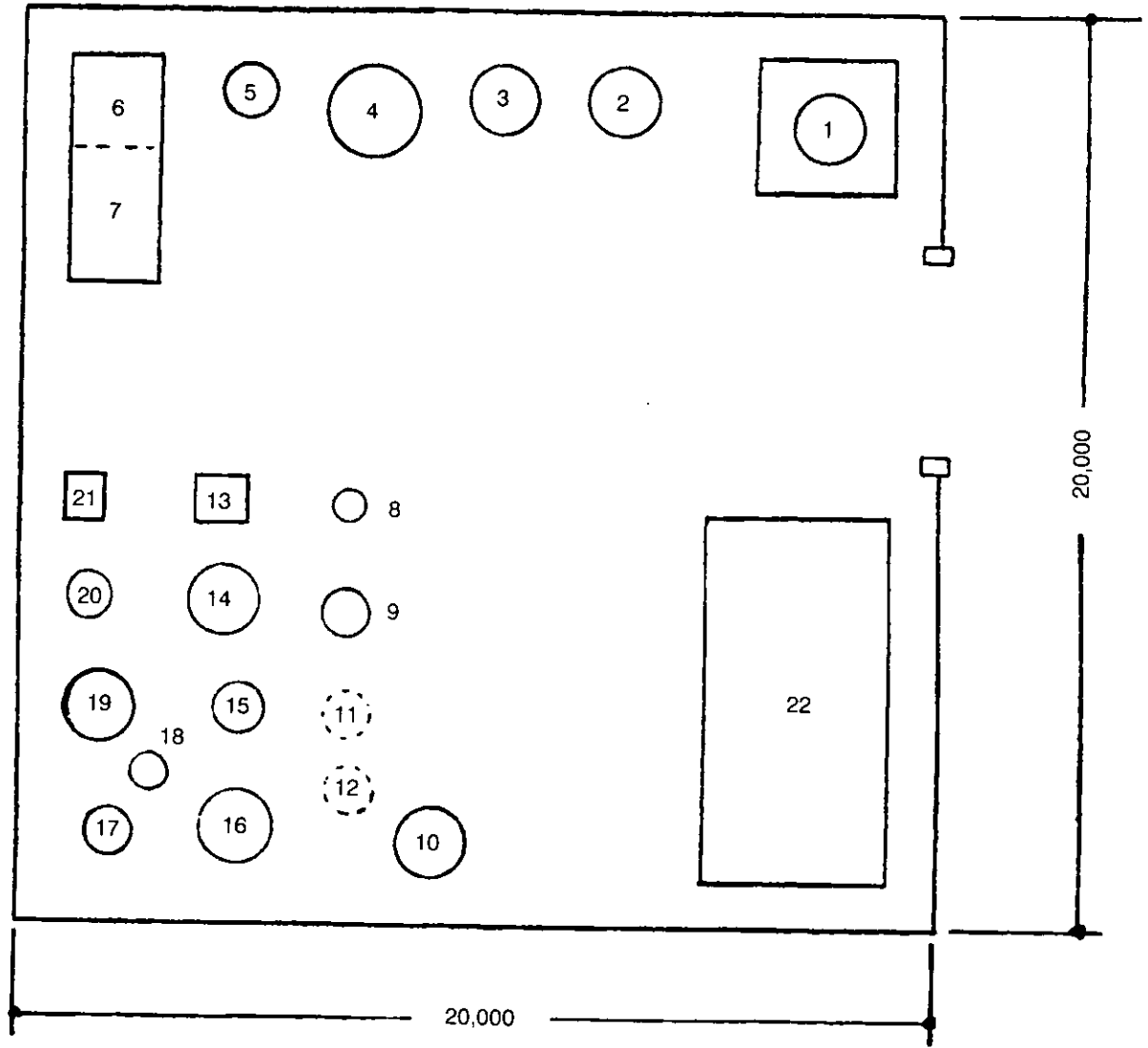
Personnel \ Size of Facility	50 m <sup>3</sup> /month	200 m <sup>3</sup> /month
Operating Personnel	5	6
Analyzing Personnel	1	1
Total	6 persons	7 persons

Note: 8-hour operations.

## 6. Construction Area

1) For 50 m<sup>3</sup>/month (400 m<sup>2</sup>)

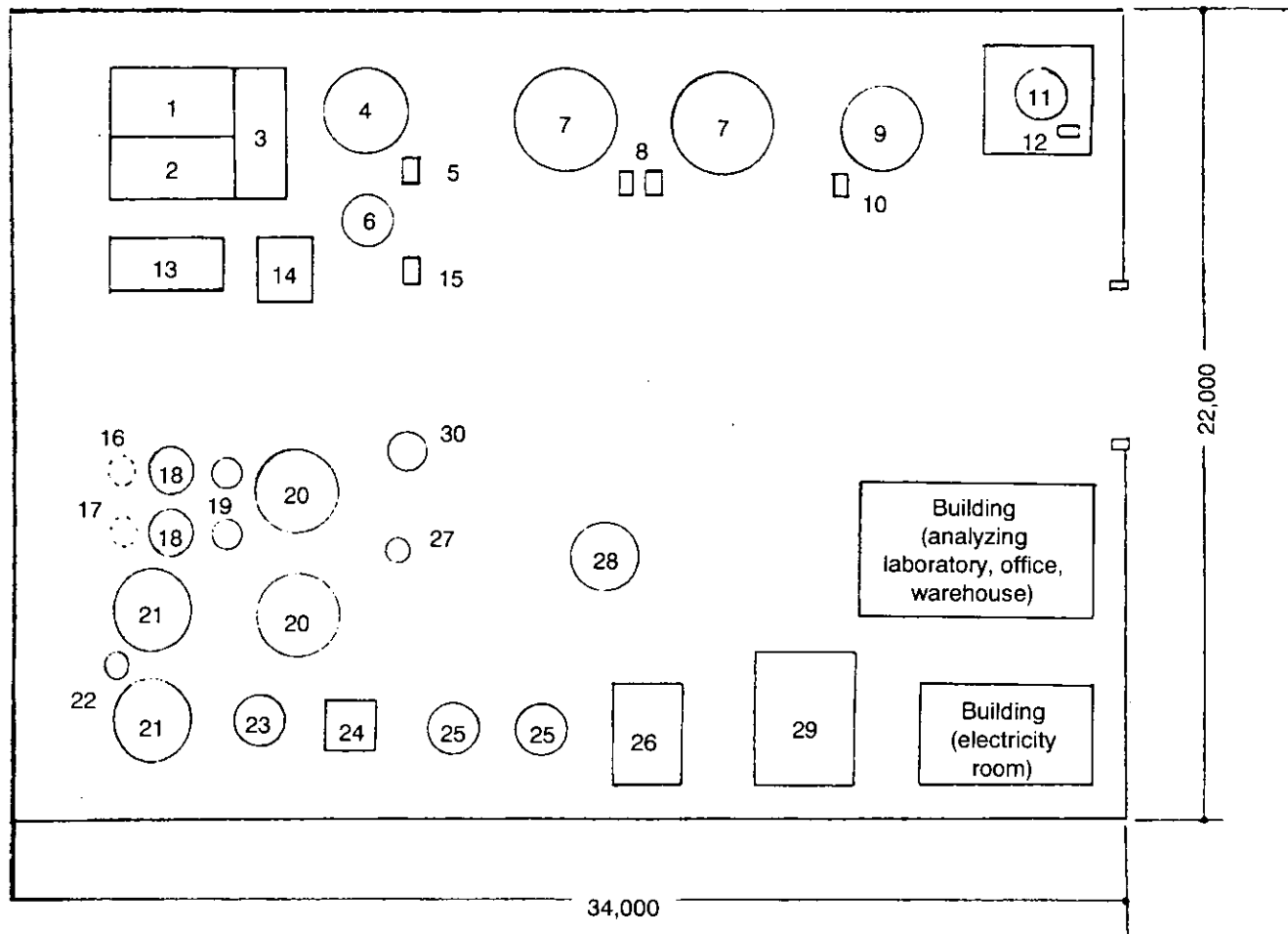
Layout of Combustion Process



- |    |   |    |  |
|----|---|----|--|
| 1  | Kerosene storage tank                         | 12 | Sulphuric acid tank  |
| 2  | Sulphuric acid storage tank                   | 13 | Filter   |
| 3  | Caustic soda storage tank                     | 14 | Neutralizing tank  |
| 4  | Concentrated cyanogen raw liquid storage tank | 15 | pH control tank  |
| 5  | Sodium hypochlorite storage tank              | 16 | Reaction chamber   |
| 6  | Filter-related facilities                     | 17 | pH control tank  |
| 7  | Filter  | 18 | Reaction chamber   |
| 8  | Aeration tower                                | 19 | Thickener  |
| 9  | Alkali absorption tower                       | 20 | Supernatant tank   |
| 10 | Incinerator                                   | 21 | Drainage pit   |
| 11 | Caustic soda tank                             | 22 | Building<br>(office, electricity room, analyzing laboratory) |

2) For 200 m<sup>3</sup>/month (750 m<sup>2</sup>)

Layout of Combustion Process



- |    |   |    |                               |
|----|---|----|-------------------------------|
| 1  | Sludge drum station                           | 16 | Caustic soda tank             |
| 2  | Sludge filter                                 | 17 | Sulphuric acid tank           |
| 3  | Filter-related facilities                     | 18 | Alkali chlorine reaction tank |
| 4  | Caustic soda storage tank                     | 19 | pH control tank               |
| 5  | Caustic soda pump                             | 20 | Neutralizing tank             |
| 6  | Sodium hypochlorite storage tank              | 21 | Thickener                     |
| 7  | Concentrated cyanogen raw liquid storage tank | 22 | Reaction chamber              |
| 8  | Concentrated cyanogen raw liquid pump         | 23 | Supernatant tank              |
| 9  | Sulphuric acid storage tank                   | 24 | Filter                        |
| 10 | Sulphuric acid pump                           | 25 | Activated carbon tower        |
| 11 | Supernatant oil storage tank                  | 26 | Drainage pit                  |
| 12 | Supernatant oil pump                          | 27 | Aeration tower                |
| 13 | Slurry pit                                    | 28 | Incinerator                   |
| 14 | In-plant drainage pit                         | 29 | Compressor, etc.              |
| 15 | Sodium hypochlorite pump                      | 30 | Alkali absorption tower       |

## C. Heated and Pressurized Air Oxidation Process

### 1. Composition of Raw liquid

	Chemical	JEC's Instructions	Quantity Actually Used
Quantities of Chemicals Dissolved in 1 m <sup>3</sup>	NaOH	61.8 kg	61.8 kg
	NaCN	60.0	60.0
	CuCN	3.8	3.8
	Zn(CN) <sub>2</sub>	8.5	8.5
	Na <sub>2</sub> [Ni(CN) <sub>4</sub> ]	10.7	-
	K <sub>2</sub> [Ni(CN) <sub>4</sub> ] · H <sub>2</sub> O	-	13.3
	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	7.8	7.8
	Na <sub>4</sub> [Fe(CN) <sub>6</sub> ]	7.4	7.4
	EDTA	0.5	0.5
	Gluconic Acid Soda	0.5	0.5

	Dissolved Component	Calculated Value of JEC's Instructions	Actual Test Liquid		Remarks
			Calculated Value	Measured Value	
Concentration of Components in Waste Liquid	Fe	ppm 2,683	ppm 2,683	ppm 2,209	① The values in parentheses ( ) were calculated on the assumption that the complex metal-cyanide ions were in the form shown in brackets [ ]. ② The differences between the calculated values and the measured values are presumed to be due to the degree of purity of the chemicals, measuring errors and other factors.
	Ni	3,009	3,015	2,520	
	Cu	2,696	2,696	2,733	
	Zn	4,734	4,734	4,458	
	Fe-CN[Fe(CN) <sub>6</sub> ]	7,494	7,494	(6,170)	
	Ni-CN[Ni(CN) <sub>4</sub> ]	5,330	5,341	(4,464)	
	Cu-CN[Cu(CN) <sub>4</sub> ]	4,413	4,413	(4,473)	
	Zn-CN[Zn(CN) <sub>4</sub> ]	7,531	7,531	(7,092)	
	Na-CN	24,761	24,761	(16,097)	
	T-CN	49,529	49,540	38,296	
F-CN	24,761	24,761	36,035		

### 3. Research Results

#### 1) Heated and Pressurized Air Oxidation Process

##### a) Reaction Conditions

Raw liquid flow rate	53 l/hr
Air volume	250 NI/min
Reaction duration	26.6 min
Reaction tower pressure	55 kg/cm <sup>2</sup>
Reaction tower temperature	235°C

Under the above conditions, it was found that although total cyanide, free cyanide and iron met the discharge standards as in the example shown below, the other items exceeded the standards, so secondary treatment is required.

pH	T-CN	F-CN	Fe	Ni	Zn	Cu	COD	NH <sub>3</sub>	SS
	ppm	ppm	ppm or less	ppm	ppm	ppm	ppm	ppm	ppm
10.5	0.05	0.004	0.3	25.6	73.3	338	233	24,664	92.5

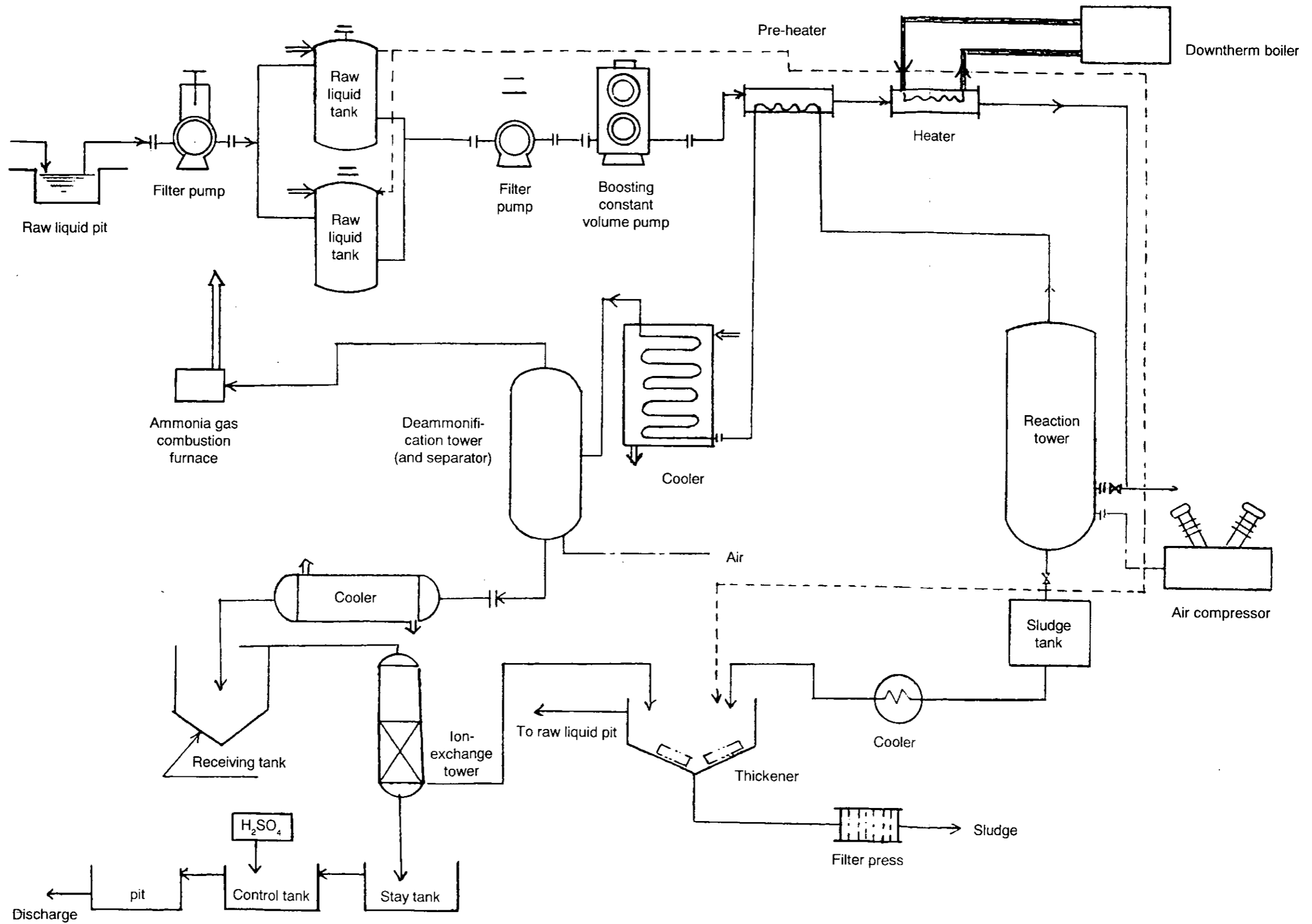
b) Judging from the results mentioned above, practically all the nitrogen content of the raw liquid was converted to ammonia which is corrosive, and, under the current circumstances, the reaction conditions for suppressing ammonia have not yet been fully ascertained.

#### 2) Study of Materials

a) The results of material tests with SUS27, SUS32, High-Steroid C (Ni alloy), and titanium were as follows.

## 2. Flow Chart

Flow Chart for Pressurized Air Oxidation Process



Location Studied	Material	Tensile Strength (kg/mm <sup>2</sup> )	Elongation (%)
Heater inlet pipe	SUS-32	78.0	55.4
Heater outlet pipe	SUS-32	77.0	53.3
Baffle plate	SUS-32	56.0	59.6
	SUS-27	68.0	47.5
	Ti	42.9	40.0
	High-Steroid C (Nickel alloy plate)	86.8	48.0
Preheater outlet pipe	SUS-32	58.0	62.0

As per the above, with respect to tensile strength and elongation, there was no problem with any of the materials as they satisfied the standards.

According to microphotographs of the metal structure, intergranular stress corrosion cracking could be seen in the heater piping. The cause of this is believed to be due to the intergranular precipitation of carbides in the molten metal structure of the weld seam resulting in cracks occurring along those grain boundaries.

- b) From the above results, while it is believed that the materials of piping and the reaction tower can be left as at present, the following measures are required to be considered with respect to the heater.
- i) Use SUS-33 and other low carbon materials.
  - ii) After fabrication, carry out a complete carbon solution heat treatment to prevent intergranular carbide precipitation.
  - iii) Change the electric heater of the heat source to a heat medium to obtain a stable and uniform heating temperature.
- 3) Secondary Treatment (Ion-Exchange Resin Treatment)

When the waste liquid, after it was subjected to the heated and pressurized air oxidation process, was treated with an ion exchange resin (type CR-Na) under the following conditions, the results, as shown in the table below, were that the treated waste liquid volume up to 80 ml/ml-resin met the discharge standards with respect to copper, zinc and nickel, but was not clear with respect to COD and other factors.

Waste liquid concentration: Waste liquid of (1)-(a) above diluted 10 times.  
SV value: 30  
Amount of resin: 10 ml



Treated Waste Liquid Volume	Cu Concentration	Zn Concentration	Ni Concentration
20 ml/ml-resin	0.1 ppm or less	0.04 ppm	0.1 ppm or less
40 ml/ml-resin	0.1 ppm or less	0.06 ppm	0.1 ppm or less
60 ml/ml-resin	0.1 ppm or less	0.12 ppm	0.1 ppm or less
80 ml/ml-resin	0.1 ppm or less	1.2 ppm	0.1 ppm or less
100 ml/ml-resin	0.2 ppm or less	7.0 ppm	0.1 ppm or less
120 ml/ml-resin	0.5 ppm or less	19.2 ppm	0.5 ppm or less
140 ml/ml-resin	1.8 ppm or less	31.4 ppm	2.5 ppm or less

### Information: Stripping Process

While it is possible to remove heavy metals by the ion-exchange resin treatment mentioned in (3)-(a) above, since it would cause running costs to escalate, basic research on an alternative method of eliminating heavy metals was carried out at the laboratory of a member of this working team, Professor Takatoshi Yoshida, of the Industrial Chemistry Department of the Nagoya Industrial University. The result was that the method was found to be extremely effective as shown below and so there are high hopes for its further research and development.

A test sample, after being treated by the heated and pressurized air oxidation method, was first adjusted with respect to its pH, and then stripped of its ammonia by injecting air for about 30 minutes while the sample was heated to 100°C in a water bath. When the pH was adjusted once again, practically all the heavy metals in the test sample became hydroxides and settled, and the quality of the clear upper water was as per the table below.

Therefore, by adjusting the pH during and after the stripping process to appropriate levels, it is believed that heavy metals can be fully removed.

Test No.		pH	Total Cyanide Concentration	Cu Concentration	Zn Concentration	Ni Concentration
	Raw Liquid	9.7	0.95 ppm	3,760 ppm	1,063 ppm	366 ppm
No. 1	After stripping at pH 9 (A)	9.7	-	1,730	22	0
	After adjusting liquid (A) to pH 9	8.0	-	750	10	0
No. 2	After stripping at pH 13.7 (B)	13.7	-	40	109	30
	After adjusting liquid (B) to pH 8	8	-	0	5	30

#### 4) Safety Measures

##### a) Measure against Explosion

As the explosion limit of ammonia in air is a concentration of 16%, operation should be carried out at below this figure.

##### b) Emergency Stop Measures

Take steps to seal off the system instantaneously, and to return untreated liquid to the raw liquid tank.

#### 5) Treatment of Metal Hydroxides Remaining in Heated and Pressurized Air Oxidation Tower

a) After operating the reaction tower for 16 consecutive hours a day, blow out the residue in the tower, cool in a cooler and separate the solids from the liquid. Return the clear upper liquid to the raw liquid tank and dewater the sludge with a filter press.

b) The quantity of sludge generated was 19.9 kg dry weight per one m<sup>3</sup> of raw liquid, and if the moisture content was assumed to be 70%, the total quantity would be 66.3 kg.

Note that the dewaterability of the sludge, judging from the stationary sedimentation curve, is believed to be good.

#### 6) Removal of Ammonia

After once cooling in a cooler after the reaction tower, remove the ammonia by aeration in an ammonia removing tower.

Decompose the ammonia in the ammonia-air mixture by combustion at 1,000°C or more in a combustion furnace.

Note: As was stated in the above paragraph entitled Information, if the stripping method is adopted for removing heavy metals, this ammonia removal method will, as a matter of course, require to be restudied.

#### 4. Construction Cost

Size of Facility	50 m <sup>3</sup> /month	200 m <sup>3</sup> /month
Total Construction Cost	JPY 101,070,000	JPY 214,390,000
Machinery Work	JPY 54,050,000	JPY 130,450,000
Instrumentation Work	JPY 6,030,000	JPY 7,200,000
Civil Engineering Work	JPY 17,800,000	JPY 32,900,000
Construction Site Expenses	JPY 16,590,000	JPY 29,840,000
Overhead Expenses	JPY 6,600,000	JPY 14,000,000

- Note 1) Civil engineering unwatering work, foundation pile driving, primary electrical wiring, and waste liquid chemicals for test operation not included.
- 2) Office and road construction, and fence, gate and other ancillary work not included.
- 3) Analyzing apparatus not included.

#### 5. Running Cost

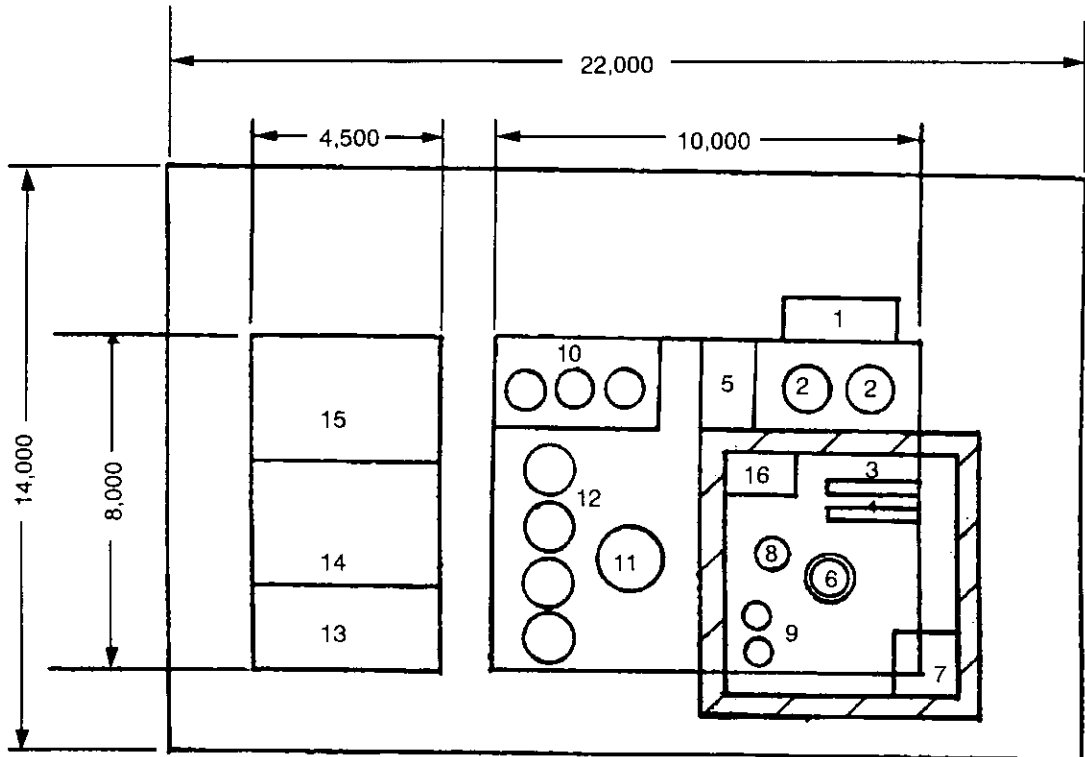
	50 m <sup>3</sup> /month			200 m <sup>3</sup> /month	
	Unit Cost	Consumption/day	Cost	Consumption/day	Cost
Electricity	6 yen/kWh	1,365 kWh	8,190 yen	4,360 kWh	26,160 yen
Sulfuric acid (98%)	12 yen/kg	166.7 kg	2,000 yen	666.7 kg	8,000 yen
Tap water	50 yen/m <sup>3</sup>	25 m <sup>3</sup>	1,250 yen	100 m <sup>3</sup>	5,000 yen
Propane	20 yen/kg	320 kg	6,400 yen	1,280 kg	25,600 yen
Hydrochloric acid (35%)	32 yen/kg	30 kg	960 yen	120 kg	3,840 yen
Caustic soda (97%)	27 yen/kg	22.5 kg	608 yen	90 kg	2,430 yen
Ion-exchange resin			42 yen		168 yen
Total			19,450 yen		71,198 yen
Running cost per m <sup>3</sup>			9,725 yen		8,900 yen

Note: These are running costs when secondary treatment with ion-exchange resin is included.

## 6. Construction Area

1) For 50 m<sup>3</sup>/month (310 m<sup>2</sup>)

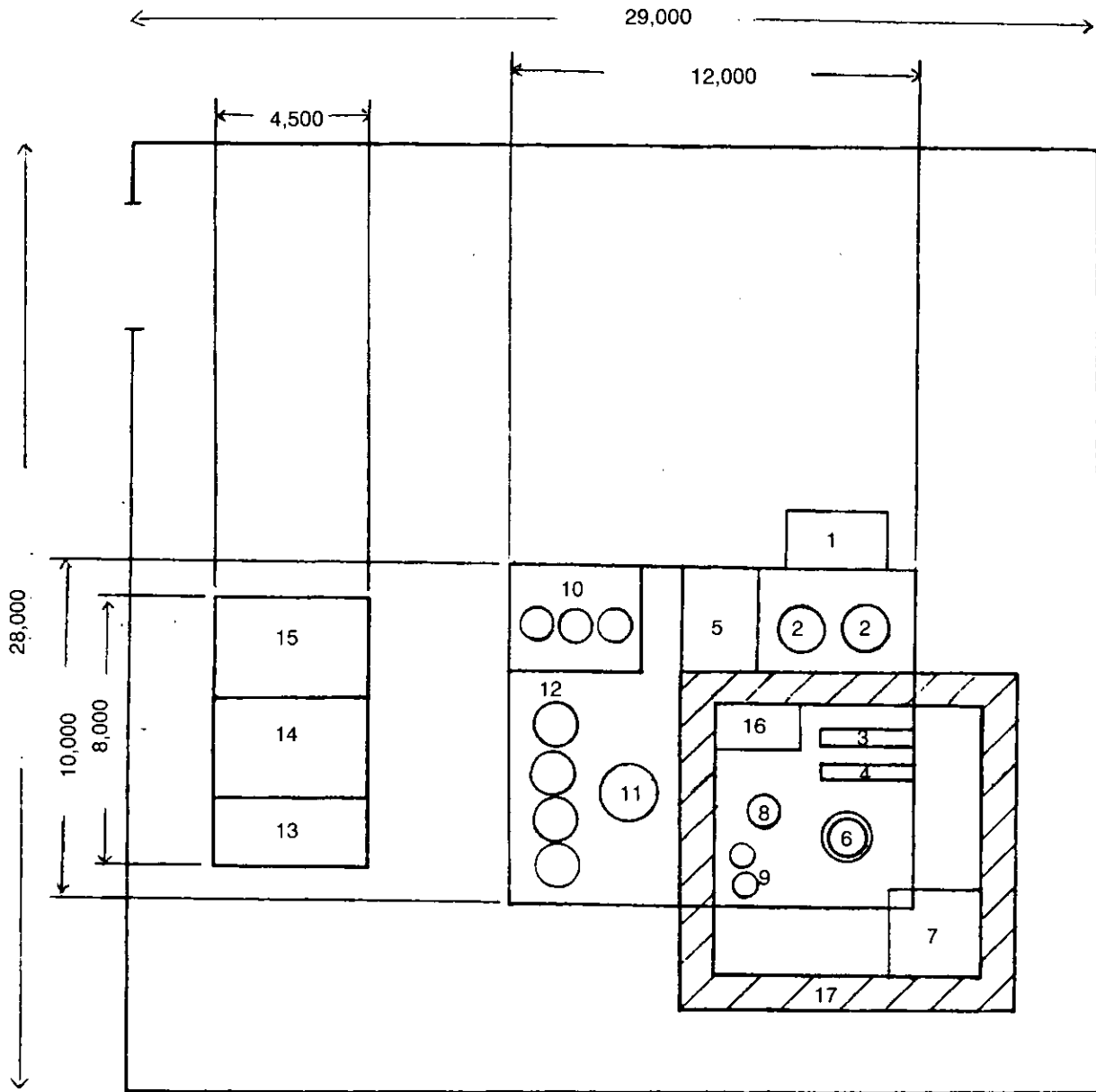
Layout of Heated and Pressurized Oxidation Process



- |    |  |
|----|--|
| 1  | Raw liquid pit                         |
| 2  | Raw liquid tank                        |
| 3  | Pre-heater                             |
| 4  | Heater                                 |
| 5  | Downtherm boiler                       |
| 6  | Reaction tower                         |
| 7  | Ammonia gas combustion furnace         |
| 8  | Deammonification tower (and separator) |
| 9  | Cooler                                 |
| 10 | Chemicals feeding tank                 |
| 11 | Thickener                              |
| 12 | Ion exchange tower                     |
| 13 | Analyzing laboratory                   |
| 14 | Control room                           |
| 15 | Office                                 |
| 16 | Compressor                             |
| 17 | Protective wall                        |

2) For 200 m<sup>3</sup>/month (810 m<sup>2</sup>)

Layout of Heated and Pressurized Oxidation Process



- 1 Raw liquid pit
- 2 Raw liquid tank
- 3 Pre-heater
- 4 Heater
- 5 Downtherm boiler
- 6 Reaction tower
- 7 Ammonia gas combustion furnace
- 8 Deammonification tower (and separator)
- 9 Cooler
- 10 Chemicals feeding tank
- 11 Thickener
- 12 Ion exchange tower
- 13 Analyzing laboratory
- 14 Control room
- 15 Office
- 16 Compressor
- 17 Protective wall

## 7. Operating Personnel

	50 m <sup>3</sup> /month	200 m <sup>3</sup> /month
Operating Personnel	7	7
Analyzing Personnel	1	1
Total	8 persons	8 persons

Note: 24-hour operations

## D. Comparison of Three Processes and Points at Issue

### 1. Technical Issues

#### 1) Matters Requiring Further Development

##### B. Combustion Process

- Treatment of the sludge containing approximately 4% cyanide that is generated from the neutralization-filtration process after aeration

##### C. Heated and Pressurized Air Oxidation Process

- Determination of optimum reaction conditions for this process, treatment of the sludge that is created in the tower, and designing of equipment giving consideration to operability, safety and efficiency

#### 2) Matters on Which Further Development is Desirable

##### A. Electrolytic Oxidation Process

- Method of automatically controlling the heat oxidation process and method of reducing the chlorine in the treated waste water
- Development of a durable graphite electrode

##### C. Heated and Pressurized Air Oxidation Process

- Determination of optimum conditions for ammonia removal and ammonia combustion methods by aeration in the ammonia removal process
- Determination of optimum conditions for removing copper and nickel by the ion-exchange resin or stripping methods

##### Matter Common to All

- Apparatus for automatic measurement of high cyanide concentrations

#### 3) Matters to be Considered in Construction of Facilities

##### A. Electrolytic Oxidation Process

- Designing of equipment for discharging out of the system the ammonia, carbon dioxide and nitrogen, etc. that are generated in the heat oxidation process and for absorbing the ammonia

B. Combustion Process

- Safety measures for the cyanide gas that is generated in aeration process

C. Heated and Pressurized Air Oxidation Process

- Employment of materials that can withstand high temperatures and high pressures

Matter Common to All

- Emergency safety measures

## 2. Cost of Constructing Facilities

	Electrolytic Oxidation Process	Combustion Process	Heated and Pressurized Air Oxidation Process
For treating 50 m <sup>3</sup> /month	JPY 83,700,000	JPY 40,500,000	JPY 101,070,000
For treating 200 m <sup>3</sup> /month	JPY 157,400,000	JPY 77,000,000	JPY 214,390,000

Note: There is not much difference even when the composition and concentration of concentrated liquid cyanide waste vary.

## 3. Running Cost

The running costs per one m<sup>3</sup> of waste liquid are as follows.

	Electrolytic Oxidation Process	Combustion Process	Heated and Pressurized Air Oxidation Process
For treating 50 m <sup>3</sup> /month	43,482 yen/m <sup>3</sup>	12,140 yen/m <sup>3</sup>	9,725 yen/m <sup>3</sup>
For treating 200 m <sup>3</sup> /month	42,740 yen/m <sup>3</sup>	11,520 yen/m <sup>3</sup>	8,859 yen/m <sup>3</sup>

Note 1) Large differences occur when the composition and concentration of the concentrated liquid cyanide waste vary. The effect of complex iron-cyanides in the electrolytic oxidation process causes particularly large variation.

For example, the above table has been calculated with an iron concentration of 1.811 ppm. but if only the iron concentration became half that, the running cost of JPY43,482/m<sup>3</sup> would become JPY30,360/m<sup>3</sup> or less.

2) Also, the running costs in the above table have been calculated based on the inclusion of 500 ppm each of only EDTA and gluconic acid soda as chelating agents, but in actual waste liquids there are inclusions of other additives which could cause running costs to vary.

3) Therefore, the running costs in the above table serve simply as yardsticks.

#### 4. Construction Area

	Electrolytic Oxidation Process	Combustion Process	Heated and Pressurized Air Oxidation Process
For treating 50 m <sup>3</sup> /month	980 m <sup>2</sup>	400 m <sup>2</sup>	310 m <sup>2</sup>
For treating 200 m <sup>3</sup> /month	1,190 m <sup>2</sup>	750 m <sup>2</sup>	810 m <sup>2</sup>

Note: Approximate 50% of the respective total areas has been allowed as unoccupied ground.

#### 5. Operating Personnel

	Electrolytic Oxidation Process	Combustion Process	Heated and Pressurized Air Oxidation Process
For treating 50 m <sup>3</sup> /month	7 persons	6 persons	8 persons
For treating 200 m <sup>3</sup> /month	7	7	8

Note 1) In the electrolytic oxidation process, only the electrolysis operation works round-the-clock; the others work 8-hours a day.

2) The combustion process works 8-hours a day.

3) The heated and pressurized air oxidation process works round-the-clock.

#### 6. Quantity of Sludge Generated

The following table shows the respective quantity of sludge generated per one m<sup>3</sup> of concentrated liquid cyanide waste, but this quantity too is subject to some variation if the composition and concentration of the waste liquid should vary.

	Electrolytic Oxidation Process	Combustion Process	Heated and Pressurized Air Oxidation Process
Quantity of sludge generated	44.2 kg	180 kg	66.3 kg
Moisture content of sludge	77.6%	69.4%	70%
Dry weight of sludge	9.9 kg	55.2 kg	19.9 kg

Note 1) The composition of the sludge generated by the electrolysis oxidation process and the heated and pressurized air oxidation process is mostly of hydroxides of metals.

2) The composition of the sludge generated by the combustion process is of complex metal-cyanides with a cyanide content of about 4% and also contains diatomaceous earth as a cake filtration agent.

The dry weight of sludge minus the diatomaceous earth is 26 kg/m<sup>3</sup> and if the moisture content of the sludge when a cake filtration agent is not used is 75%, the quantity of sludge generated becomes 104 kg/m<sup>3</sup>.



## VI. Conclusion

This investigation and study, in trying to find the most economical method for the joint treatment of the concentrated liquid cyanide waste that is discharged by the electroplating process to make it fall within the Water Pollution Control Law discharge standards [pH 5.8 to 8.6, cyanide one mg/l max., zinc 5 mg/l max., copper 3 mg/l max., iron 10 mg/l max., suspended solids 200 mg/l max (daily average 150 mg/l max.), COD 160 mg/l max. (daily average 120 mg/l max., and nickel 1 mg/l max. (Kanagawa Prefecture Pollution Control Bylaws, Otsu Area Discharge Standard)], by referring to various literature and studying the various processes being currently advocated. It was however unable to find an appropriate system that could be recommended immediately in its current form under the present technological level.

Accordingly, JEC requested Japanese private companies to carry out consecutive research on (1) the electrolytic oxidation process, (2) combustion process, and (3) heated and pressurized air oxidation process which would be effective treatment by further research and technical development.

As the result, the electrolytic oxidation process was felt to be adoptable even with the present technology despite its having problems in workability because its heat oxidation process could not be automatically controlled, and also in that durable electrodes had to be developed. The particular problem is that its running cost is high being about four times that of the other two treatment process, but this is possible to reduce significantly depending on the composition of the concentrated liquid cyanide waste, particularly the complex iron-cyanide content. Beside that, in the actual facility, there is a good possibility that the cost of the activated carbon used in the final filtration process can be lowered considerably. Accordingly there are hopes that its running cost can be brought close to that of the other two processes depending on the composition of the waste liquid. On the other hand, the advantage of this treatment process is that the cost of dumping is low due to the sludge amount being the least in the three processes. Most copper and zinc are deposited on the cathode on the electrolytic oxidation process. However, it has the demerit of chlorine existing in the treated waste water.

Except for the treatment of associated sludge, the combustion process is accepted as a nearly-established technology. The electroplating industry in Kanagawa Prefecture is currently constructing a combustion process plant that will be capable of processing 100 m<sup>3</sup> of concentrated liquid cyanide waste per month. Operation of this plant is scheduled to begin in mid June.

The use of this method requires particular attention to safety measures for the cyanide gas, which is generated by the process at a level of a few percent. Furthermore, when the amount of complex iron-cyanides in the liquid waste is small, the cyanide concentration after neutralizing and filtering reaches 1,000 ppm, which can increase operating costs for subsequent processing.

Technology to treat sludge containing approximately 4% cyanide is currently under development. This method treats the sludge along with ores at a temperature of 900°C or more in a nonferrous metal smelting process. The cyanide decomposes, and the effective components are recovered from the sludge. This technology is expected to be fully developed in the near future, providing a solution to the sludge treatment problem.

The heated and pressurized air oxidation process allows decomposition of the cyanide without adding any chemicals in the main process. This use of only heat and pressure ensures minimal secondary pollution. The small volume of sludge generation is another inherent advantage of this method. On the other hand, our investigations suggest that further research and development is required in areas such as the establishment of optimum reaction conditions for the process, removal of sludge and scale generated in the column, selection of suitable materials for the equipment, and practical design of the equipment. It is hoped that this work will be accelerated.

This investigation and study originally intended to identify an optimum treatment method to be recommended. However, regional variations (e.g., the significant differences in composition and concentration of the liquid cyanide waste), site-specific conditions (e.g., the availability of a nonferrous metal smelting plant in the immediate area), and the skill level of operators must be considered. This in turn requires that the existing condition of concentrated liquid cyanide waste generation and other local factors be investigated in depth prior to selecting a treatment method for a planned waste treatment plant.

The rapid development by instrument manufacturers of methods to automatically measure the concentration of liquid cyanide is desirable to ensure proper operation of the treatment facilities.

The investment and operating costs of treatment facilities are a significant financial burden for the small businesses that mostly comprise the electroplating industry. Accordingly, positive assistance by national and local authorities is needed.