ENVIRONMENTAL ENGINEERING COURSE
—WATER POLLUTION CONTROL—

No.15 TREATMENT OF INDUSTRIAL WASTEWATER PART 2

Mr. Hiroshi Kawahara,
Executive Researcher,
The Tokyo Metropolitan Research Institste
for Environmental Protection

JAPAN INTERNATIONAL COOPERATION AGENCY
JAPAN SOCIETY ON WATER POLLUTION RESEARCH

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(Abstract)

The standard in Japan for harmful substances and heavy metals contained in wastewater is stipulated by the "Regulation against Water Pollution". In general terms, this regulation is composed of a "Provision for Preservation of Human Health" known, in short, as the "Health Provision" and "Special Provisions" referring to such substances as Cu, Zn, Total-Cr, Mn and Fe. The criteria for wastewater is as indicated in Table 1.

Treatment of wastewater is defined as the process of employing various methods for either separating pollutant from wastewater or disintegrating such pollutant into some other stabilized and harmless substance. The processes can be roughly categorized into the following three methods:

(1) The method of decomposing organic matter and other harmful substances contained in wastewater into gas (carbonic acid gas, nitrogen gas, etc.)

(2) The method of concentrating and separating pollutant while it is contained in wastewater, such as "ion exchange method" and "reverse osmotic pressure method"

(3) "Neutralization precipitation method" and "surface separation method", the method of separating pollutant contained in wastewater by converting it into insoluble solid matter.

The optimum method is selected from those mentioned above, according to the type and form of substances contained in wastewater. However, it is rarely the case that industrial wastewater contains only one kind of harmful substance. Almost without exception, it contains a compound of pollutant, which poses many problems for undertaking the processes of separation and disintegration. It is a critical matter to be taken into account. This is also the major reason why treatment of industrial wastewater takes a complex and difficult procedure. In actual operation, treatment of industrial wastewater adopting only one of the above methods is extremely difficult and, considering the criteria and regulation for wastewater, in particular, it is more commonly the case that a combination of two methods or more are adopted for the purpose.

The following three methods are utilized for treatment of harmful substances:

(1) Applying disintegration treatment method according to the sort of harmful substance contained in wastewater, and converting pollutants into stabilized, harmless substances

(2) Recovering and separating water-soluble pollutant by means of concentration

(3) Converting water-soluble inorganic pollutant into insoluble matter by changing such conditions as the pH value, which will induce solid-liquid separation

Cyanide and organic phosphoric compound are examples of (1). Other substances are treated by methods (2) or (3). Incidentally, for methods (1) and (3), the conditions for treatment differ according to the types of treatment drug used.

Method (3) is commonly used for treating heavy metals, the precipitation-separation method being the most popular. For this treatment, one of the following three methods is employed for converting pollutant into insoluble salt:

(1) Treatment by converting pollutant into a sulphide

(2) Treatment by converting pollutant into a carbonate

(3) Treatment by converting pollutant into a hydroxide

In the above cases, the density of metal contained in the solution is determined by the level of PH

value at that certain time. It can be calculated from the solubility product; generally speaking, the smaller the solubility product, the smaller the solubility to water. On the other hand, when the level of ionic product exceeds that of solubility product, there is more tendency toward precipitation. In short, the solubility product of heavy metal salt contained in wastewater, ion density of heavy metal and density of hydrogen ion serve as key factors for separating by precipitation the heavy metals contained in wastewater converted into insoluble compound.

In reality, wastewater contains a substantial amount of other kinds of metals, which means that it is necessary to simultaneously separate other existing substances. It is therefore vital to treat wastewater, not only on the basis of theoretical values, but also on the basis of optimum conditions deducted from an accumulation of data and experiences.

The level of solubility product for metal salt are smaller in the following order:

carbonate > hydroxide > sulphide

In actual implementation, it is quite difficult to determine the conditions for treatment of wastewater containing harmful substances. The procedures for treatment are all based on chemical reactions and the results of experiments heretofore undertaken have shown to closely resemble the theoretical values. However, the ever-changing density of the harmful substances contained in industrial wastewater makes the treatment process difficult, because of the inconsistent density of the wastewater to be treated and the fixed quantity of the treatment drugs poured into the wastewater. There is a constant risk of having too much, or too little, quantity of treatment drugs. In particular, when employing the continuous processing method, the problem of how to inspect and control the amount of treatment drugs becomes very important. Whereas such treatment conditions as PH value and ORP are generally controlled by instruments, there are no means to speak of inspecting heavy metals, so that one has to resort to confirming the results through laboratory analysis. The current situation is that treatment is conducted under the speculation that a certain amount of drug poured into wastewater will result in supressing pollutant below the criterion stipulated by the Regulation against Water Pollution.

Incidentally, industrial wastewater contains a large variety of drugs other than substances which are the targets for treatment; some of which react positively to the treatment procedure, while others may cause negative reactions and even interfere with the treatment procedures. For example, brighteners and activators used for electroplating may become an obstacle for treatment of heavy metals.

On the other hand, special attention should be paid on amphoteric metal like chrome and lead when establishing the PH value for treatment. Treatment of wastewater containing a combination of cadmium, chrome and lead is particularly difficult, so that it is desirable for these pollutants to undergo a sepation procedure within their generation source. As to treatment and disposal of sludge precipitated and separated from wastewater, this process should be conducted with special care, since the sludge contains a substantial amount of pollutant. Treatment of wastewater is always accompanied by generation of sludge, so a wrong step taken for treatment and disposal of this sludge may, in turn, lead to a new source of environmental pollution. Currently, solidified disposal using concrete is conducted for isolated disposal of sludge containing pollutant. However, several problems remains to be solved in this area, including the problem of securing the place for disposal and method of disposal.

As one solution, tests are being made for recycling metal and other effective components retrieved from sludge.

Because of the difficulty in retrieving effective components from sludge containing a combination of pollutant, it will be helpful to produce separate sludge for each kind of metal.

Recycling of water is also an issue under consideration. Future prospects aim at closed circulation, but there are still a number of problems that have to be solved before this can be put into practice. Stricter regulations for wastewater has triggered more use of ion exchange resin for wastewater treatment. This method is used for the following three purposes:

(1) Using ion-exchange resin for the purpose of retrieval and recycling of effective components,

(2) Using ion-exchange resin for treatment of wastewater, and

(3) Using ion-exchange resin for the purpose of recycling water.

The following are the unique features of ion exchange resin method as compared with regular wastewater treatment method.

1) Despite quantitative limitations in wastewater treatment using ion exchange resin method, using the method for small quantities is convenient because it requires a relatively small area for installation.

2) One does not have to bother so much about density fluctuations in ion exchange resin, although it is important to pay attention to the kinds of ion in the wastewater.

3) Ion exchange resin proves effective when installed in each generation source for the purpose of retrieving effective components. For this, however, it is vital to lay hold of the relation between the exchange capacity of resin and the density of wastewater so as not to over-burden the conditions for recycling the wastewater.

4) The method had better not be adopted for treatment of wastewater containing impurities, particularly oil, activator and other organic matter.

5) Applying ion exchange resin treatment method to relatively low-concentration pre-treated wastewater will prove effective.

In addition to the above, studies are also being carried out for ion flotation method, activated charcoal adsorbent method and electrolysis reduction method.

1. Substances Harmful for Human Health

Table 1 Harmful Substances (mg/ℓ)

Pollutant	Criteria		Anal. Method	Background	
	Effl.	Envir.		Crust*1	Sea*2
CN	1	N.D.*3	Distil. - Col.*4	-	-
Hg(Alkyl)	N.D.	N.D.	Extn.*5 - G.C.*6	-	-
	(0.0005)	(0.0005)	TLC*7 - AAS*8		
Hg(Total)	0.005	0.0005	AAS (Flameless)	0.08	0.00003
Or. - P*9	1	N.D.	Col.	-	-
Cd	0.1	0.01	Extn. - AAS	0.2	0.0001
Pb	1	0.1	Extn. - AAS	12.5	0.00003
Cr(VI)	0.5	0.05	Col.	-	-
As	0.5	0.05	Col.	1.8	0.002
PCB	0.003	N.D.	Extn. - C.C.	-	-
		(0.0005)			
Cu	3	-	Extn. - AAS	55	0.003
Zn	5	-	Extn. - AAS	70	0.01
Cr(Total)	2	-	Col.	100	0.00005
Mn*10	10	-	AAS	950	0.002
Fe*10	10	-	AAS	56,300	0.01

*1 In the continental earth crust (Taylor, 1964)
*2 In the sea water (Goldberg, 1964)
*3 Non detect
*4 Colorimetry
*5 Extraction
*6 Gas chromatography
*7 Thin layer chromatography
*8 Atomic absorption spectrometry
*9 Parathion, methylparation, EPN, and Methyldimethone
*10 Dissolved

2. Emission Sources

Metal finishing

Chemical industry

Metal mines and smelters

Others: Electric, electronic, pharmaceutical, leather, paper & pulp industries, etc.

Table 2 Harmful Substances in Wastewater and Main Emission Sources

	Harmful Substances	Emission Sources	
		Effluent	High Concentration Wastewater
Liquid Organic Substances	Oils and Fats, and Surfactants	Degreasing Process	Degreased Wastewater
Solid Inorganic Substances	Abrasives, Active Carbon, and Metal Powder	Various Processes	Various Kinds of Wastewater
CN	Cyanides NaCN, KCN, etc.	Alkali Cleaning Process Electrocleaning Process Barrel Finishing Process Plating Process	Alkali Cleaning Solution Electrocleaning Solution Barrel Finishing Solution Plating Solution
	Complex Cyanide Compounds		
	$Na_2Zn(CN)_4$	Zinc Plating Process	Zinc Plating Solution
	$Na_2Cd(CN)_4$	Cadmium Plating Process	
	$Na_2Ag(CN)_4$	Silver Plating Process	
	$Na_2Ni(CN)_4$		Nickel Stripping Bath
	$Na_2Cu(CN)_4$	Copper Plating Process	Copper Plating Solution
	$NaAu(CN)_2$	Gold Plating Process	
	$K_4Fe(CN)_6$		Electrocleaning Solution
Cr	$Cr_2O_7^{2-}$	Plating Process Chromate Treatment Process Etching Process	Plating Solution Chromate Treatment Solution Etching Solution
Metals	Al Cr·Fe·Cu·Zn·Ag Cd·Sn·Au·Pb, etc.	Almite Treatment Process Various Process Etching Process	 Etching Solution
Acids	HF·HCL·HNO_3 H_2SO_4·H_3·PO_4, etc.	Etching Process Electro-polishing Process	Etching Solution
A lkalis	NaOH·KOH, etc.	Degreasing Process Various Processes	Degreasing Solution

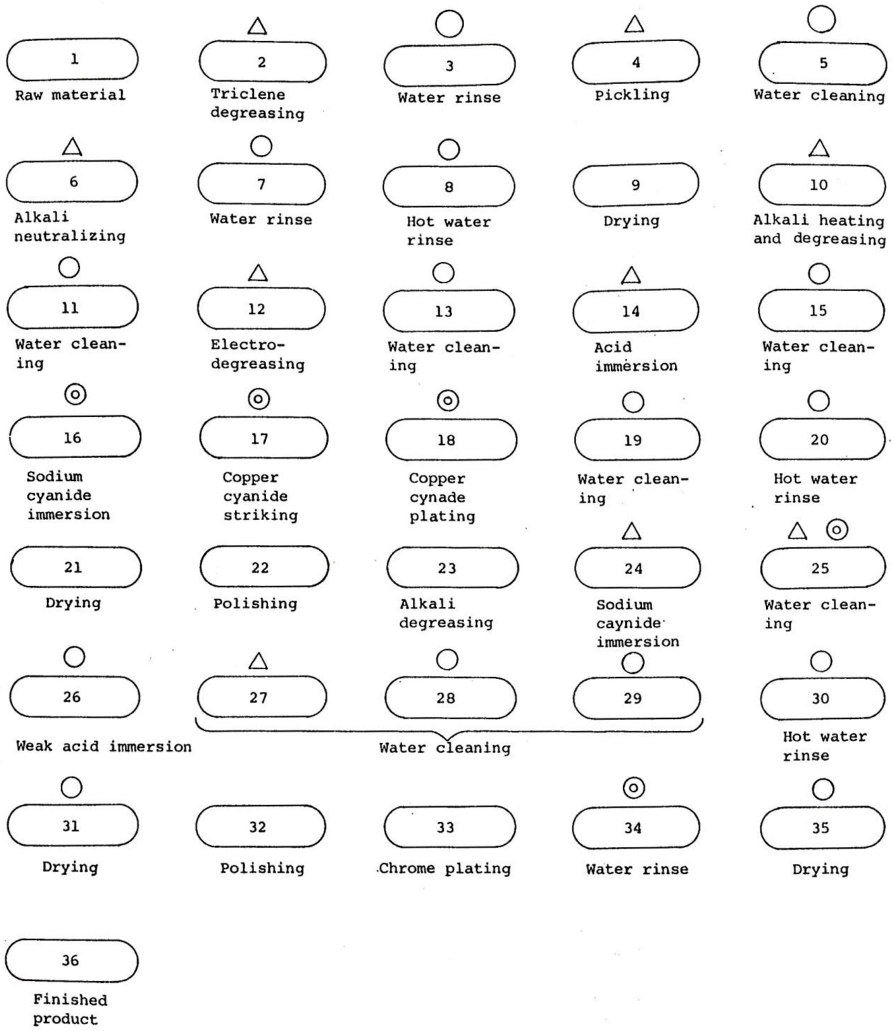

Fig. 1 Emission Sources of Represent ative Plating Processes (1)
(a) Ornamental Plating

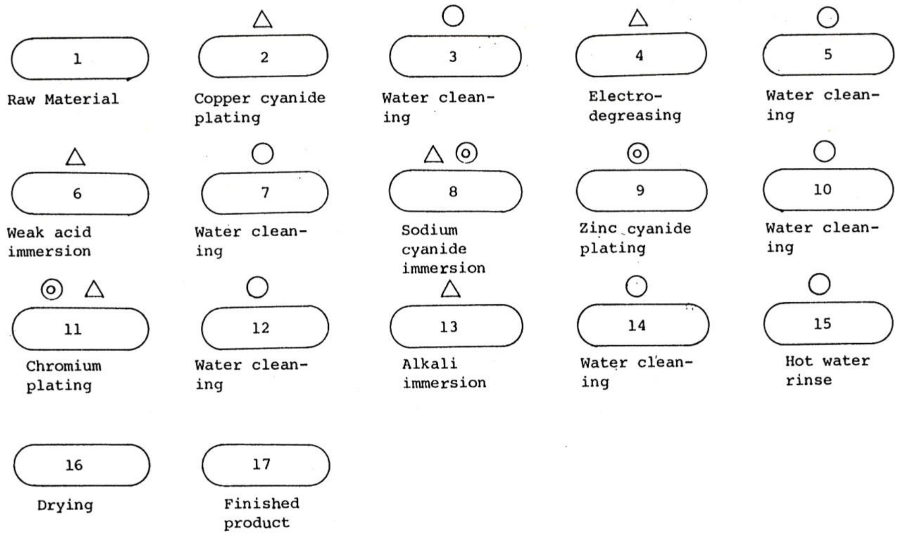

Fig. 1 Continued (2)
(b) Cromate Treatment of Zinc Plated Metal

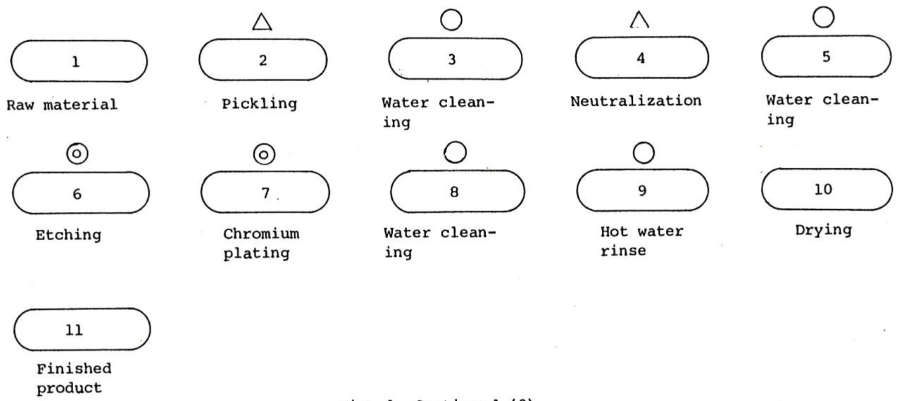

Fig. 1 Continued (3)
(c) Hard Chromium Plating

Notes
△ indicates that the pollution load increases or the process effect declines.
○ indicates that same caution as given to process marked with should be exercised.
◎ indicates that special caution must be exerted.

Table 3 Pollutant Concentration in Effluents of Different Groups at Electr. Plating Plant

Pollutant	Cn Group	Cr Group	Acid/Alkali Group
Cn	50 ∿ 100	0.2 ∿ 0.7	3.0 ∿ 4.0
Cu	0.2 ∿ 40	8 ∿ 11	0.2 ∿ 4
Ni	1 ∿ 2	8.0 ∿ 100	20 ∿ 40
Cr (Total)	0.5 ∿ 1.0	50 ∿ 100	1.0
Zn	50 ∿ 100	240 ∿ 280	30 ∿ 50
Fe	3 ∿ 5	5 ∿ 40	40 ∿ 50
pH	11 ∿ 11.5	2.7 ∿ 3.2	8.5 ∿ 9.7

3. Treatment of Wastewater Containing Cyanide, Chrome and Heavy Metals

3.1 Solution Containing CN

For decomposition of cyanide by oxidation, it is usually the case to adopt the alkali chlorine treatment called the "two-stepped cyanide oxidation method" in which the following chemical reactions take place.

$$2NaCN + 2NaC\ell O = 2NaCNO + 2NaC\ell \quad \text{(at above pH 10)} \qquad (1)$$

$$2NaCNO + 3NaC\ell O + H_2O = 2CO_2 + N_2 + 2NaOH + 3NaC\ell \quad \text{(at pH 7.5 ∿ 8.5)} \qquad (2)$$

Reaction (1) is considered to proceed as follows.

$$CN^- + HC\ell O \rightarrow CNC\ell + OH^- \qquad (4)$$

$CNC\ell + OH^-$ produced in reaction (4) turns into cyanic acid by hydrolysis.

$$CNC\ell + OH^- \rightarrow C\ell^- + HCNO \qquad (5)$$

The above treatment is controlled by pH and ORP (Oxidation Reduction Potential).

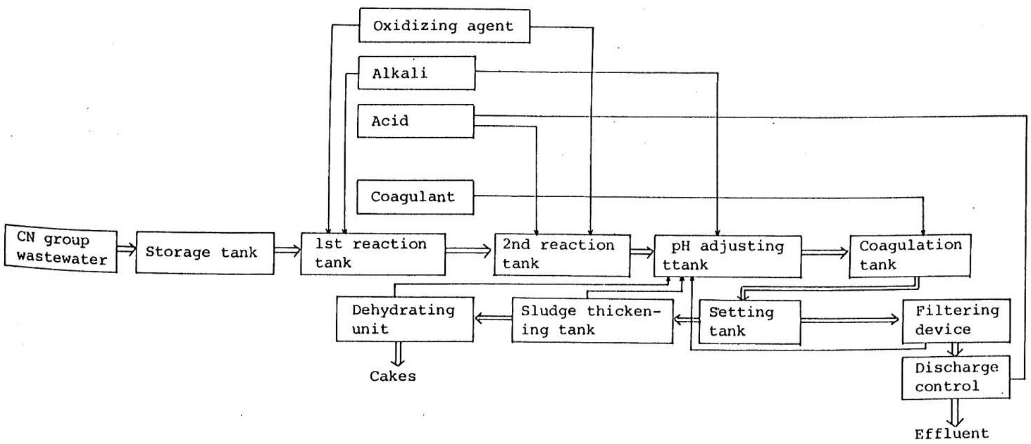

Fig. 2 Standard Flow Sheet of CN Group Wastewater Treatment

For the purpose of the same treatment, the following methods are also available.

(1) Oxidation by O_3

This method makes use of Gas-requid-reaction, but it is hardly employed because of its low efficiency.

(2) Iron complex method

$$K_4[Fe(CN)_6] + 2FeSO_4 \rightarrow Fe_2[Fe(CN)_6] + 2K_2SO_4 \quad \cdots\cdots (6)$$

$$3K_4[Fe(CN)_6] + 2Fe(SO_4)_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 6K_2SO_4 \quad \cdots\cdots (7)$$

(3) Electrolytic treatment method

This method is utilized in treating high concentration wastewater.

3.2 Solution Containing Cr (VI)

For treatment of wastewater containing chromium, it is common to resort to the reduction and neutralization method in which the following reactions take place.

Reduction (at below pH 3.0)

$$2H_2Cr_2O_7 + 6NaHSO_3 + 3H_2SO_4 = 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 8H_2O \quad \cdots\cdots (8)$$

Neutralization (at pH 8.0 ∿ 9.0)

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 = 2Cr(OH)_3 + 3CaSO_4 \quad \cdots\cdots (9)$$

or

$$Cr_2(SO_4)_3 + 6NaOH = 2CR(OH)_3 + 3Na_2SO_4 \quad \cdots\cdots (10)$$

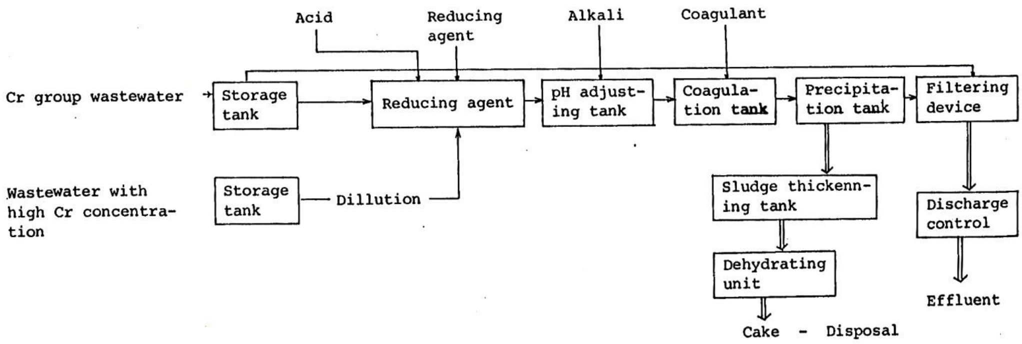

Fig. 3 Standard Flow Sheet of Cr Group Wastewater Treatment

3.3 Treatment of Acidic/Alkaline Solution

This solution contains various heavy metals which must be removed (See Table 3). In general, these heavy metals are remove by sedimentation afterturning them into hydroxides. In the process of treatment, the relationship between each metal and pH value carries a heavy weight. The optimum range of pH is shown in Table 4 for each metal.

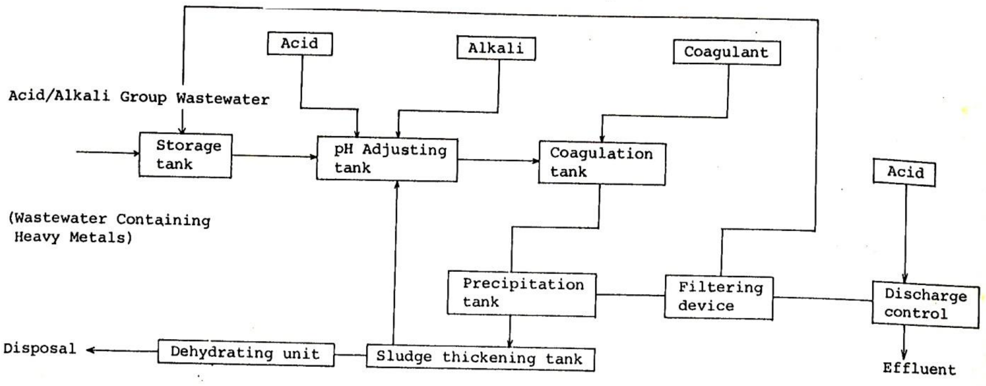

Fig. 4 Standard Flow Sheet of Acidic/Alkaline Wastewater Treatment

3.4 Hg Solution

$Hg^{2+} + S^{2} \rightarrow HgS \qquad HgS + S^{2-} \rightarrow HgS_2^{2-}$

For preventing HgS colloid formation and redissolution of HgS as complex, addition of Fe^{2+} + (or Zn^{2+}) is effective.

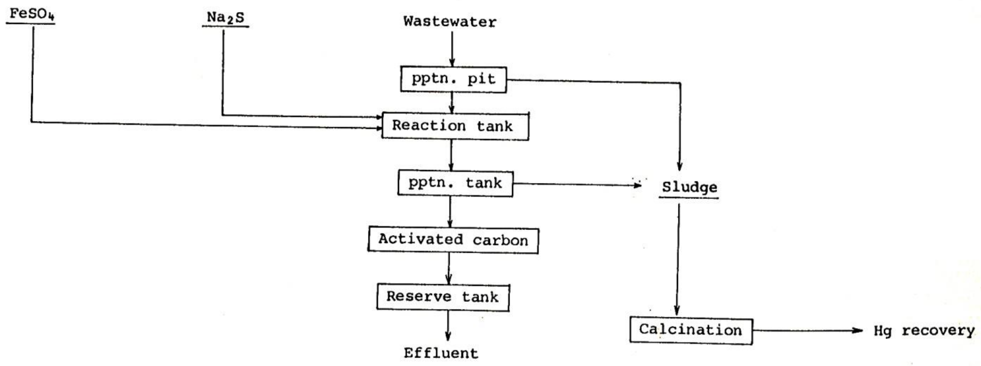

Fig. 5 Treatment of Wastewater Contg. Hg

3.5 Other Treatment Method

1) Ion Exchange and absorption

2) Ion flotation

3) Ferrite formation