2.3 Measures for the the Production Processes

2.3.1 Measures for Reducing the Wastewater Quantity (Reference 3)

The purpose of taking wastewater quantity reducing measures in the production processes is to realize the proper plant scale in planning the wastewater treatment plant by reducing the wastewater quantity or pollution load. Increased wastewater quantities or pollution loads will make the wastewater treatment plant larger than necessary and thereby increase the construction cost and operating cost of the wastewater treatment plant.

On the other hand, at the existing workshops, the present state of processes and working plans should be reviewed and the processes be improved to improve the productivity and the product quality and enhance the working safety, in addition to reducing the wastewater quantity or pollution load to be discharged.

(1) Reducing the drag-out quantity

Drag-out of plating bath or pre- or post-treatment liquor due to attachment to articles means a loss of useful components on one hand and an increase in the burden on the wastewater treatment on the other. It is necessary to take adequate care to reduce the drag-out quantity.

A. Improving the plating rack

As shown in Fig.2.3.1, the plating jig is designed to have no horizontal part so as to reduce plating bath drag-out due to attachment to articles and to ensure good separation of the liquor. Fig.2.3.2 and Table 2.3.1 show how the drag-out quantity depends on the shape of the plating rack, the method of racking and the pull-up speed.

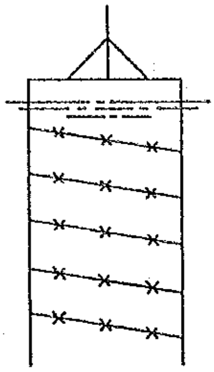

Fig. 2.3.1. Example of plating tools

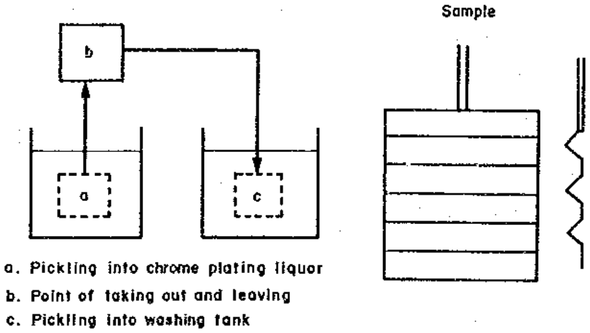

Fig. 2.3.2. Experiment about volume of liguor taken out of the bach

Table 2.3.1. Results of Experiment about Volume of Liquor taken out of Bath(Reference 3)

Kinds of experiment	Moving time (sec)	Weight of CrO_3 (g/l)	Volume of chrome plating liquor (ml/dm^2)
Hanging a flat boaed a level	2 (0) 5 (3) 10 (8) 20 (18)	0.3 0.135 0.105 0.06	1.2 0.54 0.42 0.24
Hanging an uneven board a level	2 (0) 5 (3) 10 (8) 20 (18)	1.5 1.43 1.34 1.26	6.0 5.7 5.3 5.0
Hanging an uneven board slanting	2 (0) 5 (3) 10 (8)	0.77 0.41 0.28	3.1 1.65 1.12

( ) ; the leaving time.
Liquor temp. ; the room temp.
Composition of chrome plating liquor ; CrO_3 250 g/l, H_2SO_4 2.5 g/l

B. Stopping over the plating tank

In order to minimize the drag-out quantity the article pulled up from the plating tank should be held for a while over the plating tank so that the liquor drops from the article sufficiently. In the case of automatic equipment, the article is temporarily stopped over the plating tank. In the case of hand operation, a bar should be installed over the plating tank so that the plating rack can be hung from it. Further, in the case of rack plating, a slight vibrations in up and down directions is effective. In the case of barrel plating, stopping the barrel in a slightly slanted position, or rotating it is effective.

C. Adding a direct recovery tank

In the case of rack plating, an empty direct recovery tank is installed following the plating tank as shown in Fig.2.3.3. For a while for which the finishing is not affected, the article is left to stand there so that the plating liquor attached to the article drops sufficiently. In this case, vibrating the article up and down slightly will be more effective.

The liquor recovered in the direct recovery tank has almost the same composition as the plating liquor and may be returned through a filter into the plating tank. If the liquor recovered in the direct recovery tank is to be discarded, the concentrate obsolete wastewater must be treated, but it is advisable to recover metal components prior to the treatment.

Fig.2.3.4 shows an example of the working bench for direct recovery where the article is chromated in a basket after zinc plating.

In the case of barrel plating, an empty direct recovery tank is installed following the plating tank, and for a while for which the finishing is not affected, the article should be held in a slanted position or rotated at a slow speed. In the case of hand operation or semi-automatic equipment, a tray should be mounted at the end of the chute, or a dish should be placed under the article, for direct recovery of the plating liquor.

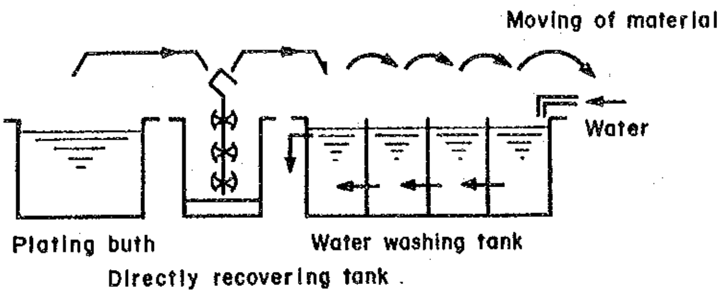

Fig. 2.3.3. Direct recovering tank on racking plating style

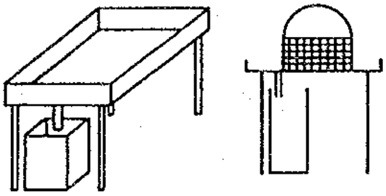

Fig. 2 .3.4. Example of direct recovering table

(2) Improving the water washing process

The function of water washing is to efficiently remove the liquor carried from the preceding process from the surface of the article, otherwise the liquor will affect the performance of the treatment liquor in the succeeding process. Wastewater treatment is mostly the treatment of wastewaters from water washing.

Therefore, reducing the washing wastewater quantity while considering the finishing of plating leads to reducing the wastewater treatment plant size and the treatment cost.

A. Improving the washing tank

The size of the washing tank should be such that the maximum article can be accommodated with some allowance. The depth of this tank should be determined by considering water level rises due to pipes and the article. The tank should be constructed considering the flow of water so that water supply and drainage may be easy.

a. Positions of water supply and drain ports

As shown in Fig.2.3.5, water is supplied from the bottom of the tank. The drain port is provided at a position farthest from the water supply port.

In order to prevent backflow, a distance of about 50 mm is necessary between the water tap and the water surface.

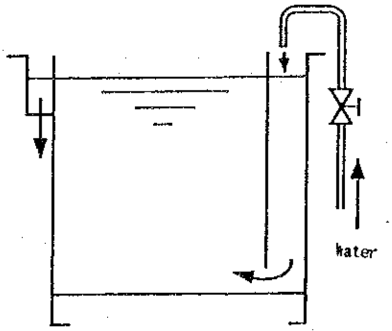

Fig. 2.3.5. Position of faucet for water and wastewater of water washing tank

b. Shape of the barrel washing tank

The water level rises greatly due to the barrel. Therefore, the distance between the water level without the barrel and the top end of the tank should have an adequate allowance. Moreover, the drain port should be sufficiently large.

Further, the tank bottom should be shaped as shown in Fig.2.3.6. so that the renewal of washing water can be quickened effectively.

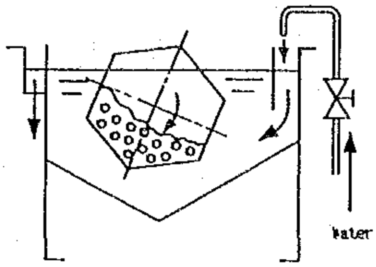

Fig. 2.3.6. Washing water tank for barrel

B. Effective washing

In some cases, water washing with supply water alone is not effective. It is advisable to add any of the following methods.

In the case of the barrel, it is difficult for the inside liquor to be replaced with the outside one. Therefore, it is advisable to bring the barrel into and out of the washing tank.

a. Spray washing

Mount a fresh water spray on the washing tank or the recovery tank to spray water to the rising article. In this case, in order to prevent the spray water from splashing, the nozzle should be directed toward 30° below the horizontal direction. If the current application bar (this bar pushes electric contacts to close to allow a current to flow) is cleaned, problems of poor contact, melting, etc. due to mist and other foreign substances are alleviated. In some processes, this method may be effective. Further, a valve or pedal is mounted to spray water during water washing only, the wastewater quantity can further be reduced.

Fig.2.3.7. shows a washing tank provided with a circulation spray at the bottom and a fresh water spray at the top. Wastewater is discharged in the same quantity as the fresh water sprayed. Thus, the water quantity can be relatively small. It is also conceivable to recover and reuse the spray washing liquor.

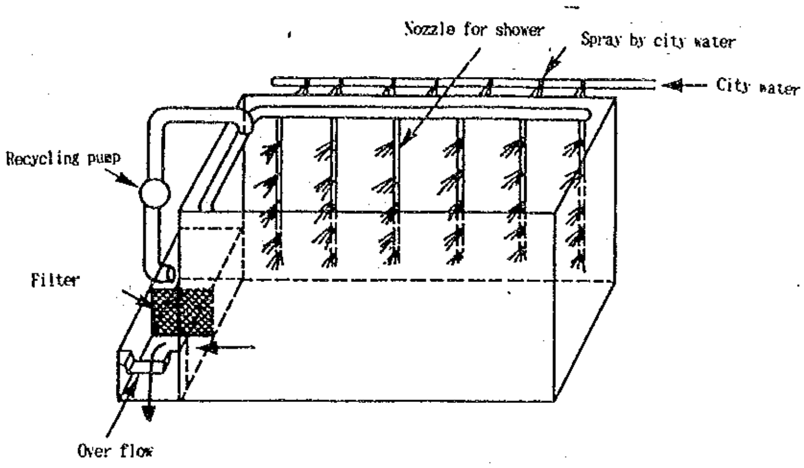

Fig. 2.3.7. An example of spray washing

b. Aeration

This method is effective for washing articles having complexed shape or uneven surfaces. To be noted is that ingress of oil or dust or dirt in the air affects the finishing.

Fig.2.3.8. shows an example of aeration.

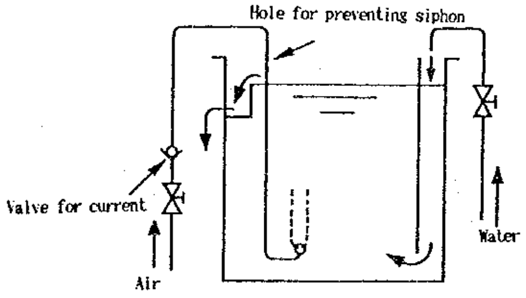

Fig.2.3.8. An example of air agitation

c. Ultrasonic washing

Ultrasonic washing uses cavitation and shock wave. This phenomenon, when repeated has a unique effect to wash out the liquor trapped in the contact portion between the article and the jig, or in the concaved portion. However, because of its very high frequency, it has a strong property of straight progress. Thus, in any portion deviated from the course of wave progress, the washing effect is liable to be degraded.

d. Hot water washing

By heating, the washing water is expanded and its viscosity is decreased so that the washing effect is improved. For heating, steam is supplied into the coil installed on the bottom or an electric heater is used. It is advisable to add agitation to improve the washing effect and to equalize the temperature. Placing the boiler drain outlet directly in the tank should be avoided as it may cause a hazard of backflow, etc.

C. Effects of multi-stage water washing, and precautions

If it is assumed that the allowable limit of pollution of the washing water is the same, it is needless to say that the washing water quantity is decreased with increasing number of washing stages.

Roughly speaking, the multi-stage water washing system is classified as parallel water washing, multi-stage counter-current water washing and batch type multi-stage counter-current water washing.

Parallel water washing is done by supplying water to each tank independently. Thus, the water quantity to be used is large, and the water saving rate by multi-stage water washing is small.

Multi-stage counter-current water washing is done by supplying water to the final tank, and feeding that water successively to the preceding tanks until it is discharged from the first tank. This method is larger in the water saving rate than parallel washing, and therefore, is used as the basic method in the water washing process in the plating factory. Fig.2.3.9. is an explanatory diagram for the multi-stage counter-current water washing tank. The water consumption by this method is expressed by $W = Dn(CO/Cn)^{1/2}$.

Batch type multi-stage counter-current water washing is done using in tanks. Once water is supplied to all tanks, further water supply is stopped. As the work progresses, the rise of the washing water concentration is noted, and periodically or non-periodically, the 1st tank is drained and then, is supplied from the 2nd tank. The 2nd tank is supplied from the 3rd tank, and so on until the final tank is drained. Then, new water is supplied to the final tank. This method is more effective in reducing the water consumption than the multi-stage counter-current method, but requires pumps for replacing and transferring of washing water.

In any case, multi-stage water washing may affect the finishing of plating. And, therefore, it is advisable to install a conductivity meter so that the allowable limit of pollution can be satisfied.

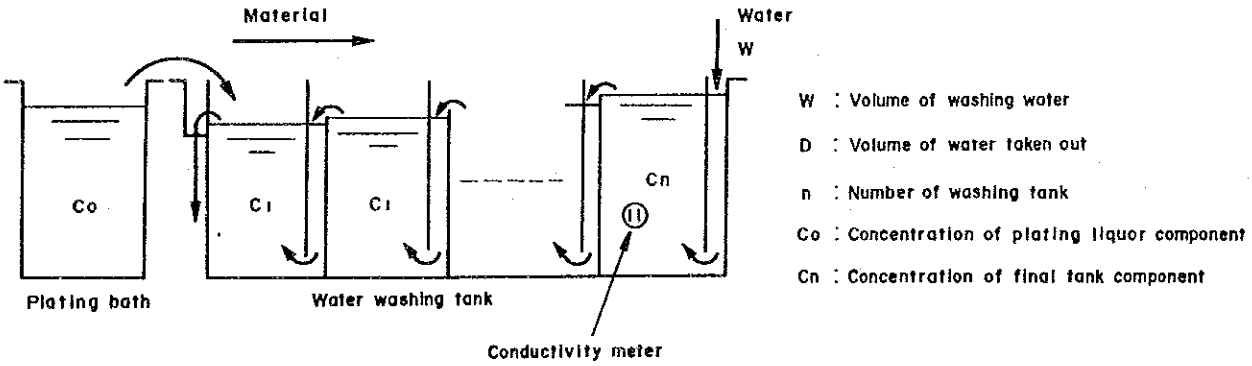

Fig. 2.3.9. Counter-current multistage washing tank

(3) Recovery and re-use of plating liquor

The liquor, which is dragged out due to attachment to the article, has the same composition as the plating liquor. Therefore, if it can be returned to the original tank, it will be advantageous for reducing the load on the wastewater treatment. In this respect, the reduction of drag-out by improving the plating rack, stopping over the plating tank, and adding a direct recovery tank, and the improved water washing effects with reduced washing water consumptions, were described in (1) and (2), respectively.

Here, some methods for returning the dragged-out liquor to the plating tank more positively will be shown. However, when attempting recovery and re-use, it is necessary to pay special attention to changes of the plating liquor with impurities contained in it and also to the decomposition of additives.

A. Atmospheric evaporating process

Gases and mists generated in the plating tank are discharged through an exhauster using a scrubber in general. In the atmospheric evaporating process, however, an atmospheric evaporator is used: the gas is brought into contact with the liquor to be concentrated in the packed layer of the evaporator and the mist is removed through the filtering effect. In this case, impurity cations are also concentrated and are removed by an additional electrolytic equipment for impurity removal.

Fig.2.3.10. shows an example of the atmospheric evaporator used in the chrome plating process.

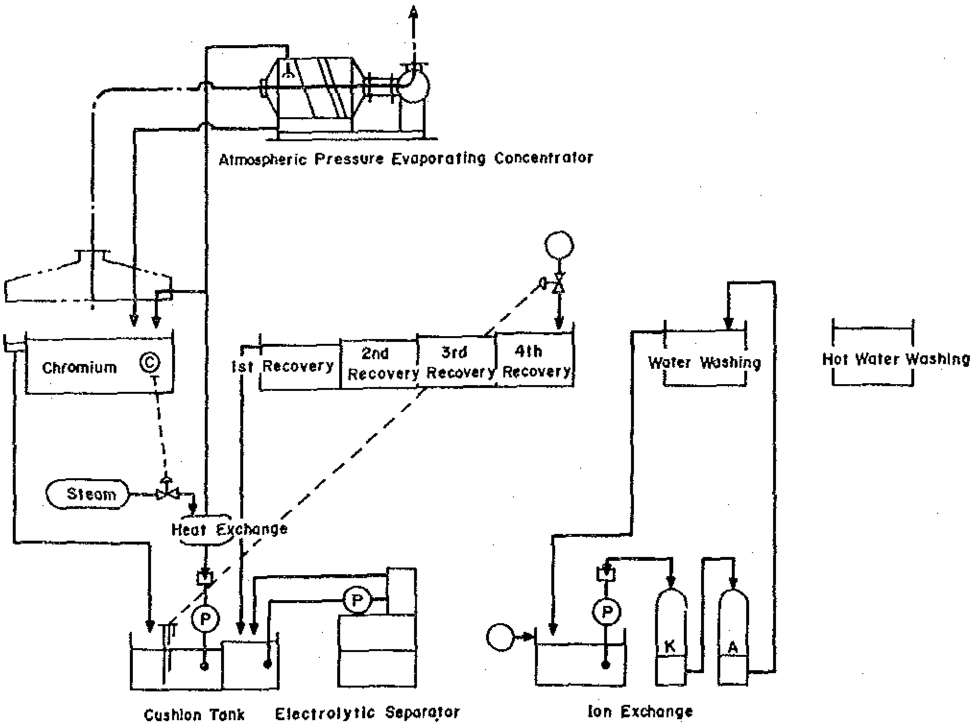

Fig. 2.3.10. An example of atmospheric pressure evaporating concentratior on chrome plating

B. Vacuum evaporating process

This method makes use of the principle that the evaporating temperature is lowered by evacuation. Before evaporation, impurity cations are removed by means of cation exchange resin, and after evaporation up to the predetermined concentration, impurity anions such as chlorine ion are removed before the liquor is returned to the plating tank.

Fig.2.3.11. shows an example of the vacuum evaporator used in the chrome plating process.

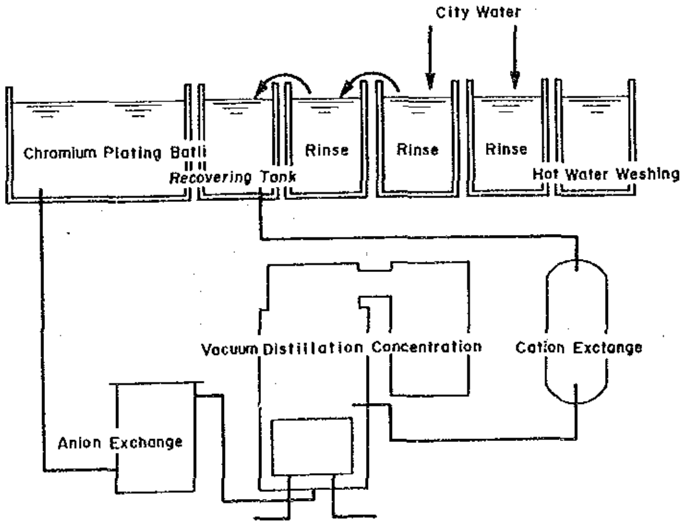

Fig. 2.3.11. Example of vacuum distillation concentration on chrome plating

C. Reverse osmosis

This method is used to concentrate and recover low concentration liquors. The permeate can be re-used. Because of continuous operation, time and labor of the operator can be saved. The applicable range is wide from low up to relatively high concentrations. Since concentration and demineralization can be done with small energy required for pump drive only, this method can be applied to concentrate and demineralize the plating liquor. However, in using this method, care is needed about restrictions on pH, SS, temperature, etc.

Fig.2.3.12. shows the principle diagram for reverse osmosis.

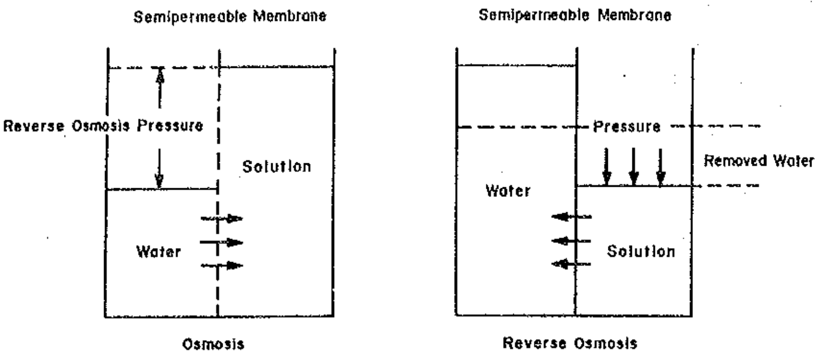

Fig. 2.3.12. Principle of reverse osmosis

2.3.2 Recovery of Valuable Substances

It is widely used to recover valuable substances such as previous metals contained in the plating liquor or to treat and reuse deteriorated liquors.

Typical techniques now in use will be introduced.

(1) Ion exchange resin method

In this method, gold and silver contained in renewal wastewaters or washing wastewaters from gold plating and silver plating are recovered by adsorbing them on ion exchange resins. It is advantageous that the recovered gold and silver can be sold.

(2) Electrolysis

This method is used to recover metals contained in renewal wastewaters from plating by precipitating them. It has been in use for a long time. Metals which can be sold profitably include gold, silver, copper, etc. This method is also effective for oxidation and decomposition of cyanides contained in cyanide wastewaters or for COD reduction of non-electroplating wastewaters.

(3) Regeneration of chrome liquor

This method is used to make chrome plating and chromate liquors reusable. These liquors must be renewed as cations are accumulated and $Cr_2O_7{}^{-}{}_2$ is changed to Cr^{3+}. However, since much $Cr_2O_7{}^{-2}$ exists, cation removal and concentration adjustment are required before reuse.

The electrolytic cell is partitioned with a diaphragm, and with renewal wastewater on the cathode side and water on the anode side, electrolysis is conducted so that $Cr_2O_7{}^{-2}$ is passed through the diaphragm and recovered on the anode.

Fig.2.3.13. shows an example of the diaphragm electrolytic cell.

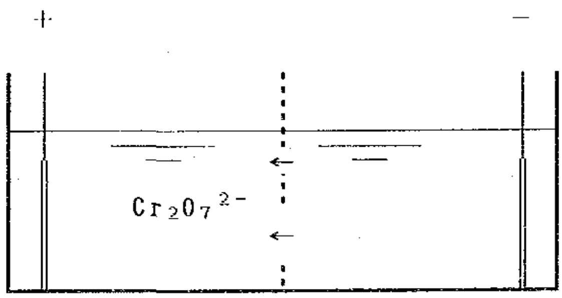

Fig. 2.3.13. Diaphrag Electrolytic Separation

(4) Diffusion dialysis

This method is used to make pickling wastewaters reusable. The pickling liquor must be renewed as metals are dissolved in it and the acid concentration is thereby decreased. However, since much free acid still exists, cation removal and concentration adjustment are necessary before reuse.

When the waste acid and water are applied alternately in the chamber partitioned with an anion membrane, the acid permeates through the anion membrane into the water side and can be recovered.

Fig.2.3.14 shows an example of the diffusion dialyzer.

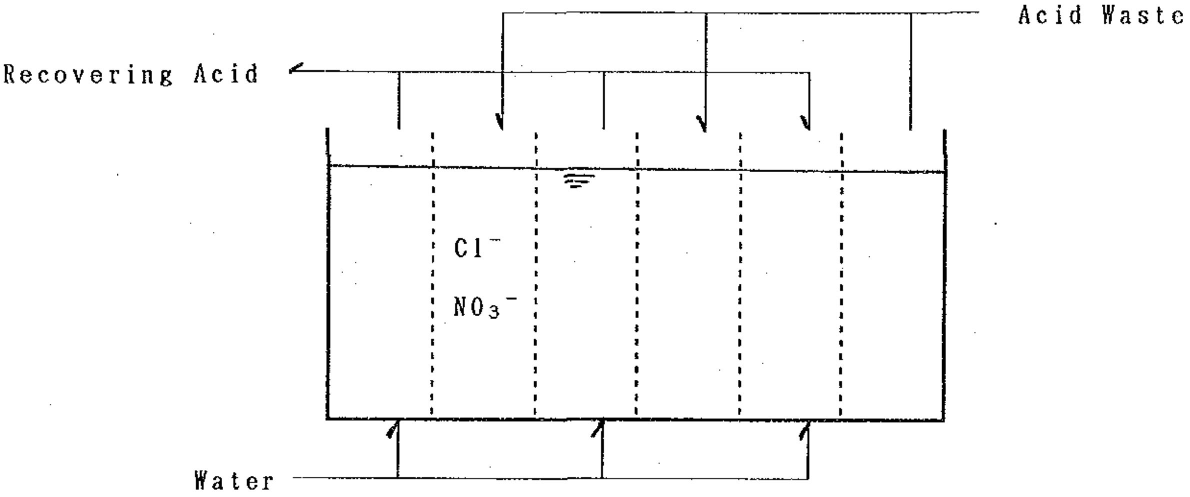

Fig. 2.3.14. Exsample of Diffuse Equipment

2.4 Wastewater Treatment

The basic steps of plating wastewater treatment are oxidation of cyanide, reduction of chrome, removal of heavy metals as hydroxides, and adjustment of pH. Fig.2.4.1 shows the flow sheet of a standard system for plating wastewater treatment consisting of these treatment steps in combination.

When the plating wastewater is treated in accordance with this treatment system, COD, phosphorus(excepting phosphorus in the nickel bath of non-electroplating), fluorine(excepting fluoborate), etc. can also be treated. Fig.2.4.2 shows the flow sheet of a batchwise treatment system.

2.4.1 Treatment of cyanide wastewaters

For the treatment of cyanide wastewaters, the alkaline chlorination method is the safest and most positive method. This method uses soda hypochloride or the like to decompose cyanide through cyanic acid to nitrogen gas and carbon dioxide.

(1) Treatment of free cyanide (Reference 3)

The treatment of cyanide with soda hypochlorite consists of two stages of reaction as shown by the following formulas. The first stage of reaction is to decompose cyanide ion to cyanic acid, and the second stage of reaction is to further decompose cyanic acid to nitrogen gas and carbon dioxide.

Heavy metals contained are treated by the neutralization method which will be described later.

First stage of reaction:

$$\mathrm{NaCN + NaOCl - NaCNO + NaCl} \tag{1}$$

Second stage of reaction:

$$\mathrm{2NaCNO + 3NaOCl + H_2O - N_2 + 3NaCl + 2NaHCO_3} \tag{2}$$

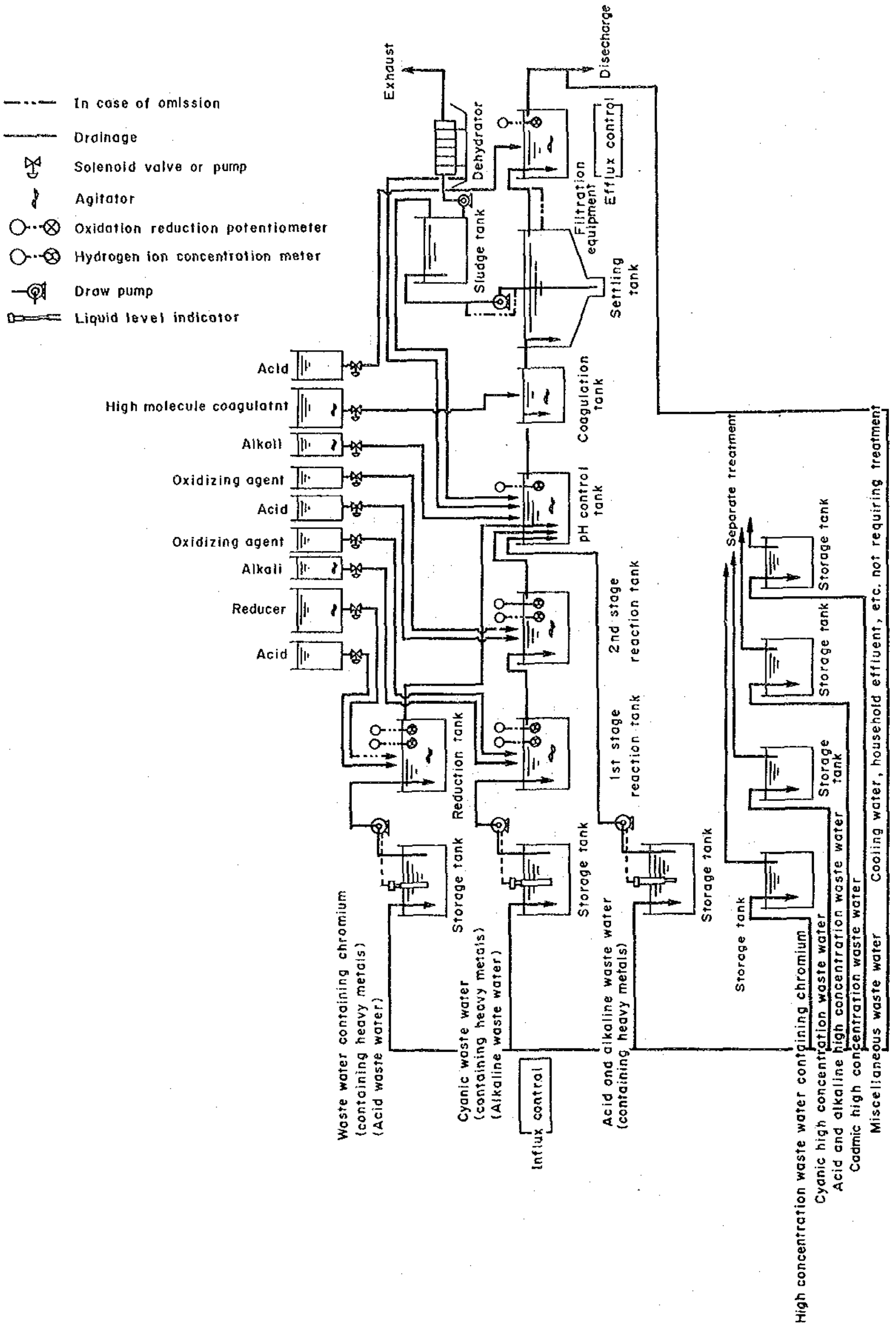

Fig. 2.4.1. The flow-sheet for standard plating wastewater treatment system

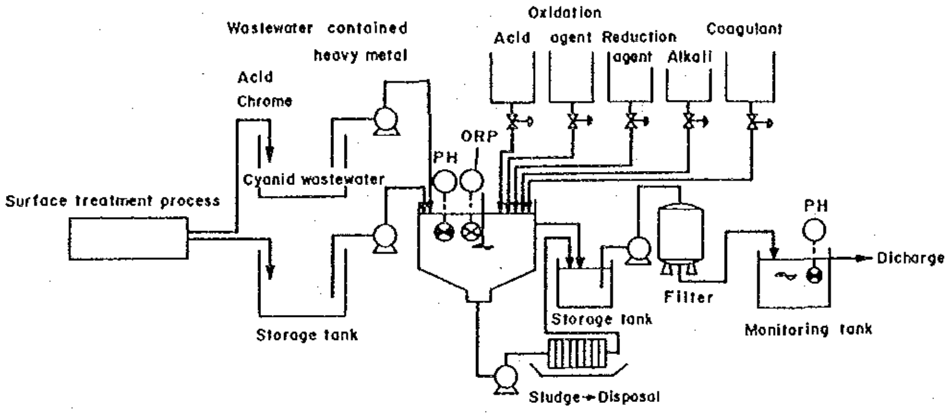

Fig. 2.4.2. The flow-sheet for plating wastewater treatment

In the first stage of reaction, cyanide is not decompose with soda hypochlorite directly to cyanic acid, but when soda hypochlorite is added to cyanide ion, chlorine cyanide is first produced by the following reaction.

$$NaCN + NaOCl + H_2O - CNCl + 2NaOH \qquad (1)$$

The reaction of Eq.(1) is slow in a neutral region, but very rapidly progresses in a strongly alkaline region. Therefore, if it is desired to proceed with the first stage of reaction to produce cyanic acid without generating chlorine cyanide, it is necessary to keep pH above 10.5.

The second stage of reaction is different from the first stage of reaction. It rapidly progresses in a low pH region. It requires 30-60 minutes or more at pH near 10, but complete within a short time (10 minutes) at pH 7.5-8.0.

In this way, in order to ensure complete decomposition of cyanide, it is necessary to proceed with the reaction in two stages at different values of pH. Reaction conditions are as follows.

First stage of reaction:
pH 10.5 min., oxidation-reduction potential 300mV min.

Second stage of reaction:
pH 7, oxidation-reduction potential 600mV

The oxidation reaction of cyanide by the alkaline chlorination method as a combination of the first stage and the second stage is as follows.

$$2NaCN + 5NaOCl + H_2O - N_2 + 5aCl + 2NaHCO_3 \qquad (3)$$

The quantity of soda hypochlorite required for complete oxidation of 1g cyanide is theoretically 7.16g, but actually an excess quantity of soda hypochlorite is required. By the way, available chlorine of soda hypochlorite which is supplied is 10-12%, and therefore, the quantity of soda hypochlorite required for decomposition of 1g cyanide is theoretically 60g.

(2) Treatment of cyanide complexes of zine, cadmium and copper (Reference 3)

Cyanide complexes of zinc, cadmium and copper can be decomposed easily with soda hypochlorite.

$Na_2[Zn(CN)_4]+4NaOCl+2NaOH - Zn(OH)_2+4NaCl+2N_2+4NaHCO_3$ (4)

In the case of cyanide complexes of copper, 1-valent copper is oxidized to 2-valent copper, and therefore, the quantity of soda hypochlorite to be added is larger than theoretically calculated.

(3) Treatment of cyanide complexes of nickel (Reference 3)

Cyanide complexes of nickel can be decomposed with soda hypochrolite, but the reaction is very slow. Therefore, if cyanide complexes of nickel are mixed in the continuous treatment equipment, decomposition of cyanide is incomplete because of short retention time in the reaction tank. It is necessary to take care to prevent cyanide complexes of nickel from making ingress in the cyanide wastewater.

For the treatment of cyanide complexes of nickel, soda hypochlorite should be fed at a small rate which agitating for a long time (24 hours min.) to proceed with the first stage of reaction and subsequently with the second stage of reaction until decomposition.

In the case of cyanide complexes of nickel, 2-valent nickel is oxidized to 3-valent nickel, and therefore, the quantity of soda hypochlorite to be added is larger than theoretically calculated.

(4) Treatment of cyanide complexes of iron (Reference 3)

Iron ion is 2-valent or 3-valent, and either reacts with cyanide radicals to form cyanide complexes of iron, called ferro cyanide or ferric cyanide, respectively.

In the case when cyanide is not completely treated in the plating wastewater treatment, cyanide is detected frequently in the treated water owing to the existence of cyanide complexes of iron.

In the case of zinc cyanide plating, iron as base metal falls in the plating tank and is eluted to form cyanide complexes of iron. These complexes are attached to the base metal, and after being washed in the subsequent washing process, appear in trace quantities in the washing wastewater. Here, to be noted is that *cyanide complexes of iron are not used as plating agent.*

Cyanide complexes of iron cannot be treated by the alkaline chlorination method. Of the cyanide complexes of iron, ferro cyanide can be removed through reaction with a metal such as zinc or copper to produce an insoluble compound.

Ferric cyanide is reduced with ferrous sulfate to ferro cyanide which can be treated as mentioned above.

(5) Electrolytic treatment of concentrate cyanide

Electrolytic treatment of concentrate cyanide is used as pre-treatment by the alkaline chlorination method for plating liquous above 1000mg/1.

This treatment has the following advantages.

a. Anodic oxidation goes up to cyanic acid in the first stage of reaction by the alkaline chlorination method.

$$CN + 2OH^- - CNO^- + H_2O + 2e^-$$

b. Treatment cost is about 1/3 of that of the alkaline chlorination method.

c. Highly safe.

d. Useful metals can be recovered

e. Generation of final sludge is smaller than that by the alka line chlorination method.

This treatment has the following disadvantages.

a.Treatment equipment cost is relatively high

b. Treatment time is long.

c. Poor efficiency at low concentrations.

d. From cyanide complexes, metal precipitation is difficult, and therefore, treatment efficiency is very low.

e. Maintenance of electrodes is time-consuming.

Most of the equipment cost is occupied by rectifiers. In any plating factory which uses the rectifier, therefore, the equipment cost may be reduced by utilizing it during the night for electrolytic treatment.

If common salt is added in the wastewater to be treated by electrolysis, alkaline chlorine is produced by electrolysis of common salt and the wastewater is treated by the alkaline chloride method. This process, which has high efficiency is widely used.

2.4.2 Treatment of chrome wastewaters (Reference 3)

Sources of chrome wastewaters are mainly washing wastewater and renewal wastewaters from chrome plating and chromate, etching liquous using chromic acid, etc.

In the treatment of chrome wastewaters, 6-valent chrome is reduced with a reducing agent to 3-valent chrome which is then separated by neutralization.

For the reduction of chrome wastewaters containing chromic acid and concentrate wastewaters, the method using soda bisulfite($NaHSO_3$) or soda metabisulfite ($Na_2S_2O_5$) is the safest and most positive method and is used widely at present.

The reaction with soda bisulfite is as follows.

$$4H_2CrO_3 + 6NaHSO_3 + 3H_2SO_4 - 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 10H_2O \qquad (1)$$

This reduction of 6-valent chrome (Cr^{6+}) to 3-valent chrome (Cr^{3+}) progresses with a speed which increases with increasing acidity. By pH adjustment, reduced 3-valent chrome can be separated as chromium hydroxide whose solubility is very small.

When calcium hydroxide ($Ca(OH)_2$) or sodium hydroxide ($NaOH$) is used as alkali, the treatment reaction is as follows.

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 - 2Cr(OH)_3 + 3CaSO_4 \qquad (2)$$

$$Cr_2(SO_4)_3 + 6Na(OH)_2 - 2Cr(OH)_3 + 3NaSO_4 \qquad (3)$$

With either Eq.(2) or Eq.(3), chrome hydroxide is precipitated, but in the case of Eq.(3) where sodium hydroxide is used for neutralization, it is to be method that precipitates are finer and if pH is above 11, they are redissolved.

Reaction conditions are pH 3 max. and oxidation-reduction potential 250mV max for the ordinary reduction reaction or pH8.5-10 for the precipitation of chrome hydroxide.

The quantity of soda bisulfite required for the reduction of 1g chromic acid is actually a little in excess of the theoretical one. However, if it is too excessive, it affects formation of chrome hydroxide adversely. When soda bisulfite is fed in a quantity above two times chrome hydroxide is hardly precipitated. In order to prevent this, addition of aluminum salt such as aluminum sulfate is effective.

In many cases, the chrome wastewater after reduction of chromic acid is combined with the cyanide wastewater after oxidation, and treatment of heavy metals is carried out. In this treatment, however, 3-valent chrome is sometimes reoxidized with excess chlorine remaining in the treated cyanide wastewater to 6-

valent chrome which is then detected. Therefore, in attempting to combine the wastewaters together as mentioned above, it is necessary to provide for a reducing agent to remain after the combining.

2.4.3 Treatment of Heavy Metal Containing Wastewaters (Reference 3)

Wastewaters containing heavy metals are treated as acid-alkali wastewaters by neutralization. pH is adjusted with a neutralizing agent, and metal hydroxide is separated.

For the treatment of plating wastewaters containing heavy metals, the method using an alkali or acid to adjust pH and precipitating insoluble metal oxides to be separated is a positive method.

Heavy metals to be treated are mainly chrome, copper, nickel, zinc, cadmium, lead, iron, etc. The region pH required to achieve precipitation satisfying the effluent standards for treated water differs with different metals.

Main reactions of hydroxide formation are as follows:

$$Cr_2(SO_4)_3 + 6NaOH - 2Ca(OH)_3 + 3Na_2SO_4 \quad (1)$$
$$CuSO_4 + Ca(OH)_2 - Cu(OH)_2 + CaSO_4 \quad (2)$$
$$ZnSO_4 + Ca(OH)_2 - Zn(OH)_2 + CaSO_4 \quad (3)$$

2.4.4 Treatment of Chelate Containing Wastewaters (Reference 3)

Wastewaters containing chelating agents are cleaning liquous, ammonia containing plating liquous, non-electroplating liquous, cyanide bath liquous, pyrophosphoric acid bath liquous, etc.

If a chelating agent is mixed in the wastewater, chelated metals may remain in the treated water even after separation of heavy metals by precipitation as hydroxides, and as a result, metals in excess of the effluent standards are detected. To prevent this, it is necessary to take care about the method of discharge when discharging the wastewater containing the chelating agents.

(1) Coagulation-sedimentation method

By addition of a coagulant such as gluconic acid, citric acid, tartaric acid, ferric chloride or aluminum salt, for example, alum, the chelate containing wastewater can be treated effectively, for example, copper is decreased to below 1mg/l. EDTA can be treated with pH raised above 12 in the co-existence of calcium salt.

Trisodium phosphate and copper pyrophosphate are also treated by addition of calcium.

Surface activator sodium dodecylite(anion group) up to 400mg/l and dodecyl trimethyl ammonium chloride up to 1000mg/l do not affect the treatment.

Ammonia below 100mg/l does not interfere with the treatment, but if it is far beyond the limit, removal by stripping or treating by addition of chelate resin or soda sulfide is necessary.

(2) Activated carbon adsorption method

Heavy metal-EDTA complexes exist as dissolved in the form of complex anion, and therefore, are adsorbed on activated carbon in a acidic region where the activated carbon surface is charged positively.

The range of pH for good adsorption differs with different metals: 1.8-7 for 3-valent ferric complexes, 2.7-6 for 2-valent nickel complexes, 4.3-7 for 2-valent cupric complexes, and 4.7-6.8 for 2-valent zinc complexes.

(3) Treatment with sulfide

Sulfides of heavy metals have very small solubility products. Therefore, the wastewater containing chelating agents can be treated by addition of soda sulfide. However, in the case of acidic wastewaters, hydrogen sulfide gas may be generated dangerously and it is not desirable to use this method in general.

Various organic polymerized sulfides are commercially available and have good coagulating properties. When using them, it is necessary to take care about rising of COD due to excessive addition, etc.

(4) Adsorption treatment with chelate resins

The chelate resins an ion exchange resin consisting of macromolecules having the stereo-network structure added with functional groups for chelating with metal ions. It is available in various kinds. As compared with ordinary ion exchange resins, the chelate resin has a feature that the selective absorptivity foe heavy metals is much higher than for sodium and calcium ions. It is utilized for the advanced treatment to remove trace quantities of heavy metals remaining in the treated wastewater.

The adsorption rate for heavy metals differs with pH. Moreover, cyanide complexes of iron and EDTA complexes of copper are not removed. When attempting to use this method, it is necessary to note to these points.

2.4.5 Treatment of COD and BOD

In the plating factory, a variety of chemicals are used. Organic chemicals, and surface activators and other additives are quite various.

For the advanced treatment of COD, it is difficult in many cases to satisfy the effluent standards with a single treatment method alone, and it becomes necessary to use other treatment methods in combination.

(1) Coagulation (Reference 3)

By coagulation, COD or BOD is made insoluble or adsorbed on flocs of metal hydroxide, to be partly removed.

A portion of organic acids, etc. as a COD component reacts with calcium ion to produce difficult to dissolve salts. Therefore, adsorption by addition of calcium is effective in many cases. However, it is difficult to treat COD completely with adsorption alone. In practice, this method is used frequently in combination with other treatment methods to improve efficiency.

(2) Activated carbon adsorption (Reference 3)

Activated carbon has a property to selectively adsorb organic substances and therefore, it is used widely for COD treatment.

A system in which powdered activated carbon is added in the reaction tank, and a fixed bed system in which granular activated carbon is packed in a tower and water is applied through the packed layer, are widely used.

The adsorption capability of activated carbon differ with the kind of activated carbon, the kind of organic substance, concentration, pH, temperature, etc. It is said that the activated carbon has an adsorption rate of 5-50kg/kg-AC as COD. In the treatment with the activated carbon tower, the linear velocity (LV) is 5-10 m/h.

(3) Electrolytic oxidation (Reference 3)

In this treatment method, lead peroxide formed by electrodeposition of lead peroxide on titanium, or graphite is used as the anode in the electrolytic cell, and with the wastewater applied in electrolytic cell, a DC current is applied to treat the COD component by anodic oxidation.

This method is economical when used for wastewaters containing COD above 5g/l.

This method is utilized for the treatment of wastewaters containing much COD, such as cleaning liquous, non-electro nickel liquous, etc.

(4) Biological treatment (Reference 3)

In this type of treatment, COD or BOD is removed using activated sludge process, fixed bed process, rotating biological contactor process, trickling filter process, etc.

Biological treatment can remove not only COD and BOD, but also nitrogen and phosphorus simultaneously. Treatment systems with specially high effectiveness are used for general wastewater treatment.

(5) Fenton oxidation (Reference 2)

In the presence of iron catalyst, hydrogen peroxide is used for oxidation of organic substances and inorganic reducing substances contained in the wastewater.

As this catalyst, inexpensive ferrous salt is used, and the treatment is done in an acidic region. Following oxidation, neutralization is applied to convert iron to hydroxide to be separated.

This method is used widely for COD treatment of non-electro nickel liquors.

2.4.6 Treatment of fluorine (Reference 3)

(1) Treatment of fluorine

A method in which calcium salt is added in the wastewater to form difficult-to-dissolve calcium fluoride to be separated is used.

$$2F^- + Ca^{2+} - CaF_2$$

The formation of calcium fluoride does not differ significantly if pH lies in a range of 4-12. Formed calcium fluoride is in a colloidal state and so, is not easily precipitated. For this reason, the degree of treatment is actually only about 15-20mg/l. However, by adding aluminum salt or iron salt to the treated water and repeating coagulation, the degree of treatment can be improved to 3 mg/l or better.

(2) Treatment of fluoborate

Fluoboric acid and its salts used in the treatment of solda plating liquors, etc. can not be treated by the calcium salt adding method.

Aluminum salt is added to convert fluoboric acid to aluminum fluoride, and then calcium salt is added to convert aluminum fluoride to calcium fluoride to be separated.

The reaction by addition of aluminum progresses faster when heated and the fluorine concentration can be reduced to below 20 mg/l. At the room temperature, the treatment requires 24 hours and the fluorine concentration is reduced to 15mg/l.

$$3HBF_4 + Al_2(SO_4)_3 + 6H_2O - 2H_3AlF_6 + 3H_2SO_4 + 3H_3BO_3 \qquad (1)$$

$$2H_3AlF_6 + 6Ca(OH)_2 - 6CaF_2 + 4Al(OH)_3 + 4H_2O \qquad (2)$$

When low concentration wastewaters such as washing wastewaters are treated using weak basic anion exchange resins, resin treatment and desorption can be done easily.

2.4.7 Treatment of phosphorus (Reference 3)

Phosphates used in cleaning liquous, chemical polishing liquors, pyrophosphate plating liquors, etc. can be separated as difficult-to-dissolve compounds which are produced by reacting the phosphate with calcium, iron and aluminum ions.

Cleaning liquor, etc.:

$$3PO_4^{3-} + 5Ca^{2+} + OH^- - Ca_5(OH)(PO_4)_3 \qquad (pH>10)$$

Pyrophasphate:

$$P_2O_7 + 2Ca^{2+} - Ca_2P_2O_7 \qquad (pH>10)$$

When ferric salt or aluminum salt is used:

$Fe^{3+} + PO_4^{3-} - FePO_4$ (pH 5-7)
$Al^{3+} + PO_4^{3-} - AlPO_4$ (pH 5-7)

Phosphorus in the non-electro nickel plating liquor exists as hypophasphate and phosphite. Phosphite can be treated in the some way as phosphate, but hypophosphite requires oxidation beforehand. Oxidation for this purpose can be done using sodium hypochlorite, electrolysis, Fenton method, etc.

2.4.8 Treatment of nitrogen (Reference 3)

Nitrogen in the plating wastewater exists, in most cases, as ammonia state nitrogen.

(1) Excess chlorine process

Oxidation with chlorine from sodium hypochlorite, etc. is used. Ammonia is oxidized to chloramine which is further oxidized to nitrogen. This process is applied as chlorination of tap water.

$$2NH_3 + 3NaOCl - N_2 + 3NaCl + 3H_2O \qquad (1)$$

(2) Stripping

In an alkaline region, the wastewater is introduce into the packed tower where by aeration and ventilation ammonia gas is removed. It is necessary to take measures for recovering and treating the removed ammonia.

(3) Adsorption

The treatment with natural zeolite which selectively adsorbs ammonia state nitrogen in the wastewater is widely used.

The treatment with ion exchange resins is also available, but no resin which selectively adsorbs ammonia state nitrogen has yet been developed.

In either method, it is necessary to treat ammonia in the regeneration wastewater.

(4) Biological treatment

A ammonia is oxidized under aerobic conditions with nitrifying bacteria to nitrate state nitrogen, which is then reduced under anaerobic conditions with denitrifying bacteria to nitrogen gas to be dispersed into the atmosphere.

This method is used widely for denitrification of wastewater.

2.5 Reclamation

It is said that in plating factories about 70-80% of purchased raw materials fail to become products but are discharged together with washing wastewaters to the wastewater treatment plant. These raw materials are discharged together with vast volume of wastewaters and removed of toxic substances, and resulting sludges are treated and disposed of. And that, involved operations require expenses. Under these circumstances, various reclamation techniques have been developed and put into practical use.

Among the reclamation techniques, the most fundamental is water reclamation. Most of water usage in plating factories is for washing. Using ion exchange resins to treat these washing wastewaters and recycling as washing waters are used widely. And that, wastewaters from regeneration of ion exchange resins contain the pollution substances in a concentrated condition, so that the treatment equipment can be advantageously compact.

In the case of ion exchange resin, the lower the ion concentration the more the regeneration interval can be prolonged. Therefore, following the counter-current multi-stage washing tanks, a recycled water washing tank equipped with an ion exchange equipment is installed so that the effluent from ion exchange may be recycled as the washing water.

For reclamation of wastewaters with ion exchange resins, a system using first a strongly acidic cation exchange resin to remove cations in the wastewater, then a weakly basic anion exchange resin to remove the strong acid, and finally a strongly basic anion exchange resin to remove the weak acid, is used.

The investigation on this system will be conducted regarding both technical and economical aspects about the following items. Water recovery rate and reclaimed wastewater quantity, necessity of a weakly acidic cation exchange resin tower, regeneration level and regeneration cost of ion exchange resins, pollution of resins with organic substances in the wastewater method of treatment of wastewater from regeneration of ion exchange resins, etc.

The ion exchange resin equipment may be of fixed bed type, moving bed type or fluidized bed type, or of single-bed type, multi-bed type, double-bed type or mixed-bed type according to the method of water application, or of down-flow type, up-flow type, counter-flow type or outside regeneration type according to the method of regeneration. It is essential to select the most suitable type considering the purpose of using the reclaimed water, and the construction and running costs.

Fig.2.5.1. shows an example of reclamation of chrome washing wastewaters using ion exchange resins. The washing wastewaters from washing processes is passed through a strongly acidic cation exchange resin and a weakly basic anion exchange resin, which remove salts in the wastewater, and the treated water is recycled for washing purpose. The chromic acid adsorbed on the weakly basic anion exchange resin is desorbed by regeneration of sodium hydroxide to sodium chromate. This sodium chromate is converted by an H type strongly acidic cation exchange resin to chromic acid to be recovered. The recovered chromic acid is thickened and recovered in the plating bath. On the other hand, ion exchange resins are used also for refining of chrome plating bath liquous. The bath liquor is filtered, and applied to a strongly acidic cation exchange resin which removes impurities such as copper, iron and trivalent chrome, and the effluent is returned to the plating bath.

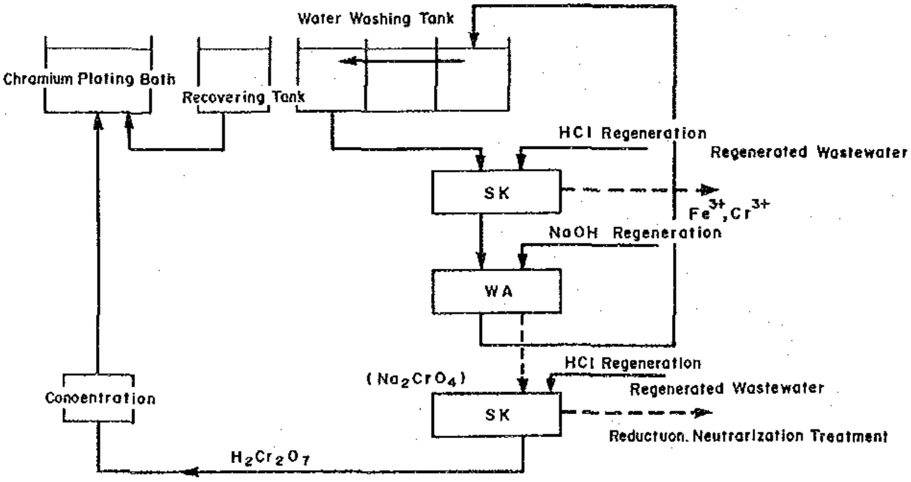

Fig. 2.5.1. Example of reclamation of washing water on chrome plating using ion exchange resin by batch system

In order to realize a closed wastewater system, it is necessary to make the wastewater from regeneration of ion exchange resins and concentrate renewal wastewaters harmless and subsequently to demineralize the harmless water. A system which concentrates the demineralized water through reverse osmosis or electric dialysis before evaporation to dryness will be economical.

Table 2.5.1 shows some features of unit operation for demineralization.

Table 2.5.1. Characteristics of Unit Operation for Demineralization

Unit Process	Ion Exchange	Rverse Osmosis	Electrodialysis	Evaporation
Mechanism	Adsorption of Disolved Ion	Membrane Filtration of Water	Membrane Filtration of Ion	Evaporation of Water
Energy	Chemical Potential	Difference of Pressure	Electric Power	Thermal
Supply	Pompe	Pompe	electrochemical Potential	Steam or Gas or Electric Power
Main Material	High-Molecular Compound	Membrane made by High-Molecular Compound	Membrane made by High-Molecular Compound	Copper
Object	Inorganic Compound	Organic & Inorganic Compound	Inorganic Compound mainly	High Concentration Waste water
Concentration (1)Object (2)Desalinated water (3)Concentrated water	 < 500 mg/l < 10 mg/l 1 〜 1.5 %	 500 mg/l 〜 2 % 50 〜500 mg/l 4 〜 6 %	 0.1 〜 3 % 200 〜 500 mg/l 7 〜 10 %	 3 % < < 200 mg/l Solid
Adding Chemicals	Acid & Alkaki	—	—	—
Waste water	Regenerated Waste water	Concentrated Waste water	Concentrated Waste water	Salt (Solid)
Cost of Operation	Low	Middle	Middle	High
Maintenance	Regeneration of Risin	Cleaning of Membrane	Cleaning of Membrane	Removing of scale
Pretreatment	Sand Filter	MF + pH control	Mf + pH control	—

2.6 Sludge Treatment

The sludge as hydroxides of heavy metals is thickened in the settling tank or through the filter, then dehydrated through a filter press, and the harmless dehydrated cake is disposed of as an industrial waste by land refilling. This is a general practice.

The dehydrator available is in a variety of types such as filter press, vacuum dehydrator etc. having different dehydration characteristics. Dehydrators capable of water contents below 80% after dehydration and cake discharge rates above 3-10 kg/m^2 should be selected.

The sludge disposal cost is high, the land available for sludge disposal is short, and the sludge contains valuable substances. From these facts, various methods of sludge treatment are being tried, and their practical use is progressing.

(1) Solidification (Reference 4)

If the sludge generated from plating wastewater treatment is disposed of by land filling as it is, problems of soil pollution, etc. with ground infiltration may occur. It is, therefore, necessary to suppress elusion of contained metals and also to convert the sludge to a hard solid having the highest possible strength.

In this method, the sludge is mixed with cement, plastics, glass, etc. and solidified before being used for land filling or disposed of by ocean disposal.

(2) Solidification by sintering (Reference 4)

The sludge is mixed with clay, expanding scale, etc., and molded and Aimtered into a half-molten state.

Because of sintering at a high temperature, the produce is strong and stable and can be reused as light-weight aggregate, artificial grave, rooping tile, etc. If the sludge contains 6-valent chrome, sintering should be done in a reducing atmosphere such as carbon dioxide or hydrogen to prevent chrome from being eluted.

(3) Treatment after returning to the mine (Reference 4)

The sludge should be transported to my refining at a mine appropriate for its component such as nickel, copper or zinc. There, it is added in the refining process and refined to a valuable metal to be used.

From the viewpoint of re-utilization of resources or stable treatment for harmlessness, this method is excellent. Its disad vantage is that when the sludge has a complicate composition as in the case of plating wastewaters, it is difficult to satisfy the receiving standards on the transported sludge. There will be a necessity to treat the wastewater in a way appropriate to each metal contained in it.

(4) Treatment to convert sludge to ferrite

Plating wastewaters, or wastewaters thickened by ion exchange resin or other treatment, are subjected to oxidation of cyanide, reduction of chrome and neutralization, and the wastewater containing the resulting sludge is added with ferrous ion and an equivalent quantity of alkali, then applied with oxidation to convert the sludge to ferrite.

$$\mathrm{Fe^{2+} + 2OH^{-} \text{ — } FeO\cdot H_2O \overset{O_2}{\text{ — }} FeO\cdot Fe_2O_3} \quad \cdots\cdots\cdots\cdots \quad (1)$$

The ferrite obtained is stable and is utilized as a radio absorber.

2.7 Direction of New Technologies

For the treatment of plating wastewaters, reverse osmosis(RO) membranes are used more frequently than ultrafiltration (UF) membranes or micro-filtration membranes. Recently, various RO membranes have been commercialized progressively, and the range of their application is expected to be extended.

The RO membrane is an effective means for demineralization or trickening to remove dissolved substances at ion levels. When attempting to apply the RO membrane on an industrial basis in plating factories, it is necessary to study it in comparison with the ion exchange resin, electrolysis and vacuum evaporation of combinations with them from technical and economical viewpoints.

The membrane properties required are as follows:

a. Usable pH range is wide.
b. N6t vulnerable to fouling with organic substances, and highly capable of separating organic substances.
c. Usable at relatively high temperatures.
d. Resisitant to oxidation.
e. Salt rejection rate is high and its degradation with time is small.
f. Pesmeate flow is large and its degradation with time is small.
g. Operating pressure is low, and replacement of membrane elements is easy.

An example of RO application to thickening of washing wastewaters from the nickel watt bath process is shown.

In this example, the washing wastewater from the 1st washing tank is treated by three RO stages to be thickened by a factor of several to about 10.

The effluent is used directly as make-up water for the plating bath, or it is thickened and adjusted of its composition in an evaporator, then returned to the plating bath. The rejection of the RO membrane differs with the substance to be treated and is about 99% for nickel, 81 - 89% for brightening agents and 45% for boric acid. By thickening, a portion of organic substances of the brightening agent is decomposed. Therefore, prior to thickening, the organic substances should be removed through activated carbon or ion exchange resin treatment, so as to make adjustment for the change of composition due to thickening.

Figure 2.7.1. shows a nickel plating wastewater recovery system using the RO membrane. The liquor thickened through the RO membrane is further thickened in an evaporator, passed through a filter, added with chemicals for adjustment, and used as make-up water for the plating bath. The liquor rejected of salts through RO is supplied through ion exchange resins to the washing tank. (Reference 5)

On the other hand, along with the development of electronic industry, improved manufacturing techniques have required improving the quality of water to be used. Regarding the RO membranes as well as the ion exchange resins, technologies for wastewater reclamation and water ,manufacture and being investigated. This is to ensure that traces of dissolved substances leaking through the ion exchange resin should be removed through the RO membrane.

The plating wastewater treatment is not merely treating the wastewater. Besides the above mentioned items such as effective use of water, reduction of pollution load, recovery and re-use of wastewater and valuable substances, disposal of sludge, etc., it is necessary to conduct an extensive study on locating plating factories in industrial estates, realizing centralized treatment of wastewaters, etc.

It is also important to keep eyes always on new technologies. Because research and development are being continued toward the equipment, easy to operate, of resource-saving and energy-saving type, capable of energy recovery, compact and assuring stable treated water quality.

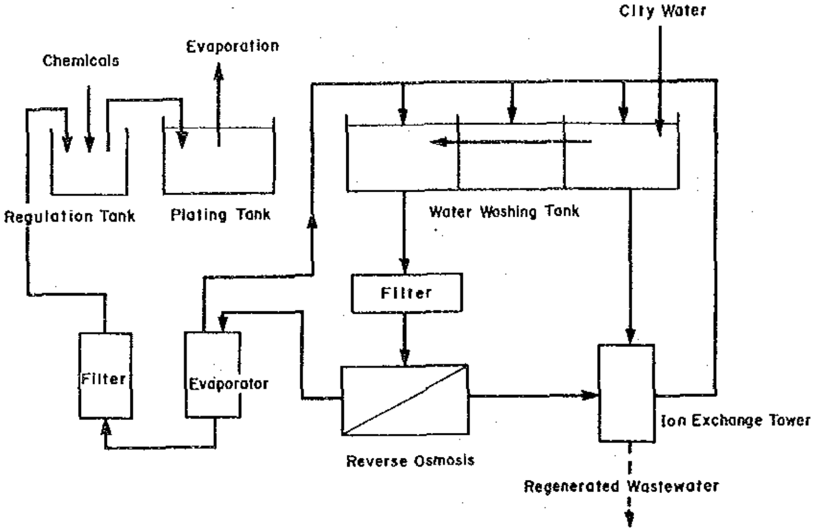

Fig. 2.7.1. Example of the recovering system on nickel plating using Reverse Osmesis

2.8 Maintenance of Wastewater Treatment Plants in the Plating Industry (Reference 3)

Regarding the operation and management of the plating wastewater treatment equipment, it is important to standardize (1) setting of treatment system and treated water quality, (2) wastewater sampling and analysis, (3) purchase and storage of treating chemicals, (4) Preparation of treating chemicals, (5) Operating procedures, (6) method of maintenance, maintenance interval and troubleshooting, (7) method of sludge disposal, (8) record and report of working details and (9) others.

The results obtained through standardization of works must immediately be reflected in the wastewater treatment operation on (1) improvement of treated water quality, (2) reduction of treatment cost, (3) extension of equipment life, (4) safety of works, etc.

(1) Maintenance of Equipment

The wastewater treatment equipment is different from general production processes in that it must never result in defects. Even if the wastewater concentration varies by a factor of 10, the treated water quality must be kept within the same limits to satisfy the effluent standards. Thus, stricter control of operation the in other production processes is demanded.

Items of equipment maintenance are as follows:

A. Periodical maintenance comprising check of oil filling, supply of chemicals, daily cleaning of electrodes, cleaning of pipings, check for concrete leaking, check of linings, etc.

B. Cleaning

C. Repair

(2) Maintenance of apparatus.

Maintenance of common apparatus of the wastewater treatment equipment is as follows:

A. Chemical tank

Daily check is to dissolve chemicals to make up for the reduced stock of chemical liquor. Maintenance is visual inspection for corrosion, leakage, cracking, swelling and painted condition.

B. Reaction tank

Daily check is to examine for tank deformation, lining cracking, swelling, etc. Maintenance is visual inspection for corrosion, leakage, cracking, swelling , painted condition and agitator.

C. Setting tank

Daily check is to examine raw water quality, coagulant feed rate, and coagulated condition. Maintenance is visual inspection of sludge condition, sludge quantity and concentration and corroded condition of inside and outside surfaces of the tank.

D. Sand filter

Daily check is to examine (1) carry-over of coagulation-sedimentation tank, (2) added quantity and feed rate of high polymer coagulant, (3) contaminated condition of backwashing water and (4) water supply rate to sand filter. Maintenance is confirmation of backwashing internal, and visual inspection for corrosion of inside and outside surfaces and painted condition.

E. Dehydrator

Daily check is to examine (1) operating pressure or vacuum degree, (2) operating condition of each apparatus, (3) presence of abnormal symptoms, (4) water content of dehydrated cake, (5) clogging of filter cloth, etc. Filter media and filter cloth should be washed at definite intervals.

F. Pumps

Daily check is to examine pumping rate and pressure, leakage of gland seal and mechanical seal, etc. If any fault is found, take actions in accordance with the instruction manual.

G. Agitator

Daily check is to examine for bent shaft in the case of proper agitator, fixed condition of the body, abnormal sounds in the bearing section, agitating condition, etc. Maintenance is (1) measurement of insulation resistance, (2) replacement and oiling of bearings, (3) adjustment of belt tension, etc.

(3) Maintenance of measuring instruments

For pH meters, ORP meters, etc., it is important to maintain the functions of the measuring instruments in the correctly isolated and stabilized condition every day.
Measuring instruments should be maintained in accordance with the instruction manual, regarding (1) indicators, (2) exclusive cables and (3) electrodes.

(4) Maintenance of pipings and wirings

Regarding pipings and wirings, the present state should be confirmed as to (1) freezing prevention measures, (2) vibration and shrink prevention measures, (3) condition of chemical feed pipes, and (4) condition and material, etc. of wirings.
(Reference 1)

(Reference Materials)

1) Environmental Pollution Department of the Ministry of Internationa Trade and Industry, Committee for Preparation of Guidance of Waste Water Treatment Technology; Guidance of Waste Water Treatment Technolo - Countermeasures for Treatment of Waste Water for Nitrogen and Phosphorus (Electroplating Industry) (1987)

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3) Fundamental Industry Department of the Ministry of International Trade and Industry, Electroplating Waste Water Treatment Study Committee; Guidance of Electroplating Waste Water Treatment (1987)

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5) Waste Water Treatment in Plating Industry - Environmental Study by Osamu Kagawa and Nobuyuki Takahashi, 35 (1981)

3. Guideline for the Dyeing Industry

3.1 Outline of the Dyeing Industry

Characteristics of the dyeing industry and wastewater therefrom are as follows.

(1) Majority of the business is performed on commission, and therefore it is difficult for individual companies to determine the contents of processing processes independently.

(2) Small processing lots cause wide fluctuations in a day and the season and the fashion also cause wide seasonal fluctuations.

(3) Most of the processing processes require chemical treatment.

(4) Used in the processes are a variety of chemicals such as dyes, pigments, acid, alkali, oxidizer, reductants, sizing agents, surface active agents, solvents, metallic chloride which have all different chemical properties.

(5) Wastewater is colored by dyes, pigments and impurities in fibers.

(6) pH of the total drainage is unstable because of the irregular continuation of the operation process involving acid and alkaline.

(7) Residues of casein and lanolin, sizing agents and surface active agents raise BOD and COD content levels in wastewater and make the wastewater effervescent.

(8) Chloride concentration in wastewater is high because various chlorides are used in the processes.

(9) The concentration of phenol and n-hexane extract in waste water is high because of the solvent used in the process.

(10) The levels of BOD, COD and n-hexane extracts concentrations in wastewater are high because of the loss of oil and desizing agents during the processes of fiber manufacturing, spinning and weaving.

(11) SS concentration in wastewater is high because of the loss of fiber flocks and so on.

(12) Main processes are implemented mostly batchwise and intermittently discharge high concentration wastewater. Consequently, the amount and quality of wastewater fluctuate widely, and, it is difficult to grasp water quality because of mutual chemical action among chemicals.

Thus, the treatment of wastewater implemented by the dyeing industry is more difficult than that by other manufacturing industries and combinations of several kinds treatment processes are required for sufficient treatment. The dyeing industry which is a water-oriented industry discharges huge amounts of wastewater. For the above mentioned reasons, wastewater treatment in the dyeing industry requires massive capital investments and operating costs which constitute a significantly large burden on management.

The following part summarizes the characteristics of the dyeing industry and describes the guidelines to implement economic wastewater treatment and reclamation.

3.2 Main Production Process and Wastewater Quality

Dyeing is classified into four categories depending on the kinds of raw materials, cotton dyeing, top dyeing, yarn dyeing (pre-dyeing) and textile or knit dyeing (post-dyeing). Dyeing can be classified roughly into two methods: dipping and printing.

Textiles for dyeing is as follows:

1) Natural fibers
   Cotton, silk, wool, ramie, etc.
2) Chemical fibers
   Rayon, acetate, etc.
3) Synthetic fibers
   Nylon, polyester, acryl, etc.

All these fibers have different characteristics and features and can be used individually or more than two kind of fibers can be twisted or mixed together. The dyeing process and methods vary according to the characteristics of the textiles, dyeing tones, textures of the textiles and the kinds of dyes to be used. When the finishing process for softening and water-proof processing is added to the production process, the process is very extensive and highly diversified.

As described above, each dyeing company uses its own unique equipment and facilities depending on the process features and processing specifications for textiles and pursues the optimum conditions. Consequently, it is not possible to define the standard process in a strict sense. However, in general, a processing is conducted based on the procedure shown in Fig. 3.2.1. (Reference 1).

The production description and quality of wastewater for each stage of process are described as follows.

(1) Wastewater from desizing

The desizing process removes sizing agents adhered to yarn or textile. In this process, sizing agents such as starch, PVA

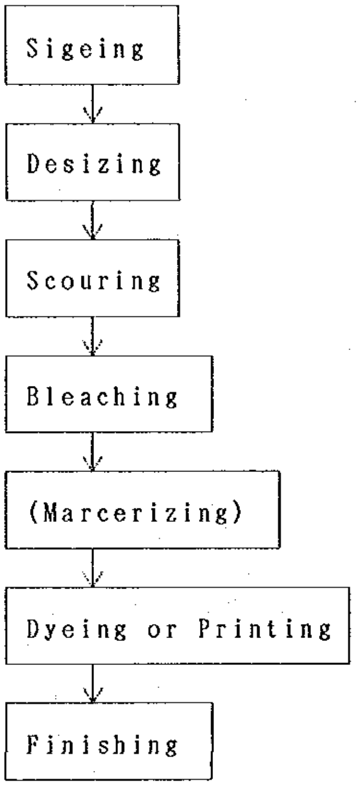


Fig. 3.2.1. Example of Separated Treatment for Dyenig Wastewater

and CMC become water-soluble through hydrolysis by enzyme or oxidizer and are then washed away. Therefore, the wastewater contains concentrated BOD and COD.

(2) Wastewater from scouring

The scouring process removes impurities adhered such as wax, fat and oil, pectin and nitrogenated organic compounds from textiles using alkaline, soap, and surface active agents, etc. The major problems in the wastewater are fine fibers, pH, SS, BOD, n-hexane extracts.

(3) Bleaching

The bleaching process removes natural color substances in textiles, using hypochlorite, hydrogen peroxide and alkaline. The wastewater contains not only pH, SS and BOD but also residual bleach.

(4) Dyeing

Surface active agents, inorganic chloride and acetic acid are used as dyes or dyeing auxiliaries in this process. Chemicals and their amounts flowing into wastewater differ according to the kinds of fibers and dyes. Generally, yarn dyeing is easier than textile dyeing. In the dye bath, a variety of chemicals are added besides dyes in order to attain a higher degree of adsorption of colors and better color development. Such chemicals are added for wetting, emulsifying, solubilization, diffusion, infiltration and color development, and large amounts of surface active agents are employed as well as inorganic chloride, organic acid, organic acid soda chloride and alkaline to that end. These auxiliaries are discharged with the wastewater without any reduction in the amount. Thus, they are seen as causes of water contamination and, making wastewater treatment difficult to implement. The wastewater in this process has complicated constitution, containing concentrated BOD and COD, oil, and occasionally including chrome and copper.

In the case of printing dyeing, quality of wastewater is affected in various forms by the printing method, fiber material, shape of the material and chemicals used. Additionally, printing paste used in this process causes a high BOD concentration in the wastewater.

(5) Finishing

Dyed textiles are treated with wrinkle-free or shrink-free processing in this process. This process employs processing agents such as melamine resin, urea-formaldehyde resin and auxiliaries such as surface active agents. With diversified textile applications, chemicals used in this process are diversified and complicated. However, this process does not discharge large amounts of wastewater because of the absence of the washing process, although such chemicals are discharged along with washing water during the washing process for processed units such as rollers. The wastewater, therefore, contains concentrated COD and BOD.

Table 3.2.1 (Reference 1) summarizes chemicals used, and pollutants and others generated in each production process. Table 3.2.2 (Reference 1) shows bleaches and dyes used for each kind of fiber.

With regard to quality of wastewater from dyeing, in general, the total drainage contains around 300 mg/l of BOD and pollution load ratios are high in the desizing and scouring processes. An example of quality and quantity of wastewater in every process is shown in the Table 3.2.3 (Reference 1).

[Reference]

Reference 1: "Pollution Prevention Business Guidance Manual (dyeing)" by Japan Small Business Cooperation

Table 3.2.1. Using Chemicals and Pollution Components in each Process

Process	Chemicals	Pollution components
Desizing	Desizing agent(Enzymatic etc.), Week acid	Desizing agent, Week acid, Sizing material, Waste fiber
Scouring	Caustic soda, Surface active agent	Alkali, Surface active agents, Waste fiber, Stained components on fiber (Wax, Pectin, Coloring matter etc.)
Bleaching	Hypochlorite soda, Chlorous soda, Peroxide(Hidrogen peroxide), Reduction agents, Alkali, Acid	Salts, Stained components on fiber, Waste fiber, Decomposeing coloring matter
Marcerizing	Caustic soda	Caustic soda, fiber
Dyeing or Printing	Dyestuff, Auxiliary, Sizing material, Surface active agen	Not exhausted dyestuff, Auxiliary, Surface active agent, Sizing material
Finishing	Resin finishing agent, Softing agent, Others	Not fixed matter

Table 3.2.2. Using Bleaching Agents and Dyestuff of each Fiber

Fiber	Useing bleaching agent and dyestuff	
Cotton, Hemp	B-1～3	D-1～7, 16
Silk, Wool	B-3, 5	D-1～3, 5, 8～12, 16
Rayon	B-1～3	D-1, 3～7, 16
Acetate	B-2, 3	D-1, 3, 5, 6, 13, 14, 16
Polyamide	B-3	D-1～10, 13, 16
Poly(vinyl alcohl)	B-2, 3	D-1, 4～6, 8～10, 13, 14, 16
Polyester	B-2	D-5, 6, 13
Polyacrylonitrile	B-2	D-3, 5, 6, 8～10, 13, 14
Poly(vinyl chloride)	B-2	
Poly(vinylidene chloride)	B-2	D-13
Polyolefine	B-2	D-3～6, 9, 13～15

(Bleaching Agent and Dyestuff List)

Bleaching Agent		Dyestuff	
No.	Kinds	No.	Kinds
B-1	Hypochlorite	D-5	Vat dye
B-2	Chlorous	D-6	Insolubility azo dye
B-3	Peroxide	D-7	Oxidation dye
B-4	Permanganate	D-8	Acid dye
B-5	Reduction type	D-9	Chrom dye
		D-10	Metal complex salt dye
Dyestuff		D-11	Mordant dye
No.	Kinds	D-12	Vagetable dye
D-1	Direct dye	D-13	Disperse dye
D-2	Reactive dye	D-14	Cationic dye
D-3	Basic dye	D-15	Oil color
D-4	Sulfer dye	D-16	Pigment

Table 3.2.3. Quality and Quantity of each Effluent

(Texistil dyeing)

Items / Process	Quantity		Qualitity								Dilution magnifications by washing water[-]
	Conc. [ℓ/kg]	Total [ℓ/kg]	Concentrated Effluent				Total Effluent				
			pH [-]	BOD[mg/ℓ]	COD[mg/ℓ]	SS [mg/ℓ]	pH [-]	BOD[mg/ℓ]	COD[mg/ℓ]	SS [mg/ℓ]	
Desizing		15 〜 25	14.0〜1.0	15700〜96600	7300〜80500	4700〜8800	10.0〜3.8	1750〜6930	247〜1300	230〜550	8 〜 16
Scouring		20 〜 40	14.0〜3.8	10000〜39000	1200〜7000	840〜2540	12.8〜6.8	1020〜2360	210〜930	70〜200	6 〜 16
Bleaching		15 〜 25	14.0〜1.0	780〜1400	500〜800	240〜1230	11.8〜3.0	120〜270	130〜400	40〜140	4 〜 6
Marcerizing		30 〜 40	14.0〜7.8	1640〜3080	840〜3920	190〜440	12.8〜9.0	40〜300	80〜620	10〜190	7 〜 14
Direct dyeing		50 〜 65	14.0〜2.5	250〜510	360〜2880	1200〜11000	10.6〜7.5	70〜100	100〜240	90〜300	4 〜 11
Sulfer dyeing		55 〜 70	14.0〜7.5	8300〜19200	11400〜77200	6300〜18900	11.5〜9.9	430〜1200	800〜2200	610〜1380	11 〜 18
Vat dyeing		150 〜 180	14.0〜1.0	2100〜4100	710〜1570	640〜5500	13.0〜9.6	230〜660	150〜490	90〜480	5 〜 12
Acid dyeing			7.8〜1.0	6390〜10800	1300〜2200	150〜310	6.0〜3.2	330〜1060	130〜520	20〜100	4 〜 14
Basic dyeing			12.8〜1.0				6.4〜5.4	70〜270	80〜240	40〜80	
Disperse dyeing			14.0〜3.1	790	790〜5500	200〜400	10.2〜4.5	180〜440	150〜430	40〜80	5 〜 12
Reactive dyeing			11.8		140〜930		10.6		20〜120	0〜40	6 〜 8
Dyeing Total			13.6〜1.0	390〜4640	410〜5880	200〜800	12.6〜4.6	30〜290	70〜350	20〜90	6 〜 17
Reactive printing		70 〜 150					9.8〜9.2	270	240	101	
Vat printing		70 〜 150					12.0〜11.6	750	160	90	
Naphtol printing		70 〜 150	11.0〜5.1	210〜380	120〜200	180〜240					
Printing total			14.0〜1.0	980〜4750	1000〜4300	400〜2300	9.8〜5.7	100〜270	120〜560	80〜230	5 〜 13
Finishing			12.1〜2.9	680〜6210	1000〜17100	460〜4400	9.6〜5.9	20〜160	20〜100	0〜150	23 〜 70
Total		150 〜 400	14.0〜3.3	1050〜2150	400〜6700	540〜1900	12.2〜4.9	150〜280	60〜600	30〜120	6 〜 12

Table 3.2.3. Quality and Quantity of each Effluent(continued)

(Yarn dyeing)

Items / Process	Quantity		Qualitity								Dilution magni-fications by washing water[-]
	Conc. [ℓ/kg]	Total [ℓ/kg]	Concentrated Effluent				Total Effluent				
			pH [-]	BOD[mg/ℓ]	COD[mg/ℓ]	SS [mg/ℓ]	pH [-]	BOD[mg/ℓ]	COD[mg/ℓ]	SS [mg/ℓ]	
Scouring	10 ～ 15	45 ～ 55	13.2		1309～1620	10～30	12.5～12.9	1240	438～518	2～13	3 ～ 5
Bleaching	10 ～ 15	75 ～ 95	11.3	430	563～728	10～70	10.4	120	110～142	0～10	5 ～ 9
Direct dyeing	12 ～ 15		9.3	1800		269	7.0～9.0	40～200	35～188		
Acid dyeing	12 ～ 15		4.3～5.7				4.3～5.4	200～500	141～400		
Sulfer dyeing	20 ～ 30		11.8～13.1	2210～3430	2212～2630	20～25	10.5～11.4	240～1300	70～530	5～10	5 ～ 10
Vat dyeing	20 ～ 30		12.8～13.2	2080	100～622	15～25	11.3～12.3	140	20～260	0～10	3 ～ 12
Reactive dyeing	12 ～ 15		10.6		112～811	35	7.5～9.5	180	20～130	0	4 ～ 10
Disperse dyeing	12 ～ 15		4.2～5.2	500～800	1705～2804	0	7.0～7.4	35～180	50～280	0	7 ～ 16
Oxidation dyeing	20 ～ 30			840							
Naphtol dyeing	20 ～ 30		4.3～13.0		4362～5847	43～426	9.5～4.2	108			
Basic dyeing	12 ～ 15			780		630	10.0～6.3	200			
Oiling			8.8		300～810	102～196	8.9～7.5				
Total		200 ～ 500	12.8～3.0	630～1230	300～920	200～1170	10.5～6.3	80～210	90～180	50～120	4 ～ 8

3.3 Measures of the Production Process

In planning wastewater policies in the dyeing industry, comprehensive survey on the quality and quantity of wastewater should be conducted and the pollution-causing route should be detected prior to the determination of the establishment and designing of a wastewater treatment plant. It is important to trace back to the production process to improve efficiency through the reduction of pollution and treatment load implemented from the early stage wastewater treatment. To reduce pollution load in wastewater, there are two measures: reducing wastewater quantity and lowering concentration of wastewater.

Measures as from the reduction of pollution load during the production process to wastewater treatment are discussed in this section.

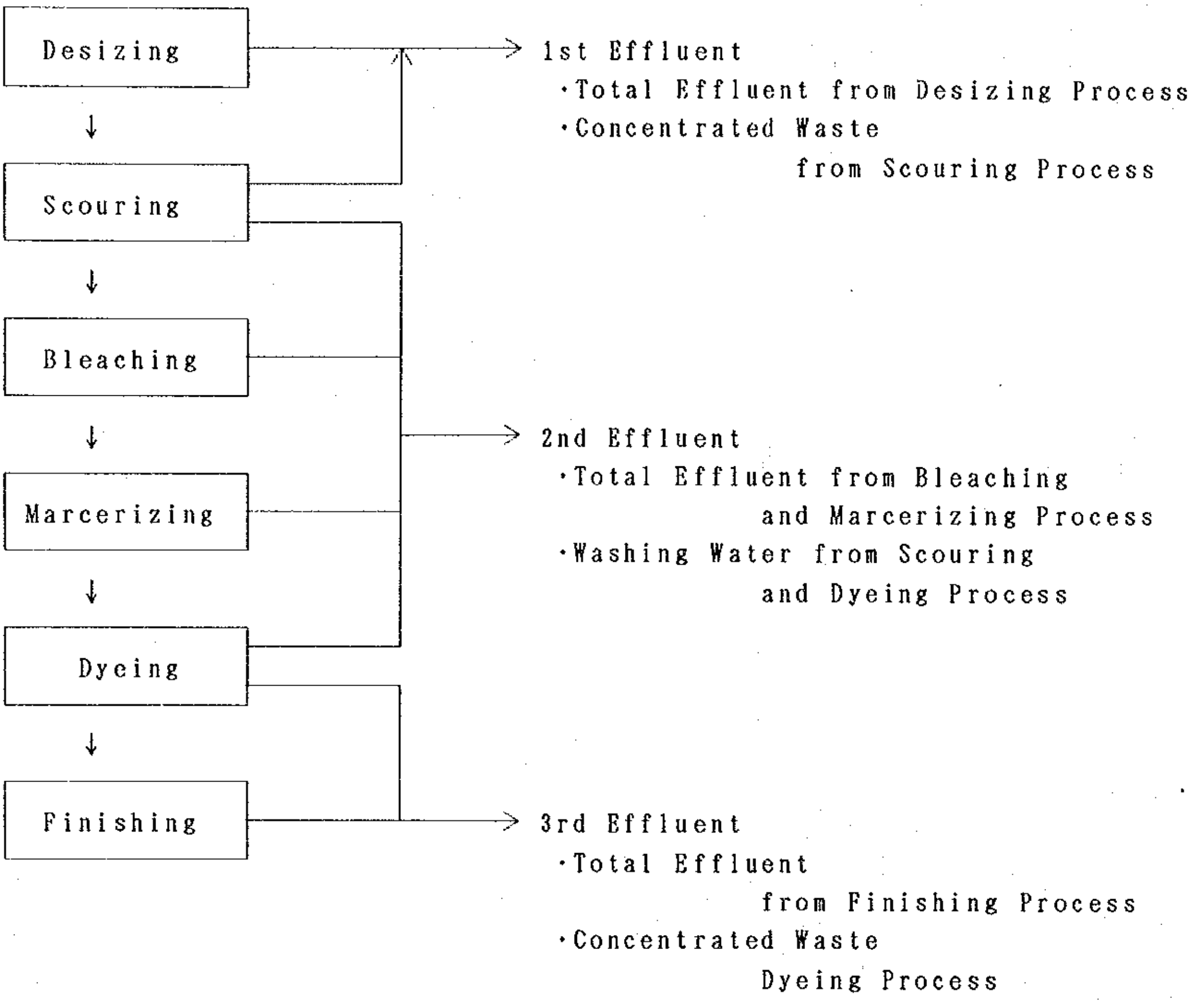
3.3.1 Reduction of waste water

(1) Sorting of wastewater

Wastewaters from the dyeing industry differ in properties according to the process stages. Hence it is obviously not wise to mix the whole wastewaters from an processes altogether before treating. Wastewater treatment should be conducted based on a type-by-type basis. It is necessary that wastewater be classified into several categories and the effluents be stored thereby and appropriate treatment be conducted for each categorized wastewater. in order to scale down the facilities. It has another advantage of heat recovery from high temperature waste water.

Fig. 3.3.1 (Reference 1) shows the 3 categories of wastewater from cotton and P/C mixed fabric dyeing.

1) 1st effluent: heavily contaminated wastewater from desizing and scouring
2) 2st effluent: less contaminated wastewater from bleaching and scouring, wastewater from mercerizing, and diluted wastewater from dyeing



Product : Cotton and P/C textile dyeing

Fig. 3.3.1. Example of Separated Treatment for Dyeing Wastewater

3) concentrated wastewater from dyeing: concentrated wastewater from dyeing and resin treatment

In sorting wastewater, it is generally sorted into two categories: low concentration water and high concentration. However, it is pragmatically difficult for the existing plants to sort and treat wastewater because of the present wastewater treatment systems.The sorting of wastewater is not practiced in most of the plants in reality.

(2) Water conservation

After the survey on water consumption at the dyeing facilities, excessive water consumption was observed in many cases. In the case of continuous washing, it will be possible to save considerable amount of water by adopting counter current washing method.

The reduction of the total amount of wastewater enables the down-sizing of the whole system for wastewater treatment as well as the reduction of treatment costs. Even with the present treatment equipment,less wastewater conduces to more stable operation due to more energy that each device san save.

However, water conservation is limited to a certain degree. For the dyeing factories that need to keep using great amounts of water continuously, it is required to reduce the water consumption to a minimum with which production and wastewater treatment should not even be interfered.

(3) Dehydrated dyeing process

Great expectation is placed on a dyeing method without using water as an alternative fundamental technique to prevent pollution. However, there are only a few cases while the technique is adopted. In addition to the thermo-sol dyeing and pigment resin coloring method, the sublimating transfer printing method which needs no washing or soaping is employed in such cases. The solvent dyeing method and the gaseous phase dyeing method are to materialize value-added quality and to increase quantitative productivity.

3.3.2 Reduction in wastewater concentration

(1) Change of chemicals

A change of chemicals affects product quality and is difficult to realize; however, it needs to be reviewed whether the present chemicals can be changed to any other alternatives which have a smaller pollution load or require smaller dosages. however, if any change is made, some organic chemicals whose BOD per unit weight are extremely low, might have biological toxicity. Consequently, due caution is required in choosing the right chemicals.

(2) Saving of chemicals

It is necessary to review dyeing methods and conditions to reduce the consumption of chemicals (used at present) for more efficient use of dyes.

In most of the cases, chemicals are used not individually but the from of mixture. The mixture ratio differs according to the object material and processing process, and, in usual cases the mixture liquid is discharged after the process. In the mixing operation, excessively or improperly mixed liquid is also discarded. Searching efforts should be made to reduce the amount of unused chemicals to be discarded. From the viewpoint of production technology, the rearrangement and the integration of the mixtures of chemicals and in addition to the change of chemicals should also be examined.

Liquid compounds are kept in the bag of processing machines and are used for processing. Reducing the capacity of these bags leads to the reduction in the amount of a liquid compound abandoned at the replacement and of such compound with a different one contributes to the significant decrease of pollution load.

(3) Examination of materials for dyeing

A considerable percentage of the pollutants in the dyeing plants is from the spinning and weaving processes. Sizing agents from the desizing process and oil from the scouring process are such examples. It might be difficult for the dyeing industry, whose majority of business is entrusted processing business, to reduce the consumption of such agents; however, tracing back to the above-mentioned processes to find measures coping with the situation, taking into consideration the whole textile consideration.

(4) Recovery and reuse

Recovery and reuse of pollutants in wastewater brings about a considerable reduction in pollution load. The recovery of the sizing agent from wastewater produced from the desizing process, caustic soda from the wastewater in mercerizing process, and certain dyes from the dyeing process have already been attempted. However, very few chemicals are remunerable when recovered and reused. It is only caustic soda that might be remunerable when recovered of the decrease in the amount of sulfuric acid to be used for neutralization in the waste water treatment.

With regard to the scouring and bleaching liquids that are kept in the bag of the processing machine, careful handling is required. A light pollution load and small dosages of chemical agents are expected, if wastewater is treated with these treatments in the ascending order of concentration and only the chemicals running short are replenished and the waste of liquid in bag is minimized. In this case, the apparatus to measure the concentration of each chemical and to control chemical consumption would be necessary.

3.3.3 Summary of the measures to be taken in the processes

In the above sections, the measures to reduce wastewater up to the point of the treatment of wastewater are described from two different viewpoints: the reduction of wastewater and the lowering of concentration of wastewater. Table 3.3.1 shows the summary of measures to reduce pollution load of the wastewater in each process.

[Reference]

Reference 1: Maki et al, "Industrial Pollution", 24, 341 (1988)

Table 3.3.1. Summary of Remedies to Reduse Pollution Load of Wastewater in each Process

Process	Selecting and saving of chemicals	Saving of process water	Improvment of process & equipment	Throughgoing of control	Separation of treatment for concentrated & diluted waste water
Desizing	Improvement of desizing agent		Raising the efficiency of water washing & dehydration		
Scouring Bleaching	Quantifing proper for scouring & bleaching agent	Raising the efficiency of water washing & dehydration	Continueing & recycling		Recycling of process water & separation of washing water
Dyeing	Improvement & quantifing proper for processing aid & auxiliary (level dyeing agent, dispersant agent, color former & mordant)	Lowering the liquor ratio Swich the overflow-washing to batch-washing	Utilizing low liquor ratio dyeing, buble dyeing, nonaqueous dyeing & radio frequency heating	Qualifing the operating temparature, pressure & time schedule	Recycling of dyeing liquor effluent Separation of washing water
Printing	Improvement & quantifing proper for processing aid & auxiliary (level dyeing agent, dispersant agent, color former & mordant)	Correcting of liquid ratio Swich the overflow-washing to batch-washing	Raising the efficiency of printing, heeting, water washing & dehydrating Utilizing radio frequency heating	Qualifing the operating temparature, pressure, time schedule, wringing condisition	Separation & recycling of remained sizing agent, dye & pigment
Finishing	Improvement & quantifing proper for processing aid, auxiliary & sub-material	Correcting of liquid ratio	Raising the efficiency of treatment, finishing & dehydrating	Qualifing the operating temparature, pressure, time schedule, wringing condisition	

3.4 Wastewater Treatment

An outline of the unit treatment and operation in the wastewater from dyeing is described herein, and, the wastewater treatment in the general dyeing factories is also explained with examples.

3.4.1 Outline of the treatment of wastewater from dyeing

The dyeing industry is one of the water consuming industries and the wastewater treatment process varies according to the textile and processing method. Dyeing industrial waste water has following features.

(1) Wastewater per output is of large quantity.

(2) Timewise fluctuation in water quality and quantity are wide.

(3) Various chemicals are contained.

(4) Irresolvable organic substances, surface active agents(foam), and dyes (coloring) are contained.

(5) Heavy metals and organic chloride are occasionally contained.

(6) A large amount of reducing inorganic chloride (sulfur compound) is contained.

Organic substances such as pH, BOD and COD have so far been under control mainly for living environmental protection in Japan. However, in recent years, coloring forming in addition to the above-mentioned substances have been taken up as problems. Coloring and foaming in the dyeing wastewater are attributable to the dyes and auxiliaries. They exist in extremely small amount as organic substances to constitute BOD and COD, but, since biological resolution is difficult, they are regarded as irresolvable. Furthermore, since the components that cause coloring and foaming coexist with other organic substances of high concentration in many cases, selective removal is very difficult.

There is no special method of treating dyeing wastewater. The reality is that the conventional treatment technologies are combined to meet the requirement of the object plants according to the waste water features and drainage standard.

The present main processes of the treatment of dyeing waste water are aerobic bacteria treatment processes represented by the activated sludge process, sedimentation and surface separation process by coagulant, activated carbon adsorption process and chemical oxidization by ozone. In general, the bacteria treatment process is employed for the removal of BOD and other treatment processes are employed for the removal of COD and color components. To attain high removal rate of the COD and coloring as well as BOD components, the single treatment is not feasible technically or economically and it is more likely to combine several processes to that end.

3.4.2 Unit process and operations in the dyeing wastewater treatment

Generally, the wastewater treatment process can be classified into the two: physical or chemical treatment and biological treatment; but, fundamentally, they consist of 1) dissolution or digestion of pollutant 2) separation or removal 3) neutralization. In the following part unit-by-unit treatment and process operation in the dyeing wastewater treatment are explained.

(1) Screening

A. Objective

Removal of the coarse out of SS such as (fiber flocks, cloth clocks and others)

B. Equipment

Bar screen, mesh screen, drum screen and others.

C. Problem and consideration

Since most of the main pollutant in the dyeing wastewater can be are dissolved or colloidal, screening is not highly effective in reducing pollution. If the mesh opening is inappropriate, even the flock cannot be removed. However, it is important as the pre-treatment of wastewater. The wastewater is usually treated through the wide mesh first and then through the fine mesh. The screen is easily clogged (especially in the case of the adhesive substance such as sizing scum); therefore that careful washing is required.

(2) Natural sedimentation

A. Objective

Removal of medium-size SS (flocks, sand, sizing scum and others)

B. Equipment

Sedimentation basin and clarifier

C. Problem and consideration

Separation efficiency is not high with very high current speed. The structure of the equipment should facilitate the removal of the sludge.

(4) Coagulation sedimentation and coagulation flotation

A. Removal of particle-sized SS, colloidal substances, oil substances, BOD and COD (dye, pigment, sizing agent, resin) and others.

B. Equipment

Horizontal type, slurry recirculation type, sludge blanket type, and cylinder type

C. Problems and matters to be considerated for

many of the direct dyes and acidic dyes are soluble substances. Other dyes do not readily dissolve because of the operation of the dyeing process, but they do not precipitate easily but are dispersed as particles. Additionally, cohesion efficiency declines, affected by the surface active agent. Therefore, in some cases excessive coagulant is added ,which leads to the increase in the amount of sludge and chemical costs. Agglutination is influenced by the liquor temperature, features of the pollutant and concentration. Consequently, it is absolutely necessary to conduct a prior survey and analysis without imitating the other cases to decide on the operation conditions such as optimum coagulant, the procedure of coagulant addition, and the amount of addition (inorganic substances 200-1,000 mg/l for inorganic substances and 1-3 mg/l for organic substances). Wit regard to the retention time (5-10 min.) and revolution speed (10-60 cm/min.) of agitator, the optimum conditions should be decided on after the test of flock growth.

In the selection of the coagulant, it is better to use a high polymer coagulant together to reduce amount of the sludge to a minimum when the treatment costs for sludge is taken into consideration.

Inlet and outlet of the sedimentation basin should be cleaned for prevention of the short flow turbulent flow and the scum should be removed completely. Also, the removal of the accumulated sludge on the inclined plate is necessary and due attention should be paid to the maintenance of the sludge collector and any overload in the case of power failure.

For the pressure flotation basin, it is more effective to use the new water because the amount of air solved in the water is in proportion to the pressure and in inverse proportion to the temperature. Attention should be paid to the flock so that it may not destroyed in entering the flotation basin , and, the water surface and the skimmer should be carefully adjusted.

Decolorization by coagulation treatment is possible for the disperse type dyes such as disperse dyes and the vat dye with the decolorization effect of around 90%, but for the water soluble type dyes such as reactive, acidic and direct dye, the separation by coagulation is difficult. However, when the ferrous sulfate is used as coagulant, its reducing process functions for decolorization. In many cases, 600 mg/l of ferrous sulfate or 200 mg/l of calcium hydroxide is used. In the sulfuric acid band, along with the liquid temperature, the solubility of the flock rises and the decolorization effect declines. Therefore, careful temperature control is required.

(5) Neutralization and pH adjustment

A. Objective

Neutralization or pH adjustment

B. Equipment

Neutralization tank and others

C. Problem and materials to be considerated for

Electrode should be cleaned once a day and should be checked by the standard liquid once a month, because colloidal substances such as sizing agent tend to cover up the pH electrode and hamper the accurate indication.

(6) Biological treatment

A. Objective

Removal of soluble BOD and COD (acetic acid, sericin and others) and colloidal BOD and COD components (starch paste and others)

B. Equipment

Diffused aeration tank, contact aeration tank, trickling filter, and rotating disk contactor, etc.

C. Problem and matters to be considered for

There are activated sludge process, contact aeration process, trickling filter process and rotating disk contactor process. The biological treatment is more effective for the wastewater with higher BOD such as the desizing wastewater for cotton. However, it is difficult to treat dyes, aromatic compounds, ABS, and synthetic pastes(PVA, etc.) in general. In order to raise the treatment efficiency, the aeration tank should retain the untreated water for at least 5-6 hours with the proportion between BOD, nitrogen, and phosphorus at 100: 5: 1. The appropriate pH is 6-7 and water temperature is 20-30°C. It is desirable to maintain the DO concentration at the outlet of the aeration tank at 4-5 mg/l in terms of the prevent ion against bulking. In order to prevent bulking, it is also necessary to maintain the quality and quantity of the wastewater without any sudden fluctuation.

Biological treatment process is an effective measure to remove BOD in the wastewater and there are many actual cases with the dyeing wastewater treatment. However, pollutants in the dyeing wastewater have some components to inhibit the microbic activity. In planning on wastewater treatment, cultivation and treatment tests for sludge should be conducted, in case of the wastewater containing any inhibitors the preventive substance the appropriate pre-treatment process should be reviewed.

For example, the oxidizer represented bleaching powder, soda and hypochlorite, hydrogen peroxide in the wastewater from the bleaching process can be the inhibitory substance for the microbic activity, depending on its concentration. In such a case, as a pre-treatment prior to biological treatment, it is necessary to conduct a treatment of reduction by using sodium sulfite in advance. In the dyeing and processing plant for cotton, strong alkaline wastewater is discharged from the marcerizing process and the dyeing process using reactive dye. If they flow directly into the biological treatment equipment, it would be the shock load to the microorganism; therefore,prior neutralization is necessary.

Considerable amounts of irresolvable substances such as synthetic paste (PVA, etc.), dye, surface active agent are contained in the dyeing waste water. Especially, PVA is frequently used as the sizing agent in the yarn testing process and it increases the COD value in the wastewater in the plant that has the desizing process. Consequently, PVA becomes a great obstacle for COD reduction by biological treatment. Concentrated organic substances and surface active agent are rather small in the dye, but they are the cause of coloring and foaming in the treated water. physic chemical treatment in addition to biological treatment is required to remove these irresolvable substances.

(7) Sedimentation

A. Objective

Separation of SS (sludge) after biological treatment

B. Equipment

Sedimentation basin, clarifier

C. Problems and matters to be considered for

The retention time of the treated water should be 3-4 hours and surface load should be 20-40 m^3/day. Sludge collected is constantly sent back to the biological treatment process by the rake as returnable sludge to stabilize the biological treatment. It is also necessary to set up a dam to prevent any floating sludge from overflowing.

(8) Ozone oxidization

A. Objective

Taking advantage of the oxidative power of ozone, irresolvable organic substances in waste water should be oxidized and dissolved, and decolorized as well as simultaneously.

B. Equipment

Ozone generator + ozone reaction tower

C. Problems and Matters to be considered for

The key is how to make ozone and wastewater contact each other and the react in an efficient manner. For the treatment of the dyeing wastewater, the diffuser method and the injection method are widely adopted. The injection amount of ozone is determined based on the COD value. Concerning the diffuser method, since injection gate of ozone and inflow gate of the treated water are situated separately, the gaseous amount should be changed according to the pollution amount. The injection method, the ozone concentration should be determined according to the pollution amount because the gaseous amount is stable.

The ozone injection amount is set at 35 mg/l for less than 80 mg/l of COD, 45 mg/l for 80-130 mg/l of COD, and 50 mg/l for 130-200 mg/l of COD and contact time is set at 25 min. as the standard.

Ozone oxidization is effective not only in decolorization but also in COD removal. BOD, however, occasionally increases, and thus,thorough preliminary tests should be conducted. It is rare to employ ozone treatment alone but it is employed together with the activated carbon adsorption process.

Attention should be paid to the fact that ozone treatment makes the treated water foamy and trivalent chrome can be oxidized into hexavalent chrome in alkaline.

(9) Fenton oxidation

A. Objective

Irresolvable organic substances in wastewater should be oxidized and decolorized as well simultaneously.

B. Equipment

Fenton oxidization tank

C. Problems and Matters to be considered for

Fenton oxidization is oxidation-dissolution reaction of organic substance, using radical hydroxyl that is generated through the reaction of hydrogen peroxide and ferrous substance (Fenton reagent). Its oxidizing capability is equal to ozone's and it is highly effective in decolorization and the removal of COD, but it produces a large amount of sludge.

(10) Other oxidization treatment

A. Objective

Removal of soluble BOD and COD components and color

B. Equipment

Ultra-violet radiation tank, electrolytic bath

C. Problems and matters to be considered for

There are several process of using oxidizer such as soda hypochlorite, using UV oxidization process, electrolytic oxidization and coagulation.

The UV method is not advantageous when oxidizing deeply colored wastewater because of its narrow range of transmission,

With UV only oxidization speed is so that oxidizer such as chlorine is added. It is not suitable for treatment involving a large amount of treatment.

In the electrolytic oxidation and electrolytic oxidation-coagulation, an electrochemical oxidative reaction is tiggerd on the anode and an oxidatve reaction is triggered on the cathode by chlorine generated. Neither method is suitable for treatment involving a large amount of wastewater.

(11) Reduction treatment

A. Objective

Removal of color, etc

B. Equipment

C. Problems and matters to be considered for

There are some cases where hydrosulfite is used for decolorization reaction. This method is effective in decolorization and produces no sludge, but an inappropriate amount in addition increases COD; therefore, care should be taken in handling hydrosulfite.

(12) Activated carbon adsorption treatment

A. Objective

Adsorption and removal of surface active agent and dye, and removal of COD.

B. Equipment

Fixed bed adsorption tank, moving bed adsorption tank, fludized bed tank, etc.

C. Problems and matters to be considered for

Application and efficacy differ according to the form and kind of the activated carbon (granulated or powdered type). Usually, it is more common to use granulated activated carbon because of its easiness in recycling. In order to fill in the column, the fixed bed type or the moving bed type is employed. In fixed bed type, it is better to apply the upstream for current type when the velocity of the current is and apply the downstream current type when the high velocity is high, and, the activated carbon should be replaced with a new one and recycled when adsorption turns saturated. As for the moving bed type, the activated carbon near the inflow gate turns saturated adsorption first, and thus, the activated carbon in this area should be discharged and recycled continuously or intermittently and then should be reduced at the outflow gate for continuous treatment.

In deciding on the treatment facilities for the dyeing wastewater, it is necessary to choose the optimum combinations among unit-by-unit and equipment in consideration of the characteristics of the effluent, quality of the treated water, construction costs and operating costs.

3.4.3 Examples of combination among unit process and operations in the dyeing wastewater treatment

Combinations among unit process and operations that are explained in the above section and examples of application to the dyeing wastewater treatment are describe in this section.

(1) Coagulation and floatation process (Reference 1)

Process	Bleaching, dyeing and sizing for the cotton yarn
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dyeing process (reactive dye is employed) Drainage from the sizing process
Treated amount	600-800 m^3/day
Flowchart	Fig. 3.4.1
Water quality	Table 3.4.1

(2) Coagulation and floatation process + ozone oxidization process (Reference 1)

Process	Printing of cotton fibrics
Wastewater	Drainage from the printing process (reactive dye and pigment are employed)
Treated amount	180-250 m^3/day
Flowchart	Fig. 3.4.2
Water quality	Table 3.4.2

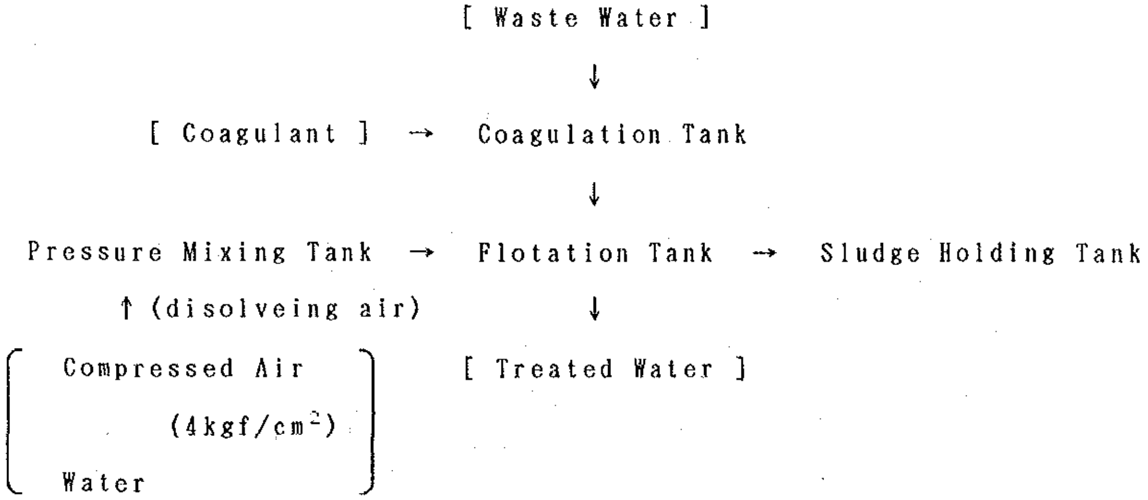


Fig. 3.4.1. Flow Diagram of Coagulation and Flotation Treatment

Table 3.4.1. Quality of Wastewater and Treated Water
(Coagulation and Flotation Treatmnt)

Items		Waste Water	Treated Water
BOD	[mg/ℓ]	500	60 - 75
COD	[mg/ℓ]		85 - 100
SS	[mg/ℓ]		70 - 80
n-Hex	[mg/ℓ]		5 - 20

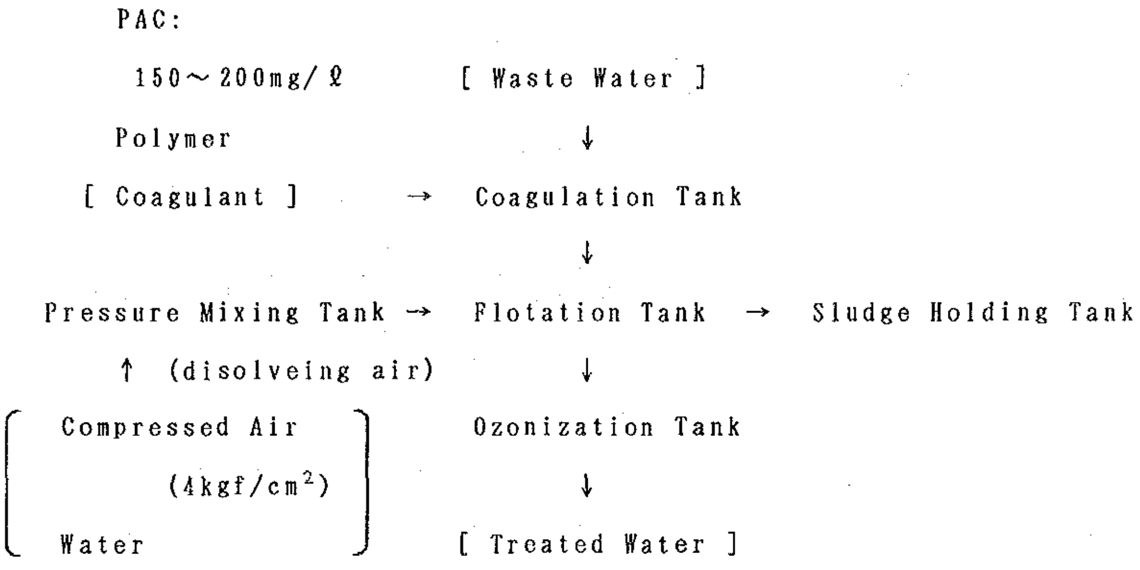


Fig. 3.4.2. Flow Diagram of Coagulation, Flotation and Ozonization Treatment

Table 3.4.2. Quality of Wastewater and Treated Water (Coagulation, Flotation and Ozonization) Treatment

Items	Waste Water	Treated Water
BOD [mg/ℓ]	250 - 350	80 - 130

(3) Coagulation and sedimentation process + ozone oxidization process (reference 1)

Process	Bleaching, dyeing and finishing of acrylic fibers
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dyeing process (cation dye and dispersed dye are employed) Drainage from the softening process
Treated amount	500 m^3/day
Flowchart	Fig. 3.4.3
Water quality	Table 3.4.3

(4) Activated sludge process + coagulation sedimentation process 1 (reference 1)

Process	Bleaching and dyeing of cotton yarn and textile (printing and dipping dyeing)
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dipping dyeing process (reactive dye is employed) Drainage from the printing dyeing process (reactive dye is employed)
Treated amount	270 m^3/day
Flowchart	Fig. 3.4.4
Water quality	Table 3.4.4

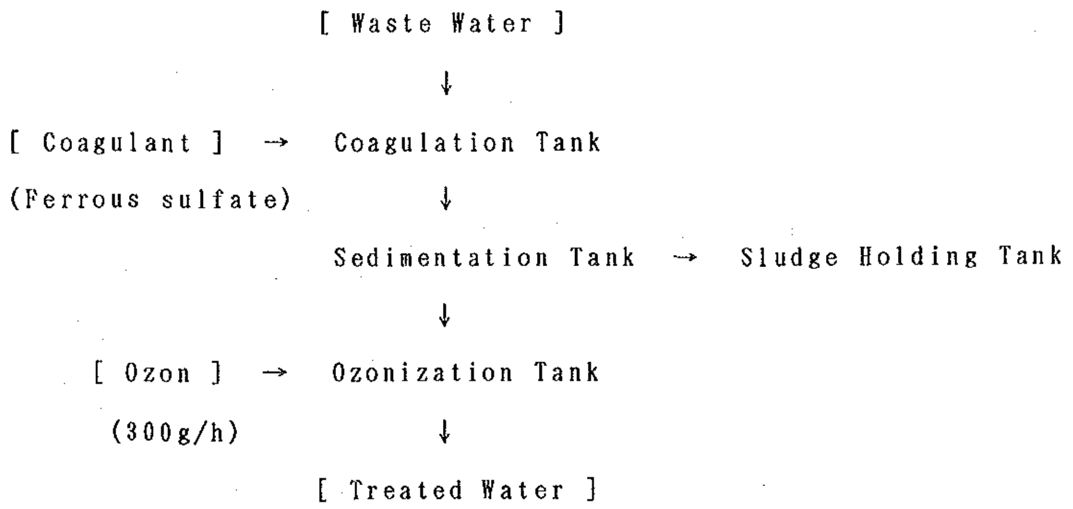


Fig. 3.4.3. Flow Diagram of Coagulation, Sedimentation and Ozonization Treatment

Table 3.4.3. Quality of Wastewater and Treated Water (Coagulation, Sedimentation and Ozonization Treatment)

Items	Waste Water	Treated Water
BOD [mg/ℓ]	100	50 - 70
COD [mg/ℓ]	120	

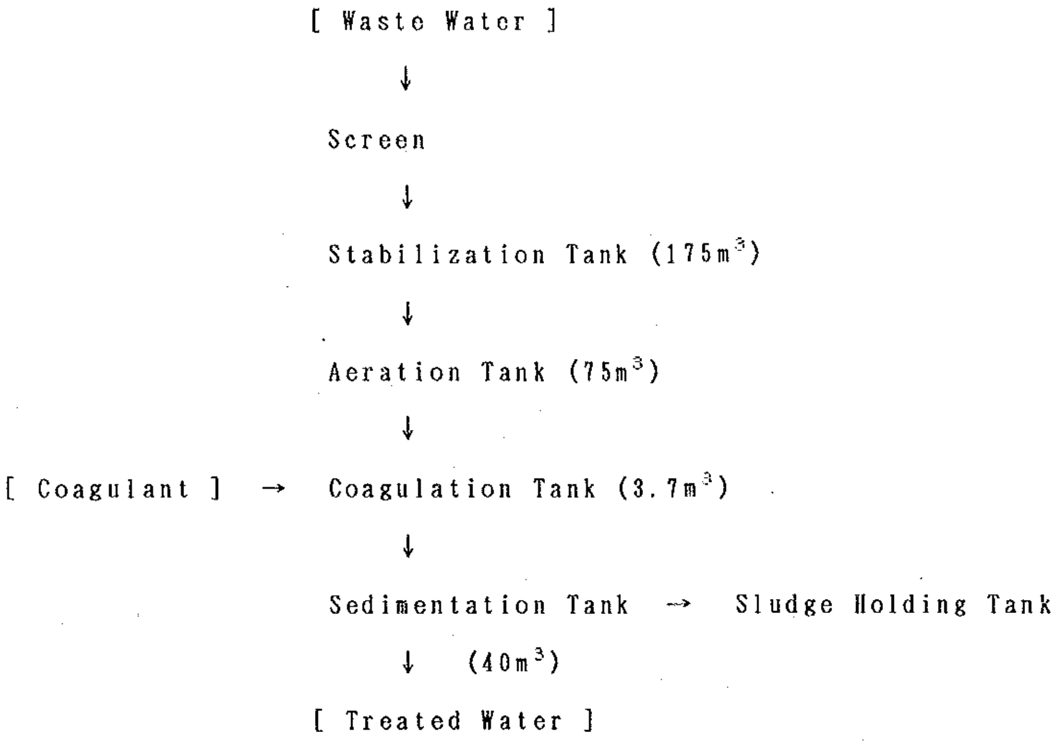


Fig. 3.4.4. Flow Diagram of Activated Sludge, Coagulation and Sedimentation Treatment (No.1)

Table 3.4.4. Quality of Wastewater and Treated Water (Activated Sludge, Coagulation and Sedimentation Treatment(No.1)

Items		Waste Water	Treated Water
BOD	[mg/ℓ]	300	15
COD	[mg/ℓ]	450	70
SS	[mg/ℓ]	50	
n-Hex	[mg/ℓ]	20	

Others	Sludge conversion ratio of BOD is about 39%. For the better separation of solid and liquid, coagulation sedimentation process is adopted subsequently.

(5) Activated sludge process + coagulation and sedimentation process 2

Process	Dyeing of polyester/rayon mixed textile
Wastewater	Mixed drainage (dispersed dye and direct dye are employed)
Treated amount	1,000 m^3/day
Flowchart	Fig. 3.4.5
Water quality	Table 3.4.5
Others	Cation coagulant is used for the removal of the color. Bulking occurs in using the sulfide dye. Defoaming agent is used for the effervescent problem.

(6) Activated sludge process (+ preliminary ozone oxidization) (Reference 1)

Process	Printing of cotton textile
Wastewater	Drainage from the printing process (reactive dye and pigment)
Treated amount	350 m^3/day
Flowchart	Fig. 3.4.6
Water quality	Table 3.4.6

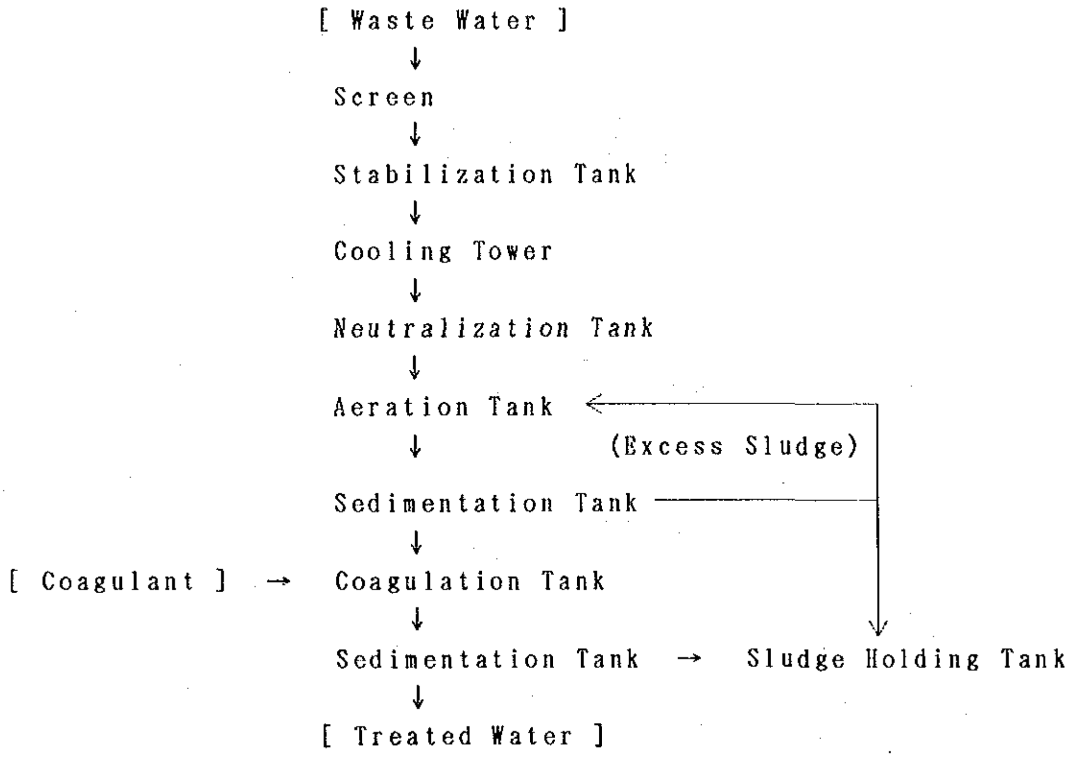


Fig 3.4.5. Flow Diagram of Activated Sludge, Coagulation and Sedimentation Treatment(No.2)

Table 3.4.5. Quality of Wastewater and Treated Water (Activated Sludge, Coagulation and Sedimentation Treatment(No.2)

Items		Waste Water	Treated Water
pH	[-]	6 - 13	6 - 7
BOD	[mg/ℓ]	214	20
COD	[mg/ℓ]	281	100
SS	[mg/ℓ]	40	20
n-Hex	[mg/ℓ]	32	<1
Temp.	[°C]	50	35

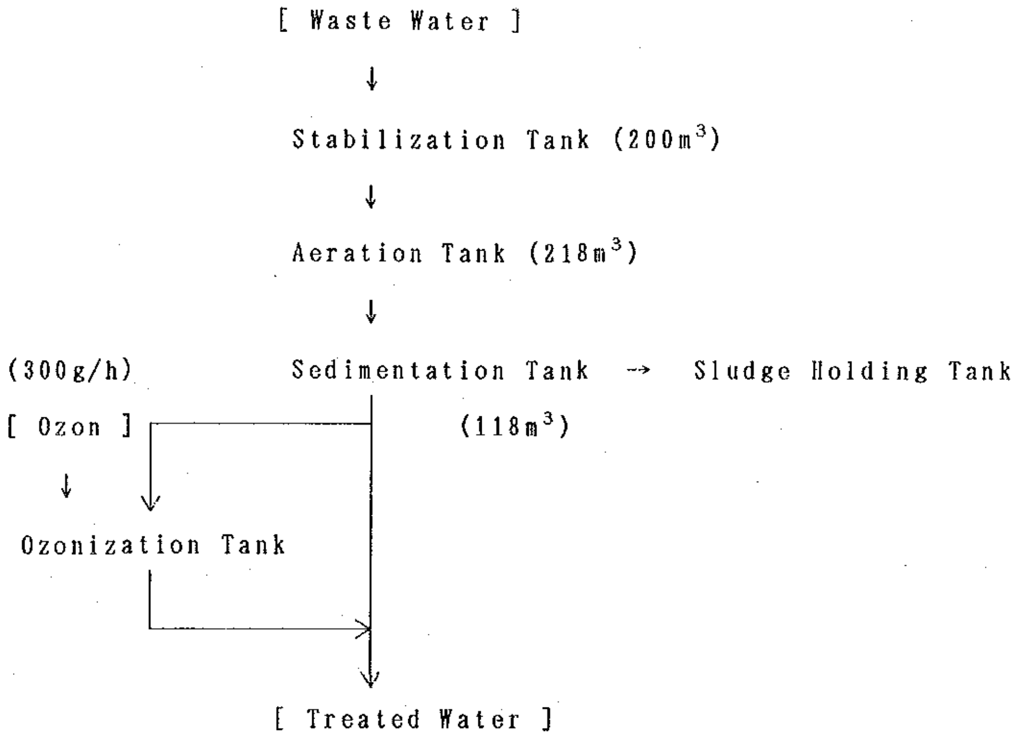


Fig. 3.4.6. Flow Diagram of Activated Sludge (+Ozonization)Treatment

Table 3.4.6. Quality of Wastewater and Treated Water
(Activated Sludge +OzonizationTreatment
Treatment

Items	Waste Water	Treated Water
BOD [mg/ℓ]	545	30
COD [mg/ℓ]	200	70 - 90
n-Hex [mg/ℓ]	30	

Others	Ozone oxidization equipment is prepared for the case of insufficient decolorization.

(7) Activated sludge process+ activated sludge process (Reference 1)

Process	Bleaching, dyeing and finishing of the acrylic fabrics
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dyeing process (cation dye and dispersed dye are employed) Drainage from the softening process
Treated amount	750 m^3/day
Flowchart	Fig. 3.4.7
Water quality	Table 3.4.7
Others	The amount of the excessive sludge is 100ton/year (water content 82-83%). In order to dear with the increased drainage with the increase in process amount, the aeration, the aeration tank is additionally installed.

(8) Trickling filter process (Reference 1)

Process	Bleaching and dyeing of cotton textile
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dyeing process
Treated amount	400-500 m^3/day

[Waste Water]

↓

Stabilization Tank (600m^3)

↓

1st Aeration Tank (200m^3)

↓

2nd Aeration Tank (200m^3)

↓

Sedimentation Tank → Sludge Holding Tank

↓ (280m^3)

[Treated Water]

Fig. 3.4.7. Flow Diagram of Tow Step Avtivated Sludge Treatment

Table 3.4.7. Quality of Wastewater and Treated Water
(Tow Step Activated Sludge Treatment)

Items	Waste Water	Treated Water
BOD [mg/ℓ]	100	1 ~ 3
COD [mg/ℓ]	120	33 - 46
n-Hex [mg/ℓ]		22 ~ 27

Flowchart	Fig. 3.4.8
Water quality	Table 3.4.8

(9) Rotating disc contactor process + coagulation sedimentation process

Process	Dyeing of acrylic, woolen and cotton yarn (bleaching is applied in part)
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the bleaching process Drainage from the dyeing process (cation dye, reactive dye, and direct dye are employed.)
Treated amount	600 m^3/day
Flowchart	Fig. 3.4.9
Water quality	Table 3.4.9
Others	When cation dye and direct dye are used, sulfuric band is used as the coagulant and when reactive dye is used, cation coagulant is used.

(10) Coagulation and pressure floatation process and activated sludge process

Process	Marcerizing and printing of cotton textile
Wastewater	General drainage sorted into the following two processes 1) Activated sludge treatment process is adopted for the drainage from the marceriz-

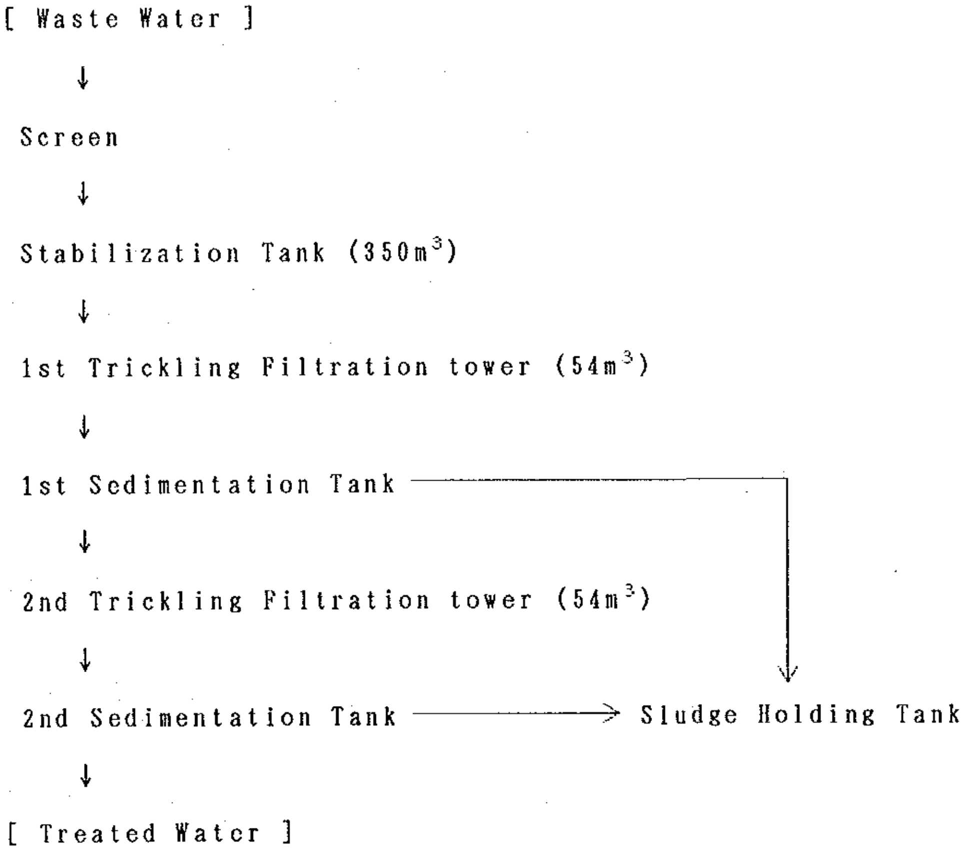


Fig. 3.4.8. Flow Diagram of Trickling Filtration Treatment

Table 3.4.8. Quality of Wastewater and Treated Water (Trickling Filtration Treatment)

Items		Waste Water	After 1st Sedimentation	Treated Water
pH	[-]	7.8	7.9	
BOD	[mg/ℓ]	160	100	60
COD	[mg/ℓ]	220	180	135
SS	[mg/ℓ]	55	55	
n-Hex	[mg/ℓ]	30	17	

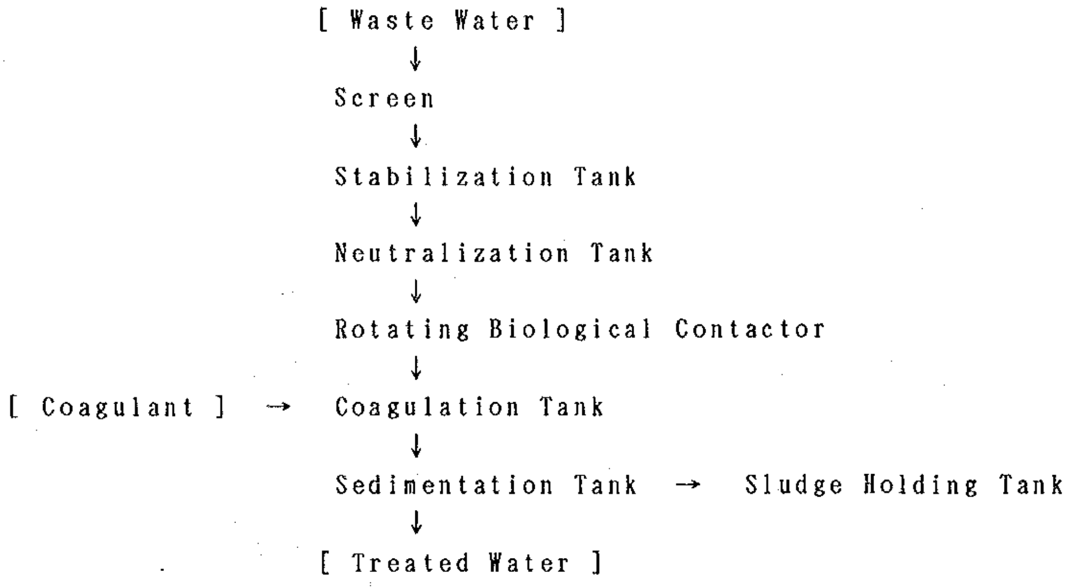


Fig. 3.4.9. Flow Diagram of Rotating Biological Contacting, Coagulation and Sedimentation Treatment

Table 3.4.9. Quality of Wastewater and Treated Water (Rotating Biological Contacting, Coagulation and Sedimentation Treatment)

Items	Waste Water	Treated Water
pH [-]	4 - 10	6 - 7
BOD [mg/ℓ]	110	17
COD [mg/ℓ]	180	60
SS [mg/ℓ]	20	20
n-Hex [mg/ℓ]	22	7
Temp. [°C]	26	25

ing process.
2) Coagulation and pressure floatation process + activated sludge process are adopted for the drainage from the printing process.

Treated amount	5,400 m^3/day
Flowchart	Fig. 3.4.10
Water quality	Table 3.4.10

(11) Activated sludge process + contact aeration process + coagulation and sedimentation process + activated carbon adsorption process

Process	Scouring, dyeing and finishing of polyester textile
Wastewater	Mixed drainage from the processes mentioned as follows: Drainage from the scouring process Drainage from the dyeing process (dispersed dye is employed.) Drainage from the finishing process
Treated amount	630 m^3/day
Flowchart	Fig. 3.4.11
Water quality	Table 3.4.11
Others	Since this plant conducts the raw material processing, hydrolytic substances in fibers (ethylene glycol and terephthalic acid) are included in the drainage from the scouring process, and water, is highly polluted. However, since the drainage standards are strict, highly advanced treatment of COD is

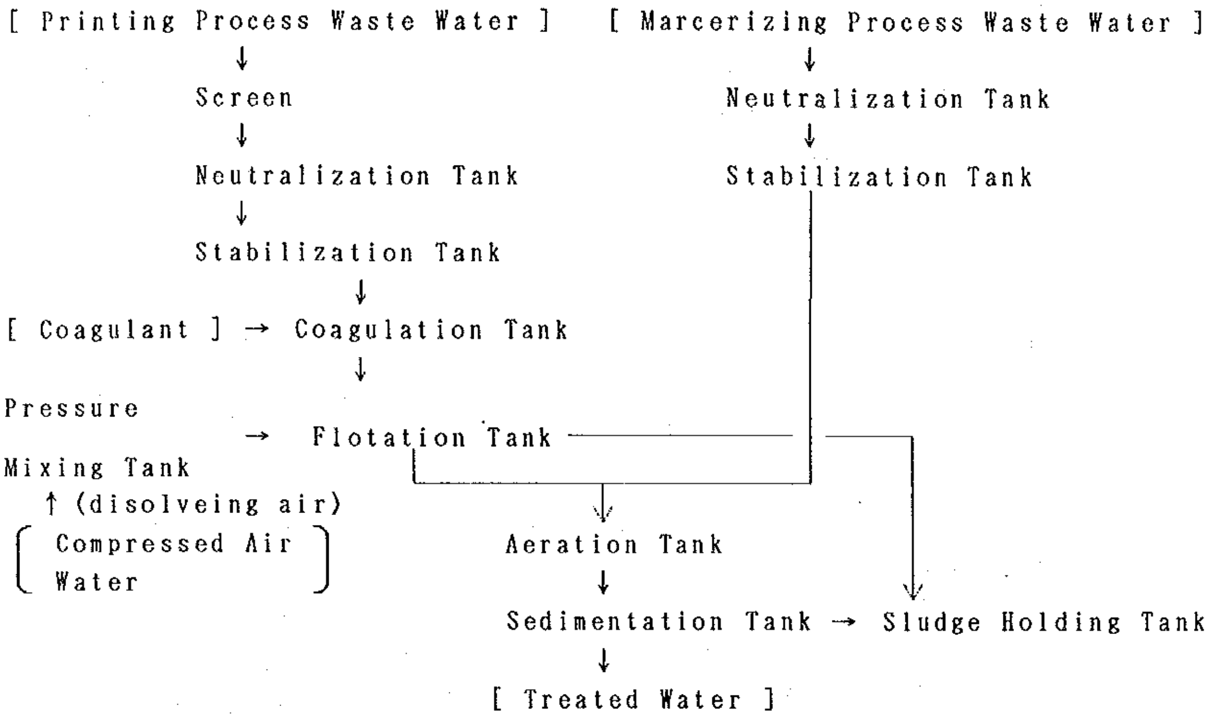


Fig. 3.4.10. Flow Diagram of Coagulation, Flotation and Activated Sludge Treatment

Table 3.4.10. Quality of Wastewater and Treated Water (Coagulation, Flotation and Activated Sludge Treatment)

Items		Printeing Procrss Waste Water	Marcerizing Process Waste Water	Treated Water
pH	[-]	8.5	-	6 - 7
BOD	[mg/ℓ]	120	60	18
COD	[mg/ℓ]	260	70	45
SS	[mg/ℓ]	80	15	20
n-Hex	[mg/ℓ]	35	-	3

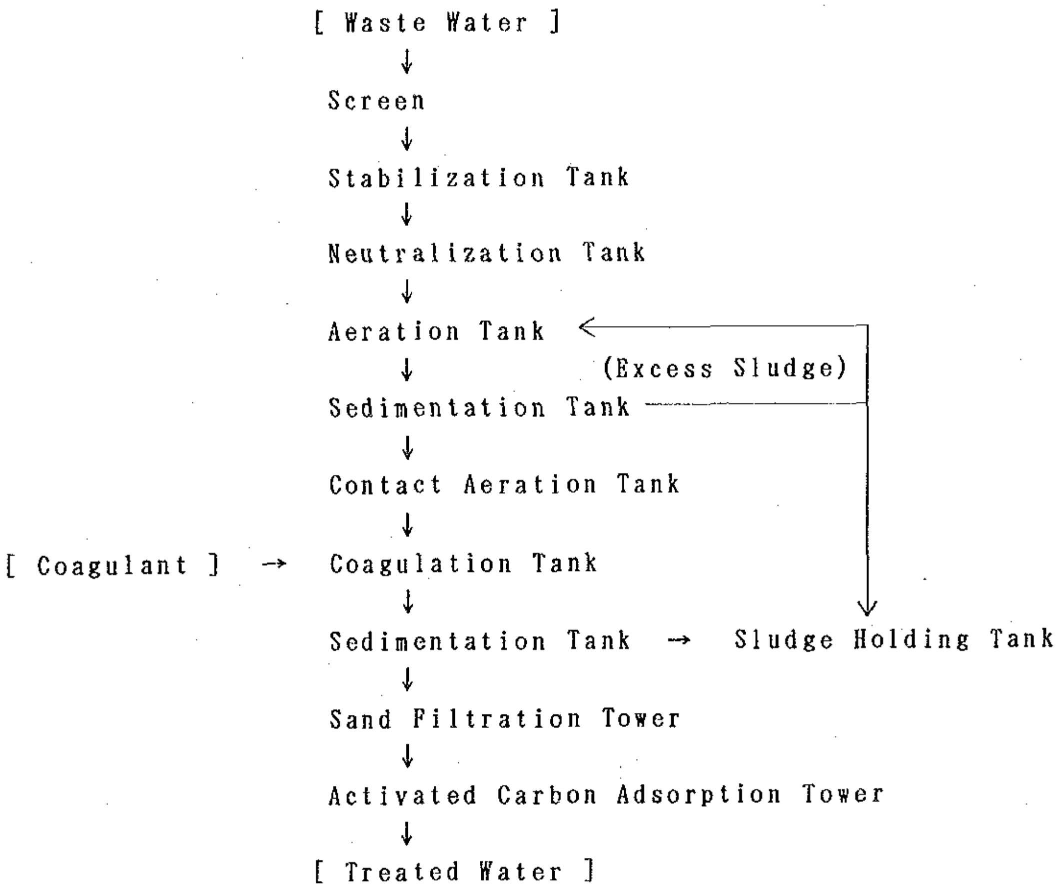


Fig. 3.4.11. Flow Diagram of Activated Sludge, Contact Aeration Coagulation, Sedimentation and Adsorption Treatment

Table 3.4.11. Quality of Wastewater and Treated Water (Activated Sludge, Contact Aeration Coagulation, Sedimentation and Adsorption Treatment)

Items	Waste Water	Treated Water
pH [-]	12	5.8 - 8.6
BOD [mg/ℓ]	850	< 12
COD [mg/ℓ]	460	12
SS [mg/ℓ]	20	20
n-Hex [mg/ℓ]	22	5
temp. [°C]	35	

conducted.

3.4.4 Items to be considered for in the planning, selection and management of the treatment system

Restricting the subject to the dyeing wastewater treatment, items to be considered are described in the planning, selection and management of the treatment system.

(1) Since the quality and quantity of the wastewater from the dyeing plant fluctuate widely according to the season, the past achievements need to be reviewed and a future plan must be well formulated in planning on wastewater treatment.

(2) In planning on waste water treatment, it is necessary to consider which is more efficient the integrated treatment or treatment by contents, considering the properties of waste water from each process drainage standards, and the possibility of recycling.

(3) Since the treatment process might be restricted by the chemicals used in the processing process, the chemicals to be used in the process should be reviewed carefully from the viewpoint of waste water treatment.

(4) Hazardous substance to affect the human health such as heavy metals might be contained in the drainage because of the consumption of certain chemicals. In such a case the appropriate treatment is required regardless of the drainage amount or the place.

(5) In the coagulation and sedimentation treatment, treatment performance is influenced by the fixed pH value and the temperature in treatment conditions. Consequently, thorough examination in advance is required.

(6) In the biological treatment, since substances that have

adverse effects on the organism might be contained in the drainage, it is necessary to prepare satisfactory countermeasures in advance.

(7) Treatment flow should be decided on, considering the proper ties of the wastewater, drainage standards, and economic feasibility (construction costs and operating costs), etc. The implementation of the table test is prerequisite for the confirmation of treatment capability. The specification of the treatment facility should be decided on based on the results of the table test.

3.5 Reclamation

The reclamation of the wastewater in the dyeing industry as a whole is described in this section.

3.5.1 The status quo of the waste water reclamation

Although the dyeing industry is one of the typical water-consuming industries, there are very few cases where reclamation work the wastewater from dyeing in reality. Main reasons are as follows.

1) The water quality required for the dyeing is very high.
2) Presently, the rate of city water is lower than wastewater treatment costs for reclamation.

In order to implement the reclamation of the wastewater from dyeing, it is necessary to develop advanced treatment technology requiring lower water treatment costs. For the time being, it is considered to remove SS by sand filtration and to conduct high-level decolorization by the ozone oxidization process or the activated carbon absorption process and to reclaim the wastewater to be used in less influential process such as soaping and desizing processes. For more effective water reclamation, it is necessary to sort wastewater by types and to separate it by concentration, and the appropriate treatment process for each wastewater should be adopted.

3.5.2 Some consideration item on the quality of reclaimed water

Items on the required quality for reclaimed water differ depending on the processing process and processing content. However, in addition to items on general drainage standards, the following items on water quality should be considered for, taking account of the influence on the product.

(1) Residue of the general evaporation

Since it is concerned that SS substabces might cause mechanical problems such as the blockade of the nozzle and might adhere to the product, it is necessary to remove SS substances to the level undetectable by the analyzer. It is possible that the soluble substances could have an adverse effect interfering with dyes and auxiliaries when used in the dyeing process. It is more likely that soluble substances erode apparatus and piping in higher concentration. Consequently, it is necessary to remove soluble substances to a maximum before re-use. Yamada (Reference 1) estimates that the maximum conductivity is 1,5000 S/cm when the reclaimed water is used for the process bath of the dyeing itself.

Regarding the facilities to remove soluble substances, demineralizer such as ion exchanger, RO equipment, and evaporator are required after removal of the organic substances and SS substances is completed for the most part.

(2) Color

The color of water does not have serious adverse effect on the product with certain hues, but the color of the reclaimed water (residual dye) might have fatal effects on the product when it is used in the finishing process. Although complete decolorization could be impossible, the water should be decolorized to the level that does not affect the product, or should be used only in the process that does not affect the product.

Regarding the decolorization degree of the reclaimed water, there is no official data at present and it is one of the tasks for the future. In order to decolorize the dyeing wastewater to the level that does not look colored, the quality of the treated water should be less than 10 degree in colorimetry, and less than 0.01 order in maximum absorption of the dissolved coloring component at wave length when measured in adsorbance. However, even at the same absorbance level, the strength of the color felt by the naked eyes differs according to the color. Consequently, the absorbance of the treated water can be relatively high for the blue and greenish color but should be a low value for the reddish color because the red tends to look relatively strong.

Dye concentration in the dyeing wastewater varies according to the kind of dye and the form of the dyeing process, but the general value is around 1,000 mg/l for the drainage from the dyeing process and about 200 mg/l for the general drainage. In general molecular weight of dye is several hundred and molecular absorption coefficient in maximum absorption at wave length is over 10,000 in many cases. Considering these conditions, it is required to attain more than 99.9% of the dye removal rate in the drainage from the dyeing process and more than 99% in the general drainage.

Regarding reclamation and treatment methods, oxidization treatment by ozone and chlorine and activated carbon adsorption treatment are possible. Coagulation treatment and biological treatment are necessary as pre-treatment to reduce treatment costs.

(3) Metals

If iron or manganese is contained in the reclaimed water in the dyeing process, the hue of the product would be influenced. Caution also is required for the heavy metals possibly contained in the reclaimed water which might react with other chemicals.

As for the treatment facilities, demineralizer that is described in (1) is required.

(4) Hardness components

Hardness components such as calcium and magnesium adhere to the surface of the product as scale and cause uneven dyeing. It is also possible that they have adverse effects on the surface active agent and finishing chemicals.

(5) Others

1) pH is a very important factor and it should be kept around

neutral.

2) Since oxidizer and reductant have adverse effects on the chemicals used in the manufacturing process, it is necessary that they should not go into the reclaimed water.

3.5.3 Items to be studied at the reclamation

In planning the re-use of the treated dyeing wastewater within the plant, there are items to be studied on. The following is summary of such items.

1) The treatment system for each process should be planned, re viewing the amount of city water and drainage as well as water quality, and considering the integration opportunities for re-use, process should be derived into two - the process in which reclamation and re-use are supposedly relatively easy and the other in which they are not.
2) The minimum water quality that can be used in each process should be provided.
3) Not only total wastewater treatment but also treatment for each process should be studied on. It is because that this can contribute to the recovery of chemicals and minimize adverse effects even though impurities may exist in the reclaimed water.
4) With regard to the treatment facilities, microfilter (MF) and counter-permeation equipment which have be rapidly developed in the field of water treatment in recent years should be examined in terms of long-range operation, running cost and flexibility of treatment.

3.5.4 Test case of the reclamation of wasters

In the dyeing industry the reclamation of wastewater is at the research stage. The majority of the research is case studies for the water quality and influence of the treated water on the product. What level of reclaimed water can be reused for certain processes and the influence of the reclaimed water on the product when reused in manufacturing process are studied. As for the reclamation process,

1) ozone treatment
2) activated carbon adsorption treatment
3) membrane treatment such as ultrafiltration(UF) and reverse osmosis(RO)

have many cases being studied.

Nagasawa (Reference 2) estimates the costs for reclamation tests conducted for the wastewater from wool dyeing plants and synthetic fiber dyeing plant. According to the test results, as for the effluent from the woolen textile dyeing factories, it is indicated that the wastewater from the woolen cloth dyeing process can be used for the same process if reclaimed and the wastewater from the crabbing process can be used for the same process if reclaimed and that the total effluent from scouring process be used for the woolen cloth dyeing process after being reclaimed. As for the effluent form the synthetic fiber dyeing factories, it is also indicated that total effluent can be treated with biological treatment, activated carbon and coagulation treatment to be reused in the whole process after being reclaimed.

[Reference]

Reference 1: Yamada, "Water Re-use Technology" 12, 14 (1986)
Reference 2: Nagasawa, "Water Re-use Technology" 12, 33 (1986)

3.6 Sludge Treatment

In Japan, in general, the sludge generated at the treatment of dyeing wastewater is entrusted with outside companies engaged in treatment after dehydration. Outside dealers directly, or occasionally after incineration taken the sludge into the final disposal plant and bury it in the ground.

However, a part of the plants that discharge massive dehydrated sludge have their own incinerators for in-house sludge incineration. Also there are some cases where emission from boiler generated at the time of sludge incineration is used for the neutralization of wastewater. The incinerators are rotary kiln or fluidized bed furnace types. As for other treatment examples, there is also one case where excessive sludge from the aeration tank is returned to dust as fertilizer for the plants. The composition of the sludge in that case is:

Water content : 80.79%
Total carbon : 8.54%
Nitrogen : 1.19%
Phosphoric acid: 0.30%
Potassium : 0.05%
Lime : 0.03%
pH : 4.97

However, it is possible that toxic substances such as heavy metals are contained in the sludge generated in the treatment of dyeing wastewater, and, therefore, great care should be paid in planning on burying sludge.

[Reference]

Reference 1: Maki et al, "Industrial Pollution" 24, 341 (1988)
Reference 2: Onari, "Industrial Water" 403, 29 (1992)

3.7 Direction of New Technologies

The new technologies for future advanced treatment and reclamation are described in this section.

3.7.1 Treatment by the membrane separation process

Wastewater treatment using membrane has been rapidly developed in recent years as means for energy and resource conservation. Membrane separation is applied to wastewater treatment in the form of either UF to separate the solute with molecular weight from 500-1,000 and over or RO to separate the solute with low molecular weight such as inorganic chlorite. Recently, the application of membrane reactor by the combination of the membrane and biological treatment reactor is being practiced.

(1) UF

UF is being practiced for the in manufacturing of ultra pure water, separation and recovery of amino acid and protein, separation and concentration of fermentatable components, concentration of fruit juice and recovery of electrolytic deposition paint. As for application for the treatment of wastewater from the dyeing industry, various issues are studied on such as separation of various dyes and re-use of permeated water out of the dyeing wastewater. There are some plants which have already commercialized the recovery and re-use of PVA from the desizing wastewater through UF. In this particular case, wastewater with 0.1% PVA is concentrated to 10-15 times before re-use. The amount of the permeated water is almost completely maintained and washing should be conducted after a day's work with 90°C hot water to keep the stable function, and, recovery rate of PVA is high, which all means this is a paying business. Regarding the case with S company in the U.S.A., wastewater from the desizing process with 1-1.5% PVA is concentrated to 10% PVA by the UF equipment after the pretreatment to remove fiber flocks by filter action is conducted. However, as for the permeated water, only thermal energy is recovered by the heat exchanger because of the accumulation of the soluble impurities from the process.

(2) RO

RO is used for the desalination of sea water and salt water, manufacturing of ultra-pure water and concentration of juice, coffee, etc. In a water recycling test using the low pressure compound membrane RO of the secondarily treated water, continuous stable operation for 10,400 hrs was recorded and water re-use costs were 68 yen/m^3 and 50,000 m^3/day. Therefore, there a possibility for commercialization (reference 2) and there are also some other cases where RO membrane applied to the recycling of wastewater. With regard to the dyeing industry, research activities are being for the recovery and removal of dyes and surface active agents, and, the feasibility of application wastewater reclamation and re-use is also studied on. However, in the reclamation of wastewater, the treatment of the concentrated water remains as a problem to be reviewed.

(3) Membrane reactor

The application of the membrane reactor technology which is the combination of membrane and biological treatment into wastewater treatment started in the United States in 1960, and, it began to be adopted for the reclamation of building drainage in 1979 in Japan, too. Its compactability and good quality of the treated water have attracted attention. More recently, it has come to be applied to wastewater treatment and human waste treatment, and, the commercialization of the technology has been considered for. Recently according to big project named "Aqua Renaissance '90" by the Ministry of International Trade and Industry in Japan, combined membrane anaerobic bioreactor has been developed and various information is available. The role of the membrane separator in the membrane reactor is to separate bacteria and dissolved substances in the water treated by the reactor and to return the separated concentration liquid to the reactor. Consequently, the concentration of microorganism in the reactor is retained at a high level, and, the retention time of undissolved substances is extended remarkably so that it becomes possible to attain high efficiency of the reactor, improvement of the treated water quality and stabilization of the treatment. However, filtration capability is heavily dependent upon the features of the water to be treated. In order to conduct efficient and stable treatment, either the selection of the appropriate form of membrane that is suitable for the features of pre-treatment is required.

3.7.2 Other technology

Most of the unit-by-unit process and operations in the dyeing wastewater treatment have been well established for years, and, there are few cases where additional technologies for unit-by-unit process and operations have been newly developed since then. As for the direction for the new technologies focused on:

1) improvement of the efficiency of the present unit-by-unit process and operation
2) combination among the present unit-by-unit process and operations

With regard to the improvement of the efficiency of the present unit-by-unit process and operations, for instance, the development of the immobilization of bacteria, AUSB process, UASB process in the field of biological treatment is in progress. The UASB process began to be applied to the treatment of concentrated wastewater from such as the wastewater from in alcohol fermentation in recent years. However, there are no cases where these are applied to the dyeing wastewater treatment so far.

With regard to the combination among unit-by-unit process and operations, "membrane treatment process + biological treatment process" mentioned in the previous section is one of the examples. Besides, "activated carbon absorption process + biological treatment process (BAC treatment process)", "ozone treatment process + UV treatment process" are at the research and development stage.

In "activated carbon absorption process + biological treatment process", microorganism is immobilized with activated carbon as carrier, and pollutants adsorbed to the activated carbon are dissolved by the microorganism cultured on the activated carbon surface. This process was developed as an advanced treatment process for water purification plants but was applied to the dyeing waste water treatment in several cases. It is effective in removing the surface active agent such as ABS as well as color. In "ozone treatment process + UV treatment process" the reactivity of ozone is improved by radiating UV onto ozone for radical formation. The reactivity of ozone improves by the combination with oxidizer such as hydrogen peroxide and chlorine. However it has not been applied to the dyeing waste water treatment.

[Reference]

Reference 1:	Kawasaki et al, "Advance Membrane Separation Handbook" 235 (1987)
Reference 2:	Inoue et al, "Nitto Technology Report" 26, 45 (1988)

3.8 Other Items to be considered For

In the dyeing industry, since the products change every year or every quarter being affected by the external factors such as social development and economic trend, operational conditions and the quality and quantity of the plant drainage are not stable. Another characteristic is a wide variety of chemicals used in the plant. Therefore, it is quite difficult to predict future changes in the dyeing waste water and treatment itself is very difficult to conduct. In the dyeing wastewater treatment, at present, the most common process is the physico-chemical combination of the coagulation and sedimentation (or floatation) process and biological treatment such as the activated sludge treatment process. Usually, each company changes its treatment process in its own way. It seems that there there will be no cases where treatment conditions and process never change since atoll. It is common to plan on wastewater treatment facilities based on long-range plans and socio-economic tendency. However, it is a very macro-view and it is difficult to predict the influence on the present drainage. It is almost impossible to design the facility that can respond to any changes in the future. However, as for the wastewater treatment facilities it is necessary to prepare for the future changes to some degree from the stage of designing, which may highlight several problems in design.

It is expected in future that environmental purification will be globalized and the restrictions against the pollution will be reinforced further. The drainage standards so far have restricted pH, BOD, and COD as living environmental items and heavy metals and toxic substances as health-hazardous, but, recently, nitrogen and phosphorus which are eutrophication substances and surface active agents as foaming components have been focused on as another objects for restriction. Furthermore, in Japan, the recent trend shows that such chemicals as organic chlorine compounds (carbon tetrachloride, etc.) are also included as hazardous substances in the environmental standards, and, sooner or later the similar tendency would also be observed in Korea.

It is technically quite possible to treat wastewater to a higher level than the drainage standard levels and to the level whose water quality is good enough for reclamation. However, at present, such advanced treatment is not easily accessible in terms of costs, As measures to perform better treatment of the dyeung wastewater, the development of economically appropriate advanced treatment equipment is required as well as the review and improvement of the current dyeing process itself.

VI. Introduction of the Japanese astewater Treatment and Reclamation Systems

VI. Introduction of the Japanese Wastewater Treatment and Reclamation Systems

1. Central Wastewater Treatment Systems at Plating Industrial Estate

1.1 Keihinjima Central Plating Industrial Estate

1.1.1 Outline of Keihinjima Central Plating Industrial Estate

Keihinjima Central Plating Industrial Estate was established as part of the Tokyo metropolitan government policy of centralizing pollution-causing factories, comprising twenty-two (22) electro-platers, one (1) metal equipment manufacturer and one (1) metal plating material supplier which all used to exist in cities. (11 companies out of 22 electroplating companies are combined into one (1) cooperative association. Thus, the total number of companies belonging to the association is 14.)

Servie water is being supplied to each office. However, wastewater is treated within the estate and then discharged into the public sewerage.

The following is a profile of Keihinjima Central Plating Industrial Estate:

Location:	2-chome, Keihinjima, Ohta-ku, Tokyo
Establishment:	June, 1977
Area:	19,801m^2
Total Number of Companies:	14
Total Number of Employees:	500 (altogether)

An outline of the companies within the estate is shown in Table 1.1.1.

1.1.2. Survie Water and Wastewater

Table 1.1.1 Outline of Members of Keihinjima Chuo Electroplaters' Society
(Keihinjima Chuo Plating Industrial Estate)

No	Capital of the enterprise (¥1,000)	Number of employees	Item	Contents of plating
1	48,000	43	Electronic calcuculator, NC machine tool	Copper, gold, rhodium, nickel
2	37,500	49	Electronic equipments and parts	Precious metals
3	20,000	30	Home electronics equipment, Parts for motorcar	Plating on plastics, various alloy plating
4	9,000	13	Home electronics equipment, accessories	Copper, nickel, tin, gold, silver
5	40,000	16	Parts for sewing machine, *medical instruments*, lighting equipments	Copper, nickel, chromium, brass
6	8,000	38	Parts for motorcar, parts for home electronics equipment	Metal plating, plating on plastics, copper
7	16,000	15	Chandelier, Lighting equipments, others	Gold, copper, nickel, chromium
8	16,000	47	Parts for communication equipments, precision parts	Copper, nickel, chromium, Zinc
9	2,000	12	Parts for communication equipments, home electronics equipments	Gold, silver, rhodium, solder
10	15,000	19	Audio equipments, combustor	Alumite and color alumite
11	50,000	46	Parts for *precision optical instrument*	Copper, nickel, chromium, gold
12	246,000	62	Parts for motorcar, parts for communication equipment	Preciouis metals, electrodeposition
13	45,000	30	(Other items: Industrial chemicals, adrasives, acid, equipment)	
14	8,000	13	(Other items: Automatic plating equipment, semi-automatic plating equipment)	

This estate is located on an island (Keihinjima) which was reclaimed from Tokyo Port, and, thus, the capacity of water supply and drainage is limited. Twenty-two (22) companies out of all the resident companies used to use 1600m^3 of water a day; however, the amount of water planned to be allocated was only 180m^3 a day. The rationalization of city water usage was, therefore, a key issue. In order to accomplish this, before the resident companies moved in, careful studies were conducted on individual companies' water saving efforts during the manufacturing processes, the first wastewater treatment process for, and complete wastewater treatment at the central wastewater treatment plant.

1.1.3. Cooperative Treatment of Wastewater

(1) Transport of wastewater to the centrak wastewater treatment plant

Wastewater produced at each factory goes through the first treatment process within the factory whenever necessary and is classified by contents and stored in different reservoirs located in each factory and then is transported through pipes to the central treatment plant.

Prior to transport, examinations of the classified wastewaters are conducted. These examinations affect the calculation of the costs for wastewater treatment. The cost of well treated wastewater is lower than that of incompletely treated wastewater.

There are seven (7) transport pipes installed for: 1) cyanide, 2)chromate, 3) acid/alkaline, 4) acid-coppery, 5) chelate-contained, 6) concentrated acid, and 7) nickelous. As for the nickel-contained, because of high temperature of bath, water is used as a supplementary source for bath. Thus,7) is not being treated at present.

Concentrated wastewater and the ion exchanger needing repairing due to deteriorated exchange capacity are transported individually to the central wastewater treatment plant.

(2) Treatment at the central wastewater treatment plant

Three (3) staff members are situated at the central wastewater treatment plant, in charge of the checking of wastewater transport as well as analysis and treatment of wastewater (including the repairing of the ion exchanger.)

A large amount of acid/alkaline wastewater is continuously treated; however, all the rest is treated batchwise system.

Each wastewater treatment method is as follows:

1) Treatment of cyanide wastewater

- Wastewater from washing
  Wastewater is treated with alkaline chlorine oxidation and then undergoes the coagulation sedimentation processes. The treated water is further treated along with acid/alkaline wastewater.
- Concentrated reclaimed water in the ion exchanger
  After electrolysis (collection of coppery substances) is conducted, the wastewater is treated along with wastewater from washing.

2) Treatment of chromate wastewater

- Wastewater from washing, etc.
  After ion exchange is completed, residual substance are neutralized. The treated water is then treated again along with acid/alkaline wastewater.
- Concentrated reclaimed water in the ion exchanger
  Ternary restoration (Recycling of resources)

3) Treatment of acid/alkaline wastewater

a) Drop pH to 3 or below (1st-stage treatment)
b) Add sodium hydroxide and sodium sulfide to raise pH up to about 9 (2nd neutralization process) and treatments by coagu-

lation sedimentation is performed.

c) The treated water is rapidly filtrated and adjusted to the optimum pH and then discharged.

4) Treatment of acid-coppery wastewater

- Wastewater from washing
  After ion exchange is completed, the wastewater is treated
- Concentrated reclaimed water in the ion exchanger
  After electrolysis (collection of coppery substances) is conducted, the wastewater is treated along with acid/alkaline wastewater.

5) Others

In regard to chelete-contained wastewater, after analysis is conducted to confirm the wastewater has really been treated at individual factories, chelate-contained wastewater is duly received and moved into a reservoir for acid/alkaline wastewater awaiting the final pH adjustment. In regard to concentrated acid wastewater, it is used for the first neutralization of acid/alkaline wastewater (for dropping PH to 3 orbelow.)

The amounts of classified wastewaters are as follows:

a) Cyanide:	11m^3/day
b) Chromate:	10m^3/day
c) Acid/alkaline:	100m^3/day
d) Acid-coppery:	3m^3/day
e) Chelating:	3m^3/day

The use of water at the estate and the wastewater treatment system are shown in Figure 1.1.1.

(3) Quality of treated water

The quality of sampled wastewater is shown in Table 1.1.2.

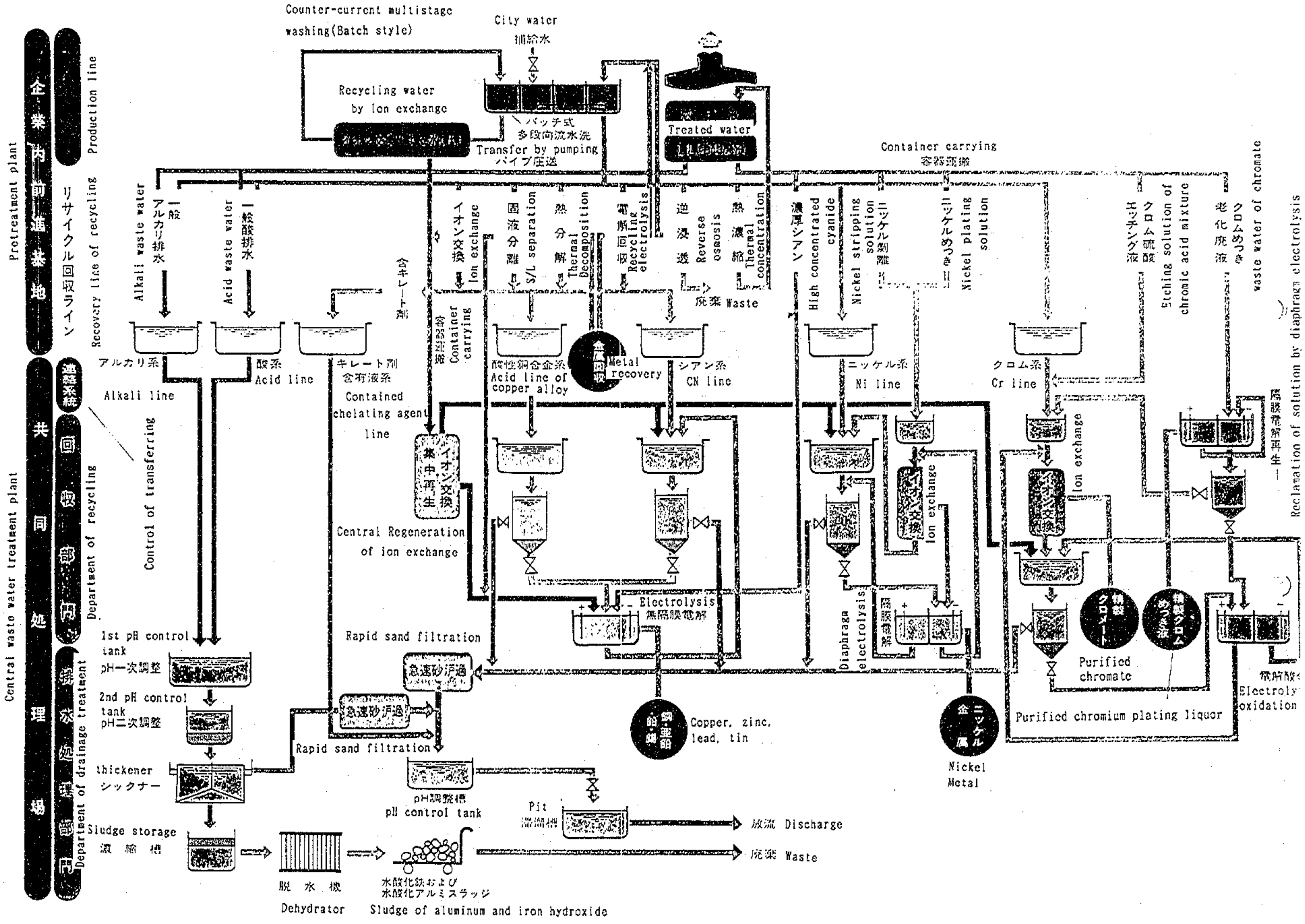


Figure 1.1.1 Waste water treatment system (Keihinjima Chuo Plating Industrial complex)

Table 1.1.2 Quality of water discharged

(Keihinjima Chuo Electroplating Industrial Estate)

Item	pH	Cu	Zn	Fe	T-Cr	Cr	n-Hex	T-CN	F
Quality of treated water	7.1	0.2	0.2	2.0	0.2	0.0	1.6	0.1	2.5
Effluent standard	6~9	3	5	10	2	0.5	30	1	15

Note: Unit used in above table is [mg/l], except one for pH.

Every numerical value shown in the table satisfies the criteria for dischargeable wastewater. (This estate is located in a drainage-provided area; and, thus, wastewater to be discharged must be adequately pollution-free in accordance with the sewage control laws.)

(4) Wastewater treatment costs

The costs of the treatment of wastewater at the estate reach approximately only one (1) percent of the proceeds on the average. The costs used to be three (3) to four (4) percent when the companies were operating individually in cities. Hence, the current situation is considered more favorable to the firms in the estate.

The following are the reasons considered for the materialized retrenchment in wastewater treatment costs:

1) Due to water saving efforts that helped reduce the amount of discharged wastewater, the scale of the wastewater treatment plant can remain small and costs for additional quipment and related extension work can be saved and chemicals used for wastewater treatment can stay at moderate amounts.
2) Joint efforts can save manpower needed for the treatment of wastewater.
3) The amount of city water used in the entire estate has .lm4 reduced to one tenth (1/10) of the previous volume, which helps service water and drainage rates stay one tenth (1/10) accordingly.

1.2. Jonan Denka Cooperative and Higashi-koujiya Plating Center

1.2.1. Outline of the Cooperative

The complex of the cooperative was built for the electro-plating firms in Jonan area in Tokyo in conformity to a master-plan named "Pollution Prevention and Joint Efforts by Tokyo Metropolitan Electro-plating Industry" which was determined at the Tokyo Renovation Promotion Conference held in 1970.

In the beginning, fifteen (15) electro-plating firms expressed their wish to join the cooperative; however, the final decision was reached on the total number of nine (9).

Service water is supplied to each member company, and, wastewater is discharged into the public sewerage after being treated jointly by the complex residents.

The member companies are cooperating in purchasing raw materials, receiving orders and in the research and development of planting technologies in order that they may be able to manufacture more and higher quality products which would not materialize among individual firms before.

A profile of the complex is as follows:

Location: 6-chome, Higashi-koujiya, Ohta-ku, Tokyo
Establishment: September, 1975
Total Number of Companies: 9
Total Number of Employees: 300 (altogether)

An outline of the companies is given in Table 1.2.1.

1.2.2. Service Water and Wastewater

As mentioned above, each firm in the complex uses service water, and wastewater produced is treated by all resident companies in cooperation.

In order to realize a plan to establish a complete "pollution-free plating center," four-or-more-stage countercurrent

Table 1.2.1 Outline of Members of Keihinjima Chuo Electroplaters' Society (Jonan Denka Association)

No	Capital of the enterprise (¥1,000)	Number of employees	Item	Contents of plating
1	5,000	10	IC lead frame	Silver, passive state treatment of stainless steel
2	10,000	140	Parts for aircraft, parts for measuring instrument	Gold, silver, cadmium, zinc
3	10,200	18	Stereo, TV, electronic equipment	Zinc
4	5,000	12	Parts for motorcar, parts for office equipments	Nickel, tin, silver
5	10,000	20	Electronic parts, parts for precision instrument	Gold, silver, copper, nickel
6	7,100	18	Office equipments, communication equipment, equipment for amusment	Copper, bright nickel plating, chromium
7	9,000	20	Parts for motorcar, machine tools	Copper, bright nickel plating, chromium
8	4,000	7	Parts for signals, parts for electronic meters	Copper, nickel, chromium, zinc
9	6,000	25	Parts for motorcar, parts for light electric applirent	Copper, semi-bright nickel plating, chromium

washing and spray washing including recovery within the production line are performed for water saving purposes at each resident company in the complex. In addition, wastewater is embanked on the floor and different pits are built for classified wastewaters in an attempt to prevent the outflow of wastewater by inundation for the sake of complete prevention against pollution.

Water which has been through reclamation processes at the wastewater treatment plant is used at two resident companies in the complex (re-use of reclaimed water). The atotal mount of reclaimed water being used is approximately 70m^3 per day.

1.2.3. Cooperative Treatment of Wastewater

(1) Capacity of treatment

The wastewater treatment device has a capacity of 400m^3 per day. Wastewater classified by contents and collected for joint treatment work. Types of wastewaters and how much these different types of waters can be individually treated are described below:

1) Cyanide zincous:	60m^3/day
2) Cyanide-coppery:	50m^3/day
3) Acid/alkaline ironic:	140m^3/day
4) Acid/alkaline coppery:	60m^3/day
5) Nickel	30m^3/day
6) Pyrophosphoric acid coppery:	10m^3/day
7) Chromate-related:	50m^3/day

(2) Treatment System

Wastewater treatment system is shown in Fig. 1.2.1.

(3) Water Quality

There is no data for water quality but according to the

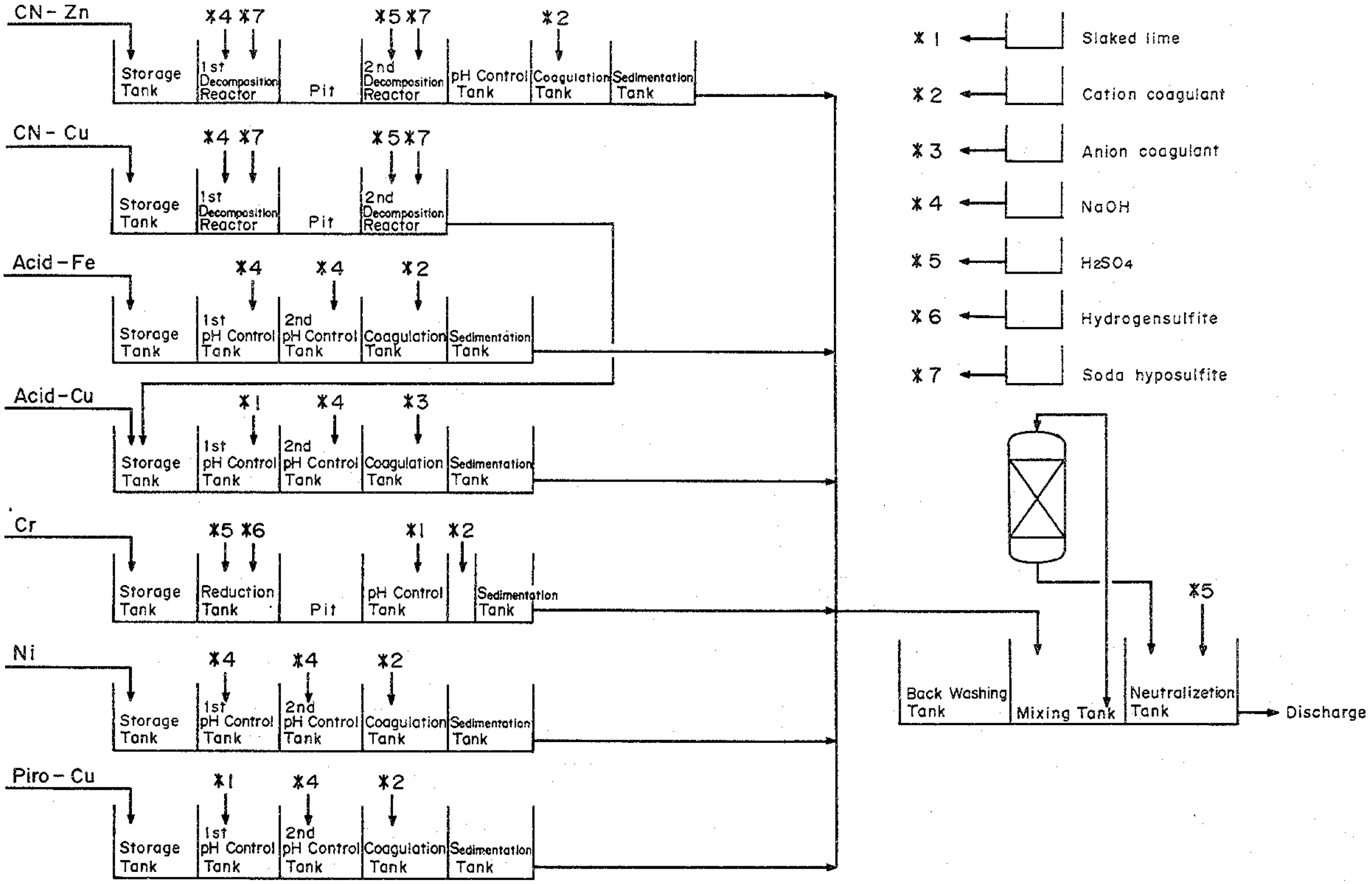


Figure 1.2.1 Waste water treatment system (Jonan Denka Association)

public sewage system, the quality of wastewater seems to be almost the same as that of Keihinjima Central Industrial Estate.

(4) Treatment Costs

The costs of wastewater treatment amount to 250 yen per cubic meter. Discharging reclaimed water into the public sewerage costs 250 yen per cubic meter, and the service water rate is 400 yen per cubic meter. Thus, each individual company is supposed to pay 900 yen per cubic meter for water-related affairs.

2. Central Wastewater Treatment Systems at Dyeing Industrial Estate

2.1 Hyogo Prefecture Textile Dyeing Industrial Cooperative

2.1.1 Outline of the Cooperative

Hyogo Prefecture Textile Dyeing Industrial Cooperative is organized in Nishiwaki City, Hyogo Prefecture and in its neighborhood rural section.

This area has prospered as a yarn fabric-producing (yarn dyeing) district. In the past, most of the yarns were made of cotton, and, thus, the main method of dyeing was hank dyeing. With synthetic fibers including polyester-synthesized and cotton mixed fabrics as the most recent main fabrics, "cheese dyeing and beam dyeing" are the most common dyeing methods.

Sixteen (16) companies are affiliated with the Cooperative. Eleven (11) out of the sixteen (16) companies are taking part in the operation of a central wastewater treatment facility. Other wastewater produced by the remaining five (5) companies is treated at five (5) different facilities separately.

This Cooperative was organized at a social request, involving the firms which had originally been situated in this area. Unlike other industrial cooperatives, it is not that all the corporations are located in the same place. Therefore, intensive joint treatment work is conducted among the six (6) firms in the central city area, while the five (5) companies in rural areas actually treat their own wastewater on their own although they are affiliated with the Cooperative. Concerning sludge, treatment work is performed jointly by the eleven (11) corporations.

2.1.2. Service Water and Wastewater

Many of the dyeing factories affiliated with the Cooperative mainly use industrial water issuing from rivers; however, the volume of water from the rivers is not sufficient, and, thus,

Table 2.1.1 Outline of Member work shops of central waste water treatment facility (Hyogo pref. textile dyeing industrial enterprise cooperative)

No	Capital of the enterprise (¥1,000)	Number of employees	Amout of water used (m /day)			
			diluted water	concentrated water	Total	
1	8,000	150	3,100	500	3,600	Central waste water treatment plant
2	100,000	400	4,200	450	4,650	
3	80,000	250	4,900	400	5,300	
4	12,000	80	2,200	400	2,600	
5	14,000	40	1,700	300	2,000	
6	8,000	80	1,200	150	1,350	
7	20,000	80	3,300	500	3,800	
8	24,000	80	2,500	450	2,950	
9	30,000	80	2,200	400	2,600	
10	7,000	25	1,600	200	1,800	
11	10,000	25	2,000	250	2,250	

Note: Contents of processing in above table are all "thread dyeing of synthetic fiber".

they pump up underground water whenever they need more. However, underground water is not very affluent; and, thus, they have a very poor source of water despite the fact that this district has a long history of taking part in the textile industry.

In regard to the discharging of wastewater, this district is covered by "The Regulations on Special Measures for the Preservation of the Environment of Seto-naikai," and criteria for discharging wastewater are severer than those of other districts.

2.1.3. Cooperative Treatment of Wastewater

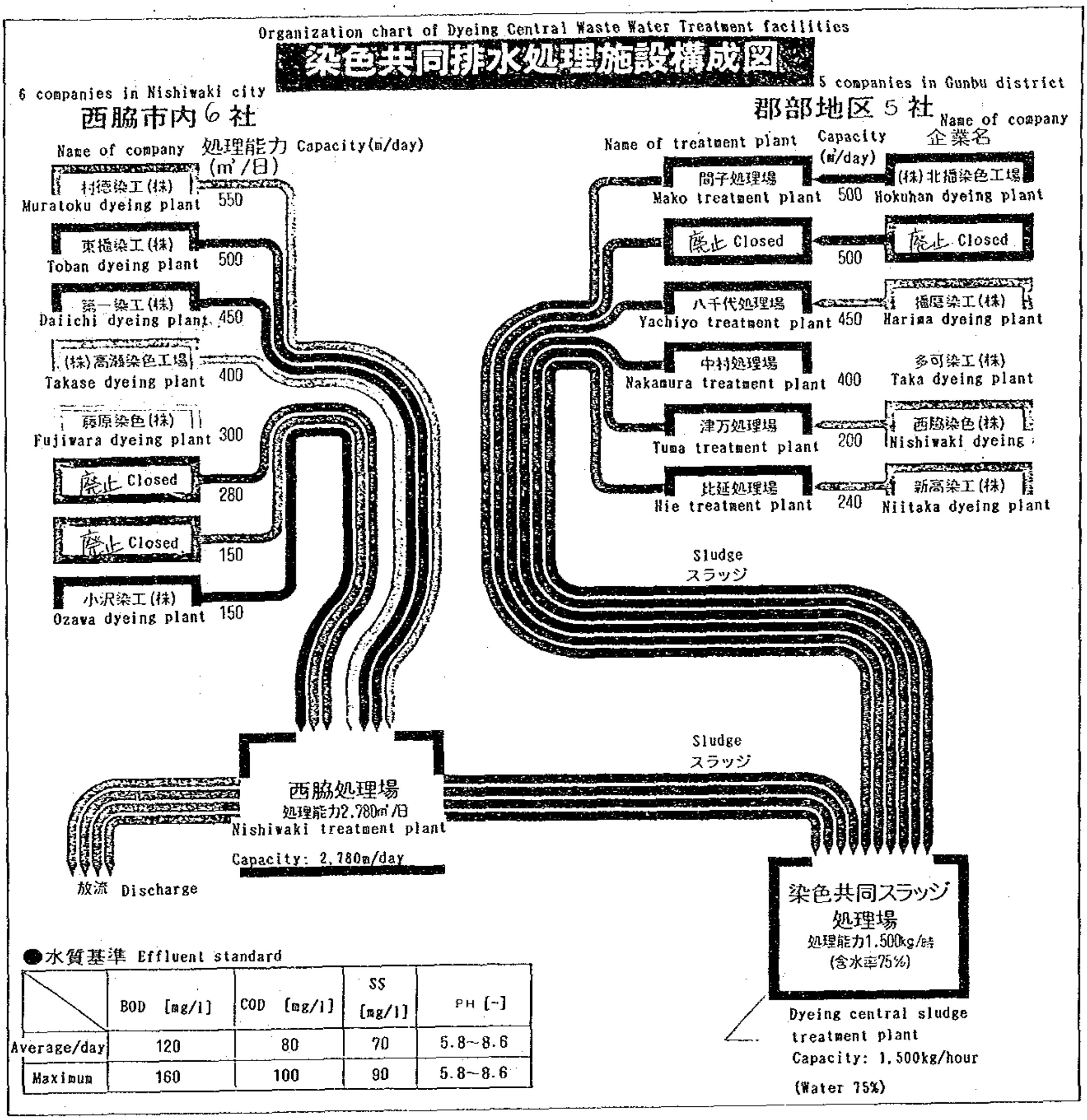
(1) Method of treatment

The central wastewater treatment facility initially started its operation with its main purposes of coagulation and sedimentation. In connection with the above mentioned, "The Regulations on Special Measures for the Preservation of the Environment of Seto-naikai" and others, the facilites has been through extension work twice in order to improve the function of the facility:

- November, 1970: The treatment facility started its operation with a coagulation and sedimentation device equipped.
- June, 1978: An activated sludge treatment device was added to the system in order to be used after the coagulation and sedimentation processes.
- October, 1981: An COD for automatic measuring and recording device and wastewater quantity were added in accordance with the areawide total total pollution load control.

The organizational structure of the treatment facility is showen in Chart 2.1.1.

First of all, wastewater is separated into concentrated wastewater and diluted wastewater at each factory, and the con-



●水質基準 Effluent standard

	BOD [mg/l]	COD [mg/l]	SS [mg/l]	PH [-]
Average/day	120	80	70	5.8~8.6
Maximum	160	100	90	5.8~8.6

Fig. 2.1.1 Organization chart of Central Waste Water Treatment plant
(Hyogo pref. Textile Dyeing Industrial Union)