VOLUME IV PROPOSAL ON PRODUCTION PROCESS

This volume analyzes various kinds of data of each factory obtained through the study we have conducted recently and makes a proposal on production process with respect to countermeasures against environmental pollution based on the experience and knowledge of each specialist of the study team. It is regrettable, however, that we could not collect enough data in the limited period of time for the field survey. We cannot help saying it is partly because each factory was less aware of the importance of data on production process and had little understanding of numerical control on production process. Each factory was not well trained for data acquisition and arrangement in daily operation.

Therefore, this volume describes the following two subjects before making a proposal to each factory on production process.

① Numerical analysis in production process

② Introduction of the Japanese production control method

1. Importance of Data in Production Process

As mentioned before, since each factory was less aware of the importance of data and collected data was not arranged in order, we will introduce the methods of data acquisition, arrangement and application.

1.1 Method of Data Acquisition

(1) Purpose of Data Acquisition

When proceeding with a job, the method is generally determined by achievements in the past, experience or custom. At a job site like factory, however, it is important to proceed with a job based on facts. To this end, data have to be acquired first and then action based on information obtained from the data has to be taken. A correct judgment is always necessary for proper action, and the data from the job site is absolutely required as a basis for correct judgment.

Since data form the basis of action and judgment, data have to be gathered and arranged in the method fit for the purpose. In other words, the purpose of data collection has to be considered thoroughly when data collection is started.

① Are data collected for grasping the present condition?

Ex. When the dispersion of material and product quality is examined

② Are data collected for analysis?

Ex. When the relation between cause and result is studied

③ Are data collected for process control?

Ex. When judgment has to be made whether the process is normal or abnormal

④ Are data collected for adjustment?

Ex. When a measure to maintain the defined normal state has to be taken

(2) Correct Data

When collecting data, it is most important that the acquired data represent fact properly.

To this purpose, it is required to give heed to the following two points.

① Are data collected so that they may represent fact?

(A matter of the method of sampling)

② Are data collected, arranged and compared so that they may represent fact?

(A matter of the statistical method for data arrangement)

(3) Mental Attitude Toward Data

It is important to take up the following mental attitudes when handling data actually.

① Take action based on data.

Form a habit to talk each other based on data.

Think much of the fact represented by data.

② What is the purpose of data collection?

Make it clear. Same as mentioned in section (1).

③ Consider to collect data for everything.

It is really required to make every possible effort or contrive to obtain data. The original data may be acquired through such efforts and contrivances.

1.2 Method of Data Arrangement

The selected factories of this study are chemical factories.

Generally speaking, the basic data of operation in the chemical factory are called "process specification sheet" and the following materials are prepared in the stage of designing facilities.

① Process Flow Diagram (PFD)

The process flow diagram illustrates the production process from raw materials to finished products, and operating temperature, operating pressure, material balance, heat balance, etc. are stated in the diagram.

② Material Balance Sheet

As to materials, products and services, the following items are described for every stream number in the process flow diagram.

- Weight and flow per hour

③ Heat Balance Sheet

As to materials, products and services, the following items are described for every stream number in the process flow diagram.

- Holding heat quantity/enthalpy/temperature/specific heat

④ List of major equipment

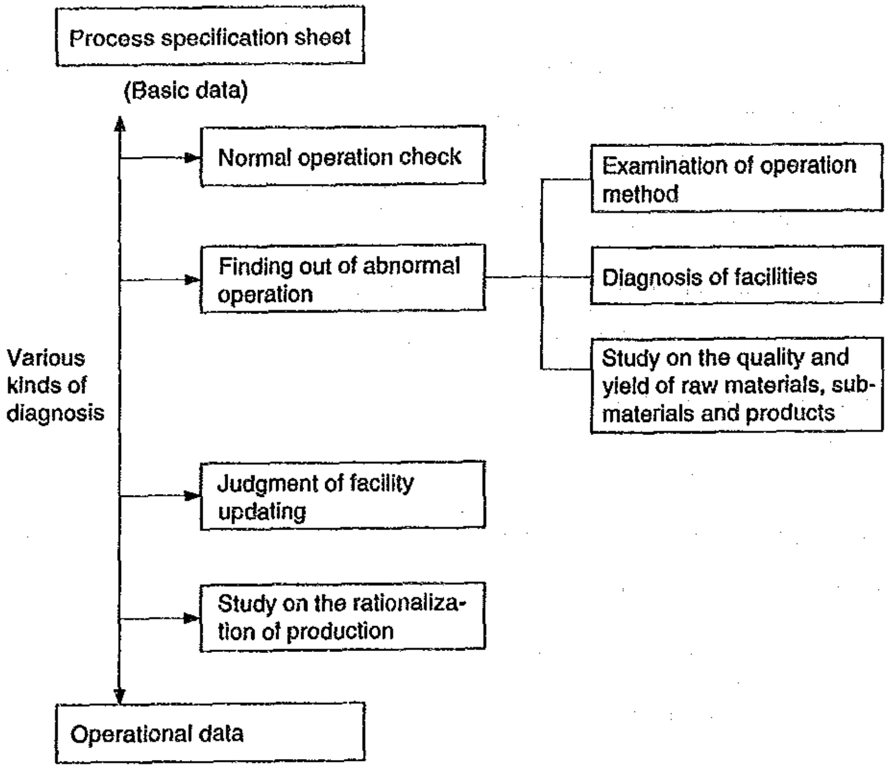
A list of major equipment carrying the descriptions of capacity, form, dimensions, material, quantity, etc.

Each factory should collect and arrange the data needed for preparing these materials.

1.3 Method of Data Utilization

Once the basic data are arranged as process specification sheet in the factory, they can be compared with daily operation data.

Fig. IV-1 Data Utilization



The following advantages can be expected through data arrangement, comparison and examination.

① Operators can understand technical contents.

② Safety operation can be secured.

③ Production cost can be reduced.

2. Introduction of the Japanese Production Control Method

(1) Features of Japanese Production Control

The Japanese industry has recently made a remarkable development and attracted a great deal of public attention all over the world. As one of technically advanced nations, Japan is now exerting a great influence upon a number of countries. The primary factor of its rapid development is a result of strenuous efforts to upgrade the quality of products and reduce the production cost, under a notion that, after the Second World War, Japan having insufficient natural sources can only survive in the world market through competition and cooperation by reinforcing its industrial productivity.

Particularly, in almost all of Japanese manufacturers, even operators at job sites have strived for the improvement of production, always aiming at a higher goal and not satisfying with the existing technical standard. "Management" is to maintain the present technical standard, while "improvement" is to raise the level of technology. Most of Japanese manufacturers continued technical improvement through "quality control (QC)." Since the latter half of 1970s, the term "quality control" came to represent the improvement of the "quality of every kind of works" covering facilities, materials and labor as well as "quality of products". It has developed into "total quality control (TQC)" which urges manufacturers from the top management to the rank and file to participate in improving all works. Therefore, it is not too much to say that the remarkable feature of Japanese production control is found in the diffusion and saturation of quality control method.

Accordingly, the concept of QC and the application of QC method to activities for improvement at job sites will be given below.

(2) Basic Concept of Quality Control

There is a term called "Demming Cycle" which defines the basic concept of quality control. Producers should determine the quality of products in the process of manufacturing not from the producer-centered (product-out) concept but from the consumer-oriented (market-in) concept. Based on a clear concept of laying stress on the quality of products and responsibility for the quality, manufacturers are required to establish a link of following four in-house activities such as survey, design, production and marketing.

① To survey and study thoroughly users' demand for quality

② To plan and design products which will satisfy users' demand

③ To manufacture products as designed

④ To market products to users and check their satisfaction

The Demming Cycle emphasizes that manufacturers should take corrective measures against claims and offer repair services to users, should any troubles be caused. They are also required to examine user-friendly functions and users' satisfaction, and make strenuous efforts to commercialize products which may satisfy users in the future by repeating procedures from ① to ④. The basic concept of Demming Cycle is that manufacturers can win the confidence of users through these activities and enjoy everlasting prosperity as manufacturers.

(3) Control Cycle

The Demming Cycle which defines the basis of quality control is described here from a different angle.

What kinds of products should manufacturers provide? The activity in the stage of planning and designing will show clearly the target of production. It is an activity in the stage of making a plan for producing goods ······ "Plan".

The activity in the stage of manufacturing will be the one in the stage of carrying out the plan ······ "Do". If produced goods are what users really need, sales may increase. On the contrary, if users are not satisfied with the products, sales may decrease.

In the stage of marketing, it is required to check whether finished products are reflex of users' demand or not ······ "Check". Should any inconvenience be caused in the stage of marketing, corrective actions should be taken to meet the claim or after sales service should be provided. All these information should be fed back, as users' dissatisfaction with the existing products, to planning and used for the development of improved products from the next time. The activity in this stage means to take positive action for the following step ······ "Action". The above-mentioned cycle is called "Demming Cycle."

The Demming Cycle is a normal way of thinking, however, it is not easy to translate the idea into action. Plans are mapped out every year, but they are not necessarily implemented as planned. Plans are scheduled but they are not carried out as planned. People often start taking action without a definite plan.

(4) Application of QC Method to Activities for Improvement at Production Sites

There exists not a single Demming Cycle in an enterprise but also multiple Demming Cycles in various areas of each enterprise such as sales, procurement, design, research & development and production departments.

For instance, the production department has a feedback loop which includes production planning, execution, check, and feedback to reform the plan.

By adopting this QC procedure into every unit of small or large job site, Japanese manufacturers are making great efforts for improvement.

Methods for various improvements are shown in Fig. IV-2: Method for making improvements by QC and in Table IV-1: Actual method for making improvements by QC.

Fig. IV-2 Method for Making Improvements by QC

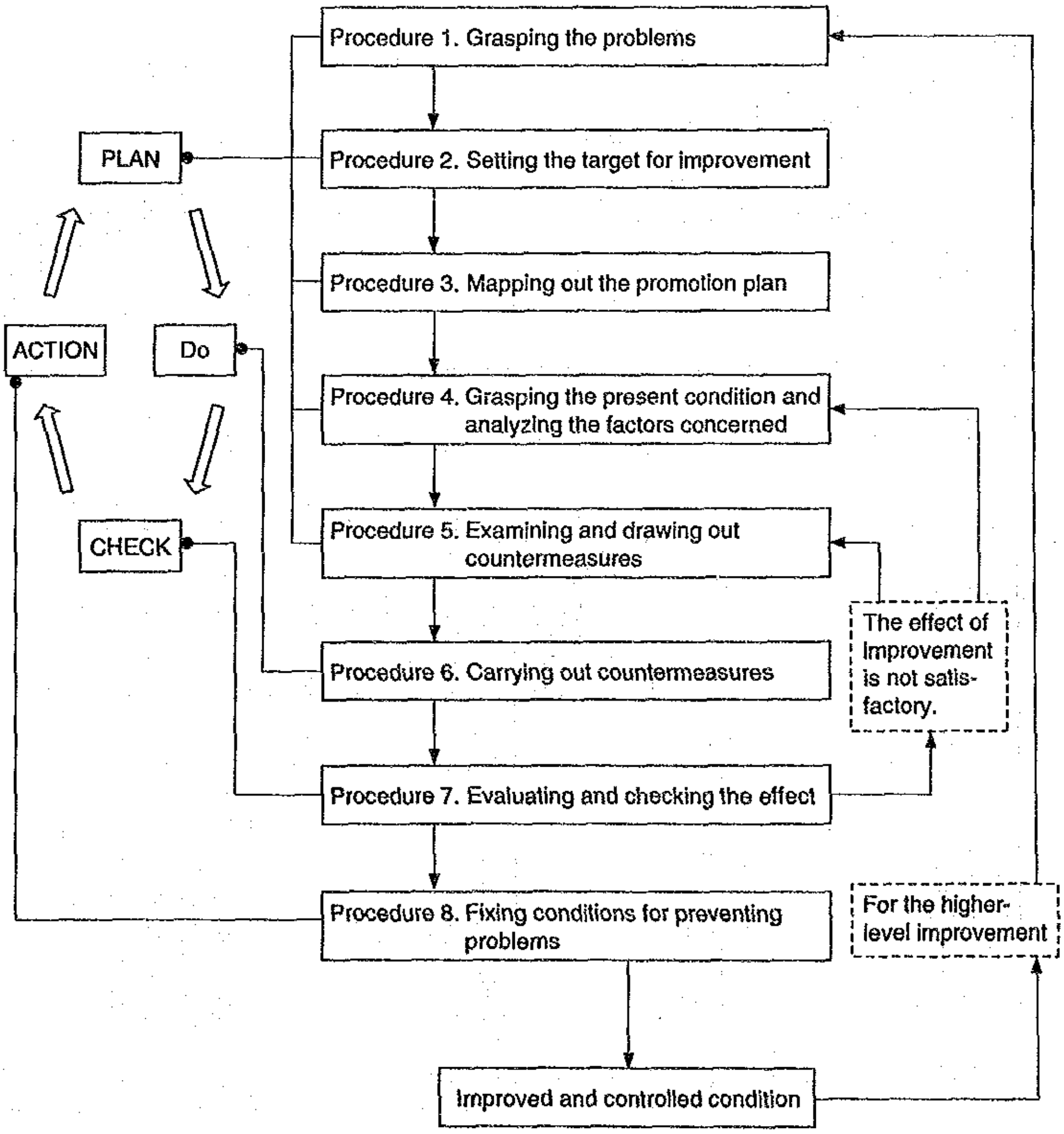


Table IV-1 Actual Method for Making Improvements by QC (1/2)

	Procedure	Contents	Actual method
PLAN	1. Grasping the problems	① Based on the company's policy and target ② Grasping fact based on data ③ Listing problems	• Realize fully the duty at the job site and make it known to people in subordinate positions • Comprehend the present conditions (occurrence of trouble) based on scientific facts by collecting practical data. • List problems for each item such as quality, cost price and delivery by using a checklist.
	2. Setting the target for improvement	① Priority system ② Setting the theme for improvement ③ Setting the target for improvement	• Select important items by using a Pareto diagram (A diagram with value-conversion is effective.) • Select themes from importance, emergency, expected effect, expenses anticipated for solution, etc. • Set the target and degree definitely.
	3. Mapping out the promotion plan	① Determining groups and responsible persons for improvement ② Mapping out the schedule ③ Allotting roles to responsible persons	• Make blueprints.
	4. Grasping the present condition and analyzing the factors concerned	① Integrating factors into the characteristic diagram ② Data collection ③ Statistical analysis and arranging the results of analysis	• Make a characteristic diagram based on your technical knowledge and experience to integrate factors into the diagram. • Collect factual materials and data by using a check sheet. • Analyze the data in the past, selected daily data and experimental data by applying statistical methods such as histograms, graphs, control charts, scatter diagrams, testing and estimation to integrate all results.

Table IV-1 Actual Method for Making Improvements by QC (2/2)

	Procedure		Contents	Actual method
PLAN	5.	Examining and drawing out countermeasures	① Listing countermeasures ② Selecting an implementation plan ③ Making a definite implementation plan	• Make a list by utilizing rich ideas, orginality and comprehensive knowledge and experiences. • Select the best implementation plan viewed from profitability, technical aspect and operability. • Confirm the 5W1H in the plan to allot roles, and also make a schedule plan.
Do	6.	Carrying out countermeasures	① Preparatory operation for implementation ② Adoption of data ③ Troubleshooting	• Make tentative standards for operations and procedures, and promote better understanding among the persons concerned. • Adopt data to check the effect. • Prepare to cope with unanticipated troubles.
Check	7.	Evaluating and checking the effect	① Result check ② To procedure 8 ③ To procedure 4 or 3	• Analyze data by statistical methods, and evaluate the effect by comparing the result with the initial target. • If the effect is recognized as planned, go to procedure 8. • If the effect is not satisfactory, go to procedure 4 or 3.
Action	8.	Fixing conditions for preventing problems	① Improving equipment and jigs ② Revising operational standards and drawings ③ Teaching and training	This is a step to secure the effect of improvement (which you improved them with much efforts) by fixing the condition for preventing problems so that they may not return to the previous state before you are aware of it.

3. Proposal on Production Process of Each Factory

To be true to the object of this study, the proposal on production process intends to improve the production process which will reduce the industrial pollution of water and atmospheric air. The proposal is not aimed at the rationalization of production process to increase the production capacity and reduce the production cost. It is also not aimed at the alteration of the current production process by going into its basic process. Therefore, we sampled and analyzed waste water and exhaust gas during the period of the field survey.

The analysis values obtained in the field study show polluted substances were commonly high in density and a large quantity of waste were discharged and exhausted. In other words, a part of products or by-products was discharged or exhausted. To collect waste as much as possible and to discharge only unavoidable waste will improve productivity and prevent environmental pollution.

With the object of reducing the environmental pollution, we examined the possibilities of resource recycling and energy saving at each factory.

3.1 SIAPE

The production process adopted by SIAPE has already been fixed. True to the purpose of our study, this chapter makes a potential proposal for improvement from the viewpoint of environmental pollution control.

However, by studying the proposal for improvement based on the regulation values of waste water and exhaust gas (to be stated in Volume V and VI), we cannot help making a proposal which may affect a part of basic production process. Therefore, it is considered necessary for SIAPE and each process owner to investigage thoroughly about the influence of process performance.

3.1.1 Sulfuric Acid Plant

(1) Comparison of Exhaust Gas Treatment Method

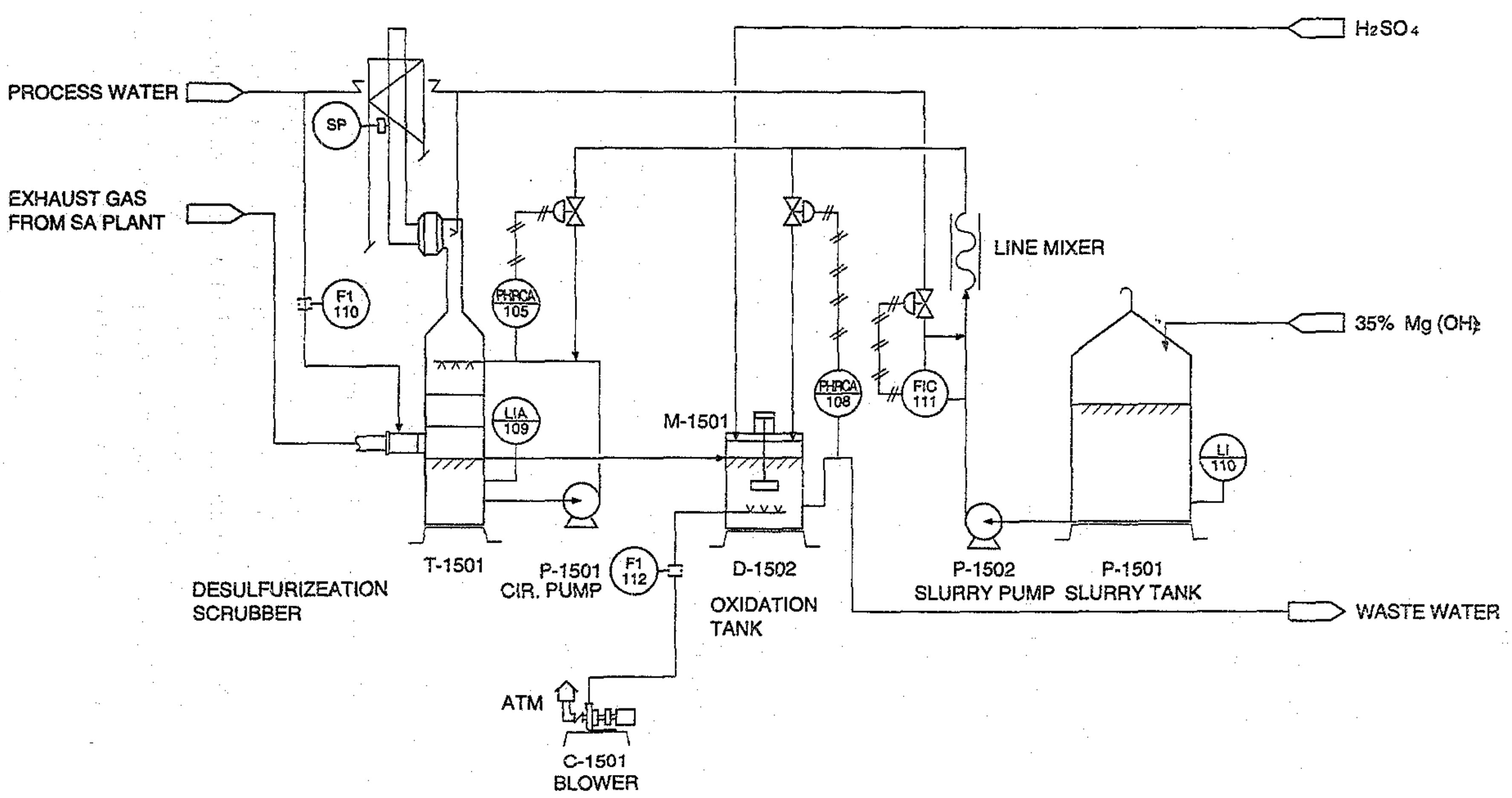
The existing sulfuric acid plant does not discharge waste water which will cause environmental pollution. However, it is required to take measures to conform to the values for regulating exhaust gas. The possible treatment of exhaust gas from the sulfuric acid plant is categorized as follows.

① Wet system

The wet system uses water solution such as magnesium hydroxide, caustic soda and ammonia to eliminate SO_2 and SO_x in the form of sulfate.

For instance, the general flowchart of the wet system is given in Fig. IV-3.

Fig. IV-3 Desulfurization Flow Sheet (Wet System)



② Dry system

Basically, this system allows solid materials to absorb or react to SO_2, SO_x and NO_x. Activated cokes, calcium carbonate, etc. are used as solid materials.

For instance, a dry system is given in Fig. IV-4.

③ Use of high chimney

Using a high chimney is the simplest way to reduce the concentration of harmful gas on the ground, but it does not reduce the discharge at all.

④ Adoption of new process which allows to increase the recovery rate of raw sulfur

(2) Application to Sulfuric Acid Plant

All systems above have been adopted in Japan and other countries, and we have analyzed as follows based on the present situation of SIAPE.

① Wet system

Waste water treatment is required, because any treatment systems adopted will discharge sulfate in the form of solution. This system allows to collect and utilize it as by-product. Besides, the wet system is very effective in a country like Japan where no regulations exist for SO_4 discharge.

② Dry system

The dry system will be large in scale, and equipment used in the system are very expensive. It will be required to examine the dry system if the regulation of exhaust gas becomes more strict in Tunisia in the future. Under the current conditions, however, we exclude it from our study.

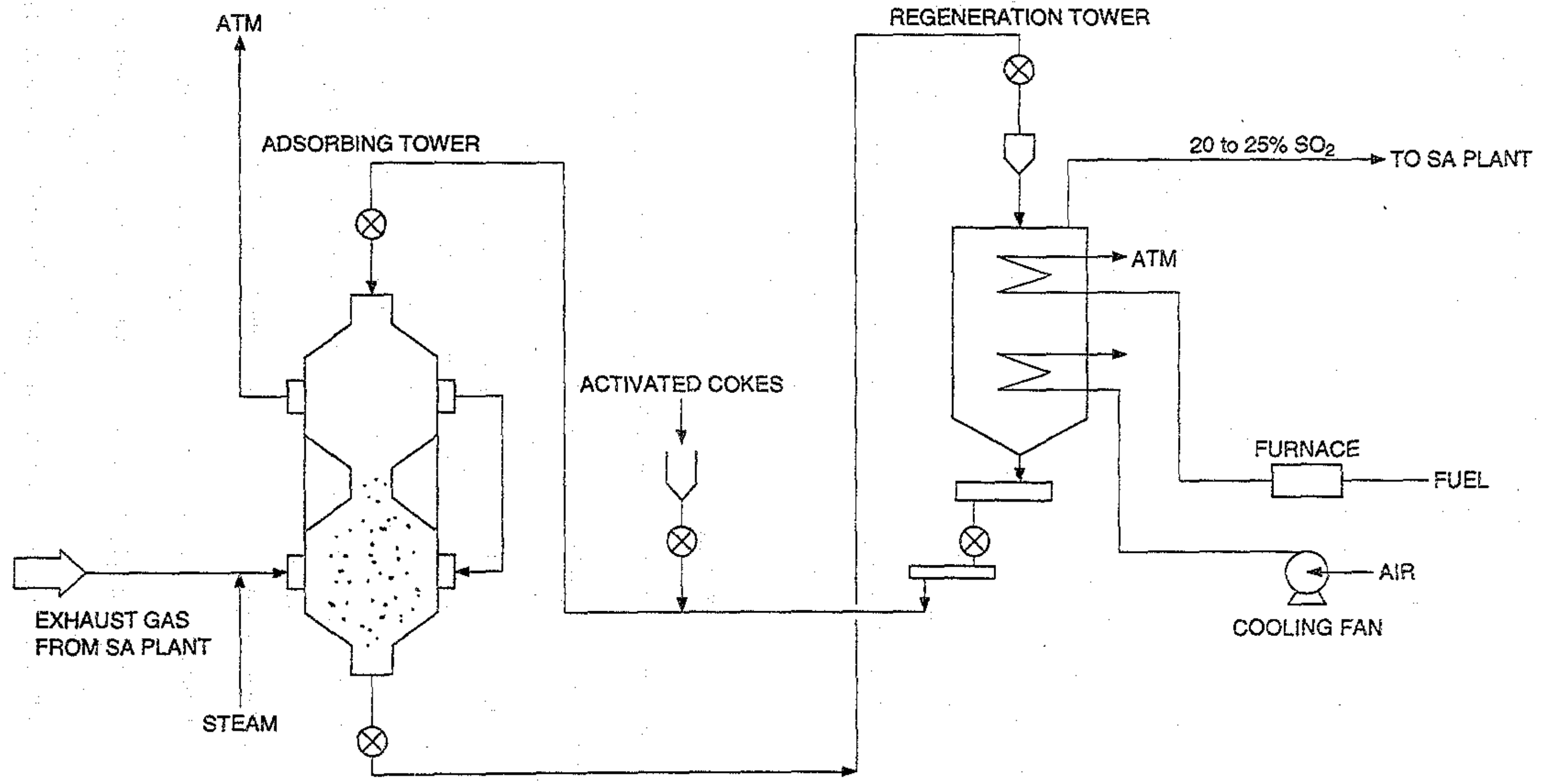
③ Use of high chimney

This is the system which we want to propose to SIAPE.

④ Adoption of new system which allows to increase the recovery rate of raw sulfur

The SCSA (single contact, single absorption) system is adopted in the SIAPE sulfuric acid plant. This system generally ensures a sulfur recovery rate of 98-98.5%. On the other hand, the DCDA (double contact, double absorption) system provides a recovery rate of more than 99.5%. Accordingly, the DCDA system emits less SO_2 and SO_x into the atmosphere than the SCSA system, and is regarded as an effective method in respect to environmental pollution. Additionally,

Fig. IV-4 Desulfurization Flow Sheet (Dry System)



since an increase in the market price of raw sulfur is now making the business condition of SIAPE more serious, this system should be studied carefully.

As a result, we will make the following proposal for environmental pollution control in the sulfuric acid plant.

1) There is no regulations for SO_4 in the tentative standard for waste water proposed by Japanese side.

   Therefore, wet system can also be applied.

   While, as for INNORPI, there is a regulation for SO_4.

   In this case, wet system can not be considered because the load for waste water treatment will increase.

2) We propose to adopt DCDA system because only the exhaust gas is the object to be considered in sulfuric acid plant. This proposal seems to be effective in respect to the efficient use of sulfur. We also have heard from SIAPE that the GABES sulfuric plant had already decided to adopt this system.

3) The method of building a higher chimney is excluded from our proposal, because we are making a proposal of 1) and 2).

3.1.2 Phosphoric Acid Plant

(1) Improvement of Facilities Viewed from Exhaust Gas Treatment

There exist no regulations of exhaust gas in Tunisia now, and SIAPE considers itself free from any troubles. However, fluorine is discharged more than defined with reference to the proposal offered from Japan. Therefore, we propose to replace the present gas scrubber at least with a more efficient gas treatment facility.

For the gas scrubber, alkaline washing with caustic soda is significantly effective for eliminating fluorine gas. Judging from the regulations of exhaust gas, alkaline washing does not seem to be indispensable, so it is recommended to provide for facilities to be installed when regulations become more strict.

(2) Improvement of Facilities Viewed from Waste Water Treatment

Under the existing circumstances, all water used in the scrubber is utilized to make gypsum slurry, and gypsum slurry is carried to Tabia, where water evaporates partially and remains partially with gypsum in Tabia. The rest of water circulates back to the plant and is used for washing gypsum in the filter process, and then it is utilized to make gypsum slurry. So far as this is repeated, a closed circuit is adopted. Since the volume of water evaporated from and remained in Tabia must be properly replenished, we propose to use waste water discharged from the factory for make-up water after treatment. The quality of waste water after treatment is enough to be used adequately as make-up water.

3.1.3 TSP Plant

Exhausted fluorine gas is not adequately treated in the TSP plant for the same reason as in the PA plant. Therefore, we propose to replace the existing gas treatment facilities in the TSP plant with more efficient facilities.

Concerning the waste water, the discharged water from the gas treatment facilities must be treated, but treatment must be conducted in several steps to meet the regulations.

3.1.4 Treatment of Waste Water from the Factory

The present condition of waste water from the factory is given in Fig. III-7 in Volume III.

Treatment of waste water must be performed respectively in accordance with the later-mentioned case setting. Water after treatment circulates back to the phosphoric acid plant, and it is used around filters.

3.1.5 Environmental Pollution Control in the Phosphoric Fertilizer Plant

Environmental pollution control for the sulfuric acid plant was described in section 3.1.1.

Here we explain environmental pollution control in the phosphoric acid plant and TSP plant for your information as these environmental pollution control will accompany the present process of SIAPE with the change. We account for the methods peculiar to the phosphoric acid and TSP plants, because the general treatment methods of waste water and exhaust gas will be stated in Volumes V and VI.

The target materials of environmental pollution control common to the phosphoric acid and TSP plants are fluorine, phosphoric acid and dust. The following measures should be taken against these materials which cause environmental pollution.

(1) Fluorine

Phosphate rock is used as raw material commonly in the production of phosphoric acid and TSP. From 2.8% to 3.4% of fluorine is contained in raw phosphate rock, and fluorine gas is generated by each chemical reaction in production process.

- Chemical equations for the generation of fluorine in the manufacturing process of phosphoric acid:

$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HF$

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$

$H_2SiF_6 + \text{Heat/Acid} \rightarrow SiF_4 + 2HF$

- A chemical equation for the generation of fluorine in the manufacturing process of TSP:

$2CaF_2 + 4H_3PO_4 + SiO_2 \rightarrow SiF_4 + 2CaH_4(PO_4)_2 \cdot H_2O$

In either cases, generated fluorine gas is generally washed in the scrubber before it is emitted into the atmosphere. On the other hand, such a measure is taken as to calcinate phosphate rock and upgrade it to reduce the content of fluorine in the phosphate rock.

Organic matters can be eliminated through calcination, and it is a matter to be considered carefully, if phosphate rock used in SIAPE contains a comparatively high percentage of organic substances.

Regardless of the kind of manufacturing process, fluorine gas is generated according to the above-mentioned chemical reaction. In case of phosphoric acid plant, however, the volume of fluorine generated as gas depends on the place of origin of the phosphate rock. It is regarded as from 2% to 5% of all fluorine contained in phosphate rock, and most fluorine remains in phosphoric acid solution and gypsum. Several methods are available to collect fluorine contained in the phosphoric acid solution from the standpoint of environmental pollution control, and they are explained below. The collected fluorine is used for aluminum industry and the production of cryolite.

1) Collection of Fluorine from Concentrator of Phosphoric Acid

The purpose of concentration varies according to the demand for reducing the transportation cost of phosphoric acid and the requirements of fertilizer production process (mainly water balance in the process).

If the dihydrate process like that of the SIAPE phosphoric acid plant is adopted, phosphoric acid of 28-30% P_2O_5 is usually produced, and the density of P_2O_5 is often raised to 50-54%. Concentration is executed by vacuum heating, and fluorine remaining in phosphoric acid is evaporated by this operation and then collected. The volume of fluorine evaporation depends on the place of origin of phosphate rock, production process of phosphoric acid and density of P_2O_5. When phosphoric acid is concentrated up to 54% P_2O_5, about 80-85% of fluorine contained in the 28-30%

phosphoric acid solution is said to be evaporated. Therefore, the efficient collection of fluorine is an effective means for environmental pollution control, and it is still more effective, if the use of collected fluorine is decided.

An example of the process to collect fluorine from the concentrator is given in Fig. IV-5 (Swift process is well known.)

2) Other Collecting Methods

Condenser is used as the phosphoric acid concentrator, and fluorine can be collected from cooling water for the condenser. An example is given in Fig. IV-6.

3) Efficiency in Using Concentrated Phosphoric Acid

Waste water discharged from the factory of SIAPE as process discharge water is from the scrubber of the TSP plant. The fact of that plant discharge water is produced shows water can not be evaporated in process due to water and heat balances inside the plant.

In the TSP plant, 28% P_2O_5 phosphoric acid is used without concentration. If it is replaced by concentrated phosphoric acid, the amount of water previously evaporated in concentration can be used for gas washing, and the amount of water for washing can be evaporated in process again. Therefore the method of using concentrated phosphoric acid is effective in view of reducing the volume of waste water and absorbing fluorine gas. The flow sheet of this relation is given in Fig. IV-7.

(2) Phosphoric Acid and Dust

It is rather resulted from the performance of equipment than the production process that phosphoric acid and dust are contained in waste water and exhaust gas.

Therefore, the removable of phosphoric acid and dust is a matter to be coped with from the aspects of hardware and preventive maintenance and it is effective to take measures against the items described in Volume III as the problems of SIAPE.

3.1.6 On Gypsum in Tabia

The field survey has not reached the conclusion that the sedimentation of gypsum in Tabia itself is a cause of environmental pollution.

As long as the phosphoric acid plant continues operation in SIAPE, abandoned gypsum is accumulated in Tabia. Accordingly, the effective use of gypsum should be considered.

However, the facilities for assuring the effective use are generally very expensive.

Fig. IV-5 Flow Sheet for Fluorine Collecting Facilities

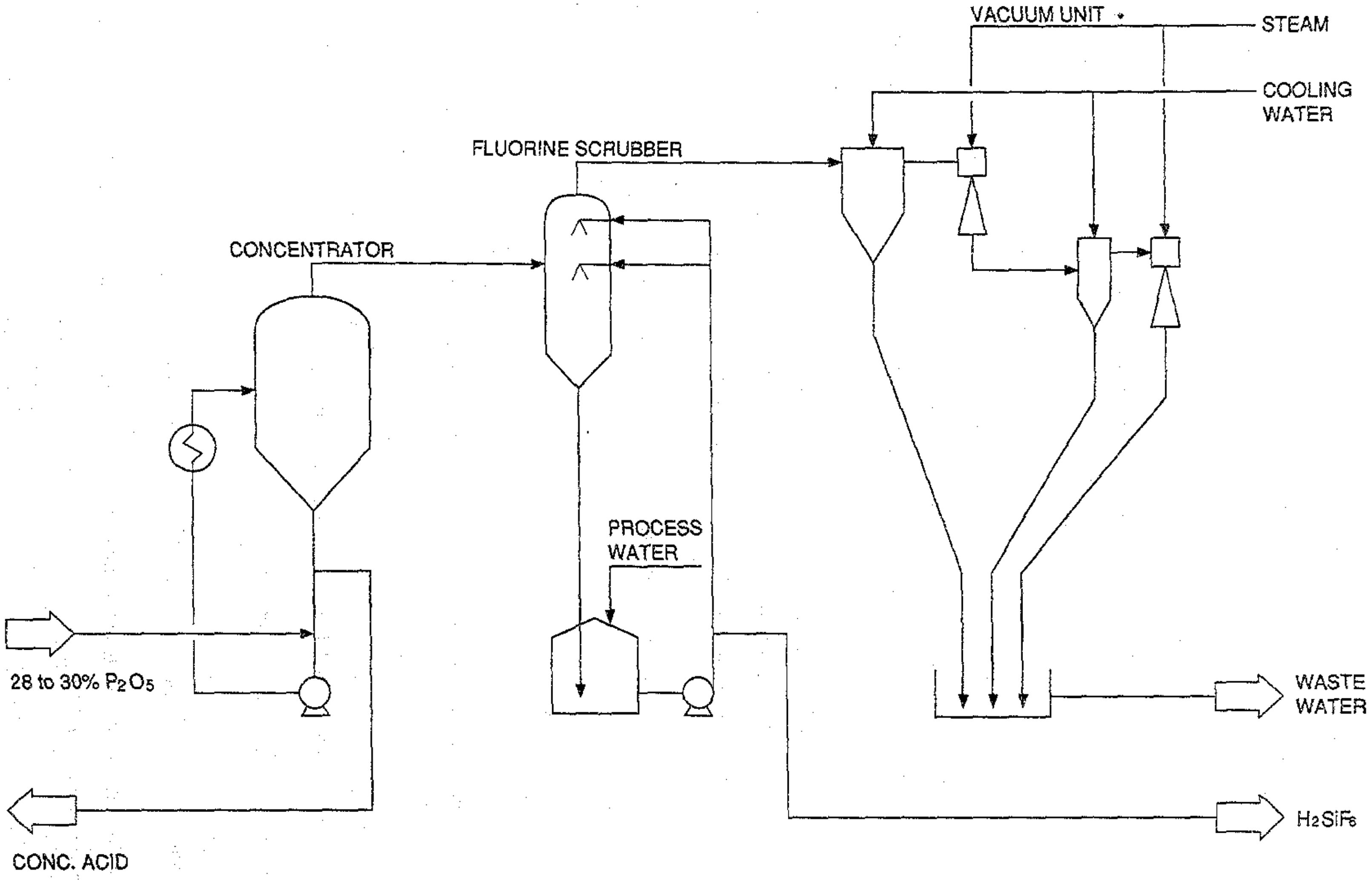


Fig. IV-6 Flow Sheet for Fluorine Collecting Facilities (from cooling water for P_2O_5 condenser)

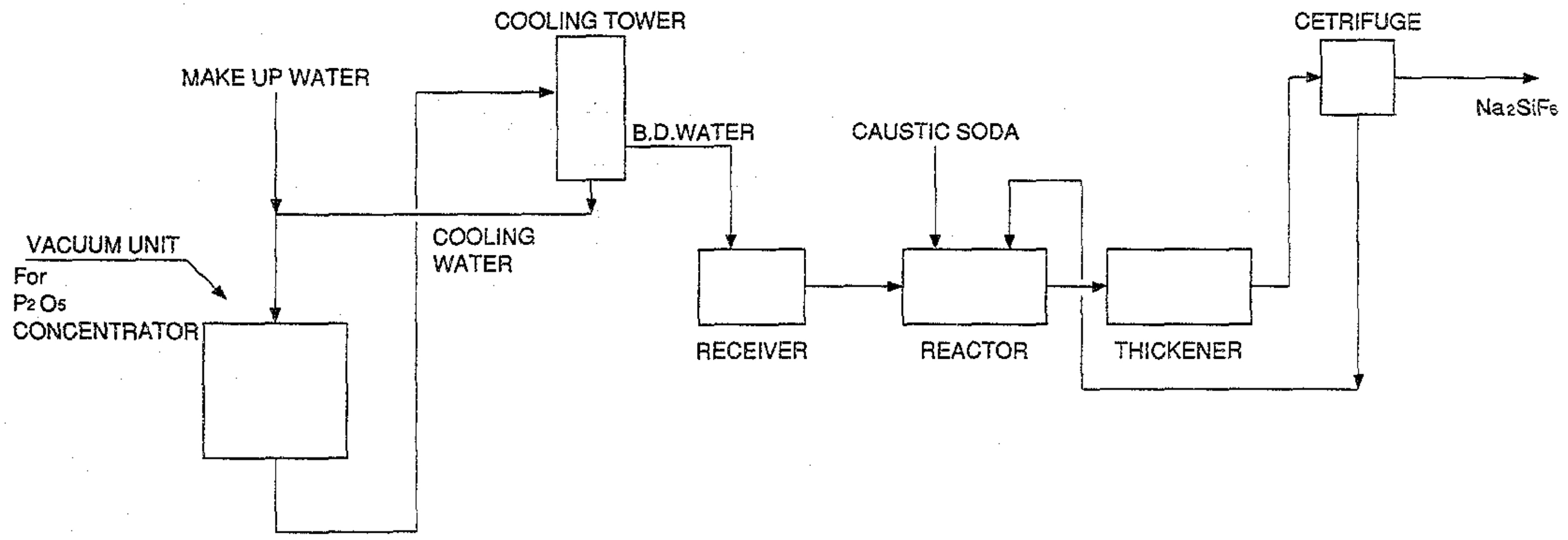
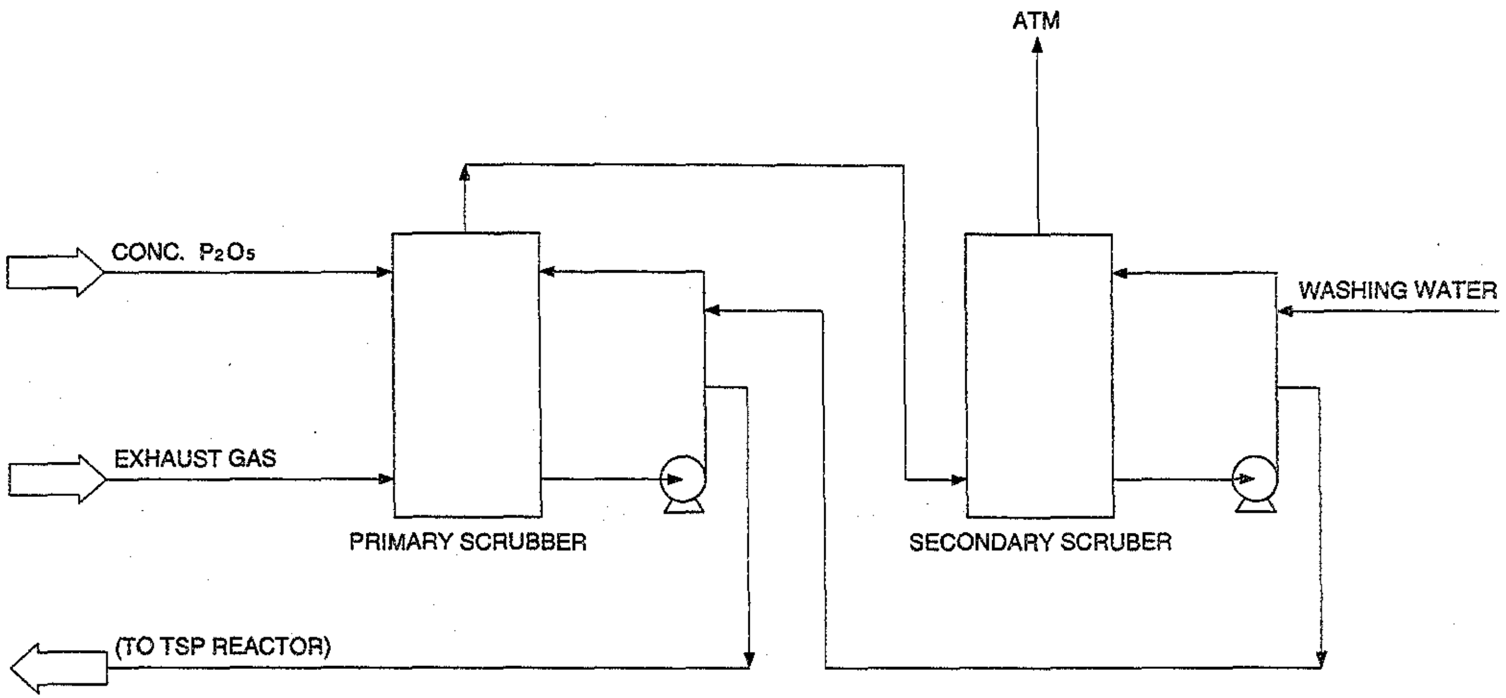


Fig. IV-7 Flow Sheet for Exhaust Gas Washing in the TSP Plant



Note: *The use of concentrated phosphoric acid enables gas washing in the two stages.

*The use of concentrated phosphoric acid is likely to absorb gas washing water in the TSP process.

Therefore, in this study, considering that it is important to take the appropriate countermeasures against waste water and exhaust gas, we only explain measures for effective use.

(1) Utilization of Gypsum

When one ton of phosphoric acid is produced from the phosphoric acid plant, roughly 4.5 tons of gypsum is produced as a by-product.

SIAPE produces 400 tons of phosphoric acid daily, i.e. it produces about 1,800 tons of gypsum as a by-product. Therefore, it is required to consider the volume utilization of gypsum. To this end, the following utilization is available.

1) Utilization of Gypsum as Filler of NPK Fertilizer

Filler (NPK-grade conditioner) is required by many factories of NPK fertilizer. The consumption of filler depends on the quality grade of NPK products, and filler is usually consumed from 50 to 300 kg per one ton of NPK fertilizer.

2) Production of Sulfuric Acid

One utilization of gypsum is to produce sulfuric acid by using SO_4 of gypsum. The "Mueller-Kuhe" process is a well-known process, which used natural gypsum for operation in the past but now also uses phospho gypsum. The actual results of constructing plants utilizing phospho gypsum are found in Austria and South Africa, with Chemie Linz as a licenser.

The production of sulfuric acid by using gypsum seems advantageous for the factories of phosphoric fertilizer, but this process consumes a great deal of energy and is not always regarded as an economical method, because the market price of sulfur has declined recently. For this reason, there seems no movement in the industry to construct sulfuric acid plants using gypsum.

3) Production of Ammonium Sulfate

The possible utilization of gypsum is to use SO_4 of gypsum as ammonium sulfate or $(NH_4)_2SO_4$, and the ICI process is well known in the industry. Many factories are in operation as effective use of phospho gypsum.

This method requires carbon dioxide gas and ammonia as raw materials, and calcium carbonate is produced as a by-product. Additionally, as for calcium carbonate, the production of quick-lime and carbon dioxide gas can be considered.

(2) Gypsum-Ammonium Sulfate Plant

The utilization of gypsum is explained in the previous section. Here we will outline the gypsum-ammonium sulfate plants which are in operation at present in several countries in where phosphoric acid plants exist. The reason why we are referring to the gypsum-ammonium sulfate plant are as follows.

- The effective utilization of gypsum in large volumes is expected.
- Ammonium sulfate as a commercial product can be produced.
- The utilization of calcium carbonate produced as a by-product can be considered.

However, the marketability of ammonium sulfate in Tunisia and availability of carbon dioxide gas and ammonium as raw material were not included in this study, and they may be discussed separately.

1) Production of Gypsum-Ammonium Sulfate

Basic reaction formulae are given below.

$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$ .... (A)

$(NH_4)_2CO_3 + CaSO_4 \bullet 2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$ .... (B)

First produce ammonium carbonate from ammonia and carbon dioxide gas, then produce ammonium sulfate and calcium carbonate from ammonium carbonate and gypsum.

Formula B shows ammonium sulfate is obtained as water solution, which is concentrated and crystallized to obtain ammonium sulfate as a product.

2) Outline of Gypsum-Ammonium Sulfate Process

This process consists of the following six sections.

a) Carbonation section

b) Reaction and gas scrubbing section

c) Filtration section

d) Neutralization section

e) Evaporation and crystallization section

f) Drying section

① Carbonation Section

Carbon dioxide gas and ammonia (gasified in case of liquid ammonia) produce ammonium carbonate in the carbonation section according to formula A mentioned before.

② Reaction and Gas Scrubbing Section

Supply multiple reactors installed in parallel with gypsum and ammonium carbonate. At this time, ammonium sulfate solution and calcium carbonate are produced according to formula B mentioned before.

Reactors are equipped with heating coils to provide the required heat of reaction. Process fluid after reaction is slurry and is generally referred to as magma. Unconverted gas (ammonium) is washed in the cleaning tower and collected.

③ Filtration Section

Magma consists of ammonium sulfate solution and calcium carbonate, and the latter is separated through the filter. Calcium carbonate is taken out of the section by the conveyor.

④ Neutralization Section

Here the PH of ammonium sulfate solution is adjusted by sulfuric acid to make crystals in the following section.

⑤ Evaporation and Crystallization Section

Ammonium sulfate solution after adjusting PH, is treated with multistage evaporator/crystallizer which consist of one evaporator and two crystallizers. At evaporator, excess water in ammonium sulfate solution is evaporated to near the saturate solution. Then its solution is fed to the crystallizer where the solution is concentrated to the slightly super saturate condition to make the ammonium sulfate cyrstals. The crystal slurry from the last cyrstallizer is fed to the centrifuge in order to separate crystals.

⑥ Drying Section

Ammonium sulfate separated by the centrifugal separator is dried with hot air to make the finished product.

3.2 SNDP

With an aim to take a measure against oil leakage, we have carried out our study for SNDP. After the first field survey made in June 1991, we have pointed out the following two points as main causes for oil leakage.

- Leakage of oil from tanks, pipelines, etc.
- Drain of oil from the oil separator

During the time of our study, however, the factory executed construction to make an independent pipeline for receiving product oil and made a plan to increase the capacity of the oil separator, i.e. SNDP took measures corresponding to proposals made by the study team.

Therefore, we have outlined "Safety Standards for Hazardous Material Storage Tanks" with an aim to maintain and control the tanks of hazardous materials in large volumes.

(1) General Description of Preventive Maintenance Standards

1) Range of Preventive Maintenance Standards

Hazardous material storage tanks (flat-bottom, cylindrical type tank)

2) Kind of Inspection

① Overhaul inspection

- Appearance visual inspection
- Plate thickness inspection
- Weld inspection
- Bottom plate form inspection

② Uneven sinkage measurement

③ Tightness test by filling water

3) Time of Inspection

The time of each inspection is given in Table IV-2.

Table IV-2: Inspection Cycle

	10,000 k*l* or more	1,000 k*l* or more	Less than 1,000 k*l*
Overhaul inspection	5 yrs. or less.	10 yrs. or less	More than 10 yrs.
Sinkage measurement	Once/yr. or more	Once/yr. or more	Once/yr. or more
Tightness test by filling water	When required	When required	When required

4) Inspection Records

Items in inspection records are as follows.

① Check items before inspection

- Name and No. of equipment
- Name of manufacturer
- Manufacturing date
- Material
- Design pressure and temperature
- Minimum allowable thickness
- Operating pressure and temperature
- Setting pressure of safety valve
- Pressure of air tightness test
- Pressure of pressure test

② Items to be recorded in inspection

- Date of inspection
- Location and thickness of main section
- The highest surface temperature and its location in the main section before operation stops (provided that the operational temperature is 300°C or more, or –30°C or less).
- The appearance inspection of main section and the result of defect inspection
- Pressure of air tightness test

- Pressure of pressure test
- Next scheduled inspection
- Person in charge of inspection

(2) Uneven Sinkage Measuring Method

Of the above-mentioned items, the uneven sinkage measuring method of hazardous material storage tanks is explained below.

1) Relevant Tanks

Of the outdoor storage tanks of hazardous materials, all tanks of 200 times or more of defined quantity and with a capacity of 100 k*l* or more

2) Measuring Method

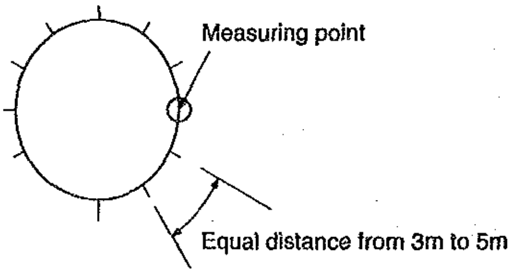
① Measuring instruments

Measurement is executed by automatic leveling

② Setting the measuring points

Divide the outer periphery of the side plate into the equal distance of 3m to 5m with an even number of sections, and set them as measuring points. Set more than four measuring points per unit.

Fig. IV-8 Setting Method of Measuring Points



③ Measuring range

Measure the difference of elevation (uneven sinkage) at each measuring point and also measure the absolute displacement from the standard point by setting it.

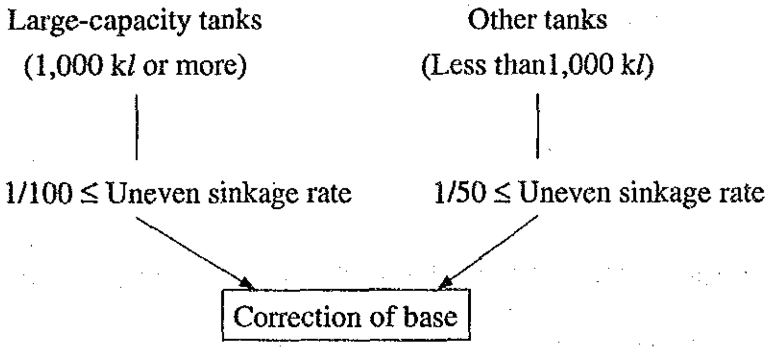
④ Judgment of measured value

From the measured values obtained in the previous step, calculate the sinkage and uneven sinkage according to the equations below.

Sinkage = (Highest measuring point) – (Lowest measuring point)

$$\text{Uneven sinkage rate} = 1/\left(\frac{\text{Tank diameter}}{\text{Sinkage}}\right)$$

Pass judgment on the calculated uneven sinkage rate as follows.

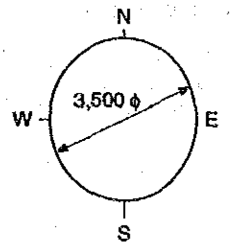


3) Examples of Judgment on Measurement

Examples of judgment are given in Fig. IV-9.

Fig. IV-9 Examples of Measurement for Uneven Sinkage

Specific tank with 1,200 kl capacity



	'89	'90	'91
N	5,111	5,109	5,109
E	5,101	5,101	5,100
S	5,124	5,124	5,130
W	5,111	5,115	5,114
Sinkage / Uneven sinkage rate	23 / $\frac{1}{152}$	23 / $\frac{1}{152}$	30 / $\frac{1}{116}$

— The highest measuring points

Result of measurement in 1991

Absolute sinkage: 5,130 – 5,124 = 6 mm

Uneven sinkage rate: 1/116 < 1/100

*No correction of base is required.

3.3 UPOTS

The source of the worst environmental pollution in the olive oil plant is margin. About 50-60 tons of margin are discharged daily (for 100 days yearly) from UPOTS, and about 100,000 tons of margin are discharged in season in the Sfax city area (total discharge from about 250 factories).

In some cases, it may weaken the business basis of small-scale factories which operate only in season to request them for process improvement including margin treatment, although it is for environmental pollution control.

Viewed from environmental pollution control, the following are the points to be dully considered when improving the process.

① Characteristics of raw materials, products and by-products.

② Kind of manufacturing process

③ Improvement of manufacturing process

3.3.1 Properties of Olive, Olive Oil and By-Products (Grignon and Margin)

When studying how to treat waste water (margin) discharged from the olive oil factory, we have to take the following steps into account.

① Treating merely waste water.

② Recovering valuable materials contained in waste water, utilizing them effectively and treating waste water later.

③ Improving the system of waste water by combining it with the modification of each process to treat waste water.

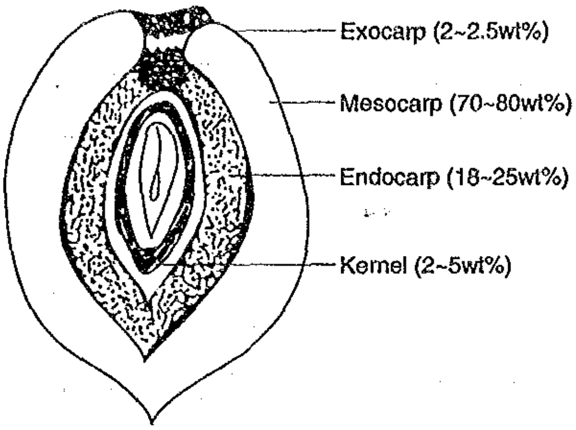
We are required to find an efficient method by executing each step separately or by combining steps. To this end, it is important to know at first the properties of olive plum, olive oil, grignon and margin. We hope this will be useful to find the potentiality of improvement.

(1) Property of Drupe of Olive

The drupe of olive is said to be classified into 20 or 30 types by its use, but we take up Chemlali olive which is mainly cultivated in Tunisia (Sfax) for oil extraction.

Its appearance is given in Fig. IV-10, and figures in parentheses indicate the component ratio of each section.

Fig. IV-10 Drupe of Olive



Chemical composition contained in each part of olive (when dried) is given in Table IV-3.

The exocarp contains a great deal of non-nitrogen content, while the mesocarp contains oil, and both endocarp and kernel contain cellulose.

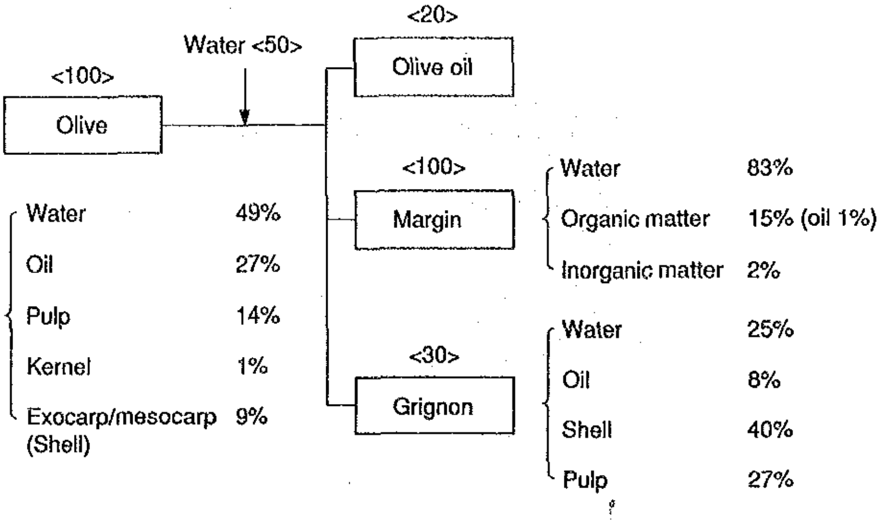
Table IV-3 Content of Drupe of Olive

(wt%)

	Exocarp	Mesocarp	Endocarp
Ash	1.6	2.3	1.2
Total nitrogen/	9.8	9.6	1.3
fat	3.4	$\boxed{51.8}$	0.8
Cellulose/	2.4	2.4	$\boxed{74.1}$
non-nitrogen extract	$\boxed{82.8}$	82.8	22.7

The component ratio of an entire drupe of olive and the component ratio of by-products are given in Fig. IV-11.

Fig. IV-11 Product Ratio of Olive

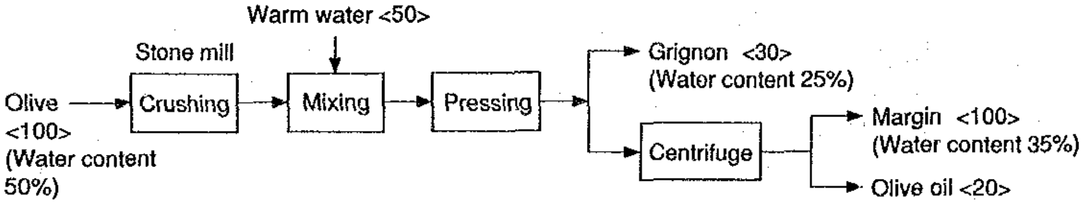


< > indicates the percentage of each part with the entire olive set as 100 (for pressing method).

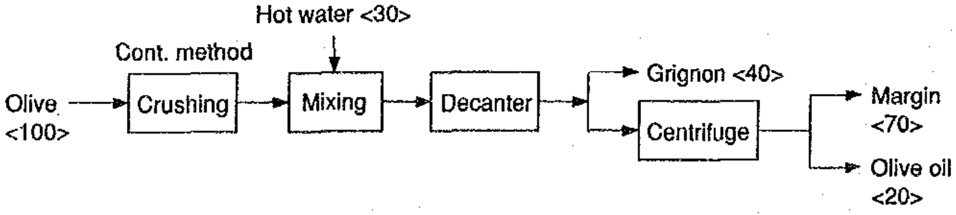
(2) Olive Oil

The methods to produce olive oil from drupe of olive will be explained in section 3.3.2 Olive Oil Production Process, and they are largely divided into pressing method (batch method) and continuous method. The quantity and quality of olive oil and by-products vary slightly depending on the production methods.

① Pressing method



② Continuous method



Figures in < > indicate the percentage of each product with drupe of olive set as 100.

Above figures, however, give only a rough idea, and the percentage may be varied largely in actual cases.

The content of olive oil is as follows. Olive oil consists mostly of saponifiable (soap-making) content (98.5-99.5%).

- Olive oil
  - Saponifiable content (98.5-99.5%)
    - Saturated fatty acidh (55-83%): (Mostly palmitic acid)
    - Mono-non-saturated fatty acid (55-83%): (Mostly oleic acid)
    - Poly-non-saturated fatty acid (3.5-22%)
  - Non-saponifiable content (0.5-1.5%)
    - Polyphenol (25-30%)
    - Alcohol (25-30%)
    - Ohters (25-30%)

Most of the saponifiable content is oleic acid. It constitutes a large part of edible olive oil, while the non-saponifiable content counts for a small portion of entire olive oil, and the latter contains important factors to determine the quality of olive oil, i.e. elements which determine the green coloring matter, red coloring matter, flavor and taste of olive oil, and Polyphenol. Polyphenol has antioxidative characteristic which ensures a long-term storage of olive oil but makes biological treatment more difficult at the same time.

The quality of olive oil is determined by various kinds of factors, and the typical elements of IOOC (International Olive Oil Council) standards are given in Table IV-4. (There are many other elements which determine the quality of olive oil.)

Table IV-4 Quality of Olive Oil

	Virgin olive oil				Refined oil	Olive oil	Extracted oil from grignon		
	Extra	Fine	Semi-fine	Lamp			Crude oil	Refined oil	–
• Odor • Taste • Color	◎ ◎ Yellow to green	◎ ◎ →	○ ○ →	× ×	Δ Δ Clear yellow	○ ○ Yellow to green		Δ Δ Clear yellow to dark yellow	Δ Δ Clear yellow to green
• Acid value • UV absorption (270 mm)	≤1.0 ≤0.25	≤1.5 →	≤3.3 ≤0.3	>3.3	≤0.3 ≤1.1	≤1.5 ≤0.9	≤1.5	≤0.3 ≤2.0	≤1.5 ≤1.7
• Water & volatility (%) • Impur. insol. ether petroleum (%)	≤0.2 ≤0.1	→ →	→ →	≤0.3 ≤0.2	≤0.1 ≤0.05	≤0.1 ≤0.05		≤0.1 ≤0.05	≤0.1 ≤0.05

Mark) ◎ Perfect Δ Acceptable

○ Good × Defective

In Tunisia, the dealing price of olive oil for ONH has been decided according to the acid number. The unit price is determined based on the following price system.

Acid No. 0.3-4.0: at 0.05 intervals

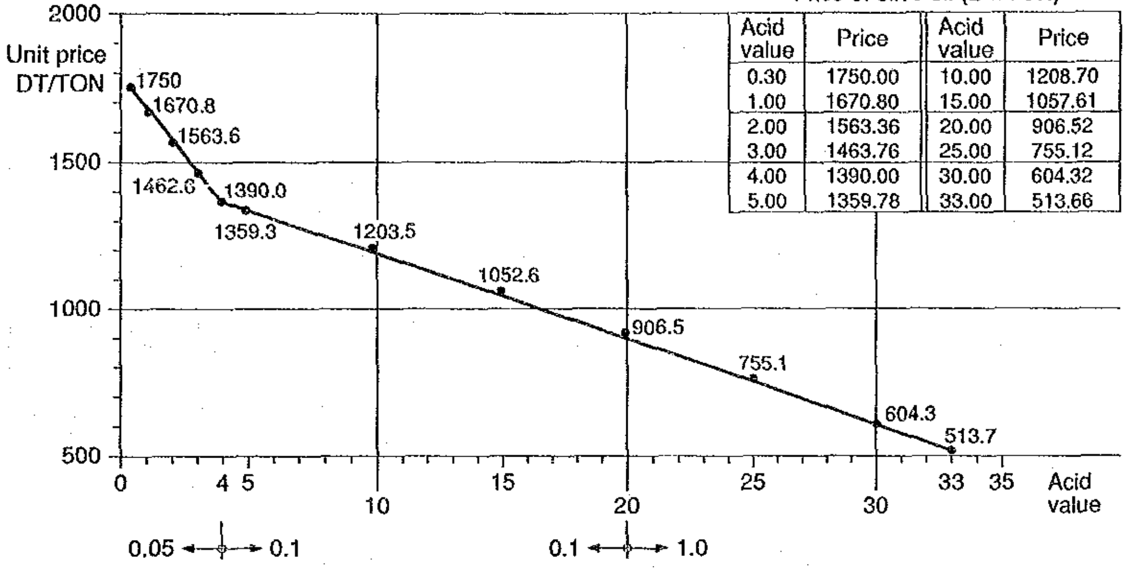
Acid No. 4.0-20: at 0.1 intervals

Acid No. 21-33: at 1.0 intervals

Fig. IV-12 illustrates the price system of olive oil.

As seen from these figures, the unit price of olive oil increases sharply when the acid number is under four, i.e. the unit price will be more profitable price as the acid number comes closely to zero.

Fig. IV-12 Price System of Olive Oil



Price of olive oil (DT/TON)

Acid value	Price	Acid value	Price
0.30	1750.00	10.00	1208.70
1.00	1670.80	15.00	1057.61
2.00	1563.36	20.00	906.52
3.00	1463.76	25.00	755.12
4.00	1390.00	30.00	604.32
5.00	1359.78	33.00	513.66

(3) Grignon

Grignon itself contains a small quantity of olive oil. Generally, the oil content is extracted as much as possible at the grignon oil extracting factory (in some cases, soap factory), and waste grignon is produced. The physical component is given in Table IV-5.

Table IV-5 Physical Component of Grignon

(wt%)

	Raw Grignon	Waste Grignon	Remarks
Water content	25 - 30	15 - 18	
Oil	8 - 10 →	2 - 4	
Shell	43 - 56	50 - 55	Endocrap, kernel
Pulp	23 - 28	30 - 35	Exocarp/mesocarp

The chemical component of grignon (dried) is given in Table IV-6.

Table IV-6 Chemical Component of Grignon

(wt%)

	Raw Grignon	Waste Grignon	Remarks
Dried content	70 - 90	86 - 95	
Ash	3 - 15	6 - 9	
Entire nitrogen	5 - 10	12 - 16	Mostly amino acid
Fat	5 - 13 →	1 - 7	From mesocarp: mostly fat acid Oleic acid 65% Linoleic acid 18% Palmitic acid 11% Others 6%
Cellulose	32 - 48	33 - 53	From endocarp
Non-nitrogen extract	27 - 45	25 - 45	From exocarp
Others	tr	tr	Polyphenol

As a matter of fact, there is a big difference in the inclusion of oil content (fat) between raw grignon and waste grignon, but the rest are almost similar.

(4) Margin

The margin has the highest degree of pollution load, and the treatment of margin is urgently needed. To this end, it is required to understand the chemical and physical components of margin. Actually, however, we can have only rough figures as data.

To show you the outline of chemical and physical components, we give an example below.

Margin
- Water content 83%
- Organic matter 15%
  - Fat 0.2-1%, Polyalcohol 1-1.5%,
  - Protein 1.2-2.4%, Polyphenol 1-1.5%
  - Carbohydrate 2-8%, Others
- Inorganic matter 2%
  - Carbonate 21%, Potassium chloride 47%
  - Phosphorus 14%, Sodium chloride 7%
  - Others 11%

There is a big difference between the pressing method (batch method) and the continuous method, and they are given in Table IV-7. In the continuous method, values are about 50% lower than those of pressing method.

Table IV-7 Example of Component of Margin

1. Alfonso Ranalli ('91 Italy)

		Pressing Method	Continuous Method
Basic Index			
BOD	g/L	67.1	39.8
COD	g/L	148	85.1
TC	g/L	59	37.1
Density		1.054	1.023
Ash	g/L	19.5	5.8
Organic Matter	g/L	94.6	55.4
Color	*	37	40.6
Saccharose	g/L	35.2	17.3
Acidity	g/L	45.6	30.5
Polyalcohol	*	1.3	
Pectin etc.	*	1.3	

* : Ratio in organic matter

2. Fiestas Ros de Ursinos ('80 West Germany)

		Pressing Method	Continuous Method	
Basic Index				
pH		4.5 - 5	4.7-5.2	5
COD	mg/L	120 - 130,000	25-48,200	40,000
BOD	mg/L	0.1	23-44,000	30,000
SS	%	12.0	0.27-1.7	0.9
Residual Dryed (105 °C)	%	1.5	1.41-4.51	3.0
Residual Ignited (550 °C)	%		0.20-0.67	0.4
Organic Content				
Total Organic Matter	%	10.5	1.20-4.06	2.60
Total Saccharose	%	2 - 8	0.5-2.6	1.0
Total Nitrogen	%	0.5 - 2.0	0.17-0.4	0.28
Organic Acid	%	0.5 - 1.0		
Polyalcohol	%	1.0 - 1.5		1.1
Pectin	%	1.0		0.37
Polyphenol	%	1.0 - 2.4	0.3-0.8	0.5
Fat	%	0.3 - 1.0	0.5-2.3	1.0
Inorganic Content				
P	mg/L	1,100	24 - 259	96
K	mg/L	7,200	529-2,758	1,200
Ca	mg/L	700	49 - 267	120
Mg	mg/L	400	19 - 125	48
Na	mg/L	900	10 - 137	45
Fe	mg/L	70	2 - 62	16
CO2	mg/L	3,700		
SO3	mg/L	400		
Cl2	mg/L	300		
SiO2	mg/L	50		

⬚ Freqently data

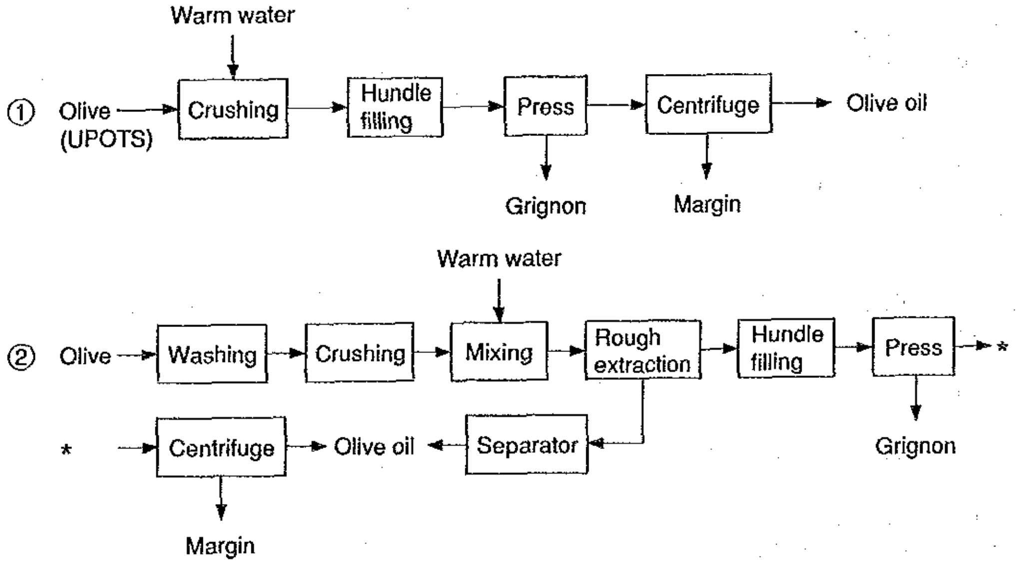
3.3.2 Types of Olive Oil Production Process

So far we have outlined the characteristics of raw materials, products and by-products. Now we proceed to the production process for them.

Broadly speaking, there are two production methods for olive oil as described in the previous section, i.e. pressing method (batch method) and continuous method.

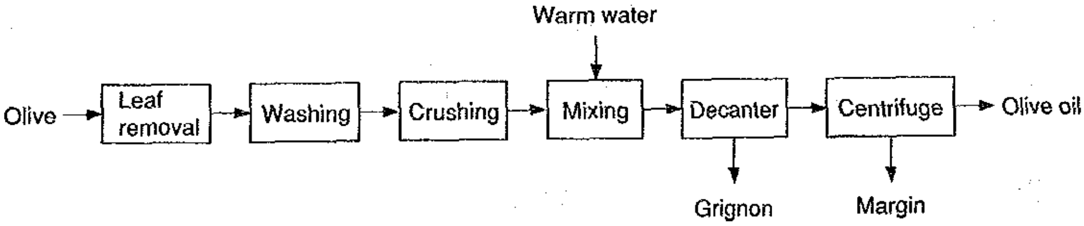
Recently, another production method like enzyme extract method is going to be established.

(1) Pressing Method (Batch Method)

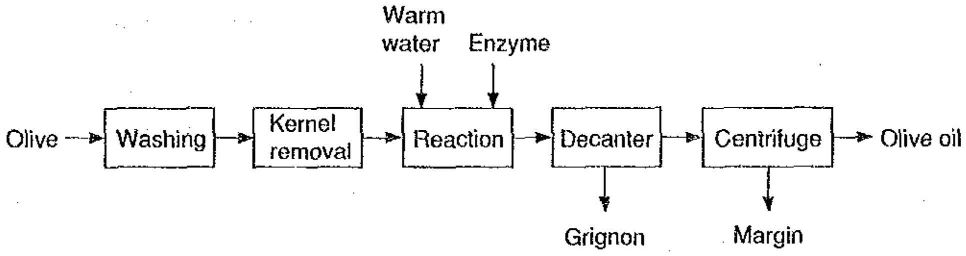


The difference between system ② and system ① is in the addition of mixing machine and rough extractor (primary press).

(2) Continuous Method



(3) Enzyme Extract Method



The pressing method has more chances of exposing raw material to air (crushing and hurdle filling) and requires a longer time for entire production process. It usually takes almost three to four hours including the primary and secondary pressing processes.

On the other hand, the continuous method takes about one hour from the start of olive processing to the completion of olive oil. From the viewpoint of acid value, the continuous method is overwhelmingly advantageous than the pressing method, but the taste of olive oil is so subtle that the continuous method is not always considered to be superior to the pressing method.

3.3.3 Improvement of Olive Oil Production Process

When taking measures to purify margin waste water, it is required to take various kinds of methods into account, i.e. to purify margin waste water directly, to decrease the volume of waste water so that its treatment may become much easier, to improve the olive oil production process so that less margin is discharged, and to reduce pollutant contained in margin. Other methods are to collect valuable materials from margin or to take advantage of margin's property (ex. combustion quality) to use it in the production process.

(1) Existing Treatment Technologies

Various kinds of existing margin treatment methods are given in Table IV-8. The table shows that almost all kinds of treatment methods have been developed, and theses on the treatment of margin may total more than 1,000.

The treatment technologies may be classified largely into about 10 categories, and they can further be divided into about 30 subdivisions ranging from the method which uses natural purifying function to the most basic physico-chemical treatment method, biological treatment method, or concentration method combined with oil production process.

Among these technologies, the biological treatment is the most popular, particularly the biological treatment of anaerobe, followed by the concentration method utilizing the heat of combustion (Grignon burning boiler). Various methods are under investigation for treatment after concentration, i.e. recovering valuable materials contained in margin or recycling oil in the extraction process by mixing margin with paste or raw grignon or using it as fuel for the grignon boiler.

The outline of major technologies is given in Table IV-9.

The table shows there are many methods to be devised by adopting or rejecting elementary technologies.

It is also feared that a new method may result in a margin treatment process, which is larger in scale and more complicated than the existing olive oil production process, and an unbalanced production process on the whole (especially for operational and technical requirements), if necessary precautions are not taken.

(2) Considerations on Process Improvement

It should be carfully studied to improve the process only with the purpose of purifying margin waste water.

For instance, the continuous method which causes less pollution of margin waste water and produces olive oil with superior acid value and the adoption of a new process to use grignon, which is now sold to soap factories, with margin inside the factory can be considered.

However, the following points should be considered carefully.

1) The change of process on a large scale will affect the business condition of the factory.

2) The pressing method (batch method) itself is a simple process. In case where multiple processes are adopted in a single factory (i.e. simple labor-intensive factory), it is unbalanced to introduce more complicated waste treatment system into the factory, if viewed from operational and technical requirements. (A seasonal factor in operation should also be considered.)

3) Process improvement should be considered to cover about 250 small-scale olive oil factories in Sfax.

It is recommended to integrate several small-scale factories into a large factory and treat waste water on a large scale. Another recommendation is not to change the present system nor the process in each factory and limit its improvement to simple rationalization by merely collecting margin discharged from each factory for treatment.

Table IV-8: Classification of Various Margin Treatment Methods Currently Available

Broad classification	Subdivision
Using natural purifying power	• Using for agriculture (as fertilizer) • Scattering over the olive firm (as fertilizer) • Discharging into the river • Drying in the lagoon • Scattering over the sand to use as fertilizer
Using as fertilizer and food for animals	• Mixing with agricultural residues, grignon, etc. or fermenting to make fertilizer • Mixing with agricultural residues, fermenting and drying to make pellets and using as food for animals • Making food through the fermentation of margin
Physico-chemical treatment	• Condensation method (lime/soda persulfate/iron sulfate/ electrolytic condensation) • Filtration concentration method (UF/RO/porous resin) • Saponification treatment • Activated carbon treatment and ultrasonic wave treatment
Heat utilizing treatment	• Drying by burning grignon • Thermal concentration by burning grignon • Atomized firing • Making fuel (Ash is used for fertilizer)
• Treatment by freezing	• Concentration through freezing
Biological treatment • Anaerobic	• Fermenting anaerobe and recovering methane
• Aerobic	• Biological treatment of aerobe
Recovering valuable materials	• Recovering polyphenol compound (as anti-oxidant) • Recovering aromatic compound and alcohol • Recovering nitrogen and protein • Collecting potassium chloride
Others	• Using for civil engineering works (agricultural maintenance and brick production) • For sampler and activated carbon (mixed with grignon)

Table IV-9 (1/2) Outline of Margin Treatment Technology (extract)

(1 lira = ¥1/10)

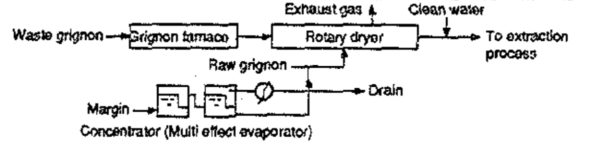
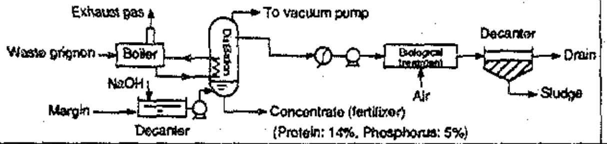
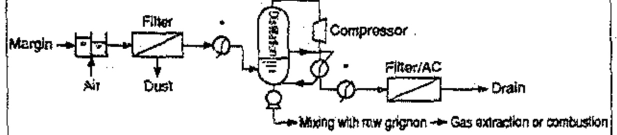
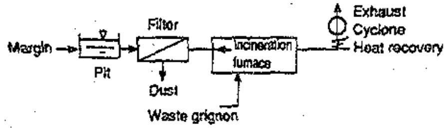
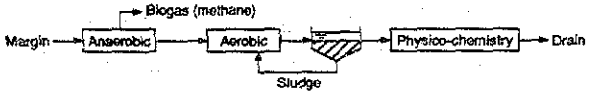
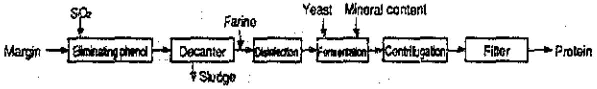
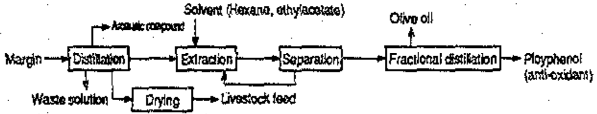
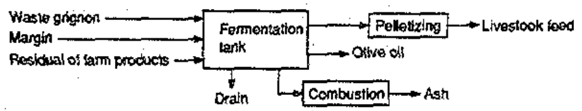
No.	Item	Outline of facilities	Treatment cost	Remarks
1	Raw grignon and margin are dried by burning waste grignon		• Construction cost for processing olive, 10 tons/day: 200 x 10^6 lire • Processing cost: 1,700 lire/m³ olive (≒ 17 lire/kg oil)	• Subsidy system is available for these facilities in Italy (capital, tax, etc..)
2	Purification of margin by distillation and biological treatment		• Treatment cost 9,660 lire/m³ margin (≒ 50 lire/kg oil) • Utility unit figure: (160 kg waste grignon/m³ margin, 15 kWh/waste grignon/m³ margin, 0.3 kg NaOH/waste grignon/m³ margin)	• It is easier to treat margin processed by continuous method than margin processed by pressing method.
3	Distillation by mechanical compressor and heat recovery		• Treatment cost: 6,440 lire/ton margin 109 lire/ton margin (for start) –3,560 lire/ton margin (Sales profit) 2,989 lire/ton margin (≒ 10 lire/kg oil)	• Additionally, a heating furnace for start-up is required
4	Atomizer incineration		• Construction cost 20 m³ margin/day treatment: 100 x 60^6 lire • Treatment cost 57 lire/kg oil, utility unit figure: 250 kg waste grignon/m³ margin	
5	Anaerobic/aerobic biological treatment			• It is a problem to keep organism alive in the season when olive waste water is not produced.
6	Produceing biomass (protein) by yeast fermentation			• Main phenol eliminating (extracting) solution 1. Absorption by gelation, bentonite and polyclar 2. Extraction by ethylacetate, ethylacetate/acetone, ethylether 3. Oxidation by caro acid
7	Recovery of valuables by distillation and extraction			

Table IV-9 (2/2) Outline of Margin Treatment Technology (extract)

No.	Item	Outline of facilities	Treatment cost	Remarks
8	Marking livestock feed through fermentation			• Is it all right to feed it to animals? Examination is still not enough.
9	Concentration by freezing		• Utility unit figure: (103 kWh/m³ margin, 100 1 water/m³ margin)	• It is not at the stage of practical use.

3.4 SIOS-ZITEX (SATHOP)

(1) Introduction

There are two soap factories in operation in Sfax. Both SIOS-ZITEX and SATHOP adopt almost similar drainage systems. Therefore, this section describes the process improvement of SIOS-ZITEX only.

At SIOS-ZITEX, waste water is discharged from several places. Here we discuss on waste water discharged from the saponification tank which is most closely related to process improvement.

For improving the existing process without changing too much, the simplest way is to recover valuable materials contained in waste water and reflect them as reduction from expenses for waste water treatment.

The valuable materials in waste water discharged from the soap factory are as follows.

- Glycerine: 2 - 8% (content)
- Salt: 2 - 3%
- NaOH: 3 - 4%

Here we examine the recovery of glycerine (sodium chloride is recovered at the same time) which is the most valuable in all and whose process has already been established in variously.

(2) Glycerine

The composite system and natural system (glycerine is produced as a by-product of soap) are available for the production of glycerine. The natural method was popular in Japan in the past, but the adoption of composite system is increasing nowadays. (The import of soap has been increased.)

Glycerine is used in all areas of industry thanks to its various features such as physical properties (hygroscopicity, solubility and viscosity), chemical properties (reactivity due to three OH groups) and nonpoisonousness to organism. The main use of glycerine is as follows, and it is regarded as an effective chemical product.

Table IV-10 Use of Glycerine

Classification	Use
Food	Solvent (perfume, colorant), crystallization inhibitor (sugar), refrigerant (frozen food), lubricant (food processing machine)
For medicine	Enema, tincture, ointment, mental stabilizer, heart medicine (nitroglycerine)
For cosmetics	Dryness inhibitor, viscosity adjuster
For lubricant	Oxygen compressor, non-oil soluble lubricant
For tobacco	Leaf shape collapse inhibitor, dryness inhibitor
For cellophane	Plasticizer (absorption 10-20%)
For urethane foam	Raw material (glycerine + PO/EO + diisocyanate)
For monoglyceride	For food, medicine, cosmetics, emulsifier for construction (monodiethyl)
For resin	Water-proof lacquer, varnish, paint (ester gum), for coating (alkyl resin)
For explosive	Dynamite (nitroglycerine)

To meet the requirements above, the quality standard of glycerine is classified as follows.

Table IV-11 Quality Standard of Glycerine (Japan)

Type	Description and subdivision
Pharmaceutical glycerine (PG)	Approved by Japanese Pharmacopoeia (84-87 wt%, ρ=1.221-1.230). • Concentrated glycerine (95 wt% or above) • Glycerine for cosmetics (meeting the raw material standard of cosmetics)
Refined glycerine (RG)	Meeting the JIS refined glycerine standard (95 wt% or above) • Glycerine for resin (passing the heat run test) • Edible glycerine (passing the test of the Food Sanitation Act)
Dynamite glycerine (DG)	Meeting the JIS requirements of dynamite glycerine (98.5 wt% or above), slightly yellow-colored

The U.S. standard of glycerine is as follows.

Table IV-12 Quality Standard of Glycerine (U.S.A.)

Type	Description
USP grade	Almost similar to concentrated glycerine approved by the Japanese Pharmacopoeia
BP grade	Similar to the USP grade, $\rho \geq 1.260$
CP grade	Almost similar to the USP grade
Industrial glycerine	Light-yellow, $\rho \geq 1.262$
Dynamite grade	Large difference in color, $\rho \geq 1.262$

(3) Outline of Process for Recovering Glycerine from Soap Waste Water

Generally, glycerine has been produced by recovering from soap waste water. The volume of soap waste water discharged at SIOS-ZITEX is $7m^3$ daily and contains about 5% of glycerine, sodium chloride, NaOH and impurities.

The process of concentration refinery method which is most popular now in soap production allows to collect high-quality glycerine efficiently.

Since soap waste water contains various kinds of impurities, it is required to remove them completely through chemical treatment before conducting concentration refinery.

The concentration process consists of double-effect vessel, concentration vessel and refinery vessel, and glycerine and sodium chloride are recovered at the same time.

(4) Description on Recovery Process

The flow sheet of recovering glycerine is given in Fig. IV-13, and the recovery process is explained along the flow.

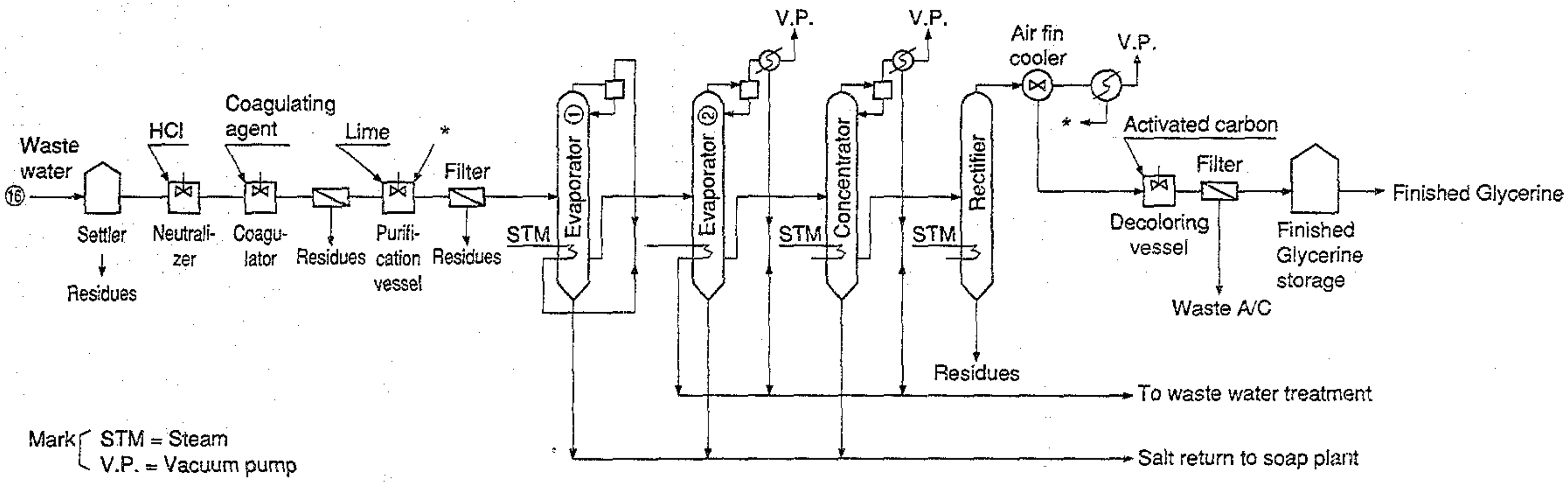
1) Settler (2 units)

Two units of settlers are used to remove impurities in soap waste water. The stationary settlers separate and eliminate fatty acid or soap content as much as possible.

2) Neutralizer

Alkalinity (caustic soda) contained in waste water is mixed with hydrochloric acid and neutralized (Sulfuric acid is also available.)

Fig. IV-13 Flow Sheet of Glycerine Recovery



3) Coagulator

Aluminum sulfate is added in the coagulator, and coagulation refinery is conducted to separate residual oil emulsion into metallic soap (aluminum soap) and colloidal sediment of sodium hydroxide. Alun can substitute for aluminum sulfate.

Additionally, lime is added and mixed, then forced filtration is conducted at PH 4.5 to separate various kinds of impurities contained, fatty acid or soap content completely.

4) Purifier

For concentration to be followed, soda ash (sodium carbonate) is added and mixed, and forced filtration is conducted at PH 8.5-9.0 again.

Residues carried out twice through above-mentioned forced filtration include metallic soap (aluminum soap), colloidal sediment of sodium hydroxide and aluminum soap.

5) Evaporator (2 units) and Concentrator

The evaporators (2 units) consist of double-effect vessels. After glycerine is heated and concentrated to 40-60% in the second vessel, it is transferred to the concentrator, where glycerine is heated at 60-80°C and concentrated to 80-90% under a reduced pressure of 50-100 mmHg to obtain crude glycerine. Sodium chloride crystallized at the bottom of above-mentioned three vessels is recovered in a form of slurry and can be used again for soap production.

6) Rectifier and Air-Cooled Heat Exchanger (3 units)

Crude glycerine is transferred to the rectifier to be heated at approximately 200°C and distilled under a reduced pressure of 40-50 mmHg, then condensed in the three units of air-cooled heat exchangers to obtain glycerine with a density of 98% or above at an yield of 80-90%.

7) Decolorizer

Since crude glycerine obtained as in a manner described above is slightly colored (light yellow) by decomposition and sometimes gives out a bit of smell, it is required to mix with activated carbon in the decolorizer and conduct forced filtration.

In some cases, it is diluted with distilled water to obtain glycerine of required density.

The arrangement drawing of facilities for recovery process is given in Fig. IV-14 and main equipment are given in Table IV-13.

Fig. IV-14 Arrangement Drawing of Glycerine Recovery Facilities

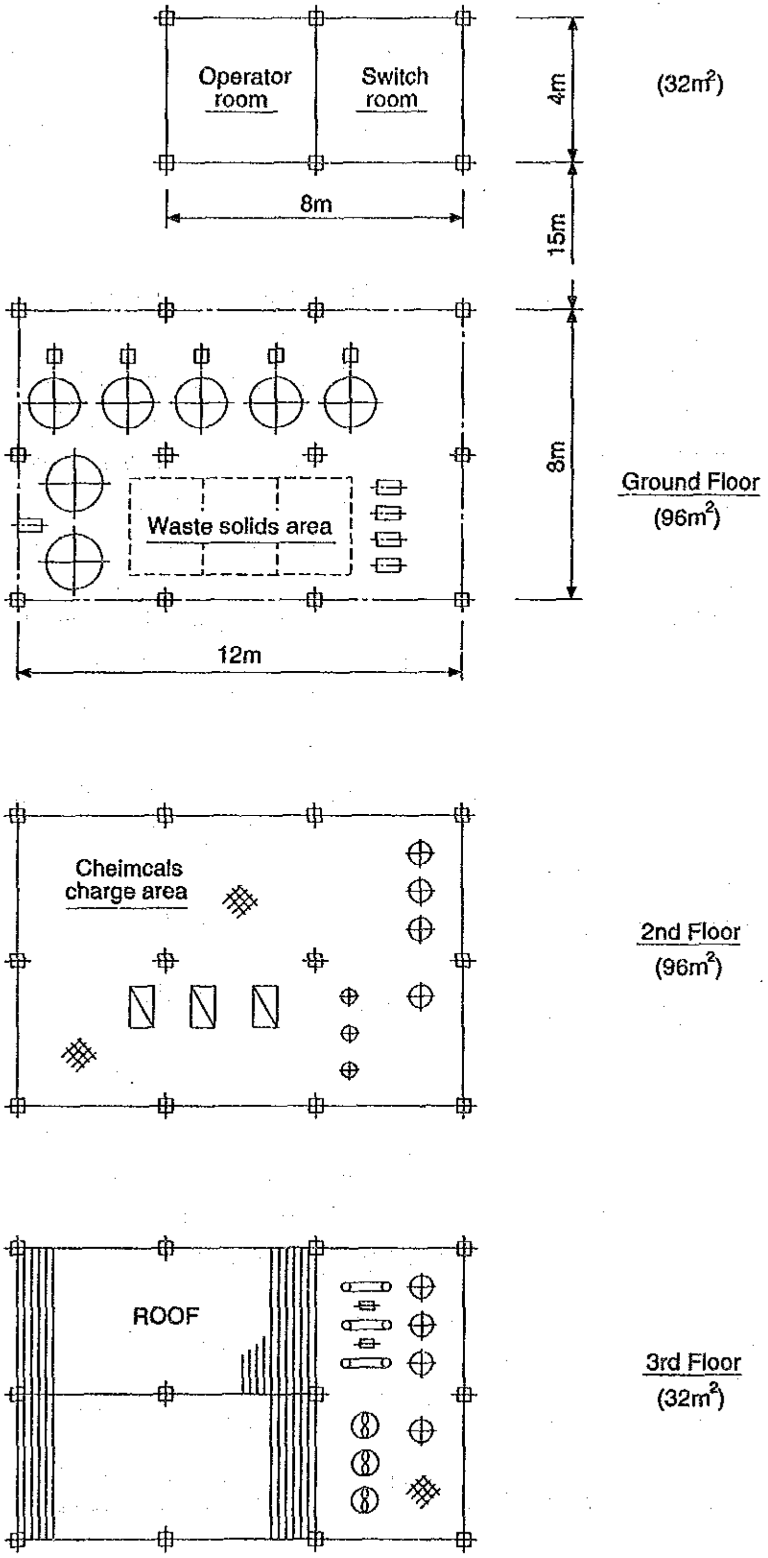


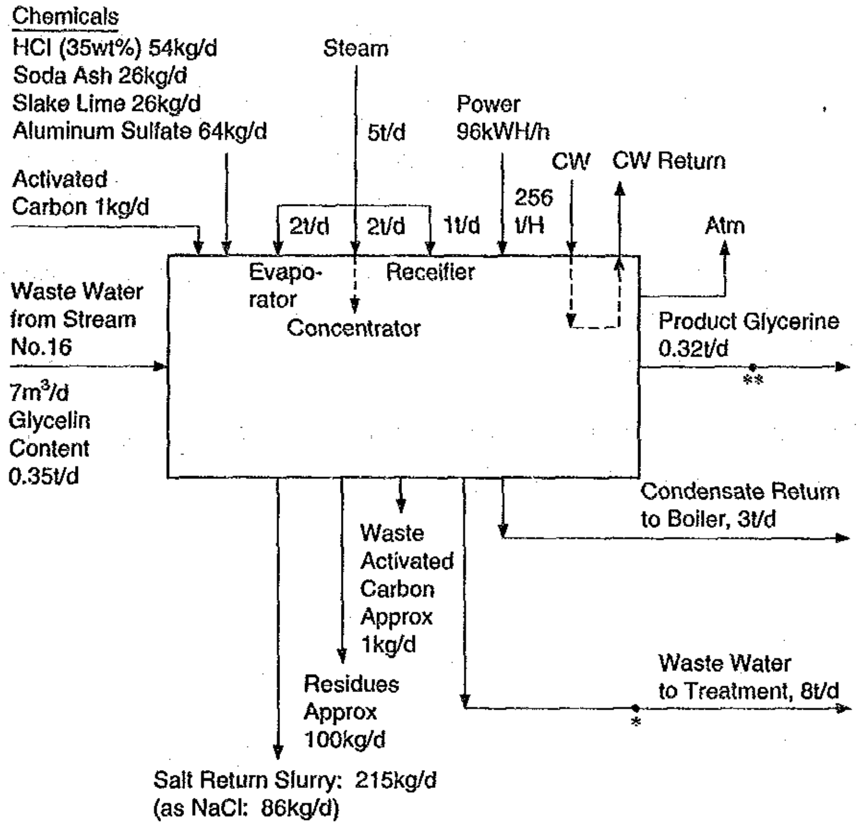
Table IV-13 List of Main Equipment (Glycerine Recovery Facilities)

Item	Quantities	Specification
Columns		
Evaporator I	1	500 $\phi \times$ 3000H, C.S., Pall Ring with Reboiler
Evaporator II	1	500 $\phi \times$ 3000H, C.S., Pall Ring with Reboiler
Concentrator	1	400 $\phi \times$ 4000H, C.S., Pall Ring with Reboiler
Rectifier	1	300 $\phi \times$ 5000H, C.S., Pall Ring with Reboiler
Vessels and Tanks		
Settler	2	Cone Roof, Cylindrical, 8 m^3, PE
Neutralizer	1	Cylindrical, 4 m^3, PE with mixer
Purification Vessel I	1	Cylindrical, 4 m^3, PE with mixer
Purification Vessel II	1	Cylindrical, 4 m^3, PE with mixer
Evaporator Feed Vessel	1	Flat Bottom, Cylindrical, 4 m^3, C.S.
Concentrator Feed Vessel	1	Flat Bottom, Cylindrical, 2 m^3, C.S.
Crude Glycelin Storage	1	Vertical Cylindrical, 1 m^3, C.S.
Accumulator I	1	Vertical Cylindrical, 0.5 m^3, C.S.
Accumulator II	1	Vertical Cylindrical, 0.5 m^3, C.S.
Condensate Vessel	1	Vertical Cylindrical, 0.2 m^3, C.S.
Decoloring Vessel	1	Conical Bottom, Cylindrical, C.S. with mixer
Finished Glycerin Storage	1	Cone Roof, 3 m^3, C.S., for 1 week storage
Heat Exchangers		
Evaporator Condenser	1	Shell and Tube, C.S./C.S., 3 m^2
Concentrator Condenser	1	Shell and Tube, C.S./C.S., 3 m^2
First Stage Air Fin Cooler	1	Air Fin, C.S., 2 m^2
Second Stage Air Fin Cooler	1	Air Fin, C.S., 2 m^2
Third Stage Air Fin Cooler	1	Air Fin, C.S., 2 m^2
Final Condenser	1	Shell and Tube C.S./C.S., 2 m^2
Filters		
Filter I	1	Press Filter, Aluninum
Filter II	1	Press Filter, Aluminum
Filter III	1	Press Filter, Aluminum
Vacuum Pumps		
Vacuum Pump I	1	Nash Pump, CS
Vacuum Pump II	1	Nash Pump, CS
Vacuum Pump III	1	Nash Pump, CS
Pumps	10	Centrifugal, 304SS and C.S.

(5) Material Balance

When glycerine is recovered through above process, various kinds of assistant agent and utilities are used. The entire material balance is as shown in Fig. IV-15.

Fig. IV-15 Material Balance of Recovering Glycerine



As shown in the figure above, the recovered percentage of glycerine is 91%.

$$0.32/0.35 \times 100 = 91\%$$

The quality of recovered glycerine at this time can be gained as following two cases by changing the operational conditions.

Table IV-14 Quality of Recovered Glycerine

Item	Refined glycerine	Pharmaceutical glycerine
Density d^{15}	1.2626 - 1.2647	1.2241 - 1.2252
PH	5.7 - 6.6	5.8 - 6.7
Glycerine content	99.0 - 99.7%	84.3 - 84.7
Chlorine (as NaCL)	<0.001%	<0.001%
Ash	tr	tr
Non-volatil content	0.01 - 0.03%	0.01 - 0.03%
Soap content (as Na_2O)	<0.01%	<0.01%

Note: The figure above shows the quality of glycerine in the position with ** marks in Fig. IV-15.

The volume of waste water discharged from the factory (No. 16) increases from $7m^3$ to $8m^3$ daily, while the degree of pollution decreases in the recovery process of glycerine. The quality of this waste water is as follows.

The quality of waste water after recovering glycerine (the quality of waste water in the position with an * mark in Fig. IV-15)

Flow	8 m^3/day
Density of residual glycerine	2,000 ppm
CODcr	2,400 ppm
BOD	1,500 ppm
SS	Neg

(6) Examination of Profitability in Brief

The profitability of facilities for recovering glycerine will be discussed below.

① Annual recovery of glycerine: 0.32 tons/day × 330 days/year = 105.6 tons/year

② Expenses for facilities: ¥203 million

③ Labor cost: ¥1.08 million (¥45,000/month × 2 persons × 12 months)

④ Variable cost: ¥6.216 million (Chemicals and utility cost)

By using the above data, annual expenses for recovering glycerine are calculated as follows. However, the depreciation rate is regarded as 10%, and a total of tax, insurance, repair cost and interest as 12.4% of all investment.

- Fixed cost : ¥46.552 million
  (Construction and facilities : ¥45.472 million)
  (Labor cost : ¥1.08 million)
- Variable cost : ¥6.216 million
- Cost (fixed cost + variable cost) : ¥52.768 million
- Sales amount : ¥28.512 million

The period of time for return on investment is calculated from the formula below.

$$\text{POT} = \frac{\text{Investment}}{\text{Pretax profits} + \text{Depreciation}} = \frac{\text{Investment}}{\text{Sales amount} - \text{Cost} + \text{Depreciation}}$$

$$= 203{,}000/(28{,}512 - 52{,}768 + 20{,}300) = -51$$

Therefore, investment on these facilities is problematical but the pollution load of waste water may be decreased and the scale of waste water treatment facilities may be smaller. It is required to compare the case of glycerine recovery plus waste water treatment facilities with the case of waste water treatment facilities only.

3.5 SMCP (TMC)

SMCP/TMC has a definite plan for business in the future and is installing facilities along the plan, which includes facilities for environmental pollution control. Under these circumstances, the factory's main subject of environmental pollution control is to recover chromic salt. However, as we consider that it is very difficult to make a profit for the enterprise if its scale is not big to a certain degree, we only introduct the current world conditions of recovering chromic salt.

(1) Recovery of Chromic Salt from Chromic Tanning Waste Water

1) Conditions of various countries

The circulatory utilizing system of chromic tanning waste water is broadly divided into two methods, i.e. one is to use chromium-contained waste water directly as next tanning water in the direct circulation system, and another is to precipitate and separate chromium as chromium hydroxide from chromium-contained waste water with alkali, and dissolve it with sulfuric acid to recycle it as tanning agent.

There is a limit in the direct circulation system, because soluble salt, oil and protein are accumulated increasingly as recycling of waste water is repeated. Therefore, it is required to precipitate, separate and collect chromium-contained sediments from waste water which exceeds the limit of validity and decrease or eliminate the amount of soluble salt, oil and protein contained in waste waster to recycle it as solution of sulfuric acid.

The following documents are available for direct circulation system.

① Williams, D.A.: U.S. Pat. 2,110,187 (1933)

② Schulls, G.W. and Schubert, A.: PB Report, 12,672 (1945)

③ Harnley, J.W.: J.A.L.C.A., 46,169 (1951)

④ Klanfer, K.: J.A.L.C.A., Supplement, No. 15,29 (1970)

⑤ Hauck, P.A.: J.A.L.C.A., 67,422 (1972)

⑥ Harenberg, O., Heldemann, E. und Allam, S.S.: Das Leder, 25,219 (1974)

⑦ Robinson, J.W.: Leather and Shoes, 168,38 (1976)

⑧ Robinson, Jr.J.W. and Howard, J.W.: Leather Manufacturer, 93, No. 8, 12 (1976)

⑨ Constatin, J.M. and Stockman, G.B.: Das Leder, 31,52 (1980)

⑩ Emanuelsson, I., Persson, C. and Horrdin, S.: Ibid, 32,125 (1981)

According to Ir. P.J. Van Vlimmeren, president of Institute for Leather and Shoe Research (TNO) of Netherlands who visited Japan in 1977, the most efficient precipitant for this method is magnesium oxide, which is effective in producing firm sediments (10% Cr_2O_3/wet weight) and features quick sedimentation (about 2.5m/h), a smaller amount of residual chromium (5 mg Cr/*l*) coexistent with formic acid and phosphate, and a comparatively low pH of supernatant (pH 8-9). Further, precipitated chromium hydroxide can be recycled as tanning agent by dissolving and adjusting it with sulfuric acid without any technical problems and deterioration in the quality of finished products.

The Japanese Association of Leather Technology visited major European and American research institutes, leather factories and waste water treatment plants in 1976 and reported that recycling of chromium from chromic tanning waste water through the sedimentation of chromium hydroxide was widely adopted by TNO of Netherlands, Centre Technique du Cucr (CTC) of France, BASF of Germany, and Carl Freudanberg Co. (a general manufacturer of leather related products in Weinheim) of Germany.

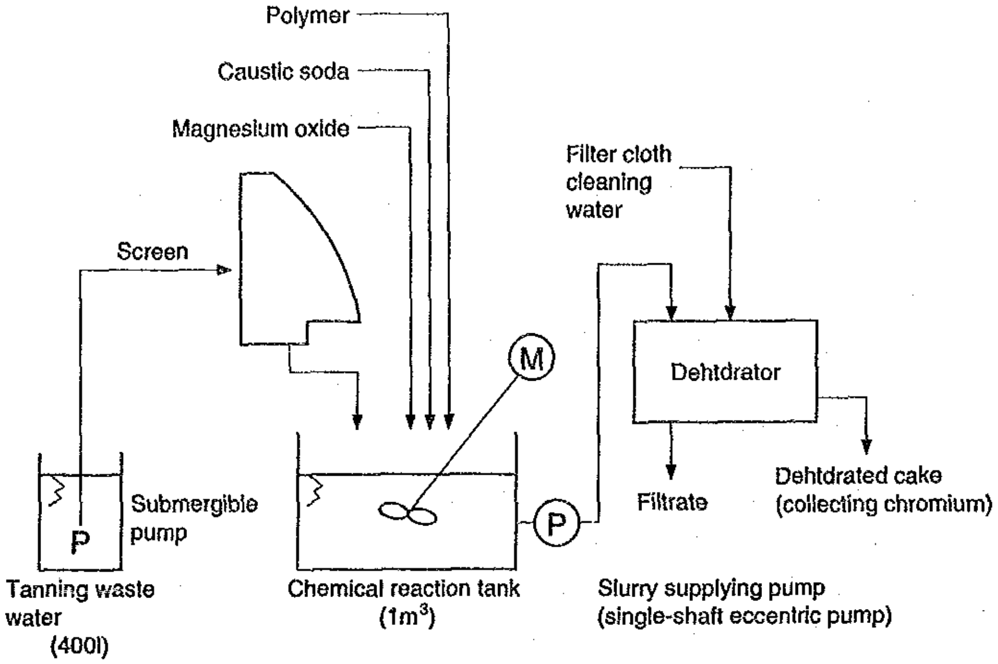
The system to precipitate, separate and dissolve chromium requires large-scale facilities and equipment like chemical reactor to collect chromium as chromium hydroxide, dehydrator to remove water from precipitated flocs, and homogenizer to dissolve chromium with acid. Beside, it requires a number of operators and huge expenses for the operation of these facilities and equipment. The system is suited for use in large factories but not for use in small factories. This is one of strong reasons why the direct circulation system is strongly recommended.

2) Practical Examples in Japan

This section outlines the "Experiment in Collecting Chromic Salt from Chrome Tanning Waste Water and Tanning with Recycled Chromium" which was conducted at the Tokyo Metropolitan Leather Technology Center in Tokyo in 1988.

Fig. IV-16 illustrates a system of recovering chromic salt from tanning waste water.

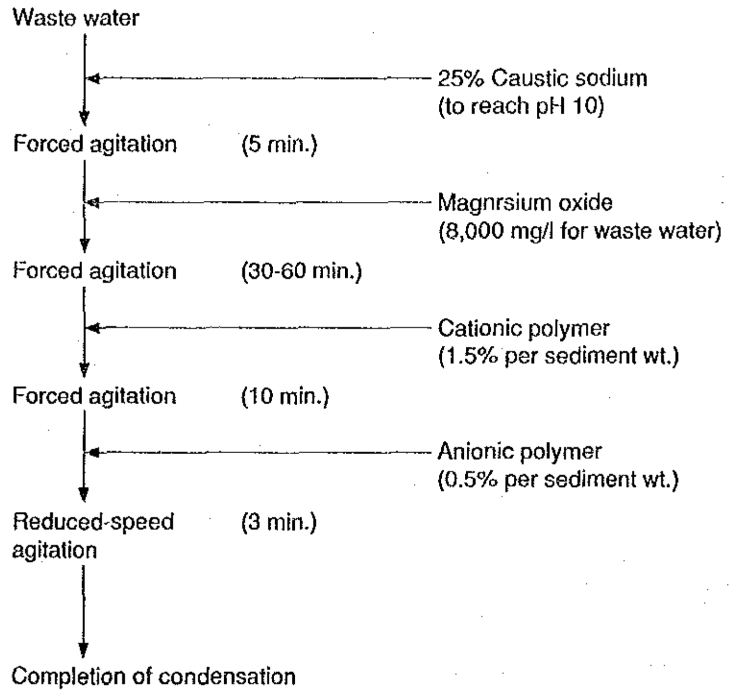
Fig. IV-16 Chromium Recovery System



Waste water was collected in two 200-liter cans (about 400 liters), and leather chips were removed by the 150 μm auto screen (wedge wire) and put into the chemical reaction tank. In the chemical reaction tank, after solution of 25% sodium hydroxide, magnesium oxide and polymer were added, agitated and mixed, waste water was transferred to the dehydrator by pump for dehydration. It is not desirable to use iron salt and lime as precipitant and condenser, because the dehydrated cake is dissolved again to be used again as tanning solution.

Fig. IV-17 shows how to condense tanning waste water.

Fig. IV-17 Condensing Method of Tanning Waste Water



A recycling test was made to dissolve dehydrated cakes with sulfuric acid for use as chromic tanning agent.

The outline of an experimental method is given below.

① Crush dehydrated cakes (65 kg).

② use hot water (30 kg) to make slurry.

③ Add and mix industrial-use concentrated sulfuric acid (20 kg) gradually to dissolve dehydrated cakes.

④ Remove undissolved lumps by using the basket of stainless net (5 mm × 5 mm).

⑤ Add hot water (40 kg) and agitate it.

Remove brown oil floated on the surface.

⑥ Blow steam into the solution to heat it up to the boiling point or so.

⑦ Leave it alone. (weighing 107.65 kg)

⑧ Add 40% caustic soda (weighing 5.8 kg) gradually and adjust pH to be 2.0 (Actually, pH was adjusted to 2.2.)

⑨ Production of recycled chromic tanning solution (116.3 kg) is completed.

The experiment was conducted by adding new tanning agent to recycled chromic tanning solution. The volume of additive agent is obtained by deducting the volume of chromium contained in recycled chromic tanning solution.

As a result,

1) The salt density of recycled tanning solution is very high at 30%. Therefore, when using it as tanning solution, it is required to dilute about four times as thin as the original tanning solution. Since the volume of recycled solution is reduced to 1/20-1/100 of the volume of used non-liquid, the entire volume can be reused here.

2) The characteristics of wet blue are almost same as compared with those of controlled leather.

3) The properties of product leather are superior to controlled leather in practicality, and there is no problem in its physical strength.

4) Dehydrating filtrate cannot meet the waste water standard of 2 mg/*l* in entire chromium. Therefore it cannot be recycled and it is treated as sludge by condensation and settlement through waste water treatment facilities.

In Japan, no factory is recycling chromium through the chromium hydroxide settlement system and reusing it as tanning solution. Entire volume is treated as sludge.

3.6 STS

3.6.1 Production Planning

The current operating time is 16 hours a day on a two-shift basis. If sales can be increased in volume by sales promotion, the three-shift system of 24-hour operation, six days a week (off on Sundays and national holidays), will make an increase in profits.

Reasons are given below.

① Since the depreciation of equipment and facilities has been finished and the labor cost is not high, the burden of fixed assets is comparatively light. An increase in production with low cost can be guaranteed.

② Equipment are more efficient rather by using them without interruption than repeating start and stop operations. (For the boiler and dryer, the repetition of thermal stress may be decreased and the working life may be prolonged.)

③ Planning the same kind of dyeing for a longer period of time will decrease the loss of dyeing chemicals and production cost.

Therefore, it may cause an increase in the number of laborers, but sales promotion must be intensified.

3.6.2 Cost Reduction Effect by Recycling Condensed Water

Air used for the dryer is heated by steam, and condensed water of steam is now discharged as effluent. However, condensed water of steam is superior in quality and can be recycled. About three tons of condensed water is discharged daily at STS. The yearly operating day is approximately 290 days, and the amount of condensed water to be recycled may be rather small as shown below, but it will contribute to water saving.

The volume of condensed water to be recycled $\doteqdot 3\text{m}^3/\text{day} \times 290\ \text{days/year} = 870\text{m}^3/\text{year}$

Amount to be recovered $\doteqdot 870\text{m}^3/\text{year} \times 0.106\ \text{TD/m}^3 = 92.2\ \text{TD/year}$

If condensed water is discharged at 80°C and the temperature of condensed water is reduced to 20°C, the yearly saving of heavy oil A will be:

$$\frac{870\ \text{m}^3 \times (80 - 20°\text{C})}{10{,}106} = 5.1\ kl$$

Where combustion heat is 10,106 kcal/kg

3.6.3 Introduction of General Energy-Saving Measures Taken By Japanese Factories

This section introduces the typical models of energy-saving measures and improvement of waste water in Japanese dyeing factories.

(1) Energy Saving in Dyeing Factories

When taking energy-saving measures, first eliminate the loss of energy. In other words, the primary object in daily operation is to eliminate 'waste' and it is required to urge all workers in the factory to participate to take energy-saving measures.

You should take the following points into account.

① Make efforts to let workers aware of energy saving and eliminate any loss nearby.

② Make a check list and examine each point.

③ Refer to precedents in the factory and cases of other factories.

④ Have the results of improvement released, and make good use of them as means for further awareness of energy saving and as reference cases.

1) Thorough Maintenance of Steam Trap

Check the steam trap for operation carefully, and you will often find troubles. For example, in the factories we investigated, about 40% of traps had some troubles. Accordingly, the periodical diagnostic system and thorough maintenance are needed.

2) Recovering Condensed Water

In some dyeing factories, condensed water is not recycled for fear that chemicals and dyes should be included into the boiler. It should be used as hot water for process or utilized in the heat exchanger to recycle heat and condensed water.

3) Improving the Operation of Dryer

In some cases, some of the final cylinders of the cylinder dryer are operated wastefully, i.e. the cylinder dryer is drying more than required. Loss can be avoided by SOP such as hutting off steam of the final cylinders according to the type of product on the line.

4) Controlling Exhaust Air Emitted from Hot Air Dryer

To minimize heat energy in exhaust air from the hot air dryer, measure the absolute temperature of exhaust air to control emission.

5) Recycling the Heat of Exhaust Air Emitted from Hot Air Dryer

Use the heat exchanger such as heat pipes, etc. to apply the heat of exhaust air for heating supply air. Heat water with waste heat and use hot water for the washing machine.

6) Illumination Check

Put light out where people are not usually working, and thin out lights to lower the entire quantity of light.

7) Decreasing the Change of Lot

In dyeing factories, especially textile printing factories, printing molds and dyes are frequently changed according to the alteration of patterns and colors. Loss of energy and chemicals is quite large during the time of replacement. Accordingly, bigger the lot becomes, more energy is saved.

(2) Improvement of Waste Water

1) Saving and Changing Chemicals and Agents

Be careful not to prepare too much when you compound chemicals or do not make mistakes in compounding chemicals. Moreover, examine to replace the present chemicals with those of smaller pollution load or those which require smaller quantity to be consumed.

2) Water Saving

By adopting counterflow for washing direction, a considerable volume of water is saved.

VOLUME V

A STUDY OF WASTE WATER TREATMENT AND RECYCLING TECHNIQUE AND PRECONDITIONS FOR PLANNING

VOLUME V A STUDY OF WASTE WATER TREATMENT AND RECYCLING TECHNIQUE AND PRECONDITIONS FOR PLANNING

1. Outline of Technique of Waste Water Treatment and Recycling

1.1 Method of Studying Waste Water Treatment and Recycling

To study the technique, the following factors are related to each other so closely that a total viewpoint is required for the procedure:

① Reduction of water use

② Recovery of superior waste water through simplified treatment

③ Pretreatment of inferior waste water

④ Overall waste water treatment plan and prediction of changes resulting from various countermeasures

⑤ Examination of recycling system of the treated overall waste water

⑥ Various case study and optimization

⑦ Technical and economic evaluation on the above items

These various factors, the main items for study and the methods to study are shown in Fig. V-1.

1.2 Notes on Waste Water Treatment

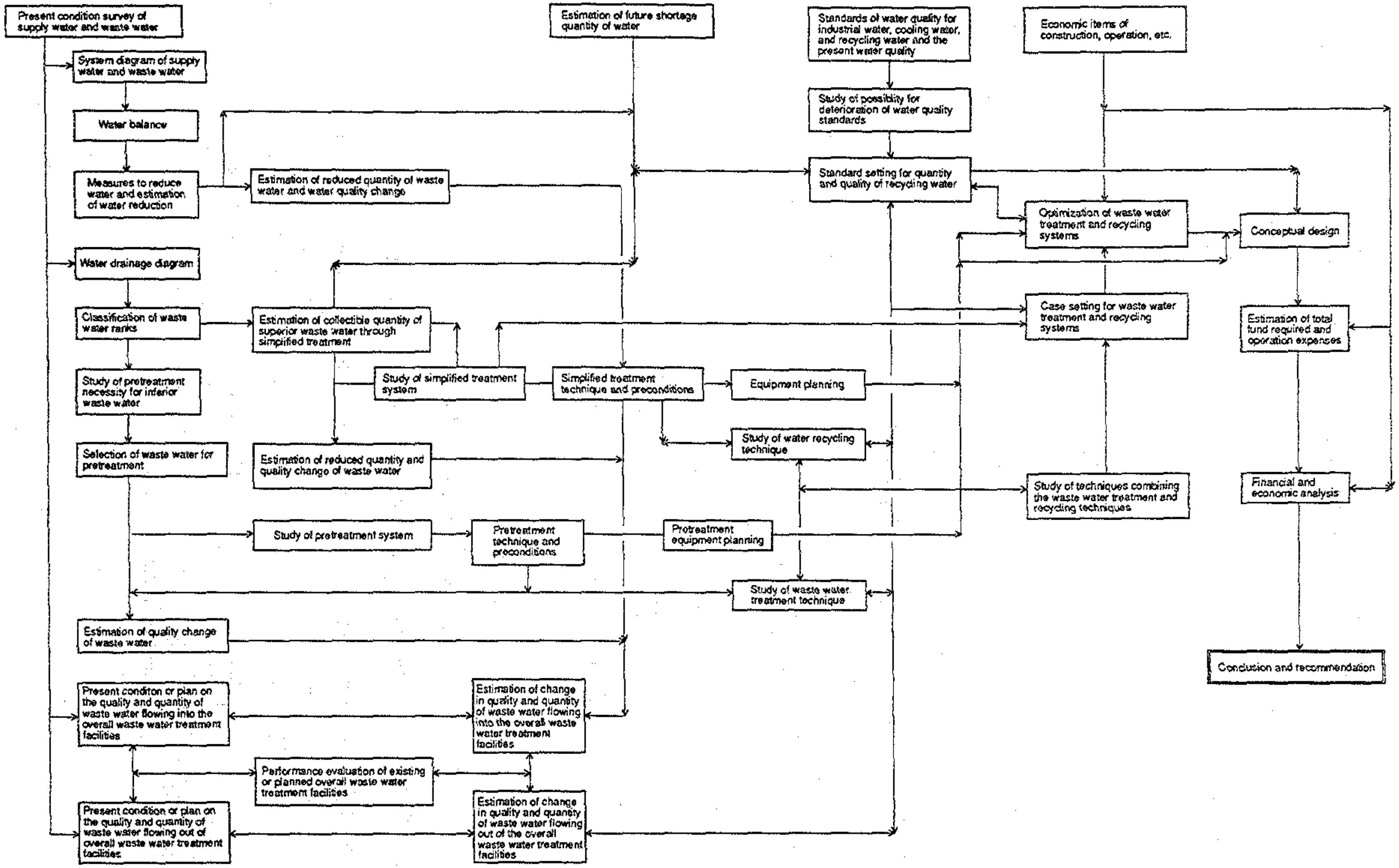
1.2.1 Necessity of Countermeasures for Generation Source

(1) Prevention of pollutant expansion at downstream

To prevent expansion of pollutant to the downstream areas, waste water must be treated when it is in a small quantity with high concentration at the generation source area. Treatment would become difficult after the waste water joins other waste water flow because of the larger quantity and lower concentration.

Thus the treatment in early stage will eventually save and reduce the expenses (cost of construction and operation).

Fig. V-1 Flowchart of Studying the Waste Water Treatment and Recycling Techniques



(2) Prevention of pollutant flow leak by accident or error

Flow leak of pollutant to other system resulting from damage or misoperation of the treatment equipment must be prevented, since that may contaminate the public water supply area and underground water.

(3) Reexamination of pollutant generation source

To reduce the pollutant discharge at the generation source area, the discharge condition and the production process must be reexamined.

1.2.2 Necessity to Separate Water Discharge Systems

There are different types of pollutant by the generation sources, so that a same type of pollutant must be separated from others for the treatment. Further, clear waste water that can be discharged without treatment must be separated completely from the waste water to be treated.

By executing the above mentioned matters, the construction cost and operation expenses of the water treatment equipment can be reduced largely.

1.3 Outline of Waste Water Treatment Techniques

1.3.1 Types of Treatment Equipment

Treatment equipment is roughly classified into the followings.

Fig. V-2 shows types and classification of treatment equipment.

① Solid-liquid separator

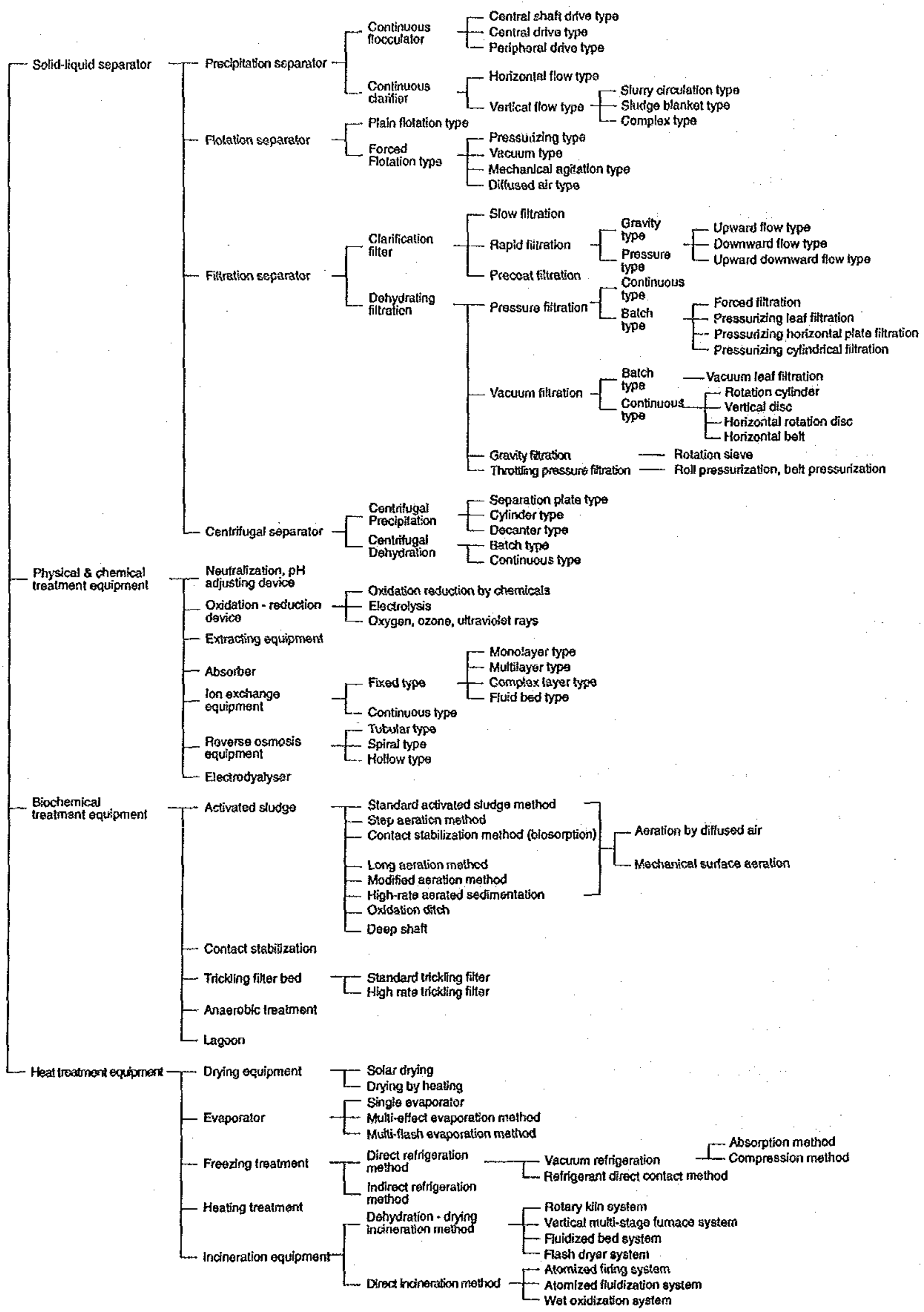
② Physical and chemical treatment equipment

③ Biochemical treatment equipment

④ Heat treatment equipment

These four items mostly cover the presently used types of waste water treatment equipment.

Fig. V-2 Types and Classification of Waste Water Treatment Equipment



1.3.2 Characteristics of Waste Water in the Selected Factories of the Study and Their Treatment Systems

The types of the selected factories of the study are varied with different characteristics of the waste water by factory. However, the common treatment objects are such factors in pollutants as suspended solids, organic substance (BOD, COD, etc.), normal hexane extracts (oil and fat, grease, etc.), and pH.

At specific factories, such factors as heavy metals, odor, and chromaticity are also treated.

Table V-1 outlines these pollutants and the primary, secondary, and high-grade treatments corresponding to them.

Some types of waste water with high salinity are discharged. In the Sfax area, the supply water itself has a high salinity. Well water has a high electric conductivity such as 5.5 to 5.7 ms/cm at the SIAPE, 14.9 to 21.9 ms/cm at the SIOS-ZITEX, and 12.0 to 12.5 ms/cm at the SMCP. Even city water measured at the TMC showed a level of 2.0 to 2.3 ms/cm which is an electric conductivity higher than that of the general drinking water in Japan.

Table V-1 Characteristics and Treatment System of Waste Water by Type of Industry

(Note) : ●●●High Concentration, ●Low Concentration

	Pollution level Kind of waste water type	pH	SS	BOD	COD	Oil content	Nitrogen compound	Phenol	Fluorine	Chromium	Iron	Other heavy metals	Phos-phorus	Sulfide	Odor	Color
Kind of industry type	Oil storage station		●	●	●●	●								●		
	Fertilizer factory	●●●	●●	●●	●●	●			●●				●●			
	Soap factory	●	●●	●●●	●●●	●										●
	Tanning and dyeing factories	●●	●●	●●●	●●●	●●●	●●			●●				●		●●●
	Sewage treatment plant		●●	●●	●●		●		●	●			●		●	●●
	Olive oil factory	●●	●●●	●●●	●●●	●	●●	●					●●			●●
Method of treatment	Primary treatment		Screen, plain sedimentation	Plain sedimentation, Coagulating sedimentation,	Plain sedimentation, Coagulating sedimentation	Plain flotation	Activated sludge, Trickling filter				Plain sedimentation and coagulating sedimentation of scales					
	Secondary treatment	Neutrali-zation	Filtration by coagulating sedimentation	Activated sludge, Trickling filtor, Methane fermentation,	Activated sludge, Trickling filtor, Methane fermentation,	Coagulating flotation, filtration	Biological denitrification	Activated sludge	Coagulating sedimentation, Filtration	Reduction - sedimentation Separation	Sedimentation, separation, and filtration as hydroxide	Sedimentation, separation, and filtration as hydroxide or sulfide	Activated sludge, Coagulating sedimentation, Filtration	Activated sludge, Chemical oxidation	Activated sludge, Chemical oxidation	Coagulating sedimentation, Oxidation and reduction by
	High-grade treatment			Activated charcoal absorption, Coagulating sedimentation and filtration after biological treatment, Reverse osmosis	Activated charcoal absorption, Chlorine, ozone oxidation, Reverse osmosis		Reverse osmosis	Activated charcoal absorption		Ion exchange Electrodyilysis	Ion exchange Electrodyalysis	Ion exchange Electrodialysis		Reverse osmosis	Activated charcoal absorption	Activated charcoal absorption, Reverse osmosis

1.3.3 Waste Water Treatment at Selected Factories of the Study

There are various types of industries in the selected factories of the study at this time, but basically, they can treat the waste water by combining the following treatment devices that are widely spread as waste water treatment equipment:

① Screen

② Oil separation (oil separator)

③ Flotation by pressure

④ Coagulating sedimentation

⑤ Biological treatment

⑥ Filtration

⑦ pH adjustment

⑧ Reverse osmosis membrane

⑨ Precision filtration

1.4 Outline of Recycling Techniques

Table V-2 outlines recycling of waste water and the devices for recycling.

Of the items listed in Table V-2, the recycling systems are the devices for coagulating sedimentation, activated charcoal absorption, ion exchange, ozone treatment, electrodialysis, and reverse osmosis.

The following items are related to the water quality problems which occur when the waste water from those factories are finally recycled:

① High concentration of COD or BOD

This is mainly caused by the organic substances that are dissolved in the water. To remove them, the following methods must be applied: oil separation, activated sludge, wet oxidation, coagulating sedimentation, activated charcoal absorption, ultrafiltration, etc.

② Waste water with high salinity concentration

The salinity contained in the water during its circulating use increases in the concentration because salt is generated during the process by the neutralizing reaction of acid and alkali, or by dissolution of impurities into the water from the process.

To remove the salinity, such methods as ion exchange, electrodialiysis, and reverse osmosis must be applied.

Table V-2 Outline of Facilities for Water Utilization and Recycling

Treatment equipment	Principle	Main treatment object	Remarks
Cooling tower	Water and air are caused to contact each other so that the evaporation latent heat of water is used for the cooling.	Temperature	① Cooling capacity depends on atmospheric temperature varying in summer and winter ② Temperature can not be lowered than atomospheric wet-bulb temparature (normally it can be lowered only to +5 C plus atmospheric wet-bulb temperature). ③ Water is mainly used for indirect cooling. Highly polluted water requires a pretreatment. ④ Operation cost is low. ⑤ Problems are noise, scales, slime, anticorrosives, and blow drainage.
Cooling water pool,	ditto	Temperature	① Cooling efficiency is lower than that of cooling tower ---> and requires the site area. ② Environmental problem may be occured if odor and noxious materials are contained. ③ Operation cost is very low. ④ Temperature can not be lowered under the atmospheric wet-bulb temperature. ⑤ Serves also as a sedimentation pond, reservoir, adjustment pond or spray pond.
Refrigerator, Cooling tower	① Cooling by latent heat of evaporation of medium with low boiling point. ② Cooling by latent heat of evaporation of water.	Temperature	① The operation cost (particularly the energy cost) is high. ② Noise problem exists. ③ Problem with removal of iron and salt content exists. ④ Refrigerator technology with high energy efficiency must be developed.
Adjustment tank	Water pool	Water quantity adjustment and storage	① Construction method varies with the water quality and quantity. ② Operation cost is very low. ③ Can be with technical ease.
Filtration, Screen, Microstrainer, etc.	Solids in the water are removed by metallic net or sand.	SS	① Operation cost is low. ② Construction cost of equipment is low. ③ Can be with technical ease.
Oil separator Coalescer, etc.	Separation by utilizing the surface phenomenon of oil and water.	BOD, COD, Oil content	① Most widely used in oil refineries.
Solid-liquid separator	Solids and water are separated by utilizing the physical and chemical characteristics.	BOD, COD, SS, Sludge	① Most widely used in coal industry.
Flotation separator	Separation by flotation by utilizing the physical and chemical characteristics on the grain surface. Suitable for separation of oil content and fibers in the waste water.	Oil content	① Widely used in food, oil, chemical, and iron and steel ndustries. ② Widely used for water for treatment and washing.
Neutralization, chemical feeder	pH adjustment and sterilization are performed.	pH and Bacteria	① Used in all industries. ② Operation cost depends largely on the raw water quality.
Softener	Chemicals are used to reduce the water hardness.	Hardness, Salt	① Widely used in food, textile, and dyeing industries. ② Usually combined with sedimentation pond, filtration device, or ion exchange equipment. ③ Effective in preventing the scales and slime.
Activated sludge process equipment	Microorganism is used to clarify the organic matters.	BOD, COD	① Treatment capacity depends on the water temperature varying in summer and winter. ② Since microbes are used, raw water with pasteurizing characteristics is not preferred.
Coagulating sedimentation	Coagulant is added to the water to increase the size of fine suspended matter in it so as to separate the coagulated grains (flocks) by precipitation.	SS, BOD, COD, Inorganic substances	① Coal, aluminum sulfate, and high polymer coagulant are used in many cases. ② Consists of a chemical injection tank, flocculation tank, sedimentation tank, etc. ③ The required operation largely depends on the quality and quantity of the suspended matter contained in the water.
Degasifier	Gas in the water is removed.	CO_2, DO	① Effective in preventing metal corrosion.
Activated charcoal absorber	Impurities in the water are removed by using absorption phenomenon on the surface of active charcoal.	BOD, COD, Oil content, Odor, Color, ABS Free chlorine	① Organic materials with low molecular weight can be removed. ② Since activated charcoal is expensive, polluted water with high concentration must be pretreated. ③ Usually a regenerating furnace of active charcoal must be constructed as attachment.
Ion exchange equipment	Ion in the water is removed by absorption.	Salt	① Chemical is used to regenerate the ion-exchange resin.2 Polluted water with high concentration must be pretreated.3 Even a compact size type is advantageous.
Ozone treatment equipment	Ozone is used for the decomposition by oxidation.	COD, BOD, Bacteria, Color, Odor, ABS	① Very little sludge is generated. ② Energy is consumed in a large quantity.
Electrodialyser	Positive ion and negative ion are separated electrically for desalting and concentration.	Salt	① Electric energy is consumed. ② Also used for salt concentration on the other hand.
Reverse osmotic pressure equipment	Salt content is removed through membrane.	Salt, organic substances, bacteria	① Membrane is expensive. ② Care must be taken for the pretreatment.

Note: Other available methods are optical treatment, electrolytic treatment, magnetic treatment, chlorine treatment, distillation, refrigeration, etc.

2. Setting of Target Quality of Waste Water

2.1 Outline of Setting

2.1.1 Adjustment of Water System Environment

Today, there has been appeal for a protection of the global environment, and the waste water from household and factories is largely affecting the water system environment. The influence ranges widely as shown below.

(1) Influence on public health

(2) Influence on water works

(3) Influence on industrial water

(4) Influence on fishery

(5) Influence on agriculture

(6) Influence on sewer

(7) Eutrophication

For Tunisia attaching a great importance to the tourism, adjustment of the water system environment must be an important problem to solve.

2.1.2 Industry and Environment

By the progress of industrial modernization expanding the production system and its scale, pollution of the environment is increased by the waste water discharged from the factories. The pollution problem is brought into the public eye when it exceeds the natural clarification capacity. Except for a very exceptional case, the waste water treatment is hardly a profitable work for enterprises. However, the waste water clarification must be implemented in view of the public nature of the enterprises and public opinion against the pollution, and under appropriate legal regulations. Nevertheless, if a high environmental standard or waste water emission standard is set exceeding the required level, that will not only lose the industrial activities but also generate a gap from the actual situation. In consideration of the type of industry and the scale of enterprise, it is necessary to establish a harmonious standard of the environment and discharge to meet the actual developing scale of the industries. This means that the discharge standard will have to be established step by step.

2.1.3 Reduction of Waste Water Load

Considering the limited natural resources, it is important to utilize the unused resources in the waste water before treating it. The existence of pollutant in the waste water means that something of value is stillflowing therein, so that its recovery must be studied first. To recover it completely, the production process needs to be reexamined, and the operation method needs to be improved. The result of our survey shows that some companies are endeavoring such recovery. However, considering the high pollution of waste water, there is still room for further recovery. It is necessary not only to increase the investment on the waste water treatment, but also to minimize the amount by recovering the valuable content therefrom as much as possible.

2.1.4 Necessity of Setting the Target

As mentioned above, the polution loading of waste water discharged from factories as a result of rationalizing the production process at the factories should be minimized, and discharging of only substances undesirable from an operational view point is the first choice. Substances unavoidably to be discharged should be disposed by water treatment. In case wastewater containing such substances is discharged into the public water area, a water quality standard will be required but such standard should adopt values within a reasonable level so that it can be harmonized with the industrial development. Tunisia has INNORPI standard as emission standard. This standard is very severe and is deemed hard to achieve at a single stroke. Therefore, it is proposed that they start the lenient standard in the beginning and make it severer step by step until the final target can be achieved. Since Japan has once provided the tentative standard according to the type of industry, the Japanese standard will be explained in the next paragraph, and then the draft tentative standard prevailing in Tunisia will be referred to.

2.2 Environmental Standard and Waste Water Standard in Japan

In Japan, the quality standard is established separately for the environment and for the waste water emission, as outlined below.

2.2.1 Environmental Standard

The basic measures for the pollution protection of water areas is to reduce the pollution load of the discharge to those areas. To attain this goal, some steps are taken such as regulations by the law, monitoring by measurement, construction of sewers and waste water treatment facilities.

The environmental standard on the water quality specifies the water quality level desirable to be attained and maintained for the public water areas. The standard consists of two factors: one for the protection of people's health and the other for the maintenance of living environment.

(1) Standard for people's health

This is the minimum standard to be conformed to at any time regardless of any other standards or economic development. Therefore, the numeric values are set to the maximum level, not the average. Nine items are object of regulations: Cd, CN, organic phosphorus, Pb, Cr^{+6}, As, total mercury, alkyl mercury, and PCB.

(2) Standard for living environment

This standard is established to protect the living environment regardless of the direct relationship with people's health, and specifies that the value is set as a daily average to be observed at 75% during the year. This standard provides a water area model corresponding to the water utilization purpose of each river, lake, and sea. Thus, the environmental standard for each public water area is set by determining the level for each item, and specifying the water area model for each public water area. Six items are objects of regulation in the public sea area (A area): pH, BOD, SS, DO, oil content, and number of colitis germs groups.

2.2.2 Waste Water Emission Standard

The waste water standard is established as the standard for emission of the waste water to observe the above environmental standard, and is divided into the standard applicable nationwide, more stringently specified standard and others. These standards are outlined below.

(1) Standard applicable nationwide

This standard shows the numeric levels of pollutants that can be treated with the currently available techniques. Basically, it is applied uniformly to all public water areas. However, the living environment items do not apply to a business companies smaller than a size 50 m^3 /day. Table V-3 lists the numeric levels.

Table V-3 (1) Uniform Standard (No. 1)

Type of harmful substance	Allowable limit
Cadmium and its compounds	0.1 mg/l
Cyanogen compounds	1 mg/l
Organic phosphide compounds (limited to parathion, methyl-parathion, methyl-dimethon, and EPN)	1 mg/l
Lead and its compounds	1 mg/l
Hexa-chromic compounds	0.5 mg/l
Arsenic and its compounds	0.5 mg/l
Mercury, alkyl mercury, & other mercury compounds	0.005 mg/l
Alkyl mercury compounds	not to be detected
P.C.B.	0.003 mg/l
Trichloroethylene	0.3 mg/l
Tetrachloroethylene	0.1 mg/l

Table V-3 (2) Uniform Standard (No.2)

Item	Allowable limit	
pH	Except sea area: 5.8 to 8.6 Sea area: 5.0 to 9.0	
BOD	160 mg/l (daily average: 120)	mg/l
COD	160 mg/l (daily average:120)	mg/l
SS	200 mg/l (daily average: 150)	mg/l
n-Hex Extract (Mineral Oil)	5	mg/l
n-Hex Extract (Non Mineral Oil)	30	mg/l
Phenol	5	mg/l
Cu	3	mg/l
Zn	5	mg/l
Soluble Fe	10	mg/l
Soluble Mn	10	mg/l
Cr	2	mg/l
F	15	mg/l
Number of colitis germ groups	Daily average: 3,000/cm^3	
N	120 mg/l (daily average: 60)	mg/l
P	16 mg/l (daily average: 8)	mg/l

(2) Tentative standard

For the standard related to living environment, a temporarily slack standard is constituted for some business types to which an application of the uniform standard may cause an economic difficulty, thus exempting them from such application for a certain period of time. At present, this exemption is applied only to tanning and fur manufacturing industries.

The history of tentative standard for tanning and fur manufacturing industries is shown in table V-4.

Table V-4 History of Tentative Standard for Tanning Industry

	1971	1979	1984	1989	1994
BOD maximum (mg/*l*)	2,300	1,100	900	900	160
Daily average (mg/*l*)			680	680	120
SS maximum (mg/*l*)	2,000	600	500	300	200
Daily average (mg/*l*)			380	250	150
n-Hex extract (mg/*l*)	50	50	50	50	30
Cr (mg/*l*)	50	20	20	10	2

(3) Regulation of total emission

In a closed water area where the pollution sources are concentrated so intensely that the environmental standard is hardly attained by the waste water standard only, both the COD concentration and flowrate are regulated by designating the business types and establishing a regulation standard of the total COD emission into such water area.

(4) More stringently specified standard

For the water areas for which the uniform standard is considered to be insufficient, a more stringently specified standard is established by each administrative division of Japan. The more stringently specified standard can also be established for a business companies discharging less than 50 cubic meters a day.

(5) Standard for prevention of eutrophication

Lakes and marshes are eutrophicated by the nitric and phosphoric content in the polluted water that flows therein, thus causing troubles by abnormal biological propagation. To prevent this, the nitric and phosphoric content is regulated for lakes and marshes by designating the areas and business types.

(6) Pollution prevention agreement

To maintain the environmental standard, the local self-governing bodies conclude, when required, a pollution prevention agreement with the enterprises or industrial group areas, to set up a stringent waste water standard for the quality regulation.

(7) Discharge standard for sewer

Sewer is a service to receive and treat the waste water from households and factories and rainwater, then discharge them to the public water area. For the waste water flowing from factories to the sewer, a standard is constituted whereby a responsibility is provided for them to set up an equipment for prevention of harmful effects if the waste water exceeds the standard.

(8) Standard of water discharge from sewage treatment plant

This is a standard for discharging water from the sewage treatment plant to public water area.

2.2.3 Subsidy and Taxation System

To promote the nongovernmental antipollution measures, several subsidiary steps are established financially and by taxation. As the financial support, subsidies are furnished at a low or no interest from corporations, banks, and government finance companies. An anti-pollution equipment is also available on lease system, and lease companies are financed by the subsidy.

Tax exempt is applied to the waste water treatment facilities, and shortening of their durability period and special depreciation are also approved.

2.2.4 Comparisons of Standard Values Between Japanese Standard and Tunisian Standard

The Japanese standard values described in the previous section are compared with INNORPI in Tunisia in Table V-5.

In Japan, the environmental standard and waste water emission standard are separated, and the emission standard is established to attain the environmental standard. For the emission standard, in consideration of the conditions of the locations such as the number and scales of enterprises in the area and the river conditions the more appropriate values are decided carefully. Furthermore, the economic and technical factors are also taken into account to provide a tentative standard.

Table V-5 Comparison of Standards between Japan and Tunisia

		JAPAN							TUNISIA	
		ENVIRONMENTAL STANDARD		EMISSION STANDARD					EMISSION STANDARD (INNORPI)	
		FOR HEALTH	FOR LIVING (PUBLIC SEA A)	UNIFORM STANDARD	MORE STRINGENT ST. (EX. SEA OF KASHIMA)		EXCLUSIVE FACILITIES (GENERAL)	EMISSION FROM SEWAGE TREATMENT PLANT	PUBLIC SEA	EMISSION TO SEWAGE TREATMENT PLANT
					FISHERIES	SEWAGE TR. PLANT				
Cd	mg/l	0.01		0.1			0.1		0.005	0.1
CN	mg/l	NOT DETECT		1			1		0.05	0.5
ORGANIC P	mg/l	NOT DETECT		1			1			
Pb	mg/l	0.1		1			1		0.5	1
Cr+6	mg/l	0.05		0.5			0.5		0.5	0.5
As	mg/l	0.05		0.5			0.5		0.1	0.1
Hg Total	mg/l	0.0005		0.005			NOT DETECT		0.001	0.01
Hg Alkyl		NOT DETECT		NOT DETECT			NOT DETECT			
PCB	mg/l	NOT DETECT		0.003			0.003			
TRICHLOROETHYLENE	mg/l			0.3						
TETRACHLOROETHYLENE	mg/l			0.1						
pH			7.8-8.3	5.0-9.0	-	5.8-8.6	5-9	5.8-8.6	6.5-8.5	6.5-9
BOD	mg/l			160	AVE. 90	AVE. 20	600	20	30	400
COD Mn	mg/l		2	160	AVE. 90	AVE. 20				
COD Cr	mg/l								90	1000
SS	mg/l		25	200	AVE. 120	AVE. 40	600	70	30	400
SEDIMENT	ml/l								0.3	
DO	mg/l		> 7.5							
OIL	mg/l		NOT DETECT						20	30
MINERAL	mg/l			5	-		5		10	10
NON MINERAL	mg/l			30	-	MAX. 10	30			
CHLORINE SOLVENT	mg/l								0.05	0.1
ABS	mg/l								2	5
PHENOL	mg/l			5	-	1	100		0.05	1
I CONSUMPTION	mg/l						220			
Cu	mg/l			3			3		1.5	1
Zn	mg/l			5			5		10	5
Fe	mg/l			10			10		1	5
Mn	mg/l			10	-	1	10		1	1
Cr	mg/l			2	-	1	2			
Cr+3	mg/l								2	2
F	mg/l			15			15		5	3
S	mg/l								2	3
COLON BACILLUS	/100ml		1.000MPN	3.000/cm3				3.000/cm3	2.000	
STREPTOCOCCUS									1.000/100ml	
SALMONELLA									NOT DETECT	
CHOLERA BACILLUS									NOT DETECT	
TEMP.	°C						45		35	35
Cl	mg/l								-	700
Cl2	mg/l								0.05	1
ClO2	mg/l								0.05	0.5
SO4	mg/l								1000	400
PO4	mg/l								0.1	10
Mg	mg/l								2000	300
K	mg/l								1000	50
Na	mg/l								-	1000
Ca	mg/l								-	-
Al	mg/l								5	10
COLOR									100	-
P	mg/l			16						
NO3	mg/l								90	90
NO2	mg/l								5	10
NH4-N	mg/l								30	100
T-N	mg/l			120						
B	mg/l								20	2
Sn	mg/l								2	2
Mo	mg/l								5	5
Co	mg/l								0.5	0.5
Br2	mg/l								0.1	1
Ba	mg/l								10	10
Ag	mg/l								0.1	0.1
Be	mg/l								0.05	0.05
Sb	mg/l								0.1	0.2
Ni	mg/l								2	2
Se	mg/l								0.5	1
Ti	mg/l								0.001	0.01
AGRICULTURAL CHEMICALS	mg/l								0.005	0.01

In Tunisia, on the other hand, a nationwide uniform standard is applied, which is waste water emission standard, and not the environmental standard. In the emission standard, various items other than those in Japanese standard are set up on highly stringent levels, and these are on an intermediate position between the environmental standard and emission standard in Japan. Further, the emission standard for public sea specifies the standard for discharging SO4 which is anion of salt.

It is difficult to say which one of these two standards is better. The best way will be to adopt the standard best-suited to conditions of the respective country. However, SO4 is contained in sea water in general, and regulating SO4 merely increases the investment on water treatment.

2.3 Establishment of Tentative Waste Water Emission Standard in Tunisia

Tunisia has INNORPI standard as the emission standard, but it has so many paragraphs and severe standard values compared with the Japanese emission standard. We propose Tunisia to set up the tentative standard and achieve INNORPI standard at the extreme end.

Japan advised Tunisia at the 5th field survey to set up the tentative standard and Tunisia presented Japan her draft tentative standard.

Table V-6 shows a comparison of the tentative standard values presseuted by Japan and Tunisia. This table excludes items which are not analyzed at this study or items which are deemed unrelated.

It should be noted that the Tunisian draft tentative standard specifies standard values for Cl and SO4 when waste water is discharged to ONAS Sewage Treatment Plant. Tunisian side strongly insisted on necessity of controlling salts at the 5th field survey because water treated at ONAS Sewage Treatment Plant is utilized for irrigations. Though removal of salts during waste water treatment would require an immense investment and the subsequent increase in costs for producing irrigation water, we have taken up this for our considerations as a case study.

Table V-6 Tentative Standard

		TENTATIVE STANDARD (JAPAN PROPOSAL)		TENTATIVE STANDARD (TUNISIA PROPOSAL)	TUNISIA EMISSION STANDARD (INNORPI)	
		EMISSION TO PUBLIC SEA	EMISSION TO SEWAGE TREAT. PLANT	EMISSION TO SEWAGE TREAT. PLANT	EMISSION TO PUBLIC SEA	EMISSION TO SEWAGE TREAT. PLANT
Cd	mg/l	0.005	0.1	0.1	0.005	0.1
CN	mg/l	0.05	1	0.5	0.05	0.5
ORGANIC P	mg/l	-	1	-	-	-
Pb	mg/l	0.5	1	1	0.5	1
Cr+6	mg/l	0.5	0.5	0.5	0.5	0.5
Cr+3	mg/l	2	2	2	2	2
As	mg/l	0.1	0.5	0.1	0.1	0.1
Hg Total-	mg/l	0.001	0.01	0.01	0.001	0.01
pH		6.5-8.5	5.0-9.0	5.0-9.0	6.5-8.5	6.5-9
SS	mg/l	30	800	500	30	400
BOD	mg/l	30	600	800	30	400
COD Cr	mg/l	90	2000	2000	90	1000
OIL	mg/l	20	50	50	20	30
MINERAL	mg/l	10	-	-	10	10
NON MINERAL	mg/l	-	-	-	-	-
PHENOL	mg/l	0.05	5	5	0.05	1
Cu	mg/l	1.5	3	3	1.5	1
Zn	mg/l	10	10	10	10	5
Fe	mg/l	1	10	10	1	5
Mn	mg/l	1	10	3	1	1
F	mg/l	5	15	15	5	3
S	mg/l	2	-	-	2	3
COLON BACILLUS		2,000 /100ml	-	-	2,000 /100ml	
STREPTOCOCCUS		1,000 /100ml	-	-	1,000 /100ml	
SALMONELLA		ABSENCE	-	-	ABSENCE	
TEMP.	° C	35	-	-	35	35
Cl	mg/l	-	-	2000	-	700
Cl2	mg/l	0.05	-	-	0.05	1
ClO2	mg/l	0.05	-	-	0.05	0.5
SO4	mg/l	-	-	1000	1000	400
PO4	mg/l	0.1	-	-	0.1	10
Mg	mg/l	2000	-	-	2000	300
K	mg/l	1000	-	-	1000	50
Na	mg/l	-	-	-	-	1000
Ca	mg/l	-	-	-	-	-
Al	mg/l	5	-	-	5	10
COLOR		100	-	-	100	-
NO3	mg/l	90	-	-	90	90
NO2	mg/l	5	-	-	5	10
NH4-N	mg/l	30	-	-	30	100
T-N	mg/l		-	-		

3. Classification by Quality of Discharged Water in Factories and Technical Studies

3.1 Classification by Quality of Discharged Water in Factories

3.1.1 Preparation of the Table of Waste Water Quality

Table V-7 Shows the table of the results of simplified analysis.

3.1.2 Classification of Waste Water by Quality

There are three main factors of water quality that are important for the waste water treatment and recycling as follows:

① Concentration of organic substances

② Concentration of salinity

③ Concentration of solid substances

From the simplified analysis items, these factors are represented by chemical oxygen demand (COD cr), electrical conductivity (EC), and suspended solids (SS), respectively, and are classified as follows according to the concentration:

(1) Concentration of organic substances

To be divided into three ranks as below.

① Waste water with high concentration of organic substances: CODcr ≥ 1000 mg/*l*

② Waste water with medium concentration of organic substances: 1000 mg/*l* > CODcr ≥ 100 mg/*l*

③ Waste water with low concentration of organic substances: 100 mg/*l* > CODcr

(2) Concentration of salinity

To be divided into three ranks as below.

① Waste water with high concentration of salinity: EC ≥ 5 ms/cm

② Waste water with medium concentration of salinity: 5 ms/cm > EC ≥ 0.5 ms/cm

③ Waste water with low concentration of salinity: 0.5 ms/cm > EC

(3) Concentration of solid substances

To be divided into three ranks as below.

① Waste water with high concentration of solid substances: SS ≥ 400 mg/*l*

② Waste water with medium concentration of solid substances:400 mg/*l* > SS ≥ 100 mg/l

③ Waste water with low concentration of solid substances: 100 mg/*l* > SS

The above classification criteria were applied to prepare the table of classification by waste water quality as shown in Table V-8.

Table V-7 Result of Primary Analysis (1/2)

A. PRIMARY ANALYSIS (44 POINTS)

SAMPLING POINT	SAMPLING DATE	ANALYSIS ITEMS(8)							
		TURBIDITY deg.	p H	CONDUCT' TY ms/cm	S. SOLID mg/L	C O Dcr mg/L	B O D mg/L	n-HEX mg/L	D O mg/L
SPE-01	10/07/92	2	7.2	5.7	4	<6		5	1
SPE-01	15/07/92	13	7.2	5.5	5		1		1.4
SPE-11	10/07/92	130	2.0	22.0	82	190	--	3	4.5
SPE-11	15/07/92	51	2.0	19.9	29	120	--	4	3.7
SPE-13	10/07/92	30	1.2	48.0	10	240	--	16	3.5
SPE-13	15/07/92	6	1.3	38.7	2	240	--	4	3.5
SPE-14	10/07/92	2	1.1	59.0	3	350	9	3	6.8
SPE-14	15/07/92	6	1.2	57.7	4	270	--	9	2.8
SPE-17	10/07/92	>999	2.1	18.0	31000	8700	--	4	5.7
SPE-17	15/07/92	>999	2.0	19.5	210000	5400	2200	39	1.5
SPE-18	10/07/92	110	7.3	8.9	160	190	--	3	4.6
SPE-18	15/07/92	50	9.0	6.7	66	210	130	3	3.6
SPE-19	10/07/92	25	1.6	24.0	60	220	--	10	4.2
SPE-19	15/07/92	10	1.7	20.1	11	220	--	5	3.8
SPE-20	10/07/92	14	1.8	19.0	27	260	400	6	3.9
SPE-20	15/07/92	6	1.9	14.7	7	470	--	11	3.8
SND-11	10/07/92	79	7.9	62.0	60	240	290	60	0.4
SND-12	10/07/92	72	7.3	51.0	20	550	140	34	0.5
SND-13	10/07/92	63	7.4	57.0	10	510	150	57	0.3
SZT-01	11/07/92	10	7.5	2.4	<1	6	5	3	4.8
SZT-01	14/07/92	0	7.7	2.1	<1	2	5	-	4.2
SZT-09	11/07/92	10	6.7	21.9	1	24	3	3	2.4
SZT-09	14/07/92	1	6.9	14.0	18	170	33	-	2.3
SZT-11	11/07/92	6	7.7	16.9	8	230		2	3.3
SZT-11	14/07/92	1	7.8	17.9	5	530	30	4	3.5
SZT-12	11/07/92	1	4.3	14.2	36	2000	700	23	3.3
SZT-12	14/07/92	20	4.6	15.6	57	2000	12	39	
SZT-13	12/07/92	>999	8.9	14.0	220000	170000	27000	18000	0.3
SZT-13	14/07/92								
SZT-14	11/07/92	695	6.3	2.5	20000	65000	23000	1800	1.8
SZT-14	14/07/92								
SZT-15	11/07/92	31	7.5	30.6	28	1600	160	14	0.7
SZT-15	14/07/92	27	7.8	24.5	26	1600	13	5	0.3
SZT-16	11/07/92	>999	12.3	91.7	740	44000	16000	9800	0.5
SZT-16	14/07/92	>999	12.6	>100	2600	29000	13000	5500	0
SZT-17	11/07/92	715	11.7	35.0	590	620	140	34	2.3
SZT-17	14/07/92	980	12.0	58.3	1300	550	450	20	1.5
SZT-18	11/07/92	10	8.5	2.6	1	130	26	4	4.9
SZT-18	14/07/92	2	8.0	2.5	1	32	170	4	3.9
SZT-19	11/07/92	110	5.7	14.0	70	940	530	4	3
SZT-19	14/07/92	700	6.1	14	2900	6400	2300	33	0.2
SZT-20	11/07/92	10	6.8	2.4	4	64	6	6	5
SZT-20	14/07/92	165	7.8	2.3	3	330	250	27	

Table V-7 Result of Primary Analysis (2/2)

A. PRIMARY ANALYSIS (44 POINTS)

SAMPLING POINT	SAMPLING DATE	ANALYSIS ITEMS(8)							
		TURBIDITY	p H	CONDUCT'TY	S.SOLID	C O Dcr	B O D	n-HEX	D O
		deg.		ms/cm	mg/L	mg/L	mg/L	mg/L	mg/L
SMC-01	09/07/92	94	7.4	12.5	1	15	1	<1	
SMC-01	14/07/92	0	7.1	12.0	<1	27	16	--	3.5
SMC-11	09/07/92	>999	6.8	18.4	2700	50000	5200	270	
SMC-11	14/07/92	500	7.1	15.0	99	4600	13000	210	1.9
SMC-12	09/07/92	>999	>12	25.3	7200	740000	170000	260	
SMC-12	14/07/92	>999	12.0	18.0	9700	8800	6000	310	0.1
SMC-13	09/07/92	>999	8.7	31.1	1700	550000	59000	490	
SMC-13	14/07/92	>999	8.4	25.7	820	6000	112000	510	1.9
SMC-14	09/07/92	>999	8.7	16.5	3200	640000	170000	42000	
SMC-14	14/07/92	>999	8.4	12.5	1300	190000	140000	41000	6.4
SMC-15	09/07/92	>999	8.4	15.6	420	48000	8000	330	
SMC-15	14/07/92	>999	7.8	13.0	440	4100	2700	230	1.5
SMC-16	09/07/92	288	3.0	77.6	360	11000	2400	260	
SMC-16	14/07/92	440	3.6	76.0	180	720	1900	330	1.4
TMC-01	09/07/92	3	7.7	2.0	2	8	0.4	2	
TMC-01	14/07/92	0	6.6	2.3	0.8	4			5.4
TMC-11	09/07/92	>999	3.2	36.0	690	9700	7	990	
TMC-11	14/07/92	>999	3.4	27.0	260	7200	2300	1200	4.3
TMC-12	09/07/92	>999	4.9	36.0	690	5300	1200	810	
TMC-12	14/07/92	>999	5.0	31.0	280	10000	1800	1600	4.3
TMC-13	09/07/92	63	3.6	25.0	54	6400	2900	21	
TMC-13	15/07/92	125	3.2	19.3	37	10000	6500	19	3.9
STS-01	10/07/92				<1	<6	0.1	3	
STS-01	15/07/92	0	8.0	2.3	<1	<6	<6	--	4.8
STS-13	10/07/92	>999	10.3	17.0	770	19000	--	760	
STS-13	15/07/92	>999	11.3	22.0	110	2.1	48000	400	0
STS-16	10/07/92	0	8.8	2.6	12	160	--	3	
STS-16	15/07/92	20	9.8	2.9	6	410	130	4	4.2
STS-19	10/07/92	>999	5.4	2.6	30000	130000	1	230	
STS-19	15/07/92	>999	7.8	2.8	37000	160000	100000	7	0.7
STS-20	10/07/92	28	11.3	12.0	36	510	--	7	
STS-20	15/07/92	10	11.1	5.2	13	54	47	200	4.2
STS-21	09/07/92	10	7.3	34.0	<1	2000	--	4	
STS-21	15/07/92	0	7.3	35.0	2	15	7	--	4.6
ONS-11	10/07/92	220	7.3	6.2	100	240	45	9	1.4
ONS-11	13/07/92	180	7.6	5.0	200	360	230	73	0.5
ONS-11	14/07/92	650	7.3	4.6	770			140	0
ONS-11	16/07/92	160	7.6	6.0	150	340	280	--	0.6
ONS-12	10/07/92	220	7.8	5.5	140	210	39	7	0.5
ONS-12	13/07/92	200	7.8	5.3	110	190	71	12	2.3
ONS-12	14/07/92	230	7.7	5.2	130			9	1.8
ONS-12	16/07/92	280	7.8	5.3	130	280	160	--	4.6
ONS-13	10/07/92	120	7.9	5.5	13	410	74	4	2.3
ONS-13	13/07/92	150	7.8	5.2	42	230	43	8	3.8
ONS-13	14/07/92	180	7.8	5.2	50			4	3.7
ONS-13	16/07/92	200	7.9	5.5	24	210	86	--	4.5
MRG	10/07/92	>999	4.8	32.0	3200	180000	27000	320	0.2
MRG	14/07/92	>999	4.6	--	6000		74000	290	0

Table V-8 Classification of Waste Water by Quality

Organic substance and salinity	Suspended solid matters (SS: mg/l)		
	A. Less solid matters 100 > SS	B. Medium solid matters 400 > SS ≥ 100	C. Highly solid matters SS ≥ 400
1. High concentration of organic matter and high salinity	SZT-12, SZT-15, TMC-13	SMC-16	SPE-17, SZT-13, SZT-16, SZT-17, SZT-19, SMC-11, SMC-12, SMC-13, SMC-14, SMC-15, TMC-11, TMC-12, STS-13, STS-19, MGR
2. High concentration of organic matter and medium salinity			SZT-14
3. High concentration of organic matter and low salinity	SND-12, SND-13		
4. Medium concentration of organic matter and high salinity	SPE-11, SPE-13, SPE-14, SPE-19, SPE-20, SND-11, SZT-11, SZT-20, STS-16, STS-20, ONS-30	SPE-18, ONS-11, ONS-12	
5. Medium concentration of organic matter and medium salinity			
6. Medium concentration of organic matter and low salinity			
7. Low concentration of organic matter and high salinity	STS-21,		
8. Low concentration of organic matter and medium salinity	SZT-18,		
9. Low concentration of organic matter and low salinity			
Remarks	Waste water with high concentration of organic matter: CODcr ≥ 1,000 mg/*l* Waste water with medium concentration of organic matter: 1,000 mg/*l* > CODcr ≥ 100 mg/*l* Waste water with low concentration of organic matter: 100 mg/*l* > CODcr Waste water with high salinity content: EC ≥ 5 ms/cm Waste water with medium salinity content: 5 ms/cm > EC ≥ 0.5 ms/cm Waste water with low salinity content: 0.5 ms/cm > EC For two or more analysis results, the average was used		

3.1.3 Utilizing Method of Table of Classification by Waste Water Quality

The following items can be studied using the Table of Classification by Waste Water Quality:

(1) Necessity of pretreating inferior waste water

(2) Study of recycling superior waste water of good quality

(3) Determination of superior waste water and inferior waste water using the system diagram of waste water

3.2 Study of Pretreatment Technique

3.2.1 Necessity of Pretreatment

Waste water cannot be treated immediately when it is too much polluted (with high concentration of organic matter, salinity, solid matter, or oil content). Even when the immediate treatment is enabled, a large scale of equipment must be installed at a high cost of construction requiring a high operation cost as well.

In such case, some pretreatment must be applied to the waste water to ease the operation of equipment for the subsequent treatment and reduce the cost of construction and operation.

3.2.2 Selection of Waste Water Requiring Pretreatment

The waste water requiring the pretreatment has been selected by the following criteria:

① Waste water with high concentration of organic matter: CODcr > 1000 mg/*l*

② Waste water with high salinity: EC > 5 ms/cm

③ Waste water with high concentration of solid matter: SS > 500 ms/*l*

④ Waste water with high oil concentration: Oil > 100 ms/*l*

⑤ pH: 5 > pH and pH > 10

By the above criteria, the waste water that needs the pretreatment is specified in Section 5.3.

3.2.3 Determination of Necessity of Pretreatment

For each factory, the necessity of pretreating the inferior waste water was determined.

(1) SIAPE

The waste water to be studied for pretreatment are waste water symbol SPE-13 and SPE-14.

Particularly important is scrubber waste water, of which the inferior quality item is pH (1.1 to 1.2) and fluorine. It also deteriorates the PH of joint flow with waste water from the reactor and the total waste water (1.8 to 1.9). Thus a pH and fluorine treatment equipment is required.

SPE-17 has inferior quality item pH (1.8 to 2.1), SS (31,000 to 210,000 mg/*l*), and COD (5,400 to 8,700 mg/*l*). However, it is not an object for pretreatment, because it is recovered and recycled already.

(2) SNDP

No waste water that particularly needs pretreatment is discharged from the SNDP.

(3) UPOTS

The waste water to be studied for pretreatment is the waste water symbol MGR. Its inferior quality items are pH (4.6 to 4.8), SS (3,200 to 6,000 mg/*l*), COD (180,000 mg/*l*) and oil (290 to 320 mg/*l*).

Since the COD concentration is high, method of biological treatment or wet oxidation must be studied as pretreatment equipment.

(4) SIOS-ZITEX

The waste water to be studied for pretreatment is waste water symbol SZT-13. Its inferior quality items are pH (14), SS (222,000 mg/*l*), COD (170,000 mg/*l*), and concentration of oil content (1,800 mg/*l*).

Inferior quality items of waste water symbol SZT-14 are concentration of solid matter (20,000 mg/*l*), concentration of organic matter (65,000 mg/*l*) and concentration of oil content (1,800 mg/*l*).

Inferior quality item of waste water symbol SZT-15 is COD (1,600 mg/*l*).

Inferior quality item of waste water symbol SZT-16 are SS (740 to 2,600 mg/*l*), COD (29,000 mg/*l*), and concentration of oil content (5,500 to 9,800 mg/*l*).

Therefore, by collecting the above types of waste water, and after separating the oil and solid matter, the pretreatment method must be studied. By such separation of oil and solid matter, the concentration of organic matter is largely reduced.

(5) SATHOP

The waste water to be studied for pretreatment is waste water symbol STP-13. Its inferior quality items are pH (10.5), SS (840 to 2,600 mg/*l*), and COD (58,000 to 65,900 mg/*l*).

For waste water symbol STP-16, the inferior quality items are COD (95,000 to 189,000 mg/*l*) and concentration of oil content (1,400 to 1,643 mg/*l*).

Therefore, by collecting the above types of waste water, and after separating the oil and solid matter, the pretreatment method such as biological treatment must be studied.

(6) SMCP/TMC

The waste water to be studied for pretreatment are waste water symbol SMC-11, SMC-12, SMC-13, SMC-14, SMC-15, SMC-16, TMC-11, TMC-12, and TMC-13. This means that all types of waste water have high concentration of SS, COD, and high concentration of oil content.

At present, the tanning is operated at two divided factories, but in October 1992, they will be united into one factory so that a pretreatment such as biological treatment must be studied after collecting all waste water from them and separating the oil content and solid matters.

(7) STS

The waste water to be studied for pretreatment is waste water symbol STS-13, and the inferior quality items are pH (10.3 to 11.3), COD (2,583 to 19,000 mg/*l*), and concentratiion of oil content (400 to 760 mg/*l*).

The inferior quality item of waste water symbol STS-19 are COD (130,000 to 160,000 mg/*l*) and concentration of oil content (7 to 230 mg/*l*).

The inferior quality item of waste water symbol STS-21 is COD (15 to 2,000 mg/*l*).

Therefore, pretreatment method such as biological treatment of these types of waste water must be studied by collecting them.

For the oil content, pretreatment is not required in particular because most part of the oil is considered to be decomposed microbiologically by the pretreatment of organic matter.

(8) ONAS

The ONAS does not particularly accept any waste water to be studied for pretreatment, so it is therefore not object of study for pretreatment.

3.3 Study of Waste Water Treatment Technique by Factory

To study the waste water treatment technique, it is important to grasp as an integral system the individual treatment equipment which are listed in Figure V-2, "Types and classification of waste water treatment equipment", so as to obtain the most effective treating effect with the minimum combination of the treatment equipment.

To study the waste water treatment technique, the performance and characteristics of waste water must be checked completely along with the past records of similar treatment equipment.

The main operation of waste water treatment equipment is the primary and seçondary treatment described in Table V-1, "Characteristics and Treatment System of Waste Water by Type of Industry". The tertiary treatment is performed chiefly for recycling of the waste water. However, in case there is a severe regulation standard on the water discharge, up to the tertiary treatment may be applied.

This study is based on Table V-6, "Tentative Standard", and the materials to be studied for treatment at each factory are described below.

3.3.1 SIAPE

- Materials to be studied for waste water treatment

① SEP-13
② SEP-14 } : (improvement of pH, removal of SS, oil content, and fluorine)

③ SEP-18 : (improvement of pH, removal of SS and oil content)

By treating the above sources of waste water, improvement is expected on the water quality of SEP-19 and SEP-20. COD in the waste water is also somewhat high so that the method is its reduction will be studied.

3.3.2 SNDP

- Materials to be studied for waste water treatment

① SND-11: (removal of oil content)

The performance is not sufficient by the simplified oil separator which is currently installed.

3.3.3 UPOTS

- Materials to be studied for waste water treatment

① MGR: (removal of organic matters and SS)

Concentration of the organic matters and SS contained in the margin is considerably high, so that a wide range of treatment method will be studied, such as physical and chemical treatment, biological treatment, and combustion method.

3.3.4 SIOS-ZITEX

- Materials to be studied for waste water treatment

① SZT-11: removal of organic matter
② SZT-12:
③ SZT-13:
④ SZT-14: } removal of organic matter and SS
⑤ SZT-15:
⑥ SZT-16:
⑦ SZT-17: (removal of organic matter and SS)

By treating the above sources of waste water, improvement is expected on the quality of SZT-19 total waste water.

3.3.5 SATHOP

- Materials to be studied for waste water treatment

① STP-11: removal of organic matter
② STP-13:
③ STP-16: } removal of organic matter and SS
④ STP-18:

By treating the above sources of waste water, improvement is expected on the quality of STP-19 total waste water.

The quality of waste water of STP-11 and STP-18 was estimated from the analyzed value of SIOS-ZITEX.

3.3.6 SMCP/TMCP

- Materials to be studied for waste water treatment

① SMP-11:
② SMP-12:
③ SMP-13: } (pH adjustment and removal of SS, oil content and organic matter)
④ SMP-14:
⑤ SMP-15:
⑥ SMP-16:
⑦ TMC-11:
⑧ TMC-12:
⑨ TMC-13:

Chromium waste water is excluded from the study because it is already under construction by planning.

3.3.7 STS

- Materials to be studied for waste water treatment

① STS-13:
② STS-16:
③ STS-19: } (pH adjustment and removal of SS, oil content and
④ STS-20: suspended organic matter)
⑤ STS-21:

STS-16, STS-20, and STS-21 are less polluted. However, since the factory discharges small quantity of waste water and each process is performed by batch process, all waste water from the factory is to be studied for treatment.

3.3.8 ONAS (Office National de l'Assainissement)

- Objective substances to be disposed from waste water are;

① SS (Suspended solid)

② COD (Chemical oxygen demand)

③ BOD (Biological oxygen demand)

Since waste water from various factories will be flown into ONAS sewage treatment plant, the amount of SS, COD, BOD and the volume of incoming waste water will be increased. These items as well as the existent facilities will be the objects of our study.

4. Preconditions for Planning the Waste Water Treatment and Recycling Technique by the Type of Factory

4.1 Case Setting-up of Waste Water Treatment

The eases of waste water treatment for selected factories will be settled up. The cases are classified by the standard to be applied, namely the tentative standard proposed by Japan, the tentative standard proposed by Tunisia and INNORPI standard, and the destination of treated waste water, namely ONAS plant and the sea area. Further, a case of the rationalized soap manufacturing plant is included.

Case No.1 represents the tentative standard proposed by Japan, No.2 the tentative standard proposed by Tunisia, No.3 INNORPI standard, Symbol A the destination being ONAS plant, symbol B the destination being the sea area and Case No. 4 represents a rationalized soap manufacturing plant. This can be simplified as follows:

Case No.	Designation	Standard to be applied	Remarks
1	A (ONAS)	Tentative standard proposed by Japan	
1	B (Sea area)	Tentative standard proposed by Japan	
2	A (ONAS)	Tentative standard proposed by Tunisia	
2	B (Sea area)	Tentative standard proposed by Tunisia	
3	A (ONAS)	INNORPI standard	
3	B (Sea area)	INNORPI standard	
4	A (ONAS)	Tentative standard proposed by Japan	Rationalized soap plant

Table V-9 shows standards applied to respective factories.

Table V-9 A Table of Cases for the Selected Factories

Factory	Case No.	Emission Standard					
		T.S. proposed by Japan		T.S. proposed by Tunisia		INNORPI S.	
		ONAS	Sea	ONAS	Sea	ONAS	Sea
		A	B	A	B	A	B
SIAPE	1		1B				
	2				2B		
UPOTS	1	1A					
	2			2A			
	3					3A	
SIOS-ZITEX	1	1A					
	2			2A			
	3					3A	
	3						3B
	4	4A					
SATHOP	1	1A					
	2			2A			
	3					3A	
	3						3B
	4	4A					
SMCP	1	1A					
	2			2A			
	3					3A	
	3						3B
STS	1	1A					
	2			2A			
	3					3A	
ONAS	2				2B		

Notes:
1. Case No.4A is a case of the rationalized soap manufacturing plant.
2. Cases No.2B and 3B are applying the same emission standard.
3. Inflows to ONAS Plant are assumed to have been discharged from respective factories with the same tentative standards proposed by Japan.

Table V-10 shows the waste water quality standard for various substances under tentative standard proposed by Japan, Tunisia and INNORPI standard as shown in Table V-6.

Table V-10: Waste Water Quality Standard under Various Cases

		TENTATIVE STANDARD (JAPAN PROPOSAL)		TENTATIVE STANDARD (TUNISIA PROPOSAL)	TUNISIA EMISSION STANDARD (INNORPI)	
		EMISSION TO PUBLIC SEA	EMISSION TO SEWAGE TREAT. PLANT	EMISSION TO SEWAGE TREAT. PLANT	EMISSION TO PUBLIC SEA	EMISSION TO SEWAGE TREAT. PLANT
CASE		1A, 4A	1B	2A	3A	2B, 3B
Cd	mg/l	0.005	0.1	0.1	0.005	0.1
Cr+6	mg/l	0.5	0.5	0.5	0.5	0.5
Cr+3	mg/l	2	2	2	2	2
pH		6.5-8.5	5.0-9.0	5.0-9.0	6.5-8.5	6.5-9
SS	mg/l	30	800	500	30	400
BOD	mg/l	30	800	800	30	400
COD Cr	mg/l	90	2000	2000	90	1000
OIL	mg/l	20	50	50	20	30
MINERAL	mg/l	10	-	-	10	10
PHENOL	mg/l	0.05	5	5	0.05	1
Fe	mg/l	1	10	10	1	5
F	mg/l	5	15	15	5	3
COLON BACILLUS		2.000 /100ml	-	-	2,000 /100ml	
STREPTOCOCCUS		1.000 /100ml	-	-	1,000 /100ml	
SALMONELLA		ABSENCE	-	-	ABSENCE	
Cl	mg/l	-	-	2000	-	700
SO4	mg/l	-	-	1000	1000	400
PO4	mg/l	0.1	-	-	0.1	10
K	mg/l	1000	-	-	1000	50
NH4-N	mg/l	30	-	-	30	100
				-		

Note: Items considered to be unrelated to case setting-up were excluded.

As seen in Table V-9, waste water in Cases 1A, 2A and 3A except Case of SIAPE is treated at respective factories and sent to ONAS sewage treatment plant for treatments to the level as specified in INNORPI standard for discharge to the sea area. Consequently, waste water under any cases in Sfax district is in compliance with INNORPI standard for discharge to the sea area. It may be possible to consider that waste water from all factories is sent to ONAS plant without treating at the respective factories but totally treated at ONAS plant. However, this possibility was excluded from our study for the following reasons.