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WASTE WATER AND TAIL GAS TREATMENT FOR SEMICONDUCTOR PROCESS

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1 INTRODUCTION

Various chemicals and gases are used in semiconductor manufacturing process, and these chemicals and gases are discharged to the outside in response to the individual processes.

Most of the chemicals and gases discharged from processes are harmful substances, and they cannot be discharged directly into rivers and sewage or to the air without treating them.

Those discharged from the processes must be treated with waste water treatment equipment to be water of a certain quality so that they can be discharged to rivers and sewages, and gases discharged from the processes must be treated to a certain concentration with exhaust gas treatment equipment before discharging to the air.

Treatment methods for these chemicals and gases differ depending on the kinds of chemical and gas. Therefore, it is necessary to divide discharging pipes and exhaust ducts by the individual kinds of chemical and gas in response to the treatment method, and the divided pipes and ducts must be connected to the waste water and exhaust gas treatment equipment.

This paper introduces and outlines these waste water and gas treatment equipment.

2 WASTE WATER TREATMENT

Various chemicals in large volumes are used and discharged from semiconductor manufacturing plants. For the purpose of preventing water pollution, the regulations stipulate to treat pH and fluorine at most plants, and depending on the manufactured products, manufacturing method and restricted values, the treatment is also required for BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), nitrogen, phosphorus and heavy metals.

On the other hand, there is a restriction to pump up well water for the purpose of preventing ground sinking, limitation of water supply due to lack of absolute value of industrial water, and in other cases, volume of industrial water is sufficient but drained water must be recycled after a proper treatment as the water supply cost is high. Further, depending on the local situation or policy of the plant, there is a method which does not flow out waste water outside the plant at all.

As described above, various waste water treatment methods are used depending on the conditions of the individual plants, and there are many things which cannot be discussed sweepingly. However, we examine several types of treatment method as follows.

2.1 Types and features of waste water

At present, most of the semiconductors are silicon based elements, and dry etching which does not use water has been improved considerably, but still, water is used and drained at almost everywhere in the silicon processing.

As for kinds of waste water, from the manufacturing lines, they are briefly classified into SS system waste water discharged from the shaping and cutting processes which mainly contains fine SS (Suspended Solids) of silicon, organic system waste water discharged from the processes such as decreasing process where an organic solvent is used, fluorine system waste water discharged from an etching process where hydrofluoric acid is used, and acid/alkali system waste water from processes where linsing is made by using acid and alkali. At any rate, it is hard to descriminate them completely because of the nature of each process, and it cannot be avoided to indicate types with the main components. From the sources other than the manufacturing lines, concentrated waste water of RO (Reverse Osmosis) is drained from an industrial water (super pure water) producing equipment, and recycled water is drained from an ion exchanger. These two are drained constantly, and inconstantly, RO washing waste water, RO sterilizing waste water, piping sterilizing waste water, etc. are drained.

In addition, there are various types of waste water drained after washing gases, and their systems are classified by the objective gases. Needless to say, there is a waste water required for activities of the people. When waste waters can be separated into concentrated liquid and linsing water, the waste waters should be separated for rationalization of the waste treatment. Next, as for characteristics of waste water, primarily, in many cases, acetic acid and hydrogen peroxide are contained in the hydrofluoric acid

Table 1 Types and features of waste water discharged from semiconductor manufacturing plant

Type of waste water		Component and concentration	Point to be noted at waste water treatment
Process drain	SS system waste water	Silicon power (200 ~ 300 mg/l)	Most of them are 1 μm or smaller particles.
	Organic system thick drain	Alcohol, chlorosine, Trichlen, etc. (100%)	Cannot be treated. Treated separately.
	Organic system linsing waste water	Alcohol (2~3 mg/l)	BOD, COD, Microorganism
	Fluorine system thick drain	Fluorine, acetic acid, ammonia, hydrogen peroxide (3~30%)	BOD, COD, Microorganism, Floating with O_2 bubble
	Fluorine system linsing waste water	Same as above (3~300 mg/l)	Same as above
	Acid. alkali system thick drain	Mineral acids, acetic acid, hydrogen peroxide, ammonia (5 ~30%)	BOD, COD, Microorganism, Floating with O_2
	Acid. alkali system linsing waste water	Same as above (3~300 mg/l)	Same as above
Water manufacturing drain	RO concentrated liquid	Water component x 3 to 4, Phosphorous (2~3 mg/I)	Condensative
	Ion exchange reproducing waste water	NaOH, HCI (1%)	Rapid pH fluctuation
	RO linsing waste water (Non-steady)	Polyphosphoric acid (2~3%), activator (2,000~3,000 mg/l), or ethylene diamine tetranitrate (2~3%)	Water linsing is made also after this. Poor condensation
	RO sterilizing waste water (Non-steady)	Formalin (2~3%)	Water linsing is made also after this. Trouble occurs when applied to organism treatment in one time.
	Piping linsing water drain (Non-steady)	Hydrogen peroxide (2~3%)	Water linsing is made also after this. Floating with O_2 bubble
Gas linsing water	Acid system	Same as waste water and drain	——————
	Alkali system		
	Organic system		
Living waste water	Mess hall, miscellaneous waste water	——————	
	Toilet		

system waste water and acid/alkali system waste water.

These components cause problems of BOD, COD and improper precipitation at the time of discharging after processing or when collecting water as described in 2.2—processing waste water—below.

Secondarily, phosphorus and nitrogen system chemicals are used in a large quantity, and each waste water system contains them. Phosphorus is used and drained in the form of phosphoric acid for alminum etching agent and glass tube washing solution, or in the form of polyphosphoric acid after used as scaling preventing agent of RO. On the other hand, nitrogen is used in a large quantity for etching washing in the forms of ammonia and nitric acid, and recently, it is used as an organic nitrogen contained in organic alkali chemicals. The nitrogen and phosphorus are directly restricted by discharging standards, and moreover, in the water processing equipment, they become causes of improper aggregation at the time of processing and discharging occurrence of duckweed at the time of water collection.

Tertiary, complication of nonconstant draining of industrial water manufacturing equipment is pointed out. As its name indicates, water is not drained constantly. Even if there is a basic schedule, washing and sterilization are made whenever a fault occurs on the equipment, and as a waste water processing equipment, it must always be ready to treat the waste water. Further, chemicals used at this stage are mainly formalin (COD, BOD, poisonous), ethylene diamine tetranitrate (COD, N), polyphosphric acid (phosphorus, aggregativeness), hydrogen peroxide (COD, floating at precipitation), etc. These chemicals are directly related to the restriction standards, and in many cases, they are harmful factors. Table 1 shows types and characteristics of the waste water.

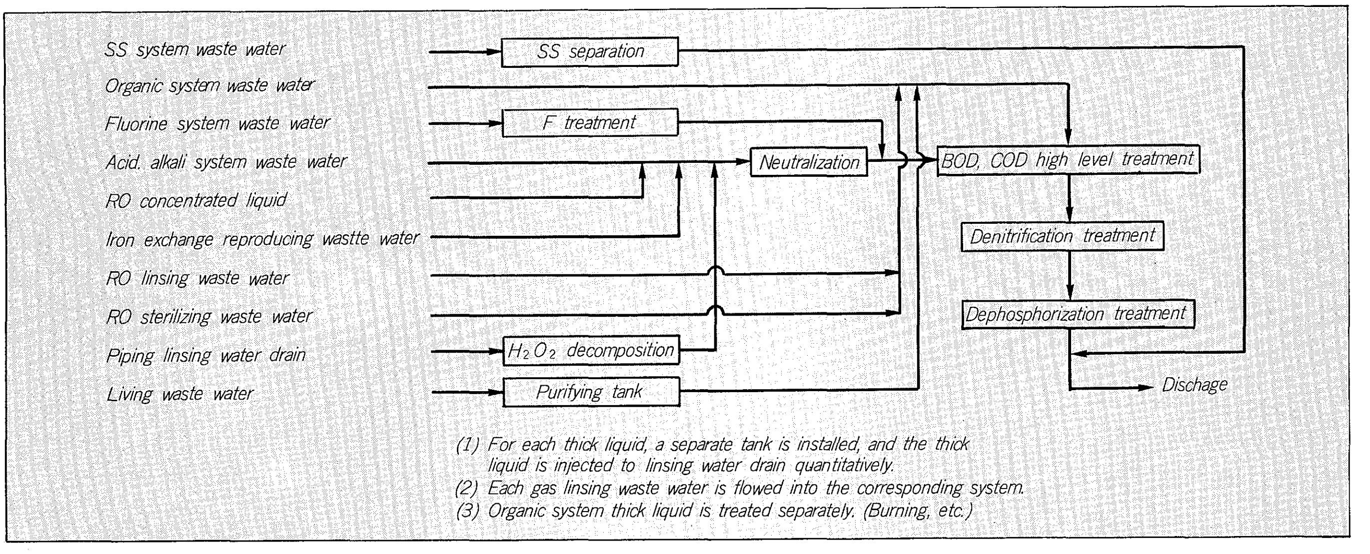
2.2 Treatment of waste water

2.2.1 Treatment and discharge system

To comply with the waste water is discharged after properly treated, and treatment process changes depending on the standards. Fig. 1 shows the changes.

For SS system waste water, only SS separation is required because this type of waste water contains SS the major component of which is silicon and no other contamination is involved. For the devices, aggregation precipitation using polyalminum chloride (PAC) or alminate salfate, or ferric trichloride and alkali, or high molecular

Fig. 1 Treatment discharge



aggregating agent and filtration by silicious earth precoat filter, or ultrafilter, etc. are used. When thick liquid is separated, concentration of organic matter is greatly reduced, and in many cases, treatment is not required for organic system waste water. When the treatment standard is severe, however, BOD and COD treatments are required. In case of water linsing, the contained organic matters are mostly methyl alcohol, ethyl alcohol, and isopropyl alcohol used in the final exchange process, and microorgainsm treatment is suited to all of them.

Fluorine system waste water is mainly from fluorine treatment. At the same time, in many cases, hydrogen peroxide is contained. Hydrogen peroxide becomes not only COD source but also causes oxygen at the fluorine aggregating and precipitating processes and bubbles cause SS components to float up. It must be noted that another component, namely, acetic acid becomes a source of BOD. For this reason, hydrogen peroxide must be eliminated before the fluorine treatment, and after the fluorine treatment, BOD treatment may also be required depending on the applicable standard.

As the practical flow, waste water is made to alkali by adding lime, and at the same time, a proper volume of ferrous salt such as ferrous sulfate is added to decompose hydrogen peroxide. As soon as making waste water to alkali by adding lime, waste water is stirred by air, a little volume of ferrous salt is added to decompose the remained hydrogen peroxide after self-decomposing the most of hydrogen peroxide. Further, depending upon fluorine treatment standard, pH is readjusted after adding aluminum salt, and then, aggregation and precipitation are made. With this treatment, fluorine is reduced to about 8 mg/1. When a lower value is required, aluminum salt is added again and aggregation and precipitation are made (double step aggregation precipitation method), or selective adsorption treatment is performed by using active almina or ion exchange resin, and thus, required value of fluorine is obtained.

Fluorine treatment completes as described above, and phosphorous generated by phosphoric acid, etc. is also treated. However, BOD caused by acetic acid and nitrogen caused by ammonia and nitric acid are not treated at all. For BOD, microorganism treatment is suited, and in many cases, active sludge method, rotary disk contacting oxidation, etc. are used. RO concentration water contains a little volume of polyphosphoric acid in the running water component which was concentrated 3~4 times, and pH is as low as 5 to 6. The item to be treated is pH, and phosphorous must be treated depending on the applicable standard. For treatment of phosphorous, aggregation and precipitation are used by means of aluminum or ferrous salt. Ion exchange recycling water is drained for a few hours in the cycle of once a day or once every eight hours, and caustic soda and hydrochloric acid are used at the time of recycling. Therefore, pH fluctuation is large. To adjust pH, treatment can be stabilized by making total volume of waste water per recycling even, and volume of used chemical can also be saved.

RO linsing waste water contains polyphosphoric acid, ethylene diamine tetraacetic acid, etc., and the waste water is separated to thick portion and thin portion which pushes and linses out the thick portion. Ethylene diamine tetraacetic acid is related to COD and nitrogen. It belongs to those the treatment of which is hard. At present, ozone ultraviolet ray treatment under thin state or acid separation under thick state is performed as the treatment. However, these methods have problems of cost and operation, and in many cases, waste water is quantitatively dilluted and discharged to other systems. Phosphorous of polyphosphoric acid is treated by aggregation.

RO sterilizing waste water is classified into several percent of formalin and dilluted liquid produced by pushing out formalin and linsing. Problem items are BOD and COD, and quantitative injection into microorganism treatment equipment is suited to treat this kind of waste water. Pipe sterilizing waste water is also classified into liquid of several percent of hydrogen perioxide and linsing water. When the concentration is equivalent to that of linsing water, the same treatment as fluorine system waste water is suited. For thick liquid, however, a large volume of ferrous salt is required, and air decomposition under alkali causes problems of bubbling. Thus, the thick liquid is treated separately. As for the method, weak ultraviolet ray is applied for a long period of time or active coal powder is added in a little volume and the liquid is stirred. For living waste water system, the treatment stipulated by the Architectural Standard is required, and after completing the treatment, higher level BOD, COD, nitrogen and phosphorous treatments are performed further depending upon the applicable standard. Out of the above described systems, those which require treatment of nitrogen are treated by microorganism treatment. The standard processing flows were explained above. Concentration, ratio of water against components and components themselves of each waste water at each plant considerably differ, and therefore, proper flows and systems should be selected in accordance with the individual plants.

2.2.2 Partial water collecting system

The water treated by a treating and discharging system can be used again for toilet purposes, spraying on the ground or water linsing which does not require high water quality. However, places to which such water can be used are limited, and only 10 to 20% of the total volume of discharged water can be used. To use the water again in a larger ratio, the water must be treated up to a level equivalent to that of pure or super pure water. However, to do so, not only those to be eliminated in compliance with various standards but also neutral salt and very small amout of organic substances which could be disregarded must be eliminated. Needless to say, in the treatment process, it must be avoided to increase salt concentration and organic components by adding chemicals. The collection and treatment objective systems are to be decided based on the volume of water to be collected, cost benefits created by the collection, etc.

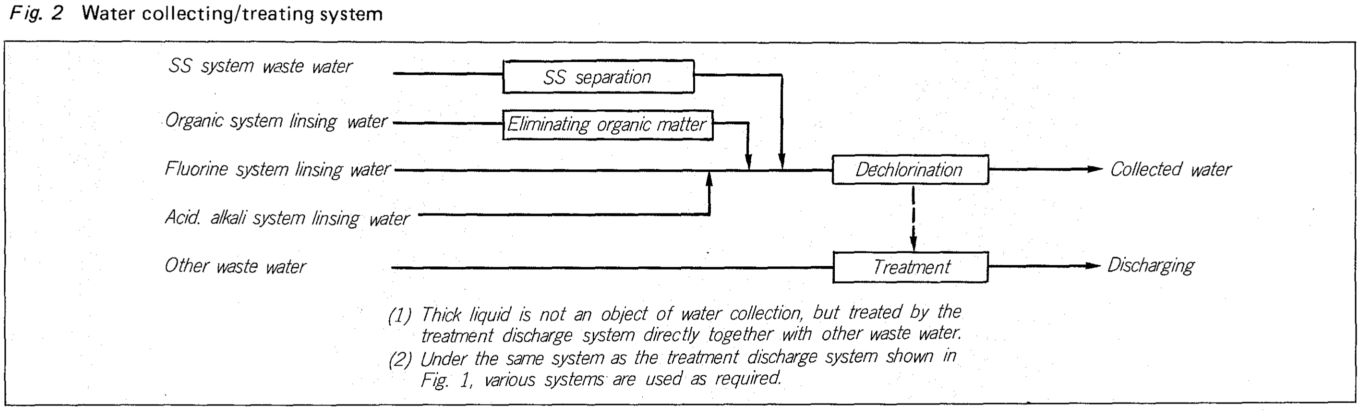
The factors which affect difficulty of water collection and water collecting cost, there are existence and nonexistence of organic matters the elimination of which from the waste water is difficult, level of salt concentration, existence or nonexistence of SS component. Water can be collected simply in a lower cost when the waste water has no organic matter and SS component and salt concentration is lower. When difficulties of water collection are compared by types of waste water, it is more difficult in the following order. Acid/alkali system linsing waste water Fluorine system linsing waste water SS system waste water Organic system linsing waste water. As for the cost, generally, the point of water collection from SS system waste water becomes the boundary, in many cases, where a merit causes. When collection of water is made up to organic system waste water, the cost increases considerably. Fig. 2 shows the fundamental water collection flow.

For SS system waste water, SS is separated alone because contamination with SS is high. For the SS separating devices, silicious earth filter, ultrafilter, aggregation/precipitation, are used.

For the treatment of organic system linsing waste water, microorganism treatment was suited in the previously discussed treatment discharge system. When collection of water is provisional, however, even if the cost increases, safer physical/chemical treatment methods are taken because of the limition of microorganism treatment, contaminations of microorganism and microparticle and stability. At present, ultraviolet ray plus H_2O_2 and ozone plus catalyst are used practically. In either case, however, the installation cost and running cost are high, and cost merit of water cost by collection of water from organic system linsing waste water cannot be expected.

SS system waste water from which SS has been eliminated, organic system linsing waste water from which organic matters have been eliminated, fluorine system linsing waste water and acid/alkali system linsing waste water are combined, and the combined water is treated to remove salt. To eliminate salt, an ion exchange device, RO device, etc. are used. Out of these devices; the ion exchange method is used in many cases because in the RO mehod, a block is anticipated due to occurrence of SS after neutralization of a fine volume of aluminum, components such as ammonia and nitric acid which cannot be separated easily are contained, salt concentration of the waste water is normally lower, and the running cost is higher than that of the ion exchange method.

Fig. 2 Water collecting/treating system



In case of the ion exchange device, not so high level is required for the purity of treated water at this stage, and therefore, taking the running cost into consideration, single floor type cation tower and anion tower are combined, and for the resin, those of microporous high frame strength which are highly resistive against contamination and oxidation agent are used. However, when concentration of peroxide hydrogen in the source water is high or when boundary surface activator is contained in other than organic system waste water, an active charcoal tower must be installed as a pretreatment method. Through the above introduced treatments, water having a higher quality than city water and well water can be obtained. Water collection of a considerably high ratio can be made by sending the collected water to those processes which do not require a high purity directly without further treating it or by using the collected water as a part of source water for the water purifying device. When water collection is made, however, the overall discharged water volume reduces, and concentration of the component increases inverse proportionally. Equipment cost required for discharging can be reduced by properly treating pH, fluorine, etc. because volume of water reduces, however, concentrations of COD, BOD, nitrogen, phosphor, etc. increase as water collection is made. Therefore, when concentrations of the components are restricted, additional equipment may be required. In this case, cost is increased by not collecting water, and when the plan is to intend reduction of water cost through a water collection, the plan must be thoroughly and carefully examined.

2.2.3 Completely closed system

In the partial water collecting system, the collecting methods were examined for all waste waters. For the completely closed system also, countermeasures can be established under the almost same idea. However, the points to be exercised are that in the partial water collecting system, waste water reproduced from the desalting equipment, reverse linsing waste water and flow out from those system from which water is not collected are involved, and city water and well water are supplied to replenish them. For this reason, even if there is a small value of component which cannot be treated by the water collecting equipment and water purifying equipment, the concentration does not exceed a certain level in accordance with the water balance. In case of the completely closed system, however, primarily, all the waste waters are subjected for collection, and the water reproduced by the desalting and purifying equipment and reverse linsing waste water are returned to the water collecting system via the post treatment. For this reason, if there is a component which cannot be treated, the concentration increases gradually, and it is anticipated that the increased concentration may affect the production line. Thus, the system must be examined more precisely. Also for the equipment, in case of a partial water collecting system, even when the equipment stops temporarily due to a fault, the problem can be solved by increasing volume of city water and well water during the stoppage. In case of a completely closed system, however, the countermeasure like this cannot be taken because volume of water kept within the system is limited to a certain range. Accordingly, it is necessary to use a safer equipment and to compose and construct a system with the sufficient countermeasures taken into considerations. Fig. 3 shows the flow.

Basically, the completely closed system differs from the partial water collecting system in the installation of an evaporator. In the partial water collecting system, various treated and discharged high concentration liquids, reproduced and reverse linsing waste water from the desalting equipment, and concentrated liquid and reproduced waste water of the water purifier are collected into the evaporator and the distilled water returned to the water collecting system. As shown in Table 2, both the evaporator installation cost and running cost are extremely high, and therefore, to set up a rational system, it is very important to reduce water flowed into the evaporator.

For this reason, a desalting equipment of high condensation ratio must be used, those reproduced liquid having a low salt concentration should be returned to the source water, and the water collecting system must be rationalized so that water will not be flowed into the evaporator.

Further important point is the rationalization of the manufacturing process and more than the treatment discharge system and partial water collecting system, a

Fig. 3 Completely closed system

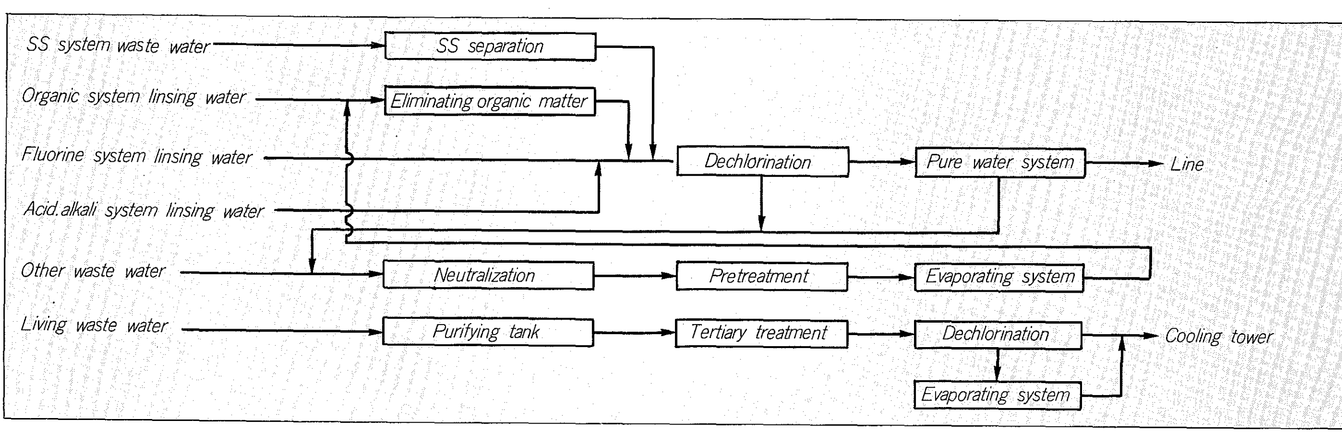


Table 2 Comparison of various water collecting equipment

Item \ Unit process	Ion exchange method IE	Reverse osmosis method RO	Evaporating method EVA
Mechanism	Resin adsorption of ion	Film asmosis of water	Evaporation of water
Energy	Chemical potential	Differential pressure	Heat
Existence or nonexistence of phase change	None	none	Liquid-Gas-Liquid
Power source	Feed pump	High pressure pump or booster pump	Steam, gas or electric power
Main material	Polystyrene system high molecular grain	Micro-porous film of cellulose acetate or polyamide system	SUS27 SUS33
Objective waste water	Low concentration nonorganic ion	Nonorganism and organism	Waste liquid with high ponetration
Applicable concentration range			
1) Source water	500ppm or less	500ppm or less	3% or less
2) Dechlorination water	10ppm or less	50~500ppm	200ppm or less
3) Concentration water	1~1.5%	4~6%	Solid
Comparison of equipment cost	1.0	1.0	50~100
Comparison of operation cost	1.0	1.0	50~100
Maintenance	Resin reproduction	Film washing	Scaling
Pretreatment	Sand filteration	Precise filteration pH adjustment	None
Operating temperature	Maximum 60°C	Maximum 40°C	70°C(reduction)
Influence of temperature	None	Affected	–

water linsing system and water using system which are advantageous to the completely close water collecting system must be used.

The evaporation pretreatment equipment is a device which eliminates and decomposes the components contained in the water which interfere the evaporator, and the device decomposes peroxide hydrogen and eliminates SS and ammonia. Out of these operations, elimination of ammonia is important. When failed from this, ammonia enters the evaporator, it evaporates together with water, ammonia is mixed into the distilled water, the water is circulated into the desalting equipment again, causing the concentration to increase gradually, and as the results, operating frequency of the desalting equipment increases, water load applied to the evaporator increases (lack of performance) and other troubles occur.

For elimination of ammonia, decomposition using oxidizing agent and deammoniausing stripping are performed. In case of a closed system, the largest problem is the nonconstant waste water within the water purifier. Out of the waste waters, pipe linsing waste water or RO linsing waste water which can be treated within the system is stored in an emergency tank temporarily and treated little by little. However, the treatment of formalin is hard within the system, and it is desirable to steralize at outside of the system or to treat the waste water at outside.

Table 3 Comparison of new RB system with the conventional method for the performance and cost (When semiconductor manufacturing plant waste water is examined)

(a) Design standard

Item	Ion	New RB system	Conventional method
Source water quality	Na	38.9 mg/l	
	Ca	0.14 mg/l	
	Mg	0.16 mg/l	
	NH_4	1.1 mg/l	
	SO_4	0.56 mg/l	
	Cl	27.8 mg/l	
	NO_3	49.6 mg/l	
	SiO_2	6.1 mg/l	
	F	5.3 mg/l	
Treated water quality	Na	0.06 or less	1.0 or less
	SiO_2	0.06 or less	0.2 or less
	F	ND	0.15 or less
	Conductivity	1 μs/cm	10 μs/cm
Volume of treated water		250m^3/cycle	

(b) Economical comparison

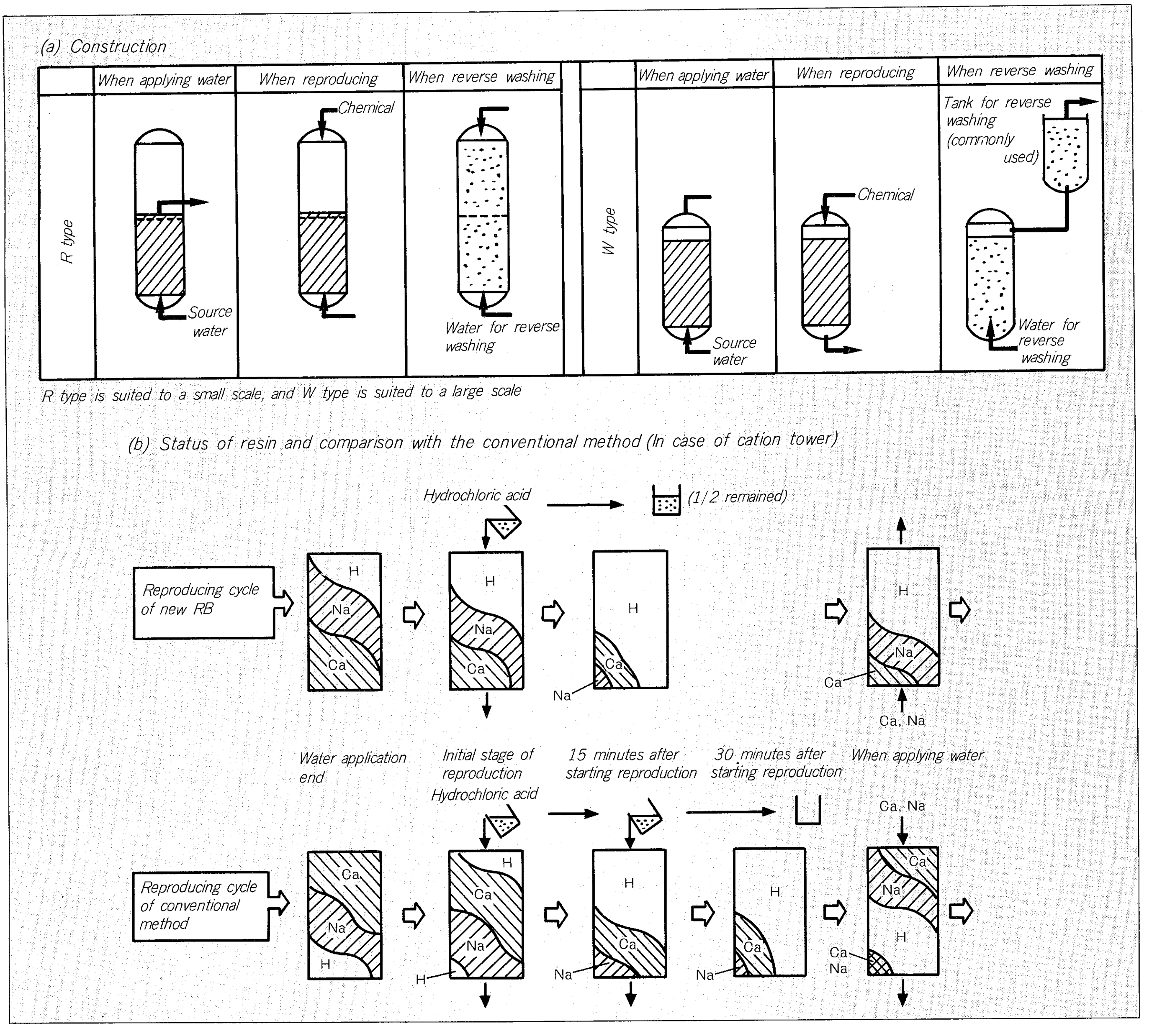
Item		New RB system	Conventional method
Reproducing chemical	HCl	23.7 kg/cycle (8.3 yen/m^3)	73.4 kg/cycle (22.3 yn/m^3)
	NaOH	30.6 kg/cycle (8.3 yen/m^3)	61.2 kg/cycle (16.6 yen/m^3)
Power consumption		68.7 kWH/cycle (4.1 yen/m^3)	93.7 kWh/cycle (5.6 yen/m^3)
Iron exchange resin	Cation resin	(0.90 yen/m^3)	(0.72 yen/m^3)
	Anion resin	(3.52 yen/m^3)	(3.11 yen/m^3)
Water for reproduction		6.8m^3/cycle (7.61 yen/m^3)	9.1m^3/cycle (10.19 yen/m^3)
Running cost		32.73 yen/m^3 2,160,000 yen/year	58.52 yen/m^3 3,860,000 yen/year
Annual running cost difference		1,700,000 yen	
Construction cost (approximately)		24,500,000 yen	23,000,000 yen

Calculation reference HCL : 76 yen/kg Water : 280 yen/m^3
NaOH : 68 yen/kg Power: 15 yen/m^3
Annual operation: 330 days/year
(Note) Water supply and sewage charge when water is not collected: 18,500,000 yen/year

2.3 Recent new technologies

As an ion exchanger, the heart of a water collecting system, recently, new RB system has invited attentions of

Fig. 4 Construction of new RB system and status of resin



the people concerned. The new system uses a counter current reproducing method as long as the operating principle is concerned, and this method is presently used so popularly in the field of pure water producing because of the features (low reproducing cost and high purity of treated water). The conventional counter current reproduction is an extension of the normal parallel current reproduction. The conventional counter current reproduction cannot wash SS components accumulated on the resin with the reverse current, and it could not be used to treat the source water which contains SS components, in the water purifier fiedls.

Further, when using waste water as the source water of a purifier again, SS may be generated also within the resin tower due to the influences of the microorganism and chemical reactions, and the conventional method could not be applied because of the SS problems. While, the new RB system solves the problems of SS with the new construction which allows reverse washing. Thus, water reproducing cost is low, level of linsing is high, and the new system can be applied to water collections. Fig. 4 shows the construction, and Table 3 shows the features.

3 TAIL GAS TREATMENT

In a semiconductor manufacturing process, various chemicals and gases are used, and people will be injured, fire may occur and air pollution will result if they are not treated or the tail gas system is separated properly. Not only the adverse effects, but as semiconductor manufacturing equipment themselves are expanded or modified frequently, tail gas treatments must be examined carefully from the beginning of the system plan, including the operations. Tail gas treatment is outlines as follows.

3.1 Types of tail gas and restriction for tail gas concentrations.

In a semiconductor manufacturing process, the harmful gas generating sources are photo-engraving, etching, diffusion process, etc. and types of the used chemical and gas vary. Table 4 shows the types of the typical gas exhausted from semiconductor manufacturing processes.

To these gases, various regulations apply when they are exhausted, and the standard is the Air Pollution Prevention Law. For prevention of the air pollution, each prefectural government has its own restrictions. Therefore, when exhausting a gas into the air, concentrations of exhausted gases must be carefully examined. Table 5 is an example of the Standard Regulation for Restriction of Public Nuisance established by Osaka Prefectural Government. The contents differ by each local government office, and therefore, the applicable standard must be carefully examined in advance.

Table 4 List of gases generated at semiconductor process

Item	Type of gas
Nonorganic system gas	Sulfuric acid, hydrochloric acid, nitric acid, flourine, ammonia, silicon compound, etc.
Organic system gas	Toluene, trichloroethylene, xylene, acetone, ethyl alcohol, etc.
Explosiveness·self-combustible gas	Hydrogen, monosilane, etc.
Special gas	Arsine, phosphine, etc.

Table 5 Standard Regulation for restriction of public nuisance (Osaka Prefecture) (March '77)

Name	Premise boundary standard	
	ppm	mg/m^3
Zinc and its compound		0.1
Acrylic ester	0.1	0.38
Acrolein	0.01	0.025
Actaldehyde	2.2	3.9
Ammonia	1	0.76
Carbon monoxide	10	13
Ammonium chloride		0.3
Hydrogen chloride	0.1	0.16
Chlorine	0.02	0.063
Cadomium and its compound		0.0005
Gasoline		5
Xylene	2	9.5
Chromic acid		0.005
Phosphoric chloride		0.1
Acetic acid	0.5	1.3
Acetate	5	17
Phosphorus trichloride	0.05	0.31
Hydrogen cyanide and cyanide		0.2
Bromine	0.01	0.071
Dioctyl phthalate		0.1
Dibutyl phthalate		0.1
Styrene	1	4.6
Asbestos		0.1
Hydrogen selenide	0.005	0.018
Substance in tar state		0.05
Nirogen oxide	0.2	0.41
Trichlorethylene	2	12
Toluene	2	8.2
Copper and its compound		0.1
Lead and its compound		0.01
Sulfer dioxide	0.2	0.57
Nickel carbonyl	0.0001	0.00076
Carbon disulfide	0.5	1.7
Pyridine	0.2	0.70
Phenol	0.2	0.84
Phthalic acid	0.1	0.66
Fluorine, hydrogen fluoride and fluoride		0.01
Benzene	0.5	1.7
Phosgene	0.005	0.022
Formaldehyde	0.1	0.13
Manganese and its compound		0.025
Methanol	5	7.1
Methyl/ethyl ketone	4	13
Mercaptane	0.05	0.14

3.2 Plan and method of tail gas treatments

3.2.1 Plan

Types of tail gas are briefly classified into organic system and nonorganic system. From a gas generating source to a treatment equipment, gas is sent through a duct. In case of a nonorganic gas, the duct is corroded shortly as it is oxidized and the duct must be of an acid resiting. Further, for the route of duct, it should be avoided to route the duct above ceiling, and it should be adequately arranged so that the duct can be checked and cleaned periodically.

Moreover, as the semiconductor manufacturing equipment are frequently expanded and modified, a spare route should be secured and a sufficient extra space should be kept. Based on the above noted points, items to be examined at the time of planning are indicated below.

(1) Type, concentration and capacity of gas generating source.
(2) Concentration of tail gas permitted by the applicable law.
(3) Used time band and room operating mode at the gas generating source.
(4) The operating method, in case of a draft chamber.
(5) Total tail gas volume and decision of number of treatment systems.
(6) Examinations for explosion, ignition, burning, etc. due to secondary reactions at the exhausting process

or mixing with air or water.

(7) Selection of material having a sufficient corrosion resistance for the duct.

(8) Depending on an equipment, when the gas is highly harmful or danger, it should be exhausted through the independent and special duct and treated separately.

(9) Influence of the installed equipment given to other equipment with wind.

(10) Countermeasures for noise and public nuisance to the vicinity.

(11) Influences of bivrations generated by a fan and pump, when installed on the roof of a building.

(12) Correspondences to modification, inspection and expansion of the duct route.

(13) Examinations on future space expansion for the equipment.

(14) Securing maintenance space and passage of the treatment equipment.

(15) Energy saving operations at the time of off duty.

3.2.2 Plans to separate tail gas duct . . . .

In a semiconductor manufacturing process, various chemicals and gases are used. Accordingly, treatment mehtod differs depending on the type of chemical or gas, and mixed exhausts through the same duct system are not allowed. For this reason, the exhaust system must be divided into five types as shown in Table 6, and duct systems must be planned in response to types of chemical and gas.

(1) Nonorganic system tail gas

The nonorganic tail gases are mainly from chemical stations where nonorganic chemicals such as ammonia, hydrochloric acid, hydrofluoric acid, sulfuric acid, nitric acid and silicon compounds are used. Since the tail gases contain highly corrosive and acidic gases, poly vinyl chloride is used for the duct. End of the duct is connected to a scrubber, and a wet treatment is made by disolving the gas into water and by discharging to the air.

(2) Organic system tial gas.

The organic tail gases are mainly from chemical stations where solvents such as acetone, trichloroethylene, ethyl alcohol, toluene and xylene are used. For the exhaust duct, steel or stainless steel plates are used. End of the duct is connected to a dry treatment system. Passing the tail gas through active charcoal, the organic solvent is adsorbed.

(3) Explosive/self-combustible gas

Explosive/self-combustible gas such as hydrogen and monosilane gas applies, and exhaust of CVD process is an example of the treatment. For the duct, stainless steel nonleak piping is used, and it must be carefully constructed so that no air flows into the duct from the joint. Further, it will be safer to flow small value of N_2 gas always through the exhaust pipe for purging. End of the duct is connected to a scrubber, and a wet treatment is made. For explosive or self-combustible tail gas, care should be exercised not to connect two or more equipment to one system because, in many cases, mixed gases may react chemically. Further, CVD process uses chlorine gas in many cases, and therefore, even if stainless steel is used, the duct must be checked periodically because it may be corroded toward a long period of time.

Table 6 Tail gas system segment and tail gas treatment

System segment	Treatment method
Nonorganic tail gas	Wet treatment
Organic tail gas	Dry treatment
Special tail gas	Wet treatment
Miscellaneous tail gas	Wet treatment
Heated tail gas	Wet treatment

(4) Miscellaneous tial gases.

Tail gas in the casing of a process equipment and tail gas of pump are miscellaneous tail gases. Since oil stays in the duct, inflammable tail gas should not be connected to tail gas of a rotary pump.

(5) Hot tial gas

Hot tial gases are those from oxidation equipment and baking furnace. End of the duct is connected to a scrubber and tial gases are discharged to the air after cooling.

Leakage or corrosion is likely to occur on a joint of the exhaust duct during a long period of time. Therefore, the exhaust duct should be installed in a proper place so that the duct can be checked easily.

3.2.3 Treatment method

Generally, harmful gases are treated by an absorbing method using scrubber or adsorption method using active charcoal. For the scrubbers, there are mechanical type and gas dispersing type, and each one of these types has several kinds. In case of a semiconductor plant, filler type or porous type is used in most cases. Fig. 5 shows a typical flow of the wet treatment method.

(1) Filler type scrubber treatment

The filler type scrubber accommodates fillers such as polypropylene and poly vinyl chloride in a tower, and with a linsing pump, sprays linsing liquid. The gas sucked by an exhaust fan goes through the system, causing the gas to contact the liquid, and thus, the gas is eliminated. This method is mainly effective for nonorganic system gases. For the linsing liquid, water or alkali water solution is used. Table 7 shows the gas eliminating efficiency of the wet treatment method.

(2) Porous disc type scrubber treatment

Instead of fillers, the porous disc type scrubber installs poly vinyl chloride plates having many number of holes in steps. When air sent by a fan passes through the holes, bubbles are made as the air contacts the liquid, and with the bubbles, gas is eliminated. This method is mainly effective for nonorganic system gases.

(3) Problem points in case of nonorganic system treatment

(a) When treating ammonia gas, it must be separated from other gas. Or otherwise, it appears to be other substance and white smoke is generated.

(b) Silane system gas should be separated from other systems and silicic acid must be eliminated before it enters the scrubber. Or otherwise, oxidized

Table 7 Gas eliminating efficiency of wet type treatment method

(Sucking concentration: 100ppm)

Name of gas	Molecular formula	Washing liquid	Eliminating efficiency (%)
Hydrogen chloride	HCl	H_2O	85~98
		NaOH	
Hydrogen fluoride	HF	H_2O	90~95
		NaOH	90~99
Chlorine	Cl_2	NaOH	92~99

Fig. 6 Typical flow of dry treatment method

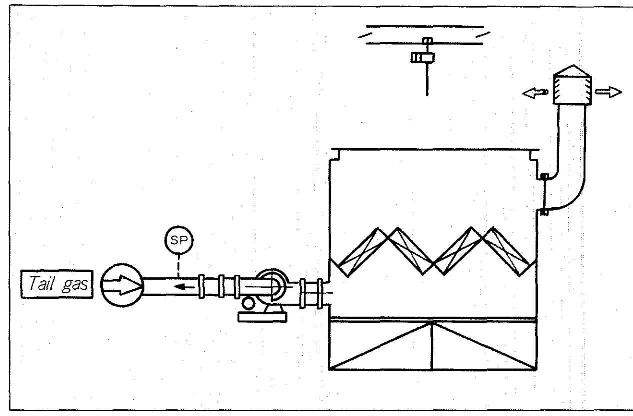
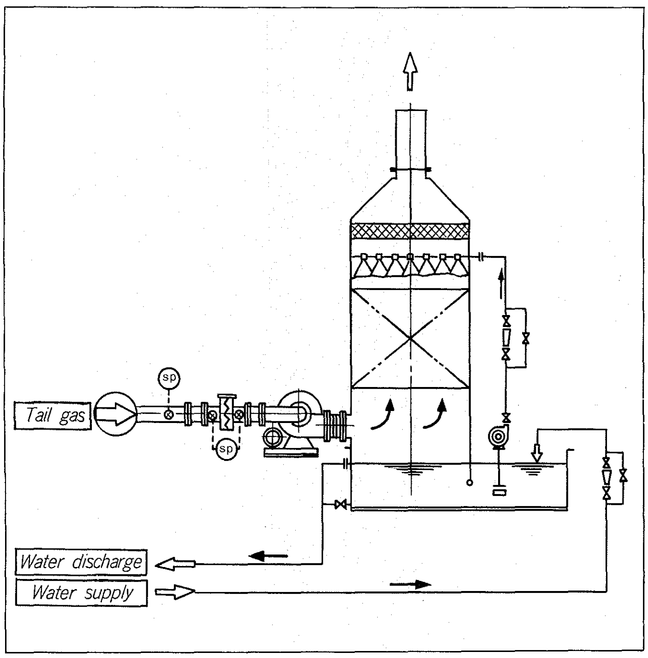


Fig. 5 Typical flow for wet type treatment system (In case of filler tower system)



silicon power sticks to the impellar of the fan, causing the performance to drop. The power also sticks to the fillers, increasing pressure loss.

(c) Tail gases including oil mist and abbrasives should not be mixed with the nonorganic system also.

(4) Active charcoal adsorption treatment.

This method is most suited to adsorb organic matters. They are adsorbed from a low to high concentrations. In case of a high concentration, hwoever, it should be noted that a fire may occur due to adsorption heat. Fig. 6 shows a typical flow of the dry treatment system.

(5) Silicious earth adsorption treatment

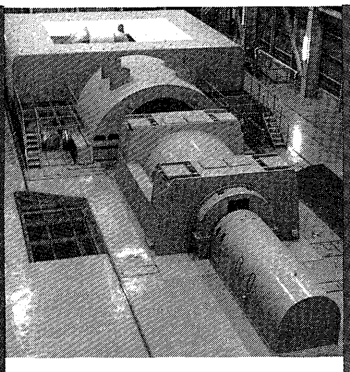
Concentration of arsine or phosphine exhausted from a semiconductor manufacturing process is extremely low, and it may be discharged as is. However, when treating it, silicious earth adsorption treatment is used. The silicious earth contains ferrous chloride as the main component and metal chlorination or metal oxide as the subsidiary component, and collects and adsorbs arsine and phosphine with the chemical oxidizing acts. The silicious earth adsorbing agent is contained in a cartridge. When yellow brown color of the adsorbing agent is faded and discolored more than 80% of the overall color, the cartridge is replaced with a new one. With this method, both arsine and phosphine, can be eliminated to 0.05ppm or 0.3ppm or less than the permissible concentrations.

4 POST SCRIPT

Both waste water treatment and tail gas treatment are of a sceneshifter in the play of semiconductor manufacturing process. However, the system configuration greatly affects the plant operating efficiency and manufacturing cost. Therefore, each plant is making all kinds of trial, and new systems will be developed. The thing that we have to do in the future is to find how should the exhausted energy be collected rather than preventions of river and air pollutions. To accomplish this target, a low cost material which is superior in resisting chemicals is required, and we are expecting such material will be developed.

Outline of Products

Power and Industrial Electrical Machinery

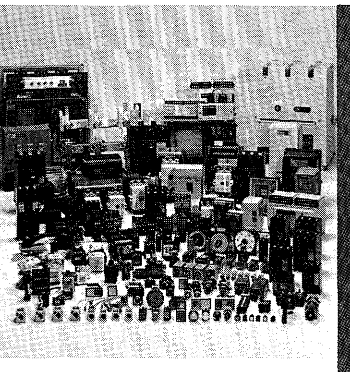


- Nuclear Power
- Power Generation and Distribution
- Transportation
- Environmental Equipment
- Industry
- Electrical Installation
- Mechatronics Equipment

Instrumentation

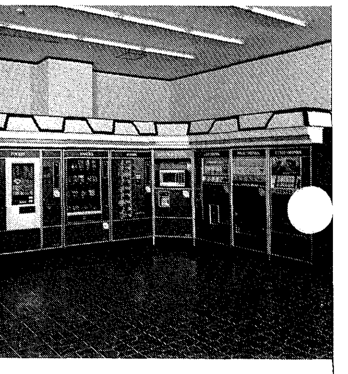
- Industrial Instrumentation
- Water Treatment
- Data Process Engineering

Standard Electrical Products



- Semiconductors
- Rotating Machines
- Standard Electrical Equipment

Vending Machines and Specialty Appliances



- Vending Machines
- Freezing & Refrigerating Open Showcases
- P.O.S. for Versatile Purpose Appliances
- Air Conditioning