Special Edition on the Environment

Effective Utilization Technology for Ultra Purewater, Chemical Liquids and Waste Materials on Semiconductor Manufacturing Plant

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Abstract

In many semiconductor manufacturing plants, in addition to "pursuit of convenience" which can be given for multifunction products at a low cost, many consumers are also demanded "pursuit of making the structure for a recirculating-type recycling plant" which positively conserve the global environment. To realize the recirculating-type recycling plant, a technical development program to be highly sustainable are required the technologies of treatment, recovery, regeneration and reuse of ultra purewater, waste water and waste chemical liquids.

In addition, to achieve further reducing of the environmental impact and decreasing in treatment cost, in constructing new semiconductor manufacturing plants, new facility technologies are needed to conform strengthened environmental regulations on depletion and degradation of water resources and plans for conservation of the natural environment and the earth's limited resources.

Figure 1 shows the breakdown of our company's investment cost in new facility equipment system for environmental conservation measures at semiconductor manufacturing plants. As shown in this figure, the measure cost to conserve the earth's environment, such as energy saving and prevention of global warming, achieve by approximately 75%. The remaining 25% is the investment cost in new facility system required for decreasing waste treatment cost and reducing the impact on the environment to conform to strengthened environmental regulations.

Technology for Treating and Recovering Ultra Purewater

Due to the need to conform depletion and degradation of water resources, techniques are required for treatment and recovery of discharge water and waste chemical liquids to remove the organic and inorganic contaminating impurities effectively and safely, so that the treated waste water can be reused as ultra purewater. In the conventional treatment method, in order to remove any contamination impurities waste water and waste chemical liquids discharged from the point of use, most of treatment system for treating waste water and waste chemical liquids was of the "one-pass" type and large amounts of chemical liquids were used only once.

In this situation, most plants, if they continued this kind of removal treatment method for a long time, the small remaining amounts of pollutants would eventually build up and rivers and streams, lakes and marshes, the oceans would reach pollution levels that growth to an environmental problem. This actual situation would eventually destroy the balance of the ecosystem in the natural world. Consequently, in view of the environmental conservation, this kind of treatment method created a large increase in the environmental impact and resulted in increased operating costs of the facility system.

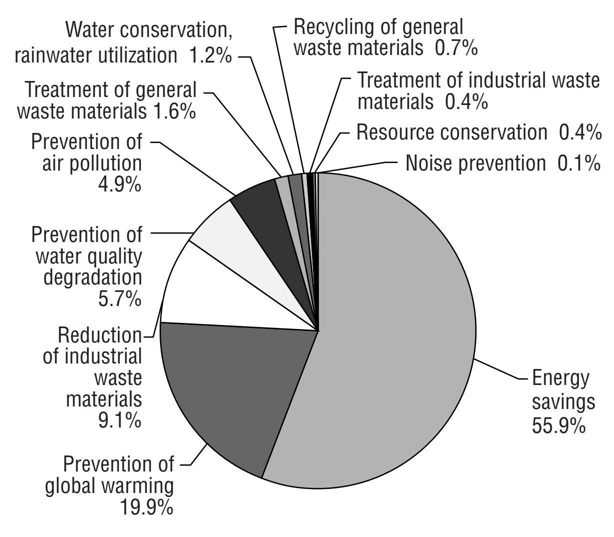

Figure 1: Breakdown of investment cost in new facility system for environmental conservation

Figure 2 shows the treatment flow of "completely closed" recovery system for ultra purewater developed at our company as a countermeasure to conserve the depletion and degradation of water resources. This system has been introduced into our plant for wafer treatment process and realized the recovery and reuse of waste water and waste chemical liquids, primarily to collect a large amounts of

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purewater used in the wafer cleaning process step.

The recovery system consists of [i] pre-treatment system for treating the industrial water, [ii] ultra purewater treatment system comprised of primary purewater producing system and secondary purewater producing system, [iii] discharge water recovery system and evaporating and concentrating system which recover each of (a) waste purewater used for the rinse cleaning, (b) waste chemical water containing chemical liquids in dilute concentrations treated at the use point, and [iv] chemical liquid recovery system which recovers concentrated waste chemical liquids which were used once at the use point.

These various kinds of system treat the waste water and waste chemical liquids discharged from the use point and return them to the use point as ultra purewater for reuse. The source water of the recovered waste water discharged from the wafer process manufacturing equipment contains many and varied kinds of chemical polluting contamination substances, such as small particles, bacteria, total organic carbon (TOC), heavy metals, etc.

These contained contamination substances are removed by optimized selective recovery methods controlled by the water quality and impurity substances concentration in recovered waste water. They are then treated by the optimal high efficiency pollution removing system. The treatment efficiency of this system has obtained 95% or more recovery rate, as compared with the totally consumption of the water used through the plant. In addition, the water quality of the recovered purewater has reached TOC concentration (the organic substances in the recovered purewater) of 0.5µg/liter or less. However, the recovery operating costs to achieve 95% recovery rate are twice, as compared with that of a system achieved 80% recovery rate.

Thus, compared to recovery system with 80% recovery rate, this system for treatment and recovery of ultra purewater, in view of a sustainable global environment preservation, is environmental freindly system which can operate in a state of most cost effectiveness and can treat and recover ultra purewater of high quality[1] .

Technology for Recycling and Resource Recovery for Waste Chemical Liquids

With the aim of reducing industrial waste materials and effective use of limited resources, we are working on the recovery of waste chemical liquids and their resource recovery in semiconductor manufacturing plants.

Up until now, waste chemical liquids used once in wafer treatment process were disposed as industrial waste materials without treating by waste water treatment system. Alternatively, after they removed chemical impurity substances by using system for treating waste water and waste chemical liquids, they delivered to an outside waste treatment maker as industrial waste materials under contract, and then treated and disposed of them. Recently, however, in order that "one-pass usage" waste water and waste chemical liquids are supplied to other existing facility system and utilized effectively, we are implementing the activities to improve a variety of treatment system.

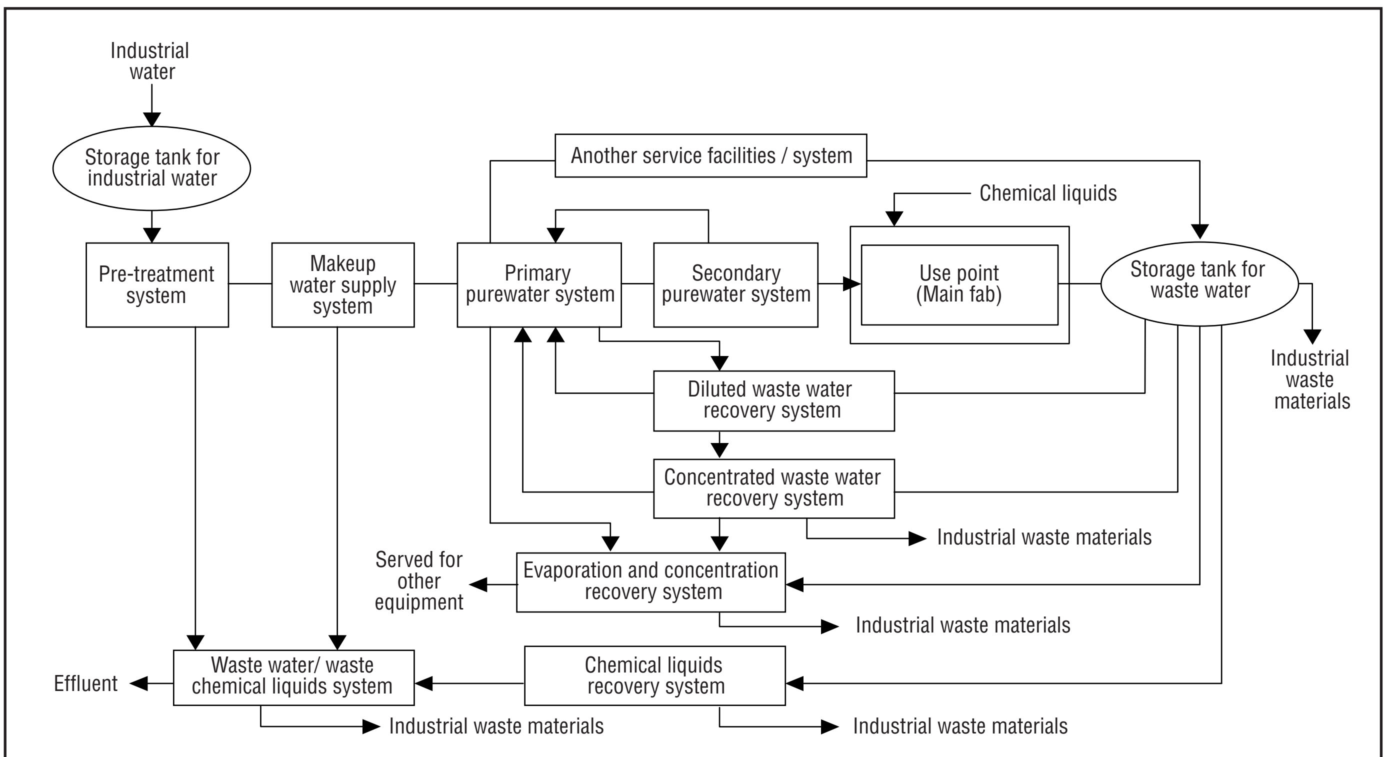

Figure 2: Treatment flow of "completely closed" recovery system for ultra purewater

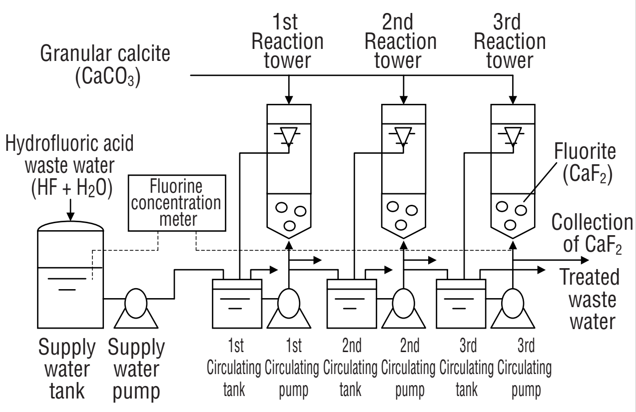

Figure 3: Treatment flow of hydrofluoric acid recovery system

We are being made to improve the operating efficiency of treatment system and the effective utilization rate of treated water treated inside the plant. Among such activities, the recovery of hydrofluoric acid liquids and their resource recovery are typical of the techniques used to reconvert waste chemical liquids to resources.

Figure 3 shows the treatment flow of system for hydrofluoric acid recovery and resource recovery.

This system can regenerate from waste chemical liquids containing hydrofluoric acid to fluorite (CaF_2) for use in producing hydrofluoric acid liquids for the chemical maker. The system utilizes a chemical direct conversion mechanism reaction by using granular calcite ($CaCO_3$). The calcite is replaced with the fluorite after directly reacted with a fluorine ion of the hydrofluoric acid. This system can obtain regeneration CaF_2 with a high purity rate of 97% or more and also a low ratio of contained H_2O moisture. The waste water treatment performance of this system has a 99% or higher level of fluorine removal rate, so that the treatment load on the existing waste water treatment system can be greatly reduced. In addition, that treated water can be effectively reused as supplement water for another facilities system.[1]

Technology for Reusing Industrial Waste Materials

In order to reduce the impact on the earth's environment as much as possible, semiconductor manufacturing plants need activities to accomplish the following: [i] reduce the amount of industrial waste materials by optimizing the treatment conditions for the recovery and neutralization of waste chemical liquids, [ii] review the frequency of exchanging chemical liquids and of cleaning the process wafer by optimizing the process treatment conditions for wafer cleaning steps, [iii] reuse the valuable resources by selective recovery and resource recovery. Recently, in order to reduce the generation of industrial waste materials, research and development of several materials to improve chemical properties of the various materials, which constitute the process equipment used in the various steps of wafer processing and waste chemical liquids treatment system is conducted at many plants.

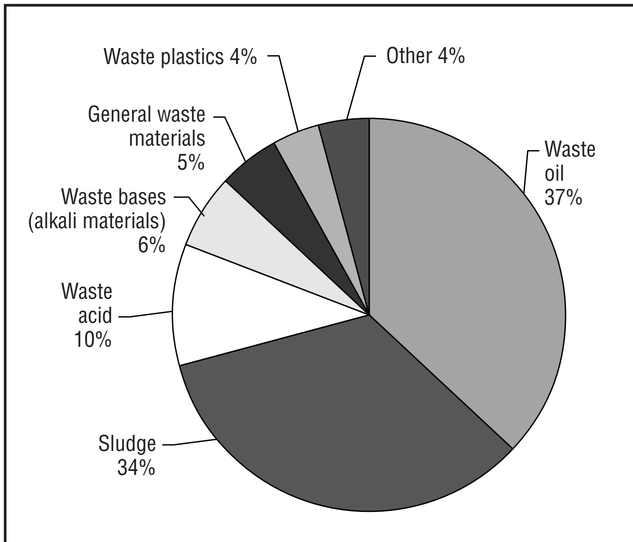

Figure 4: Breakdown of discharged amounts of industrial waste materials

Figure 4 shows the breakdown of the discharge amounts in the various classes of industrial waste materials from our semiconductor manufacturing plant.

As shown in this figure, the sum total of waste oil (including organic solvents, etc.) and sludge (organic sludge, inorganic sludge, etc.) reach by approximately 70% of the entire industrial waste materials discharged from the plants. If, in addition, waste acids (hydrofluoric acid, sulfuric acid, etc.) and waste bases (developers, etc.) are included, it is clear that discharge from the plant as industrial waste materials which can be reused by nearly 87% of the total industrial waste materials. Here we will discuss our activities for reducing these industrial waste materials, particularly our amount reduction activities, our treatment and disposal activities, and our resource recovery activities.

1. Amount reduction activities

Amount reduction activities aimed at reducing the discharge amounts of industrial waste materials from plant can achieve by optimizing the treatment conditions for the recovery and neutralization of waste water and waste chemical liquids and reducing the amount of chemical agents injected.

Figure 5 shows the treatment flow for the improved waste water treatment system reducing the chemical agent injection amount on conventional treatment system for treating waste water and waste chemical liquids. This system can treat by using a flocculation, precipitating and neutralizing method which removes and neutralizes waste chemical liquids of two lines for hydrofluoric acid line and acid/alkali line discharged from wafer processing steps, and then discharges them into rivers.

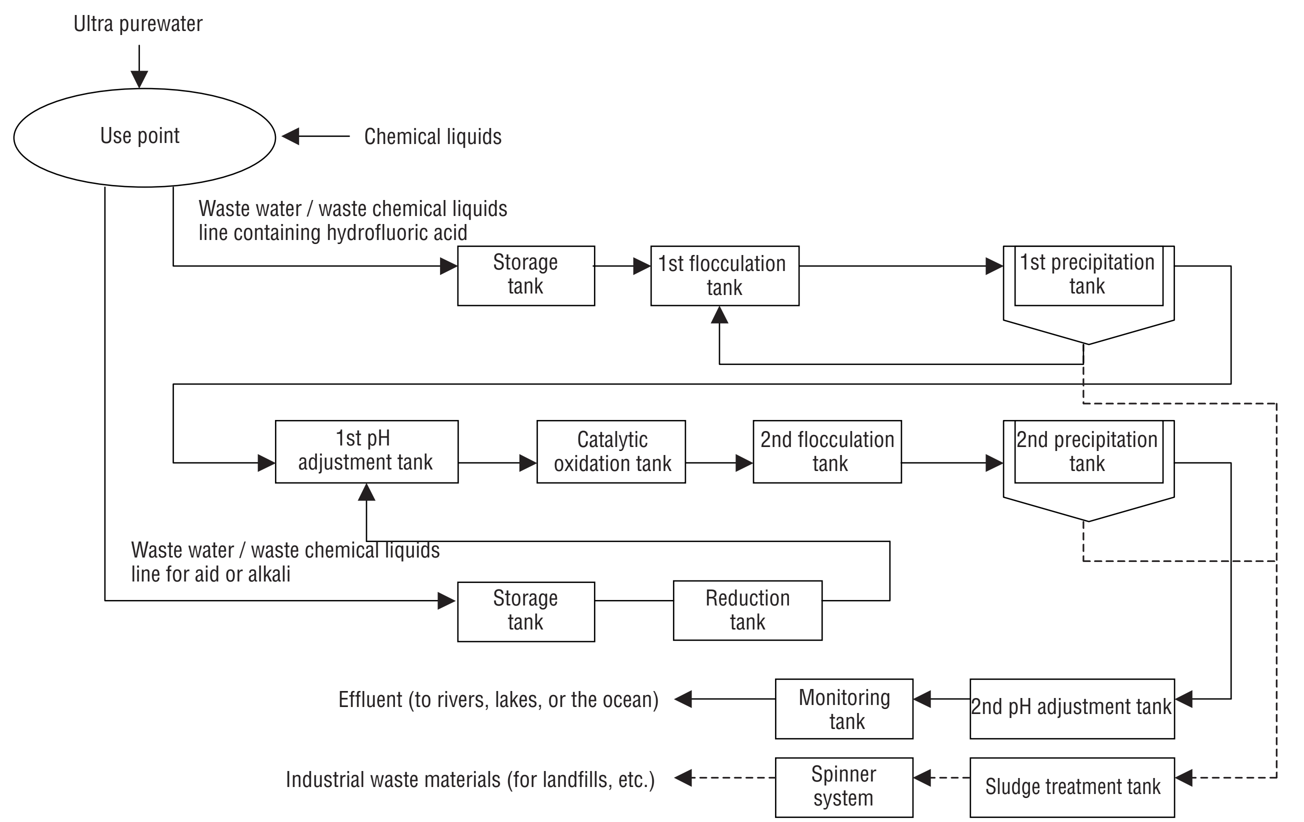

Figure 5: Treatment flow of waste water and waste chemical liquids treatment system

The special merit of this system is that, without transferring the sludge generated at the 1st precipitation tank for waste water and waste chemical liquids removal treatment line of the hydrofluoric acid, it returns them to the 1st flocculation tank where they are effectively reused as flock formation nuclei in the 1st precipitation tank. Through this kind of system improvement, the amount of neutralizing chemical agents, which must be injected and consumed in the 2nd pH adjustment tank can be greatly reduced.

As a result, by optimizing the operating conditions of this kind of removal system, in the end of fiscal 2000, we were able to achieved a large reduction level of approximately 30 tons as the amount of sulfuric acid consumed, compared to fiscal 1997. We also reduced the amount of inorganic sludge discharged as industrial waste material to about half of the amount prior to optimization and to reduce the moisture content ratio in the sludge by 70% or less. By implementing this kind of amount reduction activities, in the end of fiscal 2000, we reduced the final disposal amount of waste materials discharged from the plant by 551 tons, which achieves 70.8% reduction rate, compared with that of fiscal 1997.

2. Treatment and disposal activities

Among wafer processing steps, wafer cleaning and parts cleaning are carried out in bath of chemical liquids in which many chemicals are mixed. While the frequency of exchanging the chemical liquids in this bath is controlled by the wafer process quality control conditions determined by the number of wafer processed and the allowable polluting concentration of impurity substances, a large amounts of chemical liquids are consumed.

Large amounts of chemical liquids are also consumed due to using the chemical mixing ratios of the cleaning chemicals without changing the conventional treatment conditions. To reduce the amount of chemical liquids consumed, optimization of process treatment conditions was carried and this enabled elimination of a part of the process steps for wafer cleaning with chemical liquids.

By evaluating the reliability of the performance for the manufactured products, we are carried out wafer process improvements to extend the frequency for exchanging chemical liquids and to optimize the mixing ratio and allowable limited concentration of the chemical liquids used. As a result, by implementing such treatment and disposal activities, in the end of fiscal 2000, we greatly reduced the amounts of chemical liquids used for wafer cleaning in various wafer process steps, compared with that of fiscal 1997, by the following large amounts: hydrofluoric acid: approximately 7.3 tons, acetone: approximately 6.4 tons, sulfuric acid: approximately 12.0 tons.

3. Resource recovery activities

Classification	Type of waste	After recycling	Resource recovery method
Waste oil	Acetone	Regenerate as acetone or convert to fuel	Fuel for distiller incinerator.
	Ethanol	Regenerate as alcohol or convert to fuel	Fuel for distiller incinerator.
	IPA	Convert to fuel	After calorie adjustment, fuel for incinerator.
Sludge	Developer for negative photolithography	Convert to fuel	After calorie adjustment, fuel for incinerator.
	Inorganic sludge	Convert to raw material for cement	Calcinate after mix with cement raw materials
	Organic sludge	Convert to raw material for fertilizer	Reuse residue after composting as fertilizer
Waste acid	Mixed acids, such as sulfuric acid	(1) Regenerate as sulfuric acid (2)Reuse as a neutralizing agent	(1) Regenerate by thermal decomposition (2) Reuse as neutralizer in treatment system
	Phosphoric acid	Convert to raw material for fertilizer	At a fertilizer manufacturing plant, make fertilizers of phosphorus component
	Waste acid from etching process (sulfuric acid and H_2O_2)	Recovery of fused metal	Recovery by outside treatment maker
Waste alkalis	Developer for positive photolithography	(1) Convert to auxiliary fuel (for cement plants) (2) Cooling water for incinerators	(1) Make into a fuel product after calorie adjustment (2) Use as cooling water for exhaust gas from waste material treatment incinerator
Waste plastics	Trays, reels, magazines	Reuse. Resource recovery	Cleaning / selecting, resource recovery (for un-reused materials)
	Packaging materials, Styrofoam	Convert to recycled fuel	Make into chips after smash (use as fuel)
	Styrofoam	Convert to flower pots	Recycle flower pots by pot manufacturing makers

Table 1: Application of resource recovery for industrial waste materials

Resource recovery measures of the industrial waste materials need not only to improve each facility treatment system to enable optimal selective recovery in the plant, but also to cooperate with outside waste materials treatment makers and various parts manufacturers to effectively increase the rate of recycling and reusing for industrial waste materials.

Table 1 shows a typical application example of resource recovery for industrial waste materials. To increase the ratio of resource recovery in the plant, it is necessary to efficiently treat the waste chemical liquids discharged at each step of wafer treatment process by separating the waste liquid treatment system by the selective recovery method of approximately 20 treatment lines, which can carry out the optimal risk-avoidance management controlling to water quality and impurity substance concentration every each waste water line.

In this way, the discharged amounts of industrial waste materials, which can be efficiently reconverted into resources, are greatly reduced, while the reuse efficiency of their materials can be obtained quite high rate.

In the end of fiscal 2000, the resource recovery rate of waste materials discharged from the plant reached approximately 94%. Moreover, we will be achieved the ultimate situation of “zero emissions” (resource recovery rate of industrial waste materials is 99%) for our entire semiconductor manufacturing plant by the end of fiscal 2001.

Prospects for Zero Emission System in the Future

Recently, environmental conservation measures at semiconductor manufacturing plant have made great advances, compared with another industries.

Figure 6 shows the ideal closed loop structure for a recirculating-type facility environment required to a semiconductor manufacturing plant achieved the zero emission system in the future. To construct the zero emissions plant as shown in this figure, it is important to establish entire facility technologies that considers recycle and reuse of not only ultra purewater and chemical liquids, but also of exhaust gases containing a general gases such as N_2 or special gases such as SiH_4 exhausted from some wafer process equipment. To establish the recirculation-type recycle plant, where can be controlled entire material stream from installing in the effective resources required in the semiconductor manufacturing plant to carry the industrial waste materials used out of the plant, cooperation between five technologies is required: wafer process technology, process manufacturing equipment technology, parts manufacturing technology, facilities technology and industrial waste treatment technology.

First, from the aspect of wafer process technology, properties, it is important to know nature and final disposal method for the chemicals liquids used in the plant.

From the aspects of process manufacturing equipment and parts fabrication technologies, it is important to selective the optimal selective recovery treatment methods for many waste chemical liquids or the ideal parts and materials for the process manufacturing equipment used. Concerning the aspect of facilities technology, for the system for treatment, collection, regeneration, and reuse of ultra purewater, chemical liquids, and exhaust gases, it is important to respond to any kind of changes in volume, quality, or concentration, appropriately and safely, regardless of whether the operational status is normal or abnormal. Moreover, it

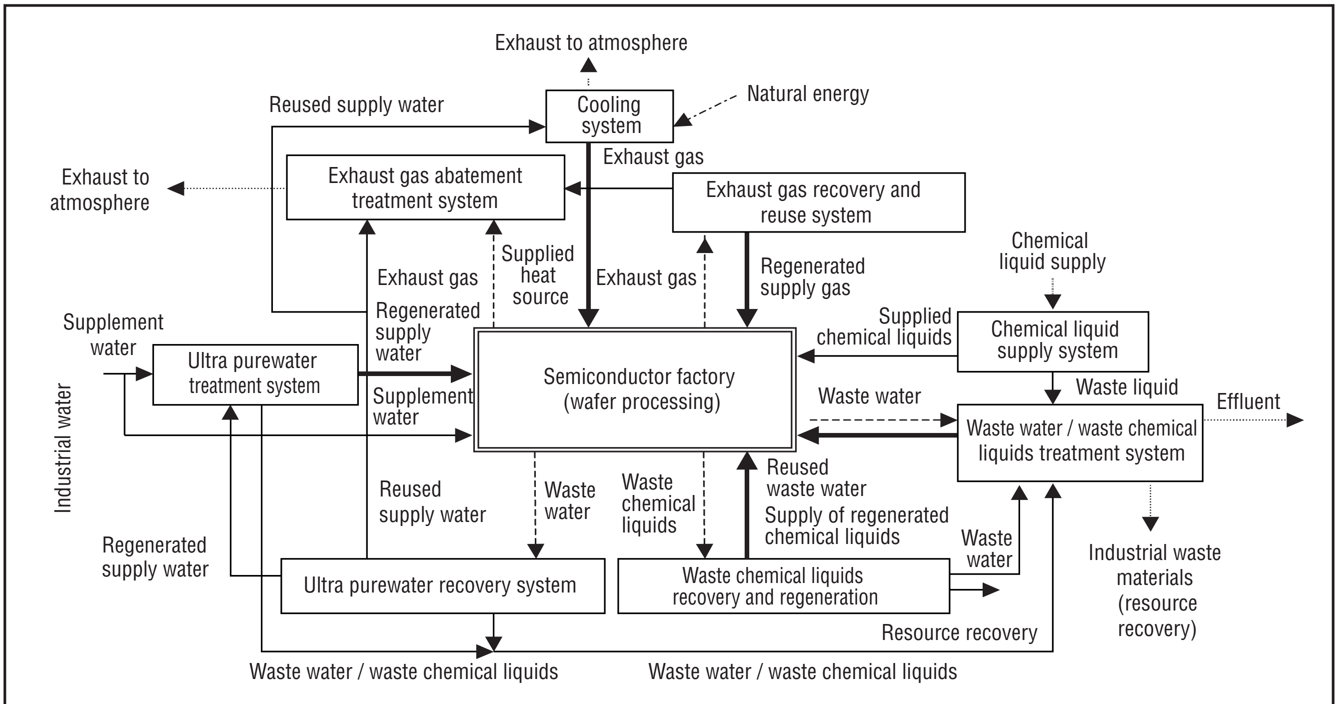

Figure 6: Ideal closed loop structure for a recirculating-type facility environment

is important that not only to strengthen the parts and materials management system from carry out of industrial waste materials until their final disposal (on April 1, 2001 a revised "Law for treatment of waste materials" has enacted), but also to construct the standard systems for a recirculation-type recycle society so it can recycle and/or reuse industrial waste materials.

Recently, to create such society, various manufacturing makers supplied parts and materials are working to construct the technical development for parts and materials of new environment friendly to reduce parts, materials useed in semiconductor manufacturing plant positively. The goal is to increase the fabrication and treatment efficiency for parts and materials by accepting industrial waste materials as a fuel source. Consequently, without five technologies described above, we can not be achieved the zero emission systems that parts and materials, which cannot be effectively utilized for nature or human society, are absolutely not discharged from plant.

In other words, if the environment friendly recirculating-type recycle plant which harmonized these five technologies, all Japan's semiconductor manufacturing plans will be become the zero emission plants in the near future.

Conclusion

In this paper, we have described that the technologies for treatment, collection, regeneration, and reuse for ultra purewater, chemical liquids and waste materials at our semiconductor manufacturing plants have most cost effectiveness and are sustainable technologies for accomplishing effective utilization of limited natural resources and conservation of the natural environment impact.

To respond further strengthening of environmental regulations, in the future we will positively incorporate a new recovery technology, such as PFC emission gas recovery technology, new technology for recovering the slurry from chemical mechanical polishing, and new developer recovery technologies. Moreover, we will address a new technology for regenerating and resuing process used chemicals, such as phosphoric acid or sulfuric acid.

By working toward further reduction in treatment cost, we will establish recirculating-type facility technologies, which can contribute to reducing environmental impact and resource recovery. In other words, it is important that some conventional facility technologies developed up to the present are kept optimal harmonization and cooperation between new facility technologies developed in the future and various other technologies. This will be able to achieve the zero emission system, to continuous to effective utilization the earth's limited energy and depleting resources.

Furthermore, the establishing of the zero-emission semiconductor manufacturing plant, which are recirculating-type recycle plants, will continuously contribute to environmental preservation. This, in turn, contributes to constructing the framework for an environmentally friendly society.

Reference

1. H.Wakamatsu, et al., "The Modern Concept of Completely Closed Ultra Pure Water System for Semiconductor Manufacturing Plant, Proceedings for The Seventh Symposium on Semiconductor Manufacturing (ISSM'98) , Vb-5, p.200, 1998.