Reduction Example of Organic Liquid Waste at a Semiconductor Manufacturing Plant

- Improvements with a bio-recycling system -

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Miyagi Oki Electric, which is the production center of the Silicon Manufacturing Company of Oki Electric Industry Co., Ltd., has and is sustaining the "Zero Emission" system since February 2002.

"Zero Emission" is a production system that produces "no waste materials" by utilizing the waste materials discharged by one manufacturing process and making them usable as raw materials for another industry. The material recovery system consists of material recycling, which reuses recycled materials as raw materials and uses thermal recycling to obtain heat.

The breakdown of material recycling of the "Zero Emission" system at Miyagi Oki Electric is 64% material recycling and 35% thermal recycling. As part of the environmental conservation activity program, efforts are currently being made to raise the material recycling rate while continued efforts are also made to reduce industrial waste.

Fig.1 depicts the breakdown of industrial waste materials of fiscal 2002 at Miyagi Oki Electric. As shown in this diagram, organic liquid waste represents 51% while dehydrated sludge accounts for 36%. Although the organic liquid waste is being used in the thermal recycling process that is currently being contracted out to an external vendor, the measures for the reduction of emissions as well as the task of diverting these materials to material recycling, have for the moment, become very urgent agendas. Further, the dehydrated sludge is currently being recycled as raw material for cement by an external cement vendor.

This paper will introduce our efforts that focused on organic liquid waste, prominent in discharge amounts, in order to formulate a means to reduce the amount of waste materials. This led to success in the realization of a massive reduction in organic liquid waste by improving the conventional organic liquid waste processing method and the decomposition process using microorganisms, through the use of surplus energy in the manufacturing plant.

Organic liquid waste and its processing technology at a semiconductor manufacturing plant

Organic liquid waste, generated at semiconductor manufacturing plants, is developer liquid waste that comes from the photolithography process and exfoliation liquids derived from the etching process.

Developer liquid waste processing, at the semiconductor manufacturing plant of Oki Electric, can be categorized in the following two broad processing categories:

The first method involves filtering liquid waste with the RO-membrane (reverse osmosis membrane). Permeate is put through an on site discharge process and released into the sewer or a river, or recycled in an ultra pure water manufacturing process after it has been processed by a high level purification process. Concentrates, on the other hand, have a concentration of percentage in the tens and thus on site processing is not possible. These are collected for thermal recycling by an external vendor.

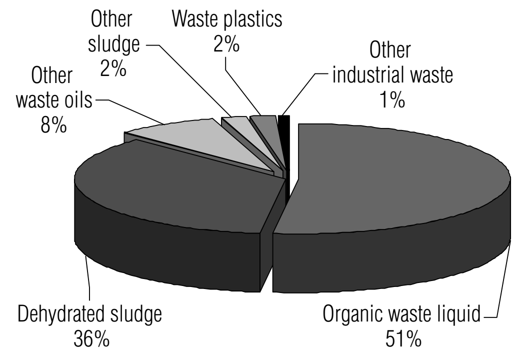

Fig. 1 Breakdown of industrial waste materials for fiscal 2002

The other method involves biological decomposition using bacteria in microorganism reactors, followed by a high level purification process at a waste water treatment facility in subsequent stages and then released into a river.

The RO-membrane processing requires a small installation space and the initial cost is quite moderate. It does, however, have a drawback with its higher running costs for its industrial waste processing and the periodical replacement of membranes.

Although the microorganism processing method requires a large space for the installation and the initial cost is quite large, there is no sludge output, operational management is simple and requires only an adjustment of air and nutrients, as well as the added advantage of not producing any industrial waste materials.

The amount of exfoliation liquids, generated in the etching process, is on the increase due to the microfabrication of semiconductor products and the accelerated rate of multilayering. These exfoliation liquids contain dimethyl sulfoxide (DMSO) as their main ingredient, which is an organic substance that contains sulfur. This DMSO is a persistent substance, which also oxidizes to become sulfuric acid by way of intermediate products of methyl sulfide and methyl mercaptan in the decomposition process.

In the etching process, once the exfoliation process has been performed, cleaning is done with isopropyl alcohol (IPA) and ultra pure water, resulting in a mixture of these substances within the exfoliation liquid. Since the drainage of ultra pure water used for cleaning has a total organic carbon (TOC) with a concentration of several hundred milligrams per liter, it is quite difficult to recover this liquid to recycle it as ultra pure water.

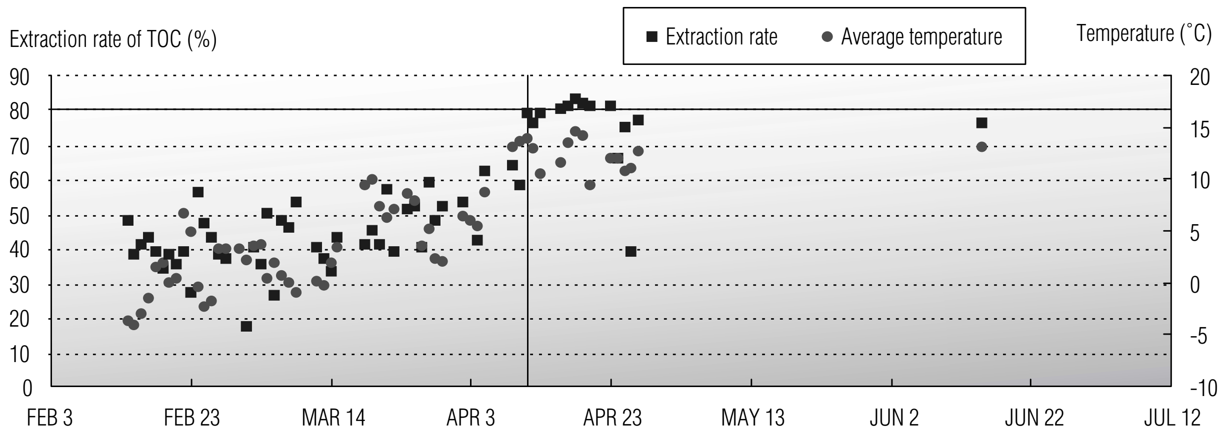

Fig. 2 Transition of the TOC extraction rate of a microorganism reactor and average outside temperature (February to July 2001)

As for the method for processing the exfoliation liquid, it would be difficult to use the RO-membrane (reverse osmosis membrane) processing method effectively to process the liquid waste, because several types of ingredients are included in the liquid, each with a different osmotic pressure. With the microorganism processing method, it is necessary to implement the processing in such a way as to ensure that accumulation does not take place in the process, as the methyl sulfide and methyl mercaptan, generated in the decomposition process, are substances with malodor.

Issues of microorganism processing

The issues relating to the control of the processing temperature and fluctuation of the concentration, are critical concerns for the microorganism processing method.

Fig. 2 shows the seasonal transition of the TOC extraction rates for the microorganism reactor between February 2001 to July 2002. Miyagi Oki Electric was initially conducting microorganism processing without implementing any heating or thermal insulation facilities. At the time the facility was designed the burden on microorganisms was small, thus the processing efficiency was complemented by a rather long decomposition time, with a holding time of 40 hours.

With the fluctuation in the production load, however, the amount of produced organic liquid waste increased, resulting in the holding time of approximately 24 hours. Fig.2 shows the transition data at this point in time. As seen in the diagram, microorganisms are reactivated when the outside temperature rises to 15°C and higher, indicating that the TOC extraction rate is highly dependant on the water quality of the treated water and the temperature.

Table 1 represents the raw water concentration of the organic liquid waste. As seen in the table, the fluctuation of concentration is extremely large. In the microorganism process it is desirable to maintain the load of the biological oxygen demand (BOD) at a certain level. Under such rapidly changing conditions an extinction of microorganisms occurred, stagnating the microorganism process with annoying malodor substances, such as methyl sulfide and methyl mercaptan, generated in the DMSO decomposition process.

Improvement method for the microorganism process

The utilization of surplus energy for controlling the processing temperature at the manufacturing plant, was our first consideration. Warm pure water was used in the cleaning processes at the semiconductor manufacturing plant. In the manufacturing process of this warm pure water, concentrated warm liquid was produced in the ultra filtration membrane (UF-membrane) process, which was in the past, processed as waste water. Further, a boiler facility was installed as an in-house heat source and supply facility and it provided steam to the plant.

Table 1 Raw water concentration of a microorganism reactor

	Concentration (mg/L)
DMSO	20 ~ 100
TMAH	500 ~ 900
IPA	1,500 ~ 4,000
BOD	1,000 ~ 4,000
TOC	500 ~ 2,000

As for the steam aspect, the plumbing laid down for the boiler facility consisted of drain pipes laid under the ground, through which the steam was blown.

It was possible to inhibit the internal temperature fluctuations of the microorganism reactor by targeting these two heat sources.

The fluctuation in concentration within the microorganism reactor, shown in Table 1, was brought about by a mixture of two organic chemicals, namely a developer liquid and an exfoliation liquid. In the past, Miyagi Oki Electric had one microorganism reactor at the 6-inch wafer factory and the other at the 8-inch wafer factory. During this time an "end-pipe measure" was implemented, which involved a conversion from individual liquid waste processing at each factory to a process where pipe connections were changed to alter the processes, in accordance with the type of liquid waste that needed processing.

Improvement effects

(1) Stabilization and improved processing capacity of the microorganism reactor

Fig.3 represents a flow diagram of the improved on site microorganism reactor. Fig.4 indicates the processing temperature and seasonal transition of the TOC extraction rate of the microorganism reactor that resulted from the improvement. Fig.5 shows the correlation between the microorganism reactor's treated water temperature and the TOC extraction rate. As shown in Fig.4, it has become possible to manage the treated water temperature, without the influence of seasonal changes. Further, it was verified that when the microorganism reactor's treated water temperature rose to 26°C or higher, the TOC decomposition rate became activated, as shown in Fig.5.

Inflow concentration of the microorganism reactor after the end-pipe measure had been implemented, is shown in Table 2. It is clear that a more stable raw water concentration was achieved, in terms of both DMSO and tetramethylammonium hydroxide (TMAH).

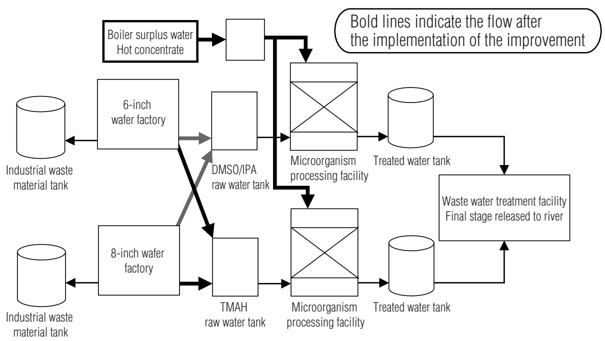

Fig. 3 Improved on site microorganism reactor flow (Black lines indicate the past flow paths, while red lines indicate the flow paths since the improvement)

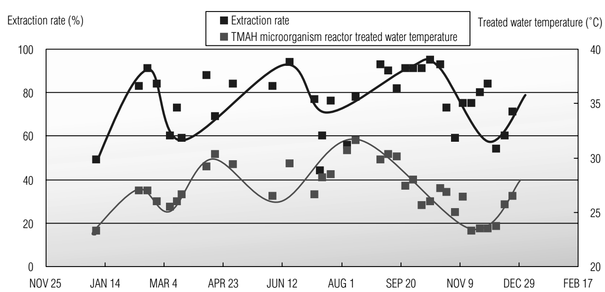

Fig. 4 Seasonal fluctuation of the TOC extraction rate of a microorganism reactor (November 2002 to December 2003)

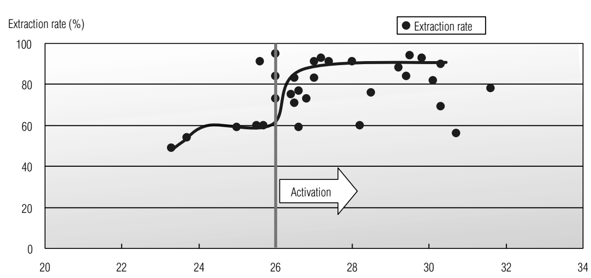

Fig. 5 Correlation between the microorganism reactor's treated water temperature and the TOC extraction rate

Table 3 is a representation of the change in the microorganism reactor's processing capacity, due to the stabilization of the concentration and temperature control. The processing capacity of the DMSO microorganism reactor improved by 1.4 times, while the processing capacity of the TMAH microorganism reactor improved by 1.5 times.

(2) Reduction of organic industrial waste materials

As the capability of microorganism reactors improved, an attempt was made to use them to reduce the amount of industrial waste material, which incidentally, is one of our objectives, by processing organic liquid waste that was previously processed as industrial waste material. Fig.6 shows the transition of the reduction (calculated amount) in organic industrial waste materials.

Since July 2003, the organic liquid waste amount has increased, although these are calculated figures, this being due to the increase in production operations arising from favorable market conditions. At the same time, processing by the microorganism reactor has stabilized resulting in a continued reduction in organic liquid waste since May 2003.

With regard to the quality of the discharged waste water, Miyagi Oki Electric abides by a pollution control agreement reached with a relevant local municipal government, which entails stricter standards than those stipulated by the Water Pollution Control Law, as well as additional conditions. For this reason it is necessary to consider the biochemical oxygen demand (BOD) for the decomposition process of organic liquid waste by using microorganism reactors. Although the Water Pollution Control Law stipulates the BOD value to be 160mg/L or lower, the pollution control agreement demands extremely stricter control with a required value of 20mg/L or less. Fig.7 shows the seasonal transitions of the BOD and TOC. It indicates that by processing organic liquid waste with microorganism reactors, instead of processing them as industrial waste materials as was the case in the past, there has been no abnormalities with the discharged waste water quality, which means the laws are being observed.

Table 2 Raw water concentration of a microorganism reactor after implementing an end-pipe measure

	Concentration (mg/L)
DMSO	100
TMAH	1,000
IPA	1,000
BOD	500 ~ 1,500
TOC	500 ~ 1,500

Table 3 The TOC load capacity of a microorganism reactor due to the improvement

(Before improvement)

	TOC load amount
6-inch wafer factory microorganism reactor	4kg/day
8-inch wafer factory microorganism reactor	55kg/day

(After improvement)

	TOC load amount
DMSO microorganism reactor	6kg/day
TMAH microorganism reactor	75kg/day

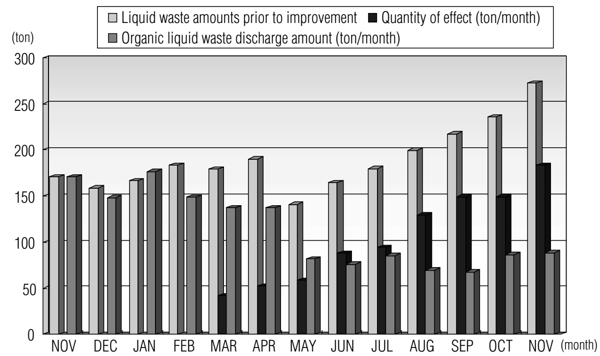

Fig. 6 Transition of a reduction in the disposal of organic industrial waste materials (November 2002 to November 2003)

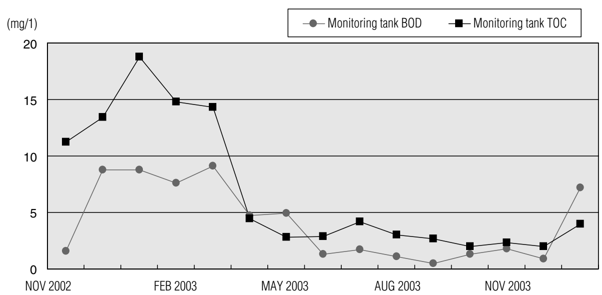

Fig. 7 Seasonal transitions of the BOD and TOC

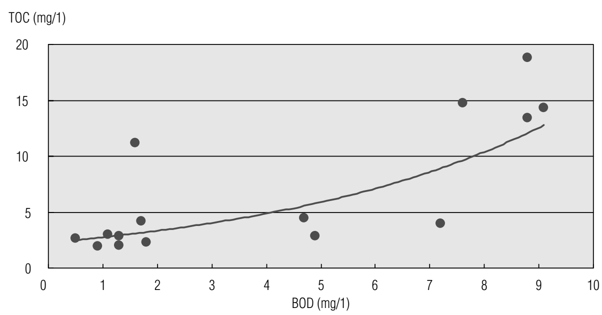

Fig. 8 Correlation between the BOD and TOC

Further, Fig.8 represents the correlation between the BOD and TOC during this period. The JIS standard requires that the measurement of the BOD be made with five days of culture. Although constant monitoring is extremely difficult, it has become possible to monitor the BOD by monitoring the TOC concentration, since there is a correlation between the BOD and TOC in low concentrations, as seen in Fig.8.

Conclusion

An attempt was made to stabilize the microorganism reactor's temperature using the on site surplus heat source, as well as stabilize the microorganism reactor's concentration using the end-pipe measure. As a result, we obtained the following:

(1) We determined that the optimal internal temperature for microorganism reactors was 26 to 36°C.

(2) We were able to reduce organic industrial waste materials by improving the capacity of the microorganism reactors by 1.4 times. The reduction effect amounted to approximately 1,500 ton for fiscal 2003.

(3) We were able to verify that the BOD, which is difficult to monitor at all times, does have a correlation with TOC that can be monitored at all times.

With the above, it was possible to improve the organic liquid waste processing capacity using the microorganism processing method and succeeded with a major reduction in organic liquid waste.

Afterword

Miyagi Oki Electric has been utilizing microorganism processing to process organic liquid waste for a very long time. Due to the diversification of organic solvents in recent years, there is an apprehensive view that substances, difficult for microorganisms to process, will be on the increase in the future. The example of the project introduced in this paper remains a phenomenological response and thus the bacteria, which decomposes wastes and the group of microbes that triggers a food chain with bacteria, have not yet been identified. Further, we also do not have enough information about the temperature variance that occurs inside microorganism reactors.

By solving such issues, it will not only be possible for semiconductor manufacturing plants, to conduct decomposition processing by establishing microorganism reactors that use bacteria and microbes that exist in nature, on site, but it will also be possible for crystal manufacturing plants that generate organic liquid waste.

Further, a “Zero Emission” organization has been established at all semiconductor manufacturing plants and, while they are all contributing to a recirculating-type society, there are many cases when organic liquid waste is thermally recycled, as mentioned earlier in this paper. It is therefore, necessary to further promote a reduction in industrial waste and at the same time conduct in house processing, with the responsible party discharging the substances. We expect that the “process that is earth-friendly and utilizes microbes that exist in nature” will mean even more developments in the future.

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