ZERO-EMISSION MATERIALS CYCLE IN PRODUCTION PROCESS AND REGIONAL SCALE

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ABSTRACT : The present paper aims to give basic information to establish zero emission material cycle including the minimization of emissions from industrial production processes and the area in regional scale. Strategies and methodologies to analyze emissions from the production processes and our human activities and to reduce those emissions by refining and/or replacing the unit process with the alternatives are introduced as well. Quantitative evaluation and management systems of any raw materials and the production process are from vie points of treatment are essential. Estabiishment of a process networking for the recycle of discharged non-products materials by the intra-process, trans-process and the trans-industries are proposed. Procedures and priorities to formulate industrial and regional zero emission system are proposed as well.

KEYWORDS : Zero-emission material cycle, Process networking and technology, Material balance, Negative flow sheet, Wastes minimization, Closed system, Optimal selection of treatments, Information system.

INTRODUCTION

Intensified human activities in a limited sphere have brought about number of conflicts between natural environment and human life. Most of the problems have been derived from emission of materials in various forms from the anthropogenic sphere. it is thus urgently needed to restructure the material cycles so that the total load to the environment is minimized. Establishment of completely closed material cycles, if possible, will not only become eco-friendly but also contribute to the maximum productivity of resources.

Figure 1 shows the evaluation of the direction of countermeasure for environmental conservation from view points of the emissions and the consumptions of energy and resources per the activity or the values for mankind. Ordinary treatments of wastewaters and solid wastes increase the consumption of resources and energy while those can reduce the discharges of wastewaters and solid wastes. Note that such treatments are transferring the pollutants from the local area to the

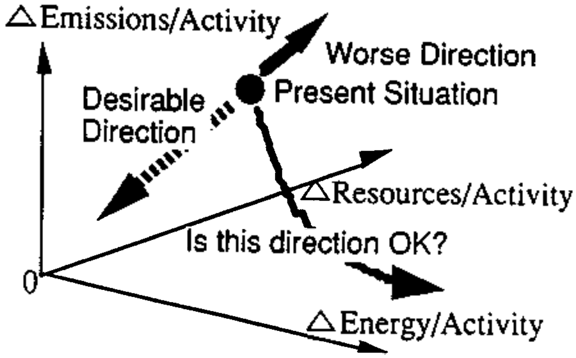

Fig. 1 Direction of enviromental conservation measures from view points of emissions discharge, energy and resources utilizations per "unit" activity or values

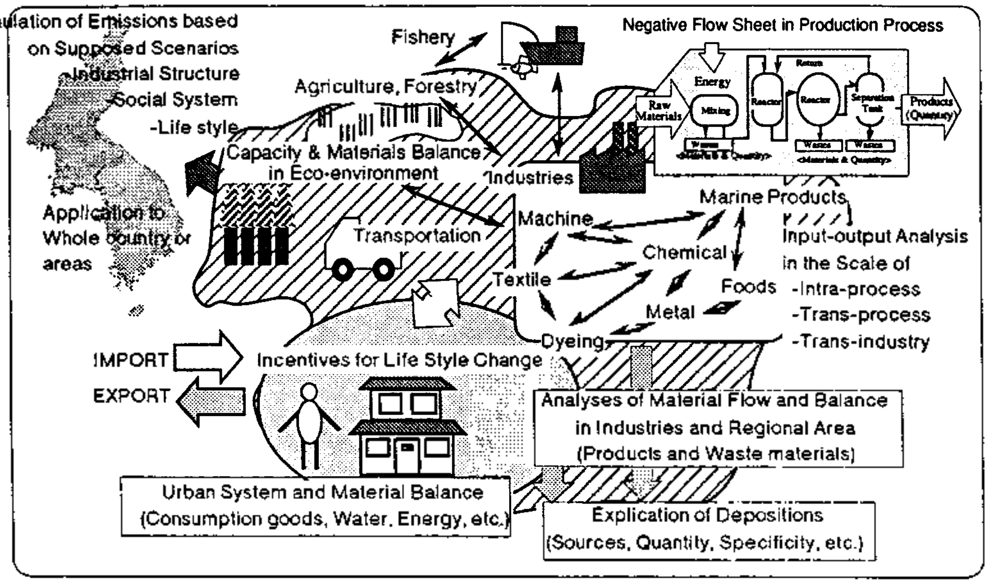

Fig.2 Materials balance and mathematical modeling to establish a zero emissions system at regional scale and application to the whole country.

global environment since the treatments discharge carbon dioxide by the consumption of fossil energies as shown in Fig. 1. Thus any counter measures should be the direction to the origin of the coordinate axes.

Approaches to minimize the pollutants from industries are categorized as shown in Fig.2. To minimize emissions to the environments what we should do first is to analyze the material flow and balances in the social system, i.e., our daily life and the production process. Input, output and accumulation in the production process and the in the local area will be clarified. What should be done next is the emission minimization at the source of emission. Production process should select any appropriate materials for less emission production. Improvement of the production process by refining each unit process and by replacing the process with alternative less emission process will be required. It is needless to say that our daily life should be changed to reduce emissions from ourselves. Source separation of wastes materials are strongly required. Third is the establishment of materials networking system. Recycle and reuse of any non-products materials are required to minimize the emissions and the utilization of energy. Development of novel technologies for reuse and recycle, i.e., the renovation of materials, are of great concern. Appropriate methods are requiredfor the quantitative evaluations of any countermeasures from view points of real emission minimization

PROCEDURES TO MINIMIZE POLLUTANTS DISCHARGE FROM PRODUCTION PROCESS

Priority for Reduction of Emission from Production Process

Figure 3 shows the procedures to reduce any emissions from the industrial production process in the order of priority. What we have to do first is the clarification of material flow and material balance in the process and the identification of pollutants discharge. Note that the control of emission at the sources has highest priority and which is followed by the treatment of emissions.

Identification of Pollution Source and Loading

First of all, the source, quality and quantity of

REDUCTION OF POLLUTANTS DISCHARGE FROM PRODUCTION PROCESSES FOR WATER ENVIRONMENT CONSERVATION

- → Reduction of pollutants discharge
  - 1)Refine or replace the raw- & sub- materials
  - 2)Refine the unit process to inctrease products yields
  - 3)Replace the process with alternatives
  - 4)Onsite treatment and closed process
- → Appropriate Selection and Operation of Existing Treatment Processes
  - 1)Characteristic evaluation of treatment processes
  - 2)Improvement of existing processes
  - 3)Appropriate selection combination of existing processes
- → Application of Newly Developed Technologies for Waste Treatments (Examples)
  - 1)Membrane filtration technologies for pollutants removal
  - 2)Anaerobic digestion for high strength wastewater treatment
  - 3)Biotechnologies for degradation of refractory organics, etc.

Fig. 3 Approaches to minimize the pollutants from industrial processes.

pollutants discharged from each production process should be clarified before considering the reduction those pollutants. Mass balance focused on the wastes materials, i.e., non-products, called'negative flow sheet' is very much useful to understand the situation of the process and to identify the pollution sources, quantity and characteristics of emissions from the process. Table 1 shows an example of pollutants from an automobile manufacturing factory. The amount of wastewater and pollutants in BOD, GOD, Oil and grease, suspended solids from the process are clarified. Huge pollutants and wastewater were discharged to produce one automobile. More detailed data of the emissions are required for all practical purpose. It can be known that most of the pollutants was discharged from the painting process of the chassis of car followed by the machining process of engine and transmission. More than 98% of the total BOD and COD were discharged from those two processes. The countermeasures for reducing the pollutants from the automobile manufacturing factory should focus on the painting and machining processes. Note that the contents in Table 1 are not enough to provide sufficient information for the consideration of appropriate procedure to the control emissions. Characteristic evaluation of the emissions are strongly required.

Reduction of Pollutants Discharge from Industrial Production Processes

Procedures to reduce pollutants discharge.

The procedures to improve the production process in chemical industry are shown in Table 2. In some cases the pollutants discharge may be easily reduced by referming the sealant and by refining or changing the raw materials. The optimization of reaction schemesand operational conditions brings about the increase in the conversion of raw materials to obtain high yield of products. Increase in the yield of products brings about the reduction in the emissions. Production process should be replaced with an alternative process to reduce or eliminate the pollutants discharge. For example, super critical carbon dioxide (SCCD) may be the preferable choice for replacing the toxic organic solvent used in the industrial extraction processes. The SCCD is a non-poiar solvent with non-toxic and non-flammable characteristics. Organic solvent extraction may be replaCed with SCCD extraction (Merz, 1997), Electrolysis using mercury electrode to produce sodium-

Table 1 Wastewater discharged from automobile and parts manufacturing process(per one car)

Products	Processing	Wastewater(l)	BOD(g)	COD(g)	Oil & Grease(g)	SS(g)
Engine, Chassis	Machining	20-200	145	100-700	80	10-400
Body	Painting	1230-4100	300-900	400-700	24-95	100 - 400
Brake	Forging & Painting	30-390	0.14-6.7	1.0-13.4	1.6-26.8	2-40
	Electroplating	20-70	0.86	0.42	-	-
Transmission	Casting	10-320	-	1-46	-	0.4-45

Table 2 Procedures to reduce the pollutants discharge from production processes

Improvement	Examples
Management & Facilities	Refine an improve the sealant, tightness and raw materials
Reaction	Change solvent, Increase the conversion, yield and product concentration
Operation	Replace the batch operation with the continuous operation
Cleaning	Improve the method and interval, cleaning the process without water

Table 3 Reduction of the wastewaters from polymerization process

Month & Year	Jan. 1965	Jan. 1973	Nov. 1973	Feb. 1974
Wastrewater(m^3/t-polymer)	36.2	17.0	8.8	0.2
Counter measure		(A)	(B) (C)	

(A) Increase in polymer concentration in liquid,

(B) Wastewater recycle from separation process,

(C) Wastewater recycle from catalyst washing and polymer drying processes.

hydroxide and chlorine from sodium chloride has been replaced with the electrolysis using ion exchange membrane to eliminate the wastes containing mercury.

An example in the reduction of wastewater discharge from a polymerization process is shown in Table 3. More than 36 m^3 wastewater was discharged from the polymerization process to produce one ton of polymer in 1965. The increased polymer concentration in the reactor was effective to cut one-half ofthe wastewater from the process. Wastewater recycle from the polymer separation process after the appropriate treatment could reduce one-half of the residual wastewater. The recycle from the catalyst washing and the polymer drying processes brought about noticeable reduction of wastewater discharge, and thus the utilization of water in the polymerization process was reduced as well. Moreover the gas phase polymerization or the liquid phase bulk polymerization processes can eliminatethe almost entire wastewaters from the polymerization process.

On-site tretment and closed process.

Top figure in Fig.4 shows the production process with separation treatment process of the mixed wastewaters discharged from different sources. It should be noted that wastewater treatment is the separation

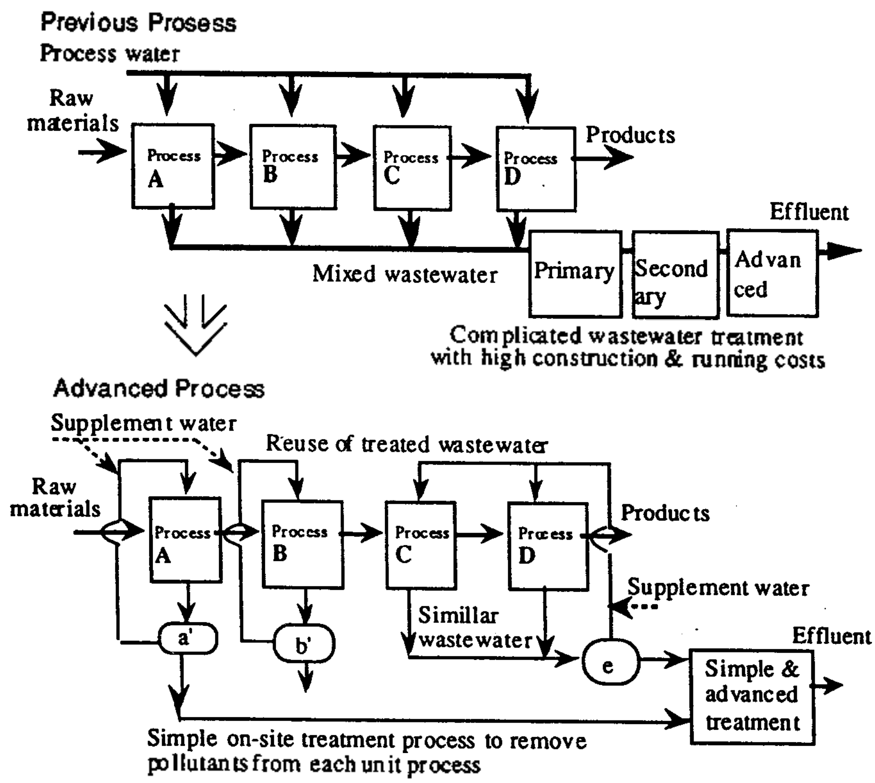

Fig. 4 Possible procedures to reduce the wastewaters from production process by incorporating the recycle systemwith onsite wastewater treatments.

process of the mixed pollutants with different characteristics from the wastewater. Mixing of the wastewaters from different sources makes the separationmore difficult due to their different characteristics for example in terms of solubilitv polarity, biological or chemical degradabilities, coagulation characteristics, molecular size, and so on. To meet the more stringent regulations applied to the effluent into the public water bodies, additional treatment, such as advanced treatment, must be required. More facilities, resources and energy are required for the advanced treatment of mixed wastewaters.

On-site treatment of wastewater with the recycle of treated waster is shown in the bottom figure in Fig.4. Wastewater is treated separately without mixing. Separation of the pollutants contained in one wastewater is easier compared to that in the mixed wastewater. Pollutants can be removed using a simple wastewater treatment process and the treated water can be recycled to the unit process from which the wastewater is discharged. Thus the closed production process can be established from view points of water utilization.

Preliminary Management of Materials in Factories

Management system of materials for zero-emission production process.

In order to establish a zero-emission production process, any raw- and sub- materials (suppiemental materials for the production) used in the processes should be managed appropriately in the factory to know the input, output and the consumption. Total management system of materials should contribute to reduce the excess use of materials and to know the effluent discharge, i.e., the wastes, from the production process. The matenal balances of chemicals enable to

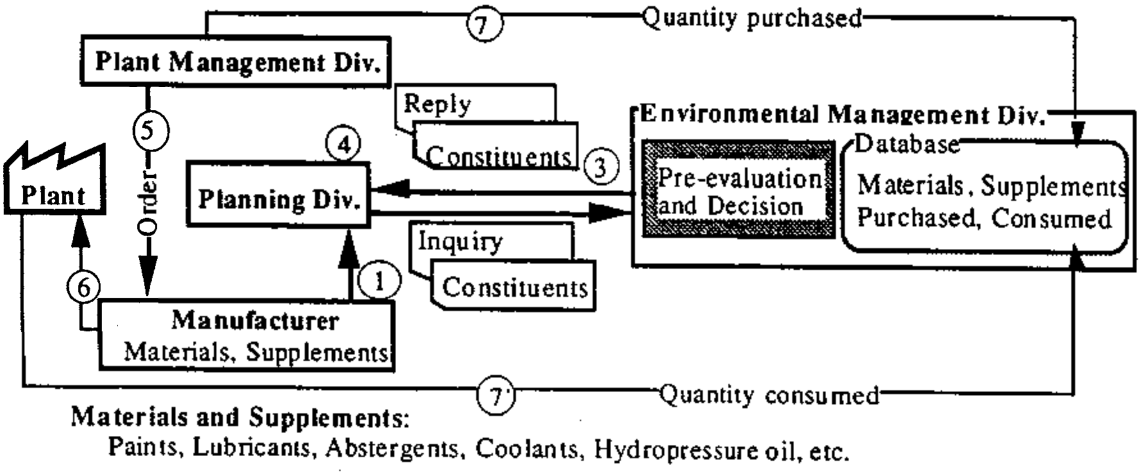

Fig. 5 Managements system of materials based on pre-evaluation system of materials in factories.

estimate the amount of wastes from the process in the forms of gas, liquid and solid by subtracting the mass of products from the input. Once such total management system is introduced, it is easy to know the constituents and the concentration of pollutants in the wastewater, exhaust gas and in the solid wastes. In the case that some materials are difficult to treat, those should be omitted from the input readily. Fig.5 shows the management system of materials in an automobile manufacturing industry (Fujie, 1997). The numbers in this figure show the steps for selecting and evaluating a new raw material or supplemental material. Key point of this system is the preliminary evaluation of materials on the basis of treatability test before using in the production process. Material balance of focused chemicals in factory should be clarified as is required in PRTR (Pollution Release and Transfer Register) system

Treatability evaluation test for the materials management system

Raw and supplemental materials should be carefully evaluated before using in the process. Any information obtained from treatability tests should be informed to the management section of production process for the reduction of the pollution by the appropriate management and/or reduction of utilization. If some material is not suitable for the treatment, it should be excluded from the process. The materials with treatment difficulties but essential in the production process must be collected separately for the appropriate treatment. Information on the constituents of raw materials and supplemental materials in the production process are very much useful to evaluate the treatability of it and to improve the production process for diminishing the effluent discharge. The procedure proposed in the present study to evaluate any materials used in the production process from view point of treatability is shown in Fig.5. Characteristics on coagulation followed by the flotation and the sedimentation, membrane filtration, biodegradation, chemical oxidation and carbon adsorption of materials are experimentally studied. Biodegradability of the materials is the most important parameters. The same procedure can be applied for treatability evaluation of wastewaters as well.

Biodegradability evaluation test

Biodegradability of organic materials and the organic pollutants in wastewaters has been evaluated

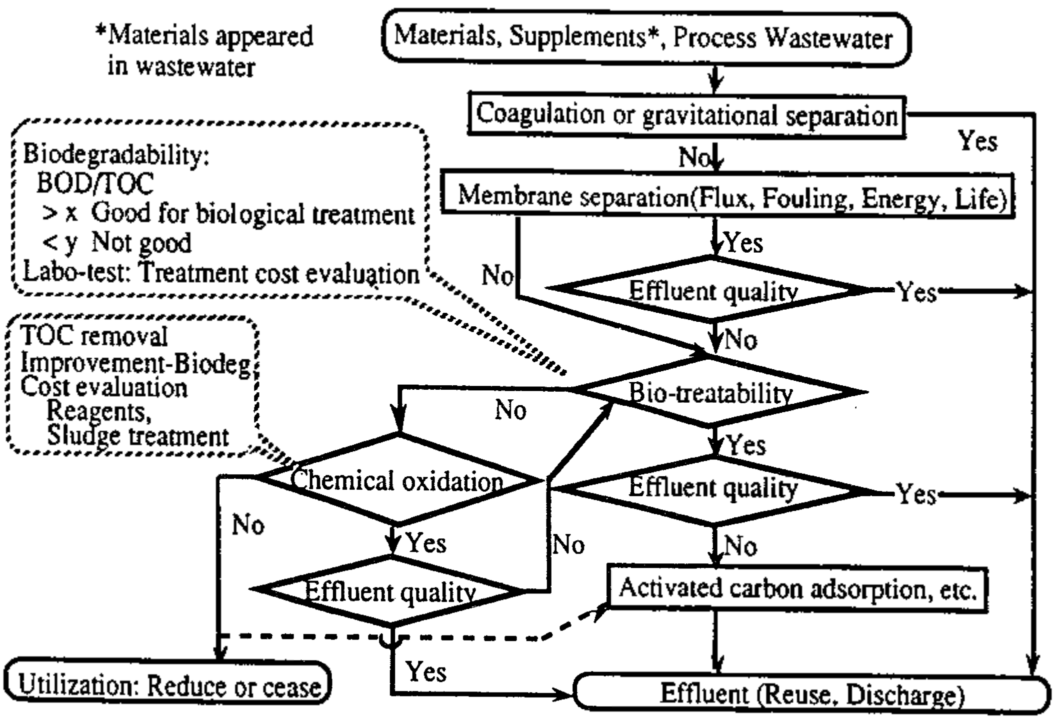

Fig. 6 Procedure to evaluate treatability of wastewaters and materials used in production process.

using the parameters such as BOD/ThOD, BOD/COD, and BOD/DOC ratios, and by the first order rate constant or Monod constants of the biological degradation (Niels,1996). Note that ThOD is the theoretical oxygen demand for the complete oxidation of organic pollutants. Relationship between the fractional removals of COD or DOC observed in the five-days BOD test (RE_b) and that in a laboratory scale submerged biofilter (RE_c) with the continuous operation is originally introduced by the authors to evaluate the characteristics of the materials contained in wastewater for the biological treatment. Principle of this method is illustrated in Fig.4. Region I with high DOC removal either in the continuous operation(RE_c) and in the BOD test (RE_b) shows that the wastewater will be satisfactory treated in the ordinary biological treatment process. Materials or wastewaters in region I-A, however, requires the appropriate acclimation course of microbes to the wastewater or chemicals for the satisfactory treatment. Materials or wastewaters in the region IV can not be treated well by the biological process since both of RE_b and RE_c, are low. Region II shows that the materialor wastewater may contain relativeiy high concentration of refractory organic pollutants.

Effective removal of those organic pollutants may not be expected even after the biological acclimation. Pre- or post- treatment using chemical or physical methods may be required to obtain a sufficient effluent quality. Optimization in the operating condition of bioiogical treatment process may be required to treat the wastewaters in the region III. Evaluated results of two of coke-oven wastewaters discharged fro¿τ a conventional coke-oven with the batch operation and a novel pilot coke-oven process with the continuous operation, respectively, are illustratively shown in Fig.5(Lim, 1997). it can be concluded that the wastewater A can be treated by the biological process to give a satisfactory effluent, but pre- or post-treatment combined with biological treatment process is required for the treatment of wastewater B to meet the regulated effluent quality.

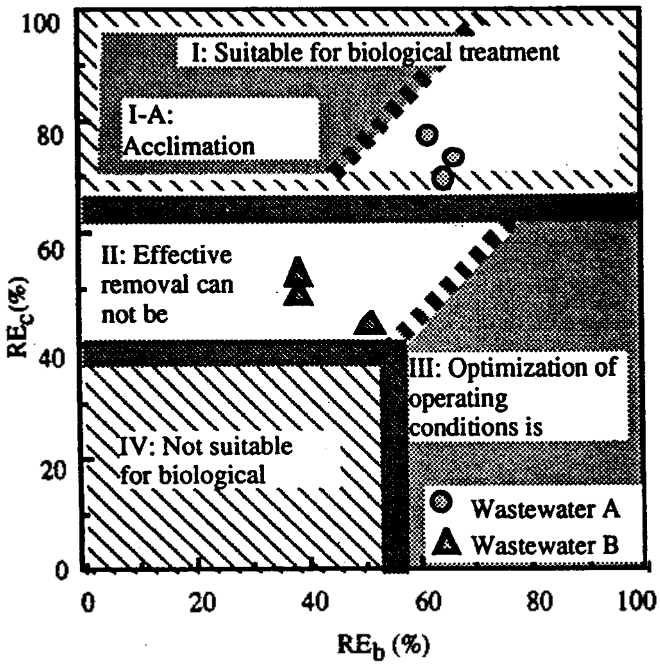

Fig. 7 Biological removal evaluation based on the relationship between DOC removal efficiency observed in BOD5 tests(REb) and that in the continuous biological treatment experiment with a small scale aerobic submerged biofilter(REc)

OPTIMIZATION OF WASTEWATER TREATMENT

Characteristic Evaluation of Existing Wastewater Teatment Processes

Before selecting the appropriate treatment process both the characteristics of existing treatment processand that of the wastewater should be clarified. Molecular size distribution analysis using the gel chromatography can be applied to identify the organic pollutants in the influent and that in the effluent(Hu, 1997), Information on such pollutants useful to select the appropriate treatment processes.

Power economy, defined as the amount of BOD removal per unit power consumption, is another essential factor to evaluate the performance of biological wastewater treatment processes. Treatment process, which give the higher power economy, can reduce the energy consumption in the wastewater treatment. Comparison of the biological wastewater treaunent processes in terms of the powereconomy and the rate of BOD removal per unit floor area of each process is shown in Fig.6 for the domestic wastewater treatment under their typical operating conditions. The land application of wastewater was the first process for the domestic wastewater treatment. This figure shows that the development of biological Ueahnent processes brought about the higher BOD removal rate but the lower power economy. The trickling filter process gives second highest power economy followed by the rotating biological contactor. Packing materials in the aeration tanks as in the submerged biofilter can increase the gas-liquid oxygen transfer rate by the breakage of air bubbles. The oxygen transfer rate in the deep shaft aerator is too high for the domestic wastewater treatment (Kubota et al., 1978).

Procedure to Select Appropriate Treatment Process

There are many principles to remove a given pollutant from wastewaters. Wastewater treatment process, which is a combination of some unit processes to meet the required effluent water quality, should be selected appropriately based upon the characteristics,

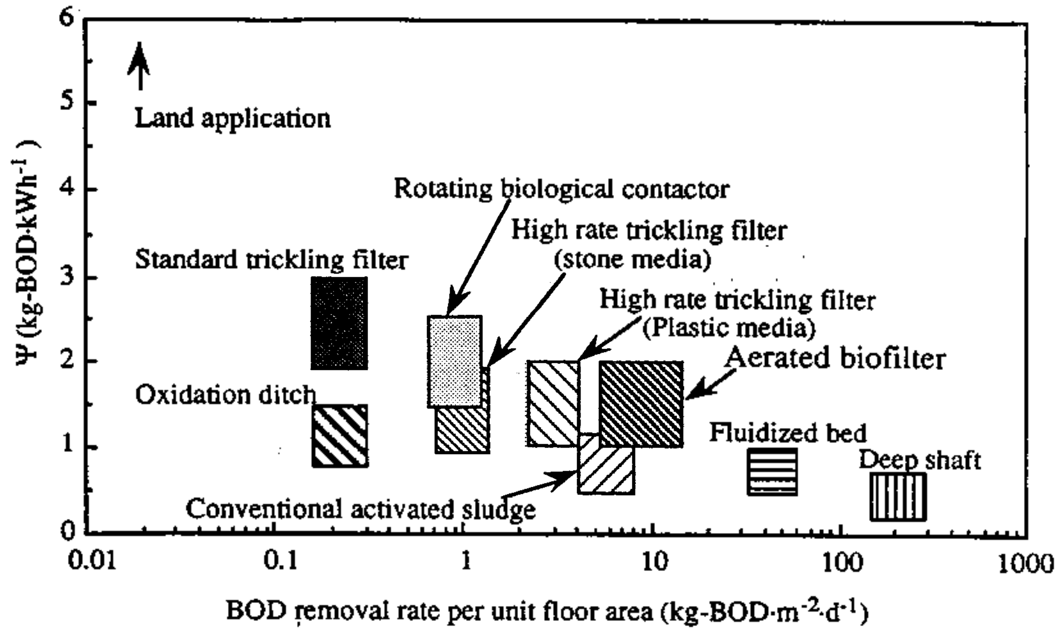

Fig. 8 Comparison of power economy characteristics of various wastewater treatment processes for domestic wastewater treatment.

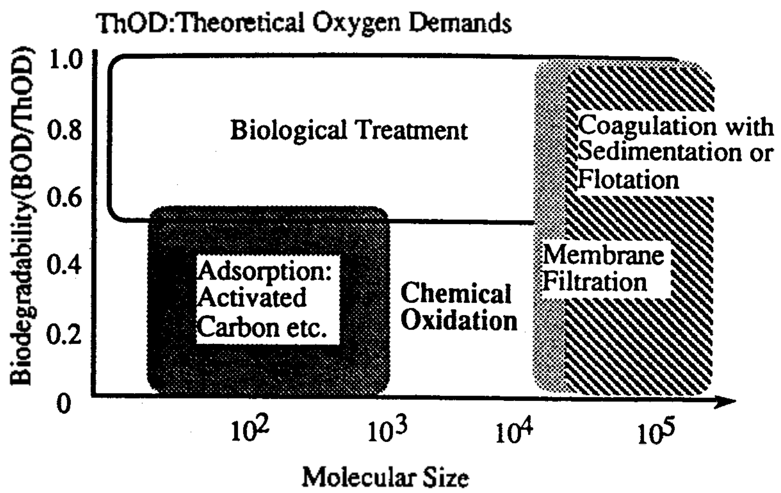

Fig. 9 Applicable treatments based upon biodegradability and molecular size of organic pollutants.

such as removal rate of pollutants, effluent water quality, energy consumption (Fujie, 1982), maintenance and so on. The characteristics of the wastewater should be evaluated quantitatively with the procedure shown in Fig.3. Figure 7 represents the applicable treatments from view points of the molecular size and the biodegradability of the pollutants. Note that the concentration is not considered here. Adsorption has never been applied to remove the pollutants in the high concentration. The biological treatment is not suitable to remove the pollutants in the very low concentration. The pollutants with a high biodegradability, i.e., the high value of BOD/ThOD ratio, can be effectively removed using the biological treatment process, and that witha molecular size large than 10,000-20,000 can be removed by the coagulation followed by the sedimentation or the flotation and by the ultra-filtration

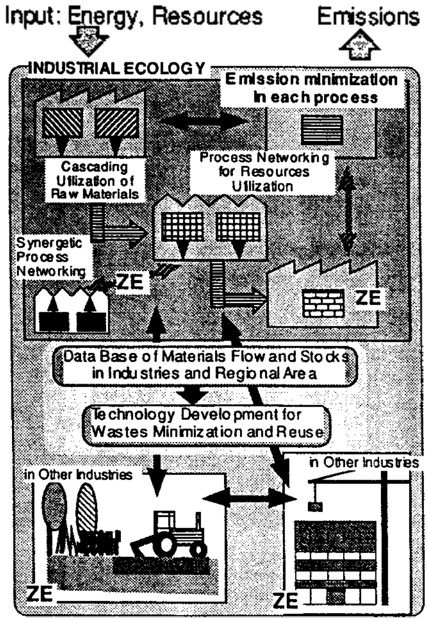

Fig. 10 Trans-process and trans-Industry material network system for emission minimization.

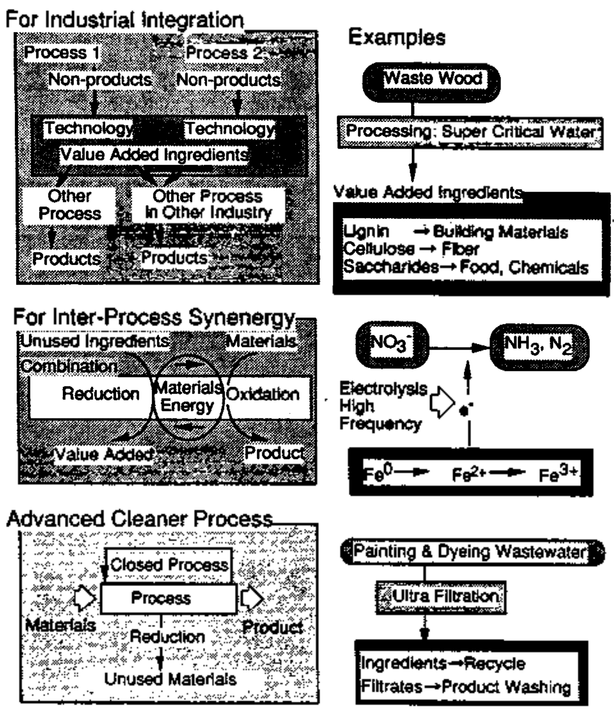

Fig. 11 Novel technology for emission minimization by process refining, materials conversion and by introducing synergitic process.

using an appropriate membrane. The less biodegradable pollutants with the smaller molecular size (<several thousands) may be removed by the activated carbon adsorption. But the less biodegradable pollutants with

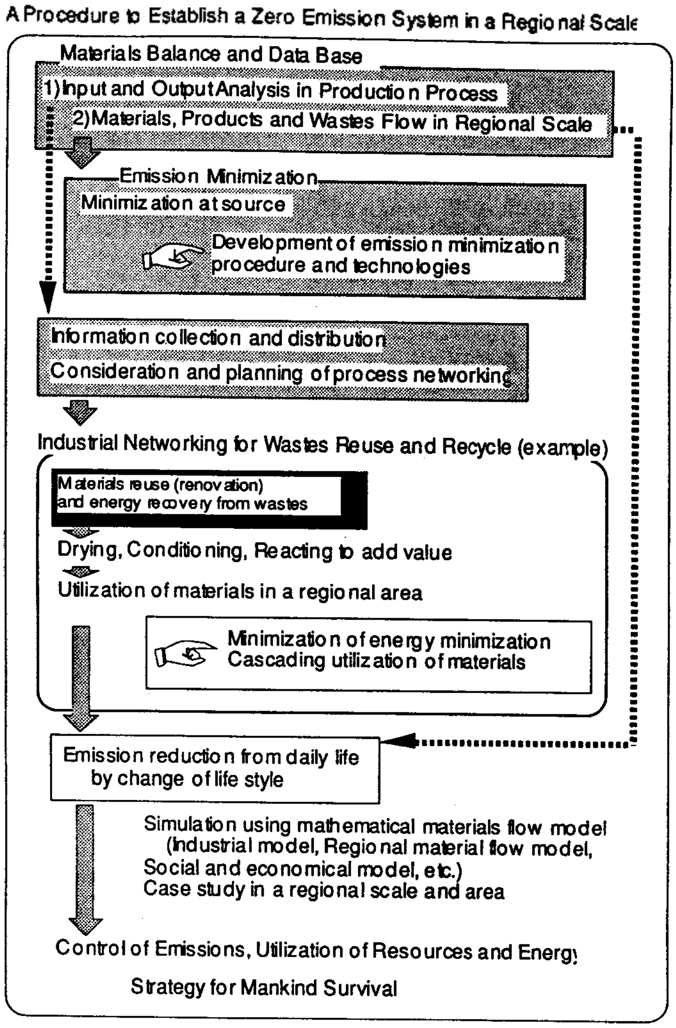

Fig. 12 Procedure and priority to minimize emissions from industries and regional area.

the larger molecular size in the range of several thousands to several tens of thousands is the most difficult for treatment with the conventional techniques because the pollutants can not be effectively removed by the coagulation and by the activated carbon adsorption. Chemical oxidation process using the Fenton's regents, Fe^{2+} and H_2O_2 and the ozonation is the alternatives for the treatment of refractory pollutants mentioned above. Chemical oxidation can be used for both the mineralization and the improvement of biodegradability of the refractory organic pollutants. Refractory pollutants in the wastewater can be treated using a combined chemical and biological oxidation process.

PROCESS NETWORKING FOR INDUSTRIAL ECOLOGY AND TECHNOLOGY DEVELOPMENT

In case the emiissions elimination from the production process is incomplete the non-products materials discharged as wastes must be reused or recycled elsewhere. The first priority is the recycle in other unit process of the same production process, i.e., intra-process recycle. The second is the trans-process recycle where the non-products waste materials are recycled to the other production process in the same industry (trans-process recycle). The final prioity is to reuse in the process of other industries (trans-industry recycle). Note that the trans-industry recycle may bring about the diffusion of pollutants to the other industry or to the environments. Appropriate treatment or conversion of waste materials are required before utilizing them n the other process. Promised technologies for the reduction of emissions by refining process, by conversion of the emissions to resources and by coupling the production and treatment by energy association (synenergitic process) and by material association. Figure 11 shows some example of novel technologies for the emission minimization by promoting the process networking.

SUMMARY

A procedure to establish zero emission system in the industry and in a regional scale is shown in Fig.12. As described previously what we should do first is to understand the present condition of materials flow and balances in the industries and in the regional area. Second is the emission minimitation at the source. Information on the characteristic properties of non-products materials, i.e. emissions, are very much desired for the utilization in the other sites and processes. Information collection and distribution system on the emissions and their characteristics are required for the establishment of material cycle system as well as the development of the emission minimization technologies. Emission reduction from our daily life is essential to establish a sound material cycle system as well. It should be noted that emission minimization associated with the reduction of energy and resources utilizations are strategies for the man kind survival in the future.

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