General paper

Contaminative Materials on Products in a Recycling System

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Abstract: The building of a sustainable material circulating system is imminent for the threatened waste disposal landfills in Japan. Now, man-aided recycling is active for the purpose of lessening waste. Although recycling originally aimed at saving resources and alleviating environmental problems simultaneously, it is nevertheless a current issue that problem of cost and environmental damages have occurred. Also, other problems include the generation of toxic substances due to the mixing of dissimilar materials in the recycling process in each industrial production field, and its progression in the future is feared. This indicates that there is a need to build a purging or purification system in recycling similar to the one originally equipped in the ecosystem. In this report, the category of the poison and the recycling process in the circulating material will be defined and the influence on the material will be examined.

Key words: Circulation, Accumulation, Contamination, Poisoning material, Purification

1. INTRODUCTION

In Japan, about 2 billion tons of industrial raw material flow a year is reported [1], though it is difficult to give an accurate account of the quantity of circulative material due to diffusion materials such as export or gas, water and air. Also, the amounts of water and air are too much to compare with these industrial raw materials. For example, water used in Japanese society is estimated at 80 billion tons in 1998 [2], which is 40 times as much as that of industrial materials. The amount of those materials used in Japan is too enormous to be handled and recycled by nature. These devastate the beautiful Japanese scenery and deprive people of comfortable life in an island located in the Temperate Zone [3-5]. Therefore, man-aided recycling has come onstage for the purpose of lessening waste [6]. The recycling rate for each product shows that the rate of steel or aluminum can is increasing by 20-40% while old recycling paper stays on the 50% level from 1986 to 1998 [7]. Although recycling originally aimed at saving resources and alleviating excessive burden on the environment simultaneously, it is nevertheless a current issue that problems of cost and environmental damages have occurred. In a man-aided recycling society, also, due to careless production and use of materials, it can be speculated that poisonous accumulation that actually degrades the physical or chemical characteristic of products or general poison will be mixed with and be generated from materials. In this paper, the preparatory concept of the accumulation and approximate value of materials life will be discussed.

2. FUNDAMENTAL MATERIALS IN JAPANESE SOCIETY

The fundamental balance and flow of materials in Japan that are used for industrial statistics are shown in Fig. 1. The raw materials for Japanese industrial uses are shown in the left column and the intermediates in the industry which are classified into energy, products and

by-products are shown in the right column in Fig. 1.

666 million tons of imported materials consist of petroleum, coal, iron ore, foods and miscellaneous materials. Although the coal mining industry in Japan has been working as well as petroleum and iron mining industry, half of foods consumed in Japan are imported. 1,164 million tons of materials are supplied in domestic resources. In particular, the materials for construction such as lime stones, and gravel occupies 90% of total domestic materials.

The right column shows the contents in the consumption state. 338 million tons of input materials, which corresponds close to 16% of total materials are used for energy, and 203 million tons are directly disposed in the production stage in the flow. By-products are 415 million ton. Some of them are recycled as law materials. 1,299 million tons of products include automobile, electric devices, foods, papers, plastics, and construction materials such as building, bridge, pavement, harbor facilities and so on. About 400 million tons of the products are used in offices and for home use.

Fig. 1. Material balance in Japanese industry(1997).

Fig. 2. Fundamental energy balance and flow in Japan (1992).

Domestic storage wastes occupy about two third to whole wastes after consumption. The greater part is waste materials from the construction industry such as concrete, cement block, asphalt for pavement and other inorganic materials. The Japanese government has been concentrating its budget on public undertakings to stimulate the economy for several decades. The large volume of construction waste is caused by this governmental policy. Less than 400million tons of input construction raw materials has been recycled.

The data on the energy balance and flow in Japan have been gathered and arranged and shown in Fig. 2[8].

Five minor sources of energy (atomic, hydraulic, coal, petroleum, and natural gas) are used for electric power plants (40%) and general uses (60%). The latter means gas for transportation, kerosene for heating, and miscellaneous uses. The supply of petroleum has been reduced from 73% in 1975 to 58% in 1992 due to the oil crisis of political oil strategy in Arab countries. Atomic energy is fundamentally accepted by Japanese society and has about a 30% share in the Japanese electric power market. The first energy supply was about 5×10^{15} kcal in 1992.

Although efficiency has been continuously improved in industry, transportation and other fields, the total energy efficiency has slightly declined from 37% in 1975 to 34% in 1992. The efforts to improve efficiency were not awarded by the business of new technology where development was much more important than the efficiency of production.

Energy flow is important when considering circulation. It is also necessary to take into account the generation of carbon dioxide. Coal, petroleum and natural gas is finally converted into carbon dioxide and water except minor wastes such as coal ash, NOx and toxic materials.

Those two materials, energy balance and their flow are fundamental and indispensable to calculate and draw the basic model of circulation in Japan.

The amount of water can be classified into three categories in Japan, and the departments of local governments measure the amounts handled. However, the

amount of water for industrial use and irrigation are vague. It appears to be from 100 billion tons to 400 billion tons in Japan. Air, which supplies oxygen for combustion, can be relatively accurately calculated by the amount of fuel. About 40 billion tons including nitrogen is used.

It should be pointed out that the amount of water and air are much larger than materials used for industry except for construction. When we discuss waste and environmental problems, the topics tend to focus on industrial waste rather than on air and water. Air and water are heavy loads on nature, as it must deal with them in place of human beings. It is one of the contradictions of constructing a circulation society.

3. BASIC MODE OF RECYCLING FOR CONSIDERING POISON ACCUMULATION

It is indispensable to construct a concept of the actual recycling flow and depict it to analyze the poison accumulation in a recycling system. The basic flow of materials in the system is shown in Fig. 3, which is actually a more complicated circulation for various concepts are proposed as a "circulation society", many materials can be recycled to use in the same or another ways. These concepts may be visualized in a simpler model in Fig. 4, in three types, difference of the circulation system between nature and human society is also pointed out. The first is very simple, where the outward line means "an active flow" and the return line "a recycling flow". Human society has functioned since the earliest times by using the materials and energy in the active flow. The recycling flow has been taken charge of by nature.

The second model includes "a purify line" to get rid of poisons and to change in quality. Although the line can hardly be noticed, human beings have been relying on it to live safely. The third is the model that takes into account the materials and energy which are necessary to drive the recycling and the purify flows.

Fig. 3. Basic flow of materials in a circulation system.

Fig. 4. Three circulation models (top: the first model, middle: the second model and bottom: the third).

The larger half circle (below) means the flow in nature and the smaller half circle (above) is the flow in human society. Since the birth of human beings, human society has been relying on nature for the recycling and purifying of waste materials disposed into the environment just like other animals. The current flow in Japan can be drawn in Fig. 5, where 1.96 billion tons of raw materials are fed to Japanese industry to produce about 500 trillion yen as its gross domestic production.

The same amount of waste is expected as an output flow from Japanese society, but about a fourth is observed as the actual waste. The residue is considered to pile up somewhere in the country.

Fig. 5. Actual current flow in Japan.

Although recycling for various target materials has been actively attempted, the recycling rate is about 10% or less at the most even if the rate is calculated based on the same as “recovery rate”. The recovery rate is calculated by the amount recovered by recycling factories regardless of re-use or not.

True recycling rate is difficult to estimate because one encounters a lot of very complicated problems in Japanese society when attempting to surveying the correct mass flow. The authors think the rate is about 2% or less because the industrial products whose ingredients are recycled materials can hardly be found in the market in Japan. For example, 300 thousand tons of PET bottles are being recovered under a recycling law newly put into operation. However, there are few consumer goods made with the recovered polyethylene terephthalate(PET). But recycling rate is considered almost zero.

4. CLASSIFICATION OF POISON IN RECYCLED MATERIALS

When observing examples at each point, for instance in the waste category, statistics such as an industrial waste and general waste are in terms of quantity. Furthermore, statistics in terms of kinds of material or products in the category exist. These statistics indicate that such products renewed with preferably minimum energy are suitable recycling materials, and regarding the high-grade products with material value, more circulation is being promoted nowadays. But in a man-aided recycling society, due to careless production and use of materials, it can be speculated that poisonous accumulation that actually degrades the physical or chemical characteristic of products or general poison mixed with and generated from materials will become common.

To identify the possibilities of the circulative problem, the sources and routes of toxins are considered in categories.

Figure 1 shows the results of classification of the poisonous characteristic materials and contaminating routes based on both the four major newspapers from August, 2000 to February, 2001, and the each productive field's references and articles. The preferable main categories are as follows:

- (1) Poison hazardous to living things and the environment.
- (2) Deteriorated material interaction between materials.
- (3) Poison generating from degraded material during or after use.
- (4) Mixing material in the recycling procedure.

“Poison” is defined as chemicals toxic to living things in general. It means the deteriorated materials as a technical term. “Poison for catalyst” is one of the typical examples. Cu and Sn are poison for processing in the steel industry, especially a deep drawing and Al weakens the strength of glass due to the fatal crack in bottles. There

Table 1. List of poisons and contaminative materials in a recycling system.

Group		Source or component	
		Generate in use	Mixed during reprocessing
Hazardous to humans	Element	---	As, Pb, Cd, Hg
	Chemical compound	Bisphenol A, Dimer, Trimer(PS), Dioxin, Dioxin Trigger	PCB, BHC, DDT in plastic
	Pathogenic	0-157, Bacteria, Vibrio-parahaemolyticus, Virus	Prion, Cancer trigger in compost
Degrade material	Metal	Grain size coarsening	Cu, Sn, Mo, Ni in Fe (Decrease of processability)
	Plastic	Polymer chain fracture	Immiscible plastic (less strength), Color agent, Additive (Bond characteristic)
	Ceramic	Crack	Al, Si, Stones, Pyroceramics (Crack), Fe (Chaging color), Organic materials

are many poisons for plastic because almost all plastics are immiscible each other, so the contamination of the different plastics in the recycling system causes degradation.

5. ACCUMULATION OF POISON IN RECYCLING

Some representative poisons or contamination in materials are impurity residues, such as tramp elements (Cu, Sn, Mo, Ni in Fe) [9] and radioactive elements [10]. Other examples are in ceramics, where impurity causes all transparent bottles to change into a blue color, or when Al-Si alloy in glass causes cracks and deterioration of the material. By evaluating the degree of the deterioration as such in the material in circulation system, meas-

Table 2. Estimating material life in a recycling system.

case	Degrade	Toxicity degree	Material life (τ)
1	small	small	$\tau_{inh.} = f(\text{fatigue}, \dots)$
2	small	large	$\frac{Q_{mpp}}{S \cdot T(t, r, \dots)}$
3	medium	small	$\frac{Q_{mpp}}{S \cdot D(t, r, \dots)}$
4	medium	large	$\frac{Q_{mpp}}{S \cdot DT(t, r, \dots)}$

Cycle: S cycle/day
 Amount of accumulated poison: D, T or DT g/cycle/kg
 The maximum permissible amount of poison: Q_{mpp} g/kg
 Material life: τ day
 Service time: t day
 Recycling ratio: r

uring the level of contamination accumulating in society and its elimination through the construction of a purification system would be possible. In the toxicology field, permissible value such as 50% of the lethal dose is applied to determine toxicity. From this point of view, we tried to analyze poisonous in circulation material in terms of contaminative or toxic substances. Table 2 shows the equations for Material Life: ($\tau_{inh.}$), defined by The Maximum Permissible amount of Poison: (Q_{mpp}), Accumulated Poison: (D) or (T), and Cycle Number (S).

In 1995, the per capita stock of steel in Japan was 12 billion tons, 62 million tons of which flowed into society and 25 million tons were disposed from economy and industry as shown in Fig. 6 [7]. Therefore, the average staying term is from 19.4 to 48.0 years. From these values and the above equation, the accumulative poison rate: $D=0.26\text{g/kg/cycle}$ is calculated. When tolerance of the Cu residual in steel is 0.4%, being avoid cracking

Fig. 6. Recycling flow of steel in Japan(1995).

Fig. 7. Extrapolated year of steel scrap.

from hot shortness, the speculative average life of steel scrap with residuals as accumulative poison is 80 years. The extrapolated curve is illustrated in Fig 7.

What the life span close to 80 years means is that the recycling scrap steel will become one of disposals. But in fact, scrap with poisoning copper diluted with higher grade for use made things more complicate. It will have to remove the copper by new methods which have been developing.

Bottles of glass, one of the major inorganic materials, have been recycled in relatively well-planned systems. One is called the "returnable system", which have no route of having glass bottles clashed into pieces called cullet [11]. The other is the "recycling system" as one way bottles, where glass bottles and other manufactured goods are objected to clash. The amount of the former is about 2 times larger than that of the latter. Fig. 8 shows recycling flow of glass bottles in Japan [12]. Notable poisons for glass are aluminum, silica, ceramics and metals as color agents such as Fe and Cu. Silicon which is reduced by aluminum weakens the strength of bottle by causing small cracks in the structure of glass, for remained silicon generated in fusion was included the sands for law material. Other kinds of silica remained for different melting points, degrade the characteristics. Metals contaminated into bottle also degrade it with changing color. That is not acceptable in market in Japan at present. Organic materials on the surface of the collected bottles to recycle are in most case vaporized during heating for melting them although the concentration does not be over current regulations. The former poisons are, however, tried to remove in the recycling system of glass bottles by applying the differences of gravity, magnetic characteristics, infrared rays, and others for more complex equipments effective for the purpose.

The life of recycling glass can not be calculated now because several methods to remove the poisons have been actively developed and the data is different in each factory of glass recycling.

Fig. 8. Recycling flow of glass in Japan (1999).

The most difficult and serious problems of recycling and poison accumulation exist in organic materials recycling such as plastics, rubber, paper, textile and woods. Most of them easily degrade under the service circumstances and generate poisonous chemicals. For example, bisphenol-A, which is a bad example of suppressor to hormones, is the main scission product from polycarbonate or in burnt fish and bread.

In addition to these drawbacks, there are other reasons for the difficulty in the recycling system, so the accurate estimation from the actual data of the materials life in the recycling system is very difficult.

Figure 9 shows the experimental results by which the poison is generated under the service circumstances (relatively higher temperature:190°C). The dimmer and trimer were detected by pyrolyzer-gas chromatography-mass spectrometry.

Fig. 9. Dimmer and trimer are generated in used polystyrene.

Table 3. Material life of representative materials in a recycling system.

Material	Products	Poison	Material life (year)
Steel	Steel scrap	Cu/ Fe	80
Glass	Bottle glass	Al/ Si/ Fe	—
Plastic	Polystyrene	Dimer, Trimer	1

Table 4. Topics of poison for material from recent newspapers.

Organic material	Usage or sort	Contaminative material
Plastic	Nylon	Dioxin
	TV cabinet	Bromine, Internal secretion disturbande system
	Building material	Formaldehyde, Toluene, Xylene
Foods	Garbage	Nail, Metal, Heavy metal, Nasty smell, Decomposition, H ₂ S(gas)
Paper · wood	Used paper	Diaper, Stapler's pad

From 4 major newspapers; Asahi, Mainichi, Nikkei, Yomiuri

For polystyrene, the materials life in a recycling system can be estimated from the quantity of dimer and trimmer (0.33g/kg), ratio of rate constant, and 10^{-4} g/kg for the maximum permissible amount of poison in case of 3 in table 2.

Table 3. lists the results of calculation of representative materials in a recycling system.

The lives of representative materials in recycling can be independently calculated without the data of fatigue and other deterioration characteristics. It appears to contribute to how long the materials can be used in recycling.

Table 4 shows the items from recent newspapers in Japan regarding the problems in the currently progressing recycling system. But long-term observation of accumulating contamination in recycling materials is limited at this time as shown in Table 4.

Only a few are known in organic material of general wastes from homes. In specified material categories, a 20% decrease in 4 years is being aimed at for food disposal. Some forms of reuses are being tried, such as half of the garbage being turned into methane gas and the rest being used as the raw material of compost by lessening weight through dehydration. For the time being, contaminative materials are removed by using magnetic power or by using the difference in specific gravity. But quantitative analysis has not often been reported yet at present.

6. REMOVAL OF POISON AND PURIFICATION IN RECYCLING

Topics regarding poison generated or mixed in recycling have been taken up to point out the necessity of

Table 5. Summary of poisons in the recycling system in Japan.

Material	Metal	Ceramic	Plastic
Products	Steel scrap	Bottle glass	Polystyrene
Poisoning material	Cu, Sn(Ni, Co, Cr, Mo)	Al, Si, Fe, Ceramics, Stone	Dimer, Trimer, Polymer alloy
Recycling rate (year)	50(1995)	80(1998)	—
Separation	Human eyes, Gravity, Magnetic power, Sensor	Human eyes, Wind power, Magnetic force, Infrared rays	Distillation, Decomposition, Gravity

Fig. 10. Detective and scavenge point of poison in a recycling system.

having a removal or purification system in our society. The representative poisons are listed up in Table 5.

Copper, tin and other some elements in ion, Al, Si, Cr and aliens in glass and deadly poisons in plastics should be paid attention to in a recycling system.

At present, the toxicity detection and removal points in the material flow in a recycling system are speculated as Fig.10.

The concept of Fig.10 is a very important model for a safely recycling society. If we ignore the detection and removal of accumulated poisons, these concentrations will reach a dangerous level, and it is not unreasonable to speculate that higher concentration of poisons will damage people susceptible to those poisons in society. Engineers who have the data and knowledge of the danger should not recycle materials without considering the detection and the removal of such poisons.

7. CONCLUSIONS

In this paper, we proposed ideas to clarify influence of accumulation of contaminative materials in a recycling system. Conclusions are as follows:

(1) For sustainable material circulative society, poison detective and purification system should be equipped in a recycling system.

(2) Poisoning materials in a recycling are classified in 2 categories. One is hazardous to humans and the other is deteriorate material.

(3) Material life time is calculated in terms of poisoning accumulation in steel scrap and polystyrene. In case of polymer, 0.6 year is obtained from the provisional equation.

(4) It is considered that the rate of accumulation of poison in a recycling of material should depend on a removal efficiency.

Acknowledgments—The authors grateful to Prof. N. Mashiko for his advice on the fundamental concept of the circulation system in Japan and Prof. S. Hirata who gave us permission to refer to one of his works on energy consumption and flow. We also thank Prof. F. Tsukehashi, Dr. M. Yukumoto, Kawasaki-steel corporation and H. Kuribayashi, Nihon Yamamura Glass Co, Ltd. for their co-operation to offer precious information on recycling of iron and steel and glass bottles. The authors also thank the fellowship of NEDO (New Energy Development Organization, Japan) for the support with Contract No. 9001940.

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