Evaluation of the Potential Amounts of Dissipated Rare Metals from WEEE in Japan

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The potential amounts of dissipated rare metals (Au, Ag, B, Ba, Cr, In, Ni, Pb, Sb, Sn, Sr, Ta, Zn and Zr) in WEEE (Cathode Ray Tube TV, liquid-crystal display TV, plasma display panel TV, refrigerator, air conditioner, washing machine, microwave oven and cleaner) have been estimated. For the estimation, the number of WEEE was also estimated using the population balance model. The composition of the WEEE were examined by interviews and the measurement using energy dispersive X-ray diffractometer. The estimated amounts of the dissipation were evaluated by both the ratio of the dissipation to domestic demand and the weight amount of the dissipation by "total materials requirement" (TMR). [doi:10.2320/matertrans.MAW200781]

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1. Introduction

Recently, in Japan, regulatory systems for waste electrical and electronic equipment (WEEE) have been established, and necessary technologies for the recycling have been developed,¹⁾ resulting in the achievement of the legal recycling rate. For example, in 2003 (3 years after the enforcement of the Home Appliances Recycling Law in Japan), about 10.5 million units of WEEE (TV, refrigerator, air conditioner and washing machine) were taken back at the 380 designated take-back sites, and 99.8% of them were subjected to recycling processes, followed by the recycling of base metals. In addition, recycling rates of 78, 63, 81 and 65% were achieved for TV, refrigerator, air conditioner and washing machine, respectively, which were better than legal standards.²⁾

However, as for current shredding recycling processes in Japan, most of rare metals are actually dissipated into recycled base metals. For example, since ferritic stainless steel including Cr, it cannot be separated from other iron-based materials by magnetic separation method, the collected materials including Cr are diluted by a large amount of pure iron in order to be used as ordinary steel. This indicates not only the downgraded utilization of ferritic stainless steel but also the dissipation of Cr into the ordinary steel. A similar downgraded utilization and dissipation occurs for other materials and elements, especially for rare metals.

Rare metals, in general, are thinly distributed in the earth, indicating that they need more cost, energy and materials to be produced than base metals. Furthermore, since they are unevenly distributed, supply shortage was frequently brought about and the market of rare metals is drastically changing world-wide. The management of these metals is thus important from the viewpoint of the material-cycle and the strategic resource utilization, especially for resource-poor Japan. In fact, national stockpiling for some rare metals is

managed by Japan Oil, Gas and Metals National Corporation (JOGMEC) in order to secure a stable supply. However, only seven kinds of rare metal are stockpiled (Ni, Cr, W, Co, Mo, Mn and V).

Recycling and reuse of the conventionally dissipated rare metals in WEEE will be one of the effective solutions, and therefore it is important to figure out the amount of the dissipation. Furthermore, evaluations of the dissipation in relation to domestic demand and environmental resource consumption, etc. should be important indices for the development of an adequate recycling scheme. However, from our investigations, few researches^{3,4)} were reported to be considering the impact (amount) of the dissipation of rare metals used in WEEE. Consequently, the aim of this study is to estimate the potential amounts of dissipated rare metals and evaluate the impact of the dissipation in WEEE in Japan.

2. Research Method

2.1 Target elements and WEEE

The rare metals (Au, Ag, B, Ba, Cr, In, Ni, Pb, Sb, Sn, Sr, Ta, Zn and Zr) and base metals (Fe, Al and Cu) were identified by componential analyses later described. In this study, the rare metals were regarded as target elements potentially dissipated. Cathode Ray Tube TV (CRT) (9 samples), liquid-crystal display TV (LCD) (4 samples), plasma display panel TV (PDP) (5 samples), refrigerator (7 samples), air conditioner (9 samples), washing machine (6 samples), microwave oven (6 samples) and cleaner (6 samples) were selected as WEEE. The estimated number of WEEE in the future was previously reported by authors⁵⁾ based on the report by Tasaki *et al.*⁶⁾ The essentials of the estimation will be briefly explained as follows;

The estimation was carried out using the population balance model,⁷⁾ that is, the difference between the domestic number shipped for a product at fiscal year t (P_t) and the

Table 1 The classification of the components for the home electric appliances.

Matrix	Details
Iron	Pure iron, coated steel, plated steel, PVC* steel, etc.
Copper	Pure copper, brass, bronze, Cu-Be-Co, conducting wire, etc.
Aluminium	Pure aluminium, Al-Cu, Mn, Mg, Sn, Zn alloys, conducting wire, etc.
Other alloys	Mg alloys, Pb alloys (excluding PWB**), Zn alloys, magnets, bond magnets, etc.
Glass	Electric glass (CRT panel), lead glass (CRT funnel and CRT neck), LCD glass, PDP glass, etc.
Plastic	Polyethylene, polypropylene, poly-styrene and foamed polyurethane, etc.
PWB**	Surface mounted components, lead-free solder (only 2002), solder, paper/phenol, paper/epoxy, etc.
Gas	Chlorofluorocarbon, etc.
Others	Rubber, ceramics, fibre, grease, etc.

* Polyvinyl chloride, ** Printed-wiring Board

number discarded for the product at fiscal year t (W_t) equals to the increase of the number in household stock from fiscal year $t - 1$ to t .

$$P_t - W_t = N_t - N_{(t-1)}, \quad (1)$$

where $N_{(t-1)}$ and N_t indicate the domestic number of possession at fiscal year $t - 1$ and t , respectively. N_t is derived from the household population⁸⁾ multiplied by the number of possession per unit household,⁹⁾ the future values of which were predicted using the logistic approximation. The number of the discarded product is estimated from their lifetime distribution functions. For the estimations of CRT, the effects of alternative products (LCD and PDP) were considered.

2.2 Determination of composition

Both the average weights and the constituent materials of the WEEE in 1997 and 2002 were examined by interviews with the Association for Electric Home Appliances in Japan, and the older data was applied to all products produced before 2001 and the later to all products after 2002. The collected data consist of nine major classifications such as iron, aluminium and plastic sorts, as shown in Table 1.

Since most of the rare metals were used as alloys or composites materials, the amounts of them were calculated by considering their compositions. The compositions of CRT glasses (neck, panel and funnel parts) were determined from the reported data.¹⁰⁾ The contents of Fe, Ba and B in bond magnet were measured using energy dispersive X-ray diffractometer (EDX). The amount of Ta in Ta capacitor was estimated based on the domestic abundance ratio (in number) of Ta capacitor to whole capacitors,¹¹⁾ the average concentration of Ta in each Ta capacitor¹²⁾ and the average number of capacitors on the printed-wiring board, the last of which was determined from actual measurements. The contents of Au and Ag on the printed-wiring board were determined from the report by Metal Economics Research Institute, JAPAN,¹³⁾ where no Pd was included on those of the WEEE. The other compositions were determined from

Table 2 Average composition for each element.

Elements	Containing materials
Au	printed-wiring board (30 ppm*)
Ag	Brazing alloy (3%**), lead-free solder (3%**), printed-wiring board (200 ppm*)
B	Bond magnets (1%*, **)
Ba	CRT panel (3.8%*), CRT funnel (0.12%*), CRT neck (0.12%*), PDP glass (3.8%***), bond magnet (3.7%***)
Cr	Stainless steel (18%**)
In	Transparent electrode (1g per 15 inch*)
Ni	Stainless steel (8%**)
Pb	CRT panel (0.28%*), CRT funnel (14.7%*), CRT neck (14.7%*), PDP glass (0.28%***), solder (40%**)
Sb	CRT panel (0.33%*)
Sn	Solder (60%**) and lead-free solder (96.5%**)
Sr	Ferrite magnet (8.3%*, **), CRT panel (5.5%*), CRT funnel (0.29%*), CRT neck (0.29%*)
Ta	Surface-mounted component*, ** (0.13%)
Zn	Plated steel (20 g/m ² ***), Zn-Al-Cu alloy (94%*)
Zr	CRT panel (1.4%*), PDP glass (1.4%***)

*: based on literatures,^{9,10,13)} interview or familiar composition, **: based on measured value

the interview and/or their familiar compositions. For example, the composition of lead-free solder, which was appeared only in results in 2002, was assumed Sn-3.0 mass%Ag-0.5 mass%Cu. Some of the incombustible materials such as Sb, probably included in plastics, were ignored in this study. The estimated compositions are summarized in Table 2.

3. Results

Figure 1 shows the estimated number of WEEE.⁵⁾ The estimated number of the discarded air conditioners, cleaners, refrigerators, washing machines and microwave ovens remains almost constant or slight increase, since the numbers of possession for the products are saturated in Japan. As for CRT, LCD and PDP, while the discarded numbers of the LCD and the PDP increase, those of CRT decrease due to the substitution effect.

The dissipated amounts of elements from the discarded products are shown in Fig. 2 (Ba, Cr, Ni, Pb, Sr and Zn), Fig. 3 (Sb, Sn and Zr) and Fig. 4 (Au, Ag, B, In and Ta), while the amounts of Fe, Cu and Al, almost of which are recycled, are about 550, 90 and 50 kton/year, respectively. From 2005 to 2015, the potential amounts of dissipated In, Ag and Sn show increasing trends due to the increases of transparent electrode (Indium Tin Oxide, ITO) for LCD and lead-free solder (Ag-Sn), while those of Pb, Sb, Zr, Ba and Sr show decreasing trends mostly due to the decrease in the usage of CRT glass.

Large amounts of Cr, Ni and Zn are dissipated since the addition of Cr and Ni to stainless steel and Zn to brass or plated steel, etc. are well-established method and better alternatives have not been found. However, it should be noted that recovery systems for Ni, Cr and Zn (stainless steel or plated steel, etc.) by manual disassembly are gradually

Fig. 1 The estimated number of WEEE.⁵⁾

Fig. 2 The potentially dissipated amounts of Ba, Cr, Ni, Pb, Sr and Zn from WEEE.

promoted¹⁴⁾ compared with those for B, Ba, In, Pb, Sb, Sn, Sr, Ta, and Zr, indicating that a larger amount of Ni, Cr and Zn will be recyclable in the future.

Since it is expected that a larger amount of lead-free solder will be continuously introduced, the dissipated amounts of Ag and Sn may be underestimated based on the compositional data in 2002. Even in recent years, most conventional solder has not been recycled in Japan due to the problem of cost. In the near future, if the problem of cost is solved for the reason that the expensive Ag is contained, the recovery of the lead-free solder will be promoted.

As for In, the amount of dissipation increases year by year due to the spread of LCD and PDP, reaching about 35 ton in 2025 through forward estimation. In addition, it should be noted that the size of LCD and PDP is progressively increasing, resulting in more dissipation. The recycling technology of In from ITO is presently under development, and the immediate application to a large-scale recycling plant is expected.

Fig. 3 The potentially dissipated amounts of Sn, Zr and Sb from WEEE.

Fig. 4 The potentially dissipated amounts of Au, Ag, B, Ta and In from WEEE.

4. Discussion

4.1 Evaluation of the dissipation compared with domestic demand

In order to evaluate the dissipation compared with domestic demand, the ratio of the dissipation to domestic demand (DDD) was proposed, and the amount of domestic demand in 2004¹⁵⁾ was used in this study, where only for Sn the data in 2001 was used. The DDD of target elements is shown in Fig. 5. The larger the DDD becomes, the lower the resource-efficiency is, which indicates that the recycling of the target element is of great significance. In the figure, “average”, “maximum” and “minimum” data were determined using the average, maximum and minimum amounts of the dissipation between 2005 and 2015. It is found from the figure that the DDDs of Ba, Sr, and Zr show large values (average 15~25% of domestic demands), while Ag, B, Cr, Ni, Pb and Zn show 2% at most, indicating the priority of the recycling for Ba, Sr and Zr is high. Since the recent domestic demands for Ba, Sr and Zr decrease due to the decrease in the demand of CRT glass, the possibility of overestimation is

Fig. 5 The ratio of the dissipation to domestic demand (DDD) in 2004.¹³⁾

considered. However, as an example, the recalculated DDD of Sr using the recent peak value of the domestic demand in 2000,¹⁵⁾ which is 152% of the domestic demand in 2004, remains the largest DDD. Much the same is true on Ba and Zr.

As for Ba, Sr and Zr, there are great differences between the maximum and the minimum, reflecting the decrease of the discarded number of CRT. In past days, CRT glasses were horizontally recycled, and the dissipation hardly occurs. However, since the domestic demand of CRT is drastically decreasing (to almost zero in 2011 by our estimation⁵⁾), it is difficult to continue the horizontal recycling within Japan in the future. After May in 2004, with the provision that phosphor materials are removed, CRT glasses were deregulated by the Basel municipal law, indicating a possibility of the horizontal recycling including overseas countries. However, this will bring about the outflow of the resources from Japan. From the viewpoint of resource risk in Japan, urgent development of recovery technology of rare metals, especially Sr, Ba and Zr, from the CRT glasses should be considered.

Furthermore, it should be noted that Sr and Ba as constituents of ferrite magnets are not recycled either. Excluding the CRT glasses, about 700 and 150 ton of Sr and Ba, respectively will be dissipated annually, while the amount of Sr occupies about 15% of the domestic demand for Sr-based ferrite magnets in 2004. Thus, both recovery and reuse of the ferrite magnets are also desirable.

4.2 Evaluation of the dissipation considering embodied environmental impact

For the evaluation of the dissipation considering embodied environmental impact, “Total Materials Requirement” (TMR) was employed as a weighting factor. TMR includes not only direct and indirect materials input but also hidden materials flow such as overburden and rock required to produce a target material.^{16,17)} The data of TMR used in this study is summarized in Table 3.^{3,18)} Although there is no available TMR data of Ba, the value was estimated to be 460 (ton/ton) from that of congener, Sr (500 ton/ton), using following relation,¹⁸⁾

Table 3 TMR of Au, Ag, B, Ba, Cr, In, Ni, Pb, Sb, Sn, Sr, Ta, Zn and Zr.^{3,16)}

Element	TMR (ton/ton)
Au	1100000
Ag	4800
B	140
Ba	460
Cr	26
In	4500
Ni	260
Pb	28
Sb	42
Sn	81
Sr	500
Ta	6800
Zn	36
Zr	550

Fig. 6 The amount of the dissipation weighted by TMR.

$$\text{TMR} \propto (\text{concentration in the crust})^{-2/3}, \quad (2)$$

where the concentrations in the crust for Ba and Sr are 425 and 375 ppm, respectively.¹⁹⁾

Figure 6 shows the sum of the dissipation weighted by TMR from 2005 to 2015. A larger amount of the weighted dissipation indicates a larger amount of materials flow, which indicates a greater significance of the recycling of the target element. The impacts of Sr (38 million ton-TMR), Ba (17 million ton-TMR) and Au (14 million ton-TMR) are outstanding. The impact of Sr is equivalent to 4.8 million ton of Fe (which TMR is 8 (ton/ton)), corresponding to about 4% of annual production of crude steel in Japan. It is suggested that the efficient utilization of Sr and Ba in discarded CRT glasses is a pressing issue, and the recovery of Au from the printed-wiring board should be actively promoted. On the other hand, despite low TMR, Ni, Pb, Cr and Zn show relatively large impacts because the absolute amounts of the dissipations are too large. It is also suggested that efforts to recycle and/or reuse the constituent materials which include the above elements are required.

5. Conclusion

In this study, the potential amounts of dissipated rare metals (Au, Ag, B, Ba, Cr, In, Ni, Pb, Sb, Sn, Sr, Ta, Zn and Zr) in WEEE have been estimated from 2005 to 2015. The dissipated amount of In shows an increasing trend, while those of Pb, Sb, Zr, Ba and Sr show decreasing trends. According to the ratio of the dissipation to domestic demand (DDD) in 2004, the DDD of Ba, Sr, and Zr are high (average 15~25% of domestic demands), while those for Ag, B, Cr, Ni, Pb and Zn show 2% at most. The evaluation of the dissipation considering embodied environmental impact was carried out based on the sum of the dissipation from 2005 to 2015 weighted by “total materials requirement” (TMR). The impacts of Sr, Ba and Au show 38 million ton-TMR, 17 million ton-TMR and 14 million ton-TMR, respectively, which are the largest among the rare metals. It is proposed that the efficient recycling of Sr and Ba from WEEE is a pressing issue, and the recovery of Au from the printed-wiring board should be actively promoted.

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