Waste Treatment using Thermochemical Materials Separation

Franz-Georg Simon, Angelika Recknagel and Gerd Kley
Federal Institute for Materials Research and Testing (BAM), Unter den Eichen 87, 12205 Berlin, Germany
Fax: 49-30-8104-1437, e-mail: franz-georg.simon@bam.de

An industrial process can be divided into 6 stages: exploitation of raw materials, production of materials, manufacture of products and goods, utilization, failure and finally generation of waste. The consumption of raw materials can be reduced by specific recycling measures. Thermochemical processes enable the enrichment of certain substances so that the substitution of raw materials for the production of products is possible. The concentrations of the heavy metals copper, zinc, lead and others in fly ash from municipal solid waste incineration are a few thousand ppm. Thermochemical treatment in an AC arc furnace provides a product with metal concentrations in the per cent region, higher than those of the respective ores. Thus just for non-ferrous metals, where the total materials requirement (TMR) is high, a more sustainable materials cycle is possible. Phosphorus as a non-metal which is used as a fertilizer everywhere in the world has a TMR of 34 tons per ton of phosphate. The use of sewage sludge which contains phosphate is controversial due to its content of pharmaceuticals and other pollutants. The ash from sewage sludge incineration can only be used in agriculture when heavy metals are removed prior to utilization by thermochemical treatment. The paper explains the technical processes in detail and discusses the sustainability of recycling processes.
Key words: arc furnace, recycling, ash treatment, phosphate, stainless steel

INTRODUCTION

An industrial process can be divided into 6 stages: exploitation of raw materials, production of materials, manufacture of products and goods, utilization, failure and finally generation of waste [1]. A wide range of non-renewable resources, often primary ones, are used in industrial processes. Even if technical development enables the extraction of resources at greater depth and of lower quality in the future – it cannot be assumed that future supplies are unlimited. One of the research challenges the emerging discipline of industrial ecology faces [2-4] will be to identify best practical options to take care of virgin resources. The consumption of raw materials can either be reduced by a more efficient use of raw materials and energy [5, 6] or by specific recycling measures. While smaller and lighter products can reduce the amount of material used, reuse and recycling can also minimize fresh input and waste output.

The success of secondary raw materials depends on three factors: efficiency of isolation of the desired materials, consumer demand for reprocessed materials and the price relative to that of primary materials. The ease of isolation explains why lead (Pb) enjoys a recovery rate today exceeding its demand by 70 per cent [7]. Lead is mainly used for automobile batteries, which are readily separated from the general waste stream. Different kind of separation options and recovery processes for certain metals are given by Wernick and Themelis [8]. Allen and Behmanesh discussed in their paper the recyclability as a function of dilution and value of the raw material [9]. For high-value materials

(e.g. gold in electronic scrap) recycling is cost-effective even when it is dilute in the waste stream. However, the evaluation of concentration distribution in waste streams undergoing recycling revealed that most metals are recycled only at high concentrations, indicating significant disincentives to make use of waste. One possibility to enrich certain substances in some kind of raw materials is the treatment by thermochemical separation which is described below.

THERMOCHEMICAL TREATMENT

Thermochemical processes are well suited for the treatment of waste materials enabling a recovery of useful elements and products. Thermochemical treatment comprises a variety of processes over a wide temperature range [10]: combustion and pyrolysis as well as partial oxidation, hydrogenation, hydrolysis, alcoholysis [11], special technologies and combinations of all these.

Treatment of waste materials in an arc furnace displays a special technology. Usually applied for scrap smelting or the production of high temperature materials [12] the furnace enables a separation of materials by applying reducing conditions and high temperatures. Fly ash from municipal solid waste incineration (MSWI) contains heavy metal compounds in soluble form (chlorides) and toxic organic compounds (dioxin and furanes) and has to be disposed of in such a way that contact with water does not cause dissipation of the contaminants. This can be achieved by solidification with cement or underground storage. However, the concentration of certain metals in fly ash (Cu, Cd, Zn, Pb) exceeds those in natural ores (see Table I). The treatment of fly ash from MSWI in an arc furnace leads to an almost complete recycling of the constituents. Toxic organic compound are decomposed by the high temperature. A reformation is prevented by

rapid quenching of the gas leaving the furnace (mainly SO_2 from thermal decomposition of sulfate in the ash, see Table I). Heavy metal compounds are either evaporated as chlorides and separated as a metal condensate on a bag filter or reduced to the elemental

form forming an alloy with iron at the bottom of the furnace. The oxides of silicon, aluminum and calcium as the main constituents of the ash form a vitrified product which is extracted from the furnace.
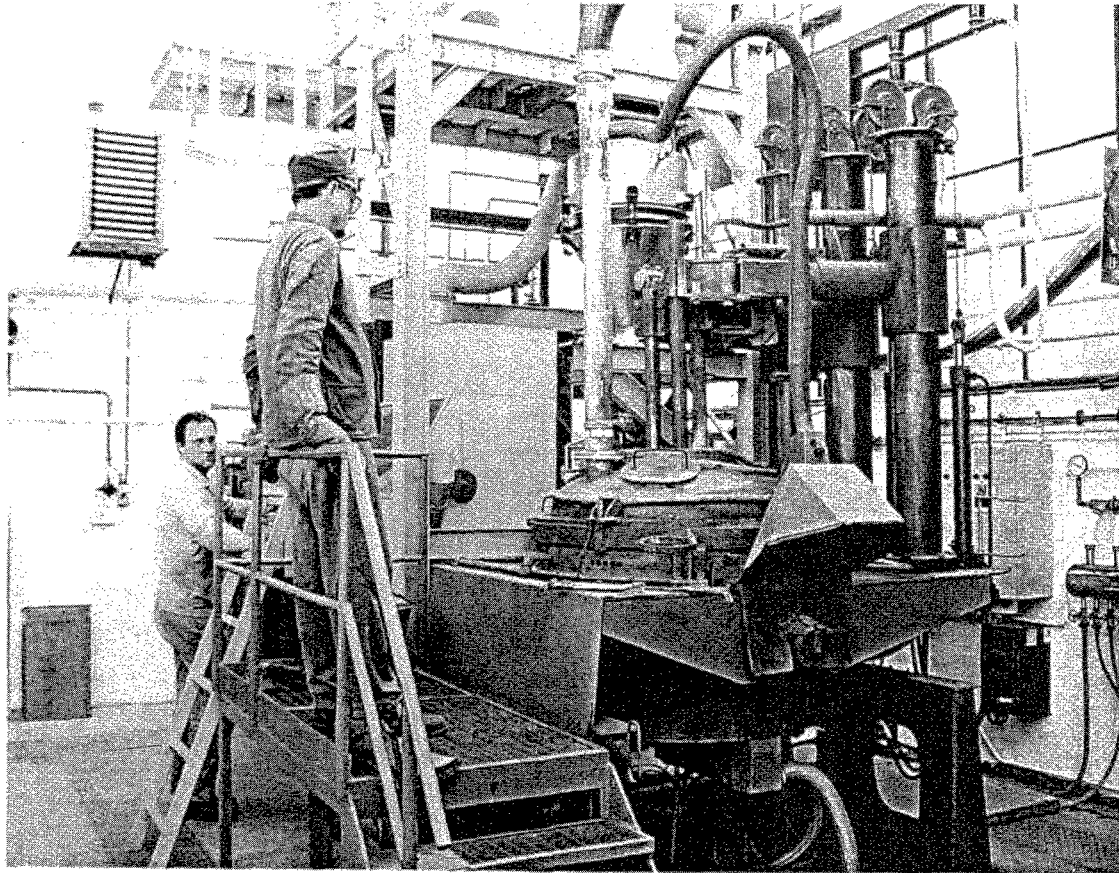

Fig. 1. BAM's AC arc furnace in operation with the three graphite electrodes at the top of the furnace

Table I. Composition of input and output of the vitrification process

%	Input Ash	Products Vitr. prod.	HM cond.	Off-gas
Si	12.40	19.50	0.18	
Ca	12.40	18.83	0.29	
Al	2.80	4.36	0.56	
Mg	3.90	5.61	n.n.	
Na	4.20	2.20	9.60	
K	3.90	0.50	17.00	
Fe	1.800	1.790	n.n.	
Cu	0.160	0.035	n.n.	
Ni	0.010	0.003	n.n.	
Zn	3.200	0.199	13.400	
Pb	1.300	0.003	4.900	
Cd	0.050	n.n.	0.152	
O	33.70	40.60	20.00	25.50
Cl	7.70	0.22	25.00	n.n.
P	0.55	0.47	0.43	n.n.
S	3.90	0.71	3.11	26.00

The melting point of ashes from MSWI is around 1200 ° C, which can easily be achieved by the arc furnace technology. Fig. 2 displays the phase diagram for mixtures of these three oxides. Typical ash compositions are in the area of low melting points. A variety of utilization paths exist for this fraction (e. g. construction material, cement clinker substitute, foam glass, mineral wool) [13].

Zinc and lead are enriched in the heavy metal (HM) condensate. Chloride can easily be removed by leaching with water.

Fig. 3 displays the mass balance of the process and the balance for the elements zinc and sulfur in the form of Sankey diagrams [14]. Thermochemical treatment in an AC arc furnace represents an effective materials separation method especially for metals enabling the recycling of valuable resources.

Elemental metals with high boiling points generated by chemical reduction (Cu, Ni, Fe) are separated by their higher density from the glassy melt. In the treatment of MSWI residues this fraction plays a minor role with 1 % only and is not mentioned in Table I. This might be different for other waste materials (see chapter 1.1).
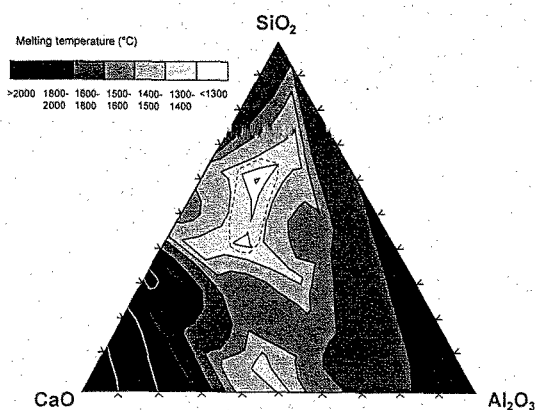
Fig. 2. Phase diagram of the three oxides of Si, Al and Ca. Ashes from MSWI usually exhibit a composition where the melting point is low (see area with dashed line).
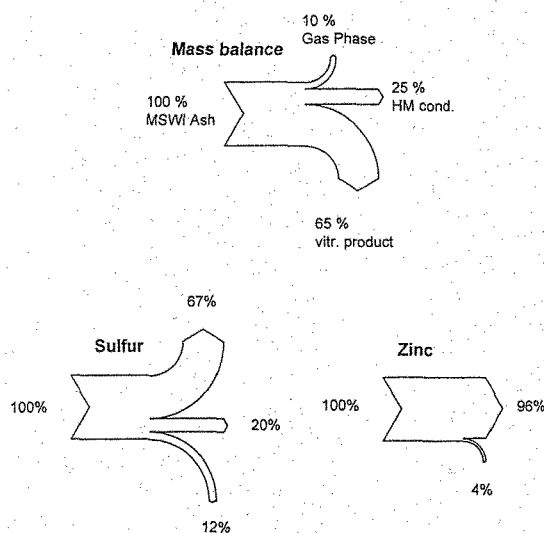

Fig. 3. Sankey diagrams [14] for the treatment of MSWI fly ash in an AC arc furnace. Zinc is almost completely transferred to the heavy metal condensate fraction. Sulfur is mainly emitted as SO₂ from the process.

1.1. Thermochemical treatment of slags from stainless steel production

In 1997, 5.7 million tons of stainless steel were produced in Europe. Stainless steel consists of chromium, nickel, manganese and iron. Chromium makes up just below 20 % and nickel some 10 % of the content. Worldwide most of the stainless steel producers employ the EAF-AOD process route. Ferrochrome and scrap are melted in an electric arc furnace (EAF). Subsequently the melt is poured into the argon-oxygen decarburization (AOD) converter. Residual carbon is oxidized with oxygen in this converter. Argon is present to avoid excessive oxidation of alloying elements, especially chromium, which is also oxidized and transferred to the slag. The AOD slag contains about 2 % of chromium oxide.

Solid residues are generated during manufacturing

of stainless steel: filter dust and slag. The filter dust amounts to 1 – 3 % of the input (120,000 tons per year). The filter dust is treated in plasma furnaces in the presence of coke. The main products are recycled metals and a material used as rock fill. The slag from stainless steel production amounts to 15 - 20 % of the input (approx. 800,000 – 1,100,000 tons per year). It is generally not used in practical applications in fear of hexavalent chromium leaching which may result in water pollution. The transmission of hexavalent chromium in the environment poses potential risk of cancer in human beings and animals and adversely alters the genetic diversity of species. In addition, the AOD slag is normally disintegrated into a powder due to the volume expansion caused by the α-dicalcium silicate to γ-dicalcium silicate phase transformation that occurs during cooling. Not only limits this its application as a construction material, but also creates an unpleasant working environment.

In today's treatment of the AOD residue the metallic granules (10 – 35 % of the slag [15]) are manually removed from the slag [16]. The remaining mineral material is not utilized due to the problems described above. Chromium occurs in the oxidation state III in the slag. The solubility of Cr-III is low. However, it is possible that chromium is oxidized to the hexavalent form, which is more mobile and is a carcinogenic species. Table II displays a typical composition of an AOD slag (adapted from [17]).

Table II. Typical composition of AOD slag without metallic granules, % by mass

SiO₂	CaO	MgO	Al₂O₃	Fe$_{tot}$	Cr$_{tot}$	Ni	Mn
28-32	45-47	4-8	2-5	2-7	1-2	0.3	0-4

A thermochemical treatment of the AOD slag in an AC arc furnace (see Fig. 1) enables a complete utilization of the constituent of the waste slag. The high temperature process facilitates an easy separation between the molten slag and liquid metal phase, which sinks down due to its higher density. The arc furnace establishes reducing conditions where chromium is transferred to the elemental form and thus to the metallic phase. The AC arc furnace itself provides reducing conditions by utilizing carbon from graphite electrodes. Use of silicon metal as reducing agent is already practiced in the reduction of chromium metals. Little is known on the use of aluminum for the reduction [18] and the reaction products from chromium reduction, SiO₂ and Al₂O₃; each of these has an influence on the composition of the slag. The use of aluminium dross, a waste material in aluminium recycling, is attractive because an increasing Al₂O₃ concentration will alter the composition and the properties of the resulting material.

A treatment of the residue in the described manner will lead to a complete recycling of the material and eliminate the risks involved in landfilling of Cr-containing wastes. Elemental chromium is recycled for the production of stainless steel. The mineral phase used as a substitute for cement clinker or light-weight aggregate replaces materials which are produced

with high energy consumption. The process will be studied in detail in a research project funded by the LIFE program of the European commission.

1.2. Recovery of phosphate from sewage sludge ash

Phosphorus is an essential element for the global biota which cannot be substituted. Phosphorus lost by dissipative use in agriculture has to be returned by fertilizers. Unlike carbon, nitrogen or sulfur, it is recycled biologically only to a minor extent (e.g. by bird droppings) [19]. The global demand for phosphorus is between 100 and 200 million tons per year. The total materials requirement (TMR) [20] or materials input per unit of service (MIPS) for phosphate is 34, i.e. for 1 ton of phosphate 34 tons of materials are transformed [6]. Therefore the utilization of phosphorus-containing waste as secondary raw material makes sense. Sewage sludge from waste water treatment displays such an type of waste. The application of untreated sewage sludge, however, is questionable: heavy metals and residues from pharmaceutical products, pesticides and herbicides are comprised and could contaminate soil or groundwater.

Sewage sludge incineration utilizes the energy content of the sludge and destroys the organic pollutants of the sludge but environmentally relevant heavy metals (Cu, Ni, Zn, Cd, Cr, Pb) remain in the ash. However, the phosphate content of the ash from sewage sludge incineration is between 10 and 20 %, much higher than in ashes from co-combustion of sewage sludge in power stations or cement plants. Heavy metal compounds have to be removed from the sewage sludge incineration ash before utilization and phosphates have to be transformed to a form utilizable for plants rather than left in form of sparingly soluble calcium and iron phosphates. Thermochemical treatment of the ash enables a separation of heavy metals. It is known that heavy metal chlorides have much higher vapour pressures than the respective oxides (see Fig. 4).
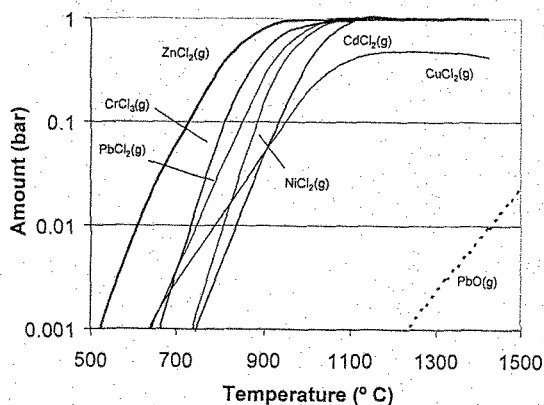

Fig. 4. Vapour pressure of heavy metal chlorides and lead oxide. From the heavy metal oxides only PbO has a significant vapour pressure in the displayed temperature region.

Displayed are six heavy metal chlorides and lead oxide. Vapour pressures of the other heavy metal oxides

are still too low at temperatures below 1500 C. A chlorinating roasting of sewage sludge ash by addition of alkaline and alkaline-earth chlorides at temperatures between 1000 and 1100 ° C leads to an almost complete evaporation of heavy metal compounds and an ash usable as a fertilizer substitute [21]. An indirectly heated rotary furnace can be used as a thermochemical reactor. The process will be studied in detail in a research project funded by the German Federal Environmental Agency.

DISCUSSION

"Pollution is nothing but the resources we are not harvesting. We allow them to disperse because we've been ignorant of their value". Stated by Buckminster Fuller, this expression is also valid for waste disposed of on a landfill without utilization. It is undoubted that our metal reserves are limited and that dissipative use of materials is unsustainable [19]. Nevertheless, more than 55 % of municipal solid wastes generated in the United States (total 231 million tons in 2000) was disposed of on landfills even without using its energy content in incineration plants (only 15 % has been incinerated) [22].

This is wasting useful resources because the content of metals and other valuable constituents is sometimes higher than in ores or other natural resources. Fig. 5 displays the relation between the price of a metal and its concentration in viable natural resources, known as the Sherwood plot [9].
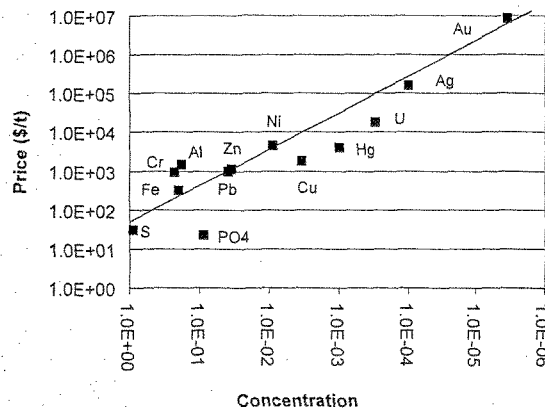

Concentration

Fig. 5. The Sherwood plot. There is a relation between the price of a substance and its concentration in viable natural resources. Price and concentration data retrieved from www.usgs.gov.

Allen and Behmanesh showed in their article that metals especially in hazardous wastes are underutilized. Reasons for that are barriers to industrial recycling [23]: technical hurdles (waste contains unwanted tramp elements, mixtures of metals which can be hardly separated [8]), economic barriers (landfilling is often a cheaper alternative disregarding external costs), legal issues (handling of waste is extremely regulated, recycling is often ruled as a form of disposal) and information and organizational barriers.

Despite these hurdles, recovery of metals or other inorganic substances (e.g. phosphates) is technically

feasible and, unlike polymer plastics, their properties can be almost completely restored. Recovery from scrap is energetically favourable because metals are predominately in elemental form, thus reduction is not necessary. Also concentrations are higher than in natural resources (i.e. area to the left from the points in Fig. 5).

Metals and other inorganic substances are non-renewable resources [24]. Dissipative use leads virtually to a complete loss of resources because a recovery is not feasible technically and economically at concentrations near those in the earth's crust (i.e. to the right from the points in Fig. 5). However, there is a variety of application for metals and metal compounds which mark a dissipative use: chromium chemicals in leather tannings, copper chemicals as wood preservatives, lead as a fuel additive, zinc for corrosion protection and so on [2]. Dissipation lowers the maximal possible recycling rate (RR). The marginal usage rate MU_R of a resource, i.e. to which extent a resource can be preserved, can be calculated from the recycling rate RR [25]:

$$MU_R = 1 + \frac{RR}{1 - RR}$$

At a recycling rate of 50 % a resource lasts twice as long as without recycling. For a ten-fold preservation a recycling rate of 90 % is necessary. Dissipation also stands for an increase in entropy. The concept of Relative Statistical Entropy (RSE) [26, 27] enables a method for benchmarking the use and the recycling of resources and wastes. A pure substance has a RSE value of 0, a substance in complete dissipation (i.e. earth's crust concentration) a value of 1. According to this concept an ideal waste treatment and recycling process is a process with optimum substance partitioning: the input is a waste material, output fractions are cleaned waste water and off-gas, an inert material with a metal concentration as low as earth's crust concentrations and a fraction with the composition of a mineral ore or even better. The thermochemical treatment of waste materials such as incineration ashes or metallurgical slags as explained in this paper approaches such an "ideal" process.

ACKNOWLEDGEMENT

REFERENCES

[1] E. Hornbogen, A definition of sustainability based on entropy production, in "R'02, Recovery, Recycling, Re-integration", Geneva (2002).

[2] R. U. Ayres, *Resources, Conservation and Recycling* 21 145-173 (1997).

[3] C. J. Andrews, Municipal Solid Waste Management, in: Ayres, R. U. and Ayres, L. (Editors), "Handbook of Industrial Ecology", Edward Elgar Publishing, Aldershot (2002).

[4] M. R. Chertow, *Social Research* 65(1) 31-53 (1998).

[5] E. U. Weizsäcker, A. B. Lovins and L. H. Lovins, "Factor 4 - Doubling Wealth, Halving Resource Use", Earthscan Publications London (1997).

[6] F. Schmidt-Bleek, "Das MIPS-Konzept", Droemer Knaur München (1998).

[7] I. K. Wernick, R. Herman, S. Govind and J. H. Ausuble, *Daedalus* 125(3) 171-198 (1996).

[8] I. K. Wernick and N. J. Themelis, *Annual Review of Energy and Environment* 23 465-497 (1998).

[9] D. T. Allen and N. Behmanesh, Wastes as raw materials, in: Allenby, B. A. and Richards, D. J. (Editors), "The Greening of Industrial Ecology", National Academy Press, Washington, DC (1994).

[10] R. Warnecke, *AbfallwirtschaftsJournal* (3) 14-21 (1996).

[11] F. G. Simon, R. Brenneis and P. Köcher, Enzymatic production of biodegradable lubricants from waste fat, in "R'02, Recovery, Recycling, Re-integration", Geneva (2002).

[12] F. G. Simon, B. Adamczyk and G. Kley, *Materials Transactions* 44(7) 1251-1254 (2003).

[13] F. G. Simon, P. Köcher and G. Kley, Products from the vitrification of residues - an example for an ecomaterial, in "4th International Conference on Ecomaterials", Gifu, Japan (1999) pp. 467-470.

[14] G. Doka, www.doka.ch/sankey.htm (2003).

[15] K. Koch, W. Münchberg, H. Zörcher and W. Rubens, *Stahl und Eisen* 112(9) 91-99 (1992).

[16] H. P. Mashanyare and R. N. Guest, *Minerals Engineering* 10(11) 1254-1258 (1997).

[17] F. A. Lopez, A. Lopez-Delgado and N. Balcazar, *Afinidad* 461(1-2) 39-46 (1996).

[18] M. Sinkai, M. Tsuno, M. Honjo, Y. Hazama and M. Sakata, *Electric Furnace Steel (Denki-Seiko)* 68(4) 287-293 (1997).

[19] R. U. Ayres, J. Holmberg and B. Andersson, *MRS Bulletin* (June) 477-480 (2001).

[20] K. Halada, K. Ijima, N. Katagiri and T. Ohkura, *Journal of the Japan Institute of Metals* 65(7) 564-570 (2001).

[21] P. Köcher, R. Brenneis and G. Kley, Verfahren zur Abtrennung von umweltrelevanten Schwermetallen aus Klärschlammaschen, Deutsches Patenamt 102 43 840.4 (2002).

[22] Office of Solid Waste, Municipal solid waste in the United States: 2000 Facts and Figures. Environmental Protection Agency, Report, EPA530-S-02-001 (2002).

[23] R. A. Frosch, Closing the loop on waste materials, in: Richards, D. J. (Editor), "The Industrial Green Game: Implications for Environmental Design and Management", National Academy Press, Washington, D. C. (1997).

[24] A. Wils, *Ecological Economics* 37 457-472 (2001).

[25] B. Spangenberg, *Müll und Abfall* (8) 502-504 (2000).

[26] H. Rechberger, *Technikfolgenabschätzung - Theorie und Praxis* 11(1) 25-31 (2002).

[27] H. Rechberger and P. H. Brunner, *Environmental Science and Technology* 36(4) 809-816 (2002).