

**AUTOMOTIVE SHREDDER RESIDUE (ASR) AND
COMPACT DISC (CD) WASTE: OPTIONS FOR
RECOVERY OF MATERIALS AND ENERGY**
Final report for study funded by Ekokem Oy Ab 2002

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Preface

Two types of solid waste streams that will be rapidly increasing in the near future, requiring more processing capacity, are automotive shredder residue (ASR, *in Finnish: autopaloittamojäte*) and waste compact discs (CDs). Both contain large fractions of polymers that may be recovered.

New EU directives on landfilling and on end-of-life vehicles (ELVs) will enforce much larger amounts of ASR to be processed. Currently around 25000 t/y is generated in Finland. A recent study by Ranta in 1999 [1] showed that for car tyre scrap there are several existing routes material and energy recovery (with an important role for cement kilns), but for the ASR fraction only a few options for future processes were mentioned. One problem is the complex composition of ASR, containing plastics such as PVC and polyurethane, textiles, glass, oils, brominated flame retardants, toxic heavy metals and possibly PCBs. The first objective of the work reported here is to re-evaluate in greater detail the options for recovery of materials or energy from ASR on a large scale, against a background of increased capacity needed for treatment of this waste and more strict legislation in the future.

Secondly, with sales of compact discs (CDs), especially writeable CDs doubling in Finland last year, increasing amounts of CDs are disposed of in waste. Worldwide, CD production is increasing with around 10% per year, being of the order of 12 billion pieces per year at the moment. Of these, almost 25% can be considered to be waste immediately, being misprints or distributed with commercial material, never to be used [67]. At a weight of 20 g per CD this implies a waste stream of several 100000 tonnes per year worldwide, excluding their packaging. CDs are mainly composed of polymers, mainly polycarbonate (PC) and small amounts of metal, for example 0.1 %-wt aluminum in a standard audio CD. As a second, smaller part of the work reported here the options for recovery of materials or energy from waste CDs in Finland will be evaluated. One objective is to verify whether recycling of the polycarbonate and the aluminum is feasible, or maybe co-firing in a pulverised coal power plant is possible.

Thus, this desk-top study will address the following two issues:

- Making an assessment of the technical options for large-scale processing of ASR in Finland, aiming at maximum recovery of energy and materials, using the suggestions by Ranta [1] as a starting point; and
- Making an assessment of the technical options for the processing waste CDs in Finland, aiming at maximum recovery of energy and materials.

For both waste streams, avoiding disposal on landfills is a first objective.

The composition of a typical ASR, with several %-wt PVC as a major plastics fraction and significant amounts of recoverable non-ferrous metal fractions makes it somewhat like an “intermediate” between two other types of problematic solid waste that have been subject of research by the authors for several years: PVC waste and waste electrical and electronic equipment (WEEE). Results from that work have so far been published in, for example:

Saeed, L., Zevenhoven, R. “Comparison between two-stage waste incineration with HCl recovery and conventional incineration plants” *Energy Sources*, 24(1) (2002) 41-57

Zevenhoven, R., Axelsen, E.P., Hupa, M. “Pyrolysis of waste-derived fuel mixtures containing PVC” *FUEL*, 81(4) (2002) 507-510

Zevenhoven, R., Saeed, L., Tohka A. “Optimisation of two-stage combustion of high-PVC solid wastes” in: *Power Production from Waste and Biomass - IV*, April 8-10, Espoo, Finland, K. Sipilä, M. Rossi (Eds.), VTT Symposium 222, Espoo (Finland) (2002), pp. 341-349

Tohka, A. Zevenhoven, R. “Processing wastes and waste-derived fuels containing brominated flame retardants” Report TKK-ENY-7, Helsinki Univ. of Technol. Espoo (Finland) (2002) ISBN 951-22-5937-0, 62 p.

Tohka, A., Zevenhoven, R. “Brominated flame retardants - a nuisance in thermal waste processing?” in: Proc. of TMS Fall 2002 Extraction and Processing Division Meeting on Recycling and Waste Treatment in Mineral Processing: Technical and Economic Aspects, Luleå (Sweden) June 16-20, 2002

Zevenhoven, R., Saeed, L., Tohka, A. “Thermal processing of chlorine- and bromine-containing wastes” in: Proc. of ECOS2002, Berlin (Germany) July 3-5, 2002, Vol 2, pp 1302-1309

Saeed, L., Tohka, A., Zevenhoven, R. “An experimental assessment of two-stage fluidised bed combustion of high-PVC solid waste with HCl recovery” accepted (after review) for presentation at the 17th Int. Conf. on Fluidised Bed Combustion, Jacksonville (FL) May 18-23, 2003. paper 87

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1. Introduction

1.1 *Automotive shredder residue (ASR)*

Auto shredder residue (ASR), also referred to as auto shredder fluff, shredder light fraction (SLF), residues from shredding (RESH) or simply “auto fluff” or “fluff”, is the fraction of an shredded end-of-life vehicle (ELV) for which recycling routes do not yet exist. After removing several recyclable parts such as bumpers (recycled into splash plates or into new bumpers [3]), air bags, batteries, fuel tanks and nowadays also tyres and sometimes even seats, the dismantled vehicle is shredded. The ASR is then obtained as the light shredder fraction from the airflow separator that separates it from the heavier metallic fraction, which is fully recyclable as a secondary raw material. ASR is a complex mixture of plastics (rigid and foam), rubber, glass, wood, paper, leather, textile, sand plus other dirt, and a significant fraction of metals. It may be feasible to remove a large plastics or non-ferrous fraction from the ASR or it may be separated into fractions that contain lighter and heavier fractions, respectively [2].

The ASR fraction is typically around 20 – 25 % of the weight of the ELV it derives from. Whilst for Finland the amount of ASR produced is around 25000 tonnes annually, this number is at least 100 times higher for North America [Ro00], which suggests that worldwide the annual production will be of the order of 10 million tonnes. Although recycling and recovery of ELV components is increasing the increasing number of vehicles will give a further rise of ASR generated for years to come. Since the mid-1990's there is, however, increased concern over how to handle this waste material and in European countries that follow EU legislations and directives, important changes are being enforced by three new directives: Directive 2000/53/EC (September 18, 2000) on End-of-Life Vehicles [5], Directive 200/76/EC (December 4, 2000) on the Incineration of Waste [6] and Directive 1999/31/EC (April 26, 1999) on the Landfill of Waste [7]. Some implications of these are limitations on what types of waste may be landfilled or incinerated (for example, car tyres may not be landfilled any longer within EU member states [7]), and especially on how ASR may be treated.

Still, in Europe ASR is mostly disposed of on landfills, despite the high concentration of organic species that will take part in chemical and biological degradation processes [2];

apparently ASR is to some extent biodegradable. At some places, ASR is incinerated or co-incinerated with other wastes or fuel, which within the EU may be restricted by the Incineration of Waste Directive when considering ASR composition or requirements to flue gas emissions control [6].

The aim of this study is to give an overview of what problem the ASR presents to modern society and what the options are for processing this waste into recovered products or materials, or energy, with a minimum of useless by-products for which landfilling is the only route. Not addressed in this work are waste car tyres or scrapped car tyres, sometimes referred to as tyre derived fuel (TDF), since for this waste stream several options for material, chemical, or energy recovery have been developed which also find use in Finland – see [1]. Examples are co-firing in cement clinker production and road construction work. Important here are the role of the Finnish tyre recycling organisation *Rengaskierrätys Oy* and the use of waste tyres as alternative fuel at the cement plant of *Finnsementti Oy* at Parainen.



Figure 1 Automotive shredder residue (above)[67] and waste compact discs (right) [76]

1.2 Compact disc (CD) waste

Compact disc waste, especially those related to computer software are often disposed of with other waste electrical and electronic equipment (WEEE) fractions, if they don't end up in the wastes from households or offices. The structure and composition of CDs and DVDs is such that when these end up on landfills or in waste incinerators not much harm will be done. Nonetheless, looking at the sheer number of CDs and DVDs that are produced should trigger considerations on their end-of-life disposal. The second, smaller part of this report deals with processes for recycling and recovery of scrapped CDs.

2. End-of-life vehicles (ELVs), automotive shredder residue (ASR)

2.1 Options for ASR treatment and disposal, legislation

Currently, except for a small part that is processed into recyclable material fractions or simply burned, ASR is almost completely disposed off on landfills, inside as well as outside the EU member countries. The ELV directive [5] mentions 8-9 million tonnes of waste generated by ELVs within the community annually, which suggests an amount of 2-2.5 million tonnes ASR. There is little incentive for recycling or recovery of, for example, the plastics fraction from ASR mainly for reasons of economy. ASR is an extremely inhomogeneous mixture of very different fractions such as plastics, metals, fibres and a lot of sand and dirt. For any material singled out the concentration is low, and although the plastics fraction in ASR usually stands for 20-40 %-wt also this material is of limited interest for recycling or recovery because it is mainly made up of four polymers being poly ethylene (PE), poly propylene (PP), poly vinylchloride (PVC) and poly urethane (PU) which all four are bulk chemicals that can be produced from virgin raw materials against low costs. Using recovered polymer fractions from ASR as secondary raw material would compromise product quality and increase costs.

Nonetheless as a result of increasingly tight regulations on local, national and sometimes international level several activities to control the rapidly increasing amounts of ASR were started during the 1990s in most industrialised countries, including all sorts of research activities addressing the environmental and health risks connected to ASR processing and disposal. Also the technologies needed for recovery and recycling of fractions in ASR received increased interest after it became clear that recyclers would have to pay a negative price, *i.e.* receive money for the ASR to be processed. This has so far resulted in small but not insignificant diversion of ASR from landfill but for the EU member states the main driving force for ASR processing will come from EU directives that recently came into force – see Table 1. There is, however, still much uncertainty about these directives and the definitions of “waste”, “dispose”, “discard”, “pre-treated waste” and “co-firing” or “co-incineration”, which makes it hard for actors in the field of waste processing to evaluate the legal and economical consequences of their (future) actions [8]. For example, ASR shows biochemical activity which is not the same as being biodegradable, and ASR can be considered the product of ELV treatment which seems to put it from into the category “waste that has been subject to treatment” from the landfill directive [7] point of view. Also, the large fraction of PVC may

classify it as hazardous waste, which may enforce incineration under specific conditions of the incineration process and flue gas clean-up [6]. In Germany, for example, under the “TA-Abfall” regulation the PCB (poly chlorinated biphenyls) content of ASR demands hazardous waste incineration as first priority route for disposal [9], which allows for energy recovery but excludes material recycling. Nonetheless, most German ASR is landfilled since hazardous waste incineration would be too expensive. Also the US most ASR (an estimated 4.7 million tonnes annually) is landfilled, in the state of California where it is categorised as hazardous waste this is significantly more expensive [10,11].

Table 1 Aspects of recent EU directives relevant for ASR processing

EU directive	Issue that relates to ASR processing
End-of-life vehicles directive 2000/53/EC 18.9.2000	<ul style="list-style-type: none"> • Preference to reuse and recycling • Integrate dismantling, reuse and recycling in design and production of new vehicles • PVC in ELV is still being examined by the Commission • After 1.7.2003 vehicles put on the market may contain no or limited amounts of Pb, Hg, Cd and Cr (VI) except for special components • ELV processing should be such that shredder residues are not contaminated by hazardous compounds, and that reuse and recovery of vehicle components are not impaired • 85 % of ELV reused / recovered and 80 % reused/recycled by 1.1.2006 • 95 % of ELV reused / recovered and 85 % reused/recycled by 1.1.2015 • Annex I removal of catalysts and metals components containing Cu, Al, Mg before shredding.
Waste incineration directive 2000/76/EC 4.12.2000	<ul style="list-style-type: none"> • Emission regulations for dust, SOx, NOx, CO, HF, TOC, PCDD/Fs, heavy metals, Hg; different for municipal waste, medical waste and hazardous waste • Hazardous waste with more than 1% halogenated organic substances has to comply with certain operational condition as to destroy PCDD/Fs • Hazardous waste with net calorific value of at least 30 MJ/kg is excluded from requirements to hazardous waste • Comply with regulations by 28.12.2005 (old) or 28.12.2002 (new)
Landfill directive 1999/31/EC 26.4.1999	<ul style="list-style-type: none"> • Encourage prevention, recycling and recovery of waste • Whole or shredder tyres may not be landfilled • Only waste that has been subject to treatment may be landfilled • 5-7 years after directive came into force: biodegradable MSW fraction reduced to 75% of 1995 values, 50% after 8-10 y., 35% after 15-17 y.

Returning to PVC it is noted in the ELV directive [5] that the European Commission is still evaluating its environmental impacts after which measures to PVC in ELVs will be proposed.

The future fate of ASR landfilling will depend on its biodegradability, whether it (or the by-products of ASR processing) is categorised as hazardous waste, and whether it makes up a small or large part of wastes that are landfilled. In the US, the 4.7 million tonnes of ASR that is landfilled represents 3.9 % of the 121 million tonnes of MSW landfilled in 1998 [11]. Within the EU there is some disagreement as to whether the dismantling of ELVs or the processing of ASR should receive more attention, with the car industry in favour of the latter [12]. As also noted by Keller [2], the EU's ELV directive statements of 85 % of ELV reused/recovered and 80 % reused/recycled by 1.1.2006, followed by 95 % of ELV reused/recovered and 85 % reused/recycled by 1.1.2015 implies that the option of energy recovery from ELVs is limited to 5 % and 10% of ELV weight, respectively, by these dates.

Based on leaching tests it can be concluded that ASR disposed on landfills will in most cases present small risks when trace metals such as Pb, Cd, Ni, Cu, As *etc.* are concerned. The situation may be different for organic hazardous compounds such as PCBs, PAHs (polycyclic aromatic hydrocarbons), or chlorine -, bromine -, sulphur – or nitrogen containing organics.

An analysis by Das *et al.* [13] addresses the recycling of automobile components from an energy impact and life cycle (LCA) point of view. One aspect is the continuously changing composition of automobile materials: for example the aluminium content has doubled between 1976 and 1992 and was expected to do so again between 1992 and 2002. This will have a large impact on energy consumption of producing an automobile: using 1 kg extra aluminium requires that 5 kg less iron is used to compensate for the increased energy input. It must not be forgotten that around to 90% of the total energy consumed by an automobile is its fuel during product life, and only around 0.2 % is consumed during ELV processing [14]. Fuel efficiency is most important to an automobile's total energy consumption. At the disposal stage, the energy consumption follows from the shredder operation plus the energy saved by using recycled raw materials instead of virgin raw materials.

Overall, the mass of an average automobile decreased during the 1980s and 1990s, at the expense of mainly iron and steel, zinc, lead and rubber. Increasing use is shown for aluminium, plastics (ABS, nylon, PE, PP and PU) and copper. The use of PVC has remained

between 7 and 12 kg per automobile of typically 1200 kg [13]. The increasing plastics fraction represents an increasing amount of material for which recovery and recycling options are limited for technical, economical or safety reasons: using recycled plastics as secondary raw material often gives a lower quality product than a product made from virgin raw material. Das *et al.* [13] consider five recycling scenarios for ELVs:

- 1 thermoplastics recycling
- 2 ASR incineration
- 3 combined thermoplastics recycling and ASR incineration
- 4 bumper and dashboard recycling
- 5 combined ASR incineration and bumper and dashboard recycling

Compared with a cradle-to-grave total energy consumption of around 550-600 GJ the most “optimistic” scenario (3) will give an energy saving of around 8 GJ, whilst the most “realistic” scenario (4) will save around 1 GJ. Incineration of all ASR would, in the US reduce the mass to be landfilled to 20-25 %, while recovery of thermoplastics would reduce its mass to around 80%. This combined with the fact that ASR represents around 1-2% of the total amount of MSW landfilled in the US and Europe explains the lack of interest in recovering recycling fractions from ASR. Nonetheless, while the production of an automobile requires increasing amounts of energy, also increasing savings of energy can be achieved by ELV processing.

2.2 *Composition and properties of ASR*

Whilst the amount of ASR that will eventually be processed for material and/or energy recovery will be dictated by legislation, it will be the composition of the ASR that will determine which process route will be selected and what materials and by-products will be obtained, besides energy recovery. At the same time, ASR processing will generate information and requirements to the upstream ELV processing. For example, the ELV dismantling and processing may complicate ASR processing when ASR qualities or quantities are not sufficiently constant over a certain time span.

As an illustration, the Appendix gives the material breakdown for mid-1990 US family sedan, which will be an important source of current and near-future ASR. A total of 9.3 %-wt of this vehicle is composed of plastics, plus a total rubber content of around 7-8 %-wt. The most important fractions are metals: 64 %-wt iron and steel, 6% aluminium plus smaller amounts

of copper, lead and a few others. The various fluids, adding up to around 5 %-wt will be almost completely drained before shredding. It is noted that the fractions of plastics used in cars, trucks, etc. is increasing at the expense of metal parts, which will further increase amounts of ASR and the urgency of recovery and recycling.

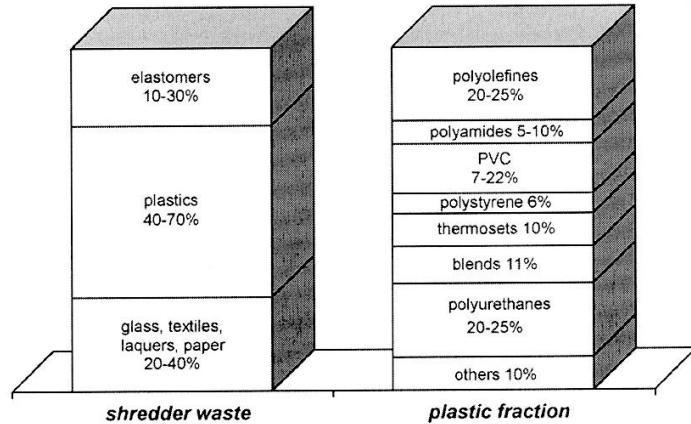


Figure 2 Typical composition of ASR and ASR plastics fraction [9].

What is described here as “ASR” is often referred to as “light” ASR (or “fluff”), besides a “heavy” ASR fraction containing smaller fractions of plastics but larger fractions of non-ferrous metals, glass and dirt. Typical compositions of ASR fractions, as collected from reporting in the open literature since the 1990s are given in Tables 2 through 5.

Table 2 Composition of typical ASR samples

%-wt	[2]	[15]	[13]	[16]	[17]	[18]
plastics	30-48	20	21.5	41		33
plastics (foam)						15
plastics (incl. coatings, textile)					83.1	
Elastomers (incl. rubber)	10-32	20	5.3	21	2.6	18
fibres (textile, wood, paper)	4-26	25	53.7	10		10
Paints, lacquer	3-10			5		
metals	~ 20		8.1		13.5	3
glass, ceramics, electric materials	3-16		3.5	19		
dust, soil, etc.	10-20		excl.			
inert (glass, sand, grit etc.)		35				
other (residues,)			7.9	4	0.6	21
oils, water	15-17					

A typical composition of an ASR and the plastics fraction is given in Figure 2 [9]. It is seen that the largest fraction are plastics, which are mainly poly olefins (PE, PP), PVC, PU (foam and rigid) nylon (poly amides, PA), poly styrene (PS) and several “blends” such as ABS (acrylonitrile-butadiene-styrene) and glass-fibre enforced polymers, all in agreement with Appendix 1.

Table 3 Typical composition data and properties of ASR – major elements

%-wt dry	[2]	[19]	[20]	[21]	[22]	[4,23]	[16]	[13]	[24,25]	[10]
C		50.8	56.6	17.5	60.2	32.8-45.1	44.5	30.0		39.7
H		6.5	7.9	2.1	6.6	4.1-6.1	5.3	3.7		4.6
N	0.9	3.0	2.7	0.5	1.7	0.6-3.1	4.5	1.7		0.92
O (diff)			21.4	17.4	7.8		6.9	7.0		11.8
S	0.6	0.3	0.2	0.25		0.2-1.0	0.2	0.3		0.25
Cl	1.8	3.7		0.05	2.5	0.1-3.4	0.5	1.4	0.5-2.0	
Al	2.0					0.74-10.5			0.7-3.0	
Ba	0.58	0.5								0.0012
Ca	4.0									
Cu	1.1	1.6				0.5-7.1	1.2		0.37-2.6	
Fe	14.1					0.9-15.7	25.7	13.0	3.3-18	
K	0.27									
Mg	0.87								0.05-0.8	
Mn	0.10								0.036-0.11	
Na	0.71									
P							0.7			
Pb	0.51	0.14				0.22-0.65	0.2		0.11-1.1	0.01
Si	7.7						2.1	9.5		
Ti							0.9			
Zn	0.90	1.2				0.8-6.1	1.9			

A British ASR fraction studied by Ambrose *et al.* [18] for the purpose of mechanical recycling of the PP fraction had a thermoplast fraction (which excludes PU foam and many other polymers) made up of 41 % PP, 17.5 % ABS, 12 % PVC, 7 % PA, 6 % PE, 3.5 % PC (poly carbonate), 13 % others. The large PVC content (that can be up to 20 %-wt in some ASRs [9]) will put restrictions on thermal processing of ASR for reasons of equipment corrosion risks by HCl, chlorine (Cl₂) and other chlorinated compounds, formation for dioxins/furans (PCDD/Fs), or a lower quality of products such as pyrolysis oils.

Table 4 Typical composition data and properties of ASR – minor elements

mg/kg	[2]	[4,23]	[16]	[24,25]	[11]	[10]	[26]*
As				20-50	57-63	11	< 2
Ag						< 6	
Br							< 20 - 90
Cd	61	50-80		< 85	14-200	160	< 0.4 - 3
Co				< 33			< 1
Cr	1200	50-660	800	1000-1800	247-770	280	8 - 39
F			500				< 30
Hg	2.1			< 4.9	0.7 - 15	1.6	< 0.1
Ni	1200	130-930		400-1500			4 - 24
Sb				180-3200			< 3 - 43
Se						5.8	
Sn	67			130-400			123 - 220
V				< 150			< 1 - 1

* Dry PU foam recovered from ELV seats

Table 5 Typical composition data and properties of ASR – other properties

	[20]	[22]	[16]	[4,23]	[24,25]	[11]	[10]	[2,27]	[26]*
Moisture (%-wt)	1.3	0.8	2.2		2-5		27.3		0.25-3.6
Volatiles (%-wt dry)	74.4	61.3	54.2				52.4		
Ash (%-wt dry)	12.1	0.8	36.2		28-61		43.2		
PCBs (mg/kg)						1.7-320		5-14	« 50 \$
PAHs (mg/kg)								10-36	
PCDD/F (µg/kg)								0.014	
Lower heating value (MJ/kg)			16.7					7-26	
Higher heating value (MJ/kg)	28.3 §	28.7			9-20		18.2		25.3-26
Density (kg/m³)			359	283-563			380		

* Dry PU foam recovered from ELV seats

\$ May be above 50 mg/kg when contaminated by ASR

§ Volume based: MJ/m³

Problematic compounds in ASR that often leads to its classification as hazardous waste are PCBs. VTT reports typical values of 10-400 mg PCB /kg ASR in the US, although typically below 100 mg/kg. In Europe (*e.g.* Germany) values are typically below 10 mg/kg. One reason for high PCB levels is the co-shredding of ELVs with scrapped refrigerators and other household equipment waste, as also occurs in Finland [28].

After PVC/chlorine and PCBs a third problematic ASR fraction are the trace elements and heavy metals. For all metals, except mercury (Hg) and cadmium (Cd), the concentration levels are about 10 × higher than in municipal solid waste (MSW). Also values for Cu, Zn, Cd, and Pb are high and for Cu the content is similar to that of exploitable ores [40,41]. The content of mercury in ASR is typically around 0.5 mg/kg, which is roughly half the Hg present in the ELV before shredding (Hg is mainly used in switches) although values up to 15 mg/kg have been reported [11]. Cd is typically found at 10-100 mg/kg in ASR, for Pb the levels are much higher, typically 500-12000 ppm (0.05-1.2 %), for chromium (Cr) typically 200-800 mg/kg, for arsenic (As) around 60 mg/kg.

A study by Mirabile *et al.* [16] on the use of ASR in blast furnaces for iron ore processing (see section 3.7) also addressed the toxicity and mutagenicity of the ASR. It was reported that the ASR (composition included in Tables 2-5) has a not-high toxicity and a weak mutagenicity.

2.3 Fuel properties of ASR

In a recent study by Pasel and Wanzl [9] different methods for thermal or thermochemical processing of fuels or other waste materials containing high-calorific fractions were listed as in Table 6.

Table 6 Thermochemical methods for recycling processes [9]

Process category	Main reactions	Requirements with respect to the feedstock	Process aim
Hydrogenation	reaction with H ₂ + thermal cleavage	homogeneous material, low content in inerts	recycling of raw materials
Hydrolysis	reaction with H ₂ O	homogeneous material, pure polycondensates	recycling of raw materials
Gasification Combustion	reaction with H ₂ O, H ₂ , O ₂ reaction with O ₂	organic matter	fuel gas, synthesis gas
Pyrolysis	thermal decomposition	organic matter	recycling of the energy content

The most suitable method must be selected on the basis of how homogeneous the material is, how much unwanted or inert fractions are present and what the aim is from the viewpoint of energy and product output. A comparison between ASR and other waste fractions, being used tyres, MSW plastics and (dry) sewage sludge, as given by Pasel and Wanzl [9] is given in Table 7.

**Table 7 Composition data on ASR compared with a few other solid wastes [9]
(maf = moisture- and ash free)**

	Shredder waste	Used tyres	Municipal waste plastics	Sewage (dry)
C (wt.%maf)	60–90	80–90	80–90	40–60
H (wt.%maf)	8–12	6–8	9–10	5–7
N (wt.%maf)	1–4	<1	<1	1–3
O (wt.%maf)	5–30	2–3	<1	23–27
S (wt.%maf)	1–3	1–3	<1	1–2
Cl (wt.%maf)	2–5	–	0–5	–
Ash (wt.%)	~ 50	6	0–5	22
Volatiles (wt.%maf)	~ 90	50–60	~ 90	60–90

Lanoir *et al.* [17] conducted a fuel characterisation study on ASR, aiming at combustion in a MSW incineration plant (MSWIP) or a cement kiln. Four features are considered most important: calorific value, ash content, chlorine content and metals content. The result of the study gave the values LHV: ~ 19 MJ/kg, ash content: ~ 38 %-wt, chlorine content: ~ 3.5 %-wt, metals: ~ 22 % (including ~ 13 % iron) - Figure 3 gives more details.

Roy and Chaala [4] give a relation between the gross calorific value, *i.e.* higher heating value of ASR and its organic content (as received), based on ten ASR samples:

$$\text{HHV (MJ/kg)} = 0.34 \times (\% \text{ organic fraction, as received})$$

Information on the behaviour of a material during thermal processes can be obtained from thermogravimetric analysis (TGA) which implies following the mass change of a solid or liquid sample at a constant or varying temperature while contained in a gas atmosphere that is oxidising, reducing or inert. Temperatures, heating rates, gas composition and often also pressure can be varied as to simulate, for example, a combustor or a pyrolysis reactor. A TGA study on a Finnish ASR made by VTT [1] showed that in a nitrogen atmosphere, the ASR sample mass decreased by pyrolysis to the final ash content (around 50-60% of the initial mass) over the temperature range 250-450°C. When an oxidising atmosphere was used the main pyrolysis stage was completed already at 400°C, followed by a slower mass loss process

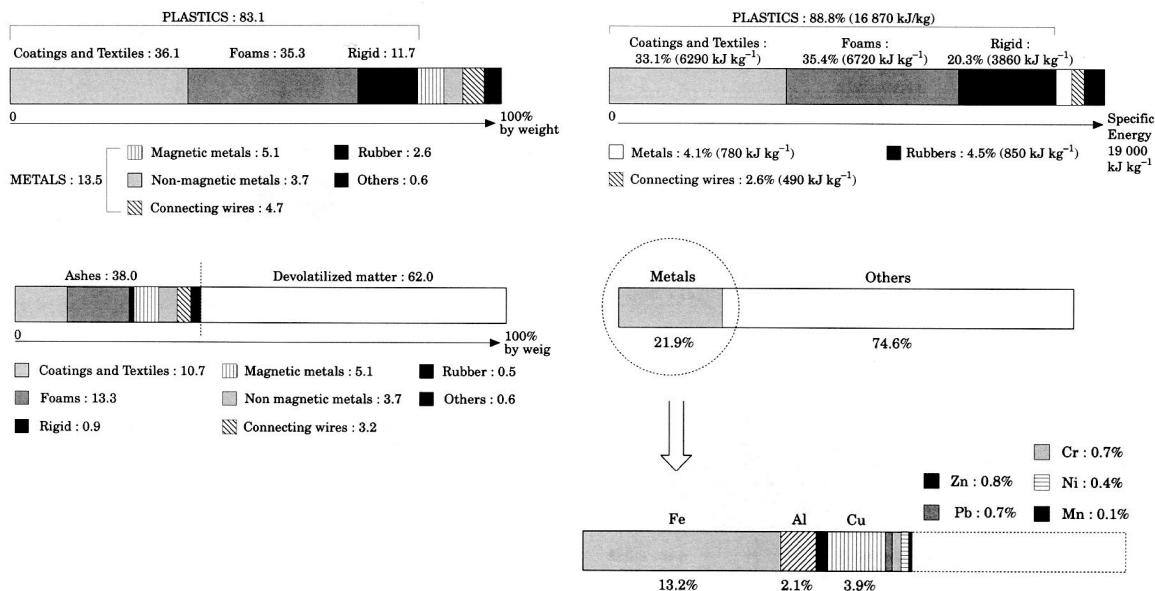


Figure 3 ASR characterisation: material fractions, energy content, ash content, metals content [17]

of a further 24 % that continued up to 600°C, which was explained from the presence of woody fractions in the ASR.

Rausa and Pollesel [20] combined TGA with Fourier transform infrared (FTIR) gas analysis (heat-up at 20 K/min in He until 850°C, followed after a certain holding time by addition of oxygen for char burnout). The result showed a maximum rate of mass loss at ~ 425 °C, with a first mass loss of ~ 15 % at 200-340°C, with (at ~350°C) 80% of the ASR chlorine as HCl, some HCN and several isocyanic acid (CNO) esters, a second mass loss of ~ 55 % at 340-550°C as “saturated medium-long chain hydrocarbons” of the -CH₂- type, the remainder of the chlorine as HCl (at ~ 490 °C), plus NH₃, H₂O, CO₂, SO₂; a third mass loss of ~ 5 % at 700-850°C of CO and CO₂; and finally a mass loss of ~ 5 %-wt resulting from char burnout after addition of O₂. Altogether, the product spectrum was ~ 60 % -CH₂-, ~ 19 % CO₂ + CO, ~ 5 % H₂O, ~ 3.5 % HCl, ~ 2.5 % NH₃, 0.4 % SO₂, plus HCN, CNO-esters etc. The final ash residue amounted to ~ 13 % of the initial sample.

In addition to this TGA/FTIR analysis, a flash pyrolysis (heat up at ~ 20000 K/s) to 600, 800 and 850°C in He was analysed, with MS/TIC (mass spectroscopy / total ion chromatography) was conducted, focussing on the formation of hazardous compound such as PAHs. It was found that while at 600°C benzene, toluene and styrene were the main aromatic products,

more alkyl/alkenyl substitutes and PAHs such as alkyl napthalenes and even the carcinogenic benzo(a)pyrene were formed at the higher temperatures 800-850°C. Formation routes to these can be Diels-Alder reactions and the production of aromatics via polyene radicals [20]. Apparently, high heating rates followed by short burnout times (or short residence times at high temperatures) may lead to high concentrations of PAHs in ASR pyrolysis product gases. (See also section 3.5 where also pyrolysis oils and chars are discussed).

Mastral *et al.* [30] made an assessment of the preferable thermal method for the processing of organic residues from car interior decoration industry. Seven organic samples were considered: two wood-type samples, three polymer foam-type fractions, a PU foam and a tyre rubber sample. Pyrolysis (referred to as thermolysis) in nitrogen or air (up to 750°C), FBC (725°C, 5 % excess O₂) and hydrogenation (400 °C, 15 bar, 30 min in H₂). It is concluded that FBC is preferable for the first two materials. For the samples containing foam, nylon, and glass fibres a pyrolysis type process is preferable: combustion of these will give problems with respect to NOx emissions and, in an FBC the melting of the glass fibres may give problems. It will instead be more feasible to remove the nitrogen from fuel oils produced by pyrolysis. Also from car tyres a good quality oil can be obtained by pyrolysis. The PU sample, hydrogenation could convert it for 67 % into gases, 32 % as oils and less than 1 % residue.

In an attempt to predict the gaseous products from ASR combustion, especially noxious gases such as NOx, HCl, SO₂, HCN, VOCs, CO) Lanoir *et al.* [31] incinerated a mixture of PVC (40 %) + PU (45 %) + tyre rubber (15 %). This synthetic mixture represents the major polymers found in ASR that may give rise to these pollutants. It was reported that there is not much interaction between the polymers, except for some interaction between tars and chlorine. Most problematic according to this study, will be CO, H₂S and VOC emissions, products of incomplete combustion, besides HCl.

Yoshiie *et al.* [32] report the chemical composition of an ASR fly ash from a CFB combustor and compared it with a fly ash from a refuse-derived fuel. The result given in Table 8, shows clearly the much higher trace element (“heavy metals”) content of ASR ash, especially for Cu, Zn and Pb, higher Fe and much lower contents of alkali and phosphorous.

**Table 8 Composition of fly ashes of RDF and ASR from CFB combustion [32].
(SD = Shredder Dust, i.e. ASR)**

Elemental composition of fly ash from CFBC burning of RDF (dry base)				Elemental composition of fly ash from CFBC burning SD (dry base)			
Major species		Heavy metals		Major species		Heavy metals	
Substance	Content (wt%)	Substance	Content ($\mu\text{g/g}$)	Substance	Content (wt%)	Substance	Content ($\mu\text{g/g}$)
SiO_2	24.2	Zn	927	SiO_2	18.7	Zn	8.29×10^3
CaO	36.6	Cu	351	CaO	28.0	Cu	1.83×10^4
Al_2O_3	11.5	Mo	346	Al_2O_3	10.0	Mo	353
MgO	2.45	Pb	288	MgO	1.74	Pb	4.08×10^3
Fe_2O_3	1.77	Cr	119	Fe_2O_3	9.23	Cr	230
P_2O_5	1.48	Ni	69	P_2O_5	0.00	Ni	977
TiO ₂	0.76	Sn	54	TiO ₂	2.30	Sn	455
Na ₂ O	2.57	Cd	41	Na ₂ O	0.96	Cd	14
K ₂ O	1.74	As	2.0	K ₂ O	0.24	As	No data
Unburnt carbon	< 1 (wt%)			Unburnt carbon	< 1 (wt%)		
S	0.31 (wt%)			S	0.74 (wt%)		
Cl	3.10 (wt%)			Cl	4.91 (wt%)		
Ignition loss	12.1 (wt%)			Ignition loss	15.48 (wt%)		

Ash from the ASR considered by Saxena *et al.* (42.8 %-wt ash, after removing large metal pieces from the ASR) shows an ash fusion temperature of around 1410°C under reducing conditions, and 1560-1690°C under oxidising conditions [10], for which Rausa and Pollesel [20] report 1080-1100°C. (Earlier, the lower value for this, *i.e.* the initial deformation temperature, was used to define the upper limit for the bed temperature in fluidised bed combustion, FBC).

Finally, a characteristic of ASR that may give problems are the self ignition properties of a stockpile. A series of tests reported by Horii and Iida [33] (who report also a heat conductivity $\lambda = 0.32 \text{ W/mK}$ for ASR) estimated that for 7-8 m high stockpiles spontaneous combustion may occur at 40-50°C self ignition temperature, with a safer value of 70-80°C for a pile 2-3 m high. For safety, spraying with water should be applied for cooling.

2.4 ASR processing in Finland

In Finland, as in most other countries, practically all ASR generated is landfilled, although Scheirs [50, p. 519] speaks of co-combustion of ASR with MSW and with coal in Finland (probably in fluidised bed incinerators). Car shredders are located at Heinola and Airaksela (both Kuusakoski Oy), Vantaa (Seutulan Uusiometalli Oy) and Lapua (Jylhän Metalliromu Oy), which cover the 80-90 % of Finnish ELVs that is being recovered. Two additional shredders will be taken into operation in the near future [28]. The largest amount of ELVs being processed by Kuusakoski Oy under the CARREC® process [28, 35]. At the end of the 1990s Kuusakoski Oy generated around 10000 t/y “fluff” from air classification after shredding, plus around 8000 t/y of a rubber-type fraction referred to as “UK-kumi” from a second, sink/float-type separation process. These fractions are both disposed of at Kuusakoski’s own landfill space [1, 42]. At the landfill at Airaksela annually from around 37000 ELVs around 4000 t of ASR is produced which is deposited at the site (data from [36]).

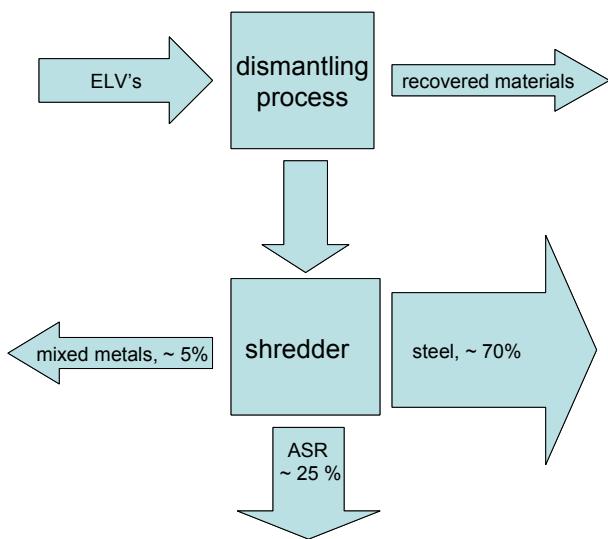


Figure 4

Simple scheme of ASR processing at Kuusakoski Oy (after [1], [35]).

The Finnish car recycling organisation *Suomen autokierätys Oy* aims at improving the possibilities for material- and energy recovery from ASR [28]. Nevertheless the Finnish Working Group for ELVs suggests for the future that “The non-recoverable part of the vehicle is disposed of in a landfill” [28]. Looking at the EU ELV directive this non-recoverable part must be less than 15 % of the ELV weight by 1.1.2006, and less than 5 % by 1.1.2015, however. For waste-to-energy (WtE) processing the waste-derived fuels from ASR should be classifiable as much as possible as Finnish SRF (solid recovered fuel) class I – see the SRF classification given in Table 9. For class II and III SRF the available capacity for WtE capacity is negligible.

**Table 9 Quality classes of Finnish SRF (solid recovered fuel)
(Finnish standard SFS 5875/2000) [37]**

(dry matter)	SRF I	SRF II	SRF III
Cl % -wt	< 0.15	< 0.5	< 1.5
S % -wt	< 0.2	< 0.3	< 0.5
N % -wt	< 1	< 1.5	< 2
P % -wt	< 0.2	< 0.4	< 0.5
Al % -wt	special	special	Special
Hg mg/kg	< 0.1	< 0.2	< 0.3
Cd mg/kg	< 1	< 2	< 4

According to Finnish statistics for 1997 (reported in 2000), 5750 tonnes of ASR were generated, listed under “waste” (not as “hazardous waste”) from manufacturing that year [34, p. 48]; and from 78 tonnes hazardous wastes from ELVs only 3 tonnes were processed at hazardous waste treatment plant [34, p. 90]. Of a total of 12750 tonnes of waste from ELVs, 4939 tonnes were landfilled [34, p. 82]. Under EWC category 16, ASR is listed under number 160105, “light residue from auto shredding” [34].

2.5 ASR processing in Switzerland

In Switzerland, one of the richest European countries, non-EU member, strong action has been taken towards ASR processing since 1991. The country has no automobile industry and the amount of ASR to be processed annually is of the order of 60000 t. Legally the ASR, referred to as RESH (REsidue from SHredding) is hazardous waste [38]. As a first short-term solution, since the mid-1990s ASR is mixed at up to 5 %-wt with MSW fractions that are incinerated, and after a start-up period (1996-1999) currently all Swiss ASR is disposed of by thermal methods, following a ban on ASR landfill that became effective as of February 1996. In year 2001, 62209 t of shredder residue (of which an estimated 40000 t from ELVs) was processed at incineration plants in Switzerland (around 29000 t) and Germany (around 21000 t) and the Citron recycling plant (see also next chapter) at Le Havre, France (around 11600 t). It must be noted that the Swiss Auto Recycling Foundation covers 80% of the costs for all this [27, 29, 39].

For the future, it is planned that for the medium-term a processing plant especially for the processing of ASR is taken into operation and in December 2001 the Reshment process (see also next chapter) was selected as the most promising technology. After finding a proper

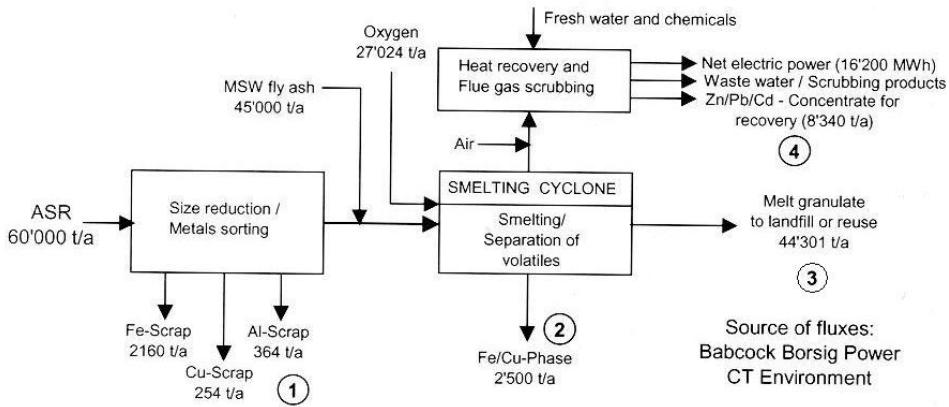


Figure 5 Simplified schematic of the Reshment process [3]

location one Reshment plant will be built that will process all Swiss ASR plus the fly ashes from MSW incinerators. A schematic of the Reshment process is shown in Figure 5.

The Reshment process by Babcock Borschig Power CT Environment is based on a smelting cyclone. After mechanical size reduction and removal of bulky material (mainly iron, copper, aluminium) a fine (< 5 mm) material composed of organic fractions, metals, metal oxides, glass and ceramics is feed to the melting cyclone furnace. At around 2000°C, under the addition of oxygen the organic fraction is decomposed, a reduced iron/copper melt (with some dissolved heavy metals such as chromium) is separated by gravity and what remains is a melt granulate that contains most of the minerals, glass and ceramics and some aluminium, which can be safely landfilled. The flue gases are cleaned after burnout in a post-combustor, which produces electricity plus a Zn/Pb/Cd slag, waste water and scrubbing products. Predicted values for metal recovery from the processed shredder residues are Al: 35%, Pb: 82%, Cd: 98%, Fe: 91.5%, Cu: 89.5%, Zn: 92% [39].

For the longer term, however, Switzerland aims at a sustainable system of automobile production, use and disposal of automobiles which a maximum of closed material cycles. This will require efforts especially from the car manufacturers, improving *e.g.* plastics labelling, producing easier to dismantle vehicles and providing lists of materials used in certain vehicles. The transition into this final stage will put strong pressures on the car dismantling and ELV components recycling business. Central issues for Swiss ASR processing, from the short-term to long-term are that its management is acceptable from an environmental point of view and that recovery, recycling and reuse methods must be technically and economically feasible and preferable over production from virgin raw materials [2, 27, 40, 41].

3. Processing of automotive shredder residue (ASR)

3.1 Mechanical recycling and material recovery

Options for recycling ASR fractions were discussed from the Australian point of view by Gomes and Thai [43]. As mentioned above, in most cases the stability of ASR against leaching is such that landfilling should not give problems. The recycling of polymers such as PET, PE and PP requires that recyclates are clean, and that applications for these materials can be found. But before that, methods for the identification of different materials should be improved and for large pieces such as PU foam or bumpers it is essential that they are removed before the shredding process. For those materials that are too contaminated for mechanical recycling, feedstock recycling (pyrolysis, hydrolysis or depolymerisation) or energy recovery are the only options, besides landfill.

Mechanical processing can give recovered fractions that may be recycled, or can be used to improve the quality of ASR by removing harmful substances, or increase its value as a waste-derived fuel [1].

A separation based on density differences allows for separating the organic (plastics) and inorganic (metals and glass) fractions in ASR – see Table 10 for some typical values for the density of components of ASR.

Table 10 Densities of ASR fractions (data from [44])

(g/cm ³)	Cu	Fe	Al	Glass	PVC	PUR	PA	Rubber	ABS	PP	Wood	Paper
Density	8.8	7.9	2.7	2.5	1.4	1.2	1.1	1.1	1.1	0.9	0.8	0.7

Density separation is also the heart of the WESA-SLF process for which a 4 t/h plant is operating at Eppingen, southern Germany [44] – see Figure 6. The ASR must be reduced to a size less than 7 mm as to assure that insulation is stripped off copper wires, which is accomplished by a two-stage comminution process. Before that, the ASR is screened to remove a fines fraction smaller than 1.2 mm, which is mainly sand. Then, the remaining ASR is cut in a rotary shear to a size below 20 mm, magnetic components are removed, the size is

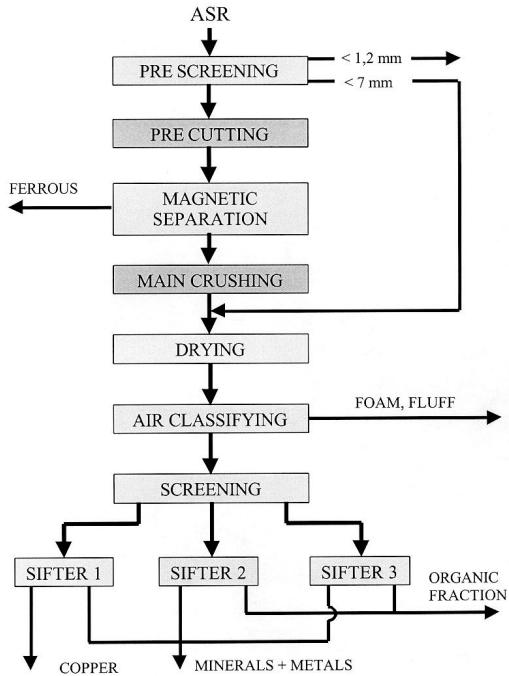


Figure 6 The WESA-SLF process for mechanical separation of ASR [44]

further reduced to below 7 mm by a double shaft cutter with an integrated sieve and it is combined with the 1.2-7 mm fraction from the first screening stage. Before the material can be further separated into different density fraction it must be dried from 5-25 % to less than 2 % moisture. After an air classification step (to remove for example foam) the material is screened in three fractions using a multi-level sieve followed by a zigzag air sifter. The four product fractions obtained are then 1) a magnetic fraction (~95 % iron), 2) a fraction containing copper granules, 3) a mixture of minerals and some metals, and 4) an organic fraction containing ~ 50 %-wt C, ~6 % H, ~ 12 % O, 1~2.5 % Cl, 20~28 % ash, < 0.5 % metal, with a calorific value > 23 MJ/kg. By making some adjustments to the process it is possible to lower the Cl-content of the organic fraction. The first two product fractions are sold to metal industry and the third fraction is further processed for copper and aluminum recovery. For the fourth, organic fraction a waste-to-energy process, use as carbon source in steel plants or use for methanol production is suggested. ASR processing costs are of the order of 60-75 €/t for this facility.

Also in Japan ASR processing receives a lot of attention: as of April 1996 ASR may be disposed of only in controlled landfills, for which the capacity is scarce. Annually around 1 million tonnes of Japanese ASR must be processed. Kusaka and Iida [45] describe a process

for sorting, compacting and solidification of ASR which basically separates the combustible and non-combustible fractions. During the sorting step the iron, non-ferrous metals and glass are extracted, during the compacting/solidification step the combustible (mainly plastics) part is processed into a fuel suitable for “dry distillation/ gasification” (see section 3.4 below). Figure 7 gives an overview of the process set-up for ASR sorting, compacting and solidification. It is seen that slaked lime, Ca(OH)_2 , is added for the purpose of trapping HCl released during the gasification process. Kusuka and Iida note that a moisture content above 20 % in the residue for solidification gives problems during the compacting/extruding/ forming rolling stage. Often large amounts of water are added to the ASR during the shredding stages to avoid fires from breaking out [45].

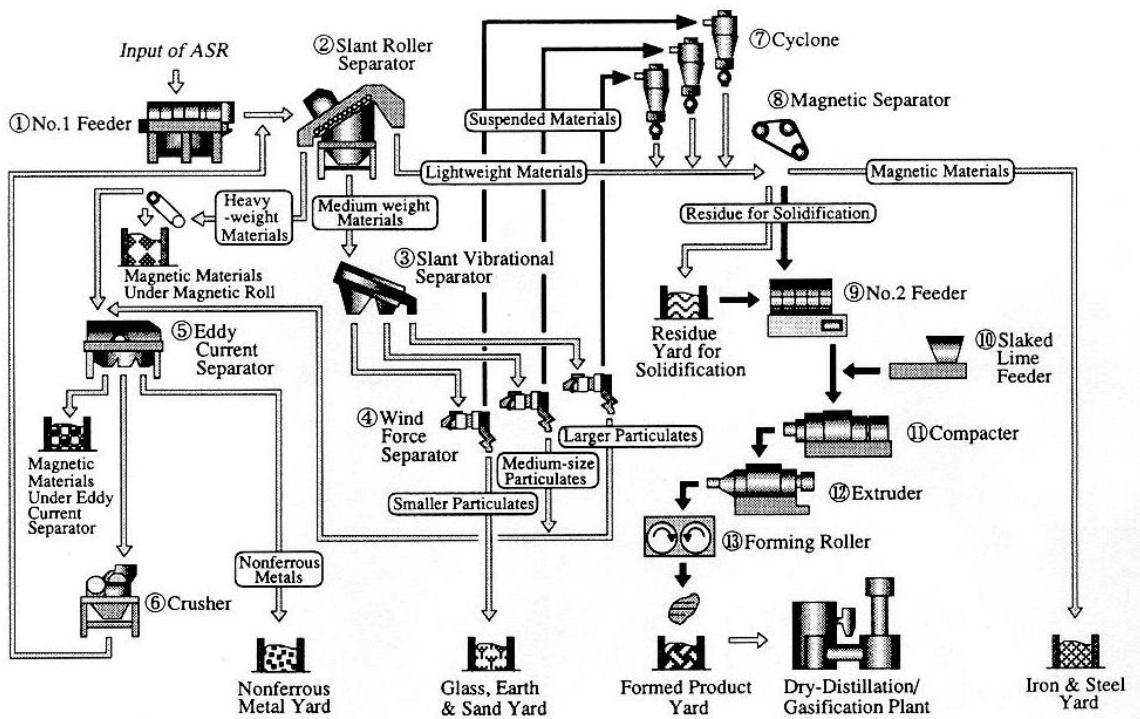


Figure 7 Flow scheme of ASR sorting, compacting and solidification [45].

Brunner *et al.* [46] made an analysis of how different materials are distributed over the different particle size classes of ASR, aiming at possibilities to remove certain size fractions as to improve recovery of for example copper, or to remove problematic species before further processing. The first finding is that the largest particles, *i.e.* > 30 mm or > 50 mm, contain mainly large metal parts or pieces of textile, wood, rigid plastics or foam. For the finer sizes it is difficult to identify such fractions. Nonetheless, analysing different size fractions gives distributions for the elements Cl, Cu, Pb, Cd and Zn as shown in Figure 8.

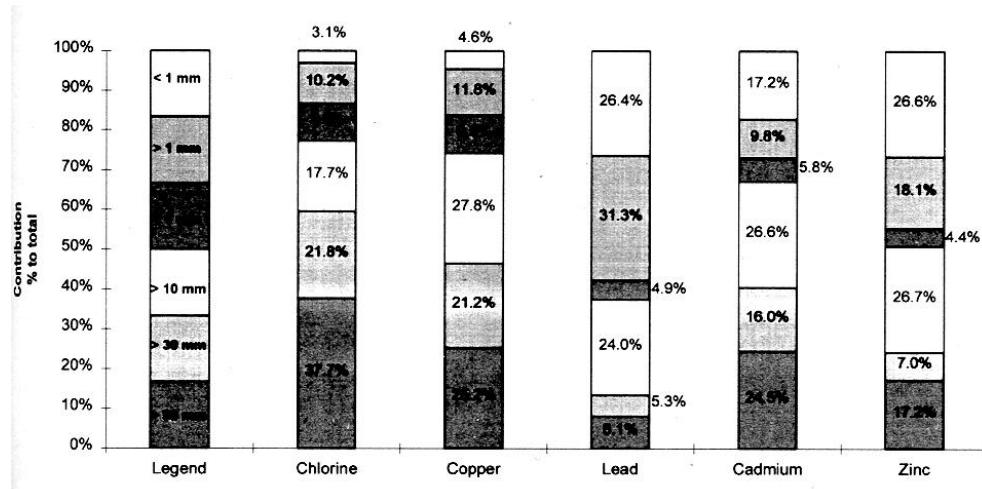


Figure 8 Distribution of several elements in ASR over size fractions [46]

As Brunner *et al.* [46] conclude, Cu is found mainly in the coarser fractions, as are also As and Cd, whilst Pb is found mainly in finer fractions. Chlorine is found for more than 60 % in the coarse fractions > 30 mm (coated textile, coated cables). For Cl, Cu, and Zn, Figure 9 shows how much of these species can be removed from the ASR when a certain size range is removed.

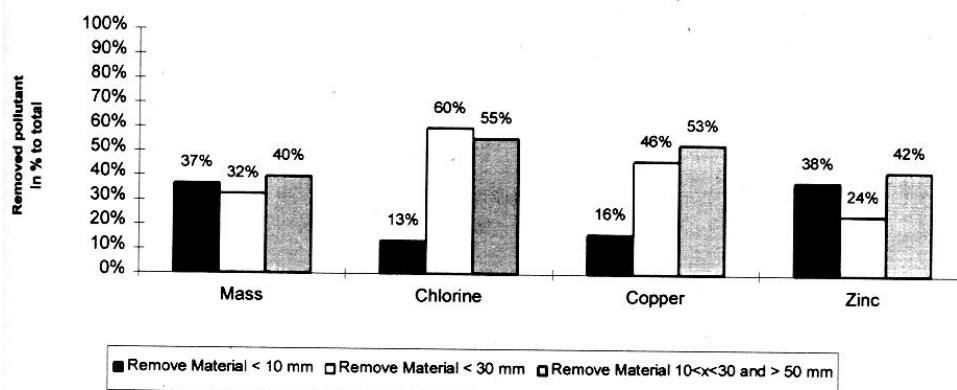


Figure 9 Analysis of how much of a certain species can be removed from ASR by removing a certain size fraction [46]

This study shows that in principle certain size fractions can be removed as to reduce the concentration of certain species. Also technically this is not too complicated. However, it would be desirable to remove *e.g.* 80 % of some material or species while not removing more than 20 % of the ASR [46]. As also the result in Figure 15 shows, this is hardly possible, especially when process economy is taken into account as well.

Flotation is an effective method for the separation of mixed plastics fractions based on differences in density, surface properties and chemical properties of polymer and additives [47]. One of the greatest challenges of this method, the separation of PVC from PET, is hardly a problem for ASR because this contains relatively large amounts of PVC and small amounts of PET when compared to other plastics-containing waste streams. By adding promoters to the water it is possible to separate also difficult mixtures, such as nylon 66 (PA 66) from PA66/ PC / ABS, as shown by Mutkowska *et al.* [48]. Addition of NaOH altered the hydrophobicity of the PA66 and ABS fractions, while leaving the PC unaffected, which eventually led to 100% selective separation efficiency for the PA66.

Ambrose *et al.* [18] analysed the recyclability of PP, which is the most abundant thermoplast in ASR. It was shown that after granulation and moulding into tensile stress samples the material fulfils the specification for high quality automotive application, even before addition of strengtheners such as talc.

Work at the Dutch organisation ARN (Auto Recycling Nederland bv) shows that PU foam seat material of good quality can be recovered relatively fast and easy but that applications for this material must be found. For transport, this bulky material must be baled to reduce costs. Other ELV materials that are recovered at ARN for recovery of plastics are bumpers, radiator grills, blinkers and rear lights, and hubcaps (wheel finishers) [49, 14]. For the future, the EU's ELV directive will enforce the processing of ASR, if the recovery and recycling is not shifted more to the ELV dismantling stage.

The glass from ELVs is sometimes removed and sold as a second-hand item, but most glass ends up on landfills with the ASR after shredding. For windshields, however, increasing recycling is seen in the US as a result of the demand of the plastic laminates used (PVB, poly vinyl butyral). This resulted in efforts to separate windshield glass from plastics, improving recovered PVB quality [11].

Weiβ and Momber [52] describe a method for treatment of carpet waste (from example from automotive components), separating the carpet fibre (plastics or textile) from its support backing material (latex, chalk-filled foam) by using a high-speed water-jet. The jet destroys the backing material whilst the fibres can be re-used.

3.2 Thermal processing of ASR – 1. Incineration / combustion

Combustion is defined as complete oxidative conversion of a fuel in order to produce heat. The stoichiometry (air factor) is $\lambda > 1$. Typical combustion reactors for low-grade fuels and wastes are based on grate firing, kiln firing and fluidised bed combustion (FBC). For waste combustion usually the term “incineration” is used since the objective is then usually not to generate heat and power but to reduce the volume. In most cases chlorine concentrations prevent the production of high temperature steam, but when energy is generated from specially prepared waste-derived fuels one refers to waste-to-energy (WtE) or energy-from-waste (EfW) processes.

The ash content (from proximate analysis) of ASR is rather high, so combustion /incineration (but also gasification) will give significant amounts of ash. Also the concentration of toxic gases and solid residues from ASR combustion as such, *i.e.* without another fuel or waste, will be very high. Examples are gaseous emissions of dioxins/furans, NOx and trace elements such as Cd and Pb, and high concentrations of many trace metals (Zn, Pb, Ni, Cd, Sb, As, Sn, ...) and organic compounds, especially chlorinated ones, in ashes, slag and gas clean-up sludge. Therefore, activities on mono-combustion of ASR are practically non-existing and reports cannot be found in the open literature.

Saxena *et al.* [10] conducted a study on ASR incineration in an FBC, with the objective to produce heat and vitrified agglomerated ash. Combustion of 5.6 mm ASR particles in a bubbling FBC with alumina as bed material at 950-1139 K, with propane as pilot fuel showed that in principle FB combustion is possible, but that the gaseous emissions (CO, HCl, NOx, SO₂) can be problematic. Fluctuations in fuel quality and fuel feeding result in CO emissions up to 1.6 %-vol, at 3.6-15 %-vol O₂. Emissions of HCl, NOx and SO₂ were up to 13000 ppmv, 400 ppmv and 1500 ppmv, respectively, and are very much depending on excess air, gas velocity, bed temperature and fuel feed rate. It was suggested to use staged combustion for better burnout of the CO, and to make compressed pellets from the ASR fuel as to reduce fuel-feeding related fluctuations. Air preheating would allow for stable combustion without pilot fuel. For the ash produced it was found that it passes a toxic characteristics leaching procedure (TCLP), for which the ASR itself gave too high leaching for lead and cadmium.

3.3 Thermal processing of ASR – 2. Co-firing

Co-combustion or co-incineration of ASR, most importantly with MSW, is an option that has been investigated at several locations in Europe. For ASR Switzerland, for example (see also section 2.4) the co-incineration with MSW (partly in German MSW incinerators) currently covers more than 80% of the ASR treatment, as the short-term solution to the problem. The objectives are the same as for MSW incineration: mineralization and immobilisation of the inorganic fraction and destruction of the organic fraction, with production of steam for district heating or electricity generation as by-products. Because of the high concentrations of trace metals and chlorine the fraction of ASR in the MSW/ASR mix should, however, not exceed 10 % of the feed as to stay within legal regulations for emissions with the flue gas and for residue treatment.

A test campaign at the MSW incinerator plant (MSWIP) at Horgen, Switzerland showed that contents of metals, chlorine and sulphur in the fly ashes, gas cleaning sludge and bottom slag increases but stays inside regulations. The copper content in the bottom slag was found to be significantly higher with 10 % ASR co-firing, and chlorine, cadmium, copper and zinc levels were significantly higher especially in the fly ashes from boiler and ESP – see also Figure 10.

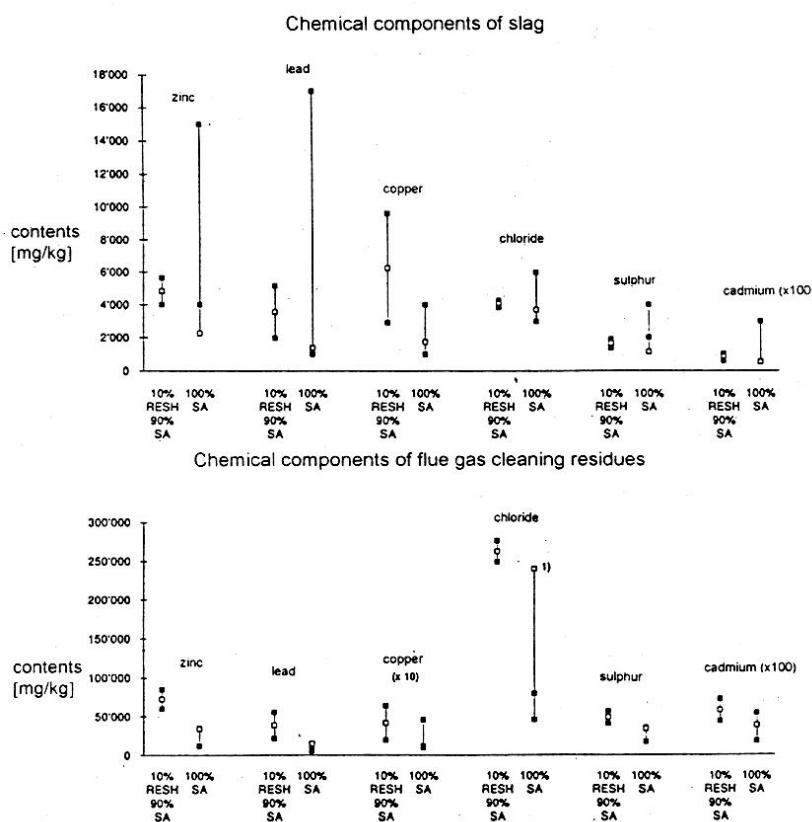


Figure 10

Comparison of the composition of the slags and flue gas cleaning residues from MSW firing and from MSW/ASR co-firing [38]

Also, increased concentrations of dioxins and furans (PCDD/Fs) and PCBs in the boiler ash were found, without becoming intolerable, however. The fly ashes and flue gas cleaning sludges are more fragile and dusty during co-firing, which has its effect on stability against leaching. Leaching tests on the residues for a certain test showed that zinc strongly exceeded the test. It was found that for a constant steam production, as a result of the higher calorific value of the ASR, an ASR amount equal to 10 % of the MSW initially fired could replace 14 % of the MSW. At this MSWIP, ASR can be co-fired with MSW at up to 10% of the energy input, but that the quality of the ashes, slag and sludges must be carefully controlled. Bottom slag must be landfilled. There was no need to make any changes to the operation of the MSWIP [38], and based on these and later tests (at Bazenheid, Switzerland for example) recently a value of 6 % was recently reported for MSW/ASR co-firing “without severe problems” [2].

In a study by the APME (Association of Plastics Manufacturers in Europe) and APC (American Plastics Council) the co-firing of ASR with MSW at higher mixing fractions than in the Swiss work was tested at an MSWIP at Würzburg, Germany [24, 25]. At this plant, during the period 1993-1996, around 4000–9000 t ASR was co-fired with 110.000-120000 t MSW, annually, *i.e.* an ASR mixture fraction of 3.6-8.4 %. With the aim of analysing operational problems and the influence of ASR on gaseous emissions and solid residue quality, one-day tests were made co-firing MSW/ASR in a 76%/24% mix (by weight), a 69%/31% mix, and a 69%/31% mix with a coarse (> 15-20 mm) ASR fraction. No operational or other problems, such as deactivation of the SCR DeNOx catalyst by As, were encountered. Overall, CO emissions were reduced and although the concentrations of dioxins/furans (PCDD/Fs) and trace elements such as Cd, As, Pb and Zn were increased by up to a factor of 6, this posed no problems to the plants gas clean-up equipment. Clean gas concentrations complied with regulations, PCDD/F concentrations were ~ 0.0025 ng (TEQ)/m³ STP. The grate ashes showed higher concentrations of especially Zn but also Cu, Sb, Ni, Sb, Pb, Sn, when compared to MSW firing, but the leachability of pollutants from this ash complied with the German LAGA standards for re-use of this material. The boiler ashes, fly ashes and baghouse residues are classified, by definition, as hazardous waste.

3.4 Thermal processing of ASR – 3. Gasification

Gasification is defined as a thermo-chemical conversion of a carbon-containing material using a gaseous compound such as water, air, oxygen and mixtures of these, producing a gaseous product. The stoichiometry (air factor) is in the range $0 < \lambda < 1$. Three main types of gasification reactors are being used: 1) moving beds (updraft, or downdraft), 2) fluidised beds and 3) entrained flow reactors. Particle sizes are of the order of 10 mm, 1 mm and 0.1 mm, respectively, for these reactors, temperatures vary from 400-500°C to more than 1500°C and residence times can very from more than an hour to less than a second. Gasification can be accomplished with air, steam, oxygen or mixtures of these, the process is exothermal (can in special cases be operated adiabatic) and produces a combustible product gas (fuel gas) plus ashes. Advantageous for ASR is that no dioxins/furans are produced because of the oxygen deficiency, that metals may be recovered from the residues partly non-oxidised, that valuable gases are produced and that the volume of the product gas is small when compared to a combustor flue gas.

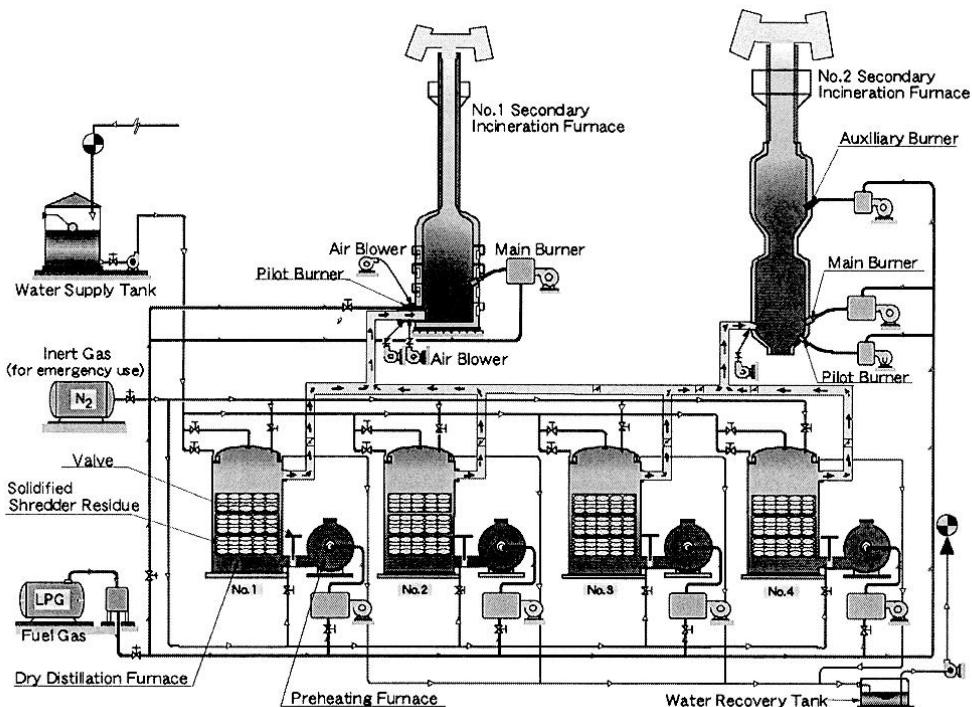


Figure 11 Schematic of the dry distillation/gasification process [53]

A process for ASR gasification, referred to as dry distillation/gasification is being developed in Japan [53]. After ASR sorting/compacting/solidification (see section 3.1) so-called “wafers” are obtained (20-30 cm × 15 cm × 2 cm) that contain mainly the plastics and other

combustible fractions of the ASR, with a heating value of ~ 25 MJ/kg and a density of ~1200 kg/m³. A schematic of the process, which aims at reducing the volume of the solidified ASR fraction to less than 20%, is seen in Figure 11.

The dry distillation gasification implies that a gas of 1000-1200°C containing 0-7% O₂ is passed over these wafers, the gases plus entrained particles are burned in a secondary combustor. The residence time for one batch is ½ – 1 hour. After the gasification, copper, aluminium and other metals, plus carbon, may be recovered from the residue.). In order to trap the HCl that is released, 1.2 %‐wt Ca(OH)₂ (giving a Ca/Cl₂ ratio 3½:1) is added to the material during the sorting/ compacting/solidification stage, which reduces the HCl concentration to a few ppmv. It was found that the temperature of the ASR during the process is preferably in the range 500-700°C: this gives a product gas with a heating value of 15.5 MJ/kg, above 700°C the amount of oxidised copper in the residue increases. The product gas contains around 30 %-vol combustibles, mainly hydrocarbons (~ 22 %-vol C_xH_y, ~ 6 %-vol H₂, ~ 2 %-vol CO), with CH₄ representing ~ 94 % of the hydrocarbons – see Figure 12. The mass loss of the solid during the process is around 50 %.

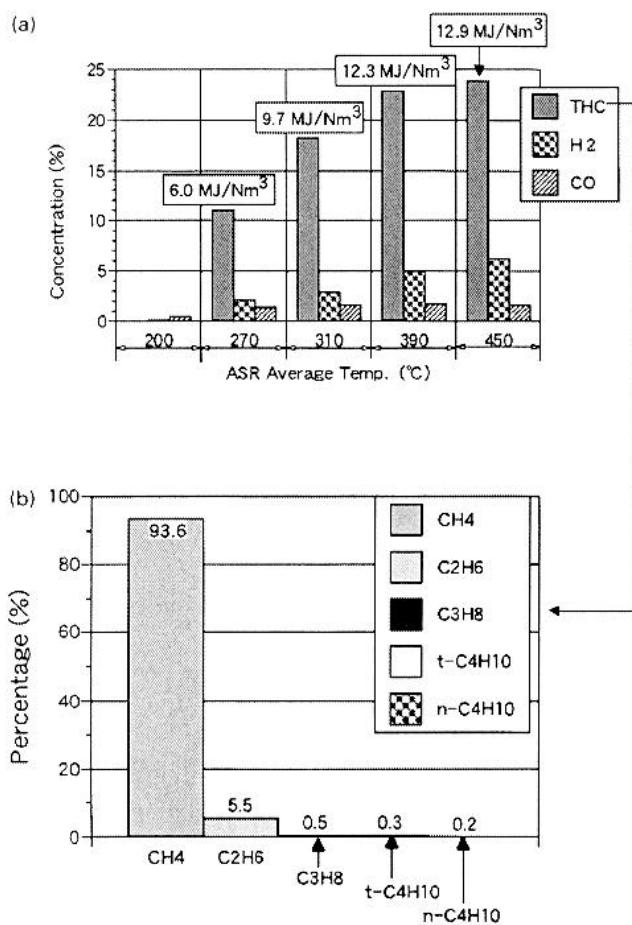


Figure 12
Product gases from the dry distillation / gasification process [53]

Also in Japan, Kondoh *et al.* [22] conducted a study comparing ASR gasification with other thermal processes. A total of five methods were compared as listed in Table 11a, the different products obtained are compared in Table 11b.

Table 11 a) (left) Thermal methods compared and b) (right) the different products from ASR processing by these methods, by Kondoh *et al.* [22]

Method	Type	Ratio of product materials (unit: %)			
		Gas	Residual	Slag	Fly ash
A	Fluidized-bed combustion furnace	Internal-circulation-type fluidized bed furnace			
B	Direct full melting	Cokes bed type	A	68.3	30.1
C	Direct gasification melting	Fluidized bed + melting furnace	B	66.1	7.2
D	Indirect gasification	Kiln-type gasification furnace	C	68.8	3.5
E	Indirect gasification reforming	Kiln-type gasification furnace + gas cracker	D	46.0	
			E	56.3	8.4
				35.3	

The conclusion from this study was that all five methods are capable of ASR processing. With increasing temperature and decreasing excess air the quality of gasification product gases (air was used as gasification agent) could be increased from 3 to 13 MJ/m³ STP. For processes B, C, D and E concentrations of the combustible fractions CO, H₂ and C_xH_y varied over the ranges 2-20 %-vol, 3-12 %-vol and 0-18 %-vol, respectively – see Table 12. Methods B, C and E give dioxin/furan concentrations of ~ 0.1 ng-TEQ/m³ STP, for A and D the level is ~ 2 ng-TEQ/m³ STP. Expressed as dioxin/furan mass per kg ASR method A, *i.e.* the combustion process gave by far the highest amount of these supertoxics.

Table 12 Product gases from ASR processing by four methods (see Table 11a) [22]

Comparison of gas compositions						
Item	Unit	B	C	D	E	
					Before cracking	After cracking
N ₂	(%)	Not measured	69.8	43.6	65.3	67.6
H ₂	(%)	3.5	3.6	6.3	3.3	11.6
O	(%)	0.2	1.6	3.3	0.6	0.3
CO	(%)	20.6	4.2	2.1	4.7	12.0
CO ₂	(%)	5.2	14.6	14.8	10.2	9.2
T-HC	(%)	0.1	0.5	12.8	17.8	1.1
Lower calorific value	(MJ/Nm ³)	3.0	4.2	10.5	13.1	3.2

At Schwarze Pumpe, in the eastern part of Germany around 450000 t/y of plastics-containing wastes are gasified (or co-gasified with coal) in a BGL (British Gas Lurgi) moving bed type gasifier. 10-20 % of the feed is ASR from which ferrous and non-ferrous metals are removed. At this SVZ plant (Sekundarrohstoff-Verwertungs Zentrum) from each tonne of ASR, which is fed to the gasifier as 8 cm pellets at up to 30 t/h, around 211 kg methanol is produced – see Obermeier in [14] and [54]. (As mentioned in section 2.5, part of Switzerland's ASR is processed at this plant).

3.5 *Thermal processing of ASR – 4. Pyrolysis*

Pyrolysis is defined as a thermo-chemical conversion of a carbon-containing material under absence of a reactive gaseous compound. The stoichiometry (air factor) equals $\lambda = 0$. Two types of pyrolysis processes can be distinguished: low temperature (in German referred to as “Schwelprozess”) operating at 400 - 600°C and high temperature processes 500 - 800°C. Advantages are the relatively low temperatures, the production of fuels that can be utilised to drive the process and no formation of hazardous gaseous pollutants such as PCDD/Fs or NOx as a result of oxygen deficiency. Drawbacks of ASR pyrolysis processing are the risk for high PCBs levels in the oil or char/solid products, which are then classified hazardous waste, and typical for pyrolysis, the formation of tars.

In one of the first studies on ASR pyrolysis, Day *et al.* [55] describe the use of commercial screw kiln process and the quality and composition of the gas, liquid and solid products. The process set-up was designed for the production of carbon black, oil and fuel gases from scrap tyres and basically a transport screw inside a reactor that is heated by a surrounding combustion chamber – see Figure 13. Solid residence time was ~ 15 min, at a feed rate of ~ 200 kg/h, for < 50 mm ASR. The non-condensable product gases were flared or used to fire the combustion chamber (replacing natural gas), the solids were separated into coarse and fine (magnetic fractions were separated as well) and an oily fraction was obtained by cooling the product gases. Reactor temperature was 700-760°C; based on an exit gas temperature of 450°C the temperature reached by the solid material in the unit was estimated at 500°C.

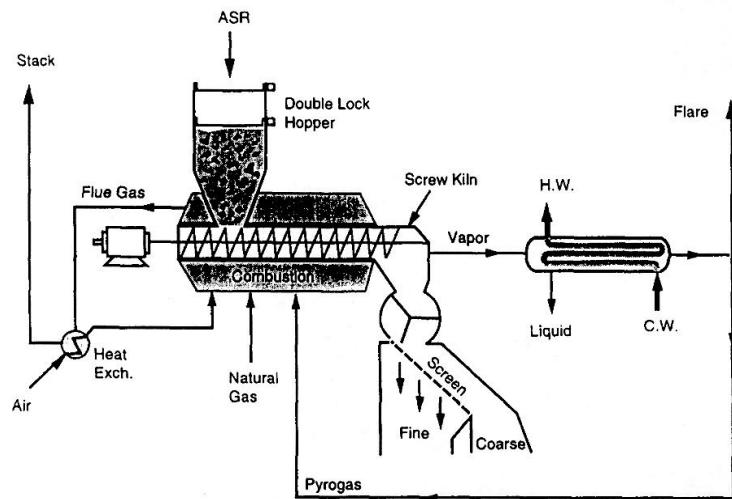


Figure 13 Set-up of the screw kiln pyrolysis process [55]

The ASR (composition included in Table 3) was pyrolysed into 26 % gases, 21 % oil, 10 % water, 11% magnetic material solids, 25 % fines plus 7 % course solids. The main gaseous components were CH₄, H₂, CO, C₂H₄/C₂H₂, CO₂, and C₂H₆, adding up to 85 %, plus fractions such as C₃H₆, benzene, toluene, butadiene and 2-methyl-1-propene. No HCl levels were reported; a small fraction of 1-chloro-3-methylbutane (C₅H₁₁Cl) was found, as well as the nitrogen-containing isocyanomethane (C₂H₃N). The heating value of this gas was measured to be 44.7 MJ/m³ (apparently HHV). In a sample of the oil fraction, the fractions of C, H, N, O, S and Cl were 86.2, 8.7, 2.4, 2.2, 0.36 and 0.18 %-wt, respectively, mainly alkyl benzenes and C₃-C₆ alkenes, with major fractions of naphthalene, (10.9 %-wt), styrene (8.3 %-wt), toluene (4.5 %-wt), 1-methyl-naphthalene (3.5 %-wt) and benzene (2.5 %-wt). Nitrogen and sulphur compounds made up 6.3 and 4.1 %-wt of the oils, respectively. Roughly, the oil contained 66 %-wt aromatics and 34 %-wt aliphatics, with an average boiling point of 258 °C (atmospheric distillation range 76-520°C), a density of 950 kg/m³, kinematic viscosity $\sim 8 \times 10^{-6}$ m²/s (23 °C) and a heating value of 41 MJ/kg (HHV). The ash content is < 0.01 %-wt. In the solids, carbon, SiO₂, Fe₂O₃, Al₂O₃ and CaO were the main fractions, at 37.8, 20.8, 8.5, 8.1 and 7.6 %-wt respectively. The 1.4 %-wt chlorine found could be in the form of CaCl₂. As for trace elements, relatively high levels of Zn, Pb and Cd were found, and almost 7 %-wt of Cu in the coarse solid fraction. A leaching test showed that the pyrolysis solids are not problematic considering leachability. The process must be further optimised to improve the quality and marketability of the solid and oil products; especially the amount of nitrogen-, chlorine- and sulphur species in the oils must be significantly reduced.

Also the ASR pyrolysis study by Rausa and Pollosel [20] mentioned above (section 2.3) focussed on oil product quality and the formation of hazardous species such as PAHs. Liquid products from ASR pyrolysis range from light oils and tars to heavy liquors, which can be difficult to dispose of in case these don't find a market. Especially the concentrations of nitrogenated and chlorinated compounds such as nitriles, pyridine and chlorobenzene prevent the use of ASR pyrolysis oils as fuels for engines *etc.* because of burnout problems. For example, the burnout of chlorobenzene within 2 seconds will require a temperature of 990°C, also PAHs such as naphthalene and benzo(a) pyrene may be released into the atmosphere as unburned fuel. Flash pyrolysis test results indicate that pyrolysis processes that combine high heating rates with short residence times at the highest temperature will give the highest yields of hazardous and/or problematic PAHs.

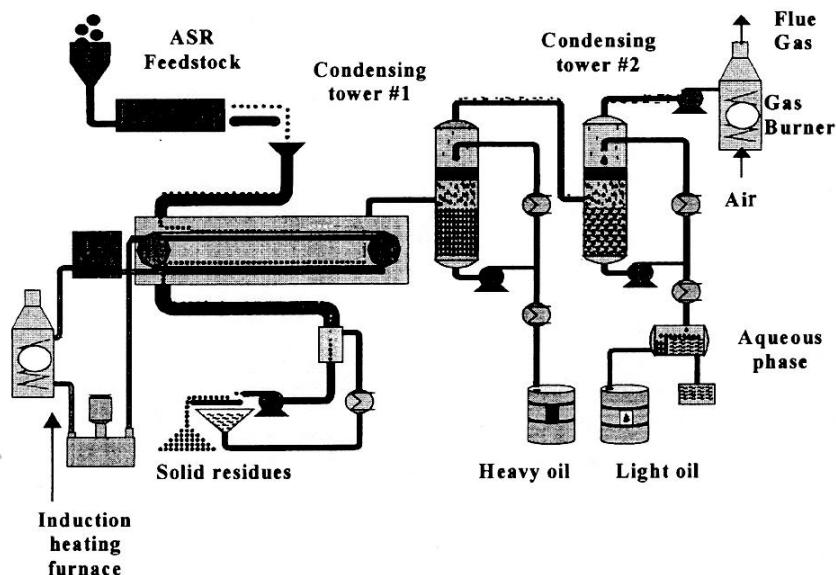


Figure 14 Flowsheet of the Pyrocycling™ process [4]

The Pyrocycling process™, patented under European, US and Canadian patents, is a process based on vacuum pyrolysis of ASR at pressures below 0.2 bar, at temperatures 450-550°C. Products are oils, char, water, gas and inert materials; the objective of the reduced pressure is to maximise the yield of oil product at the expense of gases and char [4, 23]. A process scheme is given by Figure 14. The gas can be used to heat the reactor, the aqueous fraction is disposed of after cleaning, the inert solids and char fraction are to be landfilled (after removal of large metal pieces). Overall, the products obtained from ASR Pyrocycling processing are 52 % solids, 28 % oils, 13 % water fraction and 7 % gases. The oil products, containing < 0.15 % Cl, < 1 % S, < 3 % N, and are for 33 % aromatic, 9 % aliphatic, 4 % olefinic and 25 %

alicyclic, and < 0.1 % ash, are further distilled to give a fuel oil and a pyrolytic residue (“PR”) with fractions boiling (at 1 bar) above 400°C, from 32 % of the total oil mass. This PR is similar to a petroleum bitumen (PB) and it is suggested to use it in road pavement (10 % PR + 90% PB) [23].

The gas fraction is for 95 % composed of H₂, CO₂, CH₄, CO and C₂-C₄ hydrocarbons, and has an average heating value (HHV) of ~ 24 MJ/kg. Besides some chloromethane no other organochloro compounds were found, no HCl, and besides 0.17 %-vol H₂S no significant organosulphur compounds could be detected. The metals Zn and Sn were present at 142 and 56 mg/m³ STP, respectively, in this gas. The aqueous fraction contained some chlorine, organic carbon, organic nitrogen as caprolactam (from nylon), and some Zn and Fe. The solid, finally, can be roughly separated in the metals Fe, Cu, Zn, Al, plus char and an inorganic fines fraction. These fines are derived from 47 % of the original ASR, at only 20 % of the volume of the ASR, and are composed for 68 % of minerals and metals (Fe, Zn, Al, Pb) plus for 29 % of carbon, mainly as sand and gravel coated by carbonaceous material during the pyrolysis. As an alternative for landfilling this material it may be used as filler in road pavement: it passes leaching tests according to French protocols. The Pyrocycling process allows for recovery of 64 % of the organic carbon in ASR as oils or gases. Questionable, however, is that the mass balance for chlorine could not be closed: 50 % of the ASR chlorine is found in the solids fraction, 10 % in the other fractions, and 40 % is missing [4].

Very recently Pasel and Wanzl [9] studied the effect of the process parameters temperature, time and heating rate of ASR on the products obtained from pyrolysis in nitrogen. The temperature range was 500-950°C, the heating rate in the two reactors used was ~ 6000 K/s and << 1 K/s, and the residence time (which is important for cracking reactions to occur) varied from << 1 s to more than 40 s. It was argued that a rotary kiln process followed by a catalyst bed might produce a highly valuable product stream mainly composed of aromatics with atmospheric boiling points 80 - 180°C. The combination of residence time and catalyst would improve product quality via cracking, isomerisation and aromatisation reactions. Problematic, however, is the presence of chlorine and sulphur, which give rise to corrosion and the formation of chlorinated or sulphated compounds in the pyrolysis oils (more than 10 ppm chlorine makes these oils unmarketable). Also nitrogen from the ASR may be problematic as ammonia and pyridine tend to deactivate the (acidic) catalyst [9].

The tests showed that an increased heating rate gives more liquid products. Increasing residence time or pressure both result in increased amounts of gases and chars, probably as a result of more cracking and recombination reactions. Increasing the temperature gave a more homogeneous product mix. Surprisingly, using H₂ instead of N₂ as the main gas phase caused little changes – apparently cracking reactions are faster than hydrogenation. The chlorine and sulphur content in the oil fractions were found, however, to be unacceptably high, at 1000 ppm and 2500 ppm, respectively. By using dolomite to trap these species the chlorine and sulphur content in the oil fractions could be reduced to < 1 ppm and 1400 ppm, respectively, for pyrolysis at 500°C. (At higher temperatures dolomite will catalyse cracking reactions which lowers the amount of oil product in favour of gaseous products.) As a conclusion a rotary kiln + catalyst bed is suggested to be a suitable process set-up, although a fluidised bed, operating with a higher heating rate may give more aromatics in the products. [9]. (The authors don't mention that in a fluidised bed the solid phase is much better mixed than in a kiln which would allow for adding the cracking catalyst and the dolomite for chlorine and sulphur capture to the bed. In a rotary kiln the gas and solid contacting is less good, with very different residence times for solid and gas, and hence a wider product spectrum).

Keller [27, 29] studied the pyrolysis of ASR in a 400 kg/h shaft furnace at the Swiss company for battery recycling, BATREC, aiming at the medium-term for ASR processing in Switzerland (see section 2.5). ASR (from which large pieces of foam and metal were removed) was pressed into cylinders (10 cm × 5 cm Ø), after surface melting the larger pieces were added and the material was fed into the furnace similar to battery processing. After the pyrolysis at 600°C in CO containing ~ 2 % O₂ the char was removed before it would enter the melting furnace of the plant. The pyrolysed ASR contains ~ 6 % carbon, plus up to a quarter iron and 4-5 % copper which may be economically recovered by further processing. Depending on the cooling process dioxin/furan (PCDD/F) contents may rise somewhat; PAHs and PCBs are for more than 90 % destroyed. The levels of Cd, Zn and Ni in the pyrolysed ASR are too high for landfilling of this material. Separating the pyrolysed ASR into size fractions showed that 33-65 % of the metals that may be economically recovered are found in a coarse fraction with particle size > 2 mm. Cadmium and mercury are mainly found in the finer fraction, as well as lead and zinc [27]. Thus, pyrolysis of ASR as a pre-treatment step before a melting process allows for recovery of metals, mainly iron and copper, from the ASR before further processing. This confirmed earlier work in cooperation with the Swiss Paul Scherrer Institute (PSI), showing that pyrolysis of ASR at ~ 600°C destroys largely all

organic substances, gives mineralization within a few minutes and uncovers the iron, copper and other metal fractions by removing their plastic cover, which supports the recovery of these metals [40,41].

Galvagno *et al.* [15] state that pyrolysis allows for 70 % energy recovery from ASR, against 40 % for conventional incineration. Advantages are the lower temperature, the oxygen-free environment (preventing formation of NO_x, SO_x and PCDD/Fs) and the production of useful fractions such as char, oils, metals and fuel gases, instead of ashes that are classified as hazardous wastes and pollutant-containing flue gases. Tests in a rotary kiln in an N₂ atmosphere at 550-680°C, residence time < 40 minutes, gave char yields of 59→43 %, ~ 20 % oils and 4→13 % gases with heating value (LHV) 19→30 MJ/m³ (CO, H₂, CH₄, C₂₊ hydrocarbons). The char fraction, with 47→76 % ash, 33→6 % volatiles, ~19 % carbon, 1-1.5 % S and 0.5-1 % Cl and N, shows concentrations of ash and trace elements that are roughly twice the levels in the ASR, but is not considered more dangerous than the ASR when landfilled. Recovery of copper and other metals from the solid char residue is suggested.

Also de Marco *et al.* [56] reported on the recycling of polymeric wastes by pyrolysis, including light and heavy ASR fractions (19 % and 8 % of the original ELV) in the study. Motivation for the work are that currently ~ 10 % of plastics waste is mechanically recycled and another ~ 10 % is thermally recycled, mainly by incineration, which has the drawback that recycling of inorganics is difficult, and that hazardous ashes and gaseous pollutants are formed. Pyrolysis tests at 500°C in an autoclave in N₂ with 30 min residence time show that only the heavy ASR fraction yields useful products: a recovery of ~ 29 % as fuel oil (containing 11 % water) plus a fuel gas (55 % CO, 10 % CH₄, 17 % C₂-C₄ hydrocarbons) with a heating value (HHV) of 32.4 MJ/m³. The light oil (which contained a lot of soil) yielded only ~ 10 % of its mass as oils, which contained 50 % water.

A pyrolysis kinetics study by Patierno *et al.* [21] resulted in a semi-empirical model for ASR pyrolysis based on five (first-order) chemical reactions, one of which is exothermic, the others being endothermic. The model is very sensitive to ASR composition data but gives a prediction with less than 4% error to experimental data.

3.6 Thermal processing of ASR – 5. Hybrid processes

Especially for heterogeneous materials such as ASR the most suitable methods for thermal treatment are based on so-called hybrid processes, such as:

- rotary kiln low temperature pyrolysis + combustion of the gas and/or solid residues
- gasification + combustion of the gas and/or solid residues
- low temperature pyrolysis on a grate + gasification of the solid residue at 800-1000°C.

Examples of this are the Schwel-Brenn process, the Thermoselect Process and many others; see for an overview for example the report by Juniper [57], or other recent texts on thermal processes for waste treatment [58, 59].

An important example of this is the Resment process that is being implemented for the processing of all Swiss ASR – see section 2.5. Another hybrid process is the Von Roll RCP process, for which the process schematic is shown in Figure 15.

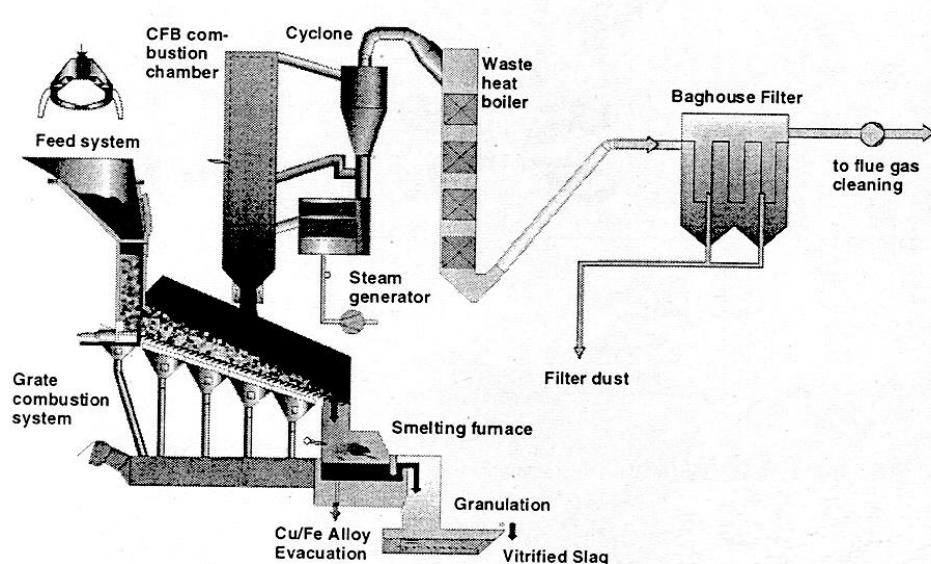


Figure 15 Schematic of the Von Roll RCP process [60]

In this process, O₂-assisted pyrolysis is followed by smelting of the solid pyrolysis residue. As the picture shows it contains four process stages: 1) pyrolysis on a grate, 2) melting of the pyrolysis residue, 3) slag treatment and 4) CFB post-combustion of the gases from the pyrolyser. The main products of this process are recovered copper and zinc, plus energy in the form of heat [60].

The TwinRec process [61] aims at converting ASR into recovered energy, copper, iron and aluminum, plus leaching-resistant construction materials. ALSTOM Power is licencing this technology from the Japanese EBARA (who use the brand name TWIG, Twin Internally Revolving Fluidised Bed Gasification) for the European market. As illustrated by Figure 16 it is based on a fluidised bed gasifier (FBG) operated at 500-600°C in with the inert materials and metals are separated from the dusts and combustibles which are fed into a cyclonic combustion chamber operating at 1350-1450°C. Iron, copper and aluminum are recovered from the bottom stream of the FBG, zinc can be recovered from the zinc, copper and lead-rich fly ashes captured from the flue gases from the combustion chamber, and a glass granulate is obtained as the bottom product from the cyclonic combustor. In Japan, this granulate fulfils soil standards and it is used by construction industry; it also passes the German LAGA limits for use in road construction. According to Selinger *et al.* [61] this process allows for 85 % re-use + recycling of ASR, 12.5 % energy recovery and 2.5 % landfill of ASR.

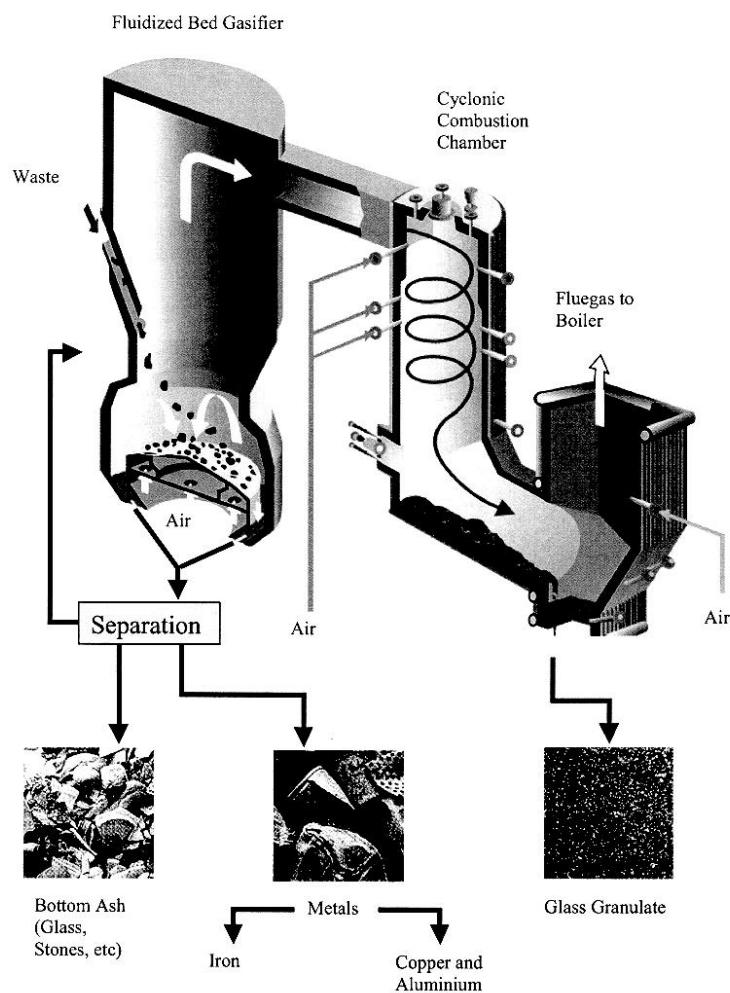


Figure 16 Schematic of the TwinRec process [61]

The overview report by Juniper [57] on pyrolysis and gasification of waste for the European region includes several hybrid-type technologies that are claimed to be capable of ASR processing. Table 25 lists these methods and some of their characteristics. Only the Prole Syngas process has a history of ASR processing.

Process name / Country	Process steps	Products
PKA / Germany	Pyrolysis followed (after removal of metals from the residue) by O ₂ -gasification	Ferrous and non-ferrous metals, syngas, inert minerals, granulated slag, HCl, gypsum, scrubber residue
Proler Syngas Process / USA (TX)	Pyrolysis followed by vitrification of the solid residue	Glassy slag, recycled metals, Syngas, some inorganic solids
Krupp Uhde Precon Process / Germany	Gasification followed by solid residue treatment in a molten metal bath	Recyclable Fe, Cu, glass, syngas, ferroalloy, ceramics, minerals, sulphur, HCl, residues
Softer Process / Canada *	Pyrolysis under vacuum	Liquid, gaseous and solid fuels, metals, minerals, ashes, residues
Compact power / UK	Pyrolysis combined with steam gasification	Ash, steam

* see also the Pyrocycling process (section 3.5)

The French CITRON process aims at the recycling of heavy metal containing wastes that also contain an organic fraction which can provide char and energy. A plant with a capacity of around 230000 t/y has been taken into use at Le Havre, France [62]. The central part of the process is a rotary hearth furnace (RHF) operating under reducing condition at ~ 1200°C. The gases from this RHF are oxidised while leaving the reactor, which leads to oxidation and condensation of vaporised metals such as Zn, Cd, Pb, except Hg. Hg is recovered separately from the gas, and the less volatile metals such as Fe, Mn, Ni, Cr, Cu, Co, Mo are recovered from the carbonaceous solid residue from the RHF. (As mentioned in section 2.5, part of Switzerland's ASR is processed at this plant).

3.7 Other processes

Wastes that contain large plastics fractions can be used as a fuel for a blast furnace, but producing raw iron (*e.g.* [63]) using ASR is not without problems. The high chlorine and copper contents cause problems: Cu makes iron brittle, chlorine gives corrosion and cooling water contamination. Polymer-containing wastes may not give a good performance when mixed directly with the furnace burden, pyrolysing at the wrong moment or the wrong position. It is usually preferable to process polymer-containing fractions externally and use the pyrolysis, gasification or liquefaction products (char, oil, fuel gas) instead [64]. The PVC and the minerals, glass, dirt *etc.* in ASR will make such pre-processing necessary.

A more detailed study by Mirabile *et al.* [16] analysed the performance of ASR as an alternative fuel in a blast furnace, *i.e.* in the so-called raceway in front of the injection tuyeres, between the (downwards) moving bed of iron ore, carbon and limestone, and the hearth of the furnace, where temperatures can range up to 2000°C. Pilot scale tests and modelling calculations were made for the three cases where pulverised coal was replaced at 0.1 %, 1 % or 10 % with ASR. It was found that the raceway temperature was reduced from 1832°C when using 100 % coal, to 1830, 1720 and 1718°C, respectively with these three ASR mixing ratios. (Pressure was 4 bar.) Despite a concentration of 0.5 %-wt Cl in the ASR no detectable levels of PCDD/Fs were found, which may be explained from the high temperatures, the reducing conditions and the gas clean-up equipment downstream. In fact, no chlorine species were detected in the off-gases at all: presumably these are bound by the ashes, cokes or the limestone (as CaCl₂). Using 10 % ASR showed erosion of the wall of the raceway by the ASR ashes. An economic study showed that replacing coal by ASR at 1-3 % is most beneficial and should not give problems. The ASR should be mixed with the coal when preparing the furnace burden [16].

Yoshiie *et al.* [32] describe the fate of trace elements and heavy metals in an ash melting process which aims, at 800-1500°C, to immobilise these elements and prevent them to be leached out after disposal of the ashes at landfills. Ashes from CFB combustion of an RDF and an ASR (see Table 5) under Reducing as well as oxidising conditions were considered. It was found that because of the high chlorine content of ASR most of the metals considered (Cu, Zn, Pb, Cd) were released to the gas phase increasingly with increasing temperature, irrespective of the gas atmosphere. On the contrary, for the RDF ash the large amount of

phosphorous (mainly phosphorous oxide) suppresses the release of the trace elements even at high temperatures, under oxidising conditions. Under reducing conditions, part of the RDF ash phosphorous was emitted regardless the temperature. This resulted in the release of especially the trace elements Pb and Zn to the gas phase. Thus, phosphorous supports the vitrification of the ashes, under oxidising conditions up to high temperatures. Pb must be present mainly as oxide (PbO) in the RDF ash, and as chloride ($PbCl_2$) in the ASR ash.

In a study by Xu et al. [65] the use of residue from ASR pyrolysis, referred to as PAF (pyrolysed automotive fluff) in concrete was reported. While the main aim was the disposal of this solid residue from ASR pyrolysis (which gives valuable pyrolysis gas and oils) it was investigated whether the quality of the resulting cement mortar is improved. With 10 %-wt PAF added to the cement it was found that strength and sulphate resistance were reduced whilst drying shrinkage was increased. A significant expansion of the PAF-added cement mortar during the first 24 h of curing resulted in many microcracks. Apparently this PAF is not a good additive for cement.

Glycolysis or alcoholysis (for PU) and hydrolysis, acidolysis or aminolysis (for PA, nylone) are chemical recycling methods for polymer fractions, which involve cleavage of polymer bonds. PU treatment results in the production of polyols and low molecular weight urethanes, PA fractions can be processed into caprolactam monomer or other monomers. It must be noted that the presence of chlorofluorocarbon (CFC) – type gases in PU foam may enforce the removal of these gases before any further processing of these foams [50, 51]. These methods can not be directly applied to ASR: a pre-separation to extract the polymers will be needed.

Ranta [1] mentions that the use of ASR as a filler or additive in asphalt or concrete may cause problems because with little is known about long-term effects such as leaching of trace elements and other toxics or deterioration of concrete structures. “Promising results” have, however been obtained from trials.

According to Galvagno *et al.* [15] ASR can be used as a fuel at cement plants, allowing for energy recovery and elimination of ashes, which are absorbed in the clinker. Disadvantages, however, are problems related to scaling, corrosion and increased volatilisation of metals such as Tl, Cd and Hg as a result of the increased chlorine concentrations. As Gomes and Thai suggest [43], PVC should be removed from the ASR before using it in cement manufacturing.

4. Compact disc (CD) waste

4.1 CDs and CD waste

At the beginning of 1980s, the Dutch and Japanese industry (Philips & Sony) introduced the world to the compact audio disc. Since then, the demand for discs and their uses have expanded into the fields of text, motion pictures and computer data storage and programming. The compact disc has become very popular among users as it can store great volumes of information in smaller packages than other types of magnetic storage media. Critical to the discs performance is the use of special polycarbonate resins that offer a range of properties, such as exceptional clarity and light transmittance, high-melt-flow rates, low moisture absorption, and high impact strength [68].

The production of compact discs worldwide reached 400 million in 1991 [69] and has increased significantly in recent years. The production of compact disc (CD-R) worldwide in 2002 was 5.225 billions pieces. Table 13 and Table 14 give some statistical information [70]. The recent advances in compact disc technology have created a higher demand for superior quality products, which has placed a more challenging role on the plastics industry.

Table 13 CD & DVD replication worldwide 2001-2003 (Millions of units) [69]

	2001	2002	2003
CD-Audio	4774	4709	4680
CD-ROM	3429	3275	3110
CD-Video	1095	1101	1046
DVD-Video	1080	1740	2415
DVD-ROM	170	298	438
DVD-Audio	6	25	60
Total worldwide CD & DVD replication	10554	11148	11749

Due to the complex manufacturing process, it has been estimated that approximately 10% of all CDs manufactured are rejected [71]. In the US alone, more than two billion polycarbonate

compact discs are manufactured each year, and around 150-200, million CDs are scrapped annually due to rejects. CDs are also destroyed because of artist's rights issues (i.e. unsold copies are destroyed). These together with some post consumer CDs are currently being reclaimed to produce grades of recycled poly carbonate (PC) [72]. Therefore, these discs are typically landfilled or granulated and sold back to the resin supplier at a nominal price.

Table 14 CD-R demand* 2001-2003 (Millions of units) [69]

	2001	2002	2003
CD-R worldwide	4170	5225	5775
CD-R North America	1565	2050	2250

* Demand = sales to wholesalers, retailer, direct marketers, etc.

The nature of the compact disc (CD) does not allow it to be easily recycled. As shown in Figure 17, the disc is a multi-layer product consisting of a thermoplastic (PC) substrate and three coatings. These coatings, aluminum, lacquer and printing, respectively make up only a small portion of the entire disc. The aluminum coating is only 55-70 nm thick, and the lacquer and printing account for approximately 20 microns to the overall thickness. In order to recover the full properties of the polycarbonate these coatings must be removed prior to recycling [69].

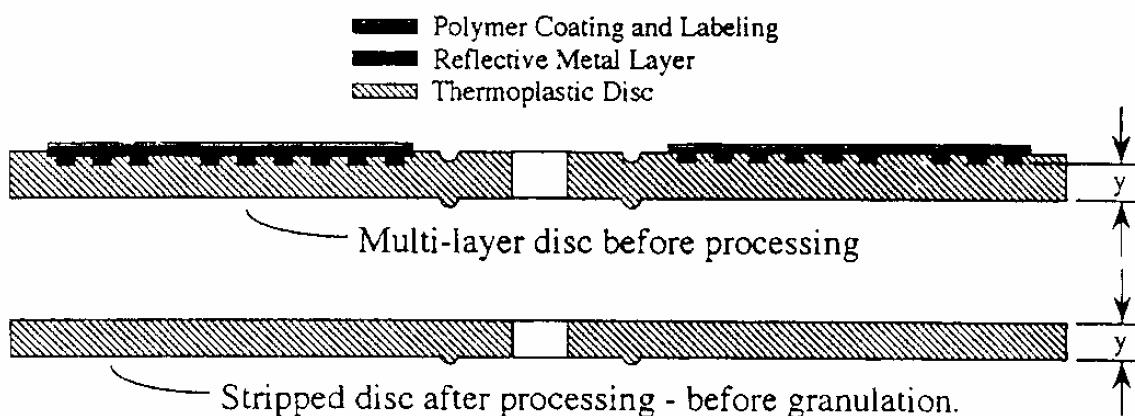


Figure 17 Molded thermoplastic disc: before and after processing - before granulation (not to scale) [69]

Generally audio compact discs are produced by injection molding from aromatic polycarbonates. The moldings thus produced are metallised with aluminum by vapor deposition and are then surface-sealed with cross-linking lacquers. In addition, they are printed with dyes. Finally, they are subjected to quality control where 10% of the compact discs are rejected because of defects [71].

A DVD (which stands for Digital Video Disc) is very similar to a CD, but has a much larger data capacity, holding about seven times more data than a CD. This is why DVDs are used for memory-intensive picture movies, while CDs are used for music. Both use the same technology. DVDs have the same diameter and thickness as CDs, and they are made using some of the same materials and manufacturing methods. The DVD, however, is made of several layers of injection molded polycarbonate plastic. Aluminum is used for protection behind the inner layers, but a semi-reflective gold layer is used for the outer layers, allowing for the laser to focus through the outer and onto the inner layers. Each layer is individually coated with lacquer, all are then squeezed together and cured under infrared light to make a single disc [73].

Polycarbonate, the main plastic of CDs is quite valuable and the gold used in gold CD-R is real gold. However, it is a very thin layer (80nm) and which can give only a few grams from a ton of discs. With a large amount of CDs, e.g. tens of kilos of scrap, it is worth getting in touch with a local recycling plant. The scrap may have some value and global pollution may be reduced somewhat [74].

4.2 CD waste processing in Finland

No activities on CD or DVD waste processing in Finland have been reported in the open literature, nor are they known by the authors. Apparently scrapped CDs are disposed of via wastes from households and offices, and probably also with waste electrical and electronical equipment (WEEE) from the information and communication technology sector.

5. Compact disc (DC) waste processing

As mentioned above compacts disc have an aluminium layer beside coatings, lacquer and printing. These materials should be separated or recovered in order to recycle the polycarbonate. There are a variety of methods for the removal of paint or plating from engineering plastics, ranging from the chemical to physico-mechanical procedures. Such techniques include chemical stripping or chemical recovery (high-temperature alkaline treatment), melt filtration, mechanical abrasion, hydrolysis, liquid cyclone, compressed vibration, cryogenic grinding, dry crushing and roller pressing [72]. This report will concentrate on the most widely used techniques for compact disc recycling, which include (1) chemical recovery, (2) melt filtration, and (3) mechanical abrasion. Other methods currently used in the recycling of multi-component materials do not seem to be feasible options for this application [69].

5.1 *Chemical stripping (chemical separation)*

Chemical stripping involves the use of solvents or aggressive chemicals to remove coatings from a polymer. Coatings are most often stripped from engineering plastics using proprietary solutions based on alkaline cleaners and inorganic salts, and is generally performed at elevated temperatures. Paint removal is initiated by submitting the parts to preliminary granulation; the paint film can then be chemically broken down in an alkaline solution at high temperatures. This approach is commonly used to remove paint from plastic auto parts such as bumpers. However, this technique requires the use of potentially harmful solvents and expensive chemical recovery equipment. Furthermore, there is the possibility of interactions between the solvent and the polymer [72].

Han [75] introduced a method for removing the lacquer and aluminum coatings from the polycarbonate of scrap CDs. The method includes immersing the discs in a perforated barrel supported for rotation in an ultrasonic tank containing an aqueous alkaline solution. The aqueous alkaline solution contains an alkaline salt or a base, preferably is a mixture of alkali metal phosphate, alkali metal hydroxide and alkali metal carbonate, wherein the metal may be either sodium or potassium. A chelating additive is selected from the alkali metal salts of citric acid, ethylenediamine tetraacetic acid (EDTA), gluconic acid and nitrilotriacetic acid. A

wetting agent is selected from the group including sodium alkylbenzene sulfonate, naphthalene sulfonate, fatty acid esters and sodium lauryl sulfate.

The alkaline solution is heated to a temperature in the range from about 55°C to 104°C and the barrel is rotated about its horizontal axis at a speed of 60-100 rpm which causes significant turbulence in the solution passing over the discs contained in the barrel. At the same time, the barrel is oscillated in the vertical direction at about one cycle/s with a displacement of about one cycle/s with a displacement of about six inches, for additionally agitating the contained discs. The best results of the process of stripping the lacquer coating are achieved in large part by applying ultrasonic energy to the alkaline solution at a frequency of 20- 40 kHz, at a power level consistent with the amount of material in the barrel. After the coatings have been stripped from all the discs contained in the barrel, the alkaline solution along with the flaked and/or dissolved lacquer and dissolved aluminum is decanted, leaving behind the stripped polycarbonate discs. The stripped discs are then washed with water at a temperature of 38°C-90°C, to remove the caustic solution. Following washing, the discs are dried using a hot air dryer. The total time required for rinsing and drying a barrel of discs is about fifteen minutes [75].

Fennhoff *et al.* [76] introduced a process for the purification of waste of thermoplastic, especially compact discs waste. This process was developed and patented by Bayer Company. Bayer has a CD recycling plant at Dormagen, Germany. In this process, the compact discs are reduced to fragments with a mean diameter of 0.1 cm to 5 cm, preferably 0.5 cm to 1.5 cm. Then the fragments are immersed in a tank containing 5% sodium hydroxide (NaOH) solution for 90 minutes at temperatures of 70°C to 95°C. This alkaline bath breaks down the lacquer and dissolves and separates the aluminum from the polycarbonate. After removal of the sodium hydroxide solution, the polycarbonate is washed with 10% acetic acid, then with softened water until neutral pH and remaining lacquer residues are rinsed out. After filtration, the polycarbonate is dried at 120°C.

The mechanical properties of the recycled compact disc obtained this way are comparable to those of virgin resin. Use of the product for manufacturing more compact discs, however, is limited by the extremely strict requirements of the industry with regard to optical properties. Instead, the recycled compact disc is used as a raw material for the production of a variety of

Bayer AG quality-assured plastics, which are then available for high-grade reuse in, for example, the electrical engineering and data processing field. Thus, Bayer seems to have closed the loop from the electrical engineering to the data processing field [77].

Chemical separation is a method widely utilised in separation processes like these. Since companies prefer to send out granulated disc flakes rather than the whole discs to be disposed of or recovered, chemical separation offers the advantage of utilizing a granulated feedstock [69]. There are, however, more disadvantages to a chemical separation process than advantages. There is a potential for an interaction between the polycarbonate and the chemicals, resulting in poor end-material properties. In addition, the recent legislation promoting the reduction in the use of hazardous materials, chemical separation may be too expensive and environmentally unattractive in the future [69].

5.2 *Melt filtration*

Melt filtration can be used to remove paint from various engineering plastics without needing to use hazardous stripping chemicals. Melt filtration has been applied successfully to remove the metal coatings of plastic products such as metallised computer housings. In this process, the plastic product is first granulated into flakes, dried and then repelletised in an extruder. During processing, the extruder screw forces the melt through a fine filter, or series of filters to remove any solid contaminants that may not have melted [72,78].

Melt filtration offers the advantage of enabling the recovery of the polycarbonate from a granulated feedstock. Polycarbonate for compact disc applications is specially fitted to have low viscosity and excellent flow properties. This polymerization process yields a lower molecular weight polymer, which results in a polymer having lower mechanical properties and thermal stability. During the filtration process, the polycarbonate is subjected to high temperatures. Taking into account the low thermal stability of this material, and the heat history of a melt filtration process, the overall properties of the resulting polycarbonate may be compromised. If this occurs, the polycarbonate may not have sufficiently high enough optical or mechanical quality to guarantee successful recovery. In addition, the granulated discs, either in a flake or powder form, may not be suitable as a feedstock for this type of process. Due to the small, inhomogeneous particle size and the extremely fine nature of the

aluminum coating, not all the contaminants may be removed [69]. Also, the protective acrylic layer softens and degrades during the process and contaminates the polymer. Besides all this during the process the polycarbonate will be exposed to additional heat history [78].

5.3 *Mechanical abrasion*

The mechanical abrasion process, also called the mechanical separation process, appears to be the best way for the recovery of polycarbonate from a compact disc since is considered to be a safe, effective, and simple process. However, it may not be a solution for other products that are constructed from several different materials, such as electromagnetic interference (EMI) shielded computer housings, which, due to the shape of the product, would not lend itself to mechanical separation [69].

Coatings can be removed from engineering plastics by mechanical abrasion processing. This has been successfully applied to the removal of coatings from polycarbonate compact discs whereby the compact discs, held on a vacuum conveyer, are exposed to a rotating wire brush. The apparatus, as shown in Figure 18, involves a rotating brush to remove the coatings and a conveyor belt to continuously move the discs. The brush removes the coatings, and the particles are carried to a special filter as to recover the aluminum. A vacuum is applied to each of the holders to provide stability while the disc is being stripped. Compressed air, inert gas, or a water mist can be applied at the interface to provide cooling and to prevent melting of the polycarbonate while being stripped. The discs, once stripped, can be saved as a whole or can be granulated [69].

The quality of recycled polycarbonate that has been mechanically stripped is only slightly lower than those of the virgin polymer. Whereas, the properties of polycarbonate from partially stripped CDs are considerably lower. For instance, the tensile modulus of fully stripped polycarbonate PC disc regrind was about 20% lower than the virgin polymer (2080 MP), while the moldings produced from the partially stripped and unstripped discs showed modulus reductions of 36% and 39% respectively. The presence of residual lacquer and aluminum layers was found to considerably affect the ultimate tensile elongation of the recycled material. The advantages of this technique are that it is easily adapted to the manufacturing environment, the equipment involved is easy to operate and is relatively inexpensive, and the process does not involve hazardous chemicals. Additionally, the flat and

round nature of the CD lends itself well to this mechanical abrasive process. In contrast to chemical stripping and melt filtration, mechanical abrasion uses whole discs rather than granulated flakes [72].

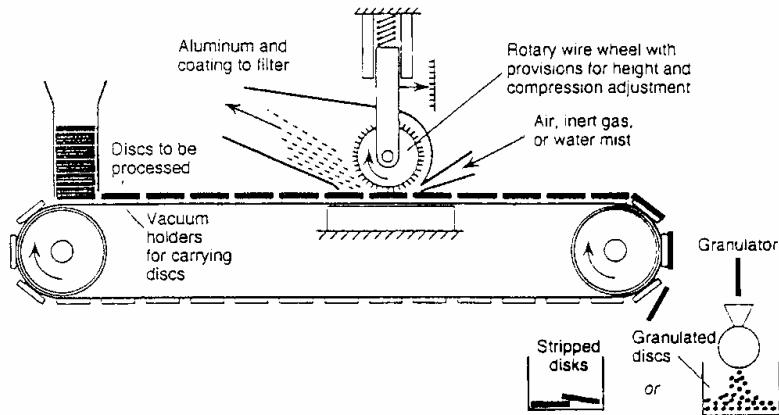


Figure 18 Schematic of compact disc processing line [69]

Figure 19 shows the laboratory apparatus suggested by Boudreau *et al.* [69], which consists of two motors, one brush, a single disc holder, a shop vacuum cleaner, and a vacuum pump. One motor rotates the brush counter-clockwise. This speed is adjustable by using different diameter pulleys to provide varying mechanical advantages. The other motor, with a variable speed controller, provides the forward and backward movement of the disc holder, by means of a rack and pinion system. The shop vacuum cleaner carries away the particles, which are in the form of water based slurry, and the vacuum pump holds the disc in place while it is being stripped.

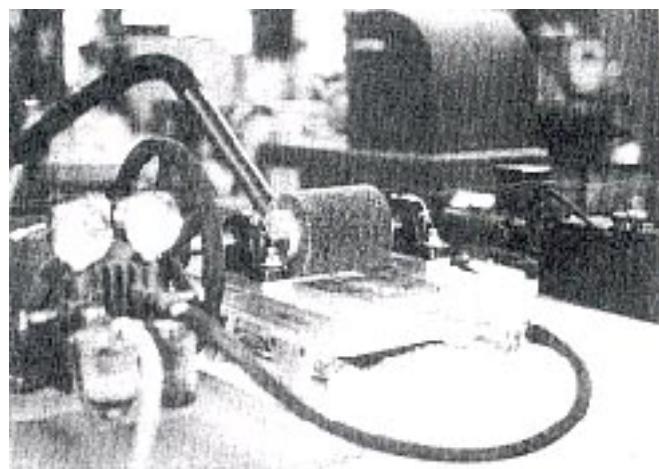


Figure 19 Laboratory apparatus suggested by Boudreau *et al.* [69]

During the final coating process before printing, some of the lacquer may drip onto the sides of the disc while the lacquer is put on during a spin casting operation. Although this particular apparatus does not include a device to clean the edges of the disc. Even though the amount of lacquer on the sides is small relative to the overall amount of polycarbonate, it is important to remove all materials that may behave as contaminants.

After being stripped, the discs are rinsed, dried with air and are ready to be granulated. The stripped disc, as seen in Figure 20, is free of any aluminum coating. The success of the removal of the coatings can be seen from the comparison of a stripped disc and an untreated disc in Figure 20. The stripped (Clean CD) and untreated (CD Flake) discs were granulated in laboratory mill with a 5 mm screen. The materials were then dried for five hours at 116°C in an air circulating oven.

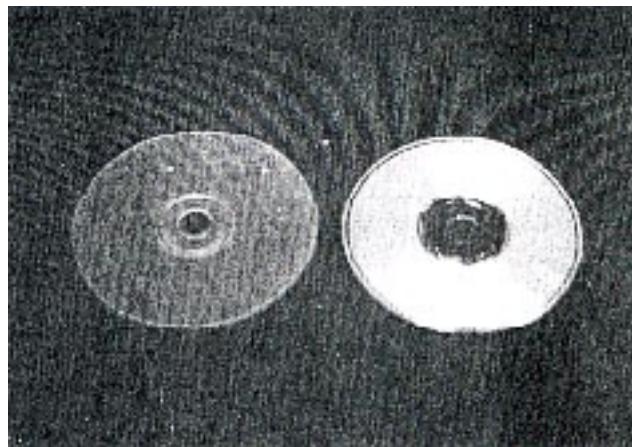


Figure 20 Stripped disc (left) and untreated disc (right) [69]

Table 15 shows some results of the flow properties as evaluated from melt flow rate calculations, demonstrate a difference between the untreated discs (CD flake) and stripped discs (clean CD). The difference in the flow rate is related to the higher melting characteristics of the aluminum and lacquer during CD flake formulation, and the difference in the density is related to the contaminants present in the CD flake formulation. The standard deviation values, represented in the parentheses, indicate an instability of the material during testing which is because both these materials are recyclates [69]. Also, in Table 16 and Figure 21 some property data are given, obtained by Boudreau *et al.* using virgin polycarbonate, fully stripped, partially stripped, and unstripped compact disc [78].

Table 15 Melt flow rate results [69]

Temperature	271.1°C	271.1°C	293.3°C	293.3°C
CD type	CD flake	Clean CD	CD flake	Clean CD
Density (g/cc)	1.07 (0.04)	1.04 (0.04)	0.996 (0.2)	0.963 (0.1)
Flow rate (g/10min)	50 (0.6)	55 (4.6)	83 (12.7)	91 (6.7)

Table 16 Tensile properties of moldings from virgin polycarbonate and reground compact discs [78]

	Virgin PC	Fully stripped	Partially stripped	Unstripped
Tensile properties:				
Initial tensile modulus (MPa)	2080	1610	1324	1270
Tensile yield strength (MPa)	60.6	60	no yield	no yield
Ultimate tensile strength (Mpa)	60.1	45.5	43.8	43.7
Yield elongation (%)	23	23	no yield	no yield
Ultimate elongation (%)	64	61	5.0	1.0

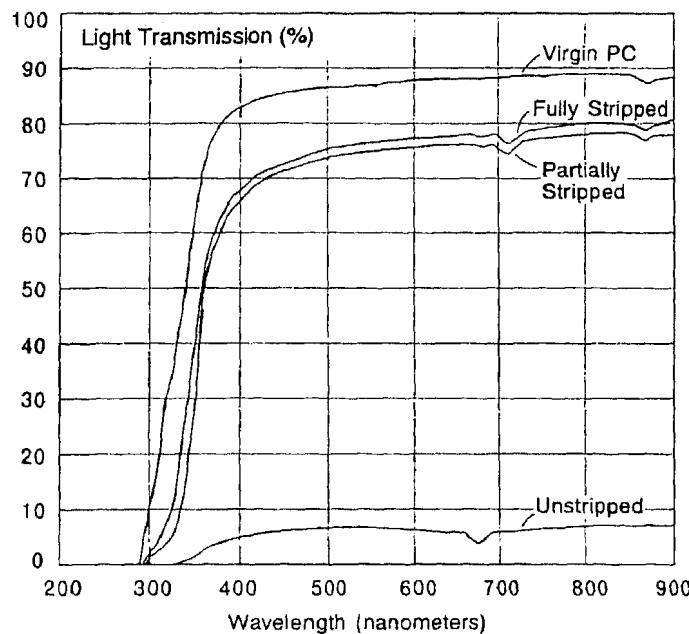


Figure 21 Light transmission from molded specimens produced from virgin polycarbonate, fully stripped, partially stripped, and unstripped compact disc [78]

DeFazio [79] suggested a mechanical apparatus to remove the coating from a compact disc by shaving. After the shaving, the discs are brushed while rotating around their centers. Figure 22 illustrates a currently manufactured compact disc (20), enlarged detail. It can be a disc of transparent polycarbonate resin, about 1 mm thick and about 12 cm in diameter. The disc's lower face (22) is generally flat and provided with multiplicity of generally cylindrical pockets (24) which are configured in a pattern that records an audio signal which can be played back by rotating the disc around its axis, while the pockets are illuminated by laser beams.

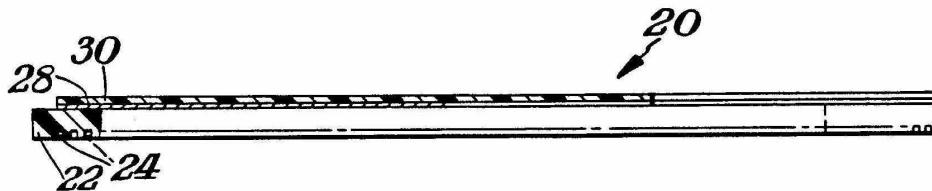


Figure 22 Schematic of a compact disc [79]

Figure 23 illustrates the apparatus for compact disc shaving technique to remove the coatings. A transporting assembly (50) is arranged to convey discs (20) from an entrance position (52) to an exit position (54) through a passageway (56) that closely fits the disc. The passageway floor has a rubbery first feed roller (60) spaced from and followed by a second rubbery feed roller (64), ending with a set of spring loaded guide rolls, (71) and (73), that urge a transported disc toward one side (74) of the passageway and also hold that disc against the disc that follows behind it in the passageway. The passageway side (74) has an edge opening through which each passing disc projects its outer edge. A motor-driven rotary brush (80) engages the projecting edges and brushes them clean of any shavings and debris. The disc is then pushed past the spring-loaded rollers by the next disc, and is thus discharged.

The passageway (56) is covered by a closely fitting roof, as noted, and through that roof a centering plunger (82) project downwardly and is spring-urged toward the line along which the disc centres are carried. When an open disc centre moves under the plunger which penetrates into the opening and momentarily holds the disc for a fraction of a second, the disc is rotated around its centre by the very rapidly rotating brush (80). Brushing action at two to ten thousand rpm is very effective. To feed the discs, the passageway floor is provided with rubbery feed rollers that pinch against feed rollers (60) and (64) to effect the feeding action. Only one of the first sets of rollers (60) is power driven. A vacuum cleaning suction input can be placed under the floor as well as near the brush to suck off the shavings and debris. Spaces

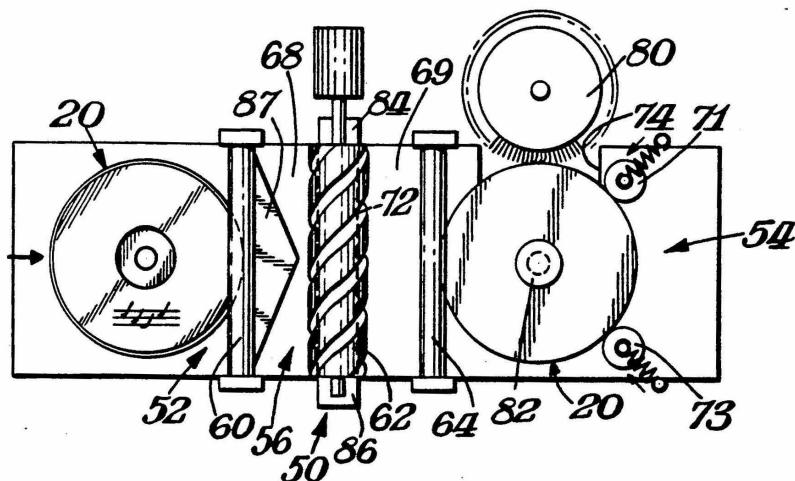


Figure 23 Schematic of apparatus for shaving off compact disc coatings [79]

(68, 69) between the rollers and the mill are provided to permit suction to remove shavings. The rubbery rollers can be backed up by all metal rolls that stiffen the pinching action of the rubbery rollers. The surface mill (62) is held between bearing blocks (84, 86), adjacent a section (72) of the floor so that the mill can be rotated around its axis at high speed, generally at over 2000 rpm, which is also raised or lowered a little as to control the shaving depth. That depth is generally about 0.05 to 0.125 mm, and can be adjusted if necessary by inspection of the brushed output without interrupting the shaving [79].

Shinomiya *et al.* [80] introduced a process for recovering the resin contained in optical information recording media having either a thin metal film layer or a printed coating film layer, coated on at least one side of a resin substrate. It which comprises the following steps: (1) passing the recording media between at least one pair of rollers to roll them; (2) feeding the rolled recording media into one end of a rotary drum having small holes, and bringing them into contact with hot water in the rotary drum while the rolled recording media are being intertwined with each other; (3) separating a substantial amount of the coating film peeled from the recording media through the small holes of the rotary drum, and extracting the recording media from the other end of the rotary drum; (4) grinding the obtained recording media; (5) feeding the obtained small pieces of the recording media into one end of a rotary drum having small holes, and bringing the small pieces into contact with hot water in the rotary drum. (6) separating the thin metal film component peeled off together with the hot

water through the small holes of the rotary drum, and taking out the small pieces of recording media from the other end of the rotary drum. With this process, the coating layer can be removed effectively from the optical information recording media and the resin component in the recording media can be selectively recovered advantageously in industry.

5.4 Other (non-thermal) methods for compact disc recycling

Polymer Reprocessors Limited (PRL) Company [81] have patented a unique, non-chemical process for the destruction of CD's and CD-ROM's, providing a high security service to media industries and offering substantial savings over increasing landfill costs by providing a complete, environmentally friendly solution (see Figure 24). A full 100% of the CDs/CD-ROMs and all packaging is recycled (paper, polycarbonate, polystyrene, paint, lacquer and aluminum). The cased CD material is delivered to a collection centre where the different parts (CD, jewel case and paper inserts) are separated. The compact discs are processed in unique and patented CD recycling machines, removing the paint, aluminum and data from the surface of the disc to be used as insulation in electric cables. The cleaned disc is then granulated, blended and compounded into a high quality injection molding grade polycarbonate for use in a multitude of applications (*e.g.* burglar alarm boxes, street lighting and lenses *etc.*). All the material obtained from the cased CD's is recycled and reused in new applications.

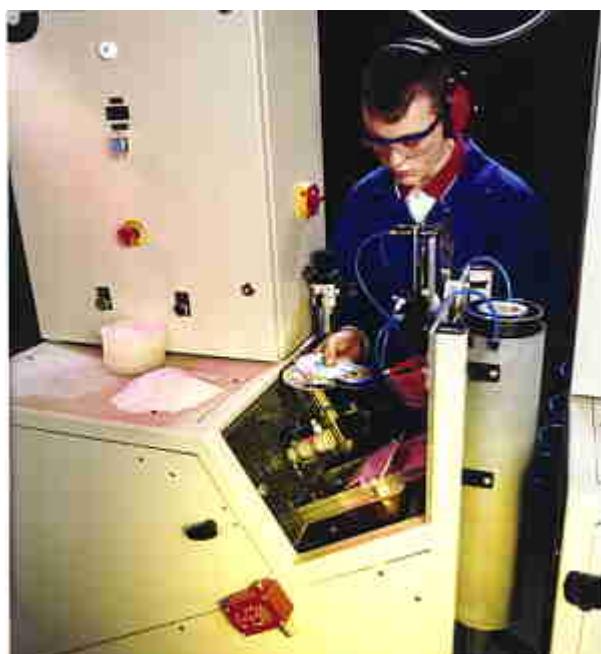


Figure 24

Picture of a non-chemical process invented by PRL [81]

Jones [82] tested the use recycled polycarbonate as a blending resin for other material formulations. Although the recycled disc grade polycarbonate has less good properties in comparison to other polycarbonate grades it does provide a valuable source of raw material. The results from the tests of compact disc polycarbonate scrap as a blending resin for other material formulations is shown to be a viable use for this recycled resin. In all the tests the blends showed improvements in tensile strength, elongation and impact.

The extent of the improvements depended on the specific blend and the property being considered. Of all the blends evaluated the 50% PC/50% ABS and 50% PC/50% bottle grade PC appeared the most favourable for further development as injection molding resins. The 50% disc PC/50% bottle PC formulation is especially advantageous since it uses two recycled resins. This utilization of readily available scrap to produce a useable resin is economically advantageous over blending the recycled disc PC with a virgin resin. This PC blend should also offer good thermal properties, and a balance of flow properties that make the resin suitable for injection molding applications. The mechanical properties, which include the tensile yield strength (σ_y), ultimate tensile strength (σ_b), yield strain (ϵ_y), ultimate strain (ϵ_b) and Izod impact for the various blends compounded in this study are given in Table 17.

**Table 17 Mechanical properties of the compact disc (CD) grade
polycarbonate scrap blends [82]**

Material	σ_y (MPa)	σ_b (MPa)	ϵ_y (m/m)	ϵ_b (m/m)	Izod Impact (J/m)
100% CD grade PC scrap	-	46.3	-	0.041	13.2
50% CD PC / 50% bottle PC	59.7	48.1	0.076	0.123	53.4
80% CD PC / 20% glass fibre	-	50.0	-	0.026	28.2
20% CD PC / 80% ABS	45.9	37.5	0.041	0.058	53.8
50% CD PC / 50% ABS	48.4	40.5	0.048	0.129	121.0
80% CD PC / 20% ABS	54.4	45.5	0.066	0.103	107.0

5.5 Thermal processing of CD waste

The methods for mechanical and chemical recycling of CD (or DVD) scrap discussed above show that the properties of the recyclate material are sensitive to temperature. For polymers such as PC thermal recycling methods are therefore not very suitable, and the presence of metals such as aluminum may interfere with feedstock recycling of PC, for which quality standards are high.

The composition of a typical CD suggest that if no recycling efforts are planned, energy recovery may be a good alternative to landfilling of the waste. At the same time, if a CD is disposed of via MSW then little or no problems will arise from their incineration in an MSWIP. Large amounts of typical CDs do, however, bring a lot of polymers and some aluminum into the process, which may cause problems. The poly carbonate will give a CD or DVD a heating value of the order of 25-31 MJ/kg [67].

The option of using CDs as alternative fuels in cement industry is limited by the amount of aluminum fed to the process, which may influence cement clinker quality. More suitable appears the co-firing of waste CDs in large-scale pulverised coal or peat boilers: there a small amount of aluminum won't do much harm and the plastics provide a lot of energy. For Finland, it may be an option to process waste CDs simultaneously with juice package waste, with aluminum recovery, at Corenso's facility at Varkaus [83,84].

6. Concluding remarks

6.1 Auto shredder residue

Current EU legislation on end-of-life vehicle (ELV) processing and landfilling of waste has resulted in increased efforts to recycle ELVs. It will inevitably lead to a reduction of the amount of ASR that is produced from a vehicle, since re-use/recycle targets are much easier reached by increased ELV dismantling than by recycling ASR fractions. Nonetheless, a wide scope of ASR processing methods based on mechanical, chemical or thermal procedures has been developed since the early 1990s, aiming at reducing the final disposal of ASR on landfills and increasing the degrees of recovery and recycling. It is noted that the driving force is from the side of legislation: the automotive industry is not too keen on extracting or re-using ELV fractions, and there is wide acceptance that ASR can safely be landfilled.

The overview given here shows that mechanical recycling methods have limited success with ASR, and also chemical treatment would require a pre-separation. From a waste-to-energy point of view, ASR falls outside the current Finnish SRF I, II, III classification. Apart from co-firing ASR with MSW at 5-10 % energy input the most promising option seems to be a hybrid process combining pyrolysis with a smelting process, such as the Reshment process that is being taken into use in Switzerland for the processing of all Swiss ASR, following a ban on landfill of ASR in Switzerland in 1996. This type of process allows for the recovery of metals, the inertisation of trace elements and the destruction of the organic fraction. Pyrolysis-based processes for ASR have a smaller environmental impact than incineration, and show a higher energy efficiency.

Most problematic is the heterogeneity of the material, the presence of PCBs, trace elements such as Cd, Ni, As, the high chlorine content in form of PVC, and the large amount of dirt, soil and other inerts that eventually will have to be landfilled after recovery and recycling efforts are exhausted.

6.2 Scrapped compact discs

Recycling of compact disc should be considered in the future because the production and the growth of the fields where these discs are used are increasing rapidly. Recycling of compact

disks is economically valuable because the quality properties of the recycled polycarbonate from old compact disk after being stripped by removing aluminum, lacquer and printing are extremely high, only slightly lower than of virgin polycarbonate. The recycled polycarbonate can be used in other application, which is preferable over final disposal on a landfill.

Each recycling method has some advantages and disadvantages. Mechanical recycling may be regarded as the simple, save and cheap way to recycle the polycarbonate. But chemical recycling is proved to be effective as being used for example by Bayer AG. Also, another way of recycling of compact disk is by using the recycled disk polycarbonate scrap as a blending resin for other material formulations has been shown to be a viable use for this recycled resin.

Already in 1998 the polycarbonate recovered from scrap CDs was amongst the four largest sources for this recyclate. For metals such as aluminum and gold the amount of material that can be recovered is extremely small as compared to the total streams of recycled aluminum and gold [67]. This makes their recovery from scrapped CDs (at this moment) economically unattractive and energy consuming.

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Auto shredder residue

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List of abbreviations

ABS	Acrylonitrile-butadiene-styrene
ASR	Automotive shredder residue
CD	Compact disc
DVD	Digital video disc
EC	European Commission
EfW	Energy from waste
ELV	End-of-life vehicle
ESP	Electrostatic precipitator
EU	European Union
EWC	European Waste Catalogue
FBC	Fluidised bed combustion
FTIR	Fourier transform infrared analysis
LHV	Lower heating value
MS	Mass spectroscopy
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
MSWIP	Municipal solid waste incineration plant
PA	Poly amide ("nylon")
PAH	Polycyclic aromatic hydrocarbon
PC	Poly carbonate
PCB	Polycyclic chlorinated biphenyls
PCDD	Poly chlorinated dibenz p dioxin
PCDF	Poly chlorinated dibenz furan
PE	Poly ethylene
PET	Poly ethylene terephthalate
PP	Poly propylene
PU	Poly urethane
PVC	Poly vinyl chloride
RDF	Refuse-derived fuel
RESH	Residue from shredding
SCR	Selective catalytic reduction (of NOx)
SLF	Shredder light fraction
SRF	Solid recovered fuel
TDF	Tyre-derived fuel
TEQ	Toxic equivalents
TGA	thermogravimetric analysis
TIC	Total ion chromatography
VOC	Volatile organic compound
WEEE	Waste electrical and electronic equipment
WtE	Waste-to-energy

Appendix

Material breakdown of a 1995 model generic US family sedan [11]

Material Breakdown of a 1995 Model Year Generic US Family Sedan

Material Category/ Material	Mass (kg)	% of Category	% of Vehicle	Material Category/ Material	Mass (kg)	% of Category	% of Vehicle
Plastics				Ferrous Metals			
ABS	9.7	7%	0.6%	Iron (Ferrite)	1.5	<1%	0.1%
ABS-PC blend	2.8	2%	0.2%	Iron (Cast)	132	13%	8.6%
Acetal	4.7	3%	0.3%	Iron (Pig)	23	2%	1.5%
Acrylic Resin	2.5	2%	0.2%	Steel (cold rolled)	114	12%	7.4%
ASA	0.18	<1%	<0.1%	Steel (EAF)	214	22%	14.0%
Epoxy Resin	0.77	1%	0.1%	Steel (galvanized)	357	36%	23.3%
PA 6	1.7	1%	0.1%	Steel (hot rolled)	126	13%	8.2%
PA 66	10	7%	0.7%	Steel (stainless)	19	2%	1.2%
PA 6-PC blend	0.45	<1%	<0.1%	Subtotal	985	100%	64.3%
PBT	0.37	<1%	<0.1%	Fluids			
PC	3.8	3%	0.2%	Auto Trans. Fluid	6.7	9%	0.4%
PE	6.2	4%	0.4%	Engine Oil	3.5	5%	0.2%
PET	2.2	2%	0.1%	Ethylene Glycol	4.3	6%	0.3%
Phenolic Resin	1.1	1%	0.1%	Gasoline	48	65%	3.1%
Polyester Resin	11	8%	0.7%	Glycol Ether	1.1	1%	0.1%
PP	25	17%	1.6%	Refrigerant	0.91	1%	0.1%
PP Foam	1.7	1%	0.1%	Water	9.0	12%	0.6%
PP-EPDM blend	0.10	<1%	<0.1%	Windshield Cleaning Additives	0.48	1%	<0.1%
PPO-PC blend	0.025	<1%	<0.1%	Subtotal	74	100%	4.8%
PPO-PC blend	2.2	2%	0.1%	Other Materials			
PS	0.007	<1%	<0.1%	Adhesive	0.17	<1%	<0.1%
PUR	35	24%	2.3%	Asbestos	0.4	<1%	<0.1%
PVC	20	14%	1.3%	Bromine	0.23	<1%	<0.1%
TEO	0.31	<1%	<0.1%	Carpeting	11	6%	0.7%
Subtotal	143	100%	9.3%	Ceramic	0.25	<1%	<0.1%
Non-Ferrous Metals				Charcoal	0.22	<1%	<0.1%
Aluminum Oxide	0.27	<1%	<0.1	Corderite	1.2	1%	0.1%
Aluminum (cast)	71	51%	4.6%	Desiccant	0.023	<1%	<0.1%
Aluminum(extruded)	22	16%	1.4%	Fiberglass	3.8	2%	0.2%
Aluminum (rolled)	3.3	2%	0.2%	Glass	42	22%	2.7%
Brass	8.5	6%	0.6%	Graphite	0.092	<1%	<0.1%
Chromium	0.91	1%	0.1	Paper	0.20	<1%	<0.1%
Copper	18	13%	1.2%	Rubber (EPDM)	10	5%	0.7%
Lead	13	9%	0.8%	Rubber (extruded)	37	19%	2.4%
Platinum	0.002	<1%	<0.1%	Rubber (tires)	45	23%	2.9%
Rhodium	0.0003	<1%	<0.1%	Rubber (other)	23	12%	1.5%
Silver	0.003	<1%	<0.1%	Sulfuric Acid- in battery	2.2	1%	0.1%
Tin	0.067	<1%	<0.1%	Textile Fibers	12	6%	0.8%
Tungsten	0.011	<1%	<0.1%	Wood	2.3	1%	0.2%
Zinc	0.32	<1%	<0.1%	Subtotal	192	100%	12.5%
Subtotal	138	100%	9.0%	GRAND TOTAL	1532		100.0%

* Adopted from Sullivan et al, 1998 (USCAR AMP Project overview).