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Shredder residues: Problematic sub- stances in relation to resource recovery

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Shredder residues: Problematic substances in relation to resource recovery

Redaktion:

Jiri Hyks, Anke Oberender og Ole Hjelmar, DHL.
Ciprian Cimpan, Henrik Wenzel, SDU.
Guilin Hu, Jesper Cramer, FORCE Technology.

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Preface

The project “**Shredder residues: Problematic substances in relation to resource recovery**” was supported by the “Miljøeffektiv teknologi 2011” programme operated by Danish EPA.

The project was executed jointly by DHI, FORCE Technology, SDU and STENA Recycling A/S. DHI was responsible for overall project management. Major contributions to the individual chapters are indicated below:

Jiri Hyks and Anke Oberender (DHI): Chapter 1-2, 5-6

Ciprian Cimpan and Henrik Wenzel (University of Southern Denmark, SDU): Chapter 3

Guilin Hu, Niels H. Pedersen, and Jesper Cramer (FORCE Technology): Chapter 4

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Abbreviations and acronyms

ABS	Acrylonitrile butadiene styrene
APC	Air pollution control
(A)SR	(Automotive) shredder residues (in this report referring to various mixtures of SR generated from simultaneous processing of ELVs and other scrap metal)
ASR	Automotive shredder residues (in this report referring to SR from shredding <i>only</i> ELVs)
BAT	Best available technology
BFR	Brominated flame retardant
BTEX	Benzene, toluene, ethyl benzene, xylene
CCA	Chromate copper arsenate (impregnated wood)
C&D waste	Construction and demolition waste
ELVs	End-of-Life-Vehicles
EPS	Expanded polystyrene
FBC	Fluidised bed combustion
GC-ECD	Gas chromatography with electron capture detector
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HIPS	High impact styrene
LIBS	Laser induced breakdown spectroscopy
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
NIR	Near infra-red
PAH	Polycyclic aromatic hydrocarbon
PBB	Polybrominated biphenyl
PBDD	Polybrominated dibenzodioxin
PBDE	Polybromodiphenyl ether
PBDF	Polybrominated dibenzofuran
PC/ABS	Polycarbonate/Acrylonitrile butadiene styrene
PCB	Polychlorinated biphenyl
PCDF	Polychlorinated dibenzofuran
PE	Polyethylene
PET	Polyethylene terephthalate
PFOS	Perfluorooctane sulfonic acid
PFOSF	Perfluorooctane sulfonyl fluoride
PGNAA	Prompt gamma neutron activation analysis
POP	Persistent Organic Pollutant
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinylchloride
RDF	Refuse derived fuel
SAN	Styrene acrylonitrile copolymer
SBR	Styrene butadiene rubber
SLF	Shredder light fraction
SR	Shredder residues (general term)

SRF	Solid recovered fuel
TBBP-A	Tetrabromobisphenol A
UPR	Unsaturated polyester resins
WEEE	Waste Electrical and Electronic Equipment
WtE	Waste to Energy
WWT	Waste water treatment
XRF	X-ray fluorescence
XRT	X-ray transmission

Summary and Conclusion

A project has been carried out to identify or confirm the presence of potentially problematic substances in SR based on:

- A desktop study focused on the latest Danish and international data on composition of shredder residues (SR), material properties and behaviour during various treatment scenarios including recycling, waste-to-energy utilisation, and landfilling;
- A discussion with the different operators; and
- A detailed characterisation of three different SR streams generated at the metal recovery plant in Grenå operated by STENA.

The results of the first two points are discussed in Chapter 2, while the results of the third point are discussed in Chapter 4. Furthermore, a desktop study was performed in order to assess the possibilities of source-separation of the problematic substances from SR using a sensor-based technology; the results of this study can be found in Chapter 3. A PGNAA sensor developed by FORCE Technology was tested on pre-treated samples of SR in order to assess its potential and future applicability on similar types of waste; the results of this experiment are shown in Chapter 4. Finally, in Chapter 5 the results of available LCA studies focusing on management of (A)SR are presented and discussed with respect to Danish conditions.

In the following text the highlights of the individual chapters are presented without discussing the possibility of source separation of the individual problematic elements prior to the shredding process. This is done in a separate paragraph at the end of this section.

Highlights of Chapter 2: Problematic substances in shredder residues with respect to further utilisation

A number of different potentially problematic¹ substances e.g. polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), BTEX, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons (TPH), PVC and “heavy metals” have been discussed with respect to their presence in SR, their potential sources as well as potential problems related to resource recovery. During the desktop study both national and international data were gathered and supplemented with relevant information from shredder plant operators. Based on available composition data (both international and Danish) it could be concluded that – from the above mentioned compounds – the PCBs, lead (Pb) and the “heavier” petroleum hydrocarbons (e.g. above C16-C20) may be regarded as “problematic” with respect to resource recovery from SR simply because their presence in SR may cause the SR to be classified as hazardous waste, thus making any further treatment (outside the process plant) more difficult if not impossible due to legislation limitations.

Polychlorinated biphenyls (PCBs)

PCBs belong to the group of persistent organic pollutants (POPs) which should ideally be destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants. Results for Danish SR indicate that PCBs (measured as the sum of seven congeners – PCB7) often have been present in SR, while sometimes the limit value for classification as hazardous waste has been exceeded. It could also be concluded from both Danish and international data that (i) PCB

¹ “Problematic” means that the substances may give rise to unacceptable environmental and/or environmental or health impacts (as reflected by legislation).

content is highly variable and sample-specific and (ii) that there appear to be “no statistically significant” differences in measured PCBs levels between the different categories of physical components of SR (e.g., fines, metals and wire fragments, soft and hard plastics, rubber, glass, fabrics, paper, and wood). In general, it has not yet been possible to identify sources of PCBs unambiguously. However, several fractions of processed metal scrap may be considered as “PCB-free” or at least “almost PCB free”. These fractions include post-1986 household appliances (white goods), ELVs and likely also large fraction of the scrap metal collected at the municipal recycling stations. Combined, these fractions represent between 20-50% (assumed) of scrap metal processed by the shredding plants and it thus seem logical to focus on the remaining 50-80% which includes scrap metal from numerous *industrial* applications such as tanks, cranes, metals structures, windmills, process plants and last but not least old ships. Moreover, literature data indicate that using PCB-containing paints as anti-corrosion protection of metal structures in a vast number of industrial application between 1950s and 1970s may be one of the major (yet largely unaccounted for) sources of PCBs to the smelters processing recycled iron/steel. For the shredding process itself, process dust is expected to be one of the main output sources of PCBs from the shredding plant. Ideally, the sludge from dust cleaning should not be sent to the landfill as landfilling of PCB-containing waste should, in line with the principles of the Stockholm Convention on POPs, be avoided if possible and POPs (including PCBs) should be destroyed or irreversibly transformed. However, exceptionally it is still permitted to dispose of POPs in an “environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or when the POP content is low”. In Denmark, shredder dust/sludge has typically been landfilled and the leaching of PCB7 is found to be mostly below the analytical detection limit.

Metals and metalloids

Various metals and metalloids have been regarded as potentially problematic for recovery of resources from SR. In general, lead (Pb) is the most critical elements with respect to classification of SR as hazardous waste. In some cases, chromium (Cr), nickel (Ni) and cobalt (Co) have been measured in SR in concentrations that may result in classification as hazardous waste; however, only if these elements were present in other than the *metallic* form – which is unlikely, since they are most likely associated with non-recovered steel.

Lead concentrations in SR has been relatively constant over the years. Furthermore, Pb is used in a number of applications including electric conductors, solder material, alloys, pipes, pigments in older paints, etc. which make source separation fairly difficult. Even if possible, the economic implications of such a separation would be very unfavourable for the shredder plant operator due to low overall recovery. It is more likely that an improved metal recovery process may help lower the Pb content of SR as hand-sorted samples (residual pieces of metals and wires were removed) of SR were shown to comply with the limits values for Pb.

Petroleum hydrocarbons

For total petroleum hydrocarbons (TPH), the hazardous waste limit value is often exceeded in Danish SR due to the contamination with petroleum hydrocarbons from the higher carbon range (above C16-C20); i.e., diesel and/or oils presumably being the main source. Thus, although the process fluids *ought to be* removed prior to the shredding, this is likely not always the case. Consequently, an improved collection scheme and/or screening procedures may be considered at the collection level, whilst some level of contamination is inevitable considering that industrial appliances and ELVs are processed. Overall, contamination with diesel/oil would not pose technical problems for recovery of metals from SR. In addition, petroleum hydrocarbons are destroyed when SR are treated thermally. It is worth mentioning that although a part of the *measured* TPH contamination certainly comes from diesel and oil, another part of the *measured* TPH contamination may be ascribed to heavy hydrocarbons present in *solid* matrix (e.g. pieces of rubber, tires etc.), the toxicity of which is rather questionable.

Brominated flame retardants (BFRs)

Though included in POPs, BFRs are not commonly measured in SR and thus only limited information is available on their contents and distribution. The bromine content has been used as a BFR indicator and it was found to increase proportionally to particle size fraction of Danish SR. This is explained by the increasing amount of plastic found in the large particle size fraction of SR. Similarly, an increasing trend in bromine content was observed for recently deposited samples compared with pre-2000 samples, indicating that more BFR-containing plastic being used and subsequently deposited. It should be noted that white goods are not considered a large source of BFRs as BFRs in these applications are generally only used for printed circuit boards, electrical connectors, some cables and in areas with a specific risk of heating. According to the statutory order of electronic waste (BEK no. 1296 of 12/12/2011) materials and components containing brominated flame retardants should be removed from the white goods prior to shredding.

As for PCBs, landfilling of BFR-containing materials should be avoided because of potential leaching. Instead, BFRs should be destroyed or irreversibly transformed. Separation of BFR-containing plastic is routinely applied in treatment of WEEE, whereas in the case of SR only some processing plants recover plastic, and only some of these plants are able to separate the BFR-containing fraction from other plastics. If, however, high-added-value applications for SR will be implemented (e.g., recycling of plastics to RDF production) or if complete destruction of BFRs is mandated by regulations, then the sensor-based sorters may provide an economically feasible solution.

BTEX

Due to their volatility, BTEX concentrations measured in Danish SR are very low and BTEX do not present any significant risk related to management of SR.

Polycyclic aromatic hydrocarbons (PAHs)

The total content of polycyclic aromatic hydrocarbons (PAHs) in Danish SR is well below the limit value for hazardous waste. The leaching of PAHs from landfilled SR is monitored and has not shown any elevated values.

Polyvinylchloride (PVC)

PVC is not hazardous itself. The fractionation of plastic in Danish SR has not been investigated and it is thus not possible to assess the amount of PVC in SR, its distribution and/or the most probable source(s). It may only be assumed that large fraction of PVC comes from furniture (metal-plastic garden furniture, office chairs), cable/wire insulation coating, and automotive parts.

Total organic carbon (TOC)

TOC is not hazardous *per se*. However, both Danish and international SR usually exceeds the TOC limit value of 6% for waste to be accepted at landfills for hazardous waste. However, similarly to the situation for TPH, this may be a legal problem but not necessarily a real problem due to the fact that the TOC analysis does not distinguish between the readily degradable fraction of TOC (e.g., paper, cardboard) and the non-degradable TOC (e.g., plastic, rubber, foam). Nevertheless, based on SR's appearance it is likely that there is more than 6% of biodegradable organic carbon present in some SR fractions.

Resource recovery

Resource recovery (material and/or energy) from SR can be realised in several ways. The evaluation of the most suitable recovery option is not straightforward and should consider a number of different aspects, such as (i) type and nature of the identified problematic substances in SR, (ii) current stage of development of screening/sorting technology (including the low-tech options), (iii) the current stage of development of the thermal-treatment technology (combustion, pyrolysis, gasification), and (iv) the environmental impacts of different SR management options. Taking these aspects

into account it becomes rather clear that landfilling of SR often is considered the worst management option since:

- Materials which can be (relatively easily) extracted from the SR and reused are deposited thereby not allowing for substitution of virgin materials in production;
- The high energy content of SR is not utilised;
- Potentially hazardous materials are deposited – the impacts from leaching of metals and organic compounds to soil and groundwater must be considered;
- Emissions of greenhouse gases from landfilled (organic) materials must be considered
- Landfill space is used for materials which (possibly) can be diverted from landfills

The overall conclusion is that although SR contains a number of problematic substances, resource recovery from SR can (and should in fact) follow the overall approach to waste management, where reuse/recycling of materials is (when feasible) preferred to utilisation of energy and finally disposal of waste. In Denmark, material recovery from SR should be complemented by energy recovery either using MSWI plants (if this will not cause severe operational problems due to fouling) or – when technologically mature – a pyrolysis/gasification process. In other countries such as Sweden and Belgium, incineration technologies typically applied to MSWI have shown to be effective with respect to utilising the energy in SR and effectively reducing the content of certain problematic substances. Co-incineration of SR is therefore one possibility to utilise energy resources from SR, and international research has indicated that co-incineration of 10-15% SR with ordinary MSW causes neither environmental nor technical problems, provided that a BAT-type plant is used. International results further show that through co-incineration at MSWI plants a large amount of the PCBs in SR can be destroyed. In addition, co-incineration of SR with BFR-containing plastic presents no environmental problem since BFRs are effectively destroyed during the incineration process; only traces of BFRs were shown to pass through the incinerator. In Denmark, co-incineration of SR in ordinary MSWI plants has been tested at FASAN and Amagerforbrænding, while tests are carried out at Reno-Nord at the moment.

As an alternative to co-incineration, gasification and/or pyrolysis seem suitable for the treatment of SR with respect to resource recovery (both material and energy). The main advantage of gasification/pyrolysis compared to incineration is that metals are not lost during the treatment and higher recovery of metals is therefore possible. However, as concluded in a number of studies, gasification/pyrolysis processes developed to treat SR from one shredder plant are generally not suitable for SR stream produced elsewhere. This is due to large heterogeneity of SR and the need for high level of optimisation of the gasification/pyrolysis process. For the same reason, a small to medium scale processes optimised for a given SR stream were suggested as the most economical solution. In Denmark, though having been under development for some years, a full-scale gasification/pyrolysis process focused on SR is not yet available. Consequently, in contrast to well established and monitored MSWI plants, the amount of data available on behaviour of different contaminants in Denmark-based gasification/pyrolysis process focused on SR is still limited.

One of the issues to be considered in connection with pyrolysis of SR is generation of PAHs during the process. As PAHs are formed during incomplete combustion of carbon containing material (e.g., wood, coal, diesel, plastic), PAHs were postulated to arise from the pyrolysis-like reaction, while during combustion, their amounts are decreasing. Pyrolysis-only treatment thus seems to be the least favourable option with respect to PAHs generation when considering energy utilisation from SR. Furthermore, considerable amounts of PBDDs/PBDFs can be formed from BFRs during pyrolysis/gasification in contrast with the incineration (combustion) in MSWI plant. Consequently, it seems necessary either to remove BFR-containing plastic from SR prior to the gasification and/or pyrolysis or to apply technology that will trap PBDDs/PBDFs from the flue gas. This would, as for incineration fly ashes, result in the generation of an additional process stream of likely hazardous material.

Highlights of Chapter 3: Overview of sensor-based technologies for substance and/or material identification

A number of sensor-based techniques are well established in the processing of different waste streams. Unfortunately, most applications are very specialised and require a very homogeneous waste stream including a limited number of material types within a limited size range, thus, their application on SR is not possible directly. Some techniques which are already applied in shredder plants may be applied for the further treatment of SR; e.g., (i) inductive sensors may be used to pick residual metals left after conventional sorting with magnetic and eddy current separators, (ii) X-ray sorters may be used to separate light and heavy non-ferrous metals, and (iii) colour sorters may be used to separate metals types based on characteristic colours.

Until recently, the SR produced by the metal recovery processes have generally been considered too heterogeneous and containing low value materials and large portion of hazardous substances. As such, there has not been much focus on development of specialised sorting systems for SR. In 2007, X-ray sensors were tested on Dutch SR in order to separate metals, inert materials (e.g., glass, stones) and chlorine-, bromine-containing materials from a coarse fraction > 10mm. Although the study has demonstrated that 15-20% of SR could be transferred into a high calorific, relatively clean fuel (low levels of problematic substances), that could potentially substitute coal in energy production, the question is what happens to the remaining 80-85% of SR. The following points summarise the reasons why sensor-based sorting has not been used for detection and sorting of problematic or unwanted materials from SR:

- Sensor-based sorting systems can only be applied for relatively coarse fractions, typically >10mm, thus covering a relatively small proportion of SR waste; many problematic substances are generally distributed over all particle size ranges;
- The material complexity and temporal variability of SR waste creates difficulties in sensor calibration as signals can be affected by fillers, various additives, plasticisers and reinforcing fibres;
- Sorting equipment costs have been unjustified relative to recovered materials or to the economic benefits brought by their use; however, the economy may change rapidly due to changes in market prices for recyclables or legislation changes (e.g., tax for landfilling of SR);
- Alternative low-technology processing and/or waste-to-energy applications represent available solutions that could be cost effective and cover a larger fraction of the SR waste stream;
- Many of the techniques have still not been developed into commercial applications.

Note that sensor resolution (smallest particle size detection), classification software and the efficiency of separation units have improved over the last couple of years (the main driver being treatment of WEEE); e.g., some equipment is able to sort particle down to 1 mm, and consequently a larger proportion of SR waste becomes available to sensor-based sorting techniques.

Highlights of Chapter 4: Assessment of applicability of PGNAA sensor technology on shredder residues

The applicability of FORCE Technology's sensor based on Prompt Gamma Neutron Activation Analysis (PGNAA) technology was meant to be assessed for detection of chlorine and bromine in different samples of SR. Preliminary tests performed in this project have shown that the method is effective for the analysis of chlorine. Unfortunately, the preliminary tests did not give a positive result for bromine as it was shown that (i) bromine gives relatively weak signal and (ii) bromine's signal is overlapped by the strong signal from chlorine. Consequently, the testing focused on the detection of chlorine alone.

Measurement of chlorine in SR samples using the PGNAA sensor showed the best results when a three-parameter model calibration was used; however, deviations between the analytically determined concentration of chlorine (chemical analysis) and the measured concentrations (using the

PGNAA sensor) were still relatively large. The large deviations of the PGNAA results seemed to be related to the inhomogeneity of SR, the calibration method and the non-uniform neutron field in the used PGNAA unit. The measuring deviations should be further reduced by improving the calibration method. For *quantitative* analysis the PGNAA sensor needs to be modified to produce a more uniform neutron field in the measuring chamber, while the calibration method needs to be improved to handle the inhomogeneity of SR.

Based on the results, it can be concluded that the PGNAA sensor developed by FORCE Technology is capable of detecting chlorine in SR with relative short response time, and it can therefore possibly be used for applications like on-line *qualitative* detection of chlorine-containing fractions of SR; i.e., for the purposes of sorting and/or characterisation of SR for chlorine-containing items (e.g. PVC).

The PGNAA sensor can be scaled up to handle objects up to 1-2 meters on conveyor belts of reasonable sizes. At the same time, the high sensitivity of the PGNAA sensor makes it possible to sort small items down to the size of a few centimetres or a few grams. Thus, the coarse part of SR with sizes over a few centimetres can be “cleaned” for chlorine-containing items by using the PGNAA sensor sorting technology. In turn, this will eliminate some of the chlorine-induced problems for recycling or energy utilisation of this fraction of SR. With a proper set-up, the PGNAA sensor sorting technology may be able to sort the fine part of SR into two streams (chlorine-rich and chlorine-poor), if there is a large variation in the chlorine concentration in the fine SR fraction.

General comment on source-separation of PCB-, Pb- and TPH-containing fractions prior to the shredding process

From the available data it is not possible to identify contamination sources of the “heavier” hydrocarbons as these are typically found to exceed the limit value for hazardous waste in all size fractions of SR. The presence of heavier hydrocarbons is an indication of contamination with diesel and/or oil. It would thus appear that an improved collection and/or screening of materials prior to the shredding process may be beneficial with special focus on ELVs, engines and appliances containing engines (e.g., lawn mowers). However, contamination with hydrocarbons is generally not causing any technical problems with respect to the shredding process and recovery of metals; it is mostly causing an economic impact related to creating/depositing of hazardous waste. If source separation of TPH-polluted materials was considered by the shredder plant operator prior to the shredding, it would be an economic evaluation of two basic scenarios: (a) current situation with little or no source-separation where more metals are recovered (though possibly polluted with TPH) while the SR would exceed limit values for TPH as well; or (b) including source-separation whereby less metals are recovered while the SR would *maybe* comply with the limit values for TPH. At the same time, it may be argued that although a part of the *measured* contamination certainly comes from diesel and oil, another part of the *measured* contamination may be ascribed to heavy hydrocarbons present in *solid* matrix (e.g. pieces of rubber, tires etc.), the toxicity of which is rather questionable.

From the available data it is not possible to identify the sources of PCBs as these were used in numerous industrial applications. The same economic evaluation as for hydrocarbons applies for PCBs and/or Pb. If PCBs and/or Pb are found to be associated with a discrete source of a relatively small volume it may be beneficial to source separate this material prior to the shredding process. If, however, PCBs and/or Pb are associated with a large fraction (volume-wise) of processed metal scrap then the separation prior to the shredding is unfavourable for economic reasons.

The extreme heterogeneity of processed material will pose significant problems for today’s sensor systems and it is highly unlikely that – in near future – incoming material will be scanned continuously for presence of the “critical elements” prior to the shredding. If needed, however, the presence of PCBs in incoming material can be assessed indirectly (by measuring chlorine) by e.g. hand-held XRF detectors which are commercially available and fast. Rather than a continuous scanning of all

incoming material the evaluation based on XRF should be carried out as spot-check or fraction-check for the “suspicious” fractions (e.g., painted scrap from old ships).

Alternatively, the PGNAAs sensor developed by FORCE Technology is capable of detecting chlorine in SR (i.e., after the shredding process) with relative short response time, and it may therefore possibly be used for applications like on-line *qualitative* detection of chlorine-containing fractions of SR; i.e., for the purposes of sorting and/or characterisation of SR for chlorine-containing items (e.g. PVC).

Highlights of Chapter 5: Environmental assessment of different management options for shredder residues

Different LCA studies provided different recommendations. However, regardless the treatment options considered, all studies have identified landfilling of SR as the worst management option since: (i) the energy content of SR is not used and significant emissions of greenhouse gases related to energy production are thus not avoided, (ii) materials which can be re-used are deposited thereby not allowing for substitution of virgin materials in production, (iii) potentially hazardous materials are deposited and related impacts from leaching of metals and organic compounds to soil and groundwater must be considered, and (iv) emissions of greenhouse gases from landfilled materials must be considered.

Konklusion og sammenfatning

Der er gennemført et projekt med det hovedformål at identificere eller bekræfte tilstedeværelsen af potentielt problematiske stoffer i shredderaffald (SR – shredder residues) baseret på:

- Et litteraturstudie med fokus på den nyeste danske og internationale viden om sammensætning, materialeegenskaber og opførsel af SR i relation til forskellige behandlingsscenarier, herunder genvinding/genbrug, energiudnyttelse fra affald og deponering;
- En diskussion med de forskellige operatører og
- En detaljeret karakterisering af tre forskellige SR-strømme genereret på metalgenvindingsanlægget i Grenå, som drives af STENA A/S.

Resultaterne af litteraturstudiet og diskussionerne er behandlet i kapitel 2, mens resultaterne af karakteriseringen behandles i kapitel 4. Derudover er der udført et litteraturstudie med henblik på at vurdere mulighederne for kildesortering af de problematiske stoffer fra SR ved hjælp af sensorbaseret teknologi. Resultaterne fra dette studie præsenteres i kapitel 3. En sensor baseret på Prompt Gamma Neutron Activation Analysis (PGNAA), som er udviklet af FORCE Technology, blev desuden testet på forbehandlede prøver af SR for at vurdere sensorens potentiale og fremtidige anvendelsesmuligheder for lignende typer affald. Resultaterne af dette forsøg er vist i kapitel 4. Endelig præsenteres i kapitel 5 resultaterne af tilgængelige LCA undersøgelser med fokus på håndtering af SR (ofte fra bilfragmentering), og resultaterne diskuteres med hensyn til danske forhold.

I det følgende præsenteres hovedpunkterne fra de enkelte kapitler. Til sidst foretages en samlet vurdering af muligheden for fraseparering af de forskellige problematiske stoffer forud for shredder-processen ved kildesortering.

Hovedpunkter fra kapitel 2: Problematiske stoffer i shredder affald i forbindelse med ressourcegenanvendelse

Indholdet af en række potentielt problematiske² stoffer som f.eks. polychlorerede biphenoler (PCB), bromerede flammehæmmere (BFR), benzen, toluen, ethylbenzen og xylener (BTEX), polycyklisk aromatisk kulbrinter (PAH), mineraloliebaserede kulbrinter (TPH), polyvinylchlorid (PVC) og "tungmetaller"/sporelementer i SR, deres potentielle kilder samt de potentielle problemer, som stofferne kan forårsage i forhold til ressourcegenanvendelse, er undersøgt og diskuteret. Både danske og internationale data er indsamlet og suppleret med relevant information fra operatørerne på danske shredder anlæg. På basis af tilgængelige oplysninger (både internationale og danske) om sammensætningen af SR kan det konkluderes, at blandt de ovennævnte forbindelser kan PCB, bly (Pb) og de 'tungere' mineraloliebaserede kulbrinter (f.eks. over C16-C20) betragtes som 'problematiske' med hensyn til ressourcegenanvendelse fra SR, alene fordi deres tilstedeværelse kan medføre, at SR klassificeres som farligt affald. Dette kan vanskeliggøre og måske endda umuliggøre enhver yderligere behandling (uden for behandlingsanlægget) på grund af lovmæssige restriktioner af håndteringen af farligt affald.

Polychlorerede biphenyl (PCB)

PCB tilhører gruppen af persistente organiske forurenende stoffer (POP), som idéelt set burde destrueres eller omdannes irreversibelt, så de ikke længere kan karakteriseres som POP'er. Resulta-

² 'Problematiske' betyder at stofferne kan give anledning til uacceptable miljømæssige og/eller miljø- og helbredstruende påvirkninger (jf. lovgivningen).

terne for dansk SR viser, at der ofte er fundet PCB (målt som summen af syv kongener - PCB7) i SR, og at grænseværdien for klassificering som farligt affald af og til er blevet overskredet. Det kan desuden konkluderes ud fra både danske og internationale data, at (i) indholdet af PCB er meget forskelligt og prøvespecifikt, samt at (ii) der ikke ser ud til at være nogen "statistisk signifikant" forskel i de målte PCB-niveauer mellem forskellige kategorier af fysiske SR komponenter (f.eks. støv/fine partikler, metal- og kabelfragmenter, blød og hård plast, gummi, glas, tekstiler, papir og træ). Overordnet set har det ikke været muligt entydigt at identificere kilderne til PCB. Visse fragmenter af behandlet metalaffald kan dog betragtes som "PCB-frie" eller i det mindste "næsten PCB-frie". Disse fraktioner omfatter husholdningsredskaber produceret senere end 1986 (hårde hvidevarer), skrottede/udrangerede biler og formentlig også store fraktioner af metalaffald opsamlet på de kommunale genbrugsstationer. Tilsammen udgør disse fraktioner ca. 20-50% (skønnet) af det metalaffald, der bliver behandlet på shredder anlæggene, og det synes derfor logisk at fokusere på de resterende 50-80%, som omfatter metalaffald fra adskillige industrielle produkter såsom tanke, kraner, metalstrukturer, vindmøller, procesanlæg og sidst, men ikke mindst gamle skibe. Desuden viser litteraturodata, at brugen af PCB-holdig maling som anti-rustbehandling af metal i et stort antal industrielle installationer mellem 1950'erne og 1970'erne kan vise sig at være en af de største PCB-kilder (som der stadig ikke kan redegøres for) til de smeltere, som behandler genanvendt jern og stål. For selve shredderprocessen anses processtøv for at være en af de væsentligste PCB-holdige affaldsstrømme fra shredder anlæg. Idéelt set burde slam fra støvfjernelse ikke sendes til deponering, da deponering af PCB-holdigt affald i henhold til principperne i Stockholm-konventionen om POP så vidt muligt bør undgås, og POP'er (inkl. PCB) i stedet bør destrueres eller omdannes irreversibelt. Det er dog stadig tilladt at bortskaffe POP på en "miljømæssigt forsvarlig måde, når destruktion eller irreversibel omdannelse ikke udgør den miljømæssigt bedste løsning, eller hvis POP-indholdet er lavt". I Danmark er shredderstøv/-slam typisk blevet deponeret, og det er konstateret, at udvaskning af PCB7 oftest ligger under den analytiske detektionsgrænse.

Metaller og metalloider

Forskellige metaller og metalloider er blevet betragtet som potentielt problematiske for genvinding af ressourcer fra SR. Overordnet set er bly (Pb) det mest kritiske stof, for så vidt angår klassificering af SR som farligt affald. I nogle tilfælde er der i SR blevet målt chrom (Cr), nikkel (Ni) og kobolt (Co) i koncentrationer, som kan føre til klassificering som farligt affald. Dette kræver dog, at disse stoffer er til stede i anden form end metallisk, hvilket ikke er sandsynligt, da de oftest forbindes med ikke-genvundet stål.

Koncentrationerne af bly i SR har været relativt konstante igennem årene. Desuden indgår Pb i en del anvendelser, som bl.a. omfatter elektriske ledere, loddemateriale, legeringer, rør, pigmenter i ældre malinger osv., og som gør kildeseparering temmelig vanskelig. Selv hvis det var muligt, ville de økonomiske konsekvenser af en sådan separering blive meget ugunstige for shredder anlægsoperatøren på grund af en generelt lav genvindingsgrad. Det er mere sandsynligt, at en forbedret metalgenvindingsproces vil kunne hjælpe med at nedsætte Pb-indholdet i SR, da det har vist sig, at håndsorterede prøver af SR (hvor rester af metaller og kabler er fjernet) kan overholde grænseværdierne for Pb.

Mineraloliebaserede kulbrinter

Totalindholdet af kulbrinter (THC/TPH) i dansk SR overskrider ofte grænseværdien for farligt affald på grund af forurening med kulbrinter med et højere kulstofindhold (over C16-C20), hvor diesel og/eller olie formentlig udgør den vigtigste kilde. Selv om procesvæskerne (benzin, olie) *burde* fjernes forud for oparbejdning i shredder anlægget, sker dette formentlig ikke altid. På indsamlingsniveau kunne en forbedring af indsamlingsprogrammet og/eller screeningprocedurerne derfor overvejes, mens det formentlig ikke er muligt at undgå en vis grad af kontaminering i betragtning af, at det er industrielle produkter og skrotbiler, som behandles. Overordnet set ville kontaminering med diesel/olie dog ikke udgøre nogen hindring for genvinding af metaller fra SR. Desuden ødelægges kulbrinterne, når SR behandles termisk. Det er desuden værd at nævne, at selv om en del af den

målte TPH-kontaminering helt sikkert stammer fra diesel og olie, kan en anden del af den *målte* TPH-kontaminering tilskrives tunge kulbrinter, som er til stede i faste matricer (f.eks. rester af gummi, dæk m.m.), som ikke nødvendigvis er tilgængelige eller specielt toksiske.

Bromerede flammehæmmere (BFR)

Selv om bromerede flammehæmmere er inkluderet i gruppen af POP-stoffer, analyseres der ikke rutinemæssigt for BFR i SR, og der findes derfor kun begrænset information om indhold og fordeling af disse stoffer i SR. Indholdet af brom anvendes som en indikator for indholdet af BFR og har vist sig at stige proportionalt med partikelstørrelsen i dansk SR. Dette forklares ved den stigende mængde plast, som er fundet i SR-fraktionen med stor partikelstørrelse. Desuden blev der observeret en stigende tendens i indholdet af brom i nyligt deponerede prøver sammenlignet med prøver fra før år 2000. Det blev derfor konkluderet, at der nu anvendes og deponeres mere BFR-holdig plast end tidligere. Det skal desuden bemærkes, at hårde hvidevarer ikke anses som en væsentlig kilde til BFR, da BFR her som regel kun indgår i printkort, i elektriske forbindelsesklemmer, i enkelte kabler og i produktdele med en specifik risiko for overophedning. Materialer og komponenter indeholdende bromerede flammehæmmere skal i henhold til elektronikaffaldsbekendtgørelsen (BEK nr. 1296 af 12/12/2011) fjernes fra de hårde hvidevarer, inden disse shreddes.

I lighed med PCB bør deponering af BFR-holdige materialer undgås på grund af risikoen for udvaskning. BFR bør i stedet destrueres eller omdannes irreversibelt. Frasortering af BFR-holdigt plast anvendes rutinemæssigt i behandlingen af WEEE, mens det kun er nogle af metalgenvindingsanlæggene, der separerer plast, og kun nogle af disse anlæg er i stand til at separere de BFR-holdige fraktioner fra anden plast. Hvis der imidlertid gennemføres "high-added-value"-applikationer for SR (f.eks. genanvendelse af plast til RDF produktion), eller hvis en total destruktion af BFR bliver påbudt ved lov, kan de sensorbaserede sorteringsanlæg vise sig at være en økonomisk gennemførlig løsning.

BTEX

På grund af BTEX'ernes flygtighed er de målte BTEX-koncentrationer i dansk SR meget lave, og BTEX udgør ikke nogen signifikant risiko i forhold til håndteringen af SR.

Polycykliske aromatiske hydrokarboner (PAH)

Det totale indhold af polycykliske aromatiske hydrokarboner (PAH'er) i dansk SR ligger langt under grænseværdien for farligt affald. Udvasningen af PAH'er fra deponeret SR overvåges og udviser ingen forhøjede værdier.

Polyvinylchlorid (PVC)

PVC er ikke i sig selv farlig. Fraktioneringen af plast i dansk SR er ikke blevet undersøgt, og det er derfor ikke muligt at vurdere mængden af PVC i SR, fordelingen og/eller de(n) mest sandsynlige kilde(r). Det er således kun en formodning, at den største del af PVC kommer fra møbler (metalplastik havemøbler og kontorstole), isolering af kabler/ledninger samt bilkomponenter.

Samlet mængde organisk kulstof (TOC)

Total organisk kulstof (TOC) er en samleparameter, og er ikke i sig selv en indikator for farlighed. Såvel i Danmark som internationalt ofte overskrider SR grænseværdien på 6% for affald, som modtages på deponeringspladser for farligt affald. Som for TPH kan dette problem imidlertid primært være af lovgivningsmæssig karakter og ikke nødvendigvis et reelt problem, da TOC-analyser ikke skelner mellem den let nedbrydelige fraktion af TOC (f.eks. papir og pap) og den ikke-nedbrydelige TOC (f.eks. plast, gummi og skum). På basis af SR's udseende må det ikke desto mindre antages, at der i nogle SR-fraktioner er mere end 6% biologisk nedbrydeligt organisk kulstof.

Ressourcenyttiggørelse

Ressourcenyttiggørelse (materialer og/eller energi) fra SR kan gennemføres på flere forskellige måder. Vurderingen af den bedst egnede løsning er ikke helt enkel og er nødt til at tage hensyn til en række aspekter som f.eks. (i) type og art af de identificerede problematiske stoffer i SR, (ii) det aktuelle udviklingsniveau inden for screenings-/sorteringsteknologi (inkl. lavteknologiske muligheder), (iii) det aktuelle udviklingsniveau inden for varmebehandlingsteknologi (forbrænding, pyrolyse, forgasning) og (iv) de miljømæssige påvirkninger af de forskellige håndteringsmuligheder for SR. Når disse aspekter tages i betragtning, bliver det tydeligt, at deponering af SR ofte må betragtes som den dårligste løsning, da:

- Materialer, som (relativt nemt) kan ekstraheres fra SR og nyttiggøres eller genanvendes i stedet bliver deponeret, hvorved muligheden for substitution af primære materialer i produktionen ikke udnyttes;
- Det høje energiindhold i SR ikke udnyttes;
- Potentielt farlige materialer deponeres, hvorfor den miljømæssige påvirkning fra udvaskning af metaller og organiske stoffer til jord og grundvand må tages i betragtning;
- Udledninger af drivhusgasser fra deponerede (organiske) materialer må tages i betragtning;
- Deponeringsplads anvendes til materialer, som (muligvis) vil kunne genanvendes/nyttiggøres.

Den samlede konklusion er, at selv om SR indeholder en række problematiske stoffer, kan (og skal) udnyttelse af ressourcer i SR følge den overordnede tilgang til affaldshåndtering, hvor genbrug eller genanvendelse af materialer prioriteres (i det omfang, det er muligt) over energiudnyttelse og sluteligt bortskaffelse af affald. I Danmark bør genanvendelse/nyttiggørelse af materialer fra SR suppleres med nyttiggørelse af energi enten i forbrændingsanlæg, forudsat at der ikke opstår korrosionsproblemer, eller – når teknologien er færdigudviklet – ved pyrolyse/forgasning. I andre lande som f.eks. Sverige og Belgien har det vist sig, at forbrændingsteknologier, som typisk anvendes til husholdnings- og industriaffald, er effektive med hensyn til udnyttelse af energien i SR og i stand til effektivt at reducere indholdet af visse problematiske (organiske) stoffer. Medforbrænding af SR er én mulighed for at udnytte energiressourcerne fra SR, og international forskning har vist, at medforbrænding af 10-15% SR med almindeligt husholdnings- og industriaffald ikke giver anledning til hverken miljømæssige eller tekniske problemer, forudsat at der anvendes BAT-teknologi. Internationale undersøgelser har desuden vist, at en stor mængde PCB i SR kan nedbrydes under medforbrænding på almindelige forbrændingsanlæg. Yderligere har det vist sig, at medforbrænding af SR med BFR-holdig plast ikke giver anledning til miljømæssige problemer, da BFR nedbrydes effektivt under forbrændingsprocessen. Det blev påvist, at kun spor af BFR passerede igennem forbrændingsprocessen. I Danmark er medforbrænding af SR i almindelige affaldsforbrændingsanlæg blevet testet på FASAN og Amagerforbrænding, mens der i øjeblikket udføres forsøg på Reno-Nord.

Som et alternativ til medforbrænding synes forgasning og/eller pyrolyse velegnet til behandling af SR med hensyn til ressourcenyttiggørelse (materialer såvel som energi). Konklusionen fra en række studier er imidlertid, at forgasnings-/pyrolyseprocesser, som er udviklet til behandling af SR fra ét bestemt shredder anlæg generelt ikke er egnede til behandling af SR, som er produceret andre steder. Dette skyldes den store heterogenitet i SR samt behovet for en høj optimering af forgasnings-/pyrolyseprocessen. Af samme årsag blev udviklingen af processer i lille til mellemstor skala, som er optimeret til en given SR strøm, anbefalet som den mest økonomiske løsning. På trods af, at de har været under udvikling i flere år, findes der i Danmark endnu ingen fuldskala forgasnings-/pyrolyse anlæg med fokus på SR. I modsætning til situationen for veletablerede og overvågede kommunale eller fælleskommunale affaldsforbrændingsanlæg er der derfor fortsat kun begrænsede data tilgængelige vedrørende forskellige forurenende stoffers adfærd i dansk-baserede forgasnings-/pyrolyseprocesser med fokus på SR.

Et af de problemer, der skal overvejes i forbindelse med pyrolyse af SR, er produktionen af PAH'er under processen. Da der dannes PAH'er under ufuldstændig forbrænding af kulstofholdige materia-

ler (f.eks. træ, kul, diesel og plast), er det blevet postuleret, at der opstår PAH'er fra den pyrolyseagtige reaktion, mens antallet af PAH'er derimod falder under forbrænding. I forbindelse med energidnyttelsen fra SR ser det således ud til, at pyrolysebehandling alene er den mindst favorable løsning med hensyn til dannelse af PAH'er. Desuden kan der opstå betydelige mængder PBDD/PBDF fra BFR under pyrolyse/forgasning i modsætning til forbrænding på et almindeligt affaldsforbrændingsanlæg. Som følge heraf må det betragtes som nødvendigt enten at fjerne BFR-holdig plast fra SR forud for forgasning og/eller pyrolyse eller at anvende en teknologi, som kan indfange PBDD/PBDF fra røggassen. Hvad angår flyveaske fra forbrænding, ville dette resultere i dannelsen af en supplerende processtrøm af formentligt farligt materiale.

Hovedpunkter fra kapitel 3: Oversigt over sensorbaserede teknologier til identifikation af stoffer og/eller materialer

En række sensorbaserede teknikker er veletablerede til behandling af forskellige affaldsstrømme. Desværre er de fleste anvendelser meget specialiserede og kræver en meget homogen affaldsstrøm, inkl. et begrænset antal materialetyper inden for et begrænset størrelsesområde, hvorfor der ikke umiddelbart er muligheder for at anvende dem på SR. Nogle teknikker, som allerede anvendes i shredder anlæg, kan muligvis anvendes til yderligere behandling af SR som i følgende eksempler: (i) induktive følere kan anvendes til opsamling af metalrester fra konventionel sortering med magnetiske separatore og hvirvelstrømsseparatorer, (ii) røntgensorteringsanlæg kan bruges til at separere lette og tunge ikke-jernholdige metaller, og (iii) farvesorteringsanlæg kan benyttes til at separere metaltyper baseret på karakteristiske farver.

Indtil for nylig er det shredderaffald, som dannes i forbindelse med metaludvindingsprocessen, generelt blevet betragtet som værende for heterogent og som indeholdende materialer af for lav værdi samt store mængder farlige stoffer til at yderligere udvinding ville være rentabel. Derfor har der ikke været meget fokus på at udvikle specialiserede sorteringssystemer til SR. I 2007 blev røntgensensorer testet på hollandsk SR med henblik på at sortere metaller, inert materiale (f.eks. glas og sten) samt chlor- og bromholdige materialer fra en grovfraktion > 10 mm. Selv om studiet har vist, at 15-20% af SR kan omdannes til et relativt rent brændstof med høj brændværdi (lavt niveau af problematiske stoffer), som potentielt ville kunne erstatte kul i energiproduktionen, er spørgsmålet, hvad der sker med de resterende 80-85% af SR. I nedenstående punkter opsummeres årsagerne til, at sensorbaseret sortering endnu ikke er blevet benyttet til at finde og frasortere problematiske eller uønskede stoffer i SR:

- Sensorbaserede sorteringssystemer kan kun anvendes til relativt grove fraktioner, typisk > 10 mm, hvilket kun dækker en relativt lille del af alt SR affald; mange problematiske stoffer er generelt fordelt over alle partikelstørrelsesområder;
- Materialekompleksiteten og den tidsmæssige variation i sammensætningen af SR affald skaber vanskeligheder for sensor kalibrering, da signaler kan påvirkes af fyldstoffer, forskellige tilsætningsstoffer, blødgørere og forstærkede fibre;
- Omkostningerne til sorteringsudstyr har været for høje set i forhold til de genanvendte materialer eller de økonomiske fordele, som er opnået igennem deres anvendelse; økonomien kan dog hurtigt ændres som følge af ændringer i markedspriser for genanvendte ressourcer eller lovgivningsmæssige ændringer (f.eks. afgifter på deponering af SR);
- Alternative lavteknologiske behandlinger og/eller affald-til-energi applikationer udgør tilgængelige løsninger, som kunne være omkostningseffektive og dække en større del af SR affaldsstrømmen;
- Mange af teknikkerne er stadig ikke blevet udviklet til kommercielt anvendelse.

Bemærk, at sensorløsningen (påvisning af de mindste partikelstørrelser), klassificeringssoftware samt effektiviteten af separationsenheder er blevet forbedret over de seneste år (med WEEE-behandling som hoveddrivkraften). Noget udstyr er f.eks. i stand til at frasortere partikler helt ned

til 1 mm, hvilket betyder, at en større del af SR affaldet bliver tilgængeligt for sensorbaserede sorteringsteknikker.

Hovedpunkter fra kapitel 4: Vurdering af anvendeligheden af PGNAA sensorteknikken på shredder restprodukter

Anvendeligheden af FORCE Technology's sensorbaserede PGNAA (Prompt Gamma Neutron Activation Analysis)-teknologi skulle have været vurderet med henblik på detektion af chlor og brom i forskellige SR-prøver. Foreløbige tests under dette projekt har vist, at metoden er effektiv for analyse af chlor. Desværre gav de foreløbige undersøgelser ikke et positivt resultat for brom, da det viste sig, at (i) brom giver et relativt svagt signal, og (ii) signalet fra brom overlappes af det stærke signal fra chlor. Som følge af dette har undersøgelsen fokuseret alene på detektion af chlor.

Måling af chlor i SR prøver ved hjælp af PGNAA-sensoren gav de bedste resultater, når der blev anvendt en tre-parameters modelkalibrering. Afvigelser mellem den analytisk bestemte koncentration af chlor (kemisk analyse) og de målte koncentrationer (ved hjælp af PGNAA sensoren) var imidlertid stadig relativt store. De store afvigelser i PGNAA-resultaterne syntes at være relateret til inhomogeniteten i SR, kalibreringsmetoden samt det uensartede neutronfelt i den anvendte PGNAA enhed. Måleafvigelseerne bør reduceres yderligere gennem forbedring af kalibreringsmetoden. Hvad angår *kvantitative* analyser, er der behov for at ændre PGNAA-sensoren, så den kan producere et mere ensartet neutronfelt i målekammeret, mens kalibreringsmetoden skal forbedres, så den kan håndtere inhomogeniteterne i SR.

På basis af resultaterne kan det konkluderes, at PGNAA-sensoren fra FORCE Technology er i stand til at påvise chlor i SR med en relativt kort responstid, og den kan derfor formentlig anvendes til applikationer som on-line *kvalitativ* detektion af chlor-holdige fraktioner af SR, bl.a. med det formål at sortere og/eller karakterisere SR med hensyn til chlor-holdige emner (f.eks. PVC).

PGNAA-sensoren kan skaleres op til at håndtere genstande på op til 1-2 meter på transportbånd af en rimelig størrelse. Samtidig gør PGNAA-sensorens høje følsomhed det muligt at sortere små genstande ned til en størrelse på nogle få centimeter eller nogle få gram. Den grove del af SR med størrelser på mere end nogle få centimeter kan således "renses" for chlor-holdige emner ved hjælp af PGNAA-sensor sorteringsteknologien. Det vil eliminere nogle af de chlor-fremkaldte problemer i forbindelse med genanvendelse eller energiudnyttelse af denne del af SR. Med det rigtige set-up kan sorteringsteknologien baseret på PGNAA-sensoren måske blive i stand til at sortere den fine del af SR i to strømme (chlor-rig og chlor-fattig), såfremt der er stor variation i chlor-koncentrationen i denne fraktion.

Generel kommentar til kildeseparering af PCB-, Pb- og TPH-holdige fraktioner forud for shredderprocessen

Ud fra de tilgængelige data er det ikke muligt at identificere kilderne til forurening med de 'tungere' kulbrinter, da disse typisk viser sig at overskride grænseværdien for farligt affald i alle størrelsesfraktioner af SR. Tilstedeværelsen af tungere kulbrinter er en indikation på forurening med diesel og/eller olie. Det ser således ud til, at en forbedret indsamling og/eller screening af materialer forud for shredderprocessen kunne være fordelagtig med særligt fokus på skrotbiler, motorer og produkter, der indeholder motorer (f.eks. plæneklippere). Generelt giver forurening med kulbrinter imidlertid ikke anledning til tekniske problemer, hvad angår shredderprocessen og genanvendelse af metaller; der er primært tale om en potentiel økonomisk effekt i forhold til dannelse/deponering af farligt affald. Hvis kildeseparering af TPH-holdige materialer skulle overvejes af shredder anlæggets operatør forud for shredderprocessen, ville det indebære en økonomisk vurdering af to scenarier: (a) nuværende situation med ringe eller ingen kildeseparering, hvor flere metaller er genvundet (selvom de eventuelt er forurennet med TPH), mens shredderaffald samtidig ville overstige grænseværdierne for TPH, eller (b) inklusive kildeseparering, hvorved færre metaller genvindes, mens shredderaffaldet måske ville overholde grænseværdierne for TPH. Samtidig kan der argumenteres

for, at selv om en del af den *målte* forurening helt sikkert stammer fra diesel og olie, kan en anden del af den *målte* forurening som tidligere nævnt muligvis tilskrives tunge kulbrinter som er til stede i *faste* matricer (f.eks. stumper af gummi, dæk osv.).

Det er ikke muligt ud fra de tilgængelige data at identificere kilderne til PCB, da disse blev brugt i adskillige industrielle applikationer. Den samme økonomiske vurdering som for kulbrinter gælder for PCB og/eller Pb. Hvis PCB og/eller Pb viser sig at være forbundet med en særskilt kilde af relativt begrænset volumen, kan det være fordelagtigt at kildeseparere dette materiale forud for shredderprocessen. Hvis PCB og/eller Pb derimod er forbundet med en stor fraktion (målt i volumen) af det behandlede metalkrot, vil separering forud for shredderprocessen være ufordelagtig ud fra et økonomisk synspunkt.

Den ekstreme heterogenitet i det behandlede materiale vil give anledning til væsentlige problemer for mange af de aktuelle sensorsystemer, og det er højst usandsynligt, at indkommende materiale i den nærmeste fremtid vil blive scannet kontinuerligt for tilstedeværelsen af "kritiske elementer" forud for shredderprocessen. Om nødvendigt kan tilstedeværelsen af PCB i indkommende materiale dog vurderes indirekte (ved at måling af chlorindholdet) f.eks. ved håndholdte XRF detektorer, som er kommercielt tilgængelige og hurtige. I stedet for en fortsat scanning af alt indkommende materiale, burde den XRF-baserede vurdering snarere udføres som stikprøver eller fraktionsprøver for de "mistænkelige" fraktioner (f.eks. malet skrot fra gamle skibe).

Alternativt er PGNAA-sensoren fra FORCE Technology i stand til at påvise chlor i SR (bl.a. efter shredderprocessen) med en relativt kort responstid, og den kunne derfor muligvis anvendes til applikationer som on-line *kvalitativ* detektion af chlor-holdige fraktioner af SR f.eks. med det formål at sortere og/eller karakterisere SR for chlor-holdige emner (f.eks. PVC).

Hovedpunkter fra kapitel 5: Miljøvurdering af forskellige disponeringsmuligheder for shredderaffald

Forskellige livscyklusvurderinger gav forskellige anbefalinger. Men uanset hvilke behandlingsmuligheder der blev sammenlignet, blev deponering af shredderaffald identificeret som den værste håndteringsmulighed, da: (i) energiindholdet i SR ikke bliver udnyttet og væsentlig udledning af drivhusgasser i forbindelse med energiproduktion således ikke kan undgås, (ii) materialer, der kan genanvendes bliver deponeret og derved ikke giver mulighed for substitution af jomfruelige materialer i produktionen, (iii) potentielt farlige materialer er deponeret og miljøpåvirkningen som resultat af udvaskning af metaller og organiske forbindelser til jord og grundvand skal tages højde for, og (iv) udledning af drivhusgasser fra deponerede materialer skal overvejes.

1. Introduction

1.1 Background

Shredder residues (SR³) are generated as a residual fraction from mechanical shredding of metal containing scrap originating from different sources and processed at recycling stations or metal recovery businesses (Fact box 1). The composition and properties of SR depend both on the input to the metal recovery process (e.g., End-of-Life vehicles (ELVs), white goods, metal containing scrap, ships being dismantled, large metal constructions, windmills etc.) and the type and effectiveness of the recovery process. Thus, SR present a highly heterogeneous mixture of different types of plastic, foam, rubber, wires, cables, wood, glass, metal and others.

SR are classified as non-hazardous waste in most of the Nordic countries. In Denmark, however, SR have been classified as hazardous waste due to their chemical composition - namely high contents of some metals and different organic contaminants (typically petroleum hydrocarbons and oils). The rules for classification of hazardous waste are currently under revision in EU (Hjelmar et al., 2009).

Until 2012, Danish SR have been exempted from landfill taxes in Denmark. This is probably the main reason why landfilling of SR has been the primary waste management option in Denmark over the last 20 years, resulting in about 1.5 million tonnes of SR being deposited. Nevertheless, as of 1.1.2012, a tax of 160 DKK/tonne of waste to be landfilled at sites for hazardous waste has been introduced. This tax is expected to increase to 475 DKK/tonne by 2015. In other words, as of 1.1.2012 landfilling of SR presents a considerable cost for the waste producer (i.e., the shredder plant operator) which will further increase in the near future. Consequently, the focus on recovery of resources from SR has been increasing lately.

In general, there are a number of different drivers for recovery of material and/or energy utilisation from SR:

- Profitable market prices of materials – especially metals (e.g., Fe, Cu, Al, Zn, stainless steel, brass);
- The presence of scarce or soon-to-be scarce elements (e.g., depletion of resources, on-going concerns regarding export quotas for rare earth elements from China);
- A favourable calorific value with respect to waste-to-energy (WtE) utilisation;
- Limited landfill space (e.g., recent closure of the SR cell at the AV Miljø landfill at Avedøre Holme);
- The uncertainty regarding the amount of resources/costs needed for the aftercare period and possible mitigation of environmental impacts related to landfilling of SR;
- Legislation such as the above mentioned landfill tax, Affaldstrategi '10 (Miljøministeriet, 2010), and/or increasing targets for recovery of materials from ELVs (European Commission, 2000).

SR composition does, to a certain extent, reflect the situation on the market. For example, an increasing trend in the relative metal content in landfilled SR was observed for Danish SR around 2008; i.e., less metals were recovered during the shredding process before the SR were landfilled.

³ SR is used as a general term describing residues originated from the shredding process; i.e., regardless the composition of the processed material.

After 2009, a decrease in the relative content of metals was observed, which indicated rather improved post-shredder material recovery at the shredding companies. This correlated very well with the fluctuations in the market demand (and prices) for scrap metal around 2008 caused by the global recession in the automotive and construction sectors. At the same time, as a side-effect of changing the relative content of metals in deposited SR, the relative content of the combustible fraction has increased in all samples deposited after 2009 when compared to samples from earlier time periods (Ahmed et al., 2012).

A typical shredder plant consist as a minimum of a hammer mill followed by a cyclone that separates the shredded material into a shredder “light” fraction (SLF), which is sometimes referred to as “fluff”, and a shredder “heavy” fraction (SHF). SLF is typically composed of light metal, paper, cardboard, various types of plastic, foam, textile, wires, wood and such, whereas SHF contains scrap iron, various non-magnetic metals, wires, high density plastic, and glass. Ferromagnetic metals are removed from both fractions by magnetic separators, while Eddy-current separators are used to remove the non-magnetic metals. At some plants, a system for separation of different types of plastic may be installed. Typically, tanks containing liquid of different density are used for separation of plastic. Alternatively, sensor-based sorting systems may be applied. SR is basically a mix of all rejected materials. As such, the composition of SR is highly dependent on the recovery process and thus may vary significantly between the different plants.

Fact box 1. Generic description of a metal recovery plant

Recent Danish studies focusing on detailed characterisation of SR (Ahmed et al., 2012; Hansen et al., 2012) showed that there is a *significant* potential for recovery of both material resources and energy from SR since considerable amounts were found of magnetic metals (e.g., scrap iron), non-magnetic metals (e.g., Al, Cu, Ni, Zn, brass) and “combustibles” (e.g., plastics, wood, foam, rubber) causing the lower heating value (LHV) of SR to be equal to or actually exceeding that of an ordinary municipal solid waste (MSW) incinerated in Denmark (LVH 9-12 MJ/kg). It was concluded, in agreement with the results of other international studies (Borjeson et al., 2000; Vermeulen et al., 2011), that utilisation of these resources (both material and energy) may, except for the obvious environmental benefits related to the material recycling and/or energy production, result in “saved” landfill capacity as well as in reducing the of resources expected to be required for the landfill after-care-period.

One of the general challenges so far – with respect to extraction of resources from SR – has been that SR contain “unwanted” substances that *may* present a barrier for efficient and environmentally sound utilisation of the resources. Examples of these substances include chlorine (found in PVC), bromine (found in brominated flame retardants), various organic compounds such as PCBs and petroleum/oil hydrocarbons, and last but not least trace elements, including “heavy metals”⁴ (Ahmed et al., 2012; Cramer et al., 2011; Poulsen et al., 2011).

While most of these substances do not in themselves constitute resources, their presence in SR is often critical with respect to further processing as – for example – a permit for treatment of hazardous waste may be required when handling SR or they simply act as impurities in the final recycle(s), thus making them less attractive for potential recycling. In addition, their presence in SR may be problematic for various energy recovering thermal processes, because they represent a potential contamination source and pathway (e.g., enhanced formation of dioxins, transfer of metals into the incineration products) and cause technology-related problems such as Cl-induced corrosion and fouling.

⁴ The term “heavy metals” are often used collectively for trace elements including both actual heavy metals such as Cd, Cu, Pb, Hg, etc. and substances which do not formally belong to this category (which is, by the way, not very well defined), such as e.g. As, which is a metalloid.

At the moment (2012), there are 5 shredder plants in Denmark (3 plants are owned by STENA A/S, and 2 plants are owned by H.J. Hansen Genvindingsindustri A/S) processing approximately 700,000-800,000 tonnes of material per year. Combined, these 5 plants produce 140,000-150,000 tonnes of SR per year (Miljøstyrelsen, personal communication).

The two companies operating shredder facilities in Denmark have fairly different approaches towards recovery of recyclables. In contrast to H.J. Hansen, who is sorting out metals (both magnetic and non-magnetic), plastic, glass and wood (as part of plastic/wood fraction), STENA is focusing on metals only. Despite momentary differences in their actual approach regarding material recovery, both STENA and H.J. Hansen are aware of the fact that “maximum recovery should ideally precede the thermal treatment as during the thermal treatment (and also during the following bottom ash treatment processes) a portion of the potentially recyclable materials (meaning metals) is lost” (personal communication). It should be noted that although partially correct, this statement implies that the bottom ash is processed using the traditional low-tech “semi-dry” technique, which has only limited recovery rates for a limited number of metals. New bottom ash treatment processes are available, which would allow for a significantly higher recovery rate for a large number of metals. This is discussed in detail in Section 2.6.

It should also be noted that the processing plants (even if owned by the same company) are operated at slightly different set-ups and receive different mixtures of incoming material (e.g., various proportions of ELVs to the other waste streams). The composition of SR therefore varies significantly between the different plants. At the same time, it is the fraction of recoverable/recyclable resources in the SR that will be the determining factor for further treatment options. Consequently, both companies are constantly investing in development and optimisation of their processes.

Typically, it has not been permitted to incinerate SR in *ordinary* municipal solid waste (MSW) incinerators due to the total contents of e.g. “heavy metals”, Cl, Br and PCBs, which (occasionally) exceed the limit values for waste to be treated in MSWI plant; this is discussed in detail in this report. However, the composition of SR has changed significantly over the last couple of years and there is still no full-scale capacity available for converting SR to secondary fuels (e.g., large-scale pyrolysis- and/or gasification plants). Some of the existing MSWI plants⁵ may consequently become a feasible option for energy recovery from SR, provided that there is sufficient and up to date knowledge of the occurrence and sources of the problematic substances in SR and their behaviour during co-incineration in the state-of-the-art MSWI plants. In addition to that, attempts can be made to source-separate some of the problematic substances from mixed SR prior to the intended thermal treatment.

1.2 Objectives

The main objective of this project is to identify the potentially problematic substances in SR based on:

- a desktop study focused on the latest Danish as well as international data and knowledge of SR composition, material properties and behaviour during various treatment scenarios including recycling, waste-to-energy utilisation, and landfilling;
- a discussion with the different operators;
- a detailed characterisation of three different SR streams generated at the metal recovery plant in Grenå (operated by STENA)

⁵ In April 2012 Reno-Nord obtained a permit to co-incinerate SR which have been pre-sorted in order to remove residual metals.

In addition:

- a desktop study has been performed in order to assess the feasibility of source-separating the problematic substances from SR using a sensor-based technology; and
- a prompt-gamma neutron activation analysis (PGNAA) sensor developed by FORCE Technology has been tested on pre-treated samples of SR in order to assess its potential and future applicability on similar types of waste.

The basic idea is that once the potentially problematic substances in different fractions of SR are identified, an attempt to target their primary sources can be made and possible source-separation techniques can be assessed. Ideally, SR with a significantly lower content of problematic substances may be generated as the result of source separation processes. These improved residues will be better suited for further material- and energy recovery with significantly reduced adverse effects on the environment, the equipment and human health.

2. Problematic substances in shredder residues with respect to further utilisation

2.1 General overview

Generally, Danish SR have been considered hazardous waste (MST, personal communication). Historically, the reasons for such classification were elevated amounts of e.g., persistent organic pollutants (POPs), petroleum hydrocarbons (TPH) and some “heavy metals” (Poulsen et al., 2011).

In addition to the above mentioned contaminants, scrap metal may contain radioactive materials. Both discrete radioactive sources which have escaped the regulatory control by being abandoned, lost or stolen (e.g., a thickness gauge from building demolitions, radiation discrete sources used for brachytherapy) and material, has been contaminated with natural or man-made radionuclides from industrial processes (e.g., pipe scale from oil and gas drilling that contains naturally occurring radioactive material) can be found in scrap metal⁶. However, scrap metal contaminated with radiation will not be accepted by the smelters, thus, in accordance with the EU-27 Steel Scrap Specification⁷ all grades should be checked for radioactivity. For example, at the Grenå plant operated by STENA, all incoming material is screened by radiation detectors both prior to the shredding, after the shredding and once more after the recovered metals are loaded on the ships to be sent to the smelters. The radioactive materials are removed from the process stream when detected (Steen Hansen, STENA, personal communication). Consequently, radioactive materials will not be discussed further in this report.

In the following text the presence of POPs (e.g., PCBs, BFRs - see Fact box 2 for details), BTEX (benzene, toluene, ethylbenzene, xylene), PAHs (polycyclic aromatic hydrocarbons), TPH, PVC and “heavy metals” in Danish SR is discussed with respect to their potential sources and with respect to potential problems they may cause in relation to resource recovery under Danish conditions. In addition, background information is provided for each of these substances and a reference to foreign experiences is given where appropriate.

Persistent Organic Pollutants (POPs) are defined as compounds long-lasting in the environment and able to travel long distances from their source. Their bio-accumulating properties and build up in the food chain is causing health impacts for current and future generations (Stockholm Convention on Persistent Organic Pollutants, 2001). Therefore, POPs should be “*destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants*”. However, exceptionally it is also permitted to dispose of POPs in an environmentally sound manner “*when destruction or irreversible transformation do not represent the environmentally preferable option*” or when the “*persistent organic pollutant content is low*”.

Historically, the original list contained 12 POPs (all chlorinated chemicals) the use of which was mainly

⁶ <http://www.epa.gov/radiation/source-reduction-management/scrapmetal.html>

⁷ http://www.efr2.org/html/downloads/EFR_EU27_steel_scrap_specification.pdf

linked to industrial applications and industrial waste (e.g., PCBs or pesticides). Over the years, however, the original list was extended for brominated and fluorinated POPs (e.g., polybrominated diphenylethers (PBDEs) and polybrominated biphenyls (PBBs)), which have been widely used as flame retardants for electronics, textiles, furniture, and insulation foam. The first fluorinated POPs added to the list were perfluorooctane sulfonic acid (PFOS) and perfluorooctane sulfonyl fluoride (PFOSF) which have been used in a range of products including synthetic carpets, textiles, dirt repelling furniture and impregnated paper.

Overall, an increasing proportion of POPs in current use is found in daily-use products mainly in the form of brominated flame retardants (BFRs). Consequently, the quantity of POPs in municipal solid waste streams is increasing. In most countries a large proportion of these wastes are still disposed of at municipal landfills. At a global scale, there is growing evidence that BFRs, including those already listed as POPs, are leaching from landfills and contaminating the environment.

POPs (namely PCBs and PBDEs) transferred by a long-range atmospheric transport have been found in environmental samples from virtually everywhere on the planet including some of the most remote locations such as Antarctica.

Fact box 2. Persistent Organic Pollutants (POPs). Source: Weber et al. (2011) and references therein; Wang et al. (2012).

2.1.1 Polychlorinated biphenyls (PCBs)

As summarised by US EPA, polychlorinated biphenyls (PCBs) were “manufactured as a mixture of various PCB congeners⁸, through progressive chlorination of batches of biphenyl until a certain target percentage of chlorine by weight was achieved. Commercial mixtures with higher percentages of chlorine contained higher proportions of the more heavily chlorinated congeners, but all congeners could be expected to be present at some level in all mixtures”.

PCBs were manufactured and sold under many different names (see Table 2.1). One of the largest producers was the Monsanto Company in the USA (production stopped in 1977), which produced several commercial mixtures of PCBs under the market name Aroclor XXXX (where XXXX reflects the level of chlorination). Similarly, in former West Germany, Bayer AG produced a range of PCB mixtures under the market name Clophen A XX (Ballschmitter and Zell, 1980); the production in Germany stopped in 1983 with 90% of the last year’s production exported. Also, Chemko company (former Czechoslovakia) manufactured large quantities of PCBs under the name Delor XXX to supply the former Eastern bloc including East Germany during 1959-1984. Note that though names may differ the mixtures are relatively comparable; e.g., Delor 103 and Delor 106 are equivalents of Aroclor 1242 and Aroclor 1260, respectively. On a global scale, some 1.5 million tonnes are estimated to have been produced⁵.

Table 2.1 Market names of selected PCB commercial mixtures (partly after Ballschmitter and Zell, 1980)

% Chlorine	Monsanto (USA)	Bayer (FRG)	Chemko (CSSR)
41	Aroclor 1016 ⁹	-	-
42	Aroclor 1242	Clophen A 30	Delor 103
54	Aroclor 1254	Clophen A 50	Delor 105
60	Aroclor 1260	Clophen A 60	Delor 106
68	Aroclor 1268	-	-

In general, PCBs have low water solubility (they are readily soluble in organic solvents), low electric conductivity, very high thermal conductivity and are extremely stable (both thermally and chemically)¹⁰. These properties made them suitable for a broad range of applications. Typically, PCBs

⁸ In total, there are 209 possible PCB congeners based on geometry and substitution positions

⁹ Reduced content of penta- and hexachlorobiphenyls compared to Aroclor 1242, which it replaced in 1971

¹⁰ http://www.chem.unep.ch/pops/POPs_Inc/proceedings/bangkok/FIEDLER1.html

were used in older electrical capacitors and transformers as coolants and dielectrics (COWIconsult, 1983). Furthermore, PCBs were used as plasticisers in paints, stabilizing additives in flexible PVC coatings, pesticide extenders, cutting oils, reactive flame retardants, lubricating oils, hydraulic fluids, de-dusting agents, casting agents, carbonless copy paper, adhesives, sealants and for many other purposes.

After being banned in the US in 1979 (their use in Europe in manufacturing of new equipment was heavily restricted as of 1985), their amounts in many waste streams decreased significantly¹¹. Today, PCBs are mainly found – except for decommissioned transformers and capacitors – in construction and demolition (C&D) waste generated from dismantling of old buildings e.g. sealants, glues, paints, thermal windows and surrounding elastic insulation foam and/or soft joints in prefabricated houses built mostly between 1950s-1980s (COWIconsult, 1983; Jensen et al., 2009). Assuming that Danish waste management system works properly PCBs from the above mentioned material fractions are not expected to enter the metal recovery process at a shredding plant. Besides C&D waste, “from the 1950s to the early 1970s, PCBs uses in anti-corrosion paints included bridges and other constructions as well as electric poles. Some of this equipment reaches the end of its useful life. Currently, there is no assessment available as to how much PCB painted scrap is entering the waste stream and the secondary metal treatment. Also, there are no data on dedicated testing of associated releases. However, it is known from measurements in EAF (electric arc furnace used at smelters) that considerable PCB loads are emitted which only can be explained by PCB input from material treated¹²”. It is the authors’ impression that scrap metal from decommissioning of industrial applications and/or ships may be the major source of PCBs to the shredding process today. However, no information is available on the amount of this type of waste processed at Danish shredder plants in comparison with the remaining material originating from municipal recycling stations and ELVs.

In 1991, US EPA published a study in which PCBs were measured in several output streams from the shredder. The study concluded that “there were no statistically significant differences in measured PCBs levels between the different categories of physical components (fines; metals and wire fragments; soft and hard plastics; and rubber, glass, fabrics, paper, and wood). It was also concluded that “scrap sources other than automobiles and white goods could be major contributors to PCBs in shredder residue” (Jody and Daniels, 2006; US EPA, 1991). This observation was confirmed in recent US study concluding that (i) shredder residue generated by shredding only autos contained very low levels of PCBs and (ii) autos, at least newer than 1983 model year, are *not* a significant source of PCBs seen in shredder residue (Duranceau and Spangenberg, 2011).

A large fraction of PCBs is known to be emitted as dust during shredding. According to Rapport nr. 34 2006 (Schleicher and Jensen, 2006), none of the Danish shredder plants can actually meet the PCB limit of 0.1 µg/Nm³ of air, which was established in 1991 as an air-quality limit for incineration of PCB-containing waste. A similar air-quality limit has not been established for shredder plants, but some of the former Danish counties have applied the value for shredder plants, also. Note that the Danish results are not unusual. Significant deposition of PCB-containing dust in the vicinity of German shredding plants have been reported (Bruckmann et al., 2011). At some occasions PCB levels were measured in the “upper mg/kg range”; i.e., between 3,000 and 9,600 mg/kg TS PCB6 *before* multiplied with factor 5. .

The Danish EPA announced around 2003 that the above mentioned limit value of 0.1 µg/Nm³ of air could be dispensed with as it is nearly impossible to achieve such low values with the existing cleaning technology used at the shredder plants (e.g. Venture scrubber for dust removal). A guidance value of 20 µg/Nm³ of air was established and concurrently, Venturi scrubbers for dust removal were imposed as BAT for shredder plants. The activated carbon and bag filters, a well-proven tech-

¹¹ In Denmark, the use of PCB was restricted in 1977 with some exceptions while the total ban came in place in 1986

¹² http://ec.europa.eu/environment/consultations/pdf/pops_consultation.pdf

nology for controlling PCBs at MSWI plants, cannot be used in shredder plants due to notorious problems with explosions.

2.1.2 Brominated flame retardants (BFRs)

Brominated flame retardants (BFRs) are organobromide compounds that have an inhibitory effect on the ignition of combustible organic materials. Similarly to PCBs, BFRs are listed as persistent organic pollutants (POPs) by the Stockholm Convention on Persistent Organic Pollutants (POPs, 2001). Unlike PCBs – the use of which was limited to industrial application – BFRs have been used in a wide range of commercial and consumer products to increase their flame ignition resistance.

Over the years, BFRs have been produced in about 70 variants with varying properties and composition. The most abundant ones are polybromodiphenyl ethers (PBDEs), polybromo-bisphenyls (PBBs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA). Note that these compounds are listed as “restricted substances” under the Directive 200/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (European Commission, 2003b).

More details are given in the fact box below.

Tetrabromobisphenol A (TBBP-A) is used primarily as a reactive flame retardant in printed circuit boards; consequently, it is mostly found in WEEE (Waste Electrical and Electronic Equipment). In addition, it may be also used as an additive in acrylonitrile–butadiene–styrene (ABS) resin, which is used in automotive trim components, automotive bumper bars, canoes, furniture, luggage, small kitchen appliances as well as toys such as Lego bricks¹³.

There are three main categories of commercial mixtures of **polybromodisphenyl ethers** (PBDEs): “penta-BDE”, “octa-BDE”, and “deca-BDE”. Historically, the lower brominated BDE – such as penta-BDE and octa-BDE – were used as the most common BFRs in printed circuit boards, cable sheets, furniture, textiles, computer housing, business machines and household appliances. After the lower brominated BDEs were banned in EU (listed as “restricted substance”; see PBBs further down) and voluntarily phased out in the US (2005), they were replaced, in some countries, with higher brominated BDEs (i.e., deca-BDE) which were initially regarded as a non-hazardous substances. However, a number of recent studies have provided evidence that the higher brominated BDEs become in fact de-brominated over time and thus form lower brominated BDE again.

Hexabromocyclododecane (HBCD) is the third most widely used BFR in the world and second in Europe. Due to its persistence and bio-accumulative and hazardous character, a global ban on HBCD is being considered under the framework of UNEP’s Stockholm Convention on persistent organic pollutants.

Polybrominated biphenyls (PBBs) were used widely as a flame retardant in production of plastics in the 1970s. After the “Michigan incident¹⁴” they were banned in the US (1977). PBBs are listed as “restricted substance” under the EU “Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (2002/95/EC)”, which was adopted in February 2003 and took effect in July 2006. Recently, PBBs were restricted in China (2007) and South Korea (2007).

Fact box 3. Examples of brominated flame retardants (BFRs) (Alaee et al., 2003 and references therein; Kefeni et al., 2011 and references therein)

The typical applications of BFRs include all sorts of plastics, printed circuit boards in electronics and polyurethane foam (e.g., furniture, car seats, mattresses, polystyrene insulation, textiles). As shown in Table 2.2. the proportion of flame retardant incorporated into the flame-retarded material

¹³ <http://designinsite.dk/htmsider/m0007.htm>

¹⁴ http://www.michigan.gov/documents/mdch_PBB_FAQ_92051_7.pdf

can range from 2 to 30% of the product by weight (Alaee et al., 2003; Weber et al., 2011). Note that “large white goods are believed to contain only small amounts of flame retarded polymers. BFR in these applications are generally only used for printed circuit boards, electrical connectors, some cables and in areas with a specific risk of heating”¹⁵.

Table 2.2 Overview of BRF content in different applications (Alaee et al., 2003 and references therein)

Polymer type	Examples of application	BFR type	BFR content
Polystyrene foam	Plastic model kits, cutlery, CD cases, different plastic housing, insulation foam, packaging material (from yogurt to TV)	HBCD	0.8-4 %
High impact polystyrene	e.g. office letter trays, roof tiles	deca-BDE, brominated polystyrene	11-15 %
Epoxy resin	Coatings, adhesives, present in composite materials such as fiberglass and carbon fibre	TBBP-A	0-0.1 % up to 20 % ¹⁶
Polyamides	Clothing, waterproof/breathable garments	deca-BDE, brominated polystyrene	13-16 %
Polyolefins	Electrical insulation, used in polypropylene (PP) and polyethylene (PE)	deca-BDE, propylene dibromo-styrene	5-8 %
Polyurethanes	Car seats, mattresses, furniture	penta-BDE	10-18 %
Unsaturated polyesters	Fiberglass reinforced plastics	TBBP-A	13-28 %
Polycarbonate	Automobile bumpers, Plexiglas, tubes, CDs, DVDs, bottles	brominated polystyrene	4-6 %
Styrene copolymers (e.g., ABS)	Drain-waste pipes, automotive trim components, automotive bumper bars, canoes, furniture, luggage, small kitchen appliances, toys (e.g., Lego)	octa-BDE, brominated polystyrene, TBBP-A	12-15 %

Similarly to PCBs, BFRs exhibit a range of hazardous effects including endocrine disruption as well as reproductive and neurodevelopmental toxicity (Tue et al., 2010). Despite the latest research by Kim et al (2011), who suggested using e.g. carbon nanofiber-filled coating to reduce polyurethane (PU) foam flammability (PU foam is used in car seats, mattresses etc.), the total BFR production capacity has increased significantly over the last 5 years, particularly in China and other developing countries in Asia (Weber et al., 2011). Naturally, a high proportion of BFRs is being exported in products from Asia, entering markets in western countries and ultimately being deposited there even though a large part of the materials may be recycled and sent back to Asia for reprocessing (e.g., WEEE and recycling of plastics in general).

Considering the hazardousness of the lower brominated PBDEs and following the precautionary principles, it has been suggested that all products containing PBDEs – both higher and lower brominated PBDEs – should be considered hazardous and special care should be taken of their treatment at the end of their useful life (Weber et al., 2011). Most importantly, it was suggested that these materials should not be considered for disposal in landfills where they will leach (Weber et al.,

¹⁵ <http://www.zerowastescotland.org.uk/sites/files/wrap/BrominatedWithAppendices.3712.pdf>

¹⁶ In epoxy resin used in production of printed circuit boards there may be up to 20% by weight of TBBPA

2011; Sakai et al., 2000). Instead, they should be either destroyed or managed in an environmentally sound manner in order not to end up in landfills or enter recycling routes.

2.1.3 Benzene, toluene, ethylbenzene, xylene (BTEX)

Benzene, toluene, ethylbenzene and xylene (BTEX) are some of the volatile organic compounds found in petroleum derivatives. They are most commonly used in paints, thinners, rubber products and adhesives. Because of their polarity and high solubility, BTEX are known as one of the major contaminants of soil and groundwater. Of the four BTEX compounds, benzene is the most toxic since it is a known carcinogen (Carc.Cat 1). The main effect of toluene is on the brain and nervous system while ethylbenzene damages liver and kidneys. Exposure to xylene causes a number of effects on the nervous system, such as headaches, lack of muscle coordination, dizziness, confusion¹⁷.

2.1.4 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) constitute a group of organic compounds present in crude oil and also emitted during incomplete combustion of carbon-containing material (e.g., wood, coal, oil). Structurally, PAHs are characterised by fused benzene rings; the simplest PAHs are phenanthrene and anthracene with three rings (Figure 2.1). Though not really a true PAH, naphthalene (only two benzene rings) is also included in the list of PAHs.

In general, PAHs are lipophilic (i.e., they dissolve in fats) and many have or are suspected of having mutagenic, carcinogenic and teratogenic properties. The higher-ring compounds are less volatile and thus found mostly in soil and sediment. Although more than 100 different PAH combinations may exist, the “group” PAH is currently defined by US EPA using the Toxic Release Inventory¹⁸. At the moment, the 16 most carcinogenic of them are more or less routinely measured worldwide; they are referred to as the “PAH US EPA 16”.

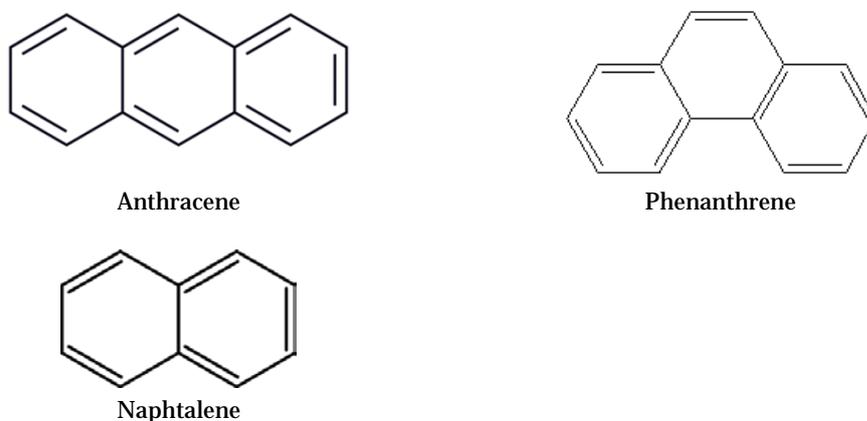


Figure 2.1 Structural formulae of anthracene, phenanthrene, and naphthalene (copyright: Wikipedia)

2.1.5 Total Petroleum Hydrocarbons (TPH)

“TPH is defined as the measurable amount of petroleum-based hydrocarbons in an environmental media. It is, thus, dependent on analysis of the medium in which it is found. Since it is measured, gross quantity without identification of its constituents, the TPH “value” still represents a mixture. Thus, TPH itself is not a direct indicator of risk to humans or to the environment”.¹⁹

¹⁷ http://www.derm.qld.gov.au/environmental_management/coal-seam-gas/pdf/btex-report.pdf

¹⁸ <http://www.atsdr.cdc.gov/toxfaqs/ifa.asp?id=121&tid=25>

¹⁹ <http://www.crccare.com/education/downloads/Presentation-TPH-Workshop.pdf>

As indicated above, TPH is a term for a wide variety of complex mixtures of C-H compounds found in petrol and oil. Some are clear or light-coloured liquids that evaporate easily, and others are thick, dark liquids or semi-solids that do not evaporate under ambient conditions. TPH are often divided into groups that act alike e.g. C6-C10 (gasoline range), C10-C14 (jet fuel range), C10-C14 & C15-C28 (diesel range), C29-C36 (mineral oil and lube oil range)²⁰. In Denmark, carbon range C6 though C35 (or C40) is analysed as TPH depending on whether the matrix is “polluted soil” or “waste” (Danish EPA, 2011).

2.1.6 Polyvinylchloride (PVC)

Polyvinylchloride (PVC) is a plastic material produced since the mid-1930s and is used for many different purposes including building materials (e.g., windows, gutters, pipes, etc.), furniture (e.g., carpets, chairs, outdoor furniture, etc.), equipment (e.g., cabinets, cable/wire insulation coating, etc.) as well as food packaging, containers and automotive parts. PVC is highly flame retardant and very resistant due to its high chlorine content. It is cheap to produce, very durable and could be long-lived. PVC contains, or used to contain, lead as stabiliser and cadmium as a pigment for red and yellow colours (Christensen, 2010).

Unlike the other listed compounds PVC itself is *not* hazardous. Nevertheless, upon combustion PVC releases high quantities of gaseous HCl, which needs to be removed from the flue gas. Furthermore, PVC was once assumed to act as a precursor of dioxin formation during the combustion. However, in modern, well-operated MSWI plants there seems to be only a small relationship between the amount of chlorine in the input and the amount of dioxins formed (Christensen, 2010; Vermeulen et al., 2011).

2.1.7 Heavy metals

As already mentioned, the term “heavy metals” has been used very loosely and often as a group name for metals and metalloids that have been associated with contamination and potential toxicity or ecotoxicity. According to the International Union of Pure and Applied Chemistry (IUPAC) the term should not be used anymore as there is a tendency to assume that all so-called “heavy metals” and their compounds have highly toxic or ecotoxic properties, which has no basis in chemical or toxicological data (Duffus, 2002). However, for the lack of better term and in order to provide consistency with the information sources used in this report the term “heavy metals” is used here. Typically, it refers to metals studied in the majority of projects: Cd, Cu, Cr, Hg, Ni, Pb, and Zn. Furthermore, metalloids (e.g., As, Sb, Mo, V) have been considered in some studies and are also referred to as “heavy metals” herein.

In general, the emissions of “heavy metals” are monitored because of the elements’ carcinogenicity or toxicity affecting the central nervous system (Hg, Pb, As), the kidneys and liver (Hg, Pb, Cd, Cu) or bones (Ni, Cd, Cu and Cr). With respect to thermal treatment of waste and associated air pollution control, the elements of the highest concern include As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn and Tl²¹.

²⁰ <http://www.deq.state.ok.us/factsheets/land/tph.pdf>

²¹ http://eny.tkk.fi/research/combustion_waste/publications/gasbook/index.htm

2.2 Composition of Danish shredder residues

Due to more stringent rules regarding material recycling (e.g., new rules for recovery of old batteries, rules for recovery of used oils, PCBs no longer being used in commercial applications, etc.) the composition of shredded material has changed significantly over the last 20 years. In addition, the efficiency of the recovery process as such has increased too by implementing more advanced sorting techniques. Consequently, composition of the residual stream (i.e., SR) has changed. Also, Ahmed et al. (2012) have shown changes in the composition of recently produced Danish SR over time presumably caused by changes in market prices of scrap metal.

Despite the large heterogeneity of SR the results of recent Danish studies focusing on composition of SR (Hansen et al., 2011a; Hansen et al., 2012; Hansen et al., 2011b; Ahmed et al., 2012; Poulsen et al., 2011) are surprisingly comparable for the total contents of metals and TPH, while somewhat larger variations are observed for PCBs and PAHs. In the following text the results of those studies are discussed in detail. In addition, an overview of the composition data is given in Table 2.3.

Hansen et al. (2011b) carried out a thorough characterisation study of SR that were disposed of at the Reno Djurs landfill near Glatved. The material that was characterised had been sampled over a 12 month period (May 2009 to May 2010). The study was focused both on the composition and the leaching properties of the landfilled SR. The results showed that none of the monitored parameters exceeded the limit values for hazardous waste, except for the total contents of PCBs (determined as 5 times the sum of PCB7), which slightly exceeded the limit value of 50 mg/kg TS (MST, 2002). In addition, TPH exceeded the limit value of 1,000 mg/kg TS (the main part of the TPH was ascribed to the C20-C40 range suggesting diesel and oil contamination), while the amount of total organic carbon (TOC) was significantly higher than the landfilling limit value of 6%; however, this result was regarded as potentially misleading because of the high amounts of plastics in the landfilled SR which would be analysed as a part of TOC.

Poulsen et al. (2011) addressed the issue of whether or not the newly produced Danish SR should still be considered hazardous waste. Based on a literature survey and composition analyses performed on three samples of Danish SR (collected over a 20-day period in May 2009 at the Reno Djurs landfill) it was concluded that “the existing data do not give an unambiguous answer on whether today's SR should be classified as hazardous waste”. However, the final conclusion from the analysis of the three SR samples was that all SR should be considered hazardous waste from a “conservative point of view”²². The total contents of Pb and TPH (suggesting diesel and oil contamination) were reported critical for the classification of SR as hazardous waste. It was also noted that a significantly higher number of samples of SR would need to be analysed for contents of metals and organic substances in order to enable a proper assessment of whether today's SR should be regarded as hazardous waste or not (Poulsen, et al. 2011).

In addition to the above mentioned studies, Table 2.3 also contains:

- data obtained by Ahmed et al. (2012) who investigated the composition of SR at the three largest sites for landfilling of SR in Denmark (Odense Nord Miljøcenter, AV Miljø and Reno Djurs);
- information on composition of SR used for the co-incineration experiments at Amagerforbrænding (Nedenskov, 2011);
- selection of the most critical contaminants and the associated limit values for classification as hazardous waste specified in the BEK 1309/2012 (Danish EPA, 2012) and the Regulation EC 1272/2008 (European Commission, 2008), respectively.

Values exceeding the limit value for hazardous waste (HW) are indicated in **red**.

²² “Conservative point of view” means that the metals are assumed to be present in their most hazardous form (e.g. as oxides, chlorides) and not in the metallic form (MST, 2002)

Table 2.3 Composition of SR determined in recent Danish studies (selected parameters are shown). All values in mg/kg TS.

Parameter	Study 1 ^a	Study 2 ^b	Study 3 ^c	Study 4 ^d	BEK 1309/2012 and Reg. EC 1272/2008
BTEX	-	12-42	-	-	1,000 ^e
TPH (C6-C40)	14,000	15,000-21,000	-	-	see below
Benzene-C10	100	110-190	-	-	1,000 ^f
>C10-C15	210	170-240	-	-	1,000 ^g or 10,000 ^g
>C15-C20	980	710-990	-	-	
>C20-C40	13,000	14,000-20,000	-	-	
PAH (US EPA 16)	1.2	28-47	1.2-41	23-28	25 ^h ; 100 ^h ; 1,000 ^h
Sum of PCB7	51ⁱ	0.9-3.1 ⁱ	13-62 ⁱ	22-44 ⁱ	50 ⁱ
TOC ²³	210,000	-	160,000-330,000	190,000-430,000	60,000
As	36	24-30	15-66	13-19	1,000 ^j
Cd	15	17-23	5-36	21-30	1,000 ^k
Co	36	28-51	25-97	24	100 ^l
Cr	890	250-270	630- 1,660	259-422	1,000 ^m
Cu	25,000	19,000-20,000	6,800-27,000	13,000-24,500	2,500 – 250,000 ⁿ
Hg	0.82	1.1-10	0.8-3.1	0.26-0.66	500 ⁿ
Ni	480	220-250	480- 1,600	222-293	1,000 ^p
Pb	4,200	3,800- 13,000	1,200-4,200	1,600-1,670	2,500 or 5,000 ^q
Sn	180	-	180-300	-	50,000 ^r
Sb	210	270-300	128-420	-	2,500 ^s
V	61	39-61	47-91	-	-
Zn	17,000	16,000-20,000	8,000-28,000	11,000-12,000	50,000 ^r

^{a)} Hansen et al. (2011b); ^{b)} Poulsen et al. (2011); ^{c)} Ahmed et al. (2012); ^{d)} Nedenskov (2011);

^{e)} A limit value of 0.1% (1,000 mg/kg TS) applies to benzene

^{g)} A limit value of 1% (10,000 mg/kg TS) applies to, jet-, diesel fuel and heavy heating oil in the interval C9-C20 (Carc. Cat 3); a limit value of 0.1% (1,000 mg/kg TS) applies to “other hydrocarbons” (incl. gasoline and light heating oil) classified as Carc.Cat2.

^{h)} Not possible to quantify as a group. A limit value of 0.0025% (25 mg/kg TS) applies to dibenzo(a,h)anthracene; 0.01% (100 mg/kg TS) applies to benzo(a)pyrene; 0.1% (1,000 mg/kg TS) applies to benzo(j)fluoranthene and benzo(k)fluoranthene

ⁱ⁾ After the result of PCB7 analysis is multiplied with a factor of 5

^{j)} A limit value of 0.1% (1,000 mg/kg TS) applies to elemental (inorganic) As

^{k)} A limit value of 0.1% (1,000 mg/kg TS) applies to elemental Cd as well as to metallic Cd

^{l)} A limit value of 0.01% (100 mg/kg TS) applies to cobalt dichloride-, sulphate-, acetate-, nitrate- and carbonate-

^{m)} A limit value of 0.1% (1,000 mg/kg TS) applies to Cr(VI) compounds; metallic Cr is not classified

ⁿ⁾ A limit value 0.05% (500 mg/kg TS) applies to organic compounds while 0.1% (1,000 mg/kg TS) applies to inorganic compounds as well as metallic Hg

^{p)} A limit value of 0.1% (1,000 mg/kg TS) applies to Ni compounds while 1.0% (10,000 mg/kg TS) applies to metallic Ni

²³ The limit for the total content of TOC in waste to be landfilled at landfills for hazardous waste (Danish EPA, 2013)

- Ⓚ) A limit value of 0.25% (2,500 mg/kg TS) applies when category “miljøfare” is considered. At the moment, no limits for “miljøfare” are set at national level, however, some municipalities (e.g. Copenhagen) use it. A limit value of 0.5% (5,000 mg/kg TS) applies to elemental (inorganic) Pb
- Ⓛ) A limit value of 5% (50,000 mg/kg TS) applies to “compounds”
- Ⓜ) A limit value of 0.25% (2,500 mg/kg TS) applies to Sb compounds, except tetr-, pentoxide, tri-, pentasulphide and tri-, pentachloride
- Ⓝ) A limit value of 25% (250,000 mg/kg TS) applies to Cu(I)-chloride and Cu(I)-oxide; however, a limit value of 0.25% (2,500 mg/kg TS) applies when category “miljøfare” is considered. Metallic Cu is not classified

2.2.1 PCBs

2.2.1.1 Landfilled SR

Hansen et al. (2012) and – in particular - Ahmed (2012) collected a large data set on the distribution of the “PCB7” congeners (i.e., PCB nr.28, PCB nr.52, PCB nr.101, PCB nr.118, PCB nr.153 and PCB nr.180) in SR samples collected from the three largest Danish landfills accepting SR: AV Miljø (AVM), Odense Nord Miljøcenter (ONM) and Reno Djurs (RNJ). Their results are discussed in the following text with respect to the scope of this study.

It should be understood that the results from the three sites *cannot* be compared directly without great caution since those sites are of different operational age and thus have received SR generated in different periods²⁴. For example AV Miljø, as the oldest site, has been receiving SR for almost 20 years (from 1990s), whereas Reno Djurs landfill has been receiving SR for only 3 years (from 2009). Furthermore, due to the differences in operation of those sites it was not possible to excavate SR samples deposited in the exact same time period despite the great effort that was made to obtain samples that were as comparable as possible for all three sites.

In Table 2.4 an overview of the different “age groups” of the tested SR samples is given for each site. For further details on the excavation, please refer to Hansen et al. (2012).

Table 2.4 Overview of “age groups” of SR samples collected at the three largest Danish landfills for SR (Ahmed , 2012; Hansen et al., 2012)

AV Miljø	Odense Nord Miljøcenter	Reno Djurs
1990-2000	2000-2001	2009-2010
2001-2004	2003-2006	-
2005-2008	2007-2009	-
2009-2010	-	-

In addition to analysis of the excavated SR, Ahmed (2012) and Hansen et al. (2012) determined SR composition as a function of *particle size*. This was done by sieving the excavated material into four pre-defined particle size fractions (>10 mm, 10-4 mm, 4-1 mm, and less than 1 mm) which were then analysed separately for a number of physical-chemical parameters including PCB7. Note that the composition of the “>10 mm” fraction was determined *after* separation of metal pieces from that fraction. Thus, if there were PCBs present in the metal fraction, these were not included in the results. However, Poulsen et al. (2011) found the amounts of PCBs in the “metal” fraction of SR insignificant compared to the other material fractions.

The distribution of PCB7 congeners in the different “age groups” of SR collected at AVM, ONM and RNJ is shown in Figure 2.4. The same y-scale is used in all figures to enable direct comparison of the results. The total amounts of PCB7 analysed in the individual samples are shown in the bottom-right corner of Figure 2.2. The red dashed line in this figure indicates the limit value of 50 mg/kg TS (before sum PCB7 is multiplied with a factor 5). It should be kept in mind that the analytical uncertainty related to PCB analysis normally is around 30% (indicated by error bars in one of the figures) and the results shown in figure below should not be used uncritically.

The distribution of the individual PCB congeners and the implications are discussed later. At this point it should be noted that, except for two samples from ONM (ONM 2000-2001 and ONM 2003-2006), all samples showed similar distribution of the 7 congeners where the abundance of a given PCB congener was decreasing with increased level of chlorination. In contrast, in ONM 2000-2001 and ONM 2003-2006 samples the most abundant congener (from the 7 measured ones) was PCB

²⁴ Highly chlorinated PCB congeners may be converted to less chlorinated PCB congeners via natural biodegradation.

no. 52. Furthermore, it seems from the data for both ONM and AVM that younger SR samples contain larger fractions of PCB no. 28. This is discussed later as well.

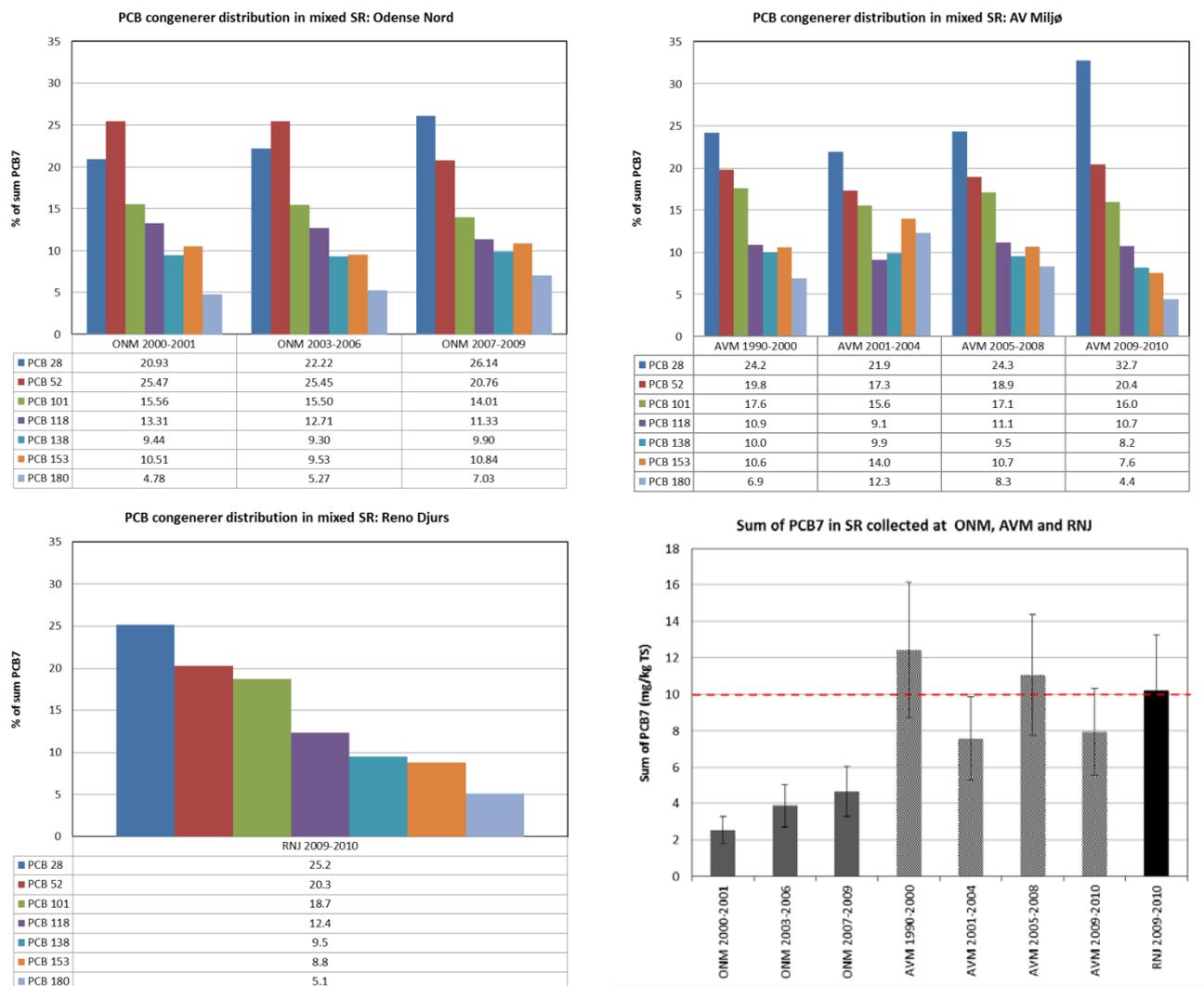


Figure 2.2 Distribution of PCB7 (shown as % of the sum of PCB7) in different “age groups” of SR samples collected at the three largest Danish landfills for SR. Bottom-right: the total amounts of PCB7 analysed in the individual samples (30% uncertainty is included for illustrative purposes). The red dashed line indicates the limit value for hazardous waste (50 mg/kg TS) before multiplying with the factor of 5.

In terms of the total content of PCB7 there seems to be no generally applicable correlation between the “age group” and the amounts of PCB7 as the results from ONM and AVM show different trends. At ONM the amounts of PCB7 seem to have increased in the last couple of years whereas a somewhat sinusoidal development has been observed at AVM. Naturally, no time trend was observed at RNJ as data were available only for a single age group.

Although a similar sampling approach was used at all three sites and the SR samples therefore may be considered equally representative, a great variation in the amounts of PCB7 was found both between the individual sites and in the case of AVM also within the same site. The lowest amounts of PCB7 were found at ONM (<5 mg/kg TS as PCB7 before multiplying with the factor of 5), whereas the total content of PCB7 both at RNJ and AVM was close to or actually exceeding 10 mg/kg TS, which would result in the limit value of 50 mg/kg TS (after multiplying with the factor of 5) being exceeded. Note that Poulsen et al. (2011) found significantly lower amounts of PCB7 at RNJ compared with the results of Ahmed et al. (2012) and Hansen et al. (2011b); see Table 2.3 for details.

Assuming that (i) the SR samples collected at all three sites had the same level of uncertainty (the same sampling methodology was used) and (ii) the analytical method used for determination of PCB7 (DIN 38407, extraction in acetone/hexane followed by GC-ECD) gives reproducible results, the different PCB7 contents at the three sites point to differences in the metal recovery process (addressed below) since the deposited SR were generated at different metal recovery plants. The lowest amounts of PCB7 were found at ONM, a site that has received SR exclusively from H.J. Hansen's plants²⁵, while the AV Miljø and Reno Djurs landfills received SR from STENA's plants. Seemingly, there is less PCB7 in SR produced by H.J. Hansen than in SR produced by STENA. It is therefore assumed that the difference in the total amounts of PCB7 may be caused by different factors associated with the operation of H.J. Hansen's and STENA's facilities, for example differences in:

- composition of the received/processed scrap (e.g., different % of ELVs – which have supposedly lower contents of PCBs than other processed materials – in the total amount of processed material);
- process set-up (e.g., recovery of metals only vs. recovery of metals and other fractions such as plastic); the more fractions are taken out the higher the chance of reducing the total PCB load in the SR;
- management of process dust (the majority of PCBs are assumed to be present in process dust);
- management of generated SR (e.g., all waste streams mixed and deposited vs. different treatment for different waste streams).

At the moment, no *detailed* information is available on the chemical composition of the processed material by STENA or by H.J. Hansen. Similarly, neither company is willing to disclose the exact process set-up in detail. This is only natural as they compete on the same market. With respect to the management of process dust, at all STENA's processing plants, the dust created during the shredding process is captured by a wet system using Venturi scrubbers (Steen Hansen, STENA A/S, personal communication), and a sludge is created from this process. Currently, the sludge is discarded together with SR going to the landfill. At STENA's plant in Grenå, an estimated 4 tonnes of dust are collected in the Venturi scrubber system each day. The daily shredding capacity of Grenå's plant is approximately 1000 tonnes of waste (Otto Jensen, Grenå's plant manager, personal communication). At H.J. Hansen's plants, a Venturi scrubber is used at the shredding plant in Hadsund, while no information was provided by H.J. Hansen regarding the technology used for cleaning off the dust at the plant in Odense.

As discussed in section 2.1.1., dust has been suggested as one of the main output streams of PCBs from the shredding plants. In 2005, 17 mg/kg TS PCB7 (before multiplying with factor 5) were found in Venturi sludge from the shredder plant at Nordhavn, Copenhagen (Schleicher, 2005). This sample thus exceeded the total content limit value for hazardous waste (the multiplication factor was, however, not clearly specified in 2005). In 2012, DHI analysed PCB7 in four process waste streams coming from the shredder plant at Grenå (this is discussed later): samples of two shredder light fractions (SLF), one shredder heavy fraction and a sample of the Venturi-sludge were analysed. The amounts of PCB7 found (before multiplying with the factor of 5) were 0.70 mg/kg TS (SLF 0-60 mm), 1.03 mg/kg TS (SLF 60-100 mm), 3.53 mg/kg TS ("heavy" fraction 0-100 mm), and 8.0 mg/kg TS (Venturi sludge)²⁶. Thus, none of the process waste streams exceeded the limit values for hazardous waste, while most of the PCB7 were found – in agreement with the literature data – in the dust. Reportedly, H.J. Hansen has no information regarding the actual amounts of PCBs in their process dust (Ole Schleicher, FORCE Technology, personal communication).

²⁵ In 2012, ONM has agreed to accept 25,000 tons of SR from STENA (Finn Andersen, Odense Nord Miljøcenter).

²⁶ The amount of PCB7 8 mg/kg TS corresponds to a daily "production" of 32 g PCB7 associated with (caught in) the process dust alone.

In addition to the testing of different “age groups”, Ahmed et al. (2012) analysed the amounts of PCB7 in different *particle size* fractions of SR. However, not all “age groups” were tested separately. Instead, at least one mixed sample representing the “average composition of SR for the respective site and period” was generated, size fractionated and tested for each site. For AVM two mixed samples were generated; one representing 1990-2008 and the other representing 2008-2010 period (Figure 2.3). Note also, that the composition of the “>10 mm” fraction was determined *after* separation of metal pieces from that fraction. Thus, if there were PCBs present in the metal fraction these were not included in the results shown in Figure 2.3. As mentioned earlier, however, Poulsen et al. (2011) found the amounts of PCBs in the “metal” fraction of SR insignificant compared to the other material fractions.

The lowest contents of PCB7 (entire sample) were determined in SR from ONM, followed by recent AVM samples (2008-2010), and samples from both RNJ and AVM (1990-2008), respectively. The limit value for the total content of PCB7 was exceeded in mixed sample AVM 1990-2008 because of high amounts of PCB7 in the largest particle size fraction. Interestingly, PCB7 were *measured* to exceed the limit value in the composite sample RNJ 2009-2010 whilst the analytical results of the individual fractions were found to comply with the limit value. On the other hand, the limit value was shown to be exceeded in two cases for the individual fractions of AVM 2008-2010 while the composite sample was shown to comply with the limit values.

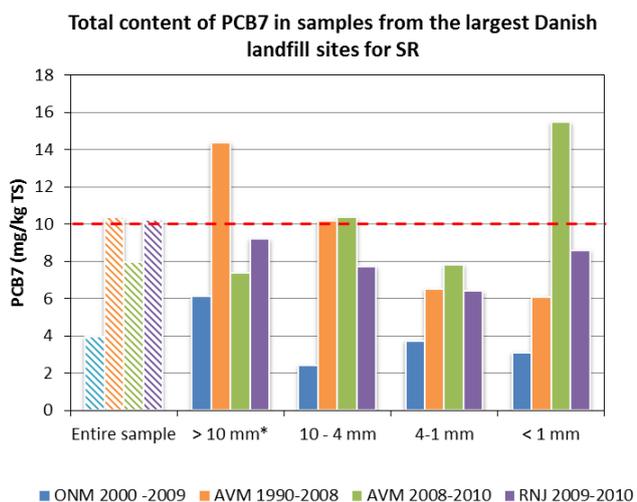


Figure 2.3 Total contents of PCB7 analysed in SR from the three largest Danish landfill sites for SR (Ahmed et al., 2012). Abbreviations: ONM (Odense Nord Miljøcenter), AVM (AV Miljø), RNJ (Reno Djurs). The red dashed line indicates the limit value before multiplying with the factor of 5.

The results of the different PCB7 congeners analysed in the different particle size fractions of the composite samples are shown in detail in Figure 2.4. As already shown in Figure 2.3, the largest amounts of PCB7 were typically found in the largest particle size fraction. Also, the amounts of the individual congeners would decrease with increasing level of chlorination. This was the case of AVM (1990-2008), ONM (2000-2009) and RNJ (2009-2010) samples. However, for AVM (2008-2010) a very different situation was observed. It could be seen that the content of PCB7 analysed in the largest particle size fraction decreased significantly compared to the sample AVM (1990-2008) and was in fact the lowest of all fractions while the amounts of PCB7 analysed in the smallest particle size fraction (<1 mm) have more than doubled. Moreover, the most abundant congener found was PCB no. 52. Despite the “transfer” of PCB7 from the largest particle size fraction to the smallest particle size fraction, the absolute content of PCB7 in SR from AV Miljø has decreased slightly; i.e.,

from 10 mg/kg TS (1990-2008) to 8 mg/kg TS (2009-2010). It is not clear what might have changed the distribution of PCB7 at AVM (e.g., PCB polluted soil, shredder process dust?).

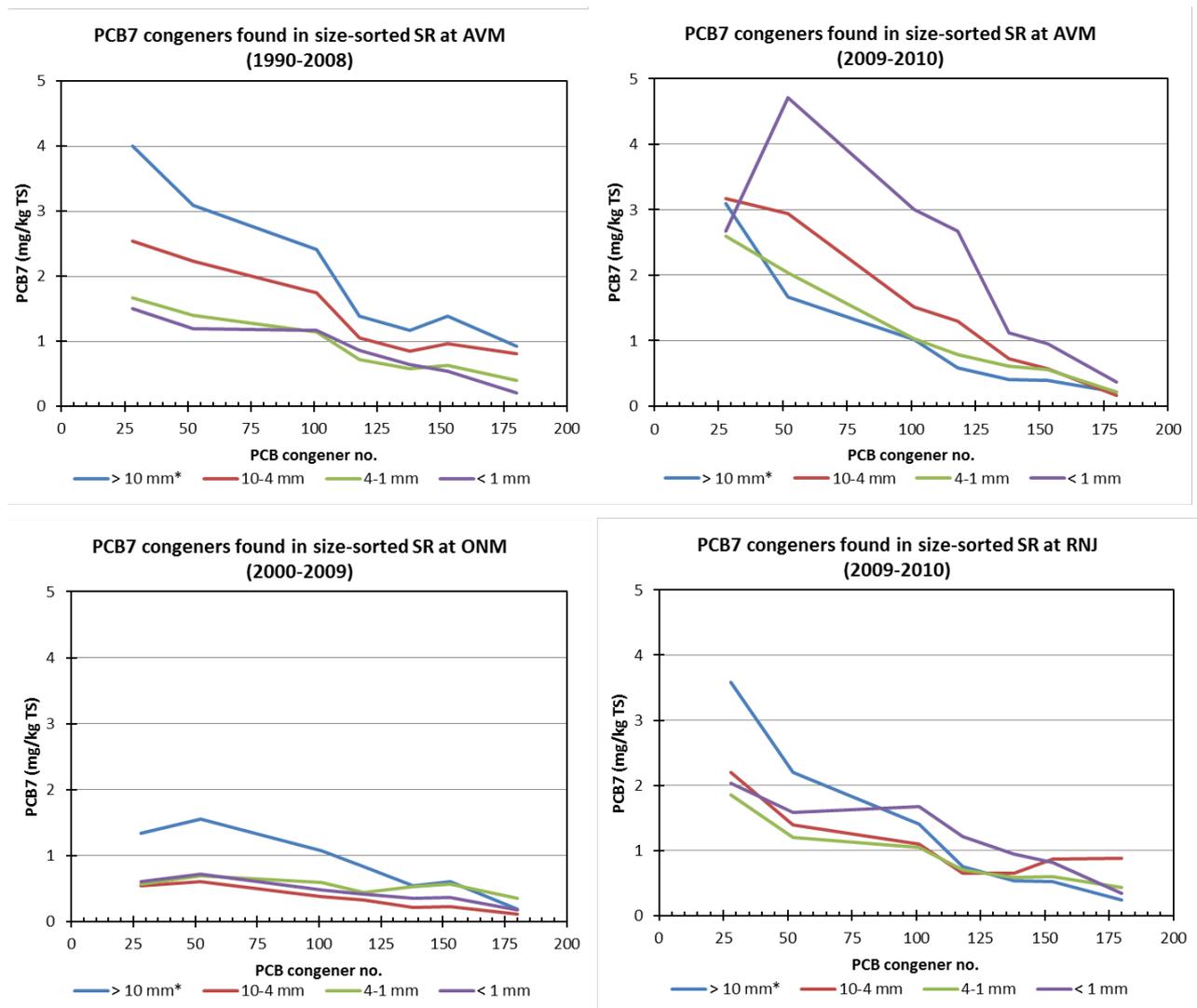


Figure 2.4 Distribution of PCB7 congeners in different particle size fractions of SR collected at the three largest Danish landfills for SR.

2.2.2 Shredder residues collected at Grenà in 2012

In this section, the results of an experiment carried out at STENA's shredding plant in Grenà are discussed. The plant in Grenà is processing approximately 1,000 tonnes of material per day. According to STENA, about 80-90% of the incoming material originates from recycling stations, other metal scrap dealers, and manufacturers while the remaining 10-20% is linked to ELVs.

After shredding by a hammer mill, the shredded material is split into two fractions by a cyclone: the shredder light fraction (SLF) and the heavy fraction (SHF). After the recyclables (metals) are collected from both the light and the heavy fraction, three waste streams are generated:

- SHF (0-100 mm) from the heavy fraction
- SLF (0-60 mm) from the shredder light fraction
- SLF (60-100 mm) from the shredder light fraction

Material with a particle size greater than 100 mm is fed back into the shredder for reprocessing. In addition to the above mentioned waste streams, one more waste stream is generated during the dust-off treatment: a sludge from Venturi-scrubber.

In this experiment, composite samples of each waste stream were collected during 20 working days. In general, a daily sample consisting of 7 subsamples (one subsample per hour) was collected for each SR stream. The subsamples were collected directly from the falling stream of SR – special care was taken to collect the entire mass of the falling stream in order to ensure that no fraction of the falling stream remained uncollected. Typically, a subsample of 5-6 kg was collected each hour yielding approximately 35-45 kg of SR from each waste stream per day. The daily samples were collected in three separate containers which had sufficient capacity to store all daily samples (i.e., the primary samples). At the end of the sampling period the primary samples were mass-reduced to laboratory samples of approximately 100-150 kg each using the "long-pile principle". The laboratory samples were sent to DHI for further treatment.

At DHI, the laboratory samples were further mass-reduced using consecutive long-piles, and two representative subsamples corresponding to a volume of approximately 26 litres were generated for each SR stream. Samples of the Venturi-sludge were taken by the sampling tube directly from the barrel. The following final samples were generated:

- SHF (0-100 mm): Sample 1 (8.8 kg) and Sample 2 (9.1 kg)
- SLF (0-60 mm): Sample 1 (8.7 kg) and Sample 2 (8.5 kg)
- SLF (60-100 mm): Sample 1 (6.6 kg) and Sample 2 (6.0 kg)
- Venturi-sludge: Sample 1 (ca. 3L) and Sample 2 (ca. 3L)

"Sample 1" was further used at DHI while "Sample 2" was sent to STENA as a back-up. The SR samples were pre-treated as indicated in Table 2.5. "Magnetic soil"²⁷ was removed by hand-held magnet in order to assess its reuse potential. Representative subsamples of all SR as well as Venturi-sludge were analysed for PCB7.

²⁷ In this project magnetic soil refers to the magnetic fraction of the "fines": a wool-like matrix (<4 mm) including mixture of soil, dust, organic material (wood, plastic, paper) and also pieces of metals

Table 2.5 Shredder waste samples collected at Grenå analysed for PCB7

Material	Pre-treatment	Comment
SLF (0-60 mm)	non-magnetic metals removed (>10 mm)	Analysed for PCB
	magnetic metals removed (>10 mm)	
	magnetic soil removed (<4 mm)	Analysed for PCB
SLF (>60 mm)	non-magnetic metals removed (>10 mm)	Analysed for PCB
	magnetic metals removed (>10 mm)	
	magnetic soil removed (<4 mm)	Analysed for PCB
	non-crushable item removed (>10 mm)	hard black plastic/polymer (not analysed)
SHF (0-100 mm)	non-magnetic metals removed (>10 mm)	Analysed for PCB
	magnetic metals removed (>10 mm)	
	wires removed (>10 mm)	
	WEEE removed (<10 mm)	
	magnetic soil removed (<4 mm)	Analysed for PCB
Sludge	Representative subsample created (sampling tube)	Analysed for PCB

PCB7 were analysed separately in the hand-sorted samples and the magnetic soil. The results are shown in Table 2.6 as (i) PCB7 analysed in the samples without magnetic soil, (ii) PCB7 analysed in the magnetic soil, and (iii) PCB7 calculated to be present in the mixed sample (using mass balance).

The amounts of PCB7 found in the mixed SHF sample were 3-6 times higher than in mixed SLF samples, while all three mixed samples were found below the limit value of 50 mg/kg TS (after multiplying with a factor 5). For the Venturi sludge 8 mg/kg TS PCB7 were found, yielding 40 mg/kg TS (after multiplying with a factor 5). Thus, although the highest amounts of PCB7 were indeed found in the composite sample of the Venturi sludge collected over 20 working days, this sample did not exceed the limit values for hazardous waste. Nevertheless, considering the uncertainty of PCB7 measurements at 30% (ALS Scandinavia, personal communication) this value should be used with caution.

It is shown in both Table 2.6 and Figure 2.5 that magnetic soil collected for SLF 0-60 mm and SHF 0-100 mm was enriched with PCB7 compared to the rest of the sample. The amounts of PCB7 measured in the magnetic soil fraction of SHF 0-100 mm were actually higher than those measured in the sludge sample. Nevertheless, none of the sub-fractions exceeded the limit value of 50 mg/kg TS. Thus, from the PCB7 point of view, this particular magnetic soil fraction was not classified as hazardous waste.

In the next step, the results of PCB7 analyses were compared congener-wise for the mixed samples. The analysed PCBs showed very different congener profile (sort of a fingerprint²⁸) for the “light” process streams (SLF 0-60 mm, SLF >60 mm, and dust) and for the “heavy” process stream (SHF 0-100); see Figure 2.6. Seemingly, the “heavy” process streams contained higher amounts of the heavier (more halogenated) congeners. The maximum was observed in congener range 80-130, whereas all three samples from the “light” process streams showed higher relative amounts of the less halogenated congeners. For the “light” streams the maximum, corresponding to 40-60% of the total PCB7, was observed for the very first congener measured (PCB no. 28) while the amounts of the other congeners were decreasing gradually towards to higher chlorinated PCB congeners.

²⁸ <http://www.exponent.com/files/Uploads/Documents/Newsletters/EFNotes2007-07.pdf>

Table 2.6 PCB7 analysed in samples collected at Grenå

Parameter	SLF 0-60 mm			SLF >60 mm			SHF 0-100 mm			Sludge
	without mag- netic soil	magnetic soil	mixed sample	without mag- netic soil	magnetic soil	mixed sample	without mag- netic soil	magnetic soil	mixed sam- ple	
All values as mg/kg TS										
PCB 28	0.31	0.88	0.36	0.38	0.25	0.38	0.19	0.57	0.20	4.65
PCB 52	0.093	0.38	0.12	0.22	0.14	0.22	0.38	0.32	0.38	1.59
PCB 101	0.047	0.24	0.065	0.15	0.11	0.15	0.83	1.3	0.84	0.498
PCB 118	0.023	0.14	0.033	0.091	0.084	0.091	0.77	1.8	0.79	0.484
PCB 138	0.036	0.25	0.056	0.087	0.13	0.088	0.72	1.3	0.73	0.424
PCB 153	0.028	0.14	0.039	0.063	0.055	0.063	0.5	2.5	0.54	0.239
PCB 180	0.017	0.09	0.024	0.035	0.032	0.035	0.13	0.33	0.14	0.110
PCB7, sum	0.55	2.1	0.70	1.03	0.81	1.02	3.5	8.1	3.6	8.0
Σ PCB7 × 5	2.8	10.5	3.5	5.2	4.1	5.1	17.5	40.5	18.1	40

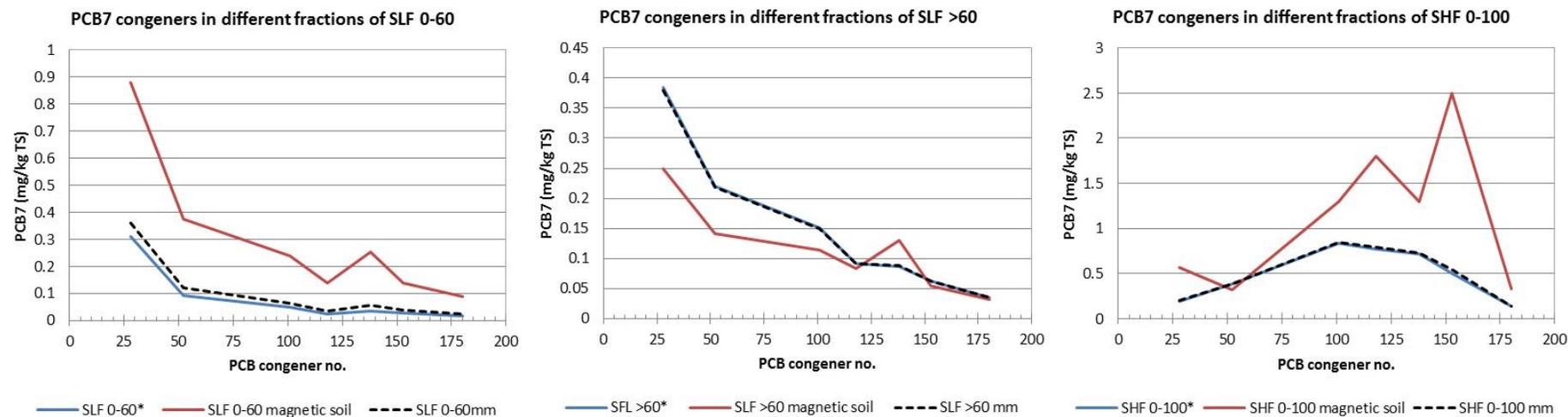


Figure 2.5 PCB7 found in different fractions of SLF 0-60, SLF >60 and SHF 0-100. Calculated composition of the mixed sample is indicated by dashed line.

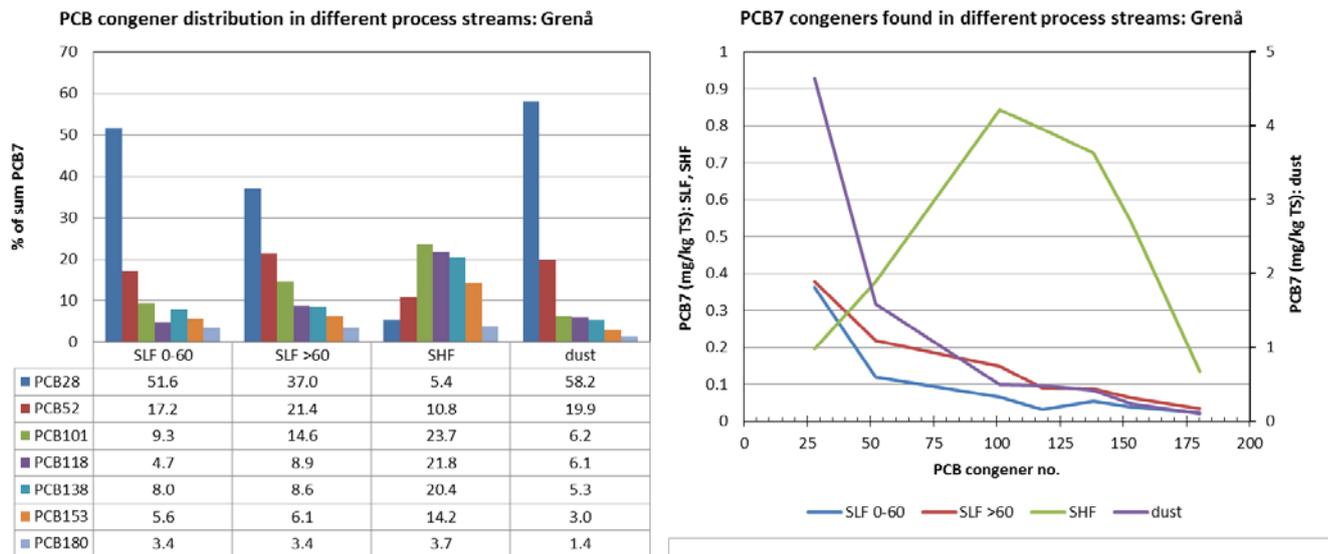


Figure 2.6 Left: Distribution of PCB7 congeners (as % of sum PCB7) in different waste streams generated at Grenå. Right: the amounts of individual congeners measured in different waste streams (mg/kg TS). Note that result of “dust” are shown on the secondary y-axes.

In Figure 2.7 the amounts of different PCB congeners found in three different Aroclor mixtures (refer to Section 2.1.1) are shown. It can be seen that the “light” SR fractions might have been contaminated predominantly by Aroclor 1016 (or Aroclor 1242, which was replaced by Aroclor 1016 in 1971), while the “heavy” fraction might have been contaminated by Aroclor 1254g (ATSDR, 2000).

As noted previously, PCB mixtures were used in numerous applications. Chapter 5 of the “Toxicological profile for Polychlorinated Biphenyls (PCBs)” (ATSDR, 2000) gives an overview of former uses of the different Aroclors (Table 2.7). Apparently, contamination of the “heavy” fraction with Aroclor 1254 or similar mixture(s) (e.g., Clorphen A50, Delor 105) may come from numerous sources/applications (e.g., hydraulic fluids, plasticisers, paints, synthetic resins, cutting oils, and sealants). Contamination of the “light” fractions (including process dust) by Aroclor 1242 or its replacement Aroclor 1016 (after 1971) would indicate slightly lower number of applications (see below Table). If contamination of the “light” fractions was caused by only Aroclor 1016, then the only remaining application seems to be capacitors²⁹. Unfortunately, fingerprints of Aroclor 1016 and 1242 are fairly similar – except for the area between congener no. 65 and congener no. 75, which is not scanned in detail while measuring PCB7 congeners. In order to confirm the presence of Aroclor 1016, the complete fingerprints are necessary (outside the scope of this project). Naturally, if Aroclor 1016 was confirmed, capacitors in the incoming waste prior to the shredding process could be targeted in order to further decrease the contamination of the “light” process waste streams (SLF and dust).

From the rather limited information obtained at Grenå, contamination of the heavy process stream seemed to be linked to different process fluids, oils, paints, rubbers and sealants. It is thus unlikely that a single source of contamination may be found without very detailed characterisation of PCBs in each material fraction. Even then it is very uncertain that the contamination source will remain constant over time and thus become an obvious target for specific source separation efforts.

²⁹ A PCB concentration of 3000 ± 1400 mg/kg TS was measured in capacitors manually separated at a WEEE recycling plant in Switzerland (Morf et al., 2007)

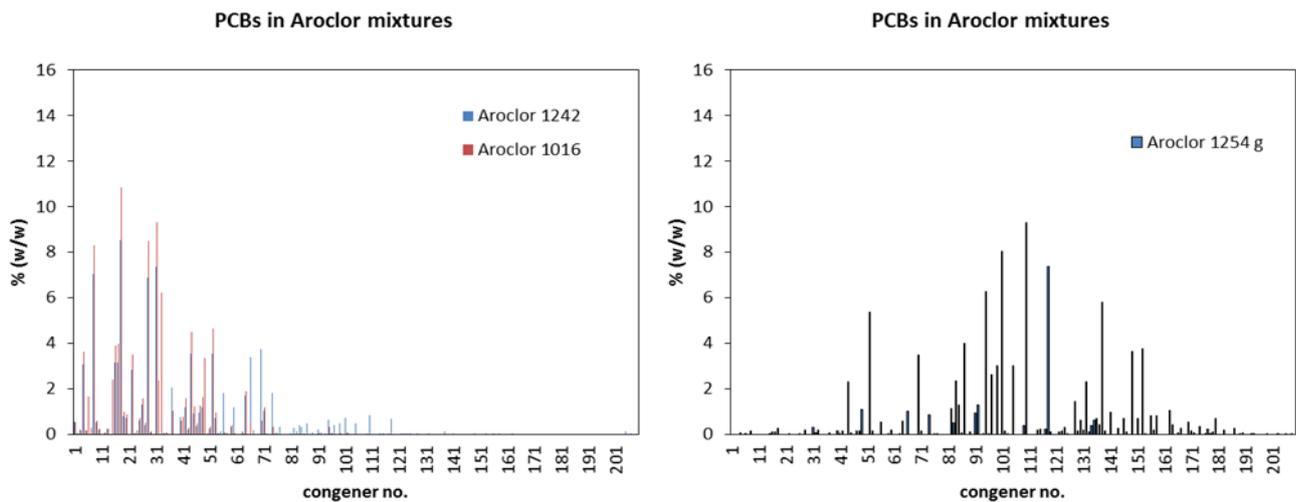


Figure 2.7 Fingerprints of Aroclor mixtures (ATSDR, 2000).

Table 2.7 Former uses of various Aroclor mixtures (ATSDR, 2000)

End use	Aroclor								
	1016	1221	1232	1242	1248	1254	1260	1262	1268
Capacitors	x	x				x			
Transformers				x		x	x		
Heat transfer				x					
Hydraulic fluids			x	x	x	x	x		
Vacuum pumps					x	x			
Gas-transmission turbines		x		x					
Rubbers		x	x	x	x	x			X
Synthetic resins					x	x	x	x	X
Carbonless paper				x					
Adhesives		x	x	x	x	x			
Wax extenders				x		x			X
De-dusting agents						x	x		
Inks						x			
Cutting oils						x			
Pesticide extenders						x			
Sealants and caulking compounds						x			

2.2.3 BFRs

BFRs are not generally measured in Denmark, and very limited information is therefore available regarding their amounts (MST, 1999), let alone their distribution in different fractions of SR. A significantly larger dataset is available for BFRs found in WEEE^{30,31}; however, components and materials from WEEE containing BFRs should be managed separately and may not – in principle – be found in significant quantities in newly produced SR.

³⁰ http://www.mst.dk/Virksomhed_og_myndighed/Kemikalier/Fokus+paa+saerlige+stoffer/

³¹ <http://www2.mst.dk/Udgiv/publications/2012/07/978-87-92779-99-1.pdf>

In order to get an indication of the possible amount of BFRs in SR, one can look at the amounts of bromine found in SR. Bromine is also not measured routinely in Denmark; however, Ahmed et al. (2012) did measure bromine in number of samples collected from the three largest sites in Denmark (Table 2.8). They found – similarly for all three sites – that the total content of bromine is increasing proportionally to the particle size fraction of SR; i.e., the largest particle size fraction contains the largest amounts of bromine. This is likely linked to the fact that the larger particle size fractions contain more plastic, rubber and foam, which are all likely to contain BFRs. In addition, it seems that the younger samples contain more bromine than the pre-2000 samples. This trend was clear for ONM and, except for the 2001-2004 sample, also for AVM. Again, this may be explained by higher use of flame-retarding materials in consumer products including cars.

Surprisingly, the highest amounts of bromine were found in the 2007-2009 samples generated by H.J. Hansen, who in fact also separate a large fraction of plastic in their recovery process. Whether this may be caused by the fact that H.J. Hansen's process is able to differentiate between non-BFR containing plastics for re-sale (BFR containing plastics are generally heavier than their non-BFR containing analogues and may be separated based on their density in float-sink separators; see Section 3.2) is unclear³². If this was the case, the reject fraction would include BFR-containing plastic and this might explain the higher amounts of bromine.

Table 2.8 Distribution of Br in Danish SR (Ahmed et al., 2012).

All values in mg/kg TS	AVM		ONM	RNJ
SR age groups	1990-2008	2009-2010	2000-2009	2009-2010
Particle size fraction				
>10 mm*	1270	830	683	934
10-4 mm	483	745	583	558
4-1 mm	229	139	180	360
<1 mm	30.1	67	73.2	60.2
Mixed sample	see below	381	271	637
Mixed sample	106 (1990-2000) 837 (2001-2004) 334 (2005-2008)		140 (2000-2001) 669 (2003-2006) 1260 (2007-2009)	

*) metals were removed prior to the analysis

Although the above data provide an indication of the potential contents of BFRs in Danish SR, the information on the exact *type* of BFR is still missing. This information is important since different types of BFRs have different environmental impact potential (see Section 2.1.2). In 2012, three samples of SR produced at the STENA's plant in Grenå were screened for a number of BFRs. The results are shown in Table 2.9. For comparison, the results of a Norwegian study focused on characterisation of SLF from (A)SR are shown in the last column (SFT, 2008a).

Values below the limit of detection are indicated **red**.

³² H.J. Hansen provided no information on that matter

Table 2.9 BFRs in SR samples collected at STENA's plant in Grenà (all values in mg/kg TS).

Parameter	SLF (0-60 mm)	SLF (60-100 mm)	SHF (0-100 mm)	Norway (SFT, 2008a)
tetra-BDE	10	10	31	10
BDE 47	1.1	3	1.0	1.7 – 17
penta-BDE	10	10	80	1 - 9.6
BDE 99	2.5	5	64	1 – 14
BDE 100	1.0	1	14	10
hexa-BDE	20	20	23	1 – 2.9
hepta-BDE	20	20	20	10
okta-BDE	50	50	50	0.25-23
nona-BDE	100	100	100	20
deka-BDE	100	100	100	18-64
di-BB	10	10	10	-
PBB	1.0	1.0	1.0	-
tri-BB	10	10	10	-
tetra-BB	10	10	10	-
PBB 49	1.0	1.0	1.0	-
PBB 52	1.0	1.0	1.0	-
penta-BB	10	10	10	-
PBB 101	1.0	1.0	1.0	-
hexa-BB	20	20	20	-
PBB 153	4.0	4.0	4.0	-
deka-BB	100	100	100	20
TBBP-A	10	10	66	10

It can be seen that many congeners of BFRs were found below the detection limits. The highest measured concentrations of BFRs were found in the “heavy” shredder fraction (SHF) with particle size 0-100 mm. Note that commercial “penta-BDE” is a technical mixture of different BDE congeners with BDE47 and BDE99 and BDE100 congeners as the most abundant. In addition, the mixture may contain around 5% BDE153/154 (hexa-BDE) congeners (La Guardia et al., 2006).

Apparently, there is more BFR-containing material in the heavy fraction than in the light fractions, likely plastic in the form of styrene polymer and/or fiberglass reinforced plastic and pieces of electronics generated from shredding ELVs and household appliances. The other most abundant BFR found in the heavy fraction was TBBP-A. TBBP-A is mainly used in epoxy resins and printed circuit boards. As an additive, it is also used in the ABS resin (acrylonitrile butadiene styrene), which is used in automotive trim components, bumpers, canoes, small kitchen appliances etc.

Overall, the results for SLF 0-60 mm and SLF 60-100 mm were comparable with the Norwegian data (using SLF-like material), whereas the results for SHF 0-100 mm were somewhat higher.

2.2.4 BTEX

BTEX are volatile compounds and as such they are not considered problematic with respect to SR management (MST, 2002). Consequently, BTEX are not generally measured in Danish SR. Poulsen et al. (2011) found between 12 and 42 mg/kg TS BTEX (Table 2.3); the largest fraction of the sum of BTEX consisted of xylenes. Nevertheless, these concentrations were roughly 2-4 orders of magnitude below the limit values for hazardous waste.

2.2.5 PAHs

Results of the analytical determination of PAHs (US EPA 16) performed by Ahmed et al. (2012) are shown in Table 2.10.

Similar to PCBs, SR deposited on ONM (generated by H.J. Hansen) showed a significantly different composition with respect to PAHs than SR deposited at AVM and RNJ. Similar levels of PAHs were found in SR deposited at AVM (until 2008) and at RNJ, whereas significantly higher amounts of PAHs were determined in SR deposited at ONM. Furthermore, notably increased amounts of PAHs were found in the SR fractions below 10 mm deposited at AVM after 2009. However, these values did not correspond with the PAH contents determined for the mixed sample containing all particle size fractions.

Table 2.10 US EPA 16 PAHs (mg/kg TS) in samples from the largest Danish landfill sites for SR (Ahmed et al., 2012).

AVM	>10 mm	10-4 mm	4-1 mm	<1 mm	All fractions
1990-2000					1.8
2001-2004	2.0	0.91	3.8	1.4	0.57
2005-2008					1.0
2009-2010	0.37	24	20	24	1.3
ONM	>10 mm	10-4 mm	4-1 mm	<1 mm	All fractions
2000-2001					28
2003-2006	55	39	19	22	41
2007-2009					39
2000-2009					30
RNJ	>10 mm	10-4 mm	4-1 mm	<1 mm	All fractions
2009-2010	1.4	0.94	1.2	1.3	1.2

2.2.6 TPH

As shown in Table 2.3, concentration of TPH found in *mixed* Danish SR ranges between 14,000 and 21,000 mg/kg TS. The largest fraction of the TPH value is associated with the carbon range C20-C40 suggesting contamination with diesel and lube oils for which the limit value is 10,000 mg/kg TS.

In 2012, DHI analysed TPH in the three process streams coming from the plant at Grenå: SLF 0-60 mm, SLF >60 mm, SHF 0-100 mm. TPH concentrations in the *individual* process streams of 17,000-38,300 mg/kg TS were found. The most polluted stream was the “heavy” fraction. In all cases, 95-97% of the TPH contamination was associated with the carbon range C16-C35; i.e., caused by diesel and mineral oils.

2.2.7 PVC

Ahmed (2012), Ahmed et al (2012), and Hansen et al (2012) investigated composition of SR with respect to the amount of “plastic” in the overall mixture. However, the fractionation of plastic has not been investigated in any study and it is thus not possible to assess the amount of PVC in SR, its distribution and/or the most probable source(s). It may be assumed that large fraction of PVC originates from furniture (metal-plastic garden furniture, office chairs), cable/wire insulation coating, and automotive parts.

2.2.8 Distribution of selected metals/metalloids

Poulsen et al. (2011) identified several elements as potentially problematic with respect to the “hazardousness” of SR. These elements included As, Cd, Co, Cr, Hg, Ni, Pb, Sb and Zn. In the following text, the distribution of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb and Zn in Danish SR is discussed.

In Figure 2.8 the distribution of the above-mentioned metals is shown for SR collected at ONM. The upper two diagrams show the contents of the individual metals in samples collected from different locations at the landfill thus representing different generation/deposition periods. In addition, each of the diagrams shows the composition of a mixed sample representing the entire 2000-2009 period. The lower two diagrams show the distribution of the same metals in the different particle size fractions of the mixed sample representing the 2000-2009 period.

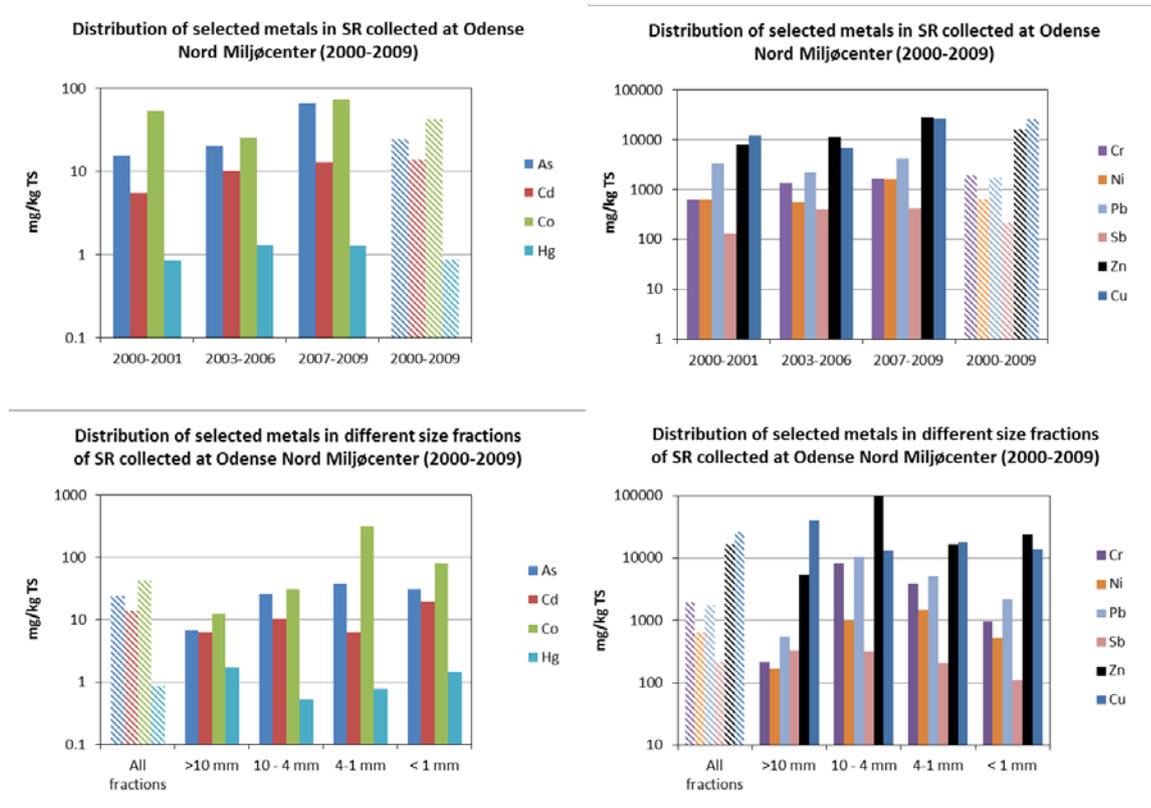


Figure 2.8 Distribution of selected metals in SR samples collected at ONM. Upper row: distribution of metals in samples obtained for different deposition periods as well as for a mixed sample representing the averaged composition on the site (pattern fill). Bottom row: distribution of metals in a mixed sample as function of particle size. Note different y-axis scale.

Similarly to Figure 2.8, the distribution of metals in the samples from AVM and RNJ is shown in Figure 2.9 and Figure 2.10, respectively. In Figure 2.9, the results for AVM are furthermore shown separately for two time periods; i.e., 1990-2008 and 2008-2010. The results for the different time periods (see Figure 2.8 and Figure 2.9) indicate slightly increased contents of As, Cd, Cr, Cu, Sb and Zn in SR from ONM while the composition of SR from AVM remains relatively unchanged – except for Cd, Cu and Hg (see also Table 2.11). This may be caused by *higher* recovery of the “clean” fractions at the shredding plant which results in higher contents of potential pollutants in the reject fractions that is landfilled.

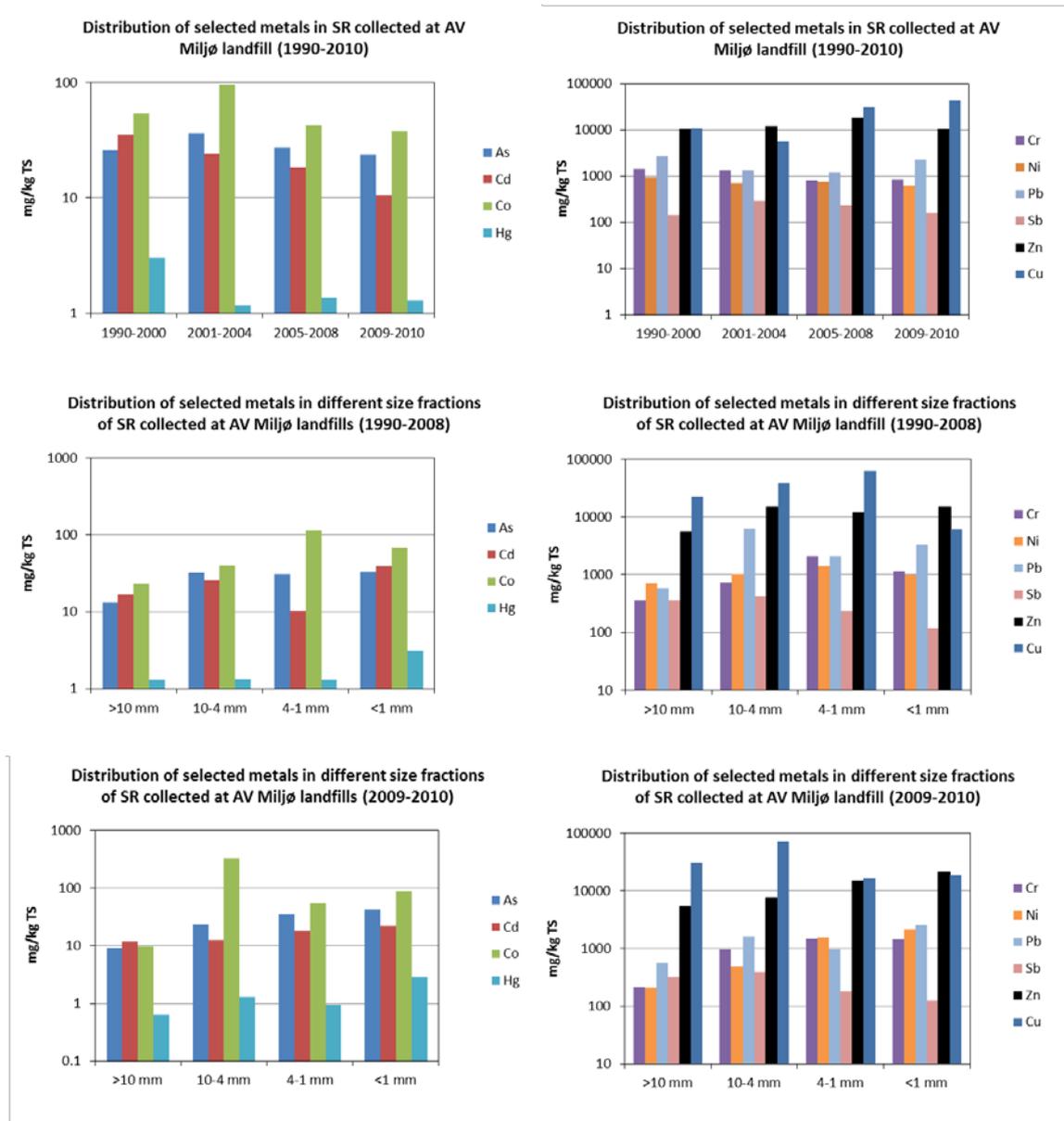


Figure 2.9 Distribution of selected metals in SR samples collected at AVM. Upper row: distribution of metals in samples obtained for different deposition periods. Middle row: distribution of metals as a function of particle size in a mixed sample representing the period of 1990-2008. Bottom row: distribution of metals as a function of particle size in a mixed sample representing the period of 2009-2010.

Table 2.11 Total composition of SR samples from ONM and AVM sites: summary of trends between 1990 and 2010.

Element	Odense Nord Miljøcenter	AV Miljø landfill	Element	Odense Nord Miljøcenter	AV Miljø landfill
As	↑	↔	Hg	↔	↓
Cd	↑	↓	Ni	↔	↔
Co	↔	↔	Pb	↔	↔
Cr	↑	↔	Sb	↑	↔
Cu	↑	↑	Zn	↑	↔

The absolute amounts of metals found in different fractions of SR collected at RNJ do not deviate significantly from the picture obtained for AVM and ONM. As data only for one “age group” are available, an evaluation of time-trends is not possible.

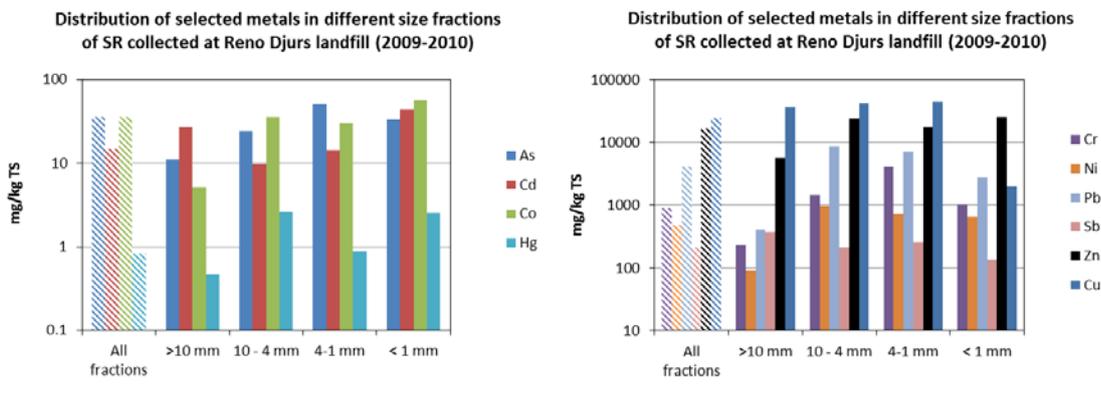


Figure 2.10 Distribution of selected metals as a function of particle size in SR samples collected at RNJ.

2.3 Shredder residue composition: European data

2.3.1 Overview

Numerous studies focused on all possible aspects of (A)SR management were carried out in the EU over the last 20-30 years (cf. Poulsen et al., 2011). Recently, an increased number of studies focusing on ASR have been carried out in e.g. Norway, Sweden and Italy. Unfortunately, because of different scope of these studies, the data obtained are not directly comparable and should be approached with great care.

In Table 2.12 examples of SR composition are given. Note that these values were obtained from different studies using different types of “residues” (e.g., pure ASR vs. (A)SR). Also, while Danish PCB data typically refer to the measurement of PCB7, German data typically refer to PCB6³³. Similarly for all studies, concentrations of some elements (e.g., Pb, PCB, or PAH) measured in SR vary by several orders of magnitude, thus illustrating the differences in chemical composition depending on SR type. It may therefore be misleading to focus on average or mean values. Instead, ranges are shown in Table 2.12 and where available, also median values are given.

Without going into details, it can be seen from the presented data that – similarly for different countries – the content of hydrocarbons (e.g., fuel, diesel, “oils”), Pb and PCB appear to cause the main problem in relation to classification of the SR as hazardous or non-hazardous. In some cases, also Ni, Co and Cr may become important in relation to SR classification if the measured content is *not* related to the metallic form.

Some of the most interesting results (within the context of this study) from different international studies are briefly discussed in this section. For full information, one should refer to the original studies.

³³ PCB₆ includes PCB nr. 28, PCB nr. 52, PCB nr. 101, PCB nr. 153, PCB nr. 138, and PCB nr. 180

Table 2.12 Examples of SR composition obtained in different countries

Parameter	Unit	Denmark ^a	Finland ^b	Germany ^c		Italy ^f	Norway ^g	BEK 1309/2012; Reg. EC 1272/2008
		Min-Max	Mix-Max	Min-Max	Median (n)	Min-Max	Min-Max	
Sum BTEX	mg/kg TS	12-42	-	-	-	-	4.1-32	1,000 ⁱ
Sum of C6-C35	mg/kg TS	14,000-21,000	-	-	-	24,000-26,000	5,100-30,000	1,000 or 10,000 ^{ij}
Sum of PAH (US EPA 16)	mg/kg TS	1,2-47	-	0.0074-715	40 (n=233)	4.0-6.4	9-32	25 ^k or 100 ^l
Sum of PCB7	mg/kg TS	0.9-51 ^e	-	0.001-297 ^d	5.0 (n=784) ^d	7.9-24.3	<0.35-22	50 ^m
TOC	%	19-43	-	20-47	32.6	33-45	-	6 ⁿ
As	mg/kg TS	13-36	-	1.7-350	38 (n=31)	0.16-16	4.2-36	1,000 ^o
Ba	mg/kg TS	2,200-5,600	-	-	-	12.8	-	-
Cd	mg/kg TS	15-30	25-400	0.23-550	38 (n=112)	11.8-23	12-63	1,000 ^p
Co	mg/kg TS	24-51	-	25-160	100	-	-	100 ^q
Cr	mg/kg TS	250-890	1,000-11,000	340-1,300	1,200	37-260	75-380	1,000 ^r
Cr(VI)	mg/kg TS	-	-	-	-	<0.2-4.9	<0.06-0.27	1,000 ^r
Cu	mg/kg TS	11,100-24,800	4,000-30,000	0.24-410,000	10,700 (n=106)	2,860-21,200	3,600-65,000	2,500 or 250,000 ^s
Hg	mg/kg TS	0.3-10	0.1-15	0.0011-48.3	1.9 (n=95)	0.12-0.42	0.56-1.9	500 or 1,000 ^s
Mo	mg/kg TS	49-144	-	45-63	54 (n=2)	19.3	-	-
Ni	mg/kg TS	220-480	400-1,500	400-2,800	1,200	33-350	130-800	1,000 or 10,000 ^t
Pb	mg/kg TS	1,600-13,000	1,000-11,000	300-14,000	5,100	410-2,500	1,500-5,500	2,500 or 5,000 ^u
Sb	mg/kg TS	210-300	-	100-678	100 (n=4)	-	-	2,500 ^v
Sn	mg/kg TS	179-193	100-400	25-90	67	55-170	-	50,000 ^w
Zn	mg/kg TS	11,000-20,000	5,000-30,000	2,000-13,000	-	1,810-19,440	7,300-28,000	50,000 ^w
Cl _{tot}	mg/kg TS	8,100-26,000	-	5,000-30,000	-	9,430-46,600	-	-
Br _{tot}	mg/kg TS	106-637	50-2100 ^h	-	-	-	-	-
S _{tot}	mg/kg TS	1,960-3,500	-	1,000-1,400	-	2,200-2,400	-	-

^a Hansen et al. (2011a, 2011b, 2012), Ahmed (2012), Ahmed et al. (2012), Nedenskov (2012); ^b Jalkanen (2006) and references therein; ^c Reihardt and Richers (2004), Sakai and Fiedler (2004), Poulsen et al. (2011); ^d Sum of 6 congeners times 5; ^e Sum of 7 congeners times 5; ^f Mirabile et al. (2002), Santini et al. (2011), Mancini et al. (2010), Viganò et al. (2010); ^g SFT (2008a); ^h Nieminen et al. (2006); ⁱ A limit value of 1,000 mg/kg TS applies to benzene; ^j A limit value of 1,000 mg/kg TS applies to "other hydrocarbons" (incl. gasoline and light heating oil) classified as Carc.Cat 2 while a limit value of 10,000 mg/kg TS applies to hydrocarbons from jet fuel, diesel and heating oil in the range C9-C20 classified as Carc.Cat 3; ^k A limit value of 25 mg/kg TS applies to dibenzo(a,h)anthracene; ^l A limit value of 100 mg/kg TS applies to benzo(a)pyrene; ^m The result of PCB7 analysis multiplied with a factor of 5; ⁿ A limit value for waste to be deposited at landfills for hazardous waste; ^o A limit value of 1,000 mg/kg TS applies to elemental (inorganic) As; ^p A limit value of 1,000 mg/kg TS applies to elemental Cd as well as to metallic Cd; ^q A limit value of 100 mg/kg TS applies to Co dichloride-, sulphate-, acetate-, nitrate- and carbonate; ^r A limit value of 1,000 mg/kg TS applies to Cr(VI) compounds while metallic Cr is not classified; ^s A limit value of 500 mg/kg TS applies to organic compounds while 1,000 mg/kg TS applies to inorganic compounds as well as metallic Hg; ^t A limit value of 1,000 mg/kg TS applies to Ni compounds while 10,000 mg/kg TS applies to metallic Ni; ^u A limit value of 2,500 mg/kg TS applies for category "ecotox". At the moment, no limits for "ecotox" are set at national level, however, some municipalities (e.g. Copenhagen) use it. A limit value of 5,000 mg/kg TS applies to elemental (inorganic) Pb. A limit value of 5,000 mg/kg TS applies for elemental (inorganic) Pb; ^v A limit value of 2,500 mg/kg TS applies to Sb compounds, except tetr-, pentoxide, tri-, pentasulphide and tri-, pentachloride; ^w A limit value of 50,000 mg/kg TS applies to "compounds"; ^x A limit value of 250,000 mg/kg TS applies to Cu(I)-chloride and Cu(I)-oxide; however, limit value of 2,500 mg/kg TS applies when category "ecotox" is considered. Metallic Cu is not classified.

2.3.2 Germany

According to the note by Sakai and Fiedler (2004) the “Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen” (LUA NRW) reported the median value of 5 mg/kg TS PCB6 in German shredder light fraction (SLF)³⁴, while 20% of the wastes actually exceeded the limit value of 50 mg/kg after multiplying the PCB6 concentrations with the factor of 5. In another report from 2005, the results of analysis of PCB6 in 8 different material fractions of SLF were reported (Lehnik-Habrink et al., 2005). The highest concentrations of PCB6 were found in textile, foam and hard plastic. It was concluded that the elevated concentrations of PCBs in these fractions were caused by point contamination with process fluids containing PCBs.

Table 2.13 PCB6 contents (mg/kg TS) analysed in different material fractions of SLF

Material fraction	PCB nr.28	PCB nr.52	PCB nr.101	PCB nr.153	PCB nr.138	PCB nr.180	Sum of PCB6
Wood	0.18	0.17	0.03	-	0.01	-	0.39
Textile	1.67	1.21	0.51	0.14	0.13	0.08	3.74
Metals	0.02	-	-	-	-	-	0.02
Foam	2.84	1.89	0.75	0.2	0.24	0.13	6.05
Paper/cardboard	0.39	0.31	0.21	0.04	0.05	0.03	1.03
Plastic-soft	0.41	0.22	0.1	0.01	0.02	0.07	0.83
Plastic-hard	2.49	2.12	0.68	0.15	0.19	0.08	5.71
Plastic-WEEE	0.28	0.19	0.02	-	0.01	0.01	0.51

2.3.3 Norway

In 2007-2008, the Norwegian Climate and Pollution Agency has carried out two studies focused on characterisation of SR from metal recovery industry. In the first study (SFT, 2008), SR samples from three different plants were collected. In total, eight SLF samples were obtained. Both mixed SLF and sorted SLF were represented; see Table 2.14 for an overview.

Table 2.14 General properties of SR samples tested in SFT (2008a).

Material origin	Type of SLF	Site 1	Site 2	Site 3
Mixed scrap metal	Coarse SLF	x	x	
	Fine SLF – mineral	x	x	
	Fine SLF – magnetic		x	
	Mixed SLF ¹			X
ELVs	Mixed SLF ¹	x		
	Mixed SLF ¹	x		

¹ Mixed SLF: not sorted into fine/coarse fraction

All samples were analysed for an extensive number of parameters including metals/trace elements, PCB7, other chlorinated compounds (e.g., chloropesticides, chlorobenzenes, organochlorides, etc.), PAHs (US EPA 16), BTEX, TPH (C5-C35; different fractionation) and BFRs (tetra-BDE, penta-BDE, tetra-BDE 47, penta-BDE 99, hexa-BDE, penta-BDE 100, hepta-BDE, octa-BDE, nona-BDE, deca-BDE, TBBP-A, decabromdiphenyl, and HBCD).

The results indicated that all eight samples had relatively high contents of “heavy metals” (especially Pb, Cu and Zn) and TPH (in particular C12-C16 and C16-C35). In addition, PCBs, trichloroethane, PAHs, BTEXs and BFRs (see Table 2.9) were found in the samples. Based on the total content of metals, all eight samples were considered as hazardous waste. The limit values for hazardous waste

³⁴ SLF: The fraction remaining after the separation of metal-containing materials. SLF contains lots of plastic, glass, sand, dust, rubber and also metals.

for TPH were exceeded in four samples while none of the samples were found to contain “hazardous” amounts of BFRs (SFT, 2008a). Notably, Danish and Norwegian data are fairly comparable considering the large heterogeneity of SR.

In a follow-up study (SFT, 2008b), the *leaching properties* of six of the above-mentioned eight samples were investigated by means of the EN 12457-2 batch test at L/S 10 l/kg (CEN, 1999) modified for the leaching of organic compounds. The leachates were analysed for the same set of parameters as the solid samples. In general, it was found that:

- the highest leaching of metals occurred in one of the samples of the coarse SLF
- the highest leaching of PCBs occurred in one of the samples of the fine grain size SLF
- the highest leaching of PAHs, BTEX and oils was found in the samples generated from shredding ELVs alone
- the highest leaching of BFRs were found in one of the samples generated from shredding ELVs alone

The leaching data were also compared with the total solid composition data. In general, 0.01-4.07% of all substances leached out in the batch leaching test. More specifically, it was found that 0.01-3.18% of metals, 0.03-0.06% of PCBs and other chlorinated compounds, 0.005-2.68% of PAH, BTEX and mineral oils, and 0.004-4.07% of BFRs leached out.

With respect to landfilling, none of the samples were found suitable for landfills receiving inert waste because of elevated leaching of metals (Cu, Ni, Pb and Zn). Samples of mixed SLF originated from shredding of ELVs and coarse SLF originated from shredding of mixed scrap complied with the leaching limit values for hazardous waste being deposited at landfills for non-hazardous waste (European Commission, 1999) – except for one sample of coarse SLF originated from shredding of mixed scrap which showed higher leaching of Pb. This sample was found to comply with the leaching limit values for landfills receiving hazardous waste.

2.3.4 Italy

In a recent Italian study (Santini et al., 2011), 630 ELVs were shredded and three samples of SLF were characterised with respect to both the total composition and the leaching using EN 12457-2 L/S 10 l/kg test (CEN, 1999). The results of this study are outlined in Table 2.15; for the full dataset refer to the original study. Santini and colleagues compared the leaching with the limit values for landfills receiving non-hazardous waste. As shown in Table 2.15, the leaching of Zn and DOC exceeded the waste acceptance criteria for non-hazardous landfills ($WAC_{non-haz}$).

In addition, the authors tried to calculate the “effective Italian ELV recycling rate”. They concluded that (Italian) ASR still contains up to 8% of metals and 40% of polymers that could be recovered. Unfortunately, no further details on how such goals may be achieved were given. Nor were the economic and/or environmental impacts of the increased recovery rate discussed.

Table 2.15 Selected physical-chemical parameters and leaching behaviour of SLF (Santini, et al., 2011)

Parameter	Unit	Solid composition	Leaching	WAC _{non-haz} ³⁵
TOC	g/kg TS	440-450	1.85-2.14 ^a	80
pH	-	-	6.7-6.9	>6
As	mg/kg TS	1	<0.1	0.2
Cd	mg/kg TS	9.9-21	0.06-0.09	0.1
Cr	mg/kg TS	73-102	<0.1	1
Cr ⁶⁺	mg/kg TS	<0.2	<1	-
Cu	mg/kg TS	5,900-21,200	1.4-1.6	5
Hg	mg/kg TS	0.17-0.42	<0.002	0.02
Ni	mg/kg TS	34.8-38.6	0.5-0.6	1
Pb	mg/kg TS	442-600	0.2-0.3	1
Se	mg/kg TS	<0.1	<0.02	0.05
Sn	mg/kg TS	55-169	<0.1	-
Zn	mg/kg TS	1,800-6,100	42-51	5
Cl _{tot}	mg/kg TS	9,500	207-250 ^b	1,500
S _{tot}	mg/kg TS	2,200-2,400	350-400 ^c	2,000
PAH (US EPA 16)	mg/kg TS	4.0-6.4	-	-

^a) as DOC (Dissolved organic carbon)

^b) as chloride (Cl)

^c) as sulfate (SO₄²⁻);

2.4 Conclusive remarks on composition of shredder residues and possible source separation of TPHs, Pb and PCBs

In the previous text the latest knowledge regarding both presence of the problematic elements and the possible sources of the problematic elements has been reviewed using international as well as Danish data. Most importantly, based on comparison of the composition data from different countries and different types of SR it appears that the contents of “heavier” hydrocarbons (e.g. above C₂₀), Pb and PCB₇ cause the main problems with respect to classification of SR as hazardous or non-hazardous waste. In some cases Ni, Co and Cr may also be considered problematic in this respect if their content is *not* related to the metallic form (pieces of stainless steel).

For “heavier” hydrocarbons the limit value of 1% (BEK 1309/2012) is often exceeded in SR. The presence of heavier hydrocarbons is an indication of contamination with diesel and/or oil. It would thus appear that an improved – in the sense of avoiding contamination – collection of materials prior the shredding process may be beneficial. Special focus should be placed on ELVs, engines and appliances containing engines (e.g., lawn mowers). At the same time, however, it should be noted that although TPH analysis allows for separation of the analysed hydrocarbons based on their polarity (i.e., polar and non-polar hydrocarbons) it may not be possible to distinguish the origin of the individual compounds. In other words, it is very difficult to determine if they are associated with liquid contaminants (e.g., diesel, oil) or the solid matrix such as rubber and tyres (Eurofins Miljø A/S, personal communication). Questions may be raised regarding the toxicity of hydrocarbons present in rubber and/or tires.

The content of Pb in SR appears to be relatively constant over time³⁶ with the median value around 5,000 mg/kg TS which is the limit value for waste to be classified as hazardous - this is also shown in results from the three Danish landfills (discussed in Section 2.2.6). Nevertheless, during the

³⁵ Waste Acceptance Criteria for landfilling (European Commission, 2003a)

³⁶ <http://www.eur2.org/html/downloads/ESG-SWEDEN-FINAL.ppt>

sorting experiments performed by DHI at STENA's plant in Grenå, none of the collected process streams were found to exceed the hazard limit for the content of Pb (5,000 mg/kg TS), provided that samples were hand-sorted for remaining metals (data not shown). In addition, the shredder-light process streams were found to comply with the limit value of 2,500 mg/kg TS, should the category "ecotox" be considered. The shredder-heavy process streams were found to comply with the current limit value of 5,000 mg/kg TS while the limit value of 2,500 mg/kg TS (ecotox) was exceeded. It should be noted that SR composition data presented in Miljøprojekt Nr. 1441 showed Pb levels around 0.13-0.15%; i.e., in compliance with both the current limit value of 5,000 mg/kg and the "ecotox" limit value of 2,500 mg/kg TS (Høstgaard et al., 2012).

PCBs in SR are often found close to or exceeding the PCB7 limit value 50 mg/kg TS (after the results of the PCB7 analyses are multiplied by the factor of 5). However, from the information collected in this study it *seems* that the PCB contamination in SR is related neither to ELVs nor to material originating from municipal recycling stations – provided that the basic principles of waste collection are fulfilled and materials possibly containing PCBs such as WEEE are collected separately. Consequently, PCBs found in SR may be related primarily to the "industrial" fraction of processed metal scrap such as scrap originating from demolition of different process plants, large scale tanks, large metal constructions and old ships. As mentioned earlier "there is no assessment available as to how much PCB-painted scrap (from the 1950s to the early 1970s PCBs were used in anti-corrosion paints included ships, bridges and other constructions as well as electric poles) is entering the waste stream and the secondary metal treatment. However, it is known from measurements in EAF (electric arc furnace use at smelters) that considerable PCB loads are emitted which only can be explained by PCB input from material treated³⁷". Similarly, no information is available on the amount of this type of waste processed at Danish shredder plants (about 50% is assumed, though) in comparison with the remaining material originating from municipal recycling stations and ELVs.

2.5 Material recovery from shredder residues

As indicated earlier, Danish SR – although still containing relatively high amounts of recyclables (e.g., metals, non-ferrous metals, plastics, glass) – have usually been landfilled. This is mainly a consequence of the high pollutant content as well as of the lack of cost-effective sorting technologies, suitable for the separation of valuable materials from the residual mix (Hansen et al., 2012; Morselli et al., 2010).

Ahmed et al. (2012) focused on physical-chemical characterisation of different size fractions of both already landfilled SR and newly produced SR with respect to potential material recovery. In general, both the deposited SR and the newly produced SR were stated to provide a significant amount of resources in terms of materials and energy. With respect to material resources the SR were characterised as containing considerable amounts of magnetic metals (e.g., scrap iron) as well as non-magnetic metals (e.g., Al, Cu, Ni, Sn, Zn, and brass). In addition, a large fraction of "combustibles" (e.g., paper, plastics, wood, foam, rubber) present in the SR causes the SR's lower heating value (LHV) to be equal to or actually exceeding that of ordinary municipal solid waste (MSW) that is incinerated in Denmark –this is discussed in next section. It was thus argued, in agreement with results from other studies carried out in Denmark as well as abroad (Borjeson et al., 2000; Vermeulen et al., 2011; Hansen et al., 2012), that utilisation of resources (both material and energy) may, in addition to the obvious environmental benefits related to the material recycling and/or energy recovery, result in "saved" landfill capacity as well as in reduced use of resources during the landfill after-care-period.

Building on the results of Ahmed et al. (2012), the possibilities of exploiting resources from the already *landfilled* SR by means of an excavation of the SR and a "low-tech" sieving approach were

³⁷ http://ec.europa.eu/environment/consultations/pdf/pops_consultation.pdf

investigated by Hansen et al. (2012). In the latter project, SR from the three largest Danish landfill sites for SR were excavated and sorted into 4 particle size fractions (the percentage of the total mass shown in parentheses): > 45 mm (11-13%), 45-10 mm (34-40%), 10-5 mm (28-30%) and < 5 mm (18-24%). Results of chemical analyses performed on each of the particle size fractions indicated that the content of Pb, Zn, TPH (especially the C16-C35 fraction) and possibly also Cu (though only when category “ecotox” (i.e. miljøfare) would be considered) exceeded the criteria for hazardous waste in each particle size fraction. In addition, one sample exceeded the limit value for total PCB content. The chemical analyses further showed that the metal content of each fraction was between 28 and 37% TS. The results also showed that the smaller size fractions were increasingly composed of minerals (sand, soil and dust). The content of Fe increased with decreasing particle size but based on the mass balance considerations, it seems likely that the iron in the smallest size fractions will increasingly occur as iron oxides. Overall, it was estimated that for particle size fractions larger than 5 mm, about 50% of the metals are present as pure metals and 50% as metal oxides. The degree of oxidation is increasing for metals present in fractions with smaller particle size (<5 mm), i.e. the proportion of metal on oxide form in fractions below 5 mm will most likely be above 50%.

By means of hand sorting Hansen et al. (2012) could remove between 11% and 10% of metals (as metal pieces) from the > 45 mm and 45-10 mm fractions, respectively. Using mechanical sorting methods, 17% and 6% were recovered as metals from > 45 mm and 45-10 mm fractions at STENA’s sorting facility. Similar results were achieved by H.J. Hansen, who recovered 12-15% of the material as metals from SR with particle sizes larger than 5 mm. The proportion of metals removed from the >45 mm and 45-10 mm fraction corresponded to approximately 9% of the total extracted quantity of excavated SR.

It was concluded that it is possible to recover a significant part of the pure metals in excavated and size fractionated SR by processing the largest size fractions in existing mechanical separation facilities. The potentials of pure metals were, based on mass balance considerations, estimated at 13-18% of the fractions larger than 5 mm (assuming 50% of metal content is “pure” metals). Chemical analysis also indicated that the carbon content was decreasing with decreasing particle size, indicating that the plastic was present as larger particles in SR. At the same time mass balances showed that the carbon in the smallest size fractions appeared in the form of wood, cardboard and paper. By hand sorting of fractions larger than 10 mm, 18-22% of the plastics were sorted out, while mechanical sorting recovered approximately 13% of recyclable plastics from the fractions larger than 5 mm.

Overall, it was concluded that:

- the landfilled SR provides a significant material resource;
- by simple size fractionation it is possible to reduce the amounts of SR deposited of at Danish sites by up to 70% (w/w);
- the fine fraction of the waste (less than 5 mm) will for the time being have to be re-deposited;
- it may be necessary to optimise the fractionation process;
- it is (environmentally) advantageous to excavate and recover the resources;
- it depends (financially) on the specific situation and circumstances if the revenues from sales of materials and the value of recovered landfill volume could cover the cost for excavation, treatment, recovery and taxes;
- no regulatory barriers were identified hindering the recovery of resources from landfilled SR.

At the same time, it was stated that it may not be possible to reclassify any of the *excavated* SR fractions (prior to other treatment than size sorting) from hazardous waste to non-hazardous waste as the content of Pb, Zn, TPH (specifically the C16-C35 range) and possibly also Cu (when limit value of 2,500 mg/kg TS for “ecotox” (i.e. miljøfare) applies) exceeded the hazardous waste criteria for all size fractions of SR and the hazardous criterion for PCB7 was exceeded for one sample.

2.6 General aspects of energy recovery from shredder residues

A large fraction of Danish SR consist of “combustibles“ (e.g., plastics, wood, foam, rubber) and has LHV higher than ordinary MSW, for which LHV typically is 9-12 MJ/kg. Seemingly, SR are thus ideal for energy recovery. However, one of the general challenges has been that SR may contain substances or materials that present a barrier for efficient and environmentally sound utilisation of the resources. Examples of these substances are in particular chlorine (in PVC), bromine (flame retardants) and PCBs (Ahmed et al., 2012; Cramer et al., 2011; Poulsen et al., 2011; Hansen et al., 2012).

While most of these substances do not in themselves constitute resources, the presence of these substances in SR is often critical with respect to energy recovery using both direct waste-to-energy (WtE) options (e.g., grate furnace, fluidised bed combustion (FBC), rotary kilns, cement kilns) and thermo-chemical processes (e.g., gasification and pyrolysis). In this perspective, the knowledge of the occurrence and sources of problematic substances in SR seems essential in order to enable a removal or reduction of these substances before applying any treatment technology for resource recovery to the SR. In general, for the direct WtE processes it could be summarised that:

- high contents of chlorine (e.g., PVC) or bromine (e.g., BFRs) will cause an extra loading on the air-pollution-control system in terms of elevated concentrations of gaseous HCl and HBr which need to be removed from the flue gas (e.g. in an acid gas scrubber);
- high contents of chlorine and bromine enhance volatilisation of “heavy metals” during combustion (Pedersen et al., 2009) and also lead to formation of a complex mixture of polychlorinated and polybrominated organic compounds (e.g. PCDD/Fs and PBDD/Fs) (Soderstrom and Marklund, 2002; Ebert and Bahadir, 2003), which in turn presents an extra load for the air pollution control system (e.g., higher volume of contaminants to be treated, increased high-temperature corrosion and fouling (Frandsen et al., 2009);
- a high content of PCBs in feed material may exceed the limit value of maximum PCB content for waste being incinerated in plants designed for incineration of non-hazardous waste³⁸, which may thus automatically result in a stop-clause for potential incineration of SR;
- a high content of PCBs in feed material may lead to transgression of limit values for working environment.

In addition to the material recovery, Ahmed et al. (2012) estimated the energy recovery potential of the excavated SR. It was found that the energy recovery potential increased with increasing particle size fraction of SR. Fractions above 10 mm showed a very favourable LHV of 7-17 MJ/kg after the removal of plastics. With plastics included, LHV was estimated between 14 and 27 MJ/kg for SR above 10 mm while the highest value was found for the fractions > 45 mm. The LHV determined for the fraction 5-10 mm was lower than expected, possibly because of poor separation of the fine fraction. The fines (less than 5 mm) had a high ash and metal content and a low calorific value and were not suitable for energy recovery. Thus, fines would have to be separated from the rest of the shredder waste prior to energy recovery and be disposed of. Leaching from the fractions less than 5 mm complied with the leaching limit values for acceptance of waste at a landfill for hazardous waste.

Note that a set-up similar to that tested by Hansen et al. (2012) has been used in Thailand to produce energy from plastics recovered from a landfill (Chiemchaisri et al., 2010). A combination of low-tech landfill mining (i.e., recovery of plastics using trommel screen), RDF production and a small-scale gasification unit was shown to be a much cheaper alternative to energy production from oil and diesel.

Over the last 20 years, thermal treatment of SR has been studied worldwide in numerous research, pilot-scale, and full-scale processes and has shown high potential with respect to energy recovery.

³⁸ The limit value of $PCB_{max} = 5 \cdot \sum(PCB_7)$ is applied (MST, 2011)

Most recently, Vermeulen et al. (2011) provided a critical review of different options for energy recovery from (A)SR. They focused on both direct WtE options and thermo-chemical processes. In the following sections the findings summarised by Vermeulen et al. (2011) are discussed in detail and, where appropriate, related to Danish conditions.

2.7 Direct Waste-to-Energy (WtE) options

2.7.1 Grate furnace combustion

Waste incineration using moving grate technology is a well-established technology for thermal treatment of waste. The moving-grate technology is fairly flexible with respect to various operation conditions, it allows for recovery of energy (often in a combined heat and power system), it reduces the volume of solid waste significantly, and advanced flue gas cleaning technologies ensure very low acid gas and particulate emissions from modern incineration plants.

In general, mono-incineration of (A)SR has not been recommended because of too high calorific value, unfavourable melting characteristics and elevated content of potentially problematic substances. As a result, most co-incineration experiments were performed with only a fraction of ASR added to the MSW waste. Typically, 10-15% of SR has been used in the incoming feed (Vermeulen et al., 2011; Pedersen et al., 2009; Nedenskov, 2011), whereas experiments with up to 20% ASR and 24-31% ASR were carried out in Sweden (Redin et al., 2001) and Germany (Marw and Vehlow, 1998), respectively. Redin et al. (2001) stated that co-incineration of 20% ASR did not affect the flue gas emissions compared to ordinary MSW, whereas the concentrations of PCBs increased by a factor of 3-5 in the flue gas and by a factor of 5 in the bottom ashes whilst all (Swedish) regulatory limits were still met. Similarly, co-incineration of up to 31% ASR (Mark and Vehlow, 1998) did not pose a significant problem for the technology itself, and all environmental limits were fulfilled. However, the concentrations of numerous "heavy metals" in fly ashes and bottom ashes increased significantly (POPs were not analysed by Mark and Vehlow, 1998). It is important to realise that the increase in the total amounts of metals and POPs in bottom ashes (fly ash is not considered as it is *always* classified as hazardous waste) has different impacts in different countries. In Switzerland, for example, bottom ashes are mostly landfilled, whereas the majority of bottom ashes is used in e.g. road constructions in Denmark.

According to Miljøprojekt 494 (MST, 1999), only traces of BFRs can pass through the incinerator. Van Caneghem et al. (2010) focused on mass balance of POPs (PCDD/F, dioxin-like PCBs, PCBs, PAHs, and HCB) in the outputs – flue gases and solid residues – from different WtE installations located in Belgium including (i) a BAT compliant grate furnace incinerating MSW and (ii) the same BAT compliant grate furnace as in (i) co-incinerating 3% plastics from WEEE recycling and 5% ASR. In order to estimate and compare the overall input and output of POPs and not just the different POP-groups separately, a POP-weighting methodology was proposed and applied to the two installations. Notably, it was found that the grate furnace incinerating a mixture of MSW, plastics from WEEE (3%) and ASR (5%) acted as a weighted POP sink because of high concentrations of PBDEs and PCBs in the input compared to the output. More specifically, co-incineration of 5% ASR and 3% plastics of WEEE in the BAT-compliant grate furnace burning MSW lowered the amount of PCBs in the output by 20–100 times compared by the input. If all the POPs (i.e. including PCBs) in the output were taken into account, the input over output ratio would range from 1 to 23. When the same incinerator was incinerating only MSW the weighted POPs in the input were about the same as at the output. This observation was consistent with other studies and explained by the fact that PCDD/Fs generated during incineration are among the main contributors to the total weighted in- and output (Van Caneghem et al., 2010; Ishikawa et al., 2007).

In Denmark, SR have been considered hazardous waste and thus full-scale co-incineration of (A)SR at ordinary MSWI plants has been problematic since these plants have no permit to incinerate such waste. Nevertheless, three major attempts to investigate potential drawbacks of co-incineration of

SR have been made at the FASAN MSWI plant in Næstved (2006-2009), the Amagerforbrænding MSWI plant in Copenhagen (2010-2011) and the Reno-Nord MSWI plant in Aalborg³⁹.

The FASAN experiment

In general, the experiment at FASAN focused on the transfer of elements during the incineration related to variations in waste input and operation conditions. As such, numerous aspects were investigated and published in specific studies, which focused on boiler-gas particle partitioning of selected elements (Pedersen et al., 2009), aerosol formation and composition (Zeuthen et al., 2007), deposit formation and composition (Frandsen et al., 2009), effects of variations in input waste and operation conditions on air emissions and residues (Astrup et al., 2011) and leaching of metals from bottom ashes (Hyks and Astrup, 2009). Sampling included fly ash, particles, stack gases, aerosols and bottom ashes. Details on the sampling can be found in the above mentioned studies.

In one of the test runs, 14% ASR were incinerated with the base-load waste, which was a mixture of 80% municipal solid waste and 20% "small combustible waste" from nearby recycling stations. Similarly to the previously mentioned studies from Belgium, Germany, Switzerland and Sweden it was documented that, even though the input waste was enriched with numerous "heavy metals" (and likely also POPs) and co-incineration of 14% ASR significantly affected the performance of the incinerator with respect to the composition of raw gas and residue quality, the *"modern flue gas cleaning systems may cope with substantial changes in waste input and still maintain relatively stable emission levels for heavy metals"* (Astrup et al., 2011). In addition, although the bottom ashes were significantly enriched with Ba, Cu, Mo, Ni, Sb, Sn and Zn (Hyks and Astrup, 2009), no significant effect on the leaching of these metals was observed when compared to bottom ashes produced by incineration of the base-load waste (the leaching of POPs was not investigated, however). It was therefore concluded that metal leaching from bottom ash was not sensitive to changes in waste input in terms of 14% of ASR in the mixture (Hyks and Astrup, 2009). A correlation ($r^2=0.86$) between waste input and the leaching was observed for Cl only, suggesting that Cl was the most prominent candidate for optimisation of leaching by controlling the composition of the incoming waste.

In 2007, the Korean Institute of Science & Technology published a study focused on characteristics and heavy metal leaching of ash generated from incineration of ASR in a dedicated ASR incineration plant (Lee, 2007). Both bottom ashes and fly ash generated from incineration of ASR were characterised in terms of particle size, compositions, and heavy metal leaching by the US EPA 1311 TCLP method. Similarly to the results of Hyks and Astrup (2009), they found very high concentrations of Cu in bottom ashes compared with ordinary MSWI residues. As a whole, the results of characterisation of ASR fly ash were in good agreement with common MSWI fly ash in terms of particle size, pH, and water-soluble substances.

The Amagerforbrænding experiment

In 2011, Amagerforbrænding carried out a full-scale experiment focused on incineration of SR. During this experiment, 12.4% SR (LHV 13.6-14.8 MJ/kg) were mixed with ordinary MSW and incinerated (Nedenskov, 2011).

The incinerated SR were generated from STENA's metal recovery process in Roskilde and could be described as a nonhomogeneous mixture of glass, rubber, wood, plastics, foam, and fabrics. The majority of the SR had a particle size <60 mm; however, pieces up to 1 m (e.g., tubes, hoses) were found occasionally. The material composition was determined prior to the incineration. Concentra-

³⁹ At the moment, co-incineration of SR is tested at Reno-Nord and no official results have been published. From the preliminary operating experience it seems that the incineration slag generated from co-incineration of SR has higher melting point compared to the slag from incineration of ordinary waste. (FORCE Technology, personal communication).

tions of numerous parameters were monitored in the flue gas before as well as after the flue gas cleaning system. Samples of bottom ash were collected separately from the line co-incinerating SR. For the purpose of the co-incineration experiment, Amagerforbrænding received a time-limited permit for incineration of max 3,000 tonnes of SR. In the permit which was issued by the Danish EPA, Roskilde (MST, 2011) a specific set of (less stringent than normally) total content limit values was given for a number of substances present in the incoming SR that “will not be destroyed during the incineration” (MST, 2011). In general, the monitored substances had been identified based on experience from other studies focusing on SR (Poulsen et al., 2011) and included As, Cd, Cr, Ni, Pb, Zn, PCBs and PAH (as a sum parameter with Cr, As, Ni; see Table 2.16). BFRs were not included based on the results of the Miljøprojekt 494 (MST, 1999).

During the test(s), a number of parameters were monitored such as flue-gas concentrations (e.g., CO, HCl, TOC, NH₃, NO_x, dust, etc.), deposit formation, and composition of solid residues. It is stated in the project report that all environmental criteria were fulfilled and that co-incineration of 12.4% SR with ordinary MSW did not cause any significant changes compared with the normal situation. More specifically, it was concluded that:

- the incoming SR was not exceeding the limit values for total composition of SR given in the (time-limited) environmental permit;
- the monitored parameters for flue gas composition fulfilled the environmental permits;
- the bottom ashes remained in Category 3 despite increased amounts of Cu in the solid phase
- the leaching properties of bottom ashes (compliance testing only) were not affected compared with ordinary bottom ashes

Table 2.16 Limit values for total content (mg/kg TS) in shredder waste co-incinerated at Amagerforbrænding.

Parameter	Amagerforbrænding ¹
As	1,000
Cd	10,000
Co	-
Cr	1,000
Hg	-
Ni	10,000
Pb	50,000
Sb	-
Zn	-
PAH	-
PCB ²	50
Benzene-C40	-
As+Cd+Cr	30,000
Cd+Cr	10,000
Cu+Ni	250,000
Zn+As	50,000
PAH+Cr+As+Ni	1,000

¹) Nedenskov (2011);

²) The limit value of PCB = 5·Σ(PCB7) (MST, 2011)

Deposit formation on the superheaters was observed after test A. However, analysis of thermal data showed that the deposit formation started already prior to the test A. During test B, no deposit formation was observed, thus, co-combustion of 12.4% SR with ordinary MSW did not seem to lead to significant formation of deposits.

Although the results of the Amagerforbrænding (and the FASAN) experiment may seem promising and are generally in agreement with the findings of Van Caneghem et al. (2010), neither experiment was long enough to provide unambiguous conclusions regarding potential operation problems caused by co-incineration of SR. A significantly longer test period (6 months as a minimum) may be required to obtain more robust conclusions regarding the effects of co-incineration of SR at MSWI plant⁴⁰. That being said, one can alternatively look at foreign experiences with long-term co-incineration of SR (e.g. Sweden). Even then, it should be realised that different plants have different temperature regimes and corrosion/fouling is thus rather plant-specific (Jonas Nedenskov, Amagerforbrænding, personal communication).

2.7.2 Fluidised bed combustion

In general, the advantages of fluidised bed combustion (FBC) compared with mass burning on a grate furnace or in a rotary kiln are (i) higher thermal efficiency due to lower level of excess air, (ii) significantly longer retention times causing better burnout, (iii) lower temperature gradients, and (iv) better emission control (e.g., NO_x). The main disadvantage is that FBC requires feed with very uniform characteristics (e.g., size, LHV, ash content etc.) and the heterogeneity of unprocessed SR (or MSW in general) was found to cause difficulties in the operation of FBC (Christensen, 2010; Vermeulen et al., 2011).

Recent studies often focus on co-incineration of ASR in FBC plants. Often, low calorific waste such as wastewater treatment (WWT) sludge is co-incinerated with high calorific non-recyclable waste from industrial sources (e.g., carpets, textiles, ASR, or RDF). During extensive tests at the largest FBC plant for WtE in Europe (the Indaver site in Antwerp, Belgium) it was found that co-incineration of a heavy ASR fraction (25%) with RDF (25%) and WWT sludge (50%) did not result in changes in emissions of NO_x, SO₂ and POPs compared with the usual feed composed of 70% RDF and 30% WWT sludge. Although the amount of bottom ashes increased by 48% and the amount of "heavy metals" in these ashes increased by 10% on the average, the bottom ashes still complied with local legal requirements for use as secondary raw materials except for Cu (Table 2.17 provides comparison with Danish limit values). The total heavy metal concentration in the flue gas also increased (by about 60%) during the co-incineration of ASR, but remained well below the local regulatory limits (Vermeulen et al., 2011).

Table 2.17 Comparison of the limit values for leaching of metals (mg/kg TS) from granular materials used in construction applications

Element	Flemish limit values ^a	Danish limit values – Cat3 ^b
As	< 0.8	< 0.1
Cd	< 0.03	< 0.08
Cr	< 0.5	< 1.0
Cu	< 0.5	< 4.0
Hg	< 0.02	< 0.002
Ni	< 0.75	< 0.14
Pb	< 1.3	< 0.20
Zn	< 2.8	< 3.0

^{a)} Arickx et al. (2007); ^{b)} Danish EPA (2010)

In Sweden, the formation of PCDD/F and PCBs as a function of Cl levels during combustion of eight artificial MSW mixtures in an experimental FBC reactor was investigated (Wikstrom and Marklund, 2001). The level of Cl was controlled by addition of plastics in to the feed and varied between 0.28% and 1.1%. A correlation between the total content of Cl in the fuel and the formation of PCDD/F was found. However, the most important variable for changes in the PCDDs/Fs and PCBs formation

⁴⁰ As mentioned earlier, co-incineration of SR is currently carried out at Reno-Nord. No official results have been released yet.

were disturbances in the combustion conditions and not the variation in the Cl content of the fuel. Notably, this observation is consistent with other studies; i.e., disturbances in the combustion process have the largest influence on the formation of PCDDs/Fs and PCBs regardless of the actual incineration technology.

In a theoretical study focused on corrosion potentials and deposit formation in FBC (Gyllenhammar et al., 2008), a range of thermodynamic calculations were performed to investigate the possibilities of co-combustion of SLF, sewage sludge and “normal” waste (MSW) at an FBC plant located at Borås, Sweden. The calculations showed that co-combustion of 20% SLF would result in high amounts of gaseous lead chlorides, while the amount of zinc chlorides would be in the same range as when firing normal waste. These chlorides were shown to condensate at a lower temperature than alkali chlorides. Therefore, deposition and corrosion problems can, theoretically, occur at lower material temperatures at superheaters, economisers and furnace walls. Nevertheless, it was concluded that co-combustion of up to 20% SLF in a boiler at 40 bar without a superheater, would not significantly increase the corrosion problems. Combustion in a boiler at 20 bar (without superheater) would decrease the risk of problems with lead chloride (and zinc chloride) deposits on the convection tubes even more.

In Denmark, FBC is used only for incineration of sewage sludge while the application of FBC for treatment of e.g. SR, MSW and/or RDF is not considered at the moment (Christian Riber, Waste to Energy - Rambøll, personal communication).

2.7.3 Rotary kiln

Rotary kilns present a robust technology for treatment of both solid and liquid waste. In the kiln and the after burner a temperature of 900-1200 °C is reached while the residence time of at least 2s allows for treatment of waste with high content of Cl (e.g., SR) or even hazardous waste. On the other hand, thermal recovery in rotary kiln is generally lower than from grate furnace or FBC (Vermeulen et al., 2011). As discussed previously, the rotary kiln was found to act as a weighed POP sink when incinerating POPs-containing waste (Van Caneghem et al., 2010).

In the Miljøprojekt 1145 (Nielsen et al., 2007) the quality of bottom ashes from 23 different Danish MSWI plants was discussed with respect to total composition and leaching properties. Factors such as the waste composition, the plant's capacity, the nominal temperature, the type of oven, and the treatment of bottom ashes were investigated. It was found that bottom ashes generated in a rotary kiln (i.e., 2 lines at Vestforbrænding and 2 lines at Reno-Nord) had significantly better quality in terms of leaching of Cu and Cr; i.e., the two metals, which may be considered “problematic” as their leaching most often exceeds the Category 1+2 limit values for material to be reused (BEK nr 1662, 2010). Unfortunately, rotary kiln(s) have not been used since 2009/2010 and both lines are scheduled to be taken down. All incoming waste is planned to be treated at two new lines (line 5, line 6), that are equipped with moving grate furnaces (Kim Crillesen, Vestforbrænding, personal communication).

2.7.4 Cement kiln

Manufacturing of cement is an energy consuming process with 30-50% of the production costs associated with energy costs. The process involves heating, calcination and sintering of blended and ground raw materials, typically limestone and clay or shale and other materials to form clinkers. Clinker burning takes place in a cement kiln at a material temperature of 1450 °C. A cement kiln is, in principle, a long rotary kiln in which the input material moves against the flow of the combustion gases. The length of the kiln ensures long retention time (up to 8s) of the combustion gases at temperatures above 1200 °C.

It would seem that a cement kiln is a perfect solution for co-incineration of a high calorific waste stream with a “problematic” composition such as (A)SR. The energy potential would be utilised

while the combustion conditions would ensure that the majority of the POPs were destroyed. Moreover, Si, Ca and Al present in (A)SR could substitute some of the mineral feedstock in cement production (Genon and Brizio, 2008; Karstensen, 2008; Vermeulen et al., 2011). On the other hand, the remaining levels of potentially problematic constituents – with respect to cement quality – such as chlorine and heavy metals may limit use of (A)SR to a low relative addition rate (Boughton, 2007).

As stated in the 2003 report “Refuse Derived Fuel, current practise and perspectives” by European Commission (Directorate General Environment), in Denmark, about 40,000 t/y of “RDF” were co-incinerated during cement manufacturing; this amount corresponded to 7% energy substitution rate (Genon and Brizio, 2008). In this case, RDF meant sewage sludge (7,500 t/y), plastics/paper (10,000 t/y), wood (>500 t/y) and other (22,000 t/y) defined as “waste textiles and unspecified non-hazardous wastes”.

2.8 Thermo-chemical processes

Similarly to FBC, SR require a certain degree of pre-treatment when used in the thermo-chemical processes (pyrolysis, gasification) because (i) PUR is difficult to crack, (ii) PVC can contaminate the pyrolysis gas, (iii) rubber forms tars and major quantities of carbonaceous residues and (iv) PP and PE tend to form waxes (Vermeulen et al., 2011).

The typical products of pyrolysis and gasification are oils, gas and solid residues (char). The relative proportion of these products depends on the type of the process and the process conditions (Zolezzi et al., 2004).

In a study from 2007, Harder and Forton summarised the global situation regarding applicability of pyrolysis and/or gasification for treatment of SR. Interestingly enough, they stated that “the SR waste stream itself is so variable that it cannot be assumed that processes developed in one place are suitable for waste streams produced elsewhere”. In their view, it was far easier to develop processes optimised for local combinations of well-characterised waste streams on a small-medium scale, since for the large scale processes, there was no clear indication emerging as to which type of process (e.g., with focus on energy production and waste minimisation or material recovery) the various stakeholders want (Harder and Forton, 2007).

Although pyrolysis/gasification has been around for many years, it should be stressed that, in contrast to many MSWI plants, thermo-chemical technology for converting SR to secondary fuels is not available in Denmark in full-scale yet. H.J. Hansen has been developing a pilot-scale test unit based on a “torrefaction” (i.e., a mild form of pyrolysis). In principle, this process was believed to allow for utilisation of the energy potential from SR via generation of pyrolysis gas, while the process allows for recovery of “clean” metals from the pyrolysis coke using the H.J. Hansen’s sorting process. It was planned to use the metal-free coke for the manufacturing of cement (Cramer et al., 2011). It was, however, shown that the coke (generated by H.J. Hansen’s process) cannot be used in cement production because of high levels of certain heavy metals (Høstgaard et al., 2012). At the moment, the process is still under development and no time estimate for delivery of an operational plant has been given. Furthermore, in contrast to Danish MSWI plants, for which data on their environmental performance is abundant, only a little information is available about the *environmental* performance of H.J. Hansen’s process.

In 2007, Joung and colleagues investigated the distribution of PCDDs/PCDFs congeners and dioxin-like PCBs in the char and slag products from ASR pyrolysis; the slag was produced from char by water cooling. They showed that slowly-cooled slag had higher total concentrations of dioxins, while the amount of dioxins-like PCBs was similar among the different slags. Water-cooled (i.e., quenched) slag produced from the char was shown to have 47 times lower concentrations of

PCDDs/PCDFs compared to the original char, while the concentration of dioxin-like PCBs was 400 times lower than that of the char. It was therefore suggested that “*slag production from char (via quenching) is an efficient way of reducing dioxins so that ASR can be recycled with the minimisation of waste to be disposed of*” (Joung et al., 2007a).

In contrast to controlled (oxygen-wise) combustion conditions in MSWI plants, considerable amounts of PBDDs/PBDFs are formed when BFR-containing material is subject to a thermal process under insufficient (oxygen-wise) combustion conditions; e.g., accidental fires, uncontrolled burning as well as gasification/pyrolysis processes (Weber and Kuch, 2003). It may thus be considered to remove BFR-containing plastic from SR prior to the gasification/pyrolysis process.

In addition, as outlined earlier, PAHs are by-products of incomplete combustion of carbon-containing fuels (both organic and fossil). In pyrolysis, the yield of PAHs is found to increase with temperature and gas phase residence time, while for gasification and combustion, it has been *postulated* that PAHs arise from pyrolysis reaction in oxygen-deficient regions (Britt et al., 2004). Nevertheless, it should be mentioned that data on generation of PAHs in different gasification/pyrolysis WtE processes are scarce, process-specific and thus not applicable globally.

2.9 Material recovery after the energy utilisation

2.9.1 Background

Solid residues from both direct and indirect thermal conversion methods still contain significant amounts of “free” metals (e.g., iron, stainless steel, Zn, Cu, Au, Ag, etc.), which may in principal be separated and recovered⁴¹, provided that there is a sufficient driving force – may it be financial, regulatory, or both – for such an activity.

The composition of bottom ashes resulting from WtE treatment is greatly affected by the incineration process itself as well as by the composition of the incoming waste (Hyks et al., 2011; Astrup et al., 2011; Nielsen et al., 2007). The same applies – to a lesser extent – for the other incineration products such as boiler ash and fly ash. While the recovery of metals from bottom ashes is a widespread option, the recovery of “valuables” from flue gas cleaning residues (including fly ash) is still at an experimental stage (STENA has e.g. been developing such a process under the name HALOSEP). As for the boiler ash, the recovery of Fe using magnetic separation was shown possible; however, the system was shown profitable only if complemented by other recovery methods (De Boom et al., 2011).

It should be realised that because of different legislative requirements, different management options are available for the utilisation of bottom ashes in different countries. In the Netherlands, for example, changes in legislation – stricter criteria for the use of processed bottom ashes in constructions – have posed challenges requiring improvements in the separation of MSWI bottom ashes. Consequently, a number of research projects were carried out, resulting in the construction of a wet⁴² physical separation pilot plant (50 t/h) in Amsterdam (Muchova, 2010).

2.9.2 Physical separation of incineration bottom ashes

“Semi-dry”⁴³ or more recent “dry”⁴⁴ physical separation can be seen as the conventional separation process. It includes coarse screening, size reduction, magnetic separation, eddy current separation

⁴¹ It should be mentioned that “free” metals present in residues from e.g. pyrolysis/gasification have higher quality (i.e., also value) than those from different combustion methods. In addition, a portion of metals present in the incoming material is lost during combustion, whereas this loss is only marginal for gasification/pyrolysis.

⁴² Involves dedicated washing steps in order to remove metals

⁴³ Bottom ash is quenched at the incinerator before being processed further

⁴⁴ Bottom ash is not quenched at the incinerator before being processed further

and possibly also aging and maturing in order to stabilize the processed bottom ashes in terms of their leaching capacity (Muchova, 2010). An example of a dry process is given in Figure 2.11.

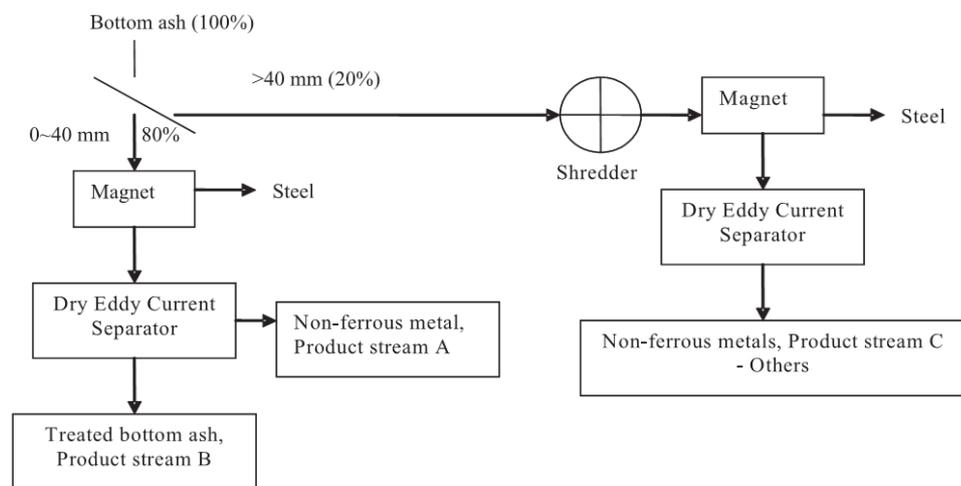


Figure 2.11 Dry separation process at the MSWI plant in Amsterdam (Hu and Rem, 2009)

In Denmark, two companies are treating most of Danish MSWI bottom ashes using the semi-dry process: Meldgaard Recycling A/S and AFATEK A/S. An estimated amount of 12,000 tonnes of valuable metals are lost annually, due to insufficient treatment of MSWI bottom ashes (AFATEK, 2011). Building on the experience from the Netherlands and Switzerland, AFATEK has announced a 5-years R&D project (starting 2011) focused on increasing the recovery of valuable resources from MSWI bottom ashes. Various optimisations of the current dry/semi-dry separation process are investigated, whilst the application of purely “wet” separation is not considered at the moment (Jens Kallesøe, AFATEK A/S, personal communication).

As noted, the pilot plant in Amsterdam is an example of a “wet” separation; for detailed information on this plant, please refer to Muchova (2010) and references therein. In the following text, the process will be described briefly. The treatment facility in Amsterdam is, in fact, a combination of the existing dry/semi-dry physical separation process and a new pilot plant based on wet physical separation. It is stated in Muchova (2010) that “the wet technology can recover virtually all metals from the size fraction >0.3mm and remove organic and fine particles from the residue”. Consequently, this combination of screening, metals recovery and washing considerably improves the quality of the residue in terms of leaching of most of the elements. In addition, a magnetic density separator provides the possibility of the recovery of precious metals from the 0-6 mm fraction.

2.9.3 Physical separation of pyrolysis/gasification residues

There are three major products of pyrolysis/gasification: gas, tar and char/coke. The gas contains mostly hydrogen, methane, propane, acetylene and butane; the exact proportion depends on the process conditions. The tar is composed of higher hydrocarbons (around C9), while the char/coke contains both hydrocarbons and metals (Joung et al., 2007b).

Compared to the rather heterogeneous MSWI bottom ashes, it may in principle be relatively easy to recover a large portion of metals from pyrolysis/gasification char/coke. As mentioned previously, both the amount and the quality (value) of metals present in pyrolysis/gasification residues is higher than those found in incineration bottom ash. The composition of the char/coke depends to a high extent on the operation conditions during the gasification/pyrolysis. Nevertheless, char/coke generally contains a high amount of recyclable metals as well as organic compounds including both aromatic and aliphatic hydrocarbons. If desired, the hydrocarbons can be extracted from the char/coke using sequential extraction and subsequently upgraded to be used as a fuel or even as a

raw material in the chemical industry (Bernardo et al., 2012). For illustration purposes – in Table 2.18 – the most recent Danish data (Høstgaard et al., 2012) are compared with the composition of char generated by pyrolysis of ASR in Japan (Hwang et al., 2007) and Korea (Joung et al., 2007b).

Table 2.18 Composition of pyrolysis char/coke (all values in mg/kg TS)

Element	Denmark	Japan		Korea
		char >1 mm	char <1mm	
Al	19,000-23,000	130,000 ^a	-	4,300-12,600
Cd	-	-	<0.05	4.8-20
Cr	-	-	587	90-195
Cu	17,000-28,000	564,000 ^b	16,100	8,200-22,200
Fe	22,000-39,000	64,000 ^c	-	39,000-89,500
Ni	-	-	-	129-218
Pb	-	-	4,190	1,500-3,100
V	-	-	-	12.7-19
Zn	-	-	12,500	5,200-8,600
Hg	-	-	-	0.02-0.084

^a) as pieces of metallic aluminium

^b) as pieces of metallic copper

^c) as pieces of “ferrous metals”

2.10 Leaching data

2.10.1 Leaching from landfilled shredder residues

Hansen et al. (2011b) investigated the SR coming to the Reno Djurs landfill in accordance with (then valid) BEK 252 on landfilling of waste (Danish EPA, 2009). This characterisation included the assessment of the leaching potential based on laboratory scale leaching tests with SR. In a follow-up study, the same authors investigated the full-scale leaching from a landfill cell containing SR at the Reno Djurs landfill site and estimated the necessary after-care period for leachate treatment (Hansen et al., 2011).

Notable differences between the results of the two studies were found. For many elements – especially the “heavy metals” – significantly higher concentrations were observed in leachates from the laboratory tests when compared with the full-scale leachate. It was suggested that this was caused by a large difference in redox conditions between laboratory scale and full-scale. Generally, in contrast to the eluates obtained from laboratory tests which showed an oxidising environment, the redox potential measured in the landfill leachate was very low; i.e., indicating reducing environment. Consequently, traces of sulphides were *measured* in the landfill leachate. Formation of fairly insoluble metal sulphides can explain the low concentrations of e.g. Cd, Co, Cu, Ni, and Zn in the landfill leachate compared to the eluates obtained from the laboratory experiments. So far, no assessment has been made on whether the sulphides might be oxidised again (e.g., by penetration of air into the landfill), how long that might take and what the influence on the leaching of the above mentioned metals might be.

In addition to the leaching of metals, the leaching of organic compounds including BTEX, TPH, PAHs, and PCBs was investigated under laboratory conditions and in full-scale. Good agreement between the full scale data and the laboratory data was found for the leaching of TPH (C6-C35), PCB7 and to some extent also for PAHs, where the results varied by factor of 10. PAH leaching observed in the laboratory test was higher than in full-scale, thus providing a conservative leaching scenario. The leaching of PCB7 from both full-scale and laboratory samples was mostly below the analytical detection limit.

In general, the leaching of PCBs from landfilled SR depends strongly on the type of leachant used; e.g. surfactants promote the leaching of PCBs (Sakai et al., 2000). Note that no measurable concentrations of surfactants (LAS, nonylphenol, nonylphenol monoethoxylate and nonylphenol diethoxylate) were found in 2009 at Reno Djurs. With respect to the scope of the herein presented study it should be noted that the leaching of BFRs was not tested, neither in lab-scale nor in full-scale.

2.10.2 Leaching from residues generated by thermal treatment of shredder residues

As already discussed in section 2.7.1, no clear correlation has been found between the increased total content of metals in residues generated from co-incineration of (A)SR and the leaching of metals from the residues (Hyks and Astrup, 2009; Nedenskov, 2011; Lee, 2007). In other words, the leaching of metals from these residues was not significantly worse/better when compared with the leaching from ordinary bottom ashes. A correlation ($r^2=0.86$) between waste input and the leaching was observed for only Cl. It was therefore suggested that Cl was the most prominent candidate for optimization of leaching by controlling the composition of the incoming waste (Hyks and Astrup, 2009).

Contrary to the situation for incineration bottom ashes, very little leaching data are available for residues generated by pyrolysis/gasification. In a Japanese study published in 2007, the leaching from char generated by pyrolysis of ASR was tested by the modified JLT-13 procedure⁴⁵, which may – to a certain extent – be comparable with the European EN 12457-2 test (CEN, 1999). The results are shown in Table 2.19.

It can be seen that the leaching of all monitored metals from the char was lower than from leaching of untreated ASR. This was explained by higher BET⁴⁶ surface of char compared to ASR and thus larger retention capacity for metals. At the other hand, Cr became enriched in the ash residue compared to the original ASR. The pyrolysis ash was separated from the char by pulverisation and sieving in order to improve the quality of the char (Hwang et al., 2007).

Table 2.19 Leaching from untreated ASR, pyrolysis char and pyrolysis ash

Element	Units	Untreated ASR	Pyrolysis char	Pyrolysis ash
pH	-	6.55	7.65	9.80
Cd	mg/l	<0.0005	<0.0005	<0.0005
Cr	mg/l	0.280	<0.001	0.610
Cu	mg/l	0.455	0.194	<0.1
Pb	mg/l	0.190	<0.002	0.115
Zn	mg/l	3.4	2.45	<0.05

⁴⁵ Batch test at L/S 10 l/kg. Distilled water is used as leachant. The leaching step takes 6 hours in a shaker set to 200 rpm.

⁴⁶ BET method is one of the most widely used techniques for estimating surface area.

3. Overview of sensor-based technologies for substance/material identification

3.1 General overview

In the previous chapter substances and compounds have been reviewed which, due to their presence or concentration in SR, are critical with regard to further treatment such as recycling, energy recovery or disposal of this type of waste. These include POPs (PCBs and BFRs), petroleum hydrocarbons (BTEX: benzene, toluene, ethylbenzene, xylene), polyaromatic hydrocarbons (PAHs), “heavy metals” and polyvinylchloride (PVC). The various SR characterisation studies conducted in recent years in Denmark have explored both the resource potential, i.e. materials and energy, and its hazardous potential. Although results between studies vary significantly it is possible to conclude that, in reference to the limit values defining hazardous waste in Denmark, the contents of PCBs and some “heavy metals” are still decisive in the labelling of SR as hazardous waste.

Without doubt, continued labelling of SR as hazardous waste would make processing of this waste for e.g. material recovery more demanding (permits needed). At the same time, it will be difficult to use SR as an alternative fuel in energy production and waste-to-energy facilities in Denmark. The reasons for the latter have been discussed in chapter 2.4.1 and chlorine, bromine and PCBs have been found critical with regard to energy recovery in MSWI plants.

Nonetheless, there are techniques that can be applied in order to reduce (by separation) certain substances or materials either directly from the input to the shredding process or from the generated/landfilled SR. This chapter will document possibilities and limitations regarding detection/identification and sorting/separation of hazardous or problematic components in waste as compiled through (i) a scientific literature review, (ii) a review of companies producing equipment, and (iii) personal communication with some of these companies.

Compared to the numerous (quantitative) analytical methods for analysis of the substances dealt with in this project, there are only a few screening methods (qualitative to semi quantitative) or bulk materials sorting methods that can be used in treatment and recycling operations. The review presented in this chapter is actually limited to screening methods, mainly in the form of handheld devices, and bulk particle sorting techniques based on sensors, similar to the technique developed by FORCE Technology which is also investigated in this project. The objective was to enhance the knowledge about techniques that can be applied on site, in a recycling plant, with the aim of identification of problem substances and materials for separation. Screening and/or sorting techniques, either still in scientific development or already in mature applications, have been identified for the following substances:

- chlorine (mainly in PVC);
- bromine (BFRs);

- “heavy metals”, metals and metalloids (As, Ag, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, S, Sb, Sn, V and Zn).

The last section of this chapter attempts to comprehensively illustrate the state of maturity of sensor-based techniques with respect to industrial sorting applications of problematic substances or unwanted materials. The main companies producing sensor-based sorting equipment are listed together with the sorting applications that they commercially offer. Examples of waste treatment plants that employ automatic sorting techniques in their operation are presented.

The study concludes with a discussion of the applicability of reviewed techniques to the treatment of shredder residues (SR).

3.1.1 Analytical measurement methods

First there is need to distinguish between types of identification and quantification techniques as used in different fields. Based on the goal of the analysis (level of precision): there are quantitative techniques which are analytical methods used in laboratory analysis (provide results per unit mass or volume within exact error limits) and semi-quantitative or qualitative methods that can provide some quantitative data or at the very least the indication that a substance is present (Bussian et al., 2010). The second category encompasses also screening methods that can be defined as rapid methods in the form of easy-to-handle tools able to identify hazardous substances and therefore verify their presence or absence, either directly in the field (e.g. at a recycling plant) or in a laboratory set-up.

The report “Study on waste related issues of newly listed POPs and candidate POPs” made for the European Commission (European Commission, 2011) contains a compilation of analytical measurement methods for the detection and quantification of new and candidate POP concentrations in different matrices including waste streams. The methods are compiled and discussed separately for each substance. The compilation comprises additionally an evaluation of available screening methods for some of the POP substances. It can be concluded, based on this reference, that different chromatographic techniques coupled with mass spectrometry are usually used for detection and analysis of the different types of BFRs (PBDEs, PBBs, HBCD). However, BFRs are difficult to identify without a thorough lab analysis, which is time consuming and not feasible to apply in sorting facilities or landfills. In the case of PCBs, gas chromatography coupled with mass spectrometry (GC-MS) or electron capture detector (GC-ECD) methods seems to be widely used. Regarding determination of POPs in waste, there are not many standard analytical methods available covering waste in general. Nevertheless, different standard methods concerning analysis in waste relevant matrices or recycling materials are available or are under preparation.

3.1.2 Sorting and separation techniques for solid wastes

Various sorting techniques are used in solid waste treatment. Conventional techniques, including dry mechanical processes and density techniques based on fluid mediums, allow the sorting of materials based on attributes such as size, density, behaviour in an air flow, magnetic susceptibility or conductivity. These attributes determine a specific behaviour of the material particles in the sorting process which then directly constitutes the basis for separation (e.g., materials will sink in a fluid that has a lower density than themselves). The limitation of such processes is that for many materials the above mentioned properties will overlap thus making it difficult to separate them from each other (Yunxia and Pretz, 2010).

Other attributes such as colour, transparency or specific chemical elements incorporated in materials cannot at all be used as sorting criteria in conventional sorting processes. However, in modern sensor-based sorting techniques these attributes (e.g. colour, density, transparency, structure, elemental composition) are detected by sensors in all particles of the processed stream and consti-

tute the basis for material or substance identification. Identified materials are subsequently separated by mechanical or pneumatic means from other materials (Yunxia and Pretz, 2010).

3.2 Mechanical and density-based separation

If the presence of problematic substances, defined in Chapter 2, determines specific properties in waste particles and if these properties coincide with the sorting principle of conventional sorting techniques it is reliably possible to sort these materials out of the waste stream. For example, if a large proportion of heavy metals and other unwanted materials are found in the fine fraction of a waste stream, then a simple screening of this material would be very effective.

In 2004, the possibilities of removal of especially “heavy metals” and chlorine in production processes for refuse derived fuel (RDF) from municipal solid waste (MSW) by the means of mechanical processes were investigated (Rotter et al., 2004). The goal was to reach quality targets demanded by legislation and the power plants that utilise these products as alternative fuels while ensuring the calorific value and yields necessary for the feasibility of the operation. The processes tested were: screening, crosswise air classification, air knife classifier, foils suction in combination with NIR plastics detection and ballistic separation.

In general, the study concluded that due to the relatively diffuse load distribution of chlorine in the different fractions of household waste, mechanical processes can hardly realise its effective removal from RDF. Furthermore, screening alone did not result in a significant removal of contaminants because the grain size distribution did not correspond to the distribution of hazardous or undesired chemicals (Pb, Cd, Cl). Specifically, all methods based on air-classification - including foils suction combined with NIR – had low yields for the recovered product (RDF); materials with a high calorific value were concentrated but the hazardous chemical content was also enriched (referring to Cl). Ballistic separation proved more effective in improving the quality of the fuel by incorporation of more of the paper fraction and thus effectively *diluting* the chlorine content.

In 2006, sink-float techniques were tested for the separation of styrene-based polymers (e.g., TV-set housing, PC housing) with and without brominated flame retardant additives (BFRs); tests were done at laboratory and small technical scale (Schlummer and Maurer, 2006). The approach was based on the fact that styrene-based polymers containing 10-20% (wt) BFRs would have significantly larger density than plastics with no BFRs.

The separation equipment consisted of a two stage sink-float process, able to split the polymers in three fractions: a light fraction, a middle density fraction and a heavy fraction. The light fraction accounted for a small weight percentage and consisted of BFR free polymers, while the middle fraction, depending on samples, accounted for 26-90% (wt) and contained 5-20% of the original bromine load. The heavy fraction contained most of the flame retarded polymers.

In an alternative study (Schlummer et al., 2006), results were reported from trials with plastic rich SR from a number of WEEE processing plants across Europe that was subjected to density separation, followed by the treatment of BFR containing polymers by a sophisticated extractive process developed for the removal of contaminants (e.g., BFRs) from plastics (Maurer and Schlummer, 2004). The density separation process generated three outputs (light, heavy and medium density) that could then be treated according to their new characteristics. The light fraction could be used as RDF as it was mostly free of BFRs and heavy metals. The heavy fraction was enriched with 95% of Cu, Sn and Cl, over 95% of Pb, 80-95% of Al, Si and K (indicating glass fibre-reinforced polymers) and around 40% of Br, Ti and Sb. This fraction has to be routed for hazardous waste disposal. The medium fraction constituted more than 50% of the whole input, was enriched in styrenic plastics and presented the rest of the Br and around 24% of Cr, 38% of Zn and 64% of Cd. This fraction was tested in further treatment to extract BFRs and produce a plastic recyclate. After the separation of

BFR additives, 70–80% of this stream was recovered as a recycle that complied with threshold values defined by European and German legislation on restriction of hazardous substances in recycled products. The study also shows that it was possible to remove a large fraction of heavy metals and BFR containing plastics with a density-based method.

The removal of contaminants, such as “heavy metals” and PVC, from SR with the intended purpose to create a fuel fraction with similar qualities as coal which would enable its use in cement kilns has been the object of a study by USEPA (Boughton, 2007). Size fractionated samples from a shredder facility were analysed for elemental composition and results were consistent with many other similar studies (e.g., studies discussed in Chapter 2). The fine fraction of SR generally had the highest content of mineral oil, the lowest calorific value and a high ash content. Problematic “heavy metals” and chlorine were distributed over all size fractions which determined the need for further treatment in order to produce a fuel fraction. In laboratory tests with density separation, using bath densities between 1100–1200 kg/m³, the majority of chlorinated plastics (up to 68%) could be removed and the heavy metals content was reduced. The study concluded that a fraction accounting for around 30 % of the total SR had fuel characteristics similar to coal. However, the remaining levels of chlorine (around 1 wt%) and heavy metals (1 ppm of mercury) could still impede its use as an alternative fuel in cement kilns.

It can be concluded that, under specific conditions, conventional sorting processes can provide simple alternatives for the separation of hazardous or problematic substances/materials such as PVC, plastics containing BFR additives and “heavy metals” as shown above. However these simple techniques are not precise, and work only within the limits of physical characteristics that might correlate with the presence of a particular substance or element of interest. Furthermore, it is impossible to differentiate between particles or materials that have the same attributes, i.e. there is no identification of the substance.

3.3 Sensor-based sorting systems

This section contains a review of screening methods in the form of handheld devices that can be utilised in a field setting, e.g. at a recycling plant. These are sensor-based systems that are relatively fast and can provide semi-quantitative to qualitative information about the presence of certain substances or chemical elements in a certain matrix (described in section 3.1.1), which is usually a single particle or a pre-treated sample from the analysed waste.

The Waste Resources Action Programme (WRAP) commissioned a large project that has run between 2004 and 2006 with the purpose of developing a process to separate brominated flame retardants (BFR) from mixed WEEE polymers. Although the main focus was on the treatment of polymers containing BFR additives, the objective was to find a ‘total process’ solution. Therefore, the costs, efficiency and yields of polymer identification and mechanical sorting techniques that could be used to separate polymers with BFR additives from non-containing ones were also assessed (Freegard et al., 2005; Freegard et al., 2006). Of the reviewed techniques, which can be categorised as screening techniques, surface ablation sliding spark and FT-mid IR appeared to be the most suitable for BFR detection with X-ray fluorescence in third place. The devices tested and a comparison between the techniques can be seen in Figure 3.1 and Table 3.1.



Figure 3.1 SSS3-FR - Sliding Spark Spectrometer for Fire Retardants detection⁴⁷, Niton XFR from Thermo Scientific⁴⁸, PolyAna from Wolfson Electrostatics⁴⁹

Table 3.1 Comparison of screening methods in the WRAP study (Freeguard et al., 2005)

Instrument type	FT-Infrared Reflectance	X-Ray Fluorescence	Sliding Spark spectral analysis
Function	Detect polymer type + <i>some additives</i>	Detect and quantify additives and bromine	Detect + quantify bromine and chlorine
Method of operation	Measures absorption of a range of IR light wavelengths on sample surface and compares with library of known reference samples to give % fit to ID type	Low power X-ray penetrates ~10mm into a sample, detector measures distinct energy peaks from fluorescence of a range of elements to give ID and % conc. of additives	High voltage spark on surface creates plasma of vaporised material. Light spectra analysed for known peaks at Br and Cl wavelength to estimate % conc.
Approx. cost €	26,500	30,000	3,900
Size	Benchtop box approx 1000 x 500 x 200mm	Handheld, bulky gun	Hand-held detector with small bench-top box
Weight	25 kilos	1.7 kilos	0.75 kilo (gun)
Portability	Zero – needs firm stable worktop + separate laptop PC	Excellent – battery powered no cables	Okay – light to carry, but needs mains power
Sample presentation and speed	Difficult with big samples and must keep still for 30 seconds	Easy – hold gun on sample for 15 – 30 seconds	Very easy – 1 second to 'fire' spark
Sample preparation	Flat non-shiny surfaces best. Dark colours more difficult, surface coatings a problem	Thicker samples better (> 5mm). Will detect surface contamination & coatings. Good for granular plastics	Clean surface required and flat area for good spark contact. Will detect dirt and coatings on surface
Measurement accuracy	Depends on closeness of match to library samples	Very good – ppm levels of elements	Sufficient – to nearest 1% on Br/Cl concentration
Measurement speed	Slow – 30 secs	Slow 15-30 secs	Fast – 1 sec
Operator skill level needed	Good technical /laboratory person	Technical operator to interpret results	Factory operator with basic training

Taurino and colleagues have concluded that the combined application of FTIR spectroscopy, DSC, Raman, EDAX, and XRF spectrometer can achieve a faster analysis of WEEE plastics, with regard to hazardous substances, compared with more in depth analytical techniques. XRF analyses focused on RoHS restricted substances, namely elements Cd, Pb, Hg, Cr, and Br (Taurino et al., 2010). In

⁴⁷ <http://www.iosys-seidel.de/sss3.html>

⁴⁸ <http://www.niton.com/RoHS-Compliance-Hi-Rel/products.aspx?sflang=en>

⁴⁹ http://www.wolfsonelectrostatics.com/02_applications/identification.html

another study it was demonstrated that Laser Induced Plasma Spectroscopy can be a rapid tool for F, Cl and Br determination in solid organic compounds with accuracy close to more advanced analytical methods (Tran et al., 2001).

The results of a study on the applicability of handheld XRF systems for waste characterisation initiated by the German states working group on waste (LAGA) demonstrated that handheld XRF instruments are useful tools for the screening of waste (Holschbach-Bussian and Vanhoof, 2010). It was concluded that reliable information can be gathered with this method regarding the presence or absence of elements, and in most cases also in terms of magnitude of the concentration levels of the elements present. This type of devices can be used to screen waste loads on hazardous substances as incoming inspection at waste handling plants and could also be used in manual sorting operations or to verify sorting outputs.

Six different waste materials were used in the field trials: construction waste, fine fraction from shredder residue, contaminated soil, waste wood, Pb granulate and bottom ash from a municipal waste incineration plant (Figure 3.2). Five handheld XRF instrument manufacturers were identified on the European market and in total 8 different instruments were evaluated. The measurements were focused on the following elements: As, Cd, Co, Cu, Cr, Hg, Mn, Ni, Pb, Sb, Tl and V, while optionally the elements Ag, Fe, Sn, Zn, S and halogens were considered.



Figure 3.2 Overview of the samples in the LAGA project

It could be concluded that the overall level of detection (LOD) for all elements and samples was around 10 to 100 mg/kg. Detailed descriptions of the devices and detailed results of tests can be accessed in the project report (Holschbach-Bussian and Vanhoof, 2010).

3.4 Sensor-based systems for bulk particle sorting

Research for the development of automatic systems that would allow for the high processing throughput characteristic to mechanical sorting processes, while being able to independently identify material types, structures or composition beyond the capabilities and limitations of the human eye (with manual sorting), was initiated as early as the 1980s. An early overview of the development and the already commercially available automatic sorters for waste processing in the late 80s and early 90s is presented elsewhere (Dinger, 1992). These already included NIR sensor systems able to automatically sort plastic containers by polymer resin and X-ray sorters for detection and separation of PVC which is a major contaminant in, for example, PET plastic streams for recycling. Re-

search and experience with the major sensing techniques are presented in the following, with special emphasis on detection and sorting of materials containing problematic/unwanted substances.

The majority of sensing techniques applied to materials sorting are spectroscopy-based, where detection and classification is achieved by spectral analysis of the interaction between matter and radiated energy in the electromagnetic spectrum (from short wavelength gamma radiation to long wavelength acoustic noise, Figure 3.3).

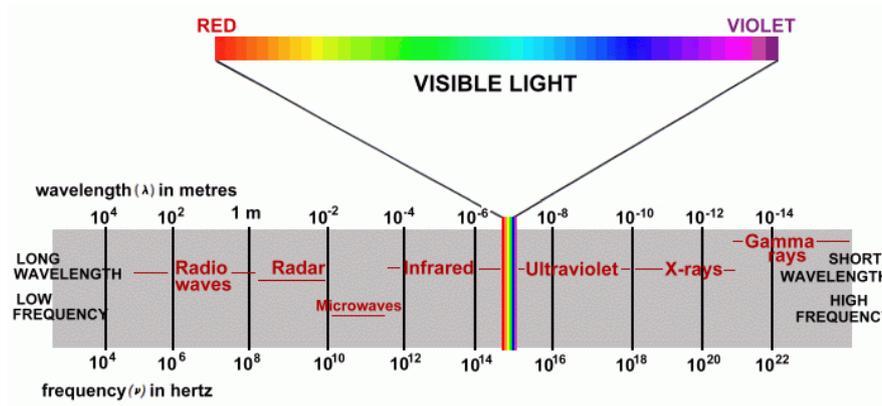


Figure 3.3 The electromagnetic spectrum⁵⁰

A sensor-based sorting unit can be described as follows:

- Materials traveling on a conveyor belt pass by a sensing unit;
- The sensing unit contains one or more sensors that detect specific attributes in all the particles in the flow; the sensor itself usually has two sub-units:
 - an emitter, which sends waves of radiation of a known intensity and frequency towards the passing material, and
 - a detector which receives the radiation after its interaction with the passing material. Depending on specific attributes of the sensed materials, the radiation, on contact, is affected by absorption, reflection, transmission, diffraction or fluorescence. The changed conditions of the detected radiation are processed and analysed by a computer system which classifies each particle according to a database of known (learned) materials.
- The last unit of a sorting machine performs the actual physical separation/extraction of detected particles usually with the aid of high speed air valves and compressed air. This separates the initial stream into “pass” and “throw-off” fractions that are then collected separately.

⁵⁰ <http://www.worsleyschool.net/science/files/electromagnetic/spectrum.html>

An overview of main sensor types that are today the basis for state-of-the-art applications in material sorting/recovery from waste streams is given in Table 3.2.

Table 3.2 State-of-the-art applications of sensor-based sorting in waste treatment

Sensor types	Sorting criteria	Detection principle	State-of-the-art applications in waste treatment
Colour Cameras and VIS (visible light) sensors	Colour, brightness	Image acquisition and processing in the visible spectrum	<ul style="list-style-type: none"> • Glass by colour • Plastics by colour (PET bottles) • Non-ferrous metals by colour (Cu, brass and 'white' metals) • Circuit boards from electronic scrap (green) • Paper sorting (by grades)
	Transparency, lustre		<ul style="list-style-type: none"> • Separation of magazines from waste paper • Separation of ceramic, stones, porcelain and heat-resistant glass • Determination of Pb content in glass
	Colour, shape (3D camera)		<ul style="list-style-type: none"> • Coins, bottle caps
NIR spectrometer	Molecular composition at the surface of materials	Spectral analysis of reflected light in the NIR region of the electromagnetic spectrum	<ul style="list-style-type: none"> • Mixed plastics by polymer type (except black coloured) • Wood and textiles from waste mixtures • Generation of RDF from municipal solid waste • PVC in RDF • Paper, cardboard and packaging • Online material flow analysis (content of moisture, chlorine and calorific value)
Inductive sensors	Electrical conductivity	Measurements of the interaction between conductive materials and an alternating magnetic field	<ul style="list-style-type: none"> • Metals from shredder residue, incineration slag, RDF • Stainless steel from metal mixtures
X-ray transmission	Density at molecular level	The attenuation of X-rays by materials combined with image processing	<ul style="list-style-type: none"> • Separate Heavy metals (Cu, brass, Zn) from light metals (Al, Mg) in shredder products • Flame retardant additives • Lead glass from panel glass (from CRTs) • Battery sorting
X-ray fluorescence	Elemental composition	Spectral analysis of fluorescent energy emitted by materials after exposure to X-ray radiation	<ul style="list-style-type: none"> • Lead glass from panel glass (from CRTs) • Ceramic and heat-resistant glass
LIBS sensors	Elemental composition	Spectral analysis of emitted energy by a plasma discharge induced by laser light	<ul style="list-style-type: none"> • Sorting of wrought and cast aluminium scrap
PNGAA sensor	Elemental composition		<ul style="list-style-type: none"> • Battery sorting • PVC sorting

3.4.1 Near Infrared spectroscopy (NIR)

In the near infrared (NIR) region of the electromagnetic spectrum (700 – 2500 nm in wavelength), electromagnetic energy (light) is absorbed by materials via the first overtones of the normal modes of vibration involving stretching of the C-H and O-H bonds. Spectral analysis of the reflected light can be used to obtain information about the chemical structure of materials.

The development of automatic sorters based on NIR has been generally motivated by the fact that it is a fast detection technique, it is robust with regard to application in industrial environments and quite inexpensive compared with other techniques (Bruno, 2000). NIR spectroscopy is the basis for the most widely used sensors for fast automatic identification and sorting applications of especially waste plastics. Numerous early studies focused on the separation of common plastic types found in household waste (e.g., PE, PET, PP, PS and PVC) with very good results (Scott and Waterland, 1995; Huth-Fehre et al., 1995). A drawback for this technique is that it cannot detect black-coloured materials due to the colour's high absorption of light in the NIR spectrum.

NIR detection is applied for the selective removal of PVC plastics in the processing of high calorific fractions for solid recovered fuels (SRF) and is also used for the selective sorting of suitable fuel components such as paper, plastics, wood and textiles from mixed waste (Pretz et al., 2004). NIR is described and included as a technique to consider for the preparation of waste to be used as fuel in the Reference Document on Best Available Techniques (BET) for the Waste Treatment Industries (European Commission, 2006).

The possibility of using NIR sensors for online monitoring of chlorine and calorific value in the production of RDF from mixed household waste and/or commercial waste was investigated by Titech GmbH and the IAR – Department for Processing and Recycling at the RWTH Aachen University (Uepping, 2008). An identification of heating value and chlorine content for the whole stream was shown possible, despite the heterogeneous nature of the above mentioned material flows. This was achieved by combining the estimated weight of the passing flow of materials with a library of known calorific values and a library of the chlorine content (both a result of extensive laboratory characterisation of waste samples) while NIR sensors provided information regarding the composition of the material flow. Online measurements correlated very well (92% confidence interval for chlorine content) with laboratory analyses, which are the standard method to measure these parameters. Nevertheless, dark and highly reflective materials were not identified, while composite materials might have been identified incorrectly. This was shown to contribute to a level of error in the online measurements.

Recently, applicability of hyper-spectral NIR imaging for detection and sorting of plastics with flame retardant additives was investigated (Leitner et al., 2009). The evaluation has been performed assuming a two-level classification scheme, first the identification of the polymer type and then the detection of the presence of flame retardants. Samples of plastic material were specially produced for the trials and amounted to a wide range of technical polymers and polymer blends containing the main groups of flame retardants in use (e.g., PBDEs). It was reported that:

- even though PBDEs did not exhibit detectable spectral features in the NIR range, their detection was possible based on the presence of the synergist Sb_2O_3 , which could be detected in a two-stage classification process after the correct identification of the polymer type;
- pure polymers can be reliably separated with hyper-spectral NIR imaging;
- after polymer classification, detection of PBDEs was possible with 99% accuracy for a number of polymers (e.g., ABS as shown in Figure 3.4);
- detection of PBDEs in PP was nearly impossible;
- the classification results might have been greatly influenced by the use of ideal samples (i.e., clean, homogenous, flat and non-overlapping)

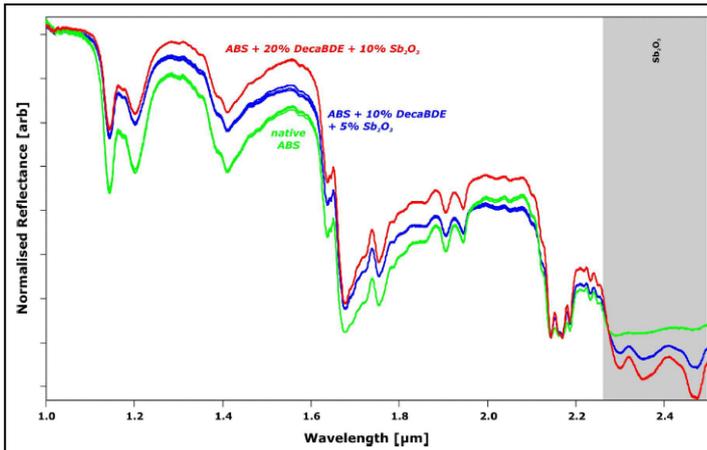


Figure 3.4 Normalised reflectance spectra of native ABS (green), ABS+20% deca-BDE / 10% Sb₂O₃ (red) and ABS+10% deca-BDE / 5% Sb₂O₃ (blue) from Leitner et al. (2009)

3.4.2 X-ray transmission techniques (XRT)

X-rays penetrate materials and are attenuated based on their atomic and material density and their thickness. To use this property in sorting applications, similar to airport baggage control systems, the attenuation is recorded by imaging line sensors and evaluated with methods of image processing. To eliminate the influence of sample/material thickness, the attenuation of the radiation intensity is recorded by two measurement channels in different wavelength ranges. This enables the mathematical calculation of the materials thickness. The identification and sorting criterion is therefore the materials specific density, independent of particle size, shape, weight of surface treatment.

Similarly to the NIR sorting systems, the first X-Ray transmission (XRT) systems were developed in the late 1980s to separate PVC from PET bottles in order to enable their recycling (Sommer and Peatman, 1993). Since 2000, Delft University of Technology has been developing imaging based on dual-energy XRT for automated sorting of especially scrap metals and for mining applications (Mesina et al., 2007; Mesina et al., 2004; Jong et al., 2004). The technique was also proved in plastic sorting, i.e. in detection of PVC and plastics with flame retardant additives (an example of XRT image is given in Figure 3.5).



Figure 3.5 Normal picture (left) and XRT image (right) of hand sorted plastic fraction. The XRT image reveals flame retardant plastics (dark blue) and PVC (pink). (Delft University of Technology)

Today industrial applications of X-ray sorting technology include (Hottenstein, 2008; Jong et al., 2004):

- separation of heavy and light metals
- separation of organics from inorganics
- separation of leaded CRT (cathode ray tube) glass from non-leaded glass⁵¹
- separation of copper from ferrous metals
- RDF production and removal of flame retardants like chlorine and bromine from mixed plastics
- mineral sorting in mining and industrial applications⁵² such as automatic ash, sulphur and chlorine reduction, classification of coal on quality types or online control of size and ash content

In 2007, Dalmijn and de Jong published results from experiments performed on SR in the Netherlands (Dalmijn and De Jong, 2007). The purpose of the study was to determine if a fuel fraction can be generated from raw SR by separation of problematic or unwanted materials by an XRT sensor. The separation efficiency of metals, inert materials (e.g., stones, glass) and chlorine/bromine containing polymers from SR was measured after one pass by the sensor. The SR samples used were first screened for < 10 mm fines, which were not further used, and the remaining materials was further separated into 10-20 mm and > 20 mm size fractions. The later size fraction accounted for an average of 25% of the SR material.

In the > 20 mm size fraction, about 50% of the incoming SLF was converted into a high calorific stream (LHV 24 MJ/kg) with chlorine and bromine content of 1.1% and 0.1%, respectively. Similarly, about 70% of the incoming “heavy” SR fraction was converted into a high calorific stream (LHV 23 MJ/kg) with chlorine and bromine content of 0.5% and 0.05%, respectively. Distribution of chlorine and bromine between the product(s) and the reject(s) is summarised in Table 3.3. Furthermore, it was reported that these results can be improved by the inclusion of pre-treatment steps such as metal removal by magnetic separation and eddy current separation and by optimising operation conditions.

Table 3.3 Mass split of Cl, Br and calorific value recovered in the fuel product and in the reject (Dalmijn and de Jong, 2007)

Shredder residue	Parameter	Feed (%TS)	Product (%TS)	Reject (%TS)
Light fraction	Chlorine	100	19	81
	Bromine	100	13	87
	Heat of combustion	100	57	43
Heavy fraction	Chlorine	100	18	82
	Bromine	100	9	91
	Heat of combustion	100	77	23

Quite recently, efficient sorting of plastics containing BFRs from mixed WEEE was achieved by using XRT technology coupled with NIR sorting (Krämer et al., 2010). In this project, samples from the WEEE processing industry were first separated using NIR sorting into three polymer types: ABS, PC/ABS and PS. Each of the three fractions was further sorted using XRT technology into two fractions: BFR-free plastics and BFR-containing plastics (Table 3.4). As the system was calibrated to reject even very low BFR concentrations the reject contained 10-30% of falsely identified parti-

⁵¹ Titech (<http://www.titech.com>)

⁵² Commodas Ultrasort (<http://www.commodas-ultrasort.com/about-us/tomra-sorting-solutions>)

cles. However, this could be improved by optimising the calibration of the sorters (Krämer et al., 2010).

Table 3.4 Original and BFR depleted polymer fractions (Krämer et al., 2010)

	ABS (wt %)		PC-ABS (wt %)		PS (wt %)	
	Original sample	Clean fraction	Original sample	Clean fraction	Original sample	Clean fraction
Bromine	3.20	0.03	0.57	0.03	1.01	0.10
Antimony	0.58	0.01	0.02	-	0.17	0.02

In the second phase of the WRAP study (Freegard et al., 2005), presented in more detail in Section 3.2, the bulk separation processes for plastics with BFR additives, as well as handheld screening systems were tested in pilot scale. Among the sensor-based sorting systems tested (commercial scale NIR, optical colour sorting system and a XRT system) only the Dual energy X-ray transmission technology developed at TU Delft proved very efficient in fast online detection of additives, not only BFRs but also heavy metals (lead, cadmium) and metal inserts in the plastic samples. This technique was not influenced by surface coatings. These tests, however, included only detection and not the separation process.

Between 2005 and 2007 the project funded by Department for Environment Food and Rural Affairs – DEFRA (UK) investigated various sorting and separation technologies available commercially for the processing of WEEE plastics. These included spectrographic and colour sorters, assessments that are not relevant for this review, and also a commercially available sorter based on XRT technology that was tested in the task of separating polymers with flame retardant additives from pure ones (Freegard et al., 2007). The samples used in the tests constituted plastic casings from computer monitors (CRT) that were shredded to a size range of 10-30mm for a first set of tests and to 30-100mm for the second set of trials. Both sets of tests revealed that an output of plastics with very low content of BFR could be generated while at the same time the reject contained around 50 % non-targeted materials (not containing BFR) which would constitute a loss of potentially recyclable plastics. The big amount of non-BFR containing plastic particles lost to reject stream was attributed to the poor shredding of the samples (the 10-30 mm samples contained also many smaller particles).

3.4.3 X-Ray fluorescence (XRF) Spectroscopy

When materials are exposed to X-ray radiation, ionisation of the atoms may occur, whereby electrons from the inner orbitals may be expelled causing electrons from lower orbitals to switch (fall to) and take their position. This movement causes the emission of secondary (fluorescent) X-rays, of low energy. The wavelength of the energy released is a function of the elements in the material, thus permitting an elemental or chemical analysis.

In 1990, the capabilities of a sorter based on X-Ray fluorescence (XRF) able to identify and sort PVC bottles were presented (Summers et al., 1990). This was the first system based on X-ray technology employed in waste treatment, followed closely by the X-ray transmission, as presented in the previous section.

XRF has mainly been researched as a technique to sort waste wood by detection of heavy metals in the treated/impregnated wood. Commercial sorters based on this technique are being used in glass sorting (e.g., lead glass, ceramics) and are undergoing development in scrap metal sorting applications (i.e. metal sorting by type).

Jacobi and colleagues reviewed the efficiency of different methods in relation to sorting of chromate-copper-arsenate (CCA) impregnated wood (Jacobi et al., 2007). While visual sorting was found effective for source separated wood coming from C&D waste, the hand-held XRF devices were the only affective tool in sorting of commingled wood waste with various degrees of surface dirt and various degrees of material degradation.

In 2004, the potential use of XRF spectroscopy and LIBS-based sensors (see next Section) in online automated separation of CCA impregnated wood from a mixed C&D wood waste were evaluated (Solo-Gabriele et al., 2004). The sorting system consisted of the detector mounted on conveyor belt followed by manual or semi-automatic removal of the identified wood pieces. The XFR detector used in the study (a commercial system) was capable of detecting the presence of CCA (As was chosen as an indicator) in different types of wood and was influenced neither by surface coating nor by increased moisture content. In addition, the system could distinguish between CCA impregnated wood and wood treated with other types of preservatives. The LIBS system developed for the same study was capable of effectively identifying CCA impregnated wood based on measurements of Cr and Ca. In a follow-up study (Hasan et al., 2011a; Hasan et al., 2011b), the authors focused on applicability of the system in a full scale sorting plant as well as optimisation of detection efficiencies. Simultaneous detection of As and Cu was used to identify CCA impregnated wood; detection of only Cu indicated copper-based preservatives that are used as replacement of CCA preservatives. Overall, 81-99% As, 75-95% Cu, and 82-99% Cr by mass were recovered into a reject stream of detected treated wood. Errors in sorting were distributed equally between the detection part and the conveyance/sorting part of the system.

3.4.4 Laser Induced Breakdown Spectroscopy (LIBS)

Laser induced breakdown spectroscopy uses a laser light focused onto the sample surface to vaporise a small amount of the material and simultaneously excite a plasma discharge. The atoms within the plasma emit light (or energy) characterised by different wavelengths. Certain wavelengths of energy are unique to different elements. The spectral analysis of the emitted energy permits the direct determination of the atomic composition while its intensity is directly proportional to the amount of the different elements.

LIBS is another relatively fast, non-contact analysis technique for which the potential for on-line high-speed applications such as sorting of plastics (including PVC) by polymer type has been tested (Sattmann et al., 1998; Gondal and Siddiqui, 2007). Unlike NIR, LIBS is applicable for dark colour polymers and contaminated surfaces; moreover, it could provide additional information such as concentration of additives (Boueri et al., 2011). Nevertheless, 1s response time for classification of polymer types (Boueri et al., 2011) is still too long for current real-time sorting applications.

LIBS has also been used for determination of fluorine, chlorine, and bromine in solids (Tran et al., 2001) or, alternatively, in fast industrial sorting (0.5-1 m/s on a conveyor belt) of WEEE plastics based on quantification of heavy metal (i.e. Cr, Hg, Cd, Pb, Sb) and bromine content (Stepputat and Noll, 2003). In the latter study, a LIBS equipped sorting system identified Cr, Hg, Cd and Pb in WEEE plastics with an accuracy of 84-95% on a conveyor belt moving at 0.5 m/s. The detection limit of 100 µg/g was reached for Cd, Cr, Hg and Sb. For Pb, the detection limit was 140 µg/g while detection limit for Br was above the concentrations found in the samples; thus, Br could not be identified directly. Nevertheless, BFRs were identified indirectly due to sufficient detection of Sb present in Sb₂O₃, which is a synergist for BFRs.

Overall, this study demonstrated that LIBS could be successfully applied for sorting of plastics containing "heavy metals" and flame retardant additives (e.g., in WEEE processing plants). However, this technique is still at research level and there are no commercially available systems yet.

3.4.5 Prompt Gamma Neutron Activation Analysis (PGNAA)

The nucleus of all elements can react with neutrons with low energy ("thermal neutrons"). The reaction is called "neutron capture" and thereby the nucleus increases atomic weight corresponding to the mass of the neutron. The nucleus becomes excited and decays momentary emitting gamma radiation with a spectrum characteristic of the actual element. The gamma ray is called "prompt gamma". The spectral analysis of the emitted energy permits the direct determination of the atomic composition while its intensity is depending on the amount of the different elements. The method is non-destructive, non-contact, sees in depth and can detect several elements simultaneously. PGNAA is indifferent to chemical composition and shape. The elements have very different affinity to thermal neutrons and some do not emit gamma rays (Pb, Li, ...). Cl and Cd have high affinity to thermal neutrons their characteristics of their gamma spectrum make them easy to detect.

PGNAA is not a new technology although it is not widespread. In addition to applications within research PGNAA is used for characterising coal at power plants, ores in the mining industry, identification of chemical warfare agents and explosives, and raw materials for cement kilns. Figure 3.6 is illustrating the working principle of a PGNAA sensor:

1. The neutron source emits fast (energy rich) neutrons
2. The moderator slows down the neutrons, henceforth being highly reactive towards certain elements
3. Neutrons reacts with said elements in the sample material with (n,gamma)-reactions
4. Gamma radiation being specific for elements participating in reactions are seen by energy resolving gamma radiation detector(s)
5. multivariate data analysis provides estimate of elemental composition for selected elements.
6. Based upon results, software then takes possible sorting action

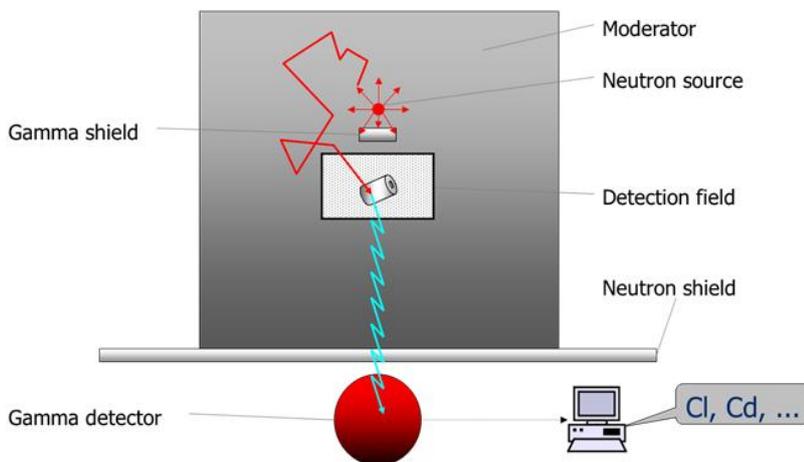


Figure 3.6 Principle of the Prompt Gamma Neutron-Activation-Analysis (PGNAA) sensor technology.

Figure 3.7 shows a typical gamma spectrum of a single detector PGNAA sensor.

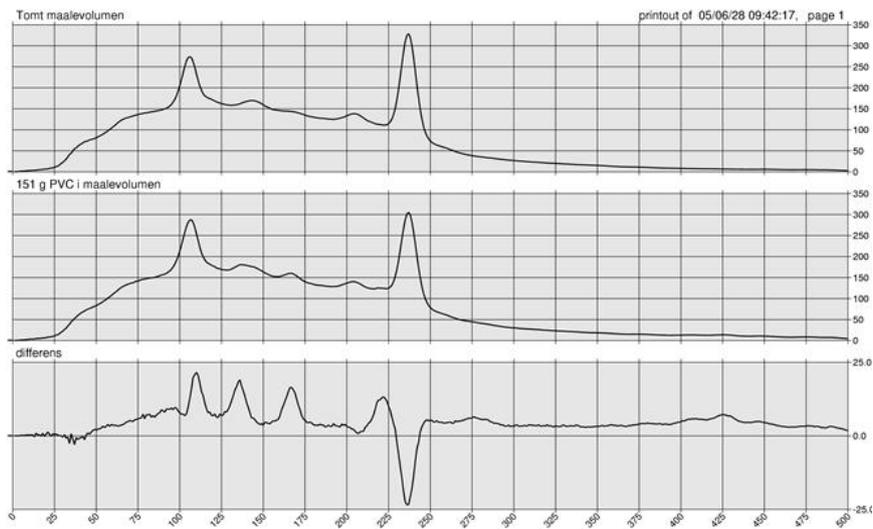


Figure 3.7 Typical spectrum of a single detector: empty, sample and difference.

Pedersen et al. (2002) have tested a sensor based on Prompt Gamma Neutron-Activation-Analysis (PGNAA) technology with the intended purpose of detection and sorting of CCA treated wood waste from mixed streams. The results revealed that it would be possible to characterize the content of Cu, Cr and As in impregnated waste wood and to develop an online sensor as a part of an automatic sorting machine.

Pedersen and Cramer (2005) showed that a PGNAA sensor had high sensitivity with regard to elements like Cl, Cd, B and Hg determining the development of the sensor for a number of applications including sorting of PVC plastics, PCB containing transformers/capacitors and NiCd batteries.

Between 2009 and 2012, in the CIP Eco-Innovation project ECOSORT, the sensor was scaled up and the first generation of sorting machines were installed in two full scale plants for the processing of two different types of waste (Figure 3.8):

- Batteries
- Industrial waste for production of low chlorine fuel for co-combustion at central power plants (installed at nomi i/s);

Figure 3.8 also shows gamma spectrum of different batteries as well as three samples of PVC.

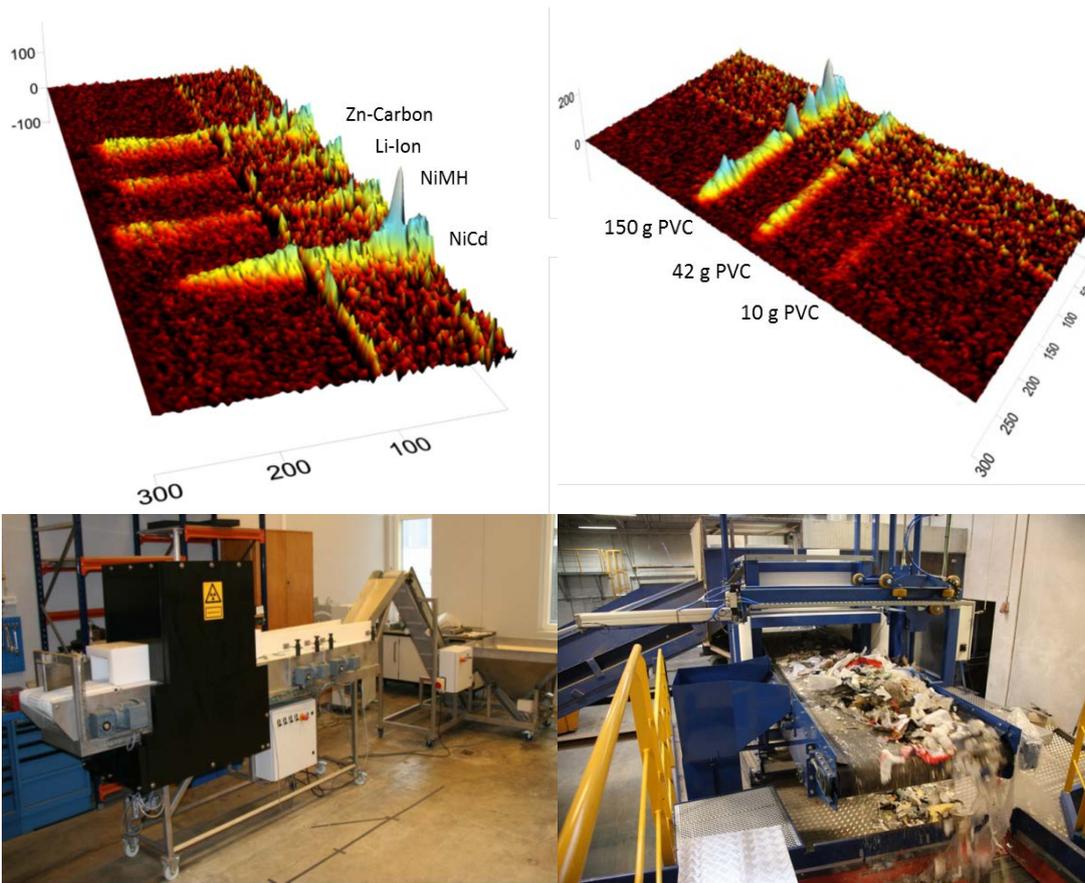


Figure 3.8 Left: Different gamma fingerprints of battery chemistries, Right: series of chlorine prompt gamma spectra showing the passage of three PVC items. Lower left: sorting system for batteries. Lower right: sorting system installed at nomi i/s.

The specifications for RDF/SRF chlorine reduction application for nomi i/s are:

- Designed for the localization of larger chlorine containing items, for subsequent removal.
- To be mounted at around conveyor after first shredder stage (material 0 – 400 mm particle size).
- Conveyor 1000 mm wide, speed 1 m/s.
- Localization of PVC items >50 g: transversal - better than 100 mm, longitudinal - better than 50 mm.
- Will also provide a tally of total chlorine.
- Capacity in actual setting: 5 tons/h
- Raw detection capacity: 20+ tons/h (handling/removal technology limited).

As part of the herein presented project, the applicability of PGNAAsensor on SR was tested on a number of SR subsamples originating from STENA's plant in Grenå. The results are documented and discussed in detail in Chapter 4.

3.5 Examples of large scale applications

3.5.1 Technology producers

The following table (Table 3.5) contains an overview of the main companies that develop and produce sorting equipment based on sensors for waste processing. The third column lists all techniques employed by the companies, while the last column lists specific applications offered within problem substance sorting.

Table 3.5 List of companies and applications offered commercially

Company	Ref	Employed Techniques	Problem substance sorting offered
TITECH, Norway	1	NIR, Colour imaging, Inductive sensor, X-ray transmission (DXRT) and X-ray fluorescence (XRF)	PVC, online monitoring of chlorine, plastics containing flame retardant additives, lead glass
RTT-Steinert, Germany	2	NIR, Colour imaging, 3D laser (shape recognition), Inductive sensor, X-ray transmission (DXRT) and X-ray fluorescence (XRF)	PVC, plastics containing flame retardant additives, lead glass
S+S Separation and Sorting Technology, Germany	3	NIR, Colour imaging, Laser camera, Inductive sensor, X-ray transmission (DXRT)	PVC
BT-Wolfgang Binder, Austria	4	NIR, Colour imaging and X-ray fluorescence (XRF)	PVC, plastics containing flame retardant additives, lead glass
EVK Elektronisch Visualisieren Klassifizieren, Austria	5	Hyperspectral and Colour Imaging	Technology supplier to other companies
Pellenc, France	6	NIR, Vision, Inductive sensor and MIR	PVC
Mogensen, Germany	7	Colour Imaging and X-ray transmission (DXRT)	PVC, lead glass
National Recovery Technologies, USA	8	NIR, Colour imaging, Inductive sensor, X-ray transmission (DXRT) and X-ray fluorescence (XRF)	PVC, plastics containing flame retardant additives
MSS, USA	9	NIR, Colour imaging, Inductive sensor, X-ray transmission (DXRT)	PVC

¹⁾ <http://www.titech.com/>

²⁾ <http://www.rtt-steinert.de/de/home/>

³⁾ http://www.sesotec.com/detectors_separators_sorting-systems/?n=25

⁴⁾ <http://www.redwave.at/en/homepage.html>

⁵⁾ <http://www.evko.at/unternehmen/?language=en&ID=89>

⁶⁾ <http://www.pellencst.com/en/1/products>

⁷⁾ http://www.mogensen.de/index_e.htm

⁸⁾ <http://www.nrtsorters.com/index.html>

⁹⁾ <http://www.magsep.com/>

3.5.2 Examples of waste treatment plants

Detection and sorting of PVC in the processing of alternative fuels by NIR sensors

Around 25 % of the mixed municipal solid waste (MMSW) in Germany is treated in mechanical-biological treatment (MBT) plants. Of the 46 plants at least 10 include NIR sensor sorter units in their process flows, with 6 plants applying this technology specifically to lower the chlorine content in the high calorific fractions processed into solid recovered fuels (Arbeitsgemeinschaft Stoffspezifische Abfallbehandlung, 2011). This is usually performed by sorting of PVC from the waste. The high quality SRF produced by some of these plants substitutes coal in coal fired power plants or cement kilns.

Another example of NIR technology application is online monitoring of chlorine, moisture and ash content in the produced SRF, which is implemented in two MBT plants in Germany, located in Neuss and Erftstadt respectively (Glorius, 2012).

Sorting of waste plastics with flame retardant additives and lead glass by XRT technology

In April 2010, Mitsubishi Electric Corp. has opened a large scale plant in Japan for the processing of shredded mixed plastics WEEE. Mitsubishi already has a large scale plant that is processing WEEE which is generating 10,000 tons per year of mixed plastics. Before the starting of the new plant, only 600 tons of these plastics were recovered for recycling into new home appliance products by conventional techniques like manual sorting. The new plant, with a total capacity of 12,000 tons/year, now recovers an additional 6,400 tons of high-purity plastics for closed-loop recycling (Plastics, 2011). The mixed plastic flakes, shredded to 10 mm, are first separated into three density groups by sink-float methods: unfilled PP, a mixture of PS and ABS and a heavy fraction containing PC/ABS alloys, PVC and highly filled plastics. The PS and ABS mixture is further separated by electrostatic separation. At the core of the plant there are the XRT separators developed independently by Mitsubishi to remove bromine-containing plastic flakes from the PP, ABS and PS fractions. The plastic is purified to comply with the European Restriction of Hazardous Substances (RoHS) Directive (European Commission, 2003b) and can therefore be used for the manufacture of new electronic appliances.

The Adamec treatment plant in Nuremberg, Germany (Figure 3.9) with an annual capacity of 35,000 tonnes input of WEEE has started operation in the summer of 2011. The proprietary treatment flow includes separation of plastics with flame retardant additives by dual-energy XRT technology (DXRT). The managers of the plant claim that 95% of the input material will be available for recycling while just 5% will have to be disposed (Lang, 2011).



Figure 3.9 A view inside the WEEE treatment plant Adamec (Lang 2011)

Another example of the use of XRT technology is the GRIAG Glasrecycling AG plant operating in Neuruppin, Germany. It is the largest cathode ray tube (CRT) processing plant in Europe with an

annual capacity of more than 120.000 tons (Beck, 2011). CRT glass from WEEE processing consists of panel glass (with aluminium and metal sulphites coatings) and funnel lead glass (iron oxide and carbon coatings). The coatings are removed in wet processes and the two glass types are separated using the XRT technology in order to be further recycled into other products.

Sorting of post-consumer batteries by XRT technology and inductive sensors

Depending on the electrochemical system, some portable batteries can contain a number of hazardous substances such as mercury (button cells), cadmium (NiCd batteries) and lead (lead acid batteries). Established collection systems in different countries usually receive all battery types in a mixture, which then has to be sorted based on electrochemical systems if sent for recycling. Sorting processes for batteries include mechanical sieving, magnetic separation, visual/manual sorting and automatic sensor-based sorting. Typical sorting rates for visual and manual sorting are 0.1 to 1 units per second with an achieved purity for battery types of 98-99% (Knudsen and Nowak, 2008). Recovery of the valuable metals in batteries is performed in metallurgical processes, either hydrometallurgical or pyrometallurgical (Bernardes et al., 2004).

One of the largest European sorting plants for batteries operates in Bremerhaven, Germany. The UNI-CYC GmbH operates a plant with a capacity of 15,000 tonnes/y. At the start of the process sieving and magnetic separation are used to sort button cells and zinc-carbon systems respectively, this is complemented by manual quality control. Larger batteries and battery packs are then manually sorted. By weight the batteries sorted manually represent around 25 % of the mass input to the plant whereas they represent only 1 % of the total number of sorted batteries. The remaining 99 % of the batteries are sorted automatically with an X-ray transmission system (Figure 3.10), developed by the company, which is able to sort 28-32 units per second at purities greater than 98 % (Knudsen and Nowak, 2008).

The following electrochemical systems are sorted in the plant:

- nickel-cadmium
- nickel metal hydride
- lithium primary
- lithium-ion
- mercury
- alkaline-manganese (with and without UV marking)
- zinc-carbon (with and without UV marking)
- lead dry cell batteries and button cells

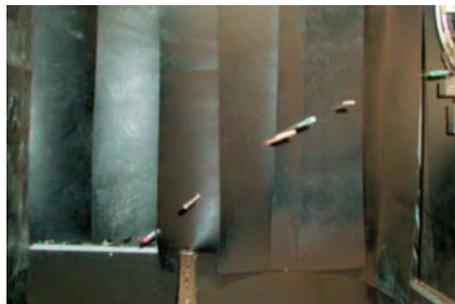


Figure 3.10 X-Ray sensor sorter at the UNI-CYC plant in Bremerhaven⁵³

⁵³ <http://www.grs-batterien.de/start.html>

3.6 Conclusions on research and maturity of sorting techniques

In the following text we attempt to comprehensively illustrate the state of maturity of sensor-based techniques with respect to industrial sorting applications of problematic substances or unwanted materials. The main companies producing sensor-based sorting equipment are listed together with the sorting applications that they commercially offer. Examples of waste treatment plants that employ automatic sorting techniques in their operation are presented.

In total, five sensor-based techniques have been reviewed (Table 3.6) with regard to sorting applications and efficiencies presented in various research papers addressing sorting of problematic substances in various waste streams. The state of maturity of these techniques has been revealed by a review of the main technology developers/sellers and secondly by presenting examples of large scale plants in the waste treatment industry.

Table 3.6 Main sensor-based techniques and applications reviewed

Sorting technique	Applications reviewed	Full scale plants	Characteristics
NIR spectroscopy	Sorting of PVC plastic	Yes	Efficient and proved technique; medium investment; does not work with dark materials
	Online monitoring of chlorine, calorific value and ash content	Yes	
	Sorting of plastics with flame retardant additives	No	Can work in specific conditions, further research is needed
X-Ray transmission	Sorting of PVC plastic	Yes	Very effective and proved technique for the presented applications; higher equipment costs
	Sorting of plastics with flame retardant additives	Yes	
	Post-consumer batteries	Yes	
X-Ray fluorescence	Sorting of PVC plastic	Yes	Efficient in both applications but can be influenced by surface coatings
	Sorting of CCA and other treated wood	No	
LIBS	Sorting of PVC plastic	No	High sensitivity in the detection of chemical elements but has longer response times compared to other techniques
	Sorting of CCA and other treated wood	No	
	Sorting of plastics with flame retardant additives	No	
	Sorting of WEEE components based on heavy metal content	No	
PNGAA	Sorting of PVC plastic	First tests 2011	Effective with detection of several chemical elements; response time and sensitivity is continuously improving
	Post-consumer batteries	First tests 2011	

NIR: Sorting of plastic material by NIR sensors is well established and used in recycling plants all over the world. Moreover, NIR is also employed in plants that process municipal, commercial or industrial waste into alternative fuels (SRF) for use in energy production processes including co-firing in coal power plants and cement kilns. In these plants NIR sorters are employed with the specific task of lowering chlorine levels by rejection of PVC materials. NIR systems have the drawback of not being able to detect dark/black materials.

With new developments in hyperspectral imaging the possibilities to detect flame retardant additives in plastics have also been tested. The first results are positive but further research is needed.

XRT techniques for bulk sorting of waste materials have been developed since the late 1980s, starting with PVC detection and sorting from PET streams. Today the technique is mature and applied in many fields in large scale applications. Several WEEE processing plants, two of which were presented in previous sections, employ the technique for separation of plastics with flame retardant additives in order to generate clean plastic outputs for recycling. An even more common application is the sorting of funnel lead glass and panel glass from CRTs. An example where the technology is applied for sorting of post-consumer batteries by type has also been presented. Reviewed research shows a direct applicability to sorting of shredder residues for the reduction of such contaminants as PVC, flame retardant additives, metals and inert material (ceramics, rocks). The main drawback of using this technique is the relative high costs of the sorters.

XRF has been studied especially for sorting of treated/impregnated wood with good results but no large scale application exists yet. Furthermore, it is used in large scale for the sorting of lead glass and commercially offered by at least one company for this task.

LIBS technology has been under research for a variety of sorting applications due to its capability of showing direct information on elemental composition and concentration in materials. The technique was successfully demonstrated in such applications as sorting of WEEE components and treated wood based on detection of various heavy metals; the detection of flame retardant additives is possible through detection of elemental synergists like Sb. This technique is not yet available in commercial applications, with at least one reason pointing at the long response time in detection (in the case of plastics). In sorting of aluminium alloys, the technique is more mature, and sorting of single piece particles on a conveyor with a speed of 3m/s has been reported (Werheit et al., 2011).

While **PGNAA** as such is a quite mature analysis technique, its application in the sorting and analysis of waste material streams is quite new; here it has proven to be efficient in detection of several chemical elements in waste materials. The first sorters have been implemented in large scale plants recently and undergo testing. While the smaller sorters, using only one detector, can only characterise one object at a time, larger sorters with an array of detectors are able to make a two-dimensional determination of location of unwanted objects on the conveyor belt.

In the various studies presented in this chapter different types of equipment have been used, from lab scale to fully developed commercially available sorting equipment. The examined materials and sample preparation are often particular to each study; therefore, the efficiencies reported in the reviewed literature have to be considered carefully and not generalised to other applications. Furthermore, one has to consider that the efficiency of sensor-based sorting techniques is dependent not only on the detection system and classification software but also largely on the limitations of the automatic separation systems (usually a pneumatic system). The latter were not included in all laboratory scale tests thus only the possibilities for detection and classifications are reported.

It can be concluded, based on the maturity of applications reviewed in this study, that although all the techniques reviewed have proven potential with regard to detection of problematic substances, only NIR spectroscopy and X-ray sensors are commercially available and are used in waste treatment plants.

3.7 Applicability of sensor-based sorting techniques in shredder residue management

As shown in the previous section, some sensor-based techniques are well established in the processing of many waste streams. However, most applications are very specialised and require a very homogeneous waste stream including a limited number of material types within a limited size range. The material stream has to be conditioned before presentation to the sorters. This can include size reduction and screening to obtain specific size ranges since sorting of heterogeneous waste types such as SR is not directly possible. An example of heterogeneous waste sorting is the use in NIR sorters to remove PVC in the processing of MSW into solid recovered fuels. In this case the waste is first screened and fines are removed while the coarse particles are usually shredded and further split into well-defined size intervals before the sorting process.

Some techniques which are already applied in shredder plants could be applied for the further treatment of SR; e.g., (i) inductive sensors are used to pick residual metals left after conventional sorting with magnetic and eddy current separators, (ii) X-ray sorters separate light and heavy non-ferrous metals, and (iii) colour sorters separate metals types based on characteristic colours. Until recently, SR left after metal recovery have generally been considered too heterogeneous, while containing low value materials and having large contents of hazardous substances. As such, there was not much focus on development of specialised sorting systems for SR.

Over the last 20 years landfilling of SR has been the main management route in Denmark. The more stringent targets related to material recovery and recycling of ELV will most likely reduce future landfilling of SR and will constitute an incentive to increase the efficiency of recovery and eventually reduce or eliminate this type of waste. Numerous initiatives have been started and post-shredder technologies have been developed (presented elsewhere). Most of these processing concepts for SR are combinations of conventional sorting techniques (e.g., sink-float, magnetic and eddy current separation, sieving). The major challenge is that a high proportion of SR needs to be recovered while residues for disposal have to be reduced.

Reviewed literature for this report has revealed studies that have applied sensor-based sorting of contaminants in plastic rich streams (usually from WEEE processing). The same techniques could be used for plastic rich streams generated from SR by conventional size splitting.

The single study conducted on SR (Dalmijn and De Jong, 2007) involved the use of X-ray sensors to separate metals, inert materials (e.g., glass, stones) and chloride/bromine-containing materials from a coarse fraction > 10mm. This fraction accounts generally for around 30% of SR, and although the study has demonstrated that 15-20% of SR could be transferred into a high calorific, relatively clean fuel (low levels of problematic substances) that could potentially substitute coal in energy production, the question is what happens to the remaining 80-85% of SR.

In another study (Boughton, 2007), after screening and removing the fine fraction, around 30% of SR (this % is highly dependent on the size distribution of particular SR used in the study) could be recovered into a high calorific fraction with sink-float techniques. Residual levels of problematic substances were still high enough to question its possible use as an alternative fuel in cement kilns.

The following list is an attempt to summarise why the reasons sensor-based sorting is not used for detection and sorting of problematic or unwanted materials in the treatment of SR:

- Sensor-based sorting systems can only be applied for relatively coarse fractions, typically >10mm, thus covering a relatively small proportion of SR waste; many problematic substances are generally distributed over all particle size ranges

- Sorting equipment costs have been unjustified relative to recovered materials or to the economic benefits brought by their use; however, the economy may change rapidly as an effect of changes in market price for recyclables or legislation (e.g., gate fee for recycling of SR)
- Alternatives like low-technology processing for/ or waste-to-energy applications represent available solutions that could be cost effective and cover a larger fraction of the SR waste stream
- Many of the techniques reviewed have not yet been developed into commercially available applications
- The material complexity and temporal variability of SR waste creates difficulties in sensor calibration as signals can be affected by fillers, various additives, plasticisers and reinforcing fibres

On the other hand, if high-value-added applications for SR will be mandated (e.g., recycling of plastics, clean alternative fuel), the sensor-based sorters are likely to be necessary in order to separate contaminants. In an alternative scenario, if complete destruction of BFRs is mandated by regulations, sensor-based sorting of BFR-containing particles would be economically justified to reduce BFR treatment costs.

Sensor resolution (smallest particle size detection), classification software and the efficiency of separation units are continuously improving due to technological evolution, e.g. some equipment is already able to sort particles down to 1 mm, and consequently a larger proportion of SR waste will become available to sensor-based sorting techniques. Furthermore, techniques that are still in development/research will become available in the near future.

For practical reasons the most effective method of improving SR waste quality and even quantity is to remove materials in the pre-treatment steps before the shredding process. The intensive shredding process based on hammer mills creates a large amount of fine material and any remaining (after manual pre-treatment in the case of ELV) hazardous substance-containing materials or components are being structurally destroyed and distributed over all resulting material streams. As a consequence of the sorting process for metals, the residue stream (SR) is then enriched with the majority of hazardous or problematic substances and materials.

The sorting processes in shredder facilities are usually optimised only for metal recovery; the inclusion of recovery for other type of materials (e.g., plastics, rubber, glass, textiles) could possibly improve the characteristics of SR waste and call for the use of more smart, sensor-based machines for sorting in shredder facilities.

Useful experience with electronic waste processing could maybe play a role in the future. In the case of WEEE, light shredding processes have been developed. Different types of shredding equipment can be applied to reduce the amount of fines and permit the removal of coarse particles including hazardous components by manual sorting. More intensive shredding is reserved for some of the fractions passing the manual sorters in order to achieve complete material liberation, especially for metals.

The same type of concepts might not be applicable in shredding of large items such as light metals scrap, ELV and white goods which constitute the input to most shredding facilities, however the development of shredding processes and materials separation should, together with design for recycling concepts, be the subject of more comprehensive research.

4. Assessment of applicability of PGNAA sensor technology on shredder residues

4.1 Introduction

As mentioned in Section 3.4.5, PGNAA sensors have been proved to be efficient in the sorting and analysis of waste material streams with the first sorters being implemented in large scale plants and undergoing testing. While the smaller sorters, using only one detector, can only characterise one object at a time, larger sorters with an array of detectors are able to make a two-dimensional determination of location of unwanted objects on the conveyor belt.

SR contain chlorine and bromine mostly originating from various types of plastics. Chlorine and bromine in SR are “problematic” substances when SR are used e.g. for energy production. Online detection of chlorine and bromine in SR may help solving the problem by, for example, enabling the removal of chlorine- and bromine-containing parts by sorting.

The PGNAA sensor technology seems to be a good candidate for identification of Cl/Br because:

- The method is non-contact and non-destructive.
- The method can detect several elements simultaneously in the whole volume of the analysed sample **if** the signals do not disturb each other.
- The method has a relatively fast response time; for large objects, the residence time can be less than 0.5 s, thus, the method is well suited for online measurement.
- The PGNAA sensor is relatively easy to scale up to handle large objects; FORCE Technology has built a sensor which can handle object size up to 1-2 meters.

Preliminary tests performed in this project have shown that the method is effective for the analysis of chlorine. Unfortunately, the tests did not give a positive result for bromine as it was shown that (i) bromine gives a relatively weak signal and (ii) the bromine signal is overlapped by the strong signal from chlorine. Consequently, the testing focused on detection of chlorine alone.

4.2 Materials and methods

4.2.1 Shredder residues

Representative samples of all process waste streams were collected over 20 working days at the STENA plant in Grenå (Section 2.2.1.2). After a series of mass reduction steps (using the long pile principle), about 100-150 kg of each waste stream was sent to DHI as the “laboratory sample”. At DHI, the laboratory samples were further mass-reduced using consecutive long-pile principle and 10 subsamples each filling the volume of a 3 l plastic bucket were generated for each of the following waste streams: SLF 0-60 mm, SLF >60 mm, SHF 0-100 mm (Table 4.1). These samples were sent to FORCE Technology to be tested in the PGNAA sensor.

No treatment other than mass reduction using the long pile was applied to the samples sent to FORCE.

Table 4.1 Amount of shredder residues (kg, wet) sent to FORCE for the PGNAA testing

Subsample	SLF 0-60 mm	SLF >60 mm	SHF 0-100 mm
1	1.66	1.12	2.1
2	1.55	1.17	2.05
3	1.36	1.04	1.31
4	1.59	0.8	2.04
5	1.5	1.18	2.19
6	1.49	1.18	1.78
7	1.45	1.05	1.59
8	1.50	1.02	2.2
9	1.36	1.48	1.68
10	1.50	1.02	2.33

4.2.2 PGNAA Measurements

The PGNAA sensor unit used for the test is FORCE Technology's own prototype unit which was designed for the characterisation and sorting of spent batteries. This unit has a measuring chamber with the dimension of 140 mm (height) x 200 mm (width) x 800 mm (length), which was well suited for the prepared samples; a sketch of the test rig in shown in Figure 4.1.

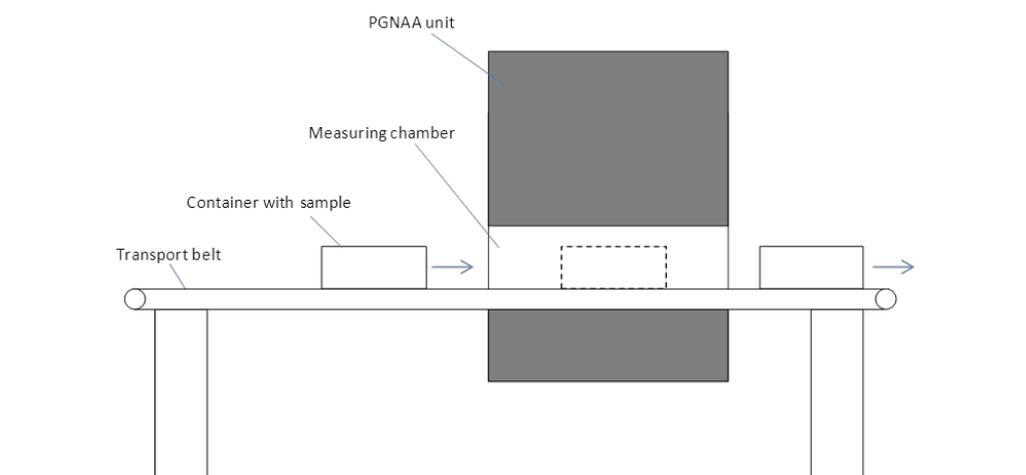


Figure 4.1 Illustration of the PGNAA sensor test rig (FORCE Technology).

For the measuring, a carton box with the dimension of about 250 mm (length) x 185 mm (width) x 50 mm (height) was used as the container for the samples. For each measuring, the carton box containing the sample was manually pushed into the middle of the measuring chamber (this can also be done by starting the conveyor belt) and stayed there for about 30 seconds for measuring. Each sample was measured in two batches as the carton box was not big enough to contain the whole sample. The concentration of chlorine was calculated by dividing the measured chlorine weight by the total weight of the sample⁵⁴.

⁵⁴ The chlorine content was determined by chemical analysis in the mixed sample of each SR stream, thus giving the average chlorine content in each SR stream

4.2.3 Calibration of the PGNAA unit for detection of Cl

The γ -ray count rate of a PGNAA sensor system is a multi-variable function of the elemental composition, density, water content and geometry of the material. Calibration is thus necessary for measuring the compositions of different materials. The calibration strategy will depend on the composition of the material itself.

For the purpose of measuring chlorine content in SR, calibrations were carried out with five different materials. The parameters obtained with these 5 materials were then used for the measuring of chlorine in SR samples. In order to find the best parameter combination for the purpose, 4 models were constructed with 2, 3, 4 and 5 parameters, respectively. The calibration materials involved in the different models were as follows:

Calibration material	NH ₄ Cl	PE	Graphite	Fe	Cu
2-parameter model	X	X			
3-parameter model	X	X	X		
4-parameter model	X	X	X	X	
5-parameter model	X	X	X	X	X

For each measurement, the weight of chlorine in the material that is in the measuring channel can be determined by using one of these 4 models.

4.2.4 Results of PGNAA sensor testing

The chlorine content of 3 x 10 samples (Table 4.1) was measured using the PGNAA sensor unit. During the test runs it was discovered that the average chlorine content determined chemically for the mixed samples may not give reasonably precise information with respect to the actual chlorine content in the individual subsamples measured by the PGNAA sensor unit. It was therefore agreed that, for the purpose of verification of the PGNAA results, 4 samples from the series of SLF 60-100mm were analysed for their chlorine content by using chemical methods after they were measured by the PGNAA unit. The results of the three series, SLF 0-60 mm, SLF 60-100 mm and SHF 0-100 mm are shown in Figure 4.2, Figure 4.3, and Figure 4.4, respectively. In each figure, the chlorine concentrations calculated using the 4 models and the average chlorine content of the same series analysed by chemical methods are shown. In Figure 4.3, the chlorine contents of the 4 *extra* samples in the series SLF 60-100 mm analysed by chemical methods are shown as well.

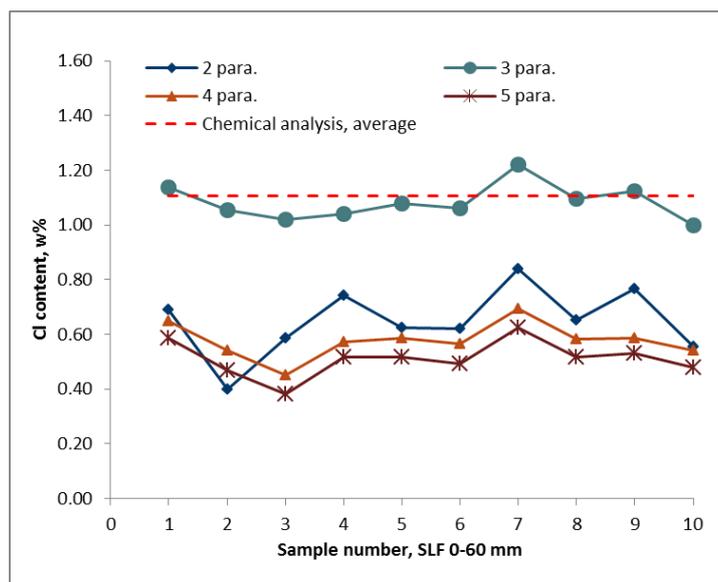


Figure 4.2 Chlorine content in SR(SLF 0-60 mm) analysed by PGNAA and chemical method. Solid lines: PGNAA results with different models; dashed line: average chlorine content analysed by using chemical methods

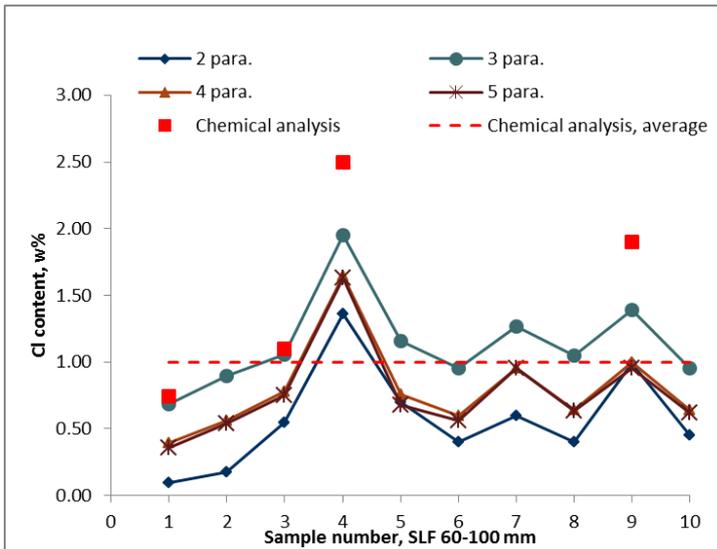


Figure 4.3 Chlorine content in SR (SLF >60 mm) analysed by PGNAA and chemical method. Solid lines: PGNAA results with different models; dashed line: average chlorine content analysed by chemical methods; square dots: chlorine content of individual samples analysed by chemical methods

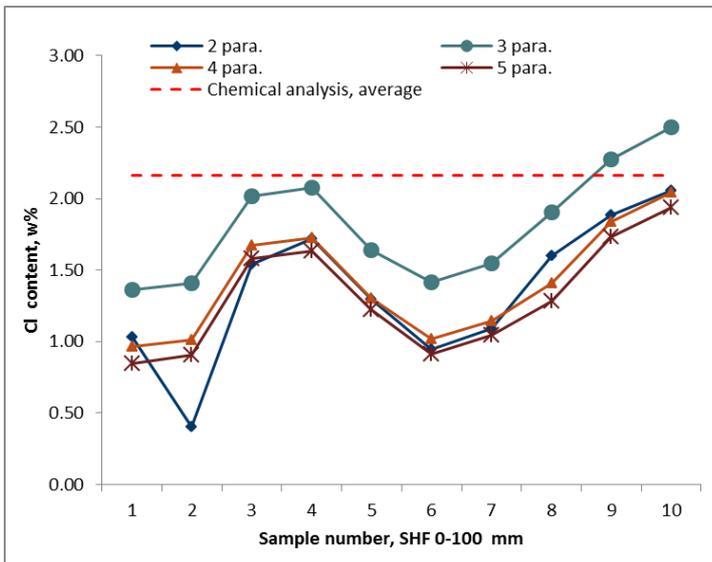


Figure 4.4 Chlorine content in SR (SHF 0-100 mm) analysed by PGNAA and chemical method. Solid lines: PGNAA results with different models; dashed line: average chlorine content analysed by chemical methods

The results shown above demonstrate that model calibration methods have great influence on the outcome of the PGNAA measurements. For the measurement of chlorine in SR samples the PGNAA sensor results based on the three-parameter model is closer to the chemically analysed results than the other models. This is clearly reflected by the relatively closer match between the three-parameter model PGNAA sensor results and the chemically analysed results (both the average (in all the three figures) and the individual analysis results (Figure 4.3)). However, even with the 3-parameter model, the deviations of the PGNAA sensor results from the chemically analysed results, which is assessed to be about $\pm 0.22\%$ for the average concentrations and about $\pm 0.38\%$ for the 4 individually analysed samples, are still quite large. Chlorine contents seem to be underestimated by the PGNAA sensor at high chlorine concentrations; especially with the 2-, 4- and 5-parameter mod-

els. The large deviations of the PGNAA results are related to the inhomogeneity of SR, the calibration method and the non-uniform⁵⁵ neutron field in the used PGNAA unit.

Nevertheless, for the purpose of qualitative characterisation, the existing design of the PGNAA sensor is considered good enough. The measuring deviations may be further reduced by improving the calibration method. For quantitative analysis the PGNAA sensor needs to be modified to produce a more uniform neutron field in the measuring chamber.

4.3 Sorting of SR with PGNAA sensor

4.3.1 Sample preparation and procedure for sorting test

Following the measurements of chlorine content, the PGNAA sensor unit was tested for its capability of sorting chlorine-containing items in SR. For this purpose, some of the large items contained in SR of the test series SHF 0-100 mm were manually selected for testing. These items were placed on the transport belt one by one and passed the PGNAA sensor continuously at a belt speed of about 0.088 m/s. In practice the belt speed can be adjusted to be faster or slower depending on the acceptable sorting quality and the design of the PGNAA sensor. Judged by the PGNAA sensor signal output which is displayed on the connected computer screen, the items coming out of the PGNAA sensor unit were manually picked up and put into two separate plastic buckets, one for chlorine-free items and one for chlorine-containing items.

4.3.2 Results of sorting test

As shown during the sorting test, the PGNAA sensor is quite sensitive to chlorine and can detect it in relatively small items. Figure 4.5 shows two chosen items, one chlorine-free and one chlorine-containing.



Figure 4.5 SR items used for demonstration of the sensitivity of the PGNAA sensor. Left: chlorine-containing material (16.8 g); Right: chlorine-free material (123 g)

In Figure 4.6 the PGNAA sensor signal output for these two items is shown. Clearly, the peak for the small (only 16.8 g in weight) and chlorine-containing item is sharp, well defined and easy to identify, while no special change in the signal can be seen with the big and chlorine-free item which passes through the PGNAA sensor about 30 seconds before the chlorine-containing item.

⁵⁵ For quantitative analysis a uniform neutron field is required.

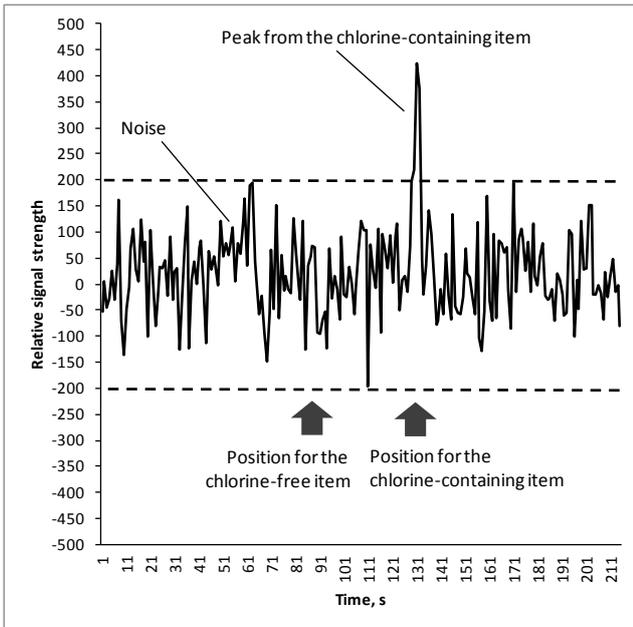


Figure 4.6 PGNAA sensor signal output for demonstration of the sensitivity of the PGNAA sensor to chlorine in shredder residue.

All hand-picked SR items were run through the sensor yielding two material fractions: chlorine-free fraction and chlorine-containing fraction (Figure 4.7). The majority of the tested items were chlorine-free plastic.



Figure 4.7 SR items sorted with PGNAA sensor. Left: chlorine-free items; Right: chlorine-containing items (Force Technology).

4.4 Applicability of the PGNAA sensor on SR

For the purpose of qualitative characterisation – as required in this project – the existing design of the PGNAA sensor is considered good enough. The measuring deviations may be further reduced by improving the calibration method. For quantitative analysis the PGNAA sensor needs to be modified to produce a more uniform neutron field in the measuring chamber, while the calibration method needs to be improved to handle the inhomogeneity of SR.

Based on the results, it can be concluded that the PGNAA sensor developed by FORCE Technology is capable of detecting chlorine in SR with short response time, and may therefore be used for appli-

cations like on-line detection of chlorine-containing fractions of SR; i.e., for the purposes of sorting and/or characterising SR with respect to chlorine-containing items (e.g., PVC, PCB⁵⁶).

The PGNAA sensor can be scaled up to handle objects up to 1-2 m on transport belt of reasonable sizes. At the same time, the high sensitivity of the PGNAA sensor makes it possible to sort small items down to the size of a few cm or a few grams. Thus, the coarse part of SR with the size over a few cm can be “cleaned” for chlorine-containing items by using the PGNAA sensor sorting technology. In turn, this will eliminate the chlorine-induced problems for recycling or energy utilisation of this fraction of SR. With a proper set-up, the PGNAA sensor sorting technology may be able to sort the fine part of SR into two streams (chlorine-rich and chlorine-poor), if there is a large variation in the chlorine concentration of the fine SR fraction.

⁵⁶ Rather than measuring PCB (via detection of chlorine) in mixed SR which have chlorine content above 50 mg/kg TS, the PGNAA sensor could identify PCB (via detection of chlorine) in some pre-treated material streams with presumably low chlorine content e.g. “metals”.

5. Environmental assessment of different treatment options for shredder residues

5.1 Life cycle assessment in general

The Society of Environmental Toxicology and Chemistry (SETAC) defines Life Cycle Assessment (LCA) as “a process used to evaluate the environmental burdens (or benefits) associated with a product, process, or activity by identifying and quantifying energy and material used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing, extracting and processing of raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal”.

In the context of this study, LCA should be seen as a tool which – when interpreted correctly – helps identifying potential impacts (both positive and negative) of different actions and process set-ups related to management of SR or waste management in general. Without LCA, it is more difficult to evaluate whether a reduction of one type of impact may result in an increase in another type of impact. However, it should be stressed that LCA has several limitations. The main weakness is that despite the availability of an ISO standard on LCA, not all LCA studies are conducted using that standard. In addition, assumptions and boundaries can be defined differently in different assessments. Thus, LCA results are generally study-specific and not directly comparable to other studies. In addition, very little inventory data may be available for some management options (typically processes still being under development) and best estimates are then required.

In the following text the results of few LCA studies focused on management of SR are discussed.

5.2 Case studies of LCA of different treatment options for (A)SR

5.2.1 USA

In 2006, Boughton and Horvath published an LCA focused on assessment of human health and environmental trade-offs of resource recovery options compared to the (then) current practice of SR landfilling in the USA. The alternative management options were chosen to include the range of technologies tested for SR (in the U.S.), while no upstream options, such as vehicle or appliance redesign or increased dismantling, were studied. The alternative management options compared were (i) using SR as feedstock in cement manufacturing, (ii) increased material recovery for recycling, and (iii) conversion to liquid fuels using a low temperature water-based hydrolysis process (Boughton and Horvath, 2006).

It was concluded that SR recovery as a fuel and mineral supplement in cement manufacturing appeared to be the most advantageous and practical near term option. However, this option should ideally include the recovery of recyclable materials with the highest value, use of residual organic materials to produce fuels or as a fuel, and recovery of mineral value by cement manufacturers (e.g.,

Si, Ca and Al present in SR could substitute some of the mineral feedstock in cement production), followed by landfilling of residuals. Furthermore, it was made clear that SR has substantial energy, material and mineral value. Consequently, rather than “waste” it should be seen as a commodity with potential uses. Policy makers should support the recovery of SR as well as the facilities interested in using these materials. Benefits would be realised by providing incentives for SR recovery and by supporting markets for SR-derived products. However, regulatory barriers inhibiting environmentally sound and economically sustainable recycling may need to be addressed (Boughton and Horvath, 2006).

5.2.2 Germany

In the SEES project (Sustainable Electrical & Electronic System for the Automotive Sector), co-funded by the European Commission within the Sixth Framework Programme 2002-2006, an LCA including “post-shredder treatment with advanced ASR recycling” was carried out (Greif et al., 2005).

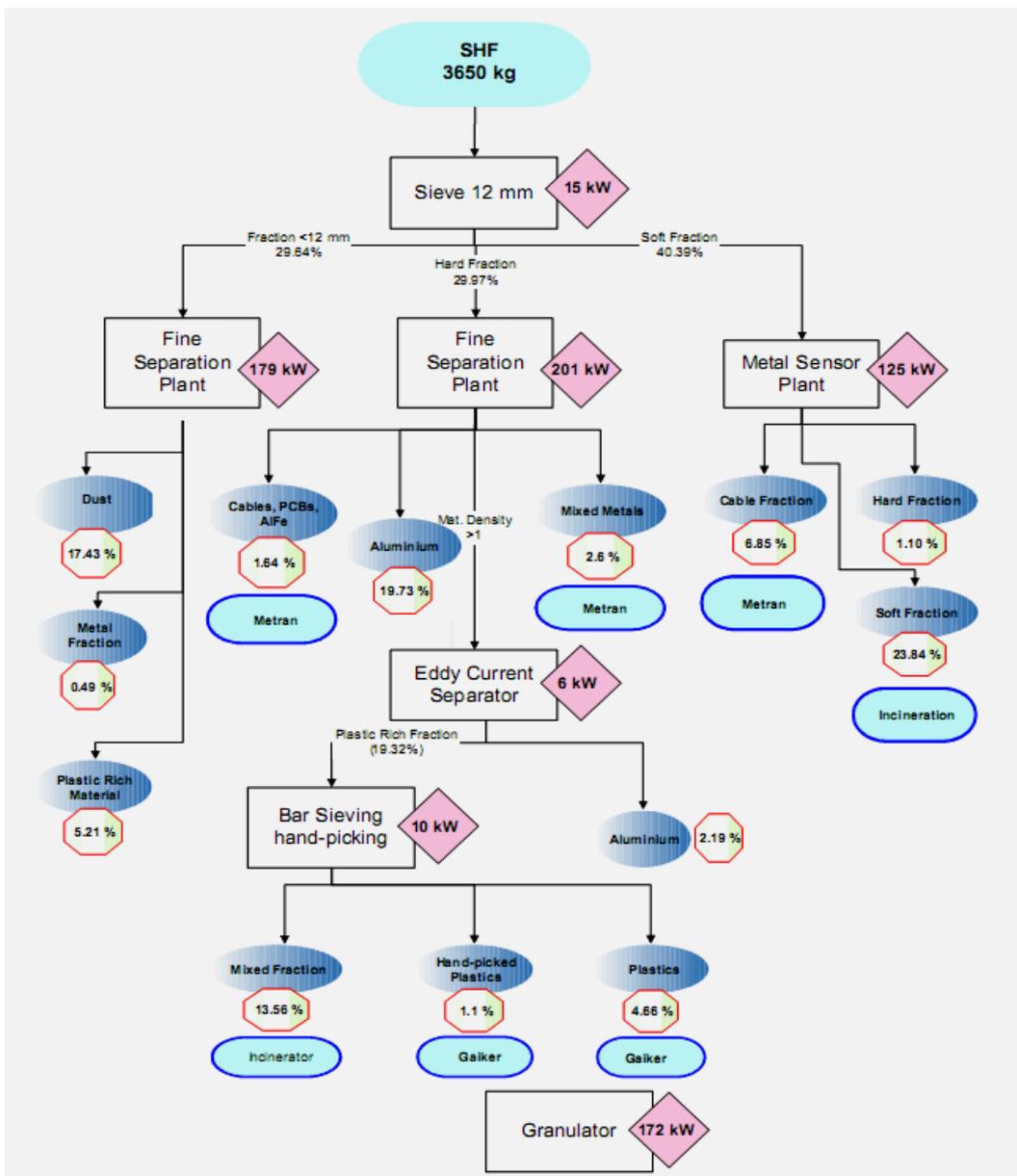


Figure 5.1 Treatment of the heavy shredder fraction (Greif et al., 2005)

The process scheme for the shredder heavy fraction (SHF) and the shredder light fraction (SLF) are shown in Figure 5.1 and Figure 5.2, respectively. It could be seen that there were numerous material fractions generated from the shredder heavy fraction, including mixed metals, aluminium, ferrous/non-ferrous metals (containing PCBs and Al/Fe) and a plastic-rich fraction. The plastic-rich fraction (density >1 g/cm³) is sorted by eddy current to regain aluminium and further plastics which would be successively sorted by bar sieving and hand-picking into three further plastic fractions (mixed, hand-picked and plastic). The SLF undergoes a sieving process (12 mm) thus obtaining three fractions: a fraction smaller than 12 mm which later on enters the fine separation plant, a soft fraction which is incinerated and a hard fraction. The material <12 mm and the remaining plastic and foam from the hard fraction treatment are processed in the fine separation plant, generating dust, metals and a plastic-rich fraction (Figure 5.2).

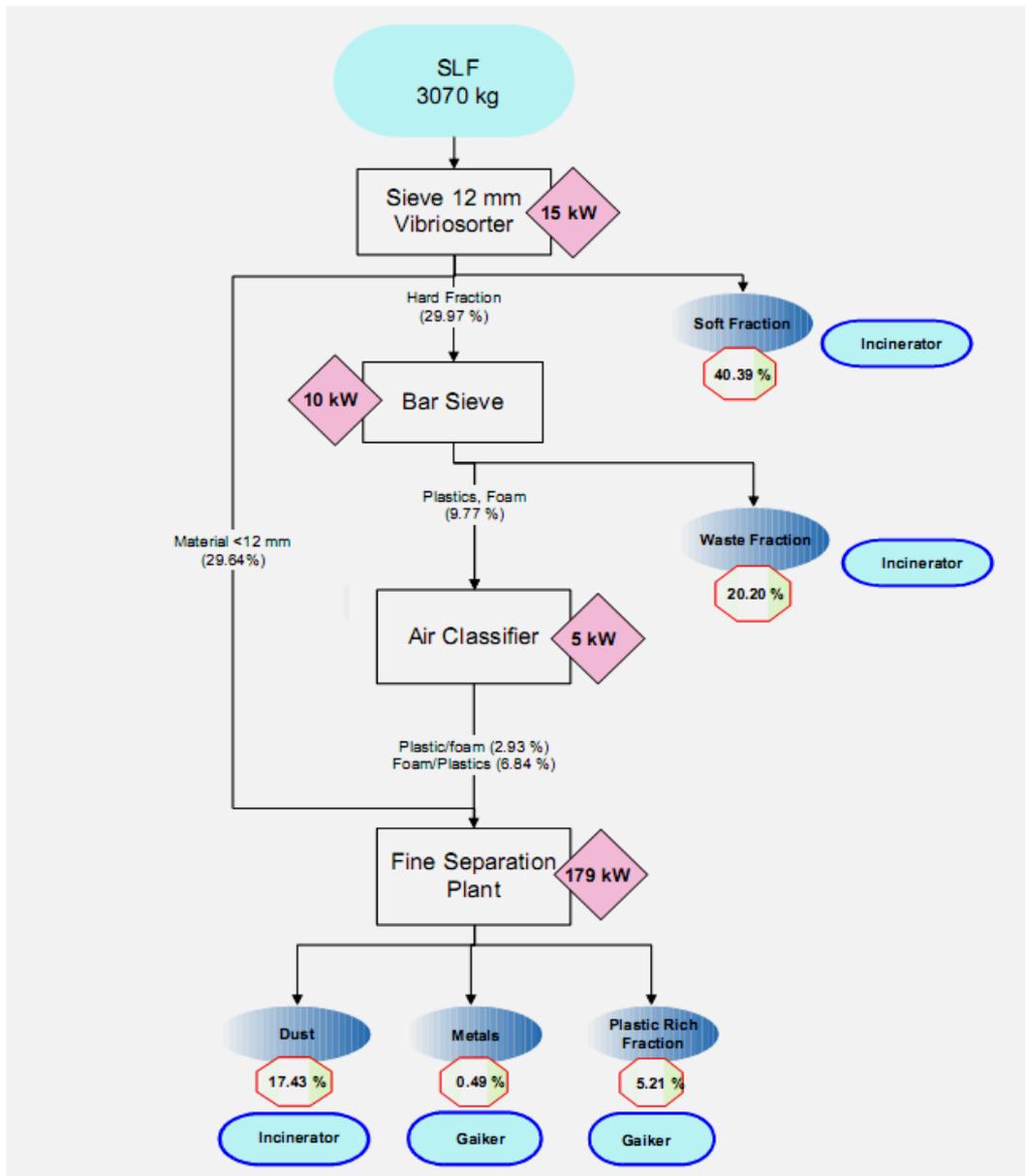


Figure 5.2 Treatment of the SLF (Greif et al., 2005)

One conclusion was that the material production, namely the production of copper, has a strong influence (production related impacts) on the overall LCA results. Accordingly, recycling of copper

has a major influence on the environmental and economic performance. For more detail please refer to the original study (Greif et al., 2005).

5.2.3 Italy

Recently, Ciacci et al. (2010) used LCA to compare several ASR management options, which were identified as “the most common management methods” in Italy (Table 5.1).

Table 5.1 ASR management strategies used in LCA (Ciacci et al., 2010)

ASR management scenario		Scenario description
1	Landfilling	ASR generated from an average Italian shredding plant is disposed of in landfill
2	Further metals recovery	Scenario 1 expanded with recovery of nonferrous metals from ASR; the residual fraction is landfilled
3	Thermal treatment with energy recovery	Scenario 2 is expanded with co-combustion of the residual fraction with MSW with energy recovery
4	Advanced material recovery and incineration with energy recovery	Scenario 2 is expanded with plastic separation; the remaining fraction is sent to co-combustion with MSW with energy recovery
5	Feedstock recycling	Scenario 2 is expanded with gasification generation syngas, which is subsequently converted to methanol

The functional unit used in the LCA study was 1,000 kg of ASR; the composition of the material is shown in Figure 5.3.

Plastics	kg	Metals and alloys	kg	Fines	kg	Textiles	kg	Rubber	kg
ABS	33.6	Aluminium	70.0	Paints	56.0	Natural	65.0	EPDM	140.0
PP	86.4	Copper	4.4	Glass	42.0	Synthetic	65.0		
PE	19.2	Steel	5.9	Sand	42.0				
PUR	168.0	Iron scrap	26.5						
PVC	67.2	Lead	0.4						
PA	28.8	Brass	2.8						
Other plastics	76.8								
Total	480.0	Total	110.0	Total	140.0	Total	130.0	Total	140.0

Figure 5.3 Composition of ASR used in LCA (Ciacci et al., 2010)

Impacts resulting from environmental loads of each scenario were quantified using the ecoindicator'99 method (PRé Consultants B.V., 1999) and for the following nine impact categories: global warming, carcinogens, respiratory diseases from organic and inorganic substances, acidification and eutrophication effects, ecotoxicity, land use, mineral and fossil fuels depletions. According to this method, results were added up yielding three end point damage indicators: Human Health, Ecosystem Quality and Resources Depletion. For further details and justification please refer to the original study (Ciacci et al., 2010).

Overall, the authors concluded that:

- landfilling of ASR (i.e., Scenario 1) was the worst option due to the impacts related to disposal of often hazardous waste

- though showing significant advantages over landfilling, ASR co-incineration without recovery of plastic should not be considered as a long-term alternative since this end-of-life strategy does not achieve the 85% recycling target for ELVs by 2015 (European Commission, 2000); in this study a recycling rate of 82.2% was reached
- Scenario 4 and Scenario 5 came out as the best options considering the environmental impacts. Moreover, they allowed for recycling rates of 86.9% and 85.8%, respectively, thus scoring as the two best management options among the five options considered.

It should be mentioned here, that under Danish conditions the availability of MSWI and the fact that all Danish plants are producing heat, power or both would most likely favour co-incineration with MSW (i.e., Scenario 4).

In another Italian study (Passarini et al., 2012), LCA was applied in order to estimate implications of different *future* scenarios, which were forecasted to happen due to larger use of polymers and non-ferrous metals (mostly aluminium) in today's car manufacturing as compared to car manufacturing in the past. In Scenario A, an increase in light material use such as polymers and non-ferrous metals (especially aluminium) in new vehicle production was predicted, while in Scenario B an improved polymer separation and recycling by reducing the different kinds of plastics used in cars, according to an eco-design-oriented strategy was considered. The basic scenario was the current situation in ASR management in Italy. Landfilling, incineration, mechanical recycling, and chemical recycling were considered as possible waste treatment options in the LCA.

The authors concluded that it is the innovative yet small-scale recycling plants that achieve the lowest impacts due to the combination of material and energy recovery. In addition, other benefits were gained from diverting large amounts of waste from landfills.

5.2.4 Denmark

Hansen et al. (2012) performed an LCA study for three SR management options (Table 5.2). In the following text the main conclusions are presented; for full details refer to the original study.

Table 5.2 SR management scenarios (Hansen, et al. 2012)

SR management option		Scenario description (for details refer to the original study)
A0	Landfilling	All SR are landfilled (reference scenario)
A1	Recovery of materials and energy (State-of-art)	SR are sieved (5 mm); <5 mm fraction is landfilled, while >5 mm fraction is processed by: (i) magnetic separation (recovered Fe) (ii) eddy current separation (recovered Al, Cu, brass) (iii) sensor-based separation (EMS + NIR) of Cu, Zn, Pb and stainless steel (iv) air classifier in order to remove paper and plastic used for production of RDF for use in power plants The residual material is landfilled.
A2	Recovery of materials and energy	SR are sieved (5 mm); <5 mm fraction is landfilled, while >5 mm fraction is processed by: (i) magnetic separation (recovered Fe) (ii) eddy current separation (recovered Al, Cu, brass) (iii) sensor-based separation (EMS + NIR) of Cu, Zn, Pb and stainless steel The residual material (includes plastic and paper) is co-incinerated in MSWI plant.

It was shown that both alternative scenarios to landfilling (A1, A2) result in significant savings in greenhouse gas emissions. This is because (i) the energy content of SR is utilised for production of heat and electricity (thus substituting energy which would otherwise need to be produced), (ii) emissions of greenhouse gas from landfills are avoided and (iii) recycling of iron, aluminium and steel “saves” emissions of greenhouse gases related to energy consumption in the production of/from the virgin material. Thus, in the overall picture, it was the avoided production of electricity and heat and the avoided use of virgin materials that were the most important factors.

Scenario A2 showed the smallest contribution to the global warming potential from the three alternatives. This was caused by the fact that no material with favourable heating value was lost in the air-classifier and all energy was utilised to produce heat and electricity. This scenario was also the most “environmentally friendly” in the other non-toxicity related impact categories (e.g., ozone depletion, acidification, eutrophication, etc.).

Finally, both alternative scenarios resulted in the same amount of “saved resources” (metals), while the reference scenario (landfilling) resulted in zero-savings (i.e., landfill-mining was not considered).

5.3 LCA-based recommendations

From the few examples given above it could be seen that different LCA studies provided different recommendations. However, regardless the treatment options considered, all studies have identified landfilling of SR as the worst management option. This is in a nutshell due to the fact that: (i) the energy content of SR is not used and significant emissions of greenhouse gases related to energy production are thus not avoided, (ii) materials which can be re-used are deposited thereby not allowing for substitution of virgin materials in production, (iii) potentially hazardous materials are deposited and related impacts from leaching of metals and organic compounds to soil and groundwater must be considered, and (iv) emissions of greenhouse gases from landfilled materials must be considered.

6. Conclusive remarks and recommendations

A number of questions concerning the feasibility of the removal of problematic substances from shredder residues have been addressed in this study. Based on the results of the study, the following answers can be given to some of these questions:

Which are the “problematic elements” with respect to resource recovery from shredder residues?

Based on available composition data (both international and Danish) it could be concluded that “heavier” hydrocarbons (e.g. above C16-C20), Pb and PCB7 may be regarded as “problematic” with respect to resource recovery from shredder residues (SR) simply because they cause SR to be classified as hazardous waste, thus making any further treatment (outside the process plant) more difficult if not impossible due to strict legislations. At some occasions, the content of Ni, Co and Cr may be considered problematic if their total measured content was *not* related to the most likely metallic form (e.g., pieces of stainless steel).

Is it possible to identify individual sources of the “heavier” hydrocarbons in shredder residues and if so, should source separation prior to the shredding process be considered?

From the available data it is not possible to identify contamination sources of the “heavier” hydrocarbons as these are typically found to exceed the limit value for hazardous waste in all size fractions of SR. The presence of heavier hydrocarbons indicates contamination with diesel and/or oil. It would thus appear that an improved collection and/or screening of materials prior to the shredding process may be beneficial with special focus on ELVs, engines and appliances containing engines (e.g., lawn mowers). However, contamination with hydrocarbons is generally not causing any technical problems with respect to the shredding process and recovery of metals; it is mostly causing an economic impact related to creating/depositing of hazardous waste. If source separation of TPH-polluted materials was considered by the shredder plant operator prior to the shredding, it would be an economic evaluation of two scenarios: (a) more metals recovered (though possibly polluted with TPH) while the shredder waste would exceed limit values for TPH as well; or (b) less metals recovered while the shredder waste would *maybe* comply with the limit values for TPH. At the same time, it may be argued that although a part of the *measured* contamination certainly comes from diesel and oil, another part of the *measured* contamination may be ascribed to heavy hydrocarbons present in *solid* matrix (e.g. pieces of rubber, tires etc.), the toxicity of which is rather questionable.

Is it possible to identify individual sources of Pb in shredder residues and if so, should source separation prior to the shredding process be considered?

Lead concentrations in SR have been relatively constant over the years. Furthermore, Pb is used in a number of applications including alloys, pipes, pigments in older paints, etc. which makes source separation fairly impossible. Even if possible, the economic implications of such separation would be very unfavourable for the shredder plant operator (see previous comment). It is more likely that an improved metal recovery process may help to lower Pb content of SR as hand-sorted samples of SR were shown to comply with the limits values for Pb.

Is it possible to identify individual sources of PCBs in shredder residues and if so, should source separation prior to the shredding process be considered?

Based on the available data it is not possible to identify the sources of PCBs unambiguously. It may, however, be plausible to consider several fractions of processed metal scrap as “PCB free” or at least “almost PCB free”. These fractions include post 1986 household appliances (white goods), ELVs and most likely also a large fraction of the scrap metal collected at the municipal recycling stations. Combined, these fractions represent about 50% (assumed) of scrap metal processed by the shredding plants and it thus seem logical to focus on the remaining 50% which includes scrap metal from numerous industrial applications (large tanks, cranes, metals structures, process plants etc.) and last but not least, old ships. Moreover, literature data indicate that the use of PCB-containing paints as anti-corrosion protection of metal structures in a number of industrial application between 1950s and 1970s may be one of the major (yet unaccounted for) sources of PCBs to the smelters processing recycled iron/steel.

The same economic evaluation as for hydrocarbons and Pb applies to PCBs. If PCBs were found (see below) to be associated with a discrete source of a relatively small volume it may be beneficial to source separate this material prior to the shredding process. If, however, PCBs were associated with a large fraction (volume-wise) of processed metal scrap (e.g., industrial structures painted with PCB-containing paints) then separation prior to the shredding is not feasible for economic reasons.

Could current sensor-based technology be used to target “critical elements” in incoming material thus facilitating source separation prior to the shredding process?

Extreme heterogeneity of incoming material will pose significant problems for today’s sensor systems and it is – in the near future – highly unlikely that incoming material will be scanned continuously for the presence of the “critical elements” prior to the shredding. If needed, however, the presence of PCBs in incoming material can be assessed by e.g. hand-held XRF detectors which are commercially available and fast (analysis takes seconds to minutes). Note that XRF does not measure PCB directly, it evaluates the presence of PCB based on measurement of chlorine. Again, rather than a continuous scanning of all incoming material the evaluation based on XRF would be carried out as spot-checks or fraction-checks (e.g., painted scrap, spot contamination with fluids).

Could the PGNAAs sensor developed by FORCE Technology be used to target “critical elements” in incoming material thus facilitating source separation prior to the shredding process?

Although the PGNAAs sensor is certainly promising technology, its use within the shredder industry is hindered by the same limitations as those applying to the other systems – in particular by the extreme heterogeneity of the incoming/processed material. At the moment, the sensor is capable of detecting chlorine qualitatively in pre-sorted samples of SR (i.e., after the shredding process), while it is assumed that improved calibration will enable it to better cope with SR’s heterogeneity. With a proper set-up, the PGNAAs sensor may be able to sort and remove the chlorine-containing objects, thus creating two material streams (one with a higher and another with a lower chlorine content). This application would be suited for e.g. generating of “low chlorine” RDF.

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Shredder residues: Problematic substances in relation to resource recovery

Detailed characterisation of shredder residues shows that certain substances in the waste may present a barrier for efficient and environmentally sound utilization of the resources. Problematic substances are identified and the possibility of source-separation of the problematic substances was assessed.



Miljøministeriet
Miljøstyrelsen

Strandgade 29
DK - 1401 København K
Tlf.: (+45) 72 54 40 00

www.mst.dk