



Danish Ministry of the Environment
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Nanomaterials in waste

Issues and new knowledge

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Nanomaterials in waste
Issues and new knowledge

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Sources must be acknowledged.

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Preface

This project has been carried out based on a tender from the Danish EPA for a project set out to cover two elements:

- i) Overview of the present knowledge and knowledge gaps in relation to nanomaterials and waste (identifying general safety and technical issues)
- ii) Recommendation of issues relevant for further studies in relation to the presence of nanomaterials in the waste and recycling cycles.

The project has been carried out by COWI A/S in cooperation with:

- The **Technology and Society Lab** at Empa - Swiss Federal Laboratories for Materials Science and Technology, an interdisciplinary research and services institution for material sciences and technological development within the ETH Domain
- **VTT** (Technical Research Centre of Finland).

The project has been carried out in the period from November 2013 to September 2014. This report forms part of a series of projects regarding nanomaterials in Denmark (“Better control of nano”) commissioned by the Danish Environmental Protection Agency (EPA).

The contact persons at the Danish EPA are Katrine Smith and Flemming Ingerslev.

Executive summary

The project aims to give

- i) An overview of the present knowledge and knowledge gaps in relation to nanomaterials and waste (identifying general safety and technical issues), and
- ii) Recommendations of issues relevant for further studies in relation to the presence of nanomaterials in the waste and recycling cycles.

The focus of the project is on consumer products ending up as waste and not production waste, and on product groups that may end up in different relevant waste streams. This focus includes addressing the nanomaterials typically contained in those product groups. In general, focus is on product types and waste streams, where information is at all available. In relation to incineration, it is considered more relevant to look at the overall load and fate of a number of nanomaterials rather than product/product categories. In general, the project focuses on engineered nanomaterials, i.e. nanomaterials manufactured/designed to provide a specific function in a product. Further, the project generally considers nanomaterials in the meaning of the recommended EU definition¹. In practice however, most of the investigated information sources do not define nanomaterials, and thus all identified information sources referring to nanomaterials in waste have been included.

Waste products from wastewater treatment are out of the scope of the project.

The project has collected information on waste types and nanomaterial content, generally given as a nanomaterial being present without information on concentration, and on how nanomaterials may be affected in the waste handling system, e.g. incineration, landfill and recycling. Little information is available on the flow of nanomaterials in organic treatment processes and their potential impact hereon.

In general, there is a limited amount of studies available regarding the fate of nanomaterials in the waste system. These studies only cover a limited number of products and nanomaterials, and care should of course be taken when trying to generalise the findings. More fundamental studies are also needed on the fate of nanoparticles. This report is a preliminary overview of the subject with the aim of pinpointing areas with need of further investigation.

Based on the accumulated information in the study, a matrix between major waste streams and most commonly mentioned nanomaterials can be set up, see Table 1. Paper is not included, since there are (at least at present) only few nanomaterials related to paper and then mainly to ink, which will primarily end up as a wastewater issue, which is out of the scope of this project.

It has not at present been possible to focus this study on the amounts of nanomaterials potentially entering the waste system as a function of the amount of nanomaterials used in the relevant types of products in Denmark, since the studies of this were not finalised sufficiently early to be included.

¹ COMMISSION RECOMMENDATION of 18 October 2011 on the definition of nanomaterial. 2011/696/EU. OJ L 275/38.

TABLE 1
MOST COMMON COMBINATIONS OF WASTE TYPES AND NANOMATERIALS

Waste type	Common nanomaterials
Metal	CNT, nano-SiO₂, nano-Ag
Plastic	CNT, nano-SiO₂, nano-TiO₂, nano-clay
Textiles	CNT, nano-Ag, nano-SiO₂, nano-TiO₂
WEEE	CNT, nano-Ag, nano-SiO₂, nano-TiO₂, nano-ZnO
ELV	CNT, nano-SiO₂, nano-TiO₂
Tires	CNT, nano-SiO₂, nano-clay
Construction & Demolition waste	CNT, nano-SiO₂, nano-TiO₂, nano-ZnO, nano-clay, nano-CeO₂

For incineration, the general agreement is that the nano-inorganics, TiO₂, ZnO, and Ag will end up primarily in the slag and to some degree in the filter ash, where the latter is primarily exported in Denmark. Only small amounts are emitted with the off-gas from the waste incinerators. CNT is assumed (and shown in a study) to be destructed, if the incinerator temperature is sufficient at all times. Any CNT not destructed is assumed also to end up in the slag.

Since the great majority of the slag is recycled in Denmark after sorting and crushing, there is a potential both for occupational health issues related to the processing of the slag and an environmental issue e.g. related to potential leaching of the nanomaterials, when the slag is used in road construction and similar.

If waste containing nanomaterials is landfilled, e.g. for non-recyclable construction waste and shredder waste, there is a potential for leaching of the nanomaterials from the waste to the leachate. However, landfill conditions typically enhance agglomeration and reduce the mobility of nanoparticles. Any organic acids in the leachate are shown to reduce the agglomeration of CNT. A single study of the potential diffusion of CNT through a HDPE membrane showed that this did not take place.

Nano-Ag was shown to inhibit anaerobic degradation, if the content was relatively high; whether this effect is specifically related to the nano-properties could be questioned. Composting of nanocellulose was feasible, and no adverse effects were observed.

For recycling, effects can be divided into three types:

- Occupational health effects in connection with the recycling processes themselves.
- Environmental impacts related to the treatment of residue from the recycling processes, which will end up either in incineration, landfill or sewage treatment, where the above statements apply.
- Introduction of residual nanomaterials into products containing recycled material, the effect of which is difficult to assess in general.

For the occupational health issues, studies related to similar processes as the ones used in recycling have shown that inflammatory effects from dust containing nanomaterials can occur, although it is sometimes not possible to distinguish these effects from the effects of dust from materials not containing nanomaterials. In any case, this points to the importance of assuring sufficient protection for workers when working with recycling of waste that may also contain nanomaterials.

A specific issue is the large amount of construction waste being recycled in Denmark. At present, there is little information as to the amount of construction material containing nanomaterials being used in Denmark or on the potential issues related to emission of nanomaterials from these products during a recycling process. Some of the issues mentioned above would also apply here, and one should note that the recycling processes carried out for construction waste are often carried out partly or entirely outdoors which may in principle give rise to environmental emissions of nanomaterials from these processes apart from the potential impact on workers. Also, due to the high degree of use of recycled construction material in road construction and similar, the potential leaching of nanomaterials from the recycled products should be assessed.

Another specific issue is the recycling of tyres. In Denmark, a very high percentage of tyres is recycled, and the granulated material is used as filler on artificial grass on football fields and for rubber tiles and carpeting used on sports arenas (also indoors) and on playing grounds for children. Potentially, the presence of nanomaterials in the tyres could lead to leaching of nanomaterials from the recycled products.

An evaluation of products containing nanomaterials with respect to the present (and incomplete) knowledge about their effects on human health and the environment, in combination with the potential content of nanomaterials in different products, could not exclude that some of the products would be characterised as hazardous waste.

An evaluation of whether the presence of nanomaterials could improve or worsen the recycling technology has been requested. This question is not possible to answer with the present available information.

The main possibilities of exposure to nanomaterials affecting occupational health in recycling processes for waste that contain nanomaterials may be:

- Exposure to fine or ultrafine dust containing free nano-objects emitted during transport, sorting, shredding, grinding or pouring of the waste containing nanomaterials
- Exposure to nano-objects in liquid media (water, solvents) due to cleaning or rinsing of the products before mechanical recycling; also exposure to contact with nano-objects on cleaning cloths from maintenance and cleaning of recycling equipment.

The following technical processes could thus give rise to workplace emissions of nanomaterials:

- Collection and sorting (dust)
- Shredding (dust), applicable to metals, plastic, textiles, WEEE, construction and demolition waste, End of Life Vehicles (ELV), tyres
- Pulping of waste paper (aerosols)
- Re-granulation of plastic (dust).

The few studies carried out as yet, primarily related to production processes for products containing nanomaterials, indicate that occupational exposure may be reduced through control techniques similar to those used in reducing exposure to aerosols and dust in general and by varying the handling procedures. Thus it might be worth investigating in more details whether appropriate risk management is in place and used at recycling operations etc.

For consumer products, uses of nanomaterials that could improve longevity could be:

- Use as coatings
- Improvement of function and thus reduction of the need for repair (where a new item may be purchased instead).

The actual importance of this is difficult to evaluate, since a number of factors influence why people purchase new items and discard the old.

Where the relevance could be greatest, is in relation to cars, where the introduction of nanomaterials could increase the longevity of an expensive consumer good. At the same time, nanomaterials are used in car motors and in the chassis to increase mileage², which is an environmental asset, although not directly related to waste.

Another area where the use of nanomaterials could be of high importance, in relation to reducing the amount of virgin resources and thus the generation of waste, is in construction products. The introduction of primarily nano-SiO₂ and nano-TiO₂ in concrete and nano-TiO₂, ZnO and CeO₂ in wood coatings could increase longevity of the constructions and thus reduce waste generation. The use of nano-SiO₂ to strengthen the construction can, in principle, also lead to use of less concrete in the construction and thus again reduce waste generation. In steel, the use of nano-iron and carbon as a means to strengthen the construction is also potentially a way to reduce waste generation. The use of nanomaterials in construction is quite novel and especially for steel still quite expensive, so little experience on the consequences is available at present.

Based on the literature review and an analysis of the Danish waste handling system, a number of ideas for further studies have been introduced:

Investigative studies:

- A. Characterize and evaluate leachability of nanomaterials from incinerator slag
- B. Characterize and evaluate leachability of nanomaterials from recycled crushed construction waste
- C. Characterize and evaluate leachability of nanomaterials from shredder waste
- D. Evaluate migration of nanomaterials through landfill liners
- E. Characterize and evaluate leachability of nanomaterials from granulated tyres.

For all the investigative studies, the development of methodology would have to be an initial part of the study, since challenges have been observed with characterization and analysis methods for nanoparticles especially in liquid media containing high concentrations of basic components. Another issue in this relation is to also investigate the potential for leaching of nanoparticles from waste products not originally containing nanomaterials, in order to evaluate the order of magnitude of a potential increase.

Analyses

- F. Obtain better overview of nanomaterials in construction waste with a focus on material with a high recycling potential
- G. Compile flow models for SiO₂ and CeO₂ (primarily relevant for slag and construction waste)
- H. Update flow models in order to describe the actual Danish situation
- I. Obtain better overview of recycling processes for textiles with nano-Ag and the potential release scenarios related to these processes.

² Primarily by reducing weight

Sammenfatning

Projektet har til formål at give:

- i) et overblik over den eksisterende viden og videnshullerne i relation til forekomsten af nanomaterialer i affald (herunder identifikation af de overordnede spørgsmål med hensyn til teknik og sikkerhed) og
- ii) anbefalinger med hensyn til hvilke forhold der bør underkastes nærmere studier for bedre at belyse betydningen af tilstedeværelsen af nanomaterialer i affaldsstrømmene, herunder affald til genanvendelse.

Projektet fokuserer på forbrugerprodukter, der ender som affald, og ikke på produktionsaffald, og på produkttyper, som kan forventes at ende i forskellige affaldsstrømme, herunder de nanomaterialer, som typisk kan forventes i disse produkttyper. Generelt vil fokus være på de produkttyper og nanomaterialer, hvor der overhovedet foreligger information. I forhold til at vurdere betydningen for de affaldsstrømme, der forbrændes, er det besluttet, at det er mere relevant at se på den overordnede belastning med specifikke nanomaterialer og deres skæbne end på specifikke produkter og produkttyper.

Projektet beskæftiger sig med bevidst fremstillede nanomaterialer, dvs. nanomaterialer som er fremstillet/designet med henblik på at tilføre produktet en specifik funktionalitet. Projektet tager i princippet udgangspunkt i EU's definition³ af nanomaterialer, men da de fleste publikationer ikke definerer nanomaterialer specifikt, er i praksis alle publikationer inddraget, hvor der refereres til nanomaterialer i affald.

Restprodukter fra spildevandsbehandling ligger uden for dette projekts område.

I projektet er indsamlet information om affaldstyper (produkttyper) og deres indhold af nanomaterialer, idet der generelt ikke angives en konkret koncentration, men alene at nanomaterialet er til stede. Derudover er der indsamlet information om, hvorledes de enkelte nanomaterialer kan forventes at opføre sig i de enkelte dele af affaldsbehandlingssystemet, f.eks. forbrænding, deponering og genanvendelse. Der er meget begrænset tilgængelig information om, hvorledes nanomaterialer kan forventes at opføre sig i biologiske behandlingsprocesser, og hvorledes disse processer evt. påvirkes af tilstedeværelsen af nanomaterialer.

Generelt foreligger der meget begrænset information om nanomaterialers skæbne i affaldsbehandlingssystemet. De foreliggende studier omfatter et mindre antal produkter og nanomaterialer, og de dragne konklusioner skal derfor ekstrapoleres med varsomhed. Der er herudover behov for flere grundlæggende studier af nanomaterialers opførsel og skæbne. Nærværende rapport giver således en indledende oversigt over emnet med det formål at pege på, hvor der især er behov for supplerende studier.

³ COMMISSION RECOMMENDATION of 18 October 2011 on the definition of nanomaterial. 2011/696/EU. OJ L 275/38.

På grundlag af den indsamlede information er der opstillet en matrice over en række primære affaldsstrømme, hvor der især kan forventes tilstedeværelse af nanomaterialer, samt hvilke nanomaterialer der er tale om, se Tabel 2. Papir er ikke medtaget, idet der (i hvert fald for tiden) kun anvendes ganske få nanomaterialer i forbindelse med papirprodukter og primært i forbindelse med blæk, som især vil ende op i spildevandsbehandlingen, der ligger uden for dette projekts rammer.

Det har ikke på nuværende tidspunkt været muligt at basere dette studie på hvilke mængder af nanomaterialer, der potentielt kan komme ind i affaldssystemet som en funktion af mængden af nanomaterialer anvendt i de relevante produkter i Danmark, da de studier der belyser dette, ikke var afsluttede tilstrækkeligt tidligt i projektperioden for nærværende projekt.

TABEL 2
DE HYPPIGST FOREKOMMENDE KOMBINATIONER AF AFFALDSTYPER OG NANOMATERIALER

Affaldstype	Typisk forekommende nanomaterialer
Metal	CNT, nano-SiO₂, nano-Ag
Plastik	CNT, nano-SiO₂, nano-TiO₂, nano-ler
Tekstiler	CNT, nano-Ag, nano-SiO₂, nano-TiO₂
WEEE (Elektronikaffald)	CNT, nano-Ag, nano-SiO₂, nano-TiO₂, nano-ZnO
ELV (Kasserede biler)	CNT, nano-SiO₂, nano-TiO₂
Bildæk	CNT, nano-SiO₂, nano-ler
Bygge- og anlægsaffald	CNT, nano-SiO₂, nano-TiO₂, nano-ZnO, nano-ler, nano-CeO₂

For affaldsforbrændingsprocessen er det generel enighed i den foreliggende information om, at de uorganiske nanomaterialer, TiO₂, ZnO og Ag, vil ende primært i slagterne og til en vis grad i flyveasken, hvor sidstnævnte hovedsageligt eksporteres i Danmark. Der emitteres kun meget små mængder med røggassen fra forbrændingsanlæggene. CNT forventes (hvilket også påvises i enkelte studier) destrueret i processen, hvis temperaturen er tilstrækkeligt høj hele tiden. Det CNT, som ikke destrueres, forventes at ende i slaggen.

Da langt hovedparten af slagge i Danmark genanvendes efter sortering og nedknusning, er der potentielt en risiko for arbejdsmiljøpåvirkninger i tilknytning til tilstedeværelsen af nanomaterialer i slaggen i forbindelse med behandlingen slagterne, og miljøpåvirkninger i forbindelse med udvaskning af nanomaterialer fra slaggen, når denne genavendes i vejkonstruktioner m.m.

Hvis affald indeholdende nanomaterialer deponeres, f.eks. i tilfælde af ikke-genanvendeligt bygningsaffald eller shredderaffald, er der potentielt en risiko for udvaskning af nanomaterialer fra affaldet til perkolatet. Forholdene i en losseplads øger dog typisk sammenkitningen af partikler, hvilket kan reducere nanopartiklernes mobilitet. Tilstedeværelsen af organiske syrer i perkolatet har dog vist sig at reducere sammenkitningen af CNT. Et enkelt studie af diffusion af CNT gennem en HDPE membran viste, at dette ikke forekom.

Nanosølv har vist sig at inhibere anaerob nedbrydning, hvis koncentrationen er tilstrækkeligt høj. Om dette skyldes materialets nanoform er dog tvivlsomt. Nanocellulose kunne komposteres uden negative effekter.

For genanvendelse kan de potentielle effekter opdeles i 3 kategorier:

- Arbejdsmiljøeffekter i forbindelse med selve genanvendelsesprocessen
- Miljøeffekter i forbindelse med behandlingen af restprodukterne fra genanvendelsesprocessen, som vil blive tilført enten forbrænding, deponering eller spildevandsbehandling; her gælder det tidligere sammenfattede
- Tilførsel af nanomaterialer til produkter med indhold af genanvendt materialer; effekten af dette er ikke mulig at fastslå på nuværende tidspunkt.

Med hensyn til arbejdsmiljø viser studier af processer, som ligner typiske genanvendelsesprocesser, at inflammatoriske effekter pga. støv indeholdende nanomaterialer kan forekomme. Det er dog ikke altid muligt at skelne effekten fra støv, som ikke indeholder nanomaterialer. I alle tilfælde peger dette på vigtigheden af at sikre tilstrækkelig beskyttelse af personalet, der arbejder med genanvendelse af affald, der kan indeholde nanomaterialer.

Et særligt punkt er den store mængde bygge- og anlægsaffald, der genanvendes i Danmark. For øjeblikket er der begrænset viden om den mængde af byggematerialer indeholdende nanomaterialer, der anvendes i Danmark, eller om den potentielle emission af nanomaterialer fra disse produkter i forbindelse med genanvendelsen af dem. Nogle af de ovenfor nævnte forhold er også relevante for denne type genanvendelse, og da en del af håndteringen af bygge- og anlægsaffald typisk foregår helt eller delvist udendørs, er der samtidigt også et potentiale for en tilsvarende påvirkning af det eksterne miljø. Derudover peger den omfattende brug af genanvendt byggeaffald i vejkonstruktioner m.m. på et behov for vurdering af den potentielle udvaskning af nanomaterialer fra disse materialer.

Et andet særligt emne er genanvendelse af bildæk. I Danmark genanvendes en meget stor andel af de brugte bildæk, og granulatet anvendes typisk som fyld på kunstgræs fodboldbaner og til gummifliser og andre gulvbelægningsmaterialer anvendt på sportsarealer (også indendørs) og på legepladser. Her kan der potentielt også frigives nanomaterialer f.eks. via udvaskning fra disse produkter.

På baggrund af det eksisterende (og ufuldstændige) vidensniveau om effekter på mennesker og miljø af bevidst fremstillede nanomaterialer i produkter, sammenholdt med det potentielle indhold af disse materialer i produkterne, kan det ikke udelukkes, at enkelte produkter, når de bliver affald, skal kategoriseres som farligt affald.

Miljøstyrelsen har i projektet udbedt sig en evaluering af, om eksistensen af nanomaterialer kan forbedre eller forværre genanvendelsesteknologien. Dette er ikke muligt at besvare på det foreliggende grundlag.

De væsentligste muligheder for arbejdsmiljømæssige påvirkninger relateret til nanomaterialer og i forbindelse med genanvendelse kunne være:

- Eksposering for fint eller ultrafint støv med et indhold af frie nanomaterialer emitteret i forbindelse med transport, sortering, neddeling eller omhældning af affald indeholdende nanomaterialer.
- Eksposering for nanomaterialer indeholdt i væsker (vand, opløsningsmidler) som følge af rengøring af produkter f.eks. før mekanisk behandling, eller eksposering for nanomaterialer på rengøringsklude m.m. fra vedligeholdelse og rengøring af udstyr.

Følgende processer kan således i princippet medføre arbejdsmiljømæssige påvirkninger knyttet til tilstedeværelse af nanomaterialer:

- Indsamling og sortering (støv)
- Neddeling (støv), relevant for metaller, plastik, tekstiler, WEEE, bygge- og anlægsaffald, kasserede biler og bildæk.
- Pulpning af affaldspapir (aerosoler)
- Granulering af plastik (støv).

De få studier, der hidtil er udført i relation til produktionsprocesser for produkter indeholdende nanomaterialer, indikerer, at den arbejdsmiljømæssige påvirkning kan reduceres via beskyttelsesforanstaltninger helt tilsvarende dem, der anvendes til at reducere eksponering for aerosoler og støv, og ved at tilrette håndteringsprocesserne. Således synes det relevante at undersøge nærmere, i hvilket omfang en hensigtsmæssig risikohåndtering er på plads og implementeret på de faciliteter, der genanvender affald.

Nanomaterialer kan forlænge forbrugerproduktets levetid f.eks. i form af:

- Belægninger (herunder maling)
- Forbedret funktion (og dermed undgåelse af reparationer, hvor det kunne blive valgt at købe nyt i stedet).

Det er dog vanskeligt at vurdere den konkrete betydning af dette, da en lang række faktorer er bestemmende for, hvorfor folk køber nyt og kasserer det gamle.

Relevansen kunne være størst for biler, hvor introduktionen af nanomaterialer kunne forlænge levetiden af et dyrt forbrugsgode. Samtidigt anvendes nanomaterialer i bilmotorer og i chassiser for at reducere brændselsforbruget⁴, hvilket er en miljømæssig fordel ikke direkte relateret til affald.

Endnu et område, hvor anvendelsen af nanomaterialer kunne have stor betydning i forhold til reduktion af ressourceforbruget og dermed affaldsgenereringen, er i byggeprodukter. Introduktionen af primært nano-SiO₂ og nano-TiO₂ i beton samt nano-TiO₂, ZnO og CeO₂ i træbeskyttelser kan medføre en forlængelse af konstruktionernes levetid og dermed genereringen af byggeaffald. Anvendelse af nano-SiO₂ i konstruktioner for at øge styrken af dem kan i princippet også føre til en reduktion i forbruget af beton i en given konstruktion og således igen til en reduktion i affaldsgenereringen. Tilsvarende effekter kunne være resultatet af anvendelsen af nano-jern og carbon i stålkonstruktioner. Anvendelsen af nanomaterialer i bygningskonstruktioner er meget nyt og især for stål stadig meget dyrt, hvorfor der endnu er meget få erfaringer med konsekvenserne af det.

På baggrund af litteraturstudiet og den tilknyttede analyse af konsekvenserne i det danske affaldsbehandlingssystem er der opstillet en række ideer til videre studier:

Undersøgelser:

- A. Karakterisering og vurdering af udvaskeligheden af nanomaterialer fra forbrændingsslagge.
- B. Karakterisering og vurdering af udvaskeligheden af nanomaterialer fra genanvendt neddelt bygge- og anlægsaffald.
- C. Karakterisering og vurdering af udvaskeligheden af nanomaterialer fra shredderaffald.
- D. Vurdering af migration af nanomaterialer igennem membraner til deponeringsanlæg.
- E. Karakterisering og vurdering af udvaskelighed af nanomaterialer fra granulerede bildæk.

⁴ Primært ved at reducere vægten.

For alle ovennævnte undersøgelser gælder, at en hensigtsmæssig og retvisende metode skal udvikles som en indledende del af projektet, idet det har vist sig problematisk at sikre sig resultater, der korrekt registrerer indholdet af de bevidst fremstillede nanomaterialer især i væskemedier med et højt indhold af basiske komponenter.

Endvidere skal undersøgelsen omfatte måling af udvaskningen af nanomaterialer fra materialer, som ikke oprindeligt indeholdt bevidst fremstillede sådanne, således at der kan skelnes mellem de generelt genererede nanomaterialer i de pågældende processer og dem, der er et resultat af "tilsætningen" af industrielt fremstillede nanomaterialer til de produkter, der ender op i den pågældende affaldstype.

Analyser:

F. Bedre overblik over tilstedeværelsen af nanomaterialer i byggevarer med et særligt fokus på produkter med et højt genanvendelsespotentiale.

G. Opstilling af flow modeller for SiO₂ og CeO₂ (især relevant for slagge og bygge- og anlægsaffald).

H. Opdatering af flow modellerne således at de beskriver den specifikke danske situation.

I. Bedre overblik over genanvendelsesprocesser for tekstiler, som potentielt indeholder nanosølv, samt opstilling af de tilknyttede frigivelsesscenarier.

1. Introduction

1.1 Background

The Danish government and the Red-Green Alliance (a.k.a. Enhedslisten) have signed an agreement called “Bedre styr på nanomaterialer” (Better control of nanomaterials). This initiative is running in 2012-2015 and focuses on the use of nanomaterials in products on the Danish market and the consequences for consumers and the environment. Under this initiative, the Danish Environmental Protection Agency has issued a series of projects on nanomaterials. These projects are aimed at:

- i) Identifying nano-related safety issues for consumers and the environment in Denmark
- ii) General knowledge building in relation to nanomaterials and environment and consumer safety.

In waste management, the presence and fate of nanomaterials is still a novel area. Knowledge and investigation methods are limited. There is no official definition of nanowaste. Still, it is inevitable that nanomaterials used in many different products or articles will end up in the waste stream. Aspects like environmental and health risks associated with nanowaste management remain unexplored. Another aspect is whether products containing nanomaterials can influence the abilities/efficiency of waste management, including recycling processes. On the other hand, prior to entering the waste management, nanomaterials might replace other materials making products e.g. smarter or stronger and thus possibly play a role in waste reduction.

1.2 Objective

The objective of the project is to:

- Establish an overview of technical, health and environmental issues related to nanomaterials and waste
- Assess possible recycling issues with relevance for environmental safety.

An overall aim of the project is to point to where further information should be sought in order to evaluate the potential risks related to the presence of nanomaterials in waste.

1.3 Scope/delimitations

The focus of the project is on consumer products ending up as waste and not production waste. Further, focus will be on articles (such as electronics and sports equipment) rather than mixture residuals (e.g. cosmetics or paint residuals in discarded tubes/containers). Waste products from wastewater treatment are out of the scope of the project.

It is the intention, not necessarily to focus on specific products, but on product groups that may end up in different relevant waste streams. This focus includes addressing the nanomaterials typically contained in those product groups.

In general, focus is on product types and waste streams, where information is at all available. Thus, the information in directly available articles and reports is an inherent delimitation of the project, since this field of study is relatively new. However, the project has also attempted to cover product

types/waste streams with specific nanomaterials that potentially could have substantial impact, but where little or no specific information is available.

In relation to incineration, it is considered more relevant to look at the overall load and fate of a number of nanomaterials rather than product/product categories.

The scope was further focused after the initial activities in the project, see Chapter2.

In general, the project focuses on engineered nanomaterials, i.e. nanomaterials manufactured/designed to provide a specific function in a product. Further, the project generally considers nanomaterials in the meaning of the recommended EU definition⁵. In practice however, most of the investigated information source do not define nanomaterials, and thus all identified information sources referring to nanomaterials in waste have been included.

⁵ **COMMISSION RECOMMENDATION of 18 October 2011 on the definition of nanomaterial.** 2011/696/EU. OJ L 275/38.

2. Approach/Methodology

The activities of the project have been divided in four work packages:

- WP1: Identification of nanomaterials in (Danish) waste streams with focus on incineration and recycling
- WP2: Fate and risk assessment of nanomaterials in (Danish) waste management systems
- WP3: Perspectives on technological aspects regarding nanomaterials and waste: Potential for substitution of raw materials, use in recycling processes or reduction of waste
- WP4: Relevant experimental follow-up studies on nanomaterials and waste.

2.1 WP1 - Identification of nanomaterials in Danish waste streams

In the absence of fully comprehensive Danish or international overviews of nanomaterials or nanomaterial containing products entering waste streams, the following on-going main information sources was, within the boundaries of this project, used in order to identify/estimate nanomaterials entering the waste streams:

- On-going activities in the OECD Working Party on Resource Productivity and Waste (WPRPW). These activities are so far reflected in the following documents of relevance for this project:
 - RECYCLING OF WASTE CONTAINING NANOMATERIALS, ENV/EPOC/WPRPW(2013)2, 17-Oct-2013 (OECD, 2013a)
 - INCINERATION OF WASTE CONTAINING NANOMATERIALS, ENV/EPOC/WPRPW(2013)2, 21-Oct-2013 (OECD, 2013b)
 - Landfilling of Waste Containing Nanomaterials and Nanowastes, Draft Reflection Paper (OECD, 2014)
- Recent Swiss modelling work of NMs in waste streams:
 - "Modelling the flows of engineered nanomaterials during waste handling" (Mueller et al., 2013)
 - "Engineered Nanomaterials concentration after the recycling process in Switzerland" (Caballero-Guzmán, 2014)
- Preliminary results from other on-going projects under the Danish 2012-2015 nano-initiative, which with different scopes/approaches have addressed NMs in products on the Danish market (project team is either involved in these project or have had draft reports made available):
 - Nanomaterials - Occurrence and effects in the Danish Environment (aiming at generating a generic overview of nanomaterials in products on the Danish market in order to estimate possible point source and diffuse releases to the environment resulting from the manufacturing and use of these) (Danish EPA, 2014a, in prep)
 - Consumer exposure and risk assessment of nanomaterials in products on the Danish market (aiming at assessing exposure and risks for Danish consumers in contact with NM containing consumer products) (Danish EPA, 2014b, in prep)
 - Supplementary survey of products on the Danish market containing nanomaterials (addressing NMs in food & feed, food contact materials, cosmetics, pesticides, medical devices and NMs used in water treatment) (Danish EPA, 2014c)

- Specifically in relation to NMs in tyres, a draft report from an on-going OECD project on nanomaterials in tyres was made available for the project (a joint activity between the Working Party on Nanotechnology (WPN) and the Working Party on Manufactured Nanomaterials (WPMN)) (OECD, 2013c); the final report is now available, at http://www.oecd-ilibrary.org/science-and-technology/nanotechnology-and-tyres_9789264209152-en
- Information from projects where VTT has been involved especially in aspects related to waste handling, e.g. the EU seventh Framework Programme (FP7) project NanoSustain.

Several of the above projects have harvested information from inventories/databases addressing products claimed to contain nanomaterials, such as the Danish “Tænk” nanodatabase⁶, The nanotech project (formerly known as the WoodrowWilson database⁷) and the BUND database⁸. Only one of these is Danish, but it has generally been assumed during those projects that products on the European market might also be available on the Danish market. This assumption is also applied in the current project.

In relation to the information harvested from these databases, a number of issues/limitations should be noted:

- Products are generally included in these databases/inventories based on nano-claims, i.e. actual content of nanomaterials has not been verified by analysis or other means by the database/inventory owners
- Products actually containing NMs, but not claimed to contain nanomaterials are generally not captured by these inventories/databases
- The identity of the possibly contained nanomaterials is often not indicated, or described rather generically.

In general, it was agreed to focus on product types/articles with known or anticipated large volumes of nanomaterials.

Knowledge of the Danish waste handling system is used to estimate, where the different types of products will typically end up.

With respect to recycling, it was agreed to focus on product types with specific properties which might influence/limit recycling. An initial review of OECD, 2013a and Caballero-Guzmán et al. (2014, in prep) was used to identify main relevant product categories. This was further supplemented with additional targeted information searches.

In relation to products on the Danish market, it was found that the on-going Danish projects (Danish EPA, 2014a-c) largely focus on mixtures/formulations which can release NMs during their production or use. The projects focus less on articles. It was therefore decided to further search the “Tænk” nanodatabase in relation to relevant products/articles known to be on the Danish market.

Specifically in relation to tyres, OECD (2013b) was used as a main information source.

Specifically for building materials, contact was made to the Danish branch organisation organising the majority of Danish building materials producers/importers (The Federation of Danish Building Industries - DI BYG), and an Internet search was conducted targeted at identifying nanomaterials in building materials.

⁶ <http://nanodb.dk/>

⁷ <http://www.nanotechproject.org/inventories/>

⁸ http://www.bund.net/themen_und_projekte/nanotechnologie/nanoproduktdatenbank/

Based on a preliminary screening of OECD (2013b) and Mueller et al. (2013), it was agreed in relation to incineration, to focus on (amounts of) nanomaterials as such rather than specific products/product types, as the fate in incineration plants to a larger extent relates to the overall volume/concentration of a nanomaterials than to specific types of products entering the incineration plants.

2.2 WP2 Fate and risk assessment of nanomaterials in Danish waste management systems

The entry point for evaluating the release and potential exposure from nanoproducts in the waste stream is the model set up by Empa and described in:

- Mueller et al., 2013. Modelling the flows of engineered nanomaterials during waste handling⁹
- The MSc study by Caballero-Guzmán from 2013 on the fate of nanomaterials in recycling processes and the paper (to be submitted) by Caballero-Guzmán et al (2014).

This is supplemented by the information gained through the literature search and other information gathering. Several published studies have for instance looked at incineration of nanoproducts. Specifically, the information obtained by VTT (The Technical Research Institute of Finland) in the EU FP7 project NanoSustain has been utilised, where VTT has investigated;

- Release potential of nanoparticles from nanoproducts under conditions mimicking landfill conditions
- Biodegradability of nanocellulose
- Incineration of CNT containing epoxy.

Where no specific information is available, the physical – chemical processes of the specific waste streams are described and their potential impact on the nanoproducts in question assessed.

It is also described, if the presence of nanomaterials will as such potentially have an impact on the waste treatment technology or will require additional steps in the waste management stream, e.g. specific sorting.

Potential waste streams are:

- Recycling, incl. a number of different mechanical, physical and chemical treatment technologies
- Incineration, encompassing also handling of residues¹⁰ and recovery of metals, and also including high temperature incineration of hazardous waste
- Landfilling
- Other chemical treatments used for hazardous waste treatment
- Biological treatment such as composting and anaerobic digestion.

As the products suggested for evaluation have been chosen in order to cover, as much as possible, all relevant material types that could in principle be recycled, all material categories addressed in the new Danish Resource Strategy are sought covered.

Potential application of the rules of classification as hazardous waste to the chosen nanoproducts is assessed.

An overall mapping of the flows and releases from the different parts of the waste treatment system is carried out, including an assessment of the related uncertainty where possible.

⁹ NC, Mueller, J Buha, J Wang, A Ulrich, B Nowack. 2013. Modeling the flows of engineered nanomaterials during waste handling. *Environ. Sci.: Processes Impacts*, 15, 251

¹⁰ Including recycling of residues

The potential exposure of humans and the environment arising from the emissions mapped is described to the level possible and, where relevant and possible, compared to the potential exposure related to similar products not containing nanomaterials. This assessment is based on our knowledge of nanorelated exposure gained from the projects carried out e.g. for the Danish EPA and of exposures from the waste management system through numerous exposure assessments and life cycle analyses for a wide range of clients. The FP7 NanoSustain project has addressed dust generated from treatment of nanoproducts (NanoSustain, 2013 f).

Where specific risks related to specific parts of the waste management system can be envisaged, this is described.

A result of this work package is also an overview of the data gaps encountered and the further investigations needed.

2.3 WP3 Perspectives on technological aspects regarding nano-materials and waste

This Work Package is based primarily on the literature search carried out and the other information collected as described previously. Specifically, the work carried out in the NanoSustain project with respect to precautionary design and improved recyclability of engineered nanomaterials will be included where relevant. This concept encompasses issues including precautionary risk aspects, resource aspects and environmental aspects. Also, information from other projects carried out by VTT (Technical Research Centre of Finland) focusing on substitution of critical raw materials with nanomaterials or use of nanoparticles in recovery of valuable metals are included.

A specific analysis of the information gathered with the aim of addressing the issues listed in the objective is carried out and presented. General tendencies are evaluated, and where the lack of information is greatest, it is pointed out.

2.4 WP4 Relevant experimental follow-up studies on nanomaterials and waste

The recommendations are based on the results of the three work packages carried out, WP1, WP2 and WP3.

The recommendations are made on the basis of consideration of the following issues:

- Relevance for recycling technologies
- Relevance for environmental safety
- The study should be realistic to carry out in the given timeframe
- Other initiatives to feed into or to collaborate with (e.g. research projects or projects in OECD, waste industry, recycling industry)
- Significance of the knowledge gaps
- The interest of national or international stakeholders in the subject, e.g. interest of the Danish EPA
- Costs versus scientific/administrative benefits.

Information collected with respect to possible experimental procedures related to nanomaterials is also included in the basis for the evaluation of which experimental studies can most successfully be carried out. In the NanoSustain project, several test methods were developed as part of the project, and VTT broadly based knowledge of how to carry out experimental work and tests with a high degree of reproducibility and overall quality is utilised in the suggestions.

3. Identification of nanomaterials in Danish waste streams

3.1 Nanomaterials in waste streams in general

Recent publications from OECD (OECD 2013a) and a Swiss research group (Caballero- Guzmán, 2014) have, at a general level, addressed the presence and fate of nanomaterials in recycling streams. As will be shown below, the publications also address nanomaterials in waste entering other types of waste treatment such as incineration.

OECD (2013a) lists the following main waste streams in which nanomaterials are potentially recycled:

- Bio waste (it is not clear from the context what this covers)
- Food waste
- Glass (bottles)
- Metal
- Paper and cardboard
- Plastic (PET and various other plastics)
- Leather and Textiles
- Waste of Electronic and Electrical Equipment WEEE
- Batteries
- Wood
- Construction and Demolition Wastes
- End of Life Vehicles ELV:
- Tires
- Recycling of residues from waste incineration plants (recovery of metals from bottom ash by mechanical separation or from fly ash by acid washing).

Not all of these streams are recycled to the same degree in Denmark at present, but the Resource Strategy has focus on recycling, so increased recycling is expected.

In relation to the identification of nanomaterials entering the recycling streams, OECD (2013a) provides two overviews, one with the nanomaterials as entry point and one with the overall waste as entry point, the tables are given in Appendix 1:. When taking a closer look at these overviews, it is apparent that both from the nanomaterial point of view and from the waste type point of view, the other main waste treatment processes: incineration and landfill are also covered by the overview. The tables are thus renamed as being general for waste handling processes.

Caballero-Guzmán (2014) models the fate of nanomaterials in recycling processes for the Swiss situation. The work addressed five nanomaterials assessed to be relevant in waste entering recycling: nano-titanium dioxide (nano-TiO₂), nano-zinc oxide (nano-ZnO), nano-silver (nano-Ag), Carbon Nanotubes (CNTs) and Fullerenes. With reference to Sun et al (2013), Caballero-Guzmán (2014) provides the overview shown, also in Appendix 1, in relation to occurrence of these five nanomaterials in various product categories. The categories not directly relevant in a Danish waste handling context within the scope of the current project have been written in *italics*.

Caballero-Guzmán (2014) notes, that not all of the above product categories enter the waste stream. Based on an analysis of available data and considering the findings in Table 17, Caballero-Guzmán (2014) estimates the main combinations of nanomaterials and product categories entering recycling streams; see Table 3.

TABLE 3
PRODUCT CATEGORIES (MARKED IN GRAY/GREEN) RELEVANT FROM THE RECYCLING PERSPECTIVE FOR THE FIVE NANOMATERIALS ADDRESSED IN CABALLERO-GUZMÁN (2014).

	Nano-TiO ₂	Nano-ZnO	Nano-Ag	CNT	Fullerenes ¹¹
Consumer electronics					
Paints					
Glass & ceramics					
Batteries & capacitors					
MedTech					
Textiles					
Metals					
Energy					
Automotive					
Motor oil (lubricants)					
Metals (coatings)					
Electronics and optics					

Based on total amounts and assessed market penetration of products, Caballero-Guzmán (2014) decided not to address Fullerenes any further. The remaining 9 product categories in Table 1 were further detailed in relation to actual relevant products within these product categories as shown in Table 17 in Appendix 1.

As supplement to the OECD and Swiss activities, the on-going Danish nanoprojects (Danish EPA 2014a-c, in prep.), The Danish Nano "Tænk" Database (<http://nanodb.dk/>) and OECD (2013c) have been reviewed to further identify nanomaterial containing products which might be relevant from a recycling perspective. In relation to nanomaterials in building materials, the relevant Danish branch organisation has been contacted, and an Internet search on nanomaterial containing building materials has been conducted.

RESULTS FROM THIS FURTHER DATA MINING HAVE BEEN INTEGRATED WITH THE FINDINGS FROM THE PREVIOUS SECTIONS, SEE

Table 4.

¹¹ Fullerenes are not evaluated in detail because of lack of concrete applications in the market and their low production compared to the other nanomaterials

TABLE 4
 INTEGRATION OF INFORMATION ON NANOMATERIALS AND THEIR PRESENCE IN RECYCLING STREAMS RELEVANT FOR DENMARK WITH EXAMPLES OF PRODUCTS IN WHICH THE NANOMATERIALS OCCUR

Waste stream	Nanomaterials	Products
Metal waste/scrap	<ul style="list-style-type: none"> • Metal oxides • CNT • SiO₂ • Nano-silver 	<ul style="list-style-type: none"> • Coatings • Coatings • Coatings • Door knobs, pet food bowls, watch chains, water taps, kitchen ware
Paper and cardboard	<ul style="list-style-type: none"> • Carbon black • Nano-TiO₂ 	<ul style="list-style-type: none"> • from ink • in special papers
Plastics	<ul style="list-style-type: none"> • Silicon dioxide, carbon black and titanium nitride¹² • CNT, SiO₂, nano-TiO₂ • Nano Titanium nitride (nano-TiN) • Nano-clay 	<ul style="list-style-type: none"> • Food packaging • PET bottles • PET bottles
Textiles and leather	<ul style="list-style-type: none"> • CNT • Nano-silver • Nano-TiO₂ • Bamboo charcoal (possibly a type of CNT but not indicated) • Silicon/SiO₂ • Nanomaterial chemistry not indicated 	<ul style="list-style-type: none"> • Any kind of textile: shirts, socks, blankets, teddy bears, slippers, sportswear, underwear, jackets, polo shirts, shorts, baby vests, gloves, bed linen, towels • Clothing • Wet suit • Textile sealant
WEEE – Electronics	<ul style="list-style-type: none"> • Carbon black • CNT • Nano-Iron oxide, ZnO, SiO₂, • Nano-silver 	<ul style="list-style-type: none"> • Plastic material • Toners • Electronic devices, plastic housings, semiconductor devices • Coatings • Flat iron, hair dryer, curling iron, computer mice and keyboards, women and men shavers, hot rollers, washing machines, air conditioners, toothbrush sterilizer, multipurpose sanitizer, vacuum cleaners, hand dryers, coffee machines, mobile phones, notebooks, electronic toilet seats, as well as air and water purifiers, air humidifier, water ionizers, refrigerators, steam iron, hair straightener, hair

¹² The positive list of the Commission Regulation (10/2011) on plastics food contact materials, allow the nanoforms of following three nanomaterials under certain conditions

Waste stream	Nanomaterials	Products
	<ul style="list-style-type: none"> Nano-TiO₂ Silicon/SiO₂ Tourmaline¹³ Platinum Nano-Phosphate Nano-gold nanomaterials where chemical identity is not disclosed 	<ul style="list-style-type: none"> trimmers, epilator Flat iron, hair dryer, curling iron, fridges, computer mice and keyboards, Hair straightener computer processors hair straightener ionic facial steamer angel grinder, bayonet saw, circular saw, compass saw, drilling machines, electronic screwdrivers, spanners, power tool sets. NB! Not clear whether the Nano-Phosphate occurs in confined batteries air conditioner headsets, iPODs, speakers, lenses, objectives, LED TVs
Batteries and solar cells	<ul style="list-style-type: none"> CNT Nano-Phosphate Nano-TiO₂ 	<ul style="list-style-type: none"> Electrodes, Li-ion batteries, solar cells Electrodes, Li-ion batteries and possibly in batteries in electric tools expected in Li-ion batteries
End of life vehicles - automotive ¹⁴	<ul style="list-style-type: none"> CNT SiO₂, TiO₂ 	<ul style="list-style-type: none"> Plastics, coatings and paints, Fuel system components and fuel lines (connectors, pump parts, o-rings), reinforcement of structural parts Plastics, coatings and paints
Tyres	<ul style="list-style-type: none"> Carbon black Highly Dispersible (HD) Silica – Conventional SiO₂ Highly Dispersible High Surface Area (HD-HS) Silica - New generation SiO₂ Nanoclay (Montmorillonite). CNT Organic nano-polymers 	-
Medical devices	<ul style="list-style-type: none"> Silicate Zirconium oxide Nano-silver Calcium alginate Zinc oxide 	<ul style="list-style-type: none"> Dental fillings/glue/implants Dental fillings/glue/implants wound dressings/plasters, coating for implants, operating tables, door knobs, handles wound dressings/plasters wound dressings/plasters,

¹³ Tourmaline is a crystal boron silicate mineral compounded with elements such as aluminium, iron, magnesium, sodium, lithium or potassium, Wikipedia, 2014.

¹⁴ Vehicles contain large amounts of electronics, so reference is also made to WEEE

Waste stream	Nanomaterials	Products
	<ul style="list-style-type: none"> • Nano-TiO₂ • Nano-copper • Nano-iron oxides 	<ul style="list-style-type: none"> • ostomy bags • wound dressings/plasters, ostomy bags • ostomy bags • polymer devices
Construction and Demolition waste ¹⁵	<ul style="list-style-type: none"> • Nano-TiO₂ • SiO₂ • Nano-ZnO • Nano-silver • Aluminium oxide • Carbon Fluorine polymers • Nano-clays • Nano-CeO₂ • Nano-Tungsten oxide • Unspecified nano-Metal oxides and Nano-polymers • CNT • Nanomaterial chemistry not specified 	<ul style="list-style-type: none"> • Coatings, pavements blocks, asphalt, sound barriers, tunnels; glass, treated wood parts, windows, ceramics, walls paints • concrete, coatings, glass • Coatings, treated wood parts, exterior walls paints and possibly in windows & ceramics • Coatings, glass, (Interior walls paints and possibly in windows & ceramics • Coatings • Coatings, glass • Coatings, treated wood parts • Treated wood parts • Glass • Glass • as replacement of steel,. anti-static and anti-fouling coating • bathroom tiles

Of the waste categories mentioned in the table, batteries and medical devices are of less interest, since they will most often be treated as hazardous waste.

The following sections provide further aspects relating to tyres and building materials, respectively.

3.2 Tyres

OECD (2013c) notes with reference to the European Commission (2012) that "Today, rubber tyres are by far the biggest commercial market for nanomaterials" and " Modern tyres achieve their high mileage, durability and road grip through the use of nanoscale carbon black and silica."

The OECD report notes that current technology is reaching its technical limits, but that application of new nanotechnology might further reduce fuel consumption (by reducing rolling resistance) as well as waste and raw material consumption (due to improved durability/better abrasion resistance) and studies in more details four widely used NMs in tyres:

- Carbon black
- Highly Dispersible (HD) Silica – Conventional SiO₂
- Highly Dispersible High Surface Area (HD-HS) Silica - New generation SiO₂
- Nanoclay (Montmorillonite).

¹⁵ See details in in Section 0

OECD (2013c) further provides an overview of some new/improved nanomaterials that are entering the market or in the research pipeline (see Table 5) and briefly outlines a number of technological, economical and possibly health and environmental challenges with these new nanotechnologies. It is noted that work is on-going to further address these issues, among others via interviews with industry experts. Further details can thus be expected in subsequent updates of the OECD report¹⁶.

TABLE 5
OVERVIEW OF SOME NEW/IMPROVED NMS THAT ARE ENTERING THE MARKET OR IN THE RESEARCH PIPELINE
(OECD, 2013C)

Technology	Description	Technology readiness
Rubber nanoparticles: “Nanopreme”	These are “traditional” tyre rubber raw materials, but produced at the nanoscale. The additive significantly reduces wear of the tyre tread and improves dry road grip by between 10% and 15%.	Market entry
Silica carbide: “Purenano”	Can improve skid resistance, as well as potentially reducing abrasion by nearly 50%.	
Core/shell Polymer nanoparticles “NanoPro Tech”	Can improve cornering and steering response and reduce heat generation (lower rolling resistance). Weight reductions can also be achieved since the core-shell particles are significantly less dense than carbon black or silica fillers.	Prototype / Market entry
Poly(alkylbenzene)-Poly(diene) (PAB-PDM) nanoparticles: “nanostrings”	Can be used to improve the mouldability of rubbers. However, current production techniques are not completely reliable.	Applied research / Prototype / Market entry
Polyhedral Oligomeric Silsesquioxanes (POSS)	A member of the silanol chemical family. POSS could improve wet traction without sacrificing rolling resistance compared to silica	Applied research
Carbon Nanotubes	May be able to reduce rolling resistance through reduced heat generation. Could improve durability – possibly even past the life of the car itself. Improved tensile strength, tear strength and hardness of the composites, by almost 600%, 250% and 70% respectively compared to pure styrene-butadiene rubber.	Basic research / Applied Research
Graphene	Graphene can be produced at a much lower cost than carbon nanotubes but offers similar characteristics to carbon nanotube composites. However, applications are at an early stage of research.	
Aerogels	Are extremely lightweight materials made up	

¹⁶ A public version of the study is now available at http://www.oecd-ilibrary.org/science-and-technology/nanotechnology-and-tyres_9789264209152-en.

Technology	Description	Technology readiness
	<p>of billions of air bubbles trapped in a matrix of nano-sized particles of silica and plastic.</p> <p>Their usefulness was initially limited because they were brittle and absorbed moisture. Reliable and cheap production at volume remains an issue. However, more recent research envisions their use to create lighter, longer-lasting tyres.</p>	
Nano-diamond	<p>Improves rolling resistance while maintaining reinforcing properties. Could help to ensure excellent abrasion resistance, braking ability and fuel efficiency. Nano-diamond applications in tyres are at an early stage of research although mature elsewhere (such as coatings); key barriers include the ability to control the size and composition during production. The production process itself is relatively slow and expensive.</p>	
Fullerenes: “bucky balls”	<p>An allotrope of carbon, that could potentially provide good reinforcement and a low rolling resistance - unfortunately they are toxic and very expensive. However, there is still interest in using their potential through blending with conventional carbon black or silica to improve tread performance.</p>	Basic research

3.3 Building materials

The Federation of Danish Building Industries (DI BYG) has been approached with the aim of collecting further information regarding types of nanomaterials used in building and construction in Denmark, since they have a large fraction of Danish building material suppliers as members. DI BYG was not in possession of specific information about nanomaterials in building materials used in Denmark and approaching their member companies did not provide any new insights.

According to a European survey among employers and workers in the construction section, nanomaterials are mostly found in cement and concrete, coatings and impregnation (Van Broekhuizen *et al.* 2009). Other applications are in glass, steel and wood, fire protection and insulation material.

A broad internet search has identified a range of NMs used in various building materials, including a range of specific products. This information is summarised in Table 6.

An important characteristic of the construction and building products is the relatively long life span of the constructions. Because of long lifespan the nanomaterials will typically enter the waste stream many decades after placed on their use. Existence of the different nanomaterials in Construction & Demolition waste depends greatly on the construction year of the building and the type of construction material.

One specific group of applications is Ag containing coatings (paints) used in facades, apparently especially in Central Europe (van Broekhuizen *et al.* 2010). The extent of the potential use of Ag containing coatings in Denmark is not known.

TABLE 6
OVERVIEW AND EXEMPLIFICATION OF NANOMATERIALS BUILDING PRODUCTS AS IDENTIFIED VIA A BROAD INTERNET SEARCH

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nanomaterial	Reference	Examples of commercial products
Concrete	Self-cleaning surface (photo catalytic)	Surface layer	TiO ₂	[1][3]	
	Ultra strong concrete	Mixed in matrix, filler to improve strength	SiO ₂ (silica fume)	[1]	
			SiO ₂	[4]	Dyckerhoff Nanodur [www.dyckerhoff.de]
	Corrosion reduction			[1]	
	Increased durability	Mixed in matrix	SiO ₂	[1]. [3]	
	Dense and strong concrete, with better water-blocking and corrosion properties	Mixed in matrix	SiO ₂	[2]	
	Improve mechanical properties	Mixed in matrix	CNT	[3]	
Mixed in matrix		Metal oxides	[4]		
Insulation material	Improved insulation properties against heat, cold, fire or a combination thereof	Aerogel (often SiO ₂ or carbon based)	Nano-porous material (internal structure consists of nano-bubbles/holes)	[1] [4]	Nansulate (http://www.nansulate.com/index.html)
Coatings	Improved surface penetration, coverage, reduced layer thickness		Not identified (nano-sized dispersions)	[1]	
	Transparent coatings	Additive in the coating	Not identified (nano-sized ingredients)	[1]	
	Photo-catalytic, self-cleaning,	Additive in the coating	TiO ₂ , ZnO, SiO ₂	[1]	

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nanomaterial	Reference	Examples of commercial products
	hydrophobic properties				
	Antibacterial properties	Additive in the coating	Ag, TiO ₂ , ZnO	[1]	
	Scratch resistance	Additive in the coating	SiO ₂ , Aluminium oxide	[1]	
	Easy-to-clean surfaces	Additive in the coating	Carbon Flourine polymers	[1]	
	Fire retardant	Additive in the coating	TiO ₂ , SiO ₂ , nano-clays	[1]	
	Insulating properties/ corrosion protection	Additive in the coating/paint	Nano-sized cells, pores and particles, not identified	[3]	
Wood	UV-protection of wood (coating)	Additive in the coating	TiO ₂ , ZnO, CeO ₂	[1]	
	Decolourisation of wood by tannin (coating)	Additive in the coating	Nano-clays	[1]	
	Water repelling wood (coating)	Not identified	SiO ₂ , alumina	[3]	
Steel	Improves strength, has favourable corrosive-resistance properties	Nano-structured surface	Not identified		MMFX steel (http://www.mmfx.com/)
	Steel alloys for improved strength and good ductility		Carbon, iron ¹⁷		Sandvik NanoFlex (http://www.smt.sandvik.com/en/products/trademarks/sandvik-nanoflex)
	Replacement of steel by CNT in steel cables ¹⁸	Not identified	CNT	[5]	
Glass	IR reflection	Surface coating	Tungsten oxide	[1]	
	Non-reflective glass	Surface structure/coating	Nano-porous SiO ₂	[1][3]	

¹⁷ According to the Nanotech project (<http://www.nanotechproject.org/cpi/products/sandvik-nanoflex-r-alloy/>) [Accessed 14.02.14]

¹⁸ Identified as future possible use of nanotechnology in the construction industry, according to researchers (The Constructor, n.d)

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nanomaterial	Reference	Examples of commercial products
	Fire or heat protection	Surface coating, transparent silica gel interlayer	Metal oxides, SiO ₂	[1]	
	Easy-to-clean properties	Surface coating	Ag, SiO ₂ , carbon fluorine, polymers	[1]	
	Photo-catalytic, self-cleaning properties	Surface coating	TiO ₂	[1]	Pilkington Activ [4]

[1]: van Broekhuizen *et al.* 2010,

[2]: Nano Connect Scandinavia, 2012.

[3]: NanoForum, 2006

[4]: Hanus *et al.* 2013

[5]: The Constructor, n.d.

3.4 Suggested focus

Based on the accumulated information in Table 16 in Appendix 1, a matrix between major waste streams and most commonly mentioned nanomaterials can be set up, see Table 7. Paper is not included, since there are (at least at present) only few nanomaterials related to paper and then mainly to ink, which will end up as a wastewater issue, and which is out of the scope of this project.

It has not at present been possible to focus this study based on the amounts of nanomaterials potentially entering the waste system as a function of the amount of nanomaterials used in the relevant types of products in Denmark.

An initial screening of the studies carried out in relation to incineration of waste potentially containing nanomaterials (see Chapter 4.1) shows that the focus in these studies is on approximately the same nanomaterials.

TABLE 7
MOST COMMON COMBINATIONS OF WASTE TYPES AND NANOMATERIALS

Waste type	Common nanomaterials
Metal	CNT, nano-SiO₂, nano-Ag
Plastic	CNT, nano-SiO₂, nano-TiO₂, nano-clay
Textiles	CNT, nano-Ag, nano-SiO₂, nano-TiO₂
WEEE	CNT, nano-Ag, nano-SiO₂, nano-TiO₂, nano-ZnO
ELV	CNT, nano-SiO₂, nano-TiO₂
Tires	CNT, nano-SiO₂, nano-clay
Construction & Demolition waste	CNT, nano-SiO₂, nano-TiO₂, nano-ZnO, nano-clay, nano-CeO₂

The further studies in this project focus on the in Table 7 mentioned waste types (rather than specific consumer products) in relation to recycling. In relation to incineration, the focus is on the nanomaterials mentioned in Table 7.

4. Fate and risk assessment of nanomaterials in Danish waste management systems

In this chapter, available information on behaviour of nanomaterials in waste products in the typical treatment types in the waste handling system is described. Estimates of the flows of the most common nanomaterials in the waste handling system is described for incineration/landfill and for the recycling sector as a further basis for the pinpointing of where the presence of nanomaterials may potentially result in exposure, either in the environment or as a potential occupational hazard in the waste handling system.

4.1 Flows of nanomaterials in waste in incineration and landfill in the Danish waste handling system

Mueller et al (2013) has modelled the flow of nanomaterials into the incinerators and onwards and directly into landfills for Switzerland. In the Swiss model, all household waste and similar waste from commerce is incinerated, while certain types of construction waste is landfilled directly¹⁹, which is also true for Denmark. The Swiss model evaluates the flow of nanomaterials based on a long list of specific consumer products containing the nanomaterials nano-TiO₂, nano-ZnO, nano-Ag and CNT. An overview of this list and the estimated release distribution in the society/environment is shown in Appendix 2:. In Appendix 2:, it can be seen that recycling only takes place in Switzerland for consumer electronics, while some of the exported waste is probably also exported in order to be recycled. A similar model has been set up based on this version of the model for Denmark taking into account the differences between the overall Swiss waste handling system and the overall Danish waste handling system, see Figure 1 for the general model and the following textbox for the legend for the flows. Since the data are here used as the basis for the estimation of the flow of nanomaterials within the system of incineration and landfilling, the potential discrepancy in where the actual recycling takes place between Switzerland and Denmark does not have an impact on the estimation of the flows of nanomaterials in incineration and landfilling in Denmark.

Sun et al (2014) have just published an update of the Swiss flow model, where recycling has been included as a sink together with production and manufacturing flows and updated information on the behaviour of the different nanomaterials in the different technical sectors. It has not been possible within the time frame of this project to update the flow model for incineration and landfill accordingly.

¹⁹ If it is not recycled

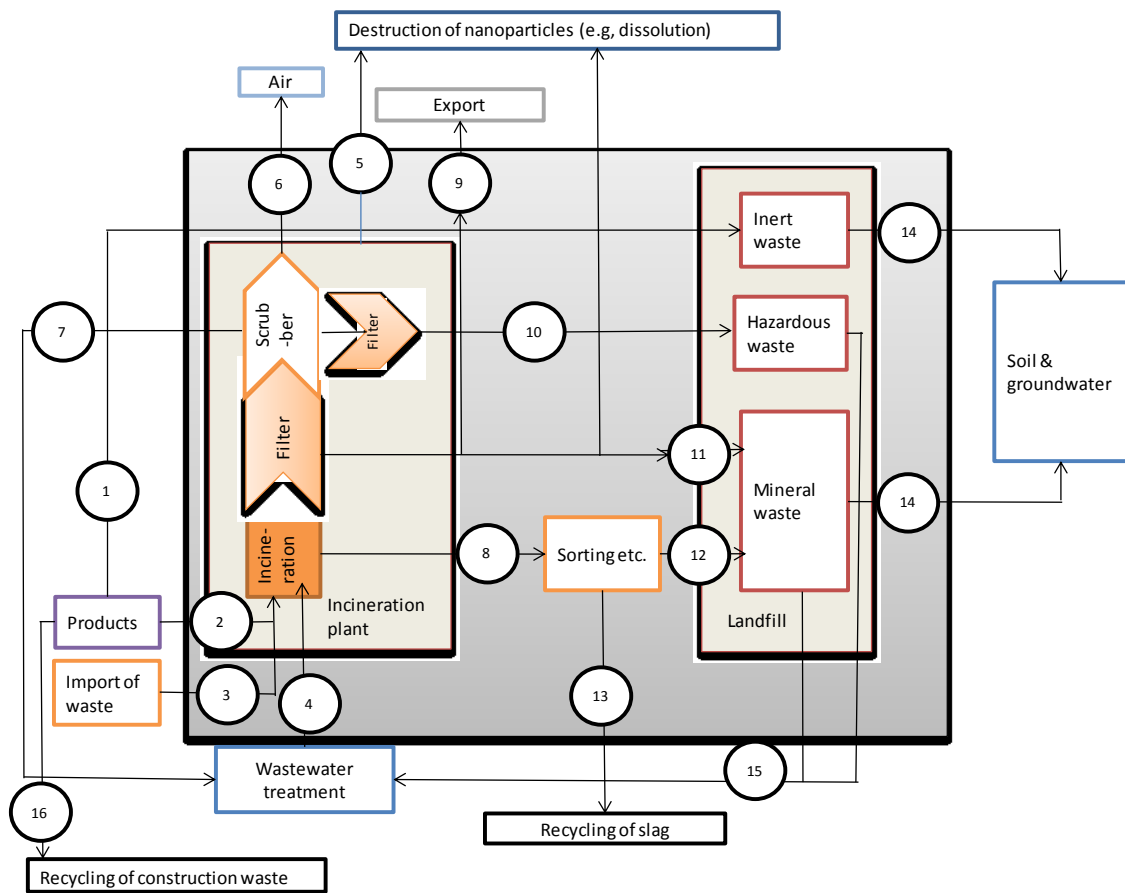


FIGURE 1 GENERAL FLOWMODEL FOR INCINERATION AND DISPOSAL OF WASTE IN DENMARK POTENTIALLY CONTAINING NANOMATERIALS, MODIFIED FROM MUELLER ET AL (2013). THE NUMBERS IN THIS FIGURE REFERS TO THE LIST OF FLOWS ON THE FOLLOWING PAGE.

Overview of processes included in the general flow model for incineration and disposal

- 1 From products to landfill
- 2 From products to incineration
- 3 Import
- 4 From sludge
- 5 Destruction
- 6 From scrubbers to air
- 7 From scrubbers to wastewater
- 8 From incineration to sorting of slag
- 9 From filter to export
- 10 From filter to hazardous waste
- 11 From filter to disposal
- 12 From sorting to landfill
- 13 From sorting to recycling
- 14 From landfill to soil
- 15 From disposal to wastewater
- 16 Recycling of construction waste

In Mueller et al (2013), four substances were modelled: nano-TiO₂, nano-ZnO, nano-Ag and carbon nanotube (CNT). These nanomaterials were chosen because they are representative for commonly used materials and products, illustrating a variety of nanomaterial with different behaviour. In the model, extrapolations from similar data were used, since no substance specific parameters for the behaviour of nanomaterials during incineration were available. The mass-based modelling showed that – despite several differences among the models for nano-TiO₂, nano-ZnO and nano-Ag (e.g. partial dissolution of nano-ZnO in acid washing of exhaust air or fly ash) – the major nanomaterial flows go from the waste incineration plant to the landfill as bottom ash²⁰. All other flows within the system boundary (e.g. with the fly ash) were predicted to be about one magnitude smaller than the bottom ash flow. In the Swiss study, a different nanomaterial distribution was found for CNTs that are expected to burn²¹ to a large extent (94%) so that only insignificant amounts remain in the system.

These evaluations are supported by a number of investigations that are further described in Chapter 4.2.

Based on this general model, specific Danish models have been set up for the 4 nanomaterials that have also been modelled by the Swiss model, see Figures 2 to 5. The basic data for the waste streams are taken from the Danish waste data system, Affaldsdatasystemet, for 2011. The flows of the nanomaterials in tonnes for 2011 have been proportioned based on the information on how much waste is incinerated and/or landfilled directly in Switzerland and Denmark respectively. The distribution of the waste between the processes is based on the latest published Danish waste statistics for 2011. In the model, the estimates related to the presence and amount of specific consumer products containing nanomaterials has not been changed from the Swiss model, since such an overview for Denmark is not available yet.

The flow models give a background for the evaluation of where nanomaterials may end up and not end up in a Danish context, and where further studies may be necessary. The estimated amounts in tonnes are based on Danish waste data and waste flows and under the assumption that the content of the specific nanomaterials in the consumer products entering the waste handling system are the same in Denmark as in Switzerland.

²⁰ Since bottom ash is landfilled in Switzerland

²¹ And thus be destroyed

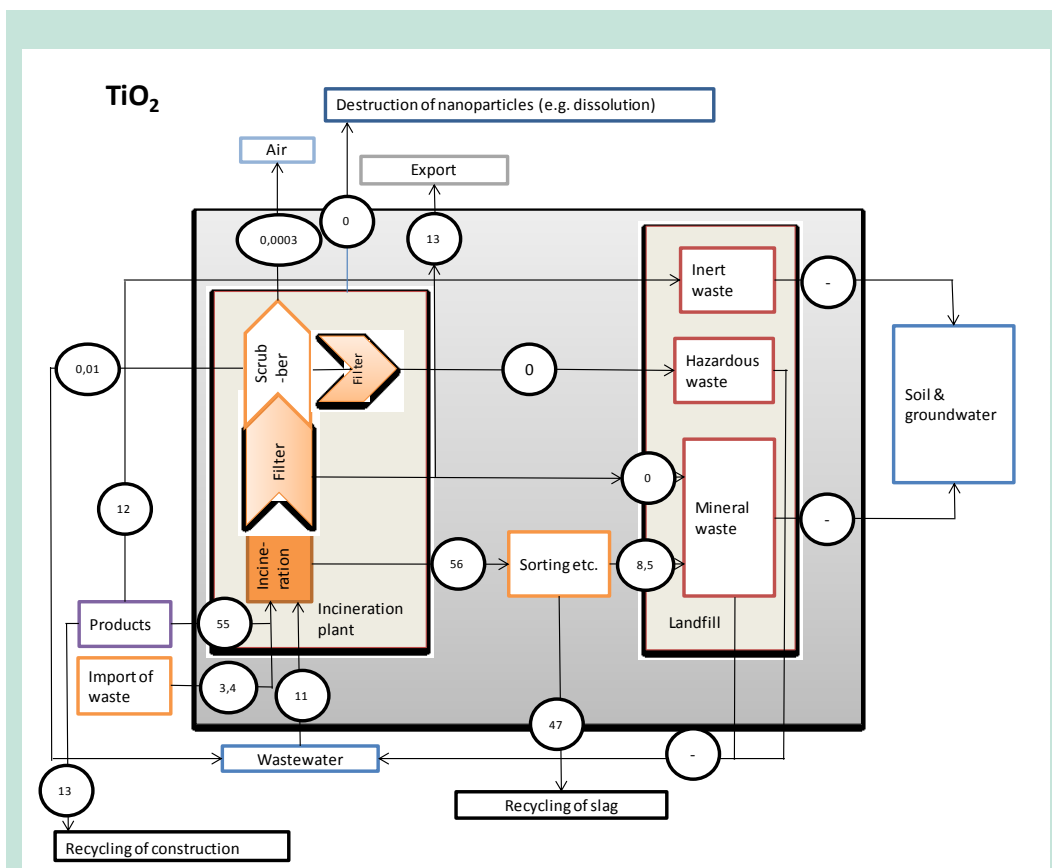


FIGURE 2
 FLOW MODEL FOR NANO-TiO₂ IN WASTE IN INCINERATION AND LANDFILL IN THE DANISH WASTE SYSTEM IN TONS PER YEAR BASED ON THE SWISS MODEL MODIFIED TO DANISH CONDITIONS BASED ON DATA FROM AFFALDSDATASYSTEMET, 2011. NUMBERS ARE IN TONNES FOR 2011.

For nano-TiO₂, Figure 2 shows that in the order of 64% of the nanomaterial going in to the waste handling system encompassing incineration and landfill will come out as either recycled slag or recycled construction waste. 22% will be landfilled and 14% will be exported as incinerator residue to Norway. Very little will be emitted to air or wastewater. These are averaged indicative numbers with a large uncertainty.

The percentages given above are based on a total of 95.3 tonnes of nano-TiO₂ goes into the waste system: 55 tonnes in waste to incineration, 13.4 tonnes in construction waste going directly to recycling, 12 tonnes in waste going to landfill, 3.4 in imported waste, and 11.5 tonnes in incinerated sludge. The recycled slag contains 47.9 tonnes TiO₂ and the recycled construction waste as mentioned 13.4 tonnes, in total 61.3 tonnes. The not recycled slag that is landfilled contains 8.5 tonnes of TiO₂, and this together with the TiO₂ in the directly landfilled waste (12 tonnes) makes up a total of 20.5 tonnes. The exported fly ash contains 4.9 tonnes of TiO₂.

The calculations for the other nanomaterials in waste are carried out in the same manner.

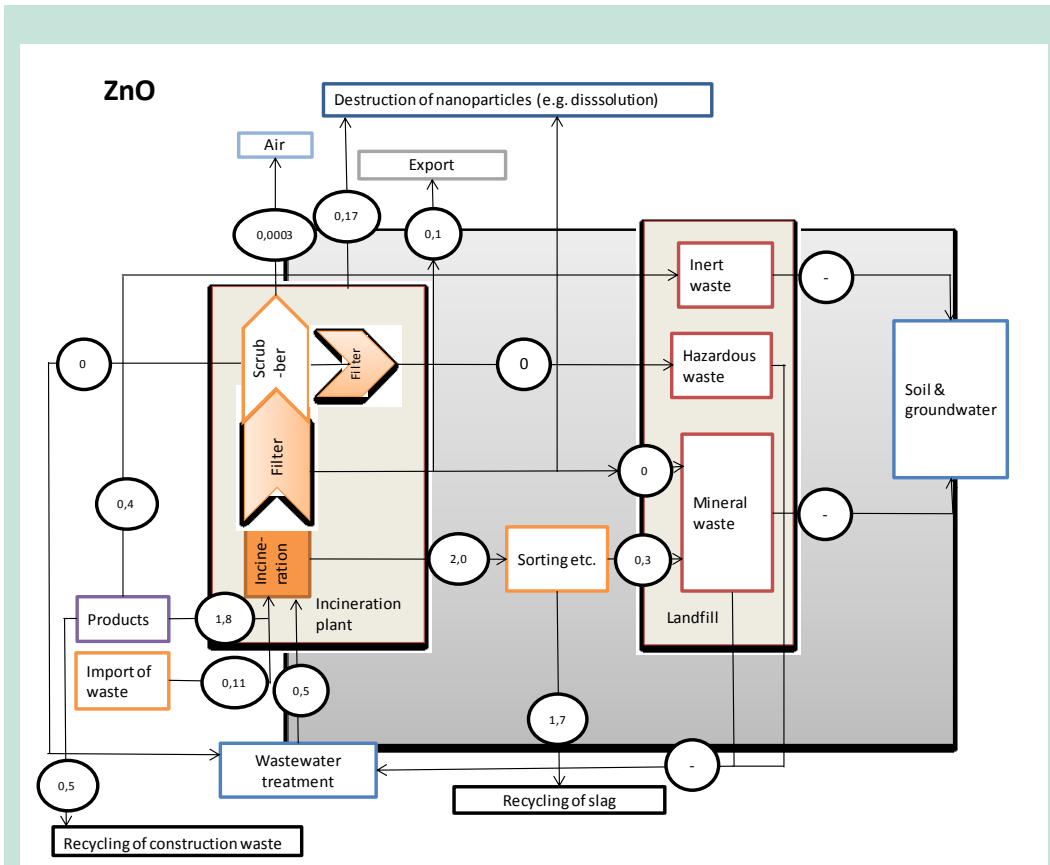


FIGURE 3
 FLOW MODEL FOR NANO-ZnO IN WASTE IN INCINERATION AND LANDFILL IN THE DANISH WASTE SYSTEM IN TONS PER YEAR BASED ON THE SWISS MODEL MODIFIED TO DANISH CONDITIONS BASED ON DATA FROM AFFALDSDATASYSTEMET, 2011. NUMBERS ARE IN TONNES FOR 2011.

For nano-ZnO, Figure 3 shows that in the order of 66% of the nanomaterial going into the waste handling system encompassing incineration and landfill will come out as either recycled slag or recycled construction waste. 21% will be landfilled and 3% will be exported as incinerator residue to Norway. App. 5% will be destroyed in the incineration process, while very little be emitted to air or wastewater. These are averaged indicative numbers with a large uncertainty.

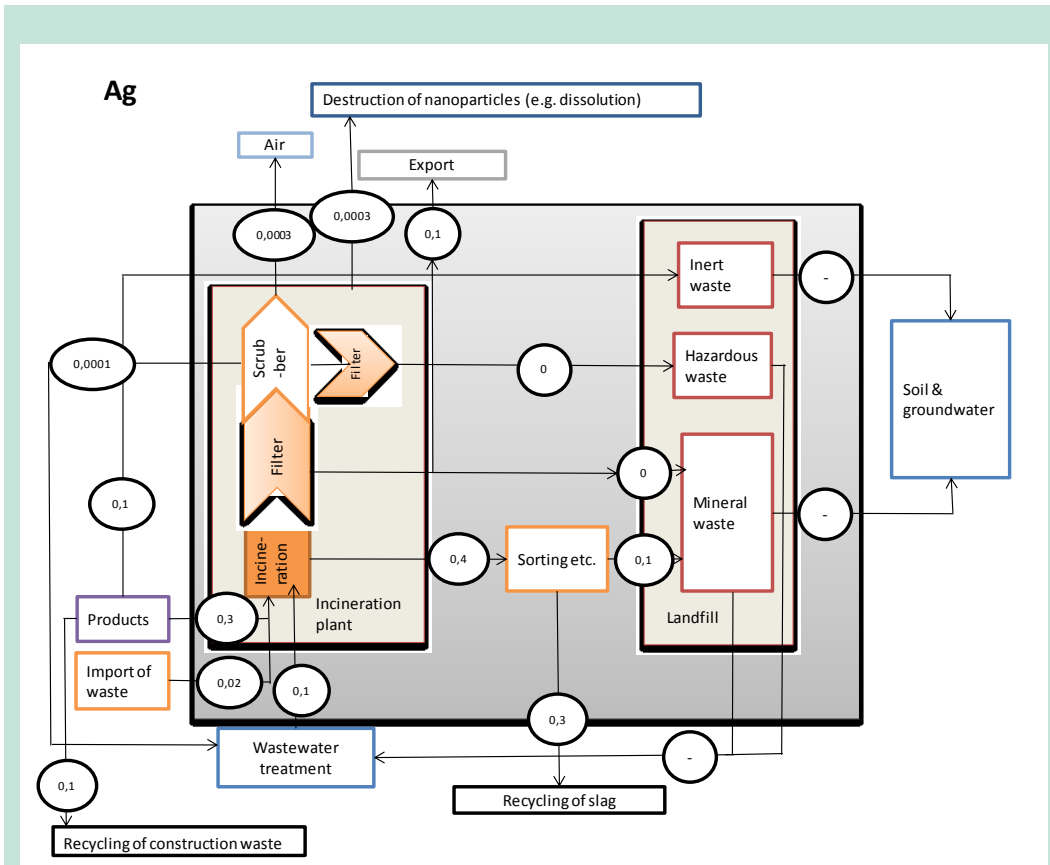


FIGURE 4
 FLOW MODEL FOR NANO-AG IN WASTE IN INCINERATION AND LANDFILL IN THE DANISH WASTE SYSTEM IN TONS PER YEAR BASED ON THE SWISS MODEL MODIFIED TO DANISH CONDITIONS BASED ON DATA FROM AFFALDSDATASYSTEMET, 2011. NUMBERS ARE IN TONNES FOR 2011.

For nano-Ag, Figure 4 shows that in the order of 68% of the nanomaterial going into the waste handling system encompassing incineration and landfill will come out as either recycled slag or recycled construction waste. 20% will be landfilled and 13% will be exported as incinerator residue to Norway. App. 0.05% will be emitted to air and wastewater. These are averaged indicative numbers with a large uncertainty.

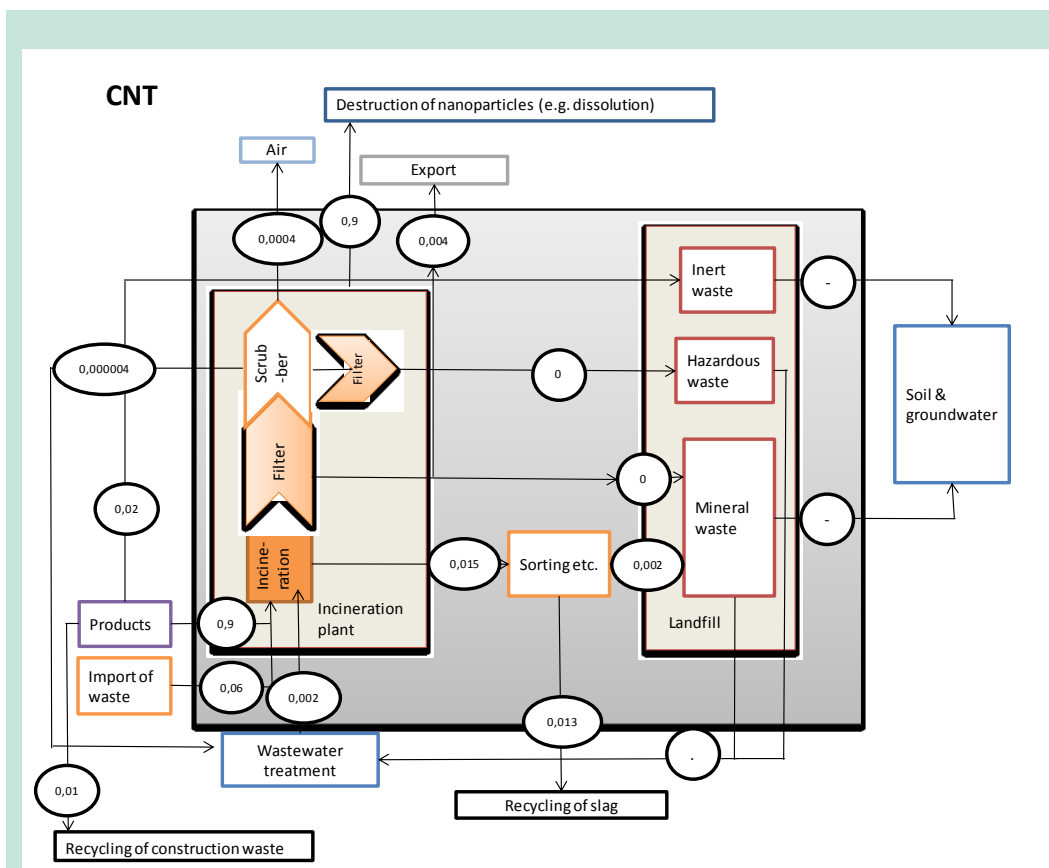


FIGURE 5
 FLOW MODEL FOR CNT IN WASTE IN INCINERATION AND LANDFILL IN THE DANISH WASTE SYSTEM IN TONS PER YEAR BASED ON THE SWISS MODEL MODIFIED TO DANISH CONDITIONS BASED ON DATA FROM AFFALDSDATASYSTEMET, 2011. NUMBERS ARE IN TONNES FOR 2011.

For CNTs, Figure 5 shows that in the order of 2% of the nanomaterial going into the waste handling system encompassing incineration and landfill will come out as either recycled slag or recycled construction waste. 2% will be landfilled and 0.4% will be exported as incinerator residue to Norway. App. 95% will be destroyed in the incineration process, while app. 0.05% will be emitted to air or wastewater. These are averaged indicative numbers with a large uncertainty.

It can be seen from the figures that a large percentage of each of the nanomaterials are recycled in construction work as both crushed and sorted construction waste or crushed and sorted waste incinerator slag. This is a quite different situation than the Swiss, where these materials are landfilled and not recycled, and points to the necessity for evaluation of the potential leaching of nanomaterials in these recycled construction materials. In Table 8, the percentages being recycled of the material entering the incineration/landfill system is summarised.

TABLE 8
 PERCENTAGE OF NANOMATERIALS ENTERING THE INCINERATION AND LANDFILL SYSTEM IN DENMARK THAT IS BEING RECYCLED THROUGH RECYCLING OF SLAG AND CONSTRUCTION WASTE AS CONSTRUCTION MATERIALS.

	Nano-TiO ₂	Nano-ZnO	Nano-Ag	CNT
Recycled percentage	64	65	68	2

4.2 Behaviour of nanomaterials in products in incineration processes

This chapter contains a review of a number of articles that address the behaviour of nanomaterials in products, when the product is incinerated. The statements in the review are all taken directly from the articles, which may in some cases lead to opposite views being expressed.

In the OECD report on incineration (OECD, 2013b), four opportunities are mentioned to exist for the (re-)formation or destruction of nanomaterials during incineration (based on Roes et al (2012):

- 1) Nanomaterials are destroyed due to combustion (for example CNT to CO₂).
- 2) Nanomaterials are destroyed or incinerated, but captured by the flue gas treatment system (for example metal oxides). These nanomaterials can be detected afterwards in the fly ash or other residues.
- 3) Certain types of nanomaterials may not get destroyed during combustion. However, the combustion products react with the other substances and form new particles (e.g. CaCO₃ to CaO and CO₂ or ZnO + HCL give ZnCL₂ + H₂O).
- 4) Bigger particles decompose and turn into new, smaller particles.

OECD (2013b) points to two main sources from which nanomaterial may enter waste incineration processes: municipal solid waste (including some residues from manufacturing of nanomaterial containing products) and sewage sludge, if it is incinerated.

Roes et al (2012) describe how nanomaterials can be destroyed, converted into other nanomaterials or left unchanged during incineration. They specifically look at the fate of nanocomposites in plastic. The assumption is that the average content of plastics in municipal solid waste is around 12%, containing 7% nanocomposites²². A model for the determination of risks related to the release of nano-objects²³ due to direct emission from incineration or leaching from the solid residues has been set up, see Figure 6. The fate of the nano-objects in solid waste incineration plants is summarised by Roes et al as follows:

- In the grate furnace, nano-objects can be destroyed, converted into other nano-objects (e.g. oxides, chlorides) or leave unchanged.
- For nano-objects that are in the range of 100 nm and larger, the efficiency of removal is highest.
- For nano-objects that are smaller than 100 nm, the removal efficiency is significantly reduced. These are partially removed by fabric filters, and wet scrubbers, but still a significant amount (up to 20%) is expected to pass²⁴ (exact amount: unknown for fabric filters; more than 35 – 50% for wet scrubbers, depending on size).
- Removed nano-objects will end up in the solid residues. Leaching from solid residues (e.g. when they are used as construction material) should be prevented.

²³ But it should be considered that the average of composites in the municipal solid waste input can vary and depends on local infrastructure.

²³ Nanoobjects are defined according to ISO, 2008 as objects that have at least one dimension in the order of 1 – 100nm, comprising nanoparticles that are nanoscale at three external dimensions, nanofibers that are nanoscale at two external dimensions and nanoplates that are nanoscale on one external dimension.

²⁴ Into the flue gas

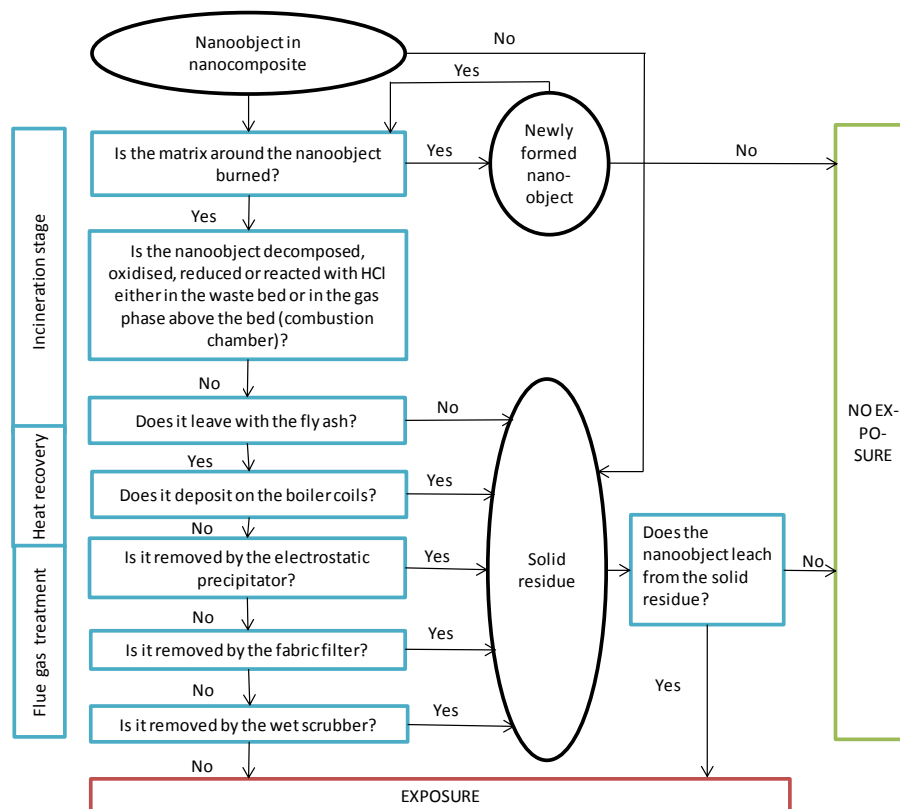


FIGURE 6
 DECISION TREE FOR THE DETERMINATION OF RISKS RELATED TO NANO-OBJECT RELEASES INTO THE ENVIRONMENT FROM INCINERATION (EITHER FROM DIRECT EMISSION OR LEACHING FROM SOLID RESIDUES), BASED ON ROES, ET AL (2012)

The risk assessment does not specifically address risks to humans exposed via the environment. It is therefore difficult to conclude whether there is a risk or not. On the other hand, it cannot be excluded that emission of materials in the nano-form rather than larger forms might increase human health risks.

Based on the amount of plastic incinerated in the US (12%, 2011), the share of nanocomposites among plastics – also in the US (7%), and the content of nano-objects in the nanocomposites (between 1 and 10%), Roes et al (2012) also calculate the potential increased nano-objects emission from solid waste incinerators due to the incineration of plastics containing nanocomposites. Especially for nanocomposites based on aluminium oxide, magnesium hydroxide, titanium oxide and fullerenes, the potential increase in the emission of nano-objects from incineration is substantial. It should be noted that the risk assessment does not take the effect of agglomeration into account. Roes et al (2012) also point to the risk of volatile heavy metal compounds condensing on particles with large surface area, making the nanoparticles carriers of all metals present in the off-gas. They finally describe the need for further research in this area, which is summarised in Chapter 7 of this report.

TABLE 9
SUMMARY OF THE RESULTS OF THE PRELIMINARY EXPOSURE ASSESSMENT FOR NANOCOMPOSITES IN INCINERATED PLASTIC IN ROES, ET AL (2012), SHOULD BE READ IN CONNECTION WITH FIGURE 6.

	Can primary nano-objects enter the fly ash stream?	Can secondary nano-objects be generated and enter the fly ash stream	Will the nano-objects be completely removed by off-gas treatment?	Is there a risk of nano-objects emission via stack
Aluminium oxide	Yes	Yes	No	Yes
Calcium carbonate	Yes	Yes	No	Yes
Magnesium hydroxide	No	Yes	No	Yes
POSS	Yes	Yes	No	Yes
Silica	Yes	No	No	Yes
Titanium oxide	Yes	No	No	Yes
Zinc oxide	Yes	Yes	No	Yes
Zirconia	Yes	No	No	Yes
Mica	Yes	Yes	No	Yes
Montmorillonite	Yes	Yes	No	Yes
Talc	Yes	Yes	No	Yes
Cobalt	Yes	Yes	No	Yes
Gold	Yes	No	No	Yes
Silver	Yes	Yes	No	Yes
Carbon black	Yes	No	No	Yes
Carbon nanotubes	Yes	No	Yes	No
Fullerenes	Yes	No	No	Yes

In Walser et al (2013), two experimental case studies were described with respect to the results of adding nanoparticles to the treatment line of a large scale solid waste incinerator with energy recovery, an electrostatic precipitator, a selective non-catalytic reduction to reduce NO_x and a wet scrubber. In the first experiment, CeO₂ was introduced by spraying 0.2 m³ nano-CeO₂ water suspension (5 wt. % CeO₂) onto app. 7 tonnes of waste at the furnace entrance during 1 hour.

In the second large scale experiment, 0.1 m³ of CeO₂ suspension (1 wt. % CeO₂) was injected directly into the space above the furnace for 2.75 hours. The conditions were sought to represent worst-case scenarios with an exceptionally high input of unattached nanoparticles (case 1) or an extremely high particle transfer to the gas phase to test the removal efficiency of the flue gas treatment (case 2).

The first case, mass balance showed that nearly 81% of nanomaterial was transferred into the slag, nearly 19% into the fly ash, and 0.02% into the quench water. In case 2, 53% of nanomaterial was found in the slag, 45% in the fly ash and 1.7 in the quench water and 0.0004% into clean flue gas. Walser et al (2013) point to the fact that emissions of engineered nanoparticles can occur during further treatment of slag such as material recovery (e.g. recovery of metals), transportation and intermediate storage, which may lead to increased exposure to workers.

Similarly, filter ash is increasingly looked at as a potential resource for the recovery of metals (zinc, lead) through acid washing. The fate of engineered nanoparticles during this process, including washouts into wastewater streams, and the subsequent metallurgical process is unclear and represents a potential risk.

In the EU NanoSustain project, the impact of using multi-walled carbon nanotubes (MWCNT) in plastic as a reinforcement agent has been evaluated (NanoSustain, 2013c & f).

To simulate the end-of-life options, composites containing carbon nanotubes (CNTs) were incinerated in a solid fuel furnace together with wood chips as a supporting fuel (Kettunen et al, 2011). The possible release of nanoparticles and CNTs during the experiment was evaluated to get information about possible risks related to incineration of CNT containing composites. The CNT composite consisted of electrical grade glass fibre with epoxy hardener, of which 52.2 wt.% is Amroy Hybtonite multiwall CNT composite containing approximately 0.5 wt.% Bayer C 150 P multiwall CNT (Bayer material science, 2008 and 2010). Three different fuel compositions were mixed: wood chips with 20 wt.%, 5 wt.% and 0 wt.% of the CNT containing composite. The average combustion temperatures in the furnace were 700-800 °C during good combustion with 20 wt.% of CNT containing composite and approximately 950-1050 °C for other conditions. During combustion, the particle number and mass concentration as well as the size distribution were measured and individual particle morphology and composition was studied by electron microscopy (EM). Raman spectroscopy was carried out on deposit and particle samples to find out possible presence of CNT structures.

Kettunen et al (2011) concluded that nanoparticles were observed in all combustion cases independent of the fuel composition when the new nanoparticle definition by EU is taken into account²⁵. However, the fraction of the nanoparticles ²⁶varied depending on the composition of the fuel. The fraction was highest for the combustion of wood chips, when nanoparticles were “counted” as individual particles and not aggregates/agglomerates.

Kettunen et al note that the combustion conditions inside the furnace were not always optimal in the CNT composite mixture cases, because of the formation of a large and hard bottom deposit on the grate of the burner. The formation of the deposit severely worsened the operation of the furnace, thus directly influencing combustion and the formation of the ash and emitted particles. As an example, the emitted particles during the 5 wt.% CNT composite combustion case were almost spherical, approximately 50 nm in diameter together with aggregates of different sizes (approx. 200 nm and larger), consisting of the primary particles. None of the combustion cases presented evidence of CNT like tubular structures in the emitted particles.

This finding was also confirmed with RAMAN spectroscopy. This was probably caused by the low amount of the CNT containing composite in the fuel mixture, and the formation of the large and hard, highly sintered bottom ash deposit that may “bind”/immobilise the species in the CNT composite in a non-volatile matrix. Thus, the results may be different with fuel mixtures with higher amounts of CNTs or depending on the matrix where the CNTs are “bound”.

Bouillard et al (2013) have investigated the incineration of CNT containing polymers (acrylonitrile butadiene styrene with a 3 wt.% content of MWCNTs). Their study showed that at low temperatures (450 °C), that is, at upstart of the incineration process, CNTs were released. This result points to the importance of running solid waste incinerators continuously (which is the case for all modern large waste incinerators due to the dioxin issue) in order to insure sufficiently high temperatures to be able to destroy the CNTs.

²⁵ EU Commission report, Review of Environmental Legislation for the Regulatory Control of Nanomaterials 2011; Available from: <http://ec.europa.eu/environment/chemicals/nanotech/>, (accessed 25.8.2013.)

²⁶ Of the particles measured

Buha et al (2014) have characterised fly ash from Swiss waste incineration plants in order to determine the ash fraction in the nano-meter range and to assess the potential content of engineered nanomaterials in this fraction. They found that the mass percentage of particles smaller than 100 nm in the fly ash was 0.1% for the incinerator only burning waste, while the number of particles smaller of 10 nm constituted 17% of the total number of particles. Comparing with modelling results for the amount of different types of nanomaterials in fly ash, they concluded that engineered nano-objects may constitute a considerable part of the fly ash particles below 100 nm.

Köhler et al (2008) have qualitatively evaluated the potential processes at which CNTs incorporated in either lithium-ion batteries or textiles with CNT enhanced polymers may be released. For some of the battery types, the casing of the battery is so resistant that it will not be damaged by incineration leading to the lack of destruction of the CNTs. This can lead to a later release of CNTs when the slag is crushed. When CNTs are used in textiles, incineration of the textiles will lead to destruction of the CNTs.

It should be noted that batteries, according to the battery directive, must be collected for recycling and not end up in an incinerator.

Petersen et al (2011) state in their review that CNTs present in nanocomposites would most likely not be aerosolized during incineration, because incineration facilities are designed to ensure that off-gases and aerosolized particulates have long residence times at high temperatures (1000 to 1100 °C) ensuring their almost complete destruction. However, non-combusted CNTs may end up in the bottom ash.

Holder et al (2013) have compiled existing information on the behaviour of nanomaterial in modern waste incinerators. Their conclusion (based on a number of the articles also referenced in this report and on some batch type experiments evaluating the impact on emission of other pollutants of the addition of nanomaterials) was that these initial studies on the incineration of nanoparticle-spiked wastes have shown that (1) some nanoparticles can penetrate through the combustion zone largely unchanged, (2) modern air pollution control equipment may be effective at removing some nanoparticles, and (3) nanoparticles can potentially impact the production or destruction of hazardous pollutants. Holder et al (2013) state that the studies reviewed, evaluated, at most, just a few particle types; therefore, these conclusions are likely specific to the particular nanomaterial investigated and cannot readily be extended to other nanomaterials.

In a figure, shown here as Figure 7, Holder et al (2013) describe the possible pathways that a nanoparticle, or nanotube or other shape, can follow inside the incinerator system. Nanoparticles may exist in the waste as free particles (i.e., a powder), dispersed in a liquid, or embedded in a solid material. This initial state is likely to determine, whether the particle will become aerosolized, which largely dictates its fate in the combustion zone.

Based on the behavior of nanoparticle fire retardants and nanoliquids, Holder et al (2013) hypothesized that nanoparticles contained within a solid or liquid system are more likely to aggregate. These larger aggregates may, or may not, burn depending upon the local conditions in the combustion chamber.

Chemical composition is also likely to play an important role in determining the fate of nanomaterials. Particles that are already oxidized, especially those with high melting points, like CeO₂, may exit the combustion zone essentially unchanged. Alternatively, reduced nanoparticles, such as aluminum, will combust given high enough temperatures. However, complete combustion may depend on the particle size and aggregation state (Holder et al 2013).

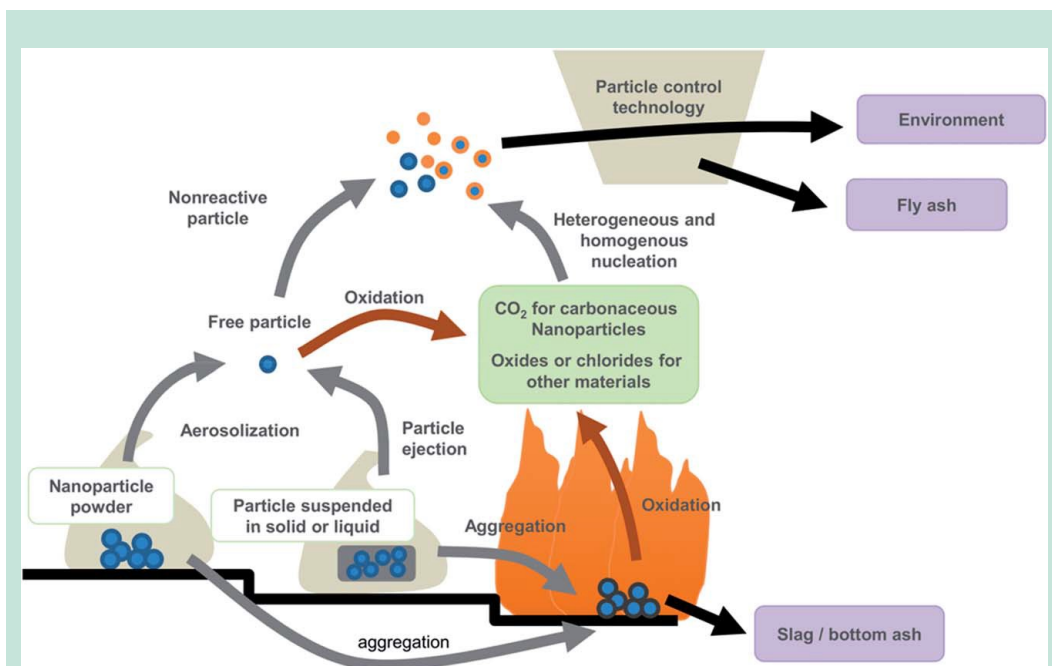


FIGURE 7
POSSIBLE PATHWAYS DESCRIBING THE FATE OF NANOMATERIALS WITHIN WASTE INCINERATORS, HOLDER ET AL (2013)

Further, according to Holder et al (2013), in the post-combustion region, aerosolized nanoparticles that persisted through the flame zone are mixed with other particles produced inside the combustion zone. Particle aggregation may occur, shifting the original size distribution toward larger diameters. Additionally, other species may condense on the nanoparticle, changing its composition, which may increase the health hazard of these particles. All of these changes may impact the effectiveness of particle control technology at removing these nanoparticles. Fabric filters are expected to be most effective among existing control technologies at removing nanoparticles and larger aggregates, regardless of particle composition. Aggregation state and particle size will be key factors in determining nanoparticle capture efficiency in other air pollution control devices (Holder et al 2013). At any point in the process, nanoparticles may impact the formation of other pollutants, particularly PAH and PCCD/F. Again, this interaction is likely to be dependent on the particle composition and available surface area. The limited experimental evidence shows that formation of pollutants can increase in some cases and decrease in others.

Holder et al (2013) summarise their findings in a table, see Table 10, with respect to expected combustion behaviour.

TABLE 10
EXPECTED INCINERATION BEHAVIOR OF SEVERAL COMMON NANOMATERIALS, HOLDER ET AL (2013)

Nanomaterial	Is combustible	Acts as a fire retardant	Can persist through combustion zone	Can cause increased emissions of other pollutants
SiO ₂	No	Yes	Yes	?
TiO ₂	No	Yes	Yes	Yes
CNT	Yes	Yes	Yes	?
CeO ₂	No	Yes	Yes	Yes
Ag	?	?	?	Yes
Fullerene	Yes	?	?	Yes

The European Commission has specifically had focus on textiles containing CNTs. They state that it is assumed that only incineration above 850°C can eliminate CNTs (OECD, 2013a).

Sun et al (2014) use their updated flow model for nanomaterials for Switzerland and the EU respectively²⁷ to calculate expected ranges of the different nanomaterials also in solid waste plus bottom ash and fly ash from solid waste incinerators, see Table 11.

TABLE 11
PREDICTED NANOMATERIAL CONCENTRATIONS IN DIFFERENT TECHNICAL COMPARTMENTS SHOWN AS MODE (MOST FREQUENT VALUE) AND AS A RANGE OF LOWER AND UPPER PERCENTILES (Q0.15 AND Q0.85), MG/KG. BASED ON SUN, ET AL (2014)

	EU			Switzerland		
	Mode	Q0.15	Q0.85	Mode	Q0.15	Q0.85
Nano-TiO₂						
Solid waste	12	8.3	20	19	14	32
WIP bottom ash	120	82	230	210	150	410
WIP fly ash	150	110	310	280	200	560
Nano- ZnO						
Solid waste	0.9	0.5	2.4	1.6	0.7	3.7
WIP bottom ash	3.5	1.9	11	5.1	2.9	16
WIP fly ash	2.8	2.7	22	4.8	4.1	33
Nano-Ag						
Solid waste	0.06	0.05	0.08	0.05	0.04	0.07
WIP bottom ash	0.23	0.2	0.4	0.2	0.2	0.3
WIP fly ash	0.38	0.2	0.9	0.3	0.2	0.8
CNT						
Solid waste	1.7	1.3	2.6	3.0	2.3	4.0
WIP bottom ash	0.2	0.2	1.4	0.4	0.4	2.3
WIP fly ash	0.4	0.3	2.9	0.6	0.6	4.7
Fullerenes						
Solid waste	0.07	0.04	0.13	0.08	0.04	0.1
WIP bottom ash	0.01	0.01	0.07	0.01	0.01	0.08
WIP fly ash	0.01	0.01	0.14	0.01	0.01	0.2

4.3 Behaviour of nanomaterials in products in landfills

This chapter contains a similar review of articles addressing behaviour of nanomaterial in landfilled products.

²⁷ The model is further described in chapter 4.1.

In the NanoSustain project concerning use of nano-ZnO as a UV reducing glass coating, leaching of ZnO from the crushed glass was also investigated in a lab-scale landfill setting (NanoSustain, 2013b & f). Test methods mimicking landfill conditions were initially studied with crushed glass and pure nano-ZnO powder mixed with glass beads in order to identify critical conditions for the release. In addition, agglomeration studies were carried out focusing on gathering information on conditions influencing the agglomeration of nanoparticles in order to support the understanding of the leaching test results. The agglomeration of nanoparticles strongly influences the fate (e.g. mobility and retardation) of the nanoparticles in landfill leachates.

Based on the results of the leaching studies, the release of Zn was dependent on the total amount Zn in the test material, and it was strongly influenced by the pH of the solution (lowest release observed at pH 9.2). Furthermore, the test results indicated that the salt concentration decreased the release (probably due to agglomeration of particles). Agglomeration studies supported these findings by detecting faster agglomeration rates with high salt concentrations. In addition, larger sized particles/agglomerates were detected at pH 9.2, which is the zero point of ZnO's zeta potential (Bacher, 2014).

According to Bacher (2014), the strong influence of salt concentration on agglomeration means that under landfill condition the release may be lower, compared to laboratory test with demineralised water. However, the leaching tests do not give information about long term behaviour of the formed agglomerates. Especially the pH needs to be taken into account in the assessment of release in landfill conditions.

Part of the NanoSustain project on behaviour of ZnO in landfills (Bacher, 2014) encompassed the development of test methods for estimating the release potential of nanoparticles from nanotechnology based products under conditions mimicking landfill conditions. Suitable methods for measuring nanoparticles in water were mapped and their reliability evaluated for the measurements as part of a release study. During the study, the standardised release tests were found to be applicable for this type of inert test materials. Critical test conditions such as using glass or potentially Teflon as equipment material were identified in order to develop a scientifically sound test method for the measurement of the release of nanomaterials.

Based on experience in the NanoSustain project, it can be stated that analysis of nanoparticles in eluates from leaching tests is very challenging, and analysis of eluates requires special analytical equipment and also expertise (Bacher et al, 2014). Today, practical tools for analysis of nanoparticles in a waste leachate containing high content of solubles are lacking. Only in case of almost inert material with a low release of salts, is it possible to characterize particles in eluates and get an indication of potential release.

The concentrations of nanoparticles in the water phase is also not constant, since nanoparticles may easily be agglomerated (and also partly decomposed into nanoparticles) with time. These analytical observations are also confirmed by Hennebert et al (2013).

Köhler et al (2008) also evaluated the fate of CNT containing batteries if they should be landfilled. Here, low pH in the landfill (if sufficient organic matter is present) can corrode the battery casings leading to release of CNT.

Nowack et al (2013) have looked at processes that may lead to release of CNTs from polymers under conditions that exist in modern managed landfills. Such processes include abrasion by the compacting processes to smaller particles and in principle degradation. Degradation of the polymer matrix, especially in the case of non-hydrolysable polymers, and release of CNTs are likely to be extremely slow. The situation in developing nations is less controlled and could lead to greater environmental releases of discarded CNT composites.

Lozano & Berge (2012) carried out laboratory-scale experiments to evaluate how organics (humic acid: 20–800 mg/L), ionic strength (100–400 mM NaCl), and pH (6–8) typical of mature leachates influence carbon nanotube surface charge, relative stability, and mobility through representative solid waste environments. Results from the batch experiments suggested that the presence of high molecular weight organics, such as humic acid, acts to stabilize carbon nanotubes present in leachate, even at high ionic strengths (>100 mM NaCl). The results also suggest that in mature landfill leachate, as long as humic acid is present, ionic strength (when represented as NaCl) will be a dominant factor influencing nanomaterial stability. Column experiments indicate that carbon nanotubes may be mobile within landfills.

These results are supported by experiments evaluating impact on aggregation of nanoparticles in water in the presence of humic, and fulvic acids (Huyng & Kim, 2008; Jaisi et al, 2008; Petosa et al, 2010; Saleh et al, 2010).

Boylard et al (2012) investigated the fate of coated zinc oxide (ZnO), titanium dioxide (TiO₂), and nano-silver (Ag) in landfills by characterising landfill leachate, evaluating the effects of nanomaterials on landfill biological processes, size fractionation of leachate exposed to coated ZnO, TiO₂, and Ag, and modelling of the chemical speciation of Zn, Ag, and Ti. Middle-aged (BOD/COD: 0.34-0.54) and mature (BOD/COD: 0.07-0.11) leachate samples were collected and characterised from MSW landfills in Florida, USA. Leachate was exposed to concentrations of 100 µg/L, 1.0 mg/L, and 100 mg/L of coated ZnO, TiO₂, and Ag, individually, in order to observe any concentration-dependent effects on biological processes, solids aggregation, and dissociation. Results were compared to a control reactor treated in the identical manner without the addition of nanomaterials.

In Boylard et al (2012), the effect of nanomaterials and their by-products on both aerobic and anaerobic biological landfill processes was evaluated by performing BOD₅ and Anaerobic Biodegradation Potential under methanogenic conditions. Any decreases in BOD₅ and BMP relative to control samples suggest inhibitory effects. The concentration of Zn, Ag, and Ti in each size fraction was quantified using ICPOES.

Boylard et al's results (2012) show that ZnO and TiO₂ did not have an inhibitory effect on anaerobic or aerobic processes when exposed to mature or middle-aged leachate. BOD₅ results after exposure to ZnO and TiO₂ were analysed, and the rate of disappearance of biodegradable matter did not vary significantly between the control and reactors exposed to nanomaterials. Additionally, the BMP test did not vary substantially over a 90-day period. This is also supported by HRTEM images that show the crystalline structure of both ZnO and TiO₂ still intact which conclude that both nanomaterial coatings were stable during the 60-day exposure time. Dispersion of hydrophobic nanomaterials was observed, presumably due to interaction between metal nanomaterials and high concentrations of humic acid in leachates.

Taghizadeh-Saheli et al (2013) carried out experiments to evaluate the potential diffusive transport of multiwall carbon nanotubes through a 0.5 mm HDPE (High Density PolyEthylene) geomembrane. Two diffusion cells contained the MWCNT dispersion in the source chamber and an identical aqueous solution but without MWCNTs in the receptor chamber; the chambers were separated by a 0.5 mm HDPE geomembrane. Two control cells, where the entire cell was filled with the MWCNT dispersion (no geomembrane), were used to quantify the MWCNT stability. Samples were taken immediately after cell set-up to confirm the initial MWCNT concentration. The cells were sampled at regular time intervals to monitor the change in the concentration of MWCNTs in both the source and receptor chambers of the diffusion cells, control cells, and blank diffusion cell. The results show that there was no detectable decrease in the concentration of MWCNTs in the source chambers of the two diffusion cells. This result suggests that sorption of MWCNTs to HDPE geomembrane or transport through the membrane was not detectable after about 1 month.

The OECD draft reflection paper (2014) on landfilling of waste containing nanomaterials and nanowaste also contains principle reflections on the behaviour of nano-objects in leachate treatment and a discussion of potential BAT technologies. Since specific leachate treatment is very near non-existent in Denmark, these discussions are not summarised here. No direct investigations of leachate treatment on nanomaterials were cited in the paper.

4.4 Behaviour of nanomaterials in products in organic processes

This chapter reviews articles that address behaviour of nanomaterials that undergo organic processes as part of the waste treatment.

Roes et al (2012) comment on the potential impacts related to treatment of biodegradable polymers containing nanocomposites: Digestion and composting may be considered suitable waste management options for these products, which may lead to compost containing nano-objects being used for soil amelioration. This could cause the nano-objects to be released, and there may even be a risk that they end up in the food chain.

If the solid output from the digester (the digestate) is instead incinerated, this would also entail a high risk of release of free nano-objects (Roes et al, 2012). The risks related to the combustion of the biogas originating from the digestion plant are probably small, since it is unlikely that the nano-objects enter the biogas phase.

In the EU NanoSustain project, production and lifecycle assessment of nanocellulose for paper and plastic products were evaluated (NanoSustain, 2013d & f). One of the findings was that nanocellulose degrades efficiently under standard composting conditions²⁸. Different kind of nanoproducs containing nano-fibrillated cellulose was evaluated using biodegradation test²⁹. According to the results, all tested products can be considered as biodegradable under composting conditions, and they also disintegrated in pilot-scale composting experiments. Compost quality was ensured using the kinetic *Vibrio fischeri* bioluminescence inhibition assay (Flash assay).

Yang et al (2012) determined the impact of Ag nanoparticles on anaerobic digestion of landfill waste. Municipal solid waste was loaded in identical landfill bioreactors (9 L volume each) and exposed to Ag NPs (average particle size=21 nm) at concentrations of 0, 1, and 10 mg Ag/kg solids. Anaerobic digestion was carried out for more than 250 days, the cumulative biogas production was recorded automatically, and the chemical property changes of leachates were analysed. There were no significant differences in the cumulative biogas volume or gas production rate between the control experiment and 1 mg Ag/kg, while landfill solids exposed to Ag NPs at 10 mg/kg resulted in reduced biogas production, accumulation of volatile fatty acids, and a prolonged period of low leachate pH (between 5 and 6). Quantitative PCR results after day 100, also the numbers of 16S rRNA gene of methanogens, were significantly reduced in the bioreactor treated with 10 mg Ag NPs/kg. The results suggest that Ag NPs at the concentration of 1 mg/kg solids have minimal impact on landfill anaerobic digestion, but at concentration of 10 mg/kg or higher Ag NPs inhibit methanogenesis and biogas production in the landfill.

Similar impacts would be expected in bioreactors for slurries based on mixed waste.

²⁸ But not in the aquatic environment.

4.5 Behaviour of nanomaterials in products in recycling processes

Finally, this chapter reviews articles that address the behaviour of nanomaterials in products that are channelled for recycling, ending in an evaluation by the authors of this study as to which processes during recycling that potentially could give rise to emission of nanomaterials to the work space. An evaluation is also given as to which processes in the further treatment of the recycled materials, where the presence of nanomaterials may give rise to emission of nanomaterials to the environment.

OECD (2013a) states that the principal challenges with safe and environmentally sound recycling procedures for waste containing nanomaterials are:

- a) Controlling the health, safety and environmental risks arising from recycling processes of waste containing nanomaterials.
- b) Controlling the technical and environmental quality of secondary materials that may be contaminated with nanomaterial from the original waste stream.
- c) Develop technologies that may be used for the recovery of the nanomaterial from the products, given suitable quantities, concentrations and economic value of the nanomaterials.

Regarding a) OECD expresses ³⁰ that the main possibilities of exposure to nanomaterials in recycling processes for waste encompassing waste that contain nanomaterials may be:

- Exposure to fine or ultrafine dust containing free nano-objects emitted during transport, sorting, shredding, grinding or pouring of the waste containing nanomaterials
- Exposure to nano-objects in liquid media (water, solvents) due to cleaning or rinsing the products before mechanical recycling; also exposure to contact with nano-objects on cleaning clothes from maintenance and cleaning of recycling equipment.
- Exposure to nano-objects that may be set free in the flue gas or to the ambient air with thermal processes (heating, welding, pyrolysis) when there is insufficient occupational control.

In evaluating the potential impact on occupational health when recycling waste containing nanomaterials, Struwe et al (2012) distinguish between two types of waste containing nanomaterials:

- a) Waste with heterogeneous composition, containing different products in their waste stream. Additionally, the different products also contain multiple diverse nanomaterials, often not even known. This category includes for example WEEE, end-of-life vehicles, paper and most plastic waste.
- b) Waste with a comparatively homogeneous composition, containing only few, normally known nanomaterials, e.g. PET-bottles, used tires, Li-ion batteries.

It seems reasonable to assume that emission control with waste of the first category will pose more difficulties, because of the diversity of products and nanomaterials and/or the complexity of the recycling technique (e.g. with WEEE, ELV³¹ or CDW). But in general, it can be supposed that the application of known techniques for workers and environment protection would also, in a general way, decrease the risk, when there are nanomaterials in the waste stream (OECD, 2013a).

Based on the list of recycling streams and the connected handling processes given in Table 16, the following technical processes could give rise to workplace emissions of nanomaterials:

³⁰ With reference to Struwe et al (2012)

³¹ End of life vehicles

- Collection and sorting (dust)
- Shredding (dust), applicable to metals, plastic, textiles, WEEE, construction and demolition waste, End of Life Vehicles (ELV), tyres
- Pulping of waste paper (aerosols)
- Re-granulation of plastic (dust).

In the further treatment of the recycled materials, the presence of nanomaterials may give rise to emission of nanomaterials to the environment through the following processes:

- Smelting of metals, de-polymerisation of plastic (nanomaterials that are not destroyed in the process may be emitted with the exhaust gas if the gas purification is not sufficient).
- Disposal or incineration of non-metallic shredder fractions from WEEE and ELV.
- Dispersion of nanomaterials with the recycled fractions (also relevant for recycled construction and demolition waste), which may either result in e.g. leaching from the products, in altered properties of the products based on the recycled materials, or in accumulation of nanomaterials in certain types of products.

For the mechanical processes, potential problems related to the presence of nanomaterials in the waste are primarily related to occupational health, and in particular to inhalation of nanomaterials containing dust. Efficiency of risk management measures to control inhalation exposure, as e.g. reviewed by Aitken et al. (2011), indicates that appropriate protective equipment seems to be efficient in reducing exposure. Thus, it might be worth investigating in more details whether appropriate risk management is in place and used.

Specifically in relation to Carbon NanoTubes (CNT), Köhler et al (2008) conclude the following: "Occupational exposure during CNT production may be reduced through control techniques similar to those used in reducing exposure to aerosols in general (e.g. state-of-the-art exhaust filters) and by varying the handling procedures. However, today's facilities and filters may not sufficiently retain nanoparticulate matter such as CNT. To avoid aerosol formation in subsequent processing steps, liquid phase or in situ processing of nanoparticles appears better than dry handling."

For the further treatment steps, the issues are similar to those relevant for incineration and landfill: the potential emission of nano-objects with the off-gas and the potential leaching from landfilled or recycled residual products from the processes.

In 2011 and 2012, the Danish National Research Centre for the Working Environment investigated the genotoxic effect of sanding dust on mice, comparing dust from paints and lacquers with or without nanoparticles with nano-TiO₂. The hazards could not be distinguished for sanding dusts with or without nanoparticles. Effects were lower for particles encapsulated in a matrix than for pure nanoparticles. The paint matrix³² seemed to be more important for the genotoxic effect than the addition of nanoparticles (Saber et al, 2012 a & b).

These results may also reflect processes relevant for recycling of construction waste, since the construction waste is subject to crushing and grinding, and the studies indicate that occupational health issues are not linked to the presence of nanomaterials, but rather to the construction materials themselves, at least with respect to the surface coatings.

³² PVA, indoor and outdoor acrylic lacquer, filler, and binder were compared. A lacquer matrix resulted in the greatest impact.

Nowack et al (2013) evaluated release of CNT used in composites in different stages of their lifecycle. They have investigated 5 different product types, where CNT is used in composite materials: sports equipment, electronics, windmill blades / fuel system parts, tires and textiles, and they conclude that release of CNT to work spaces and the environment is likely when recycling all 5 types of products.

Nowack et al (2013) specifically address CNT containing plastic. The potential recyclability of CNT-containing plastic parts is not as straightforward as other plastics not containing carbon nanomaterials, since all CNT containing plastic parts are black. With present recycling technology, it is difficult for plastic recyclers to separate different types of black plastics by plastic type. This inability to differentiate between black plastics creates a “down-cycling” where all black plastics are grouped together into one batch and shredded to create post-consumer black plastics, potentially diluting the beneficial mechanical and electromagnetic properties of the CNT enhanced material. It would also introduce CNT into post-consumer products, which would otherwise not contain nanomaterials. Depending on the products, occupational or consumer exposure is possible. Due to the colour problem, the CNT containing material may not be recycled at all, although ongoing work in plastic sorting technologies is underway to solve the colour problem in a seemingly near future.

Köhler et al (2008) also evaluated the potential fate of CNT in batteries and textiles if recycled. The batteries are typically enclosed in the electronic equipment they are serving and can only be removed by the recycling company. According to the WEEE directive, all batteries should, in principle, be removed before further processing and then be treated separately according to the battery directive (2006/66/EF and amendments).

Discarded clothing is often sold in second hand shops or abroad in developing countries. Recycling of synthetic textiles often means down-cycling in order to make building material, e.g. insulating material. If CNT containing material is introduced into recycling as a part of recyclable textiles, cross contamination is not unlikely. In this way, and in the case of textile down-cycling to technical products, the destination of the nanotubes is no longer traceable (Köhler et al, 2008).

In the "Design guide for PET Bottle Recyclability" written by van Dwongen & Dworak (2011) for UNESDA³³ and EFBW³⁴ they conclude:

Fillers or master batch additives for example titanium dioxide that can be used for opacity or for lowering the cost and polymer content of the plastic, should be avoided or their use minimised. Fillers can change the density of the plastic and can also contaminate the recycled PET stream and impact the clarity of the recycled PET resin.

The Danish National Research Center for the Working Environment have in the NANOPLAST project investigated occupational hazards related to the use of organoclays (nanoclays) in plastic in the production phase (Clausen et al 2012). They showed that the organoclays only had a short term inflammatory effect, and that the inhalable dust index was low to moderate. The specific working methods can be very important in relation to the potential exposure from a given product. It can be significant during mixing of the powder and the plastic production, even if the amount of added organoclay is small. The exposure in the working zone is high, but dilution in the background air is quite efficient in lowering the exposure. Use of CNT showed potential long term inflammatory effect, and handling of large amounts of MWCNT was difficult without causing exposure. These results from this study also point to the necessity of sufficient protection when working in recycling processes such as shredding of plastic waste containing nanomaterials.

³³ Union of European Beverages Association

³⁴ The European Federation of Bottled Waters

In the EU NanoSustain project, the impact on the recycling process of glass from nano-ZnO used in coating of glass as a UV barrier was investigated (NanoSustain, 2013, b & f). The glass was re-melted in an induction furnace. The number and mass concentration of the emitted particles from the glass samples did not depend on whether coating was applied or not, nor on the type of coating. A relatively larger amount of the particles emitted from plain window glass seemed to be larger than nanoparticles (>100 nm) compared to the ones emitted from coated glass samples.

A notable increase in the number concentration began at > 1000 °C and in the mass concentration > 1300 °C for all samples (Lyyränen J., in preparation).

A horizontal project on "Nanotechnology for Sustainable Development of Tyres" is being carried out involving the OECD Working Party on Nanotechnology and the Working Party on Manufactured Nanomaterials. The project has been developed from a proposal made to the OECD by the Business and Industry Advisory Committee to the OECD, BIAC, through the Tyre Industry Project (TIP) of the World Business Council of Sustainable Development, WBCSD.

The project has identified High-Dispersion silica and High Dispersion High Surface area silica as nanostructured silica³⁵ to be the most relevant nanomaterials to evaluate in a combined LCA and environmental impact analysis. The report has been finalised after this literature review has been finalised, but is available at http://www.oecd-ilibrary.org/science-and-technology/nanotechnology-and-tyres_9789264209152-en.

Sun et al (2014) also calculate the amount of the nanomaterials in waste products that are estimated to be recycled, which is summarised as a percentage of the overall production, manufacturing and consumption for the EU in Table 12.

TABLE 12
PERCENTAGE OF DIFFERENT NANOMATERIALS BEING RECYCLED IN THE EU, BASED ON SUN, ET AL (2014)

Nanomaterial	Percentage recycled, %
Nano-TiO ₂	18
Nano-ZnO	11
Nano-Ag	36
CNT	20
Fullerenes	51

4.6 Flows of most common nanomaterials in waste through recycling processes in the Danish waste handling system

Caballero-Guzmán (2014) has in his MSc thesis carried out a thorough analysis of the flow of the same 4 nanomaterials as evaluated for incineration and landfill (nano-TiO₂, nano-ZnO, nano-silver and CNT), but for the relevant recycling processes and for Switzerland. He has analysed, which consumer products potentially containing nanomaterials, end up in which types of recycling processes, and what the typical recycling rates are. He has then chosen the products and processes that cover the majority of the recycled amounts and carried out an analysis of the potential flows through the recycling systems and where the nanomaterials will end up. The total list of specific consumer products relevant for each type of nanomaterial is shown in Table 18**Fejl!**

Henvisningskilde ikke fundet. The assumptions, with respect to how much is recycled of the relevant nanomaterials, are shown in Appendix 3, and the recycling processes included and not included in the study are listed in Table 13.

³⁵ The tyre manufacturing industry does not use silica nano-objects.

TABLE 13
 RECYCLING PROCESSES FOR POTENTIALLY NANO-CONTAINING PROCESSES INCLUDED IN THE ANALYSIS AND PROCESSES NOT INCLUDED (DUE TO SMALL RECOVERY OF THE SPECIFIC NANO-CONTAINING PRODUCTS OR SMALL AMOUNT OF PRODUCT³⁶), CABALLERO-GUZMÁN (2014)

Recycling processes included	Recycling processes not included
WEEE general devices	Batteries
WEEE cooling devices	Printed circuit boards
Metals	Mobile phones
Cars	Glass
Concrete	Plastic
Textiles	Windows and ceramics
	Ink and toner cartridges

A description of each of the processes included is given in Appendix 4.

This model has been transferred to Danish conditions taking into account the overall recycling rates for Danish consumer products. Within the scope of this study, it has not been possible to go into details with respect to differences in the specific recycling processes between Switzerland and Denmark, but the flows can act as a preliminary estimate and pinpoint where exposure to nanomaterials may be possible.

For the 4 nanomaterials modelled, nano-TiO₂, nano-ZnO, nano-Ag and CNT, the estimated Danish flows are shown in Figure 8 to Figure 11.

The figures show where the nanomaterials, that enter the recycling system, end up after going through the different separation techniques. Since the techniques are not directed at recycling of nanomaterials, but typically metal or plastic, where they are included in composites to enhance performance, the modelling shows that the nanomaterials in many cases end up in the residue from the processes that are then sent for incineration and landfill and not in the material sent for further processing as a new product.

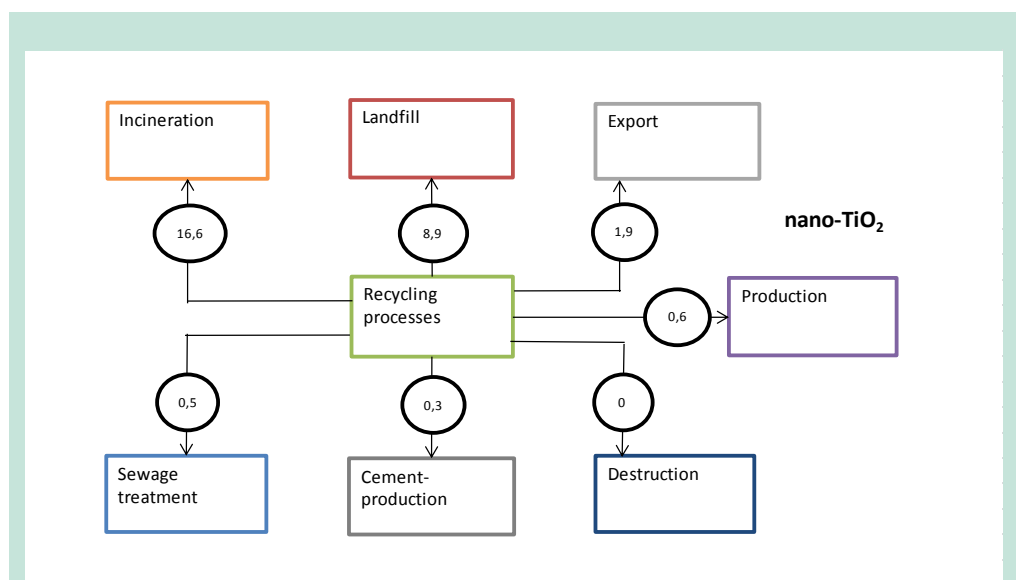


FIGURE 8
 FLOWMODEL FOR NANO-TiO₂ IN THE DANISH WASTE RECYCLING SYSTEM, TONS PER YEAR (2011), BASED ON CABALLERO-GUZMÁN, 2014. THE FLOWS ARE NOT YET BASED ON SPECIFIC DANISH CONDITIONS AND THE NUMBERS THUS INDICATIVE.

³⁶ In the Swiss system, this may not be quite the same in the Danish system.

For nano-TiO₂, Figure 8 shows that almost 90% of the nanomaterial entering the recycling processes will eventually end up in incineration or landfill. 7% is exported, of which some percentage may enter a recycling process there. App. 2% enters a production process as part of a recycled material.

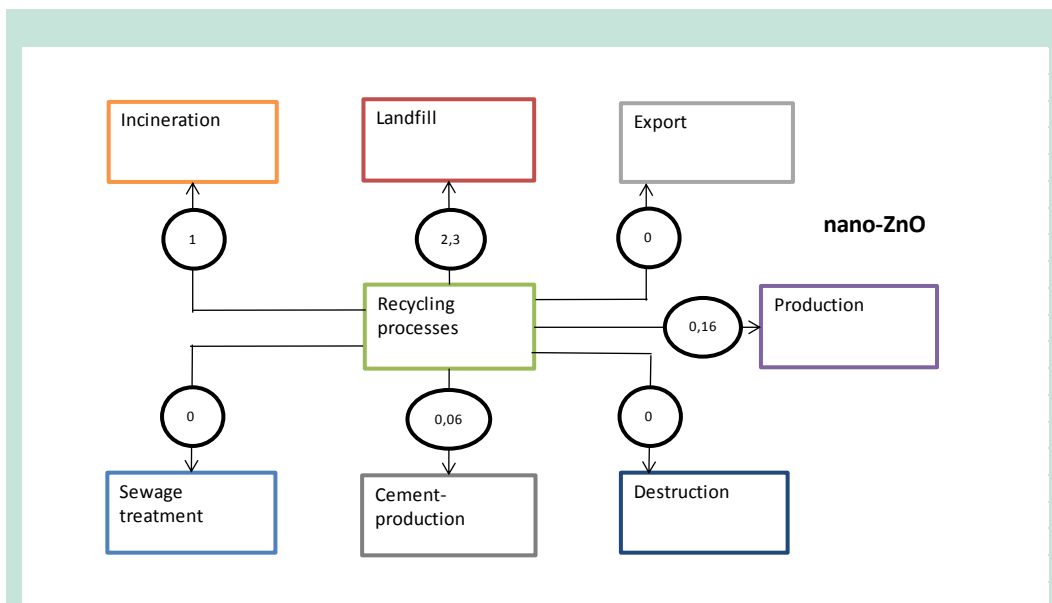


FIGURE 9
FLOWMODEL FOR NANO-ZNO IN THE DANISH WASTE RECYCLING SYSTEM, TONS PER YEAR (2011), BASED ON CABALLERO-GUZMÁN, 2014. THE FLOWS ARE NOT YET BASED ON SPECIFIC DANISH CONDITIONS AND THE NUMBERS THUS INDICATIVE.

For nano-ZnO, Figure 9 shows that more than 70% of the nanomaterial entering the recycling processes will eventually end up in a landfill, while app. 20% will go to incineration. App. 5% enters a production process as part of a recycled material.

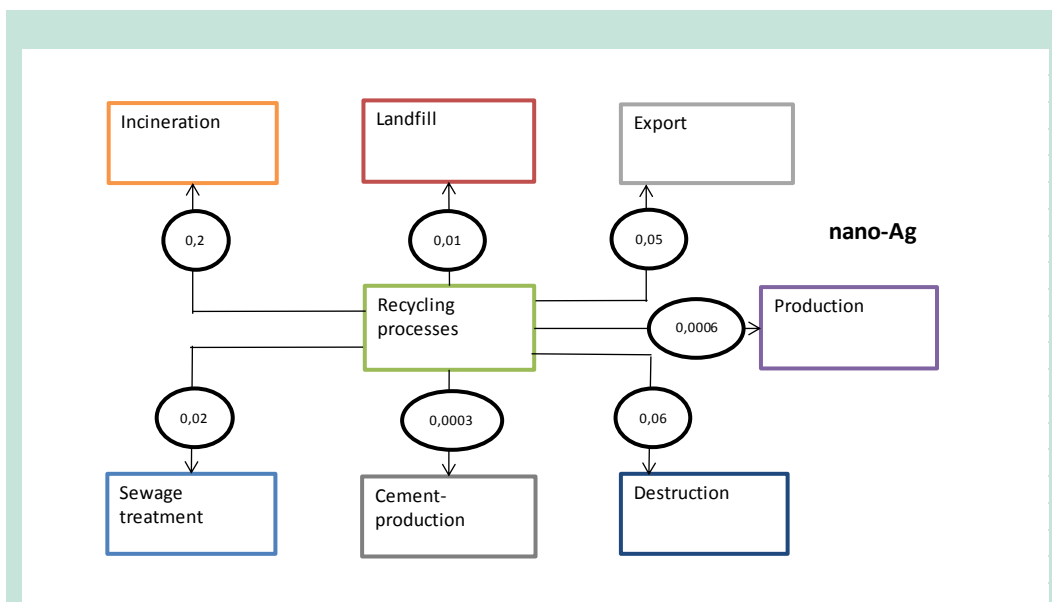
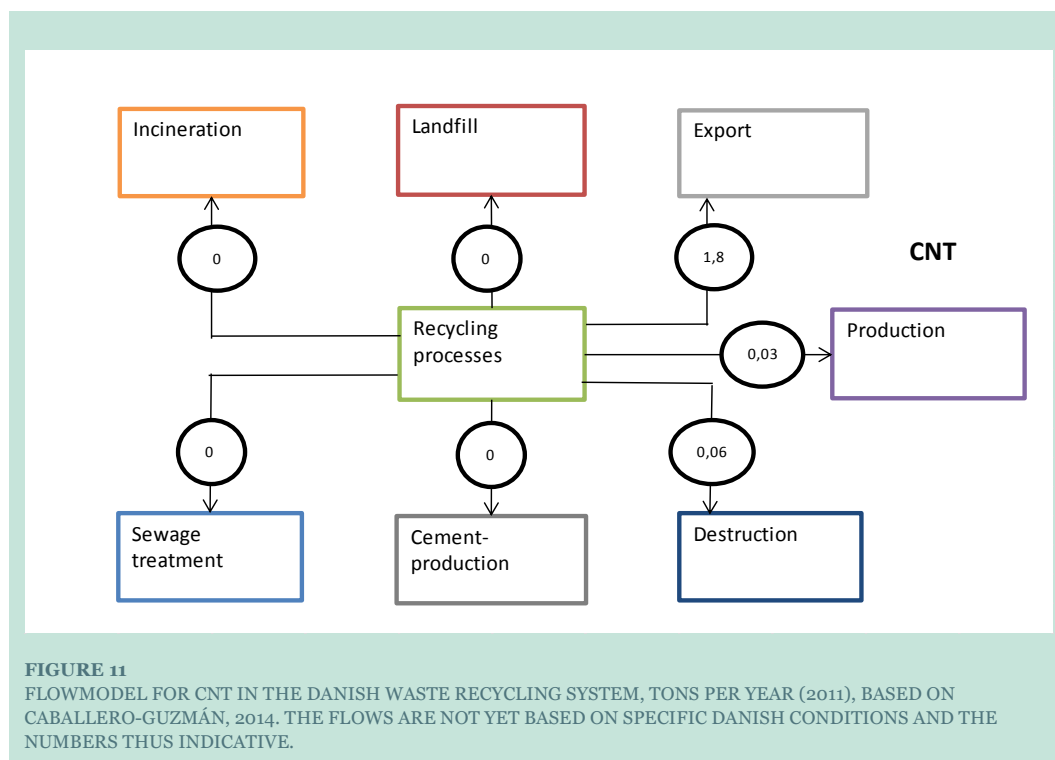


FIGURE 10
FLOWMODEL FOR NANO-AG IN THE DANISH WASTE RECYCLING SYSTEM, TONS PER YEAR (2011), BASED ON CABALLERO-GUZMÁN, 2014. THE FLOWS ARE NOT YET BASED ON SPECIFIC DANISH CONDITIONS AND THE NUMBERS THUS INDICATIVE.

For nano-silver, Figure 10 shows that app. 50% of the nanomaterial entering the recycling processes will eventually end up in an incinerator, while app. 3% can be expected to be landfilled. 17% is exported, of which some percentage may enter a recycling process there, and app. 20 % is expected to be destroyed somewhere in the recycling process.



For CNTs, Figure 11 shows that 95% of the nanomaterial entering the recycling processes is exported; of which some percentage may enter a recycling process there. 3% is expected to be destroyed somewhere in the recycling processes. App. 2% enters a production process as part of a recycled material.

The amount being exported, shown in the figures, is usually intended for further recycling, and it is uncertain how much of the nanomaterials exported will end up in recycled products. If one only looks at the fraction going directly to production of products containing recycled material, here based on the Swiss situation, the percentages of the material entering the recycling processes can be estimated, see Table 12.

TABLE 14
 ESTIMATED PERCENTAGE OF THE NANOMATERIALS ENTERING THE RECYCLING PROCESSES GOING TO FURTHER PRODUCTION

	Nano-TiO ₂	Nano-ZnO	Nano-Ag	CNT
Recycled percentage	2	5	0,2	1,5

The percentages in the table are probably too low, since the degree of recycling included in the amount exported is not included.

4.7 Potential application of the rules of classification as hazardous waste

Article 9(5) of the Classification, Labelling and Packaging (CLP) regulation (EC/1272/2008) specifies that "When evaluating the available information for the purposes of classification, the manufacturers, importers and downstream users shall consider the forms or physical states in which the substance or mixture is placed on the market and in which it can reasonably be expected to be used". Based on this, the European Commission has confirmed that nanoforms of a substance/material shall be classified differently from other forms (micro/macro form) if the properties of the nanoform differ from other forms (EC, 2008).

Due to their smaller size and increased surface area, nanoforms may exhibit higher toxicity (especially in relation to inhalation) than other forms of the same substance, when compared on a mass basis. Nanoforms might also exhibit more positive results in mutagenicity and genotoxicity testing (see e.g. Stone et al, 2010).

In general, nanoforms should, at least, be classified as other forms of the same substance chemistry. There is not yet any agreement/consensus, in relation to whether/when nanoforms of materials, including those specifically addressed in this project, should be classified stricter than other forms of the same material. There is, however, much debate related to interpretation of hazard data for nanomaterials, e.g. considering the fact that rats are more sensitive than humans in relation to inhalation (a rat has a low threshold for lung overload), and the extent to which mutagenicity/genotoxicity data in several standard test are reliable. Issues related to interpretation of hazardous data for nanomaterials are e.g. elaborated in Hankin et al (2011).

Although information is generally limited as to the amount of nanomaterials in various products/articles, the authors of this report assess that the product types mentioned in Table 7 might contain more than 0.1% (weight) nanomaterials and most of the products even higher percentages, especially in composites. As noted above, nanoforms might be more toxic than other forms of the same substance on a mass-basis (larger surface areas and larger number of particles per mass unit).

Considering the above, it cannot be excluded that waste from products containing nanomaterials sometimes should be characterised as hazardous waste.

5. Perspectives on technological aspects regarding nanomaterials and waste

Nanomaterials are typically used to enhance the properties of a specific product. In this chapter, it is discussed if this can, in some cases, lead to waste reduction, either to extend the longevity of the product or to reduce use of scarce resources.

An evaluation of whether the presence of nanomaterials could improve or worsen the recycling technology has also been requested. This question is not possible to answer with the present available information. With respect to a possible better or worse situation for the working environment related to the recycling processes, this is evaluated (based on the present knowledge) in Chapter 4.

For consumer products, uses of nanomaterials that could improve longevity could be:

- Use as coatings
- Improve function and thus reduce the need for repair (where a new item may be purchased instead).

But the actual importance of this is difficult to evaluate, since a number of factors influence why people purchase new items and discard the old.

In relation to cars, the relevance could be greatest, where the introduction of nanomaterials as described could increase the longevity of an expensive consumer good. At the same time, nanomaterials are used in car motors and in the chassis³⁷ to increase mileage, which is an environmental asset, although not directly related to waste. The OECD report (2013c) notes that current technology is reaching its technical limits, but that application of new nanotechnology might further reduce fuel consumption (by reducing rolling resistance) as well as waste and raw material consumption (due to improved durability/better abrasion resistance).

An area where the use of nanomaterials could be of high importance, in relation to reducing the amount of virgin resources and thus the generation of waste, is in construction products.

Looking at Table 6 in Chapter 3, it can be seen that the introduction of primarily nano-SiO₂ and nano-TiO₂ in concrete and in nano-TiO₂, ZnO and CeO₂ in wood coatings could increase longevity of the constructions and thus reduce waste generation. The use of nano-SiO₂ to strengthen the construction can, in principle, also lead to use of less concrete in the construction and thus again reduce waste generation.

³⁷ To decrease weight

In steel, the use of nano-iron and carbon as a means to strengthen the construction is also potentially a way to reduce waste generation.

The use of nanomaterials in construction is quite novel and especially for steel still quite expensive, so little experience on the consequences is available at present.

In conclusion, it can be said that there is little available knowledge as to the potential for waste reduction related to the use of nanomaterials, but that the issues mentioned in this chapter could be areas in which further analysis could be carried out.

6. Conclusions

This chapter contains a summary of the findings of the literature review in Chapter 4. With respect to the possibility of using nanomaterials in order to reduce the amount of waste, reference is made to Chapter 5.

In general, there is a limited amount of studies available regarding the fate of nanomaterials in the waste system. These studies only cover a limited number of products and nanomaterials, and care should of course be taken when trying to generalise the findings. In general, more fundamental studies are also needed on the fate of nanoparticles^{38,39}

6.1 Incineration

For incineration, the general agreement is that the nano-inorganics, TiO₂, ZnO, and Ag will end up primarily in the slag and to some degree in the filter ash, where the latter is primarily exported in Denmark. Only small amounts are emitted with the off-gas from the waste incinerators. CNT is assumed (and shown) to be destructed, if the incinerator temperature is sufficient⁴⁰ at all times. Any CNT not destructed, is assumed also to end up in the slag.

The actual studies of incineration of waste containing nanomaterials indicated that the presence of engineered nanomaterials in the waste could increase the amount of emitted nanoparticles substantially. There are different viewpoints on, to which extent the agglomeration of the particles may differ due to the presence of engineered nanomaterials.

Since the great majority of the slag is recycled after sorting and crushing, there is a potential both for occupational health issues related to the processing of the slag and an environmental issue related to potential leaching of the nanomaterials, when the slag is used in road construction and similar.

6.2 Landfill

If waste containing nanomaterials is landfilled, e.g. for non-recyclable construction waste and shredder waste, there is a potential for leaching of the nanomaterials from the waste to the leachate. However, landfill conditions typically enhance agglomeration and reduce the mobility of nanoparticles. Any organic acids in the leachate are shown to reduce the agglomeration of CNT. A single study of the potential diffusion of CNT through a HDPE membrane showed that diffusion did not take place.

6.3 Organic treatment

Nano-Ag was shown to inhibit anaerobic degradation if the content was relatively high; whether this effect is specifically related to the nanoproperties could be questioned. Composting of nanocellulose was feasible and no adverse effects were observed.

³⁸ New information will probably be a result of future EU projects – e.g. based on the recent Horizon 2020 call on topics related to “Assessment of environmental fate of nanomaterials”

³⁹ In this context it should maybe be noted that the 4 most common nanomaterials in the waste streams is estimated to make up app. 100 tonnes in all compared to the app 2.6 million tonnes of waste incinerated and app. 0.5 million tonnes landfilled in Denmark in 2011.

⁴⁰ That is at temperatures normal for Danish waste incinerators except at upstart.

6.4 Recycling

For recycling, effects can be divided into three types:

- Occupational health effects in connection with the recycling processes themselves.
- Environmental impacts related to the treatment of residue from the recycling processes, which will end up either in incineration, landfill or sewage treatment, where the above statements apply.
- Introduction of residual nanomaterials into products containing recycled material, the effect of which is difficult to assess in general.

For the occupational health issues, studies related to similar processes as the ones used in recycling have shown that inflammatory effects from dust containing nanomaterials can occur, although it is sometimes not possible to distinguish these effects from the effects of dust from materials not containing nanomaterials. In any case, this points to the importance of assuring sufficient protection for workers when working with recycling of waste that may also contain nanomaterials.

A specific issue is the large amount of construction waste being recycled in Denmark. At present, there is little information as to the amount of construction material containing nanomaterials being used in Denmark and also on the potential issues related to emission of nanomaterials from these products during a recycling process. Some of the issues mentioned above would also apply here, and one should note that the recycling processes carried out for construction waste are often carried out partly or entirely outdoors which may in principle give rise to environmental emissions of nanomaterials from these processes apart from the potential impact on workers. Also, due to the high degree of use of recycled construction material in road construction and similar, the potential leaching of nanomaterials from the recycled products should be assessed.

Another specific issue is the recycling of tyres. In Denmark, a very high percentage of tyres is recycled, and the granulated material is used as filler on artificial grass on football fields and for rubber tiles and carpeting used on sports arenas (also indoors) and on playing grounds for children. Studies of the potential impact from leaching from these materials have been carried out, see e.g. Klif (2012)⁴¹. Potentially, the presence of nanomaterials in the tyres could thus lead to leaching of nanomaterials from the recycled products.

6.5 Classification as hazardous waste

An evaluation of products containing nanomaterials with respect to the present (and incomplete) knowledge about their effects on human health and the environment, in combination with the potential content of nanomaterials in different products, could not exclude that some of the products would be characterised as hazardous waste.

⁴¹ showing that leaching of zinc from these applications can be an issue for sensitive surface water recipients and basically that leaching of contaminants from the tyres occur.

7. Suggestions for follow-up studies on nanomaterials and waste

This chapter first contains a summary of some of the recommendations with respect to knowledge gaps encountered in the literature. Based on this and on Chapter 4, 5 and 6, suggestions are then given as to relevant follow-up studies on nanomaterials and waste.

7.1 Recommendations from other sources

OECD (2013b) suggests that a more detailed study of nanomaterial in various waste incineration plants and co-incineration plants is necessary. Such a study could include determining the conditions that would enable the efficient removal of nanomaterial from municipal solid waste incinerator flue gas.

OECD (2014) made a long list of the areas in which further research is needed to improve the understanding of the problem and develop practical solutions related to landfilling of waste containing nanomaterials:

- a) Characterization and quantification of the issue and understanding of the chemical and environmental processes in landfills:
 - i. Identify the types and quantities of nanomaterials and their individual level of hazard, risk and exposure in products, waste containing nanomaterials and nanowaste originating from nanomaterial manufacturing;
 - ii. Understand the synergistic impacts of nanomaterials and typical contaminants in landfill leachate; specifically looking at key contaminants in leachate and studying the impact that nanomaterials have on increasing toxicity, bioavailability and transport of these contaminants;
 - iii. Understand the process of nanomaterial degradation in a landfill environment and the impact of degradation products;
 - iv. Explore whether there are air emissions of nanomaterials in or from landfills and if they are found in landfill gas.

- b) Understanding the effectiveness and constraints of current landfill methods and technologies:
 - i. Understand the impacts of microbial properties of nanomaterials on on-site landfill treatment systems and other potential impacts that nanomaterials may have on leachate treatment systems;
 - ii. Identify what key nanomaterials pass through leachate treatment systems and to what degree they are “treated” (similar to studies of nanomaterials in WWTPs) by conventional methods or other technologies;
 - iii. Determine the applicability of current BAT technologies, used in other wastewater treatment applications, to treat or remove nanomaterials in landfill leachate;

- iv. Develop effective methods of diverting nanomaterials from landfills and treating waste containing nanomaterials and nanowaste (not simply transferring them from one waste treatment method to another).

c) Understanding the applicability of a future nanomaterial classification system for waste management:

- i. Examine the potential usefulness of classifying, labelling and segregating all nanowastes and wastes containing nanomaterials, to prevent disposal in municipal landfills and ensure adequate and safe disposal.

Roes et al (2012) suggested that further research has to focus on nano-objects that especially might form a threat:

- 1) Determination of for which particles there is a risk of emission by solid waste incineration plants due to incomplete removal and net determination of their toxicity to identify those particles that form a real threat
- 2) Determination of which particles could be a serious threat to human health (toxicity tests) and then investigate whether there is a risk that they are released from waste incineration.

Roes et al (2012) point to the complexity related to non-toxic nanoparticles adsorbing volatilised metals which may increase their toxicity. Roes et al (2012) propose laboratory experiments in which the incineration and removal of nano-objects are tested for various methods of incineration and flue gas cleaning. More in vivo tests should be performed to identify those particles that form a serious threat to human health. In any case, emissions from waste incineration should be carefully monitored for the emission of nano-objects from the incineration process.

The above recommendations address incineration and landfilling, and will also be taken into consideration in the suggestions based on the all material collected and the specific Danish situation with respect to recycling of residues.

7.2 Recommendations for further studies

The recommendations are made under consideration of one or more of the following number of issues:

- Could nanomaterials have relevance for recycling technologies?
- Can nanomaterials in waste have relevance for environmental safety?
- Recommended work should be realistic to carry out within a reasonable timeframe.
- Recommendations should consider opportunities for collaboration with other initiatives (e.g. research projects or projects in OECD, waste industry, recycling industry).
- Are significant knowledge gaps addressed?
- Costs versus scientific/administrative benefits.

This has been taken into account in the suggestions made.

The suggestions for further studies are divided into actual investigative studies and more desk oriented analyses in the following, starting with the **investigative studies**.

Due to the specific situation in Denmark where large amounts of sorted slag from waste incineration and sorted construction waste is recycled, this is seen as a specific Danish priority together with an in general better overview of the situation with regard to use and recycling in Denmark of construction materials containing nanomaterials. Based on this, the following investigative studies are suggested:

A. Characterize and evaluate leachability of nanomaterials from incinerator slag

B. Characterize and evaluate leachability of nanomaterials from recycled crushed construction waste

Nanomaterials are very much associated with electric and electronic equipment and thus with WEEE. In Denmark, recycling of WEEE primarily encompasses collection and pre-treatment before exporting for further treatment. In a Danish context, the most relevant issue related to the presence of nanomaterials in WEEE could therefore be the potential consequences in the pre-treatment / landfilling of residuals from WEEE after treatment (shredder waste). The following is thus suggested as a subject for further investigation:

C. Characterize and evaluate leachability of nanomaterials from shredder waste

Since the literature review has shown that little information exists on the actual retention of nanomaterials in landfill liners, the following is also suggested:

D. Evaluate migration of nanomaterials through landfill liners

In Denmark, a very high percentage of tyres is recycled, and the granulated material is used as filler in artificial grass on football fields and for rubber tiles and carpeting used on sports arenas (also indoors) and on playing grounds for children. Potentially, the presence of nanomaterials in the tyres could thus lead to leaching of nanomaterials from the recycled products:

E. Characterize and evaluate leachability of nanomaterials from granulated tyres

For all the investigative studies, the development of methodology would have to be an initial part of the study, since challenges have been observed with characterization and analysis methods for nanoparticles especially in liquid media containing with high concentrations of basic components. More accurate analytical methods for characterization of nanoparticles in the water phase are probably needed before project studies for estimation of release of nanoparticles from waste materials can be carried out successfully. DTU Environment has pointed to the possibility of using field flow fractionation (FFF) in combination with single-particle ICP-MS for the complex matrixes that will be a result of leaching tests on waste products containing nanomaterials⁴².

Another issue in this relation is to also investigate the potential for leaching of nanoparticles from waste products not originally containing nanomaterials.

Analyses

As can be seen from the review, information is lacking on the actual use of nanomaterials in building and construction material in Denmark. Due to the previously mentioned large degree of recycling of construction and demolition waste in Denmark, it would be very relevant to get a better idea of the actual types and amounts being used, and if this is expected to increase substantially, which some studies might indicate. Therefore, the following is suggested:

F. Obtain better overview of nanomaterials in construction waste with a focus on materials with a high recycling potential

The flow models set up have primarily focused on nano-TiO₂, ZnO, Ag and CNT. Slag and construction waste may also contain nano-SiO₂ and CeO₂, and due to the large degree of recycling of these waste products and the potential leaching from them, it would be relevant to:

G. Compile Flow models for SiO₂ and CeO₂ (primarily relevant for slag and construction waste)

⁴² OECD has also setup guidelines for different issues related to the investigation of nanomaterials

The flow models set up in this report are to a large degree based on the Swiss model and only modified to a certain degree according to Danish conditions. A better overview of the actual exposure potential, especially with respect to recycling, could be obtained if the flow models were modified better to Danish conditions, which would be possible partly based on some of the broader nanostudies being carried out in Denmark at present, partly based on analysis of the actual recycling situation in Denmark, and the expected trends. It is therefore suggested to carry out a study with the aim:

H. Update of flow models in order to describe the actual Danish situation

Recycling of textiles is an issue with a lot of focus at present, e.g. through a set of Nordic projects. With regard to nanomaterials, specifically the use of nano-Ag in textiles would be relevant. Not much information is available on the actual flows of textile waste in Denmark, and a further evaluation of the consequences of the presence of nano-Ag in clothing and thus subsequently in waste, might best wait until this overview exists. A suggestion for a project is made:

I. Obtain better overview of recycling processes for textiles with nano-Ag and the potential release scenarios related to these processes

A textile project could encompass mapping of nanomaterials in the waste system for textiles based on other potential projects mapping waste handling of textiles in general.

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Appendix 1: Nanomaterials in waste streams

TABLE 15
OVERVIEW OF NANOMATERIALS IN PRODUCTS ENTERING WASTE HANDLING PROCESSES (TAKEN FROM OECD (2013A))

Nanomaterial	Consumer Products (Struwe et al. 2012) ⁴³ , (PEN 2013) ⁴⁴ , (NEEPH 2011) ⁴⁵	Construction Material (Lee 2010) ⁴⁶ , (ITA-AAS 2012) ⁴⁷
Carbon Nanotubes CNT	Electronic devices, sports equipment, composite plastics	Concrete, ceramics
Fullerene	Semi-conductor technology	
Nano-Silver (nano-Ag)	Textiles, anti-bacterial kitchenware	Antibacterial coatings and paints
Carbon Black (CB)	Tires, printing toner, plastics	
Nano-Titanium dioxide (nano-TiO₂)	Paints, coatings, composite plastics	Self-cleaning coatings
Nano-Silicium dioxide (amorphous and crystalline (nano-SiO₂))	Coatings, composite plastics, tires,	Concrete, ceramics, window coatings
Nano-Zinc oxide (nano-ZnO)	Cosmetics, coatings and paints,	
Nano-Titanium nitride (nano-TiN)	PET-bottles	
Nano-Iron oxides (nano-FeO/Fe₂O₃)	Electronic devices	Concrete
Nano-Cerium oxide (nano-CeO₂)	Fuel additive	Anti-corrosive coatings
Nano-Phosphate ® (nano-LiFePO₄)	Li-Batteries	
Nano-Copper particles (nano-Cu)	Improved steel (anticorrosive)	

⁴³ **Struwe et al. 2012:** Struwe, J. et al.; Bedeutung von Nanomaterialien beim Recycling von Abfällen; Hans Böckler Stiftung Arbeitspapier AP 270, November 2012; 2012

⁴⁴ **PEN 2013:** The Project on Emerging Nanotechnologies; Inventories on Consumer Products; PEN-Website; Washington DC; 2013; http://www.nanotechproject.org/inventories/consumer/analysis_draft/

⁴⁵ **NEEPH 2011:** EKOTEK; Guidelines for responsible management of waste nanomaterials; EU FP7 NEEPH; 2011

⁴⁶ **Lee 2010:** Jaesang Lee, Shaily Mahendra and Pedro J. J. Alvarez; Nanomaterials in the Construction Industry: A Review of Their Applications and Environmental Health and Safety Considerations; ACS Nano, 2010, 4 (7), 3580–3590; Washington DC; 2010

⁴⁷ **ITA-AAS 2012:** Gressler, S. & Gaszo, A.; Nano in the Construction Industry; Nano Trust Dossier No. 32en, August 2012, Institute of Technology Assessment of the Austrian Academy of Sciences; Vienna; 2012

TABLE 16
OVERVIEW OF SELECTED RECYCLING STREAMS WITH POSSIBLE NM CONTENT (ADAPTED FROM OECD, 2013A).

Waste type	Waste handling processes	Nanomaterials	Theoretically possible sources of nano-object emissions in the recycling process
Metal waste (scrap)	Shredding (residue may end up in landfills or incinerators), smelting	In coatings: Metal oxides, CNT, SiO ₂	Shredding, if nanomaterial ⁴⁸ can be set free from coatings Smelting: nanomaterial that are not destroyed in the melting process, insufficient exhaust gas purification
Paper and cardboard	Collection and sorting, Pulping, de-inking (wet processes)	Carbon Black (from the ink), TiO ₂ (except for special papers, TiO ₂ is not in the nanoform)	Dust from collection, transport Aerosols of ink from pulping and de-inking
Plastic	Collection & sorting, or separate collection (e.g. for PET-bottles ⁴⁹), mechanical recycling: shredding, washing, re-granulation Feedstock recycling: depolymerisation, cracking (for basic chemicals). Residue may end up in incineration	CNT, SiO ₂ , TiO ₂	Shredding and re-granulation: if nano-objects are set free. Feedstock (chemical) recycling: nano-objects that are not destroyed in the process may be emitted or end up in the cracking residues (tar). Problem of dispersion of nanomaterial to re-granulated plastics
Textiles	Collection, reuse, sorting, preparing for reuse, shredding to get fibres. Residue may end up in incineration	CNT, Ag	Shredding: if nano-objects are set free
Waste of Electronic and Electrical Equipment WEEE	Collection, dismantling, sorting by hand, Shredding and separation of the fractions, Processing of fractions (non-magnetic metals, iron, glass, plastics etc.), Further processing of the components (metal melting, material recovery of iron and non-iron metals, extraction of metals from circuit boards)	Carbon black (in plastic and in toners), CNT (in electronic devices and in plastic housings, nano-Iron oxide, ZnO, SiO ₂ , Ag (in coatings)	Any step of the procedure, depending on the nanomaterial containing component and on the specific type of nanomaterial.

⁴⁸ ENM = Engineered NanoMaterials

Waste type	Waste handling processes	Nanomaterials	Theoretically possible sources of nano-object emissions in the recycling process
Batteries	Collection, sorting. Mechanical/chemical and/or thermal treatment (various procedures, e.g. BATREC (Switzerland) ⁵⁰ for alkali- and mercury batteries, Battery Solutions (USA) ⁵¹ , Toxco (USA) ⁵² for lithium batteries, or INMETCO (USA) for Ni-Cd Batteries ⁵³ .	Electrodes with CNT or Nano-Phosphate [®] (nLiFePO ₄) ⁵⁴	In principle during mechanical, chemical or thermal treatment, dependent on the process and on the type of battery with nanomaterial.
Construction and Demolition Wastes.	Reuse of components, sorting of fractions (wood, concrete, brick, metal etc.), Metal recycling, secondary building materials, incineration and landfill	CNT, SiO ₂ , TiO ₂ , Fe ₂ O ₃ , Cu, Ag	During destruction of buildings (dust emissions), shredding, grinding if nano-objects are set free. Problem of dispersion of nanomaterial fractions of recycled material
End of Life Vehicles (ELV)	Dismantling for reusable parts (incl. tires), removal of hazardous components (e.g. batteries). Shredding and separation of fractions, metals go to smelting and refining, glass is recycled or landfilled, non-metallic shredder residues for incineration or landfill (Ostertag & Huesing, 2007)	CNT, SiO ₂ , TiO ₂ (in plastics, coatings and paints)	Shredding and sorting of fractions, smelting of metals (nanomaterial from coatings), disposal of non-metallic shredder fraction. Modern cars contain electronic components that are normally not removed before shredding, this is a possible source for nanomaterial-emissions

⁵⁰ BATREC Industries AG, in Wimmis, Switzerland: http://www.batrec.ch/en-us/unser_angebot/batterien/recyclingprozess.html# (accessed Aug 28, 2013)

⁵⁰ <http://www.batteryrecycling.com/Battery+Recycling+Process> (accessed Aug 28, 2013)

⁵⁰ Toxco Recycling Processes, <http://www.toxco.com/processes.html> (accessed Aug.28, 1013)

⁵⁰ http://www.inmetco.com/services_battery.htm

⁵⁰ http://en.wikipedia.org/wiki/Lithium_iron_phosphate#The_Physical_and_Chemical_Properties_of_LFP

⁵⁰ <http://www.nano-connect.org/content/download/79124/466758/file/ObservatoryNANO%20Factsheets%202011.pdf>.

⁵⁰ WCNM = Waste Containing NanoMaterials

Waste type	Waste handling processes	Nanomaterials	Theoretically possible sources of nano-object emissions in the recycling process
Tires	Collection, storage, refurbishment and reuse. Shredding, of metal, reuse of rubber for downcycled products or for energy recovery (incineration)	Carbon Black, silica; there are indications that future developments will include others, e.g. CNT, nanoclay (SiO ₂) or organic nano-Polymers ⁵⁵	In principle when shredding, actual tires contain nanomaterials that are bound to the rubber matrix
Recycling of residues from waste incineration:	Separation of metals bottom ash from MSWI, it contains metal residues (Iron, Aluminium, Copper, even Gold)	Nanomaterials from WCNM ⁵⁶ in the municipal waste that are not destroyed or evaporated may stay in the bottom ash.	The most efficient recovery of metals from bottom ash is done with dry ash, with dust generation: nano-objects can be emitted during pouring, sieving, mechanical and magnetic separation

TABLE 17
 PRODUCT CATEGORIES CONTAINING SELECTED NANOMATERIALS (TAKEN FROM CABALLERO-GUZMÁN (2014) WITH REFERENCE TO SUN ET AL (2013)). THE CATEGORIES NOT DIRECTLY RELEVANT IN A DANISH WASTE HANDLING CONTEXT WITHIN THE SCOPE OF THE CURRENT PROJECT HAVE BEEN WRITTEN IN ITALICS.

Nano-TiO ₂	Nano-ZnO	Nano-Ag	CNT	Fullerenes
Batteries& capacitors	<i>Cleaning agents</i>	<i>Additive to soil</i>	<i>Aerospace</i>	<i>Aerospace</i>
Cement	Consumer electronics	Coatings & cleaning agent	Automotive composites	Catalysts
<i>Cleaning agents</i>	<i>Cosmetics</i>	Consumer electronics	Consumer electronics	Composites
Coating	Filters	<i>Cosmetics</i>	Energy	<i>Cosmetics</i>
Consumer electronics	<i>Food</i>	<i>Dietary supplement</i>	Paint	Electronics and optics
<i>Cosmetics</i>	Glass & ceramics	Filter aggregates	<i>R&D (Research & Development)</i>	Energy/environment
<i>Dietary supplements</i>	Metals	Glass & ceramics	Sensors	Metals (coatings)
Filters	Paints	MedTech	Textiles	Motor oil (Lubricant)
Glass & ceramics	Paper	Metals		R&D (Research & Development)
Ink	Plastics	Paints		
Light bulbs	Textiles	Plastics		
Metals	Wood	Sanitary		
Paints		Textiles		
Paper				
Plastics				
Sports goods				
<i>Spray</i>				
Textiles				
WWTP ⁵⁷				

⁵⁷ By COWI based on the agreed approach

⁵⁷ WWTP = Waste Water Treatment Plants

TABLE 18
SPECIFICATION OF PRODUCTS WITHIN MAIN PRODUCT CATEGORIES FOR NANOMATERIALS ADDRESSED BY
CABALLERO-GUZMÁN (2014)

Product category	nanomaterial	Product category content
Consumer electronics	nano-TiO ₂	Flat iron, hair dryer, curling iron, fridges, computer mice and keyboards
	nano-ZnO	No information found
	nano-Ag	Flat iron, hair dryer, curling iron, fridges, computer mice and keyboards, woman and man shaver, hot rollers, washing machine, air conditioner, toothbrush sterilizer, multipurpose sanitizer, vacuum cleaner, humidifier, hand dryer, coffee machine, mobile phone, notebooks, electronic toilet seats
	CNT	No information found (<i>semiconductor devices in consumer electronics</i>)
Paints	nano-TiO ₂	Interior walls paints
	nano-ZnO	Exterior walls paints
	nano-Ag	Interior walls paints
	CNT	Anti-static and anti-fouling coating
Glass & Ceramics	nano-TiO ₂	Windows
	nano-ZnO	No information found
	nano-Ag	No information found
Batteries & Capacitors	nano-TiO ₂	No information found (<i>expected in Li-Ion batteries</i>)
Medical Technology	nano-Ag	Air and water purifier, operating tables, door knobs, handles
Textiles	nano-Ag	Any kind of textile: shirts, socks, pillowcase sets, blankets, sport towels, teddy bears, slippers, sportswear, underwear, jackets, polo shirts, shorts, tennis, baby vests, gloves...
Metals	nano-Ag	Door knobs, pet food bowls, watch chains, water taps, kitchen ware
Energy	CNT	Solar cells, Li-Ion batteries
Automotive	CNT	Fuel system components and fuel lines (connectors, pump parts, o-rings), reinforcement of structural parts

Appendix 2: Release of engineered nanomaterials (ENM) from consumer products

The overview given below shows the estimated distribution of different nanomaterials with the use and discarding of different types of products in Switzerland. This is given as a basis for the understanding of the Swiss model and in lieu of Danish similar data.

TABLE 19
RELEASE OF ENGINEERED NANOMATERIALS (ENM) FROM CONSUMER PRODUCTS. DATA FOR SWITZERLAND. THE VALUES REFER TO THE FRACTION OF THE TOTAL AMOUNT OF ENM RELEASED, TRANSFERRED OR DISSOLVED FROM A PARTICULAR SOURCE. BASED ON GOTSCHALK, ET AL., 2009.

Product category	STP	WIP	Atmos-phere	Land-fill	Soil	Water	REC	Disso-lution	Ex- port
nano-TiO₂									
Plastics		1.0							
Cosmetics	0.9	0.05				0.05			
Coating & Cleaning	0.9	0.05	0.05						
Batteries & Capacitors		0.28							0.73
Metals	0.05	0.05				0.05			0.9
Paint	0.2			0.5	0.25				
Light Bulbs		0.1							0.91
Glass & Ceramics		1.0							
Filter aggregates		0.28							0.73
Consumer electronics		0.28							0.73
Textiles	0.5	0.25							0.25
Dietary supplements	0.9	0.1							
Ink	0.08	0.92							
nano-ZnO									
Plastics		1.0							
Cosmetics	0.9	0.05				0.05			
Coating & Cleaning	0.9	0.05	0.05						
Textiles	0.32	0.16	0.03					0.33	0.16
Dietary supplements								1.0	
nano-Ag									
Plastics		0.95						0.05	
Metals	0.05	0.05						0.05	0.86
Cosmetics	0.73	0.04				0.04		0.19	
Coating & Cleaning	0.73	0.04	0.04					0.19	
Textiles	0.2	0.14	0.05					0.48	0.13
Paint	0.16			0.41	0.2	0.04		0.18	
Filter aggregates		0.22						0.19	0.59
Glass & Ceramics		0.81						0.19	
Consumer electronics		0.26						0.05	0.69
Dietary supplements	0.9	0.1							

Product category	STP	WIP	Atmos- -phere	Land- -fill	Soil	Water	REC	Disso- -lution	Ex- -port
CNT									
Composites		1.0							
Consumer electronics		0.28					0.73		
Fullerenes									
Composites		1.0							
Cosmetics	0.9	0.05				0.05			

Averages enlarged and reduced by 20% to build uniform model input distributions.

Appendix 3: Share of the total mass in the (Swiss) system that is recycled, by product category and nanomaterial

TABLE 20

INPUT DATA AND SHARE OF THE TOTAL MASS IN THE SYSTEM THAT IS RECYCLED, BY PRODUCT CATEGORY AND ENM IN SWITZERLAND

NOTE: SHARE IS THE MEAN MASS OF NANOMATERIALS ALLOCATED IN A PRODUCT CATEGORY (IN PERCENTAGE); RECYCLING RATE IS THE PROPORTION RECYCLED IN A PRODUCT CATEGORY; SHARE RECYCLED IS THE SHARE THAT ENTERS IN TO THE RECYCLING SYSTEM; AND RELATIVE WEIGHT IS THE PROPORTION OF THE MASS RECYCLED OF THAT PRODUCT RECYCLED TO THE TOTAL MASS RECYCLED. (BASED ON CABALLERO-GUZMÁN, 2014).

	Share	Recycling Rate	Share Recycled	Relative Weight	Accumulated Weight
nano-TiO₂					
Consumer Electronics	6.9 %	0.75	5.2 %	47.2 %	47.2 %
Paint	8.9 %	0.46	4.1 %	37.4 %	84.6 %
Glass and ceramics	1.7 %	0.79	1.3 %	12.3 %	96.9 %
Batteries and capacitors	0.4 %	0.33	0.1 %	1.2 %	98.1 %
nano-ZnO					
Paints	14.3 %	0.41	5.9 %	89.8 %	89.8 %
Glass & Ceramics	0.7 %	0.74	0.5 %	7.9 %	97.7 %
Consumer Electronics	0.2 %	0.75	0.2 %	2.3 %	100.0 %
nano-Ag					
Consumer Electronics	38.1 %	0.75	28.6 %	74.9 %	74.9 %
Med Tech	3.6 %	0.9	3.2 %	8.5 %	83.4 %
Textiles	25.1 %	0.1	2.5 %	6.6 %	90.0 %
Metals	2.4 %	0.9	2.2 %	5.7 %	95.6 %
Paints	3.0 %	0.41	1.2 %	3.2 %	98.8 %
Glass & Ceramics	0.6 %	0.74	0.4 %	1.2 %	100.0 %
CNT					
Energy	9.1 %	0.75	6.8 %	62.2 %	62.2 %
Consumer Electronics	3.1 %	0.75	2.3 %	21.2 %	83.4 %
Paint	1.4 %	0.46	6.4 %	5.9 %	89.3 %
Automotive	1.3 %	0.4	0.5 %	4.7 %	94.0 %
Fullerenes					
Motor oil(Lubricant)	24.2 %	0.8	19.4 %	50.8 %	50.8 %
Metals (coating)	16.7 %	0.9	15.0 %	39.4 %	90.2 %
Electronics and optics	3.3 %	0.75	2.5 %	6.5 %	96.7 %

Appendix 4: Description of recycling systems included in Guzmán (2013)

The recycling systems included in Caballero-Guzmán (2014) encompass:

- WEEE general devices
 - WEEE cooling devices
 - Metals
 - Cars
 - Concrete
 - Textiles

For each system, a table describing the included processes is given below.

TABLE 21
WEEE GENERAL RECYCLING PROCESSES, AFTER CABALLERO-GUZMÁN (2014)

Step	Description
1 Dismantling and depollution (manual)	Manual sorting of WEEE and removal of hazardous materials (ink cartridges, batteries).
2 Main shredding	Reduction of material to pieces of 100 mm approximately. Different types of shredding technologies can be used: grinders, chippers, hammer mills, shear shredders, all-purpose shredders and speciality shredders. This is a very abrasive process that could reach temperatures around 600°C due to kinetic energy. Dust absorbed with very strong ventilation systems. Off-gas permanently filtered
3 Sorting	The material is dropped into a large shaking hopper. This distributes the material evenly onto the conveyor system. Large material is removed from the conveyor.
4 Secondary shredding	The material then proceeds through a secondary size reduction process. Dust extracted at this stage is sent for sound environmental disposal.
5 Magnetic separation	By means of a strong magnetic field, the over-band magnet separates the ferrous (iron and steel) metals from those non-ferrous elements in the waste mix. This material is then collected in large storage containers ready for sale.
6 Eddy current separation	Electroconductive material is separated from non-electroconductive ones using Eddy Current Separators (ECS), including small particles (10mm). The ECS includes first and second hubs coupled to opposite ends of a magnet support tube. Magnets are coupled to the magnet support tube, substantially between the hubs. A motor coupled to one or both of the hubs rotates the magnet support tube and magnets to generate an eddy current in electroconductive material conveyed proximate the separator. The material in which the eddy current is created is repelled and projected away from the ECS along a predictable trajectory. An eddy current is not generated in nonconductive material conveyed proximate the separator, and thus is not projected away.
7 Waste washing	Additional steps include waste washing. Here the granulated WEEE could be passed through a washing tank where the waste is cleaned to remove adhesive residues from labels and dirt debris. Water and surfactant are typically used. NOREC™ uses acetic acid ester to remove inks and organic contaminants of waste plastics. The waste is then sieved, where the polymer is recovered and fine debris are removed. Water used in the process is normally reused repeatedly and waste materials are thoroughly rinsed and passed through to the separation method.

TABLE 22
WEEE COOLING DEVICES RECYCLING PROCESSES, AFTER CABALLERO-GUZMÁN (2014)

Step	Description
1 Preparation (disassembly, drain-off and decontamination)	Disassembly of different components such as glass, wood, cables and mercury switches. Heating of the compressor and cooling circuit to aid the flow of coolants. The liquid coolant, a mixture of refrigerants and oils is then drawn off and the compressor removed from the unit.
2 Main shredding	After preparation, refrigerators are fed-in on roller conveyors in loads of 5-11 fridges. These then are sealed to allow emission free processing, passing over time and microwave sensors. Horizontal flexible accelerating tools create an enclosed tornado. The metal and aluminium will cut the plastics and the foam up to the required sizes, dependent on properties of the materials. Grain sizes range from 0.1 mm to 100 mm.
3 Drying	The shredded material is heated up to 80°C to reduce moisture in the material in an enclosed drying stage.
4 PUR foam separation	A sieving technique is used to extract the PUR (Polyurethane) foam from the other materials. The typical size of the foam particles is less than 2 mm. The foam is then heated to 120°C, which allows the CFC's to be extracted as a vapour, which is then passed to the Cryo-condensation equipment for liquefaction in a temperature range of minus 100°C to minus 160°C. Once gathered and removed, ODS are shipped in canisters for sound environmental destruction by heating them to 2000°C, temperature at which the gasses are broken down into gas and ash.
5 Over-band magnet	Ferrous metal separation. Iron and steel (ferrous) metals are removed from the mixture of grained/sieved material using electro magnets. This material is then collected in large storage containers.
6 Eddy currents	Aluminium / copper (non-ferrous) metals are then separated from the plastics using Eddy currents (created by rapidly alternating magnetic fields). The non-ferrous material is stored in a container and the plastics are stored in a large bag.

TABLE 23
METALS RECYCLING PROCESS, AFTER CABALLERO-GUZMÁN (2014)

Step	Description
1 Sorting	Different types of metals are sorted according to their characteristics, mainly into ferrous and non-ferrous metals. This can be done manually or mechanically by means of magnetic separation, eddy currents or others. Radiation tests can also be applied in this step.
2 Shredding	Metals are shredded and crushed so they can be processed.
3 Separation	Resulting material is sorted again according to their composition or their properties. Some methods include X-ray and IR technology, electrical currents, high-pressure air flow (cyclonic separation and liquid floating systems).
4 Bailing	Once the different metals have been sorted and shredded, they are compressed into cubes or bales, which make it easier for them to be transported to smelting facilities. When the metals reach the smelting facilities, the bales are fed into a furnace where they are heated until they become molten metal.
5 Refining or recovery process	The methods applied are generically described as thermo-chemical processes and their specific characteristics depend on the properties of the metals to be recycled.
Smelter furnace Copper leaching Precious metals refinery	<p>PRECIOUS METAL REFINING PROCESS (Umicore, Hoboken, Belgium)</p> <p>The smelter furnace (first step in the Precious Metals Operations) uses the Isa smelt, submerged lance combustion technology. This involves injecting oxygen enriched air and fuel in a molten bath. The smelter separates precious metals in a copper bullion, from mostly all other metals, concentrated in a lead slag, further treated at the Base Metals Operations.</p> <p>After leaching out the copper in the leaching and electrowinning plant, the precious metals are collected in a residue that is further refined at the precious metals refinery.</p> <p>The precious metals refinery combines classical methods (cupellation) with specially developed processes (silver refinery), to enable the plant to treat all possible variations and ratios of precious metals (silver and gold) and platinum group metals (platinum, palladium, rhodium, iridium and ruthenium).</p>
Blast furnace Lead refinery Nickel leaching	<p>BASE METAL REFINING PROCESS</p> <p>The blast furnace reduces the oxidized lead slag from the smelter together with high lead containing third party raw materials and transforms them into impure lead bullion, nickel speiss, copper matte and depleted slag.</p> <p>The impure lead bullion, collecting most of the non-precious metals, is further treated in the lead refinery. Besides pure lead, the process generates special metals residues. These are, together with the main side streams of the Precious Metals Operations, further refined into pure metals and metal salts in a metals refinery to produce high quality indium, selenium, tellurium and antimonite. Some intermediates are tolled out to dedicated companies to produce tin and bismuth.</p> <p>After leaching the nickel out of the nickel speiss and turning it into nickel sulphate, the remaining precious metals residue is treated at the precious metals refinery.</p>

TABLE 24
END OF LIFE VEHICLES RECYCLING PROCESSES, AFTER CABALLERO-GUZMÁN (2014)

Step	Description
1 Removal of functioning parts	Functioning parts are removed and sold to be used as replacement parts. Larger parts made from uniform materials (e.g. bumpers) can undergo separate material recovery.
2 Detox and dismantling	Licensed disposal companies drain vehicles that have been withdrawn from circulation and strip them of pollutants. They remove the petrol/diesel, oil and other operating fluids, batteries, tyres and catalysts. Particular attention is paid to components that contain known pollutants such as asbestos, mercury and PCBs: these must be disposed of separately.
3 Shredding	Around two thirds of a car consists of metals which can be recovered as raw materials through shredding and separating. The remaining shredder light fraction mostly consists of plastics, textiles, rubber, glass and metals. This is referred to by waste specialists as RESH (residue + shredder) and usually undergoes thermal utilisation.
4 Sorting	Recyclable material is sorted and undergoes further recycling processes. The main recyclable waste fraction is metallic scrap, while the rest is mostly plastics, textiles, rubber and glass, which usually undergoes thermal utilization.
5 Metal recovery	Ferrous metal is usually melted in electric arc furnaces, where impurities are removed and new steel is produced for the car industry (or others).

TABLE 25
CONSTRUCTION AND DEMOLITION WASTE RECYCLING PROCESSES, AFTER CABALLERO-GUZMÁN (2014)

Step	Description
1 Collection	Construction and Demolition Waste (CDW) is collected on construction sites and transported to recycling facilities. CDW could be either mixed waste or only demolition concrete. Mixed waste includes concrete, bricks, tiles, gypsum, rubble and plastics. Additional input for concrete recycling includes gravel and concrete waste (concrete left over at construction sites).
2 Cleaning	Metallic components and material like plastics and textiles, or any other material which is usually not used as aggregate are removed in this step.
3 Crushing	CDW is crushed into pieces of several sizes. Some additives can be added in this step.
4 Screening and sorting	Resulting aggregate is screened and sorted according to their size and their composition (concrete waste or mixed waste), and stored.

TEXTILES

In Switzerland, TexAid and Contex control 75% of the recycling market, and their process consists of collecting and exporting 100% of the material collected. The material exported is sold as second-hand clothes (65%), sold to the car industry (15%), used in the production of recycled wool (15%) or disposed of (5%). In Denmark, different NGOs accept used clothes and textiles. Some resell the used clothes locally, while some send the reusable clothes to, typically African countries. A clear overview of the system does not exist at present. An ongoing Nordic study estimates that of the app. 14.5 kg textiles bought per person and year in the Nordic countries, app. 4.5 kg is collected as used textiles, app. 1 kg is stored / accumulated by the consumers, and app. 9 kg is incinerated and landfilled.

Nanomaterials in waste, Issues and new knowledge

This report gives a review of available information on the presence and behaviour of nanomaterials in waste with the aim at pointing to the issues most relevant for further study.



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