



Green solutions for water and waste

— science brought into action





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Foreword

The sustainable development of society is evolving away from legislation-driven to systemic strategies with balanced environmental, social and economic dimensions. At the same time, clean technologies that address the challenges and opportunities of sustainable development are growing in societal and economic importance.

Sustainable water sources and efficient use of materials are prerequisites for tomorrow's sustainable society

By definition¹, clean technology (or cleantech) refers to any products, technologies, techniques or services that cause less damage to the environment or consume less natural resources in their production or use than their alternatives. The definition is broad and encompasses renewable energy, air pollution prevention, environmental measurement and monitoring, energy efficiency, material recycling and water technologies. VTT's spearhead programme GWW – Green Solutions for Water and Waste (2011–2013) focused on two of these segments: water and waste. In addition to being prerequisites for a sustainable society, they both relate directly and indirectly to the challenges of prevention of and adaption to climate change.

Finland has an excellent sustainability performance reputation and a strong brand in the cleantech market, and has the high technological competence needed to build sustainable societies worldwide. Finland has been ranked first in the world in environmental

sustainability among 146 countries according to the Yale-Columbia Environmental Sustainability Index. In 2012 the Finnish government designated cleantech as one of the country's key economic policy priorities. Finland's Strategic Programme for Cleantech aims to double the total turnover of cleantech businesses and increase the industry's sales to EUR 50 billion by 2020.

Why are sustainable water technologies needed?

The United Nations has estimated that there is enough fresh water on our planet to support six billion people. In 2013, the global population exceeded seven billion. Long-term trends indicate that, in addition to population growth, water consumption per capita will also increase dramatically. Water recycling will become an essential requirement, and producing fresh water from the sea through different desalination technologies will become commonplace. In irrigation alone, where the vast majority of water (ca. 70%) is used globally, the World Bank estimates that we would need to "find" 45% more irrigation water to meet the increased need for food by 2050.

Europe may not be considered as heavily exposed to water scarcity as many other more southern regions, yet concerns over water security are nonetheless very real. In many southern and central European countries droughts and flooding are an almost yearly occurrence. In Europe, and globally, growing climate change consciousness is generating increasing interest in recycling and reuse

¹ Statistics Finland, http://www.stat.fi/til/yjt/2009/yjt_2009_2010-12-21_laa_001_fi.html (in Finnish).

processes as attractive and effective ways to mitigate wastewater disposal impacts and episodic drought effects.

Material efficiency and recycling become strategic

In addition to water, material recycling is shifting from being a technological and economic issue to part of national strategic policy. Globalization, population growth and the rise of emerging economies have led to increasing competition for the world's natural resources. In Europe and elsewhere, many resources are in depletion or are not easily extractable. As a consequence, both the EU and several Asian countries have developed a strong agenda to secure availability and access to industrially critical raw materials.

Recycling is a cleantech segment with high growth expectations. Globally, recycling is being driven by economic growth in emerging markets, such as China, and by legislative actions and related targets for recycling in the developed markets of Europe and North America. New innovations are called for, and the recycling sector today has an impressive R&D agenda: approximately 10% of its global turnover is spent on new technologies, research and development. There is a strong current focus on the recovery of metals and solutions for construction and demolition waste. Solving these issues means overcoming high technological challenges.

Highlights of our work

This edition of Research Highlights provides a summary of the results obtained and advances made in the GWW programme during its runtime, with the most recent research highlights showcased in detail. We discuss the search for new fresh water beyond sea and terrestrial sources – examining air-water harvesting as an emerging local solution in arid areas with high air humidity. We also present new opportunities arising from the application of fungal films in mine water treatment and the use of an industrial by-product – cast

iron chips – for arsenic removal. VTT has also been active in the development of low-fouling membranes for improved energy efficiency of membrane-based water treatment. Research and innovations aimed at whole-crop utilization, such as press cake protein capture to reduce the need for crops cultivation and by that, crop irrigation, are also addressed. This edition also presents a novel non-invasive method of carrying out elemental analysis of recycled material on a running belt. We also present key results from our research on the compostability of nanowaste.

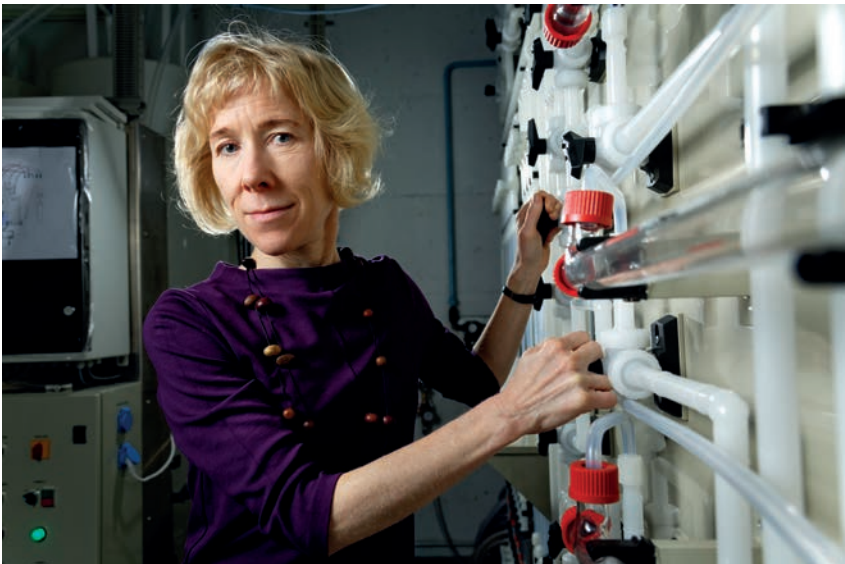
For more examples of our leading research, see the previous Highlights edition: VTT Research Highlights 4 – Green Solutions for Water and Waste².

Collaboration is the key!

Resource efficiency paves the way to reduced production costs, sharper competitiveness and new commercial opportunities. Our role at VTT is to enable this to happen. The Green Solutions for Water and Waste spearhead programme ran from 2011–2013, and this valuable work is being continued in VTT's new "Bioeconomy Transformation" and "Mineral Economy" programmes. I wish to thank all those who have collaborated with us during the past years in GWW and look forward to our continued fruitful cooperation in the latest spearhead programmes.

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² Available: <http://www.vtt.fi/inf/pdf/researchhighlights/2013/R4.pdf>.





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Science brought into action

GWW's vision of a zero-emission society translates into three core R&D areas: energy- and resource-efficient water technologies, waste valorization and smart water and waste solutions for a wide range of application areas. The main focus is on developing smart system and process optimization and diagnostics solutions for the identification of compounds for recovery or removal.

Water- and mineral-intensive industries such as the chemical, pulp and paper, and mining and metal sectors face increasing challenges in meeting their demand for mineral and water resources. More efficient methods of reuse and withdrawal need to be developed. New opportunities within sustainable development are also emerging as environmental issues gain increasing strategic importance in business.

Separation techniques for water and waste treatment

Separation in water and waste treatment occurs at several scales and a variety of different technologies are used. At the macro scale it can mean separation of solids (metals, plastics), while at the micro scale it can refer, for example, to separation of valuable chemical compounds from mine waste water. As the waste and wastewater streams we produce become increasingly complicated, new separation techniques need to be developed.

A focus on the recovery of one material can hamper the recovery of others. For example, in the extraction of materials from

electronic waste, a focus on metals separation can make the recovery of plastic material unfeasible. This is due to the fact that acidic and thermal processing for metal extraction would degrade the plastic material. Another example is separation of base metals from waste, which again can impede the recovery of high-tech metals. Waste-derived metal recovery always involves fractionation of the waste into more concentrated fractions for further cost-efficient processing. Concentrating on one metal flow can lead to the dilution of other metals in the secondary fractions. To eliminate this loss, all parts of the value chain need to be optimized.

During the course of the GWW programme VTT's greatest advances in this field relate to enhanced metal extraction methods based on new insights into the microbiological and chemical reactions taking place in the leaching process. Low-energy membrane applications have been another important development area regarding separation techniques. In particular, the development of forward osmosis in cooperation with a Singaporean university has created interest among VTT's stakeholders. The programme also boosted the development of a range of new sensor technologies for rapid monitoring of micropollutants in waters.

Mining beyond bedrock

Lower grade ores with increasing levels of contaminants as well as challenging extraction environments and tighter environmental requirements are raising the price of mined

virgin material. This production factor, coupled with globally increased industrial demand, is making mineral recycling economically feasible. Many industrial sectors, such as construction, chemicals, automotive, aerospace and machinery, are dependent on access to critical minerals. There is therefore growing interest in the recovery of high-value metals from industrial waste streams. Emerging legislative drivers regarding, for example, construction and demolition waste are also generating a need for more sophisticated processes and laying fertile ground for new value chains.

Emerging interest in the recovery of high-tech and critical metals has led VTT to study and develop processes for identifying and extracting minerals occurring in small quantities in current waste streams. Bioleaching has traditionally been seen as a potential process for the extraction of such materials. Through chemical modelling based on our expertise in chemical and microbiological reactions we have succeeded in shedding light on the black box of dissolutions and precipitations taking place in the bioleaching of various materials. This enables us to make leaching processes more effective and also to exploit materials traditionally left untapped in e.g. phosphate mining, such as overburden (soil overlying the mineral deposit) and tailings (leftover material after separation of the valuable compound). The potential of utilizing sidestreams and waste flows as phosphorus resources has been an important working area with two key aspects: extraction and recovery of the mineral itself, and increasing sewage-derived phosphorus bioavailability. Another highly interesting new resource are landfills, which are potential mines for numerous minerals and fuels that, until now, have remained practically wholly untapped.

Energy-efficient water treatment

In terms of energy efficiency of water recycling and treatment, large-scale installations are the main arena of development. Most recy-

cling and desalination systems are based on energy consuming membrane filtration technologies. This is being combated by VTT in cooperation with our partners by developing non-fouling strategies and smarter membrane materials, and by applying low-pressure technologies such as forward osmosis (FO) water treatment. This emerging technology has been a main development front of the GWW programme. During the past two years we have developed applications for biorefineries and the mining sector as well as a new support structure for FO membranes. We have also developed unique tools for deep analysis and on-line monitoring of fouling and scaling processes, as well as ways of controlling this major problem in membrane operations. Smart antifouling membrane coatings play a major role here and are a prime illustration of how a combination of different competences – in this case advanced materials and water technologies – can jointly create a competitive solution.

However, the water energy focus is not restricted to increasing the energy efficiency of membranes. It also takes vast amounts of energy to pump and deliver water for the use of society and industry each day. At VTT we have investigated ways of minimizing the need for pumping through the use of internal recycling processes and increasing the efficiency of the water distribution network, for example through leak control, to reduce overall water consumption and costs.

The water challenge is also closely tied to the sustainable use of food and biomass. The World Bank estimated in 2013 that reducing post-harvest spoilage and waste by 25% could reduce irrigation demand by 10%. VTT's work on enzyme-aided analysis and fractionation of rapeseed press cake is a prime example of innovative use of sidestreams and waste generated in the food value chain. Under the GWW programme VTT has studied organic sidestreams as a potential source of biocompounds, feed, material components and new protein fractions.

Finding new water sources and assuring water quality

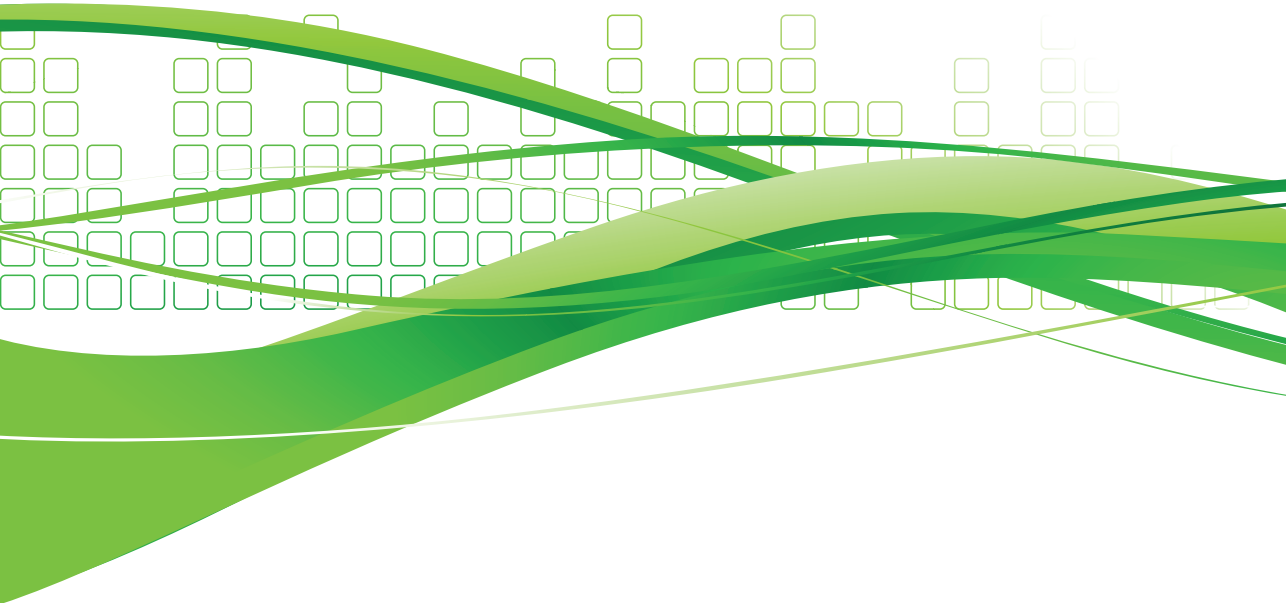
Global demand for fresh water is intensifying and the search for new sources is on. This search is not limited to the sea and terrestrial sources. Air-water harvesting is emerging as a local solution in arid areas with high air humidity. Here, the combination of smart materials in new ways offers immense potential for the generation of pioneering water harvesting technologies. Biomimetic approaches can also be used for targeted removal of pollutants from water, with the natural affinity of organisms for substances, such as heavy metals harnessed in the development of novel filter applications or cultivation of algae in waste water.

Increasing pressure on water resources intensifies the need to assure the quality of the water we use. Until now, there has been no effective alarm system capable of giving precise enough real-time information on micropollutants or microbiological contamination in natural waters or drinking water. VTT has developed affordable and easy-to-use quick tests for organic micropollutants as well as a new sensor structure with high potential for more precise identification of bacteria, viruses and endocrine disruptors.

Holistic thinking, smart solutions

VTT has pushed hard to promote holistic thinking in all focus areas of the GWW programme. A holistic approach is essential in the recycling of metals and other high-value materials, as well as in development of water solutions. In the move towards sustainable materials management, recycling must be optimized on both an economic and technological basis throughout the product life cycle. There is a need to develop not only efficient extraction technologies for the recovery of valuables from waste streams, but to manage the whole value chain. This includes smart collection and sorting, fractionation, end-use of residuals and finally – or primarily – designing recyclability into products and systems.

Waste



From X-ray aided scrap sorting ...





The challenge of elemental analysis in recycling



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Most modern consumer goods are made of a complex mix of materials. Material shredded down for recycling therefore often contains a large range of different physically or chemically tightly bounds elements. Such complex material mixtures can rarely be used directly as raw materials for further goods production. Before their physicochemical separation and purification, we typically need to analyse their elemental composition in order to be able to sort them for further treatment. Measuring the density, colour, conductivity, magnetic properties or surface spectroscopy of a material can give us a fairly good idea of the elements it contains, especially if we have some prior knowledge of the material batch. For complex products, though, these methods are simply not accurate enough.

Very few methods exist for precise analysis of elemental composition, especially if sample analysis is not possible and the bulk material must be analysed. Traditionally, the method of choice in recycling has been X-ray fluorescence spectroscopy (XRF). When properly applied, a resolution close to 1ppm material concentration can be achieved using XRF, although in rapid on-line analysis the resolution is much coarser.

X-ray material analysis

When a material sample is exposed to X-ray radiation, a small part of this energy fluoresces back to a wide space angle in the characteristic energy of each material. Corresponding to the different electron orbit transitions, several

Acknowledgements

VTT's long-term partner Kuusakoski Oy is acknowledged for the cooperation in the development of high-tech solutions for the recycling of valuable materials, together with VTT's spin-off Advacam Oy and the Czech Technical University.

possible lines in the energy spectrum can be observed. These are typically two K and two L lines and, depending on the element, usable low energy lines are found between about 3keV and 25keV at one or the other of these line pairs. Material classification is based on spectrum detection using energy-discriminating silicon or compound semiconductor detectors. **Unlike many other methods, measurement is completely independent of the chemical or crystalline structure of the material, and most materials are not damaged by the radiation. This enables us to illuminate the whole bulk within the penetration depth of the X-rays.** In contrast, some other analysis methods, such as LIBS (Laser Induced Breakdown Spectroscopy) are restricted to only small samples, and the spectra also depend on the sample chemistry.

There are many practical challenges regarding the use of XRF and detection of

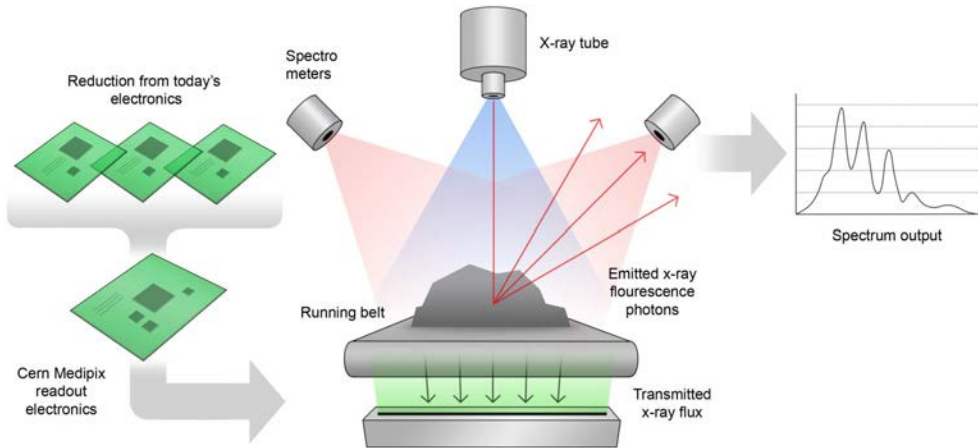


Figure 1. The new recycling analysis technology will utilize the CERN Medipix technology in a multipixel X-ray readout array providing each pixel with independent energy measurement for up to eight energy windows, in addition to the typical gross transmission X-ray image. The figure shows how typical legacy XRF spectrometers are oriented in an off-axis direction above the belt in order to receive only the fluorescent flux (but losing the origin of the rays). By contrast, the readout array below the sample can recover the spectrum at high spatial resolution.

characteristic energies, but the major drawback of present XRF devices is that the fluorescent energy is scattered in random directions, and thus such imaging like in transmitted X-ray viewing is not possible. The only means of enhancing spatial discrimination is to bring the detector close to the analysed material, which is difficult to achieve in the case of randomly shaped objects. In principle, multi-slot collimators could be used, but the characteristic low intensity of the fluorescent flux makes this impractical.

VTT spin-off takes radiation research further

A pioneering new approach to imaging X-ray spectrometry is being developed by VTT spin-off Advacam Oy. Their technology allows non-destructive X-ray imaging and material discrimination of microscopic features. Advacam utilises the state-of-the-art radiation

detector technology licensed from the CERN particle physics laboratory, VTT as a part of a large research consortium has further developed the detector technology and this is now being commercialised by Advacam. The radiation detection technology makes it possible to measure both the energy and the direction of origin of radiation emanating from the target under exposure. This measurement is utilised in elemental analysis for efficient sorting in recycling plants. Figure 1 shows an illustrated comparison of legacy XRF and the new approach under development. A key enabler is the integration of the CERN Medipix pulse processor for each pixel, so that a high flux can be analysed in high resolution without suffering too much from the high background that would otherwise cover the characteristic radiation [1, 2].

Because the arrangement shown in Figure 1 also measures the gross material X-ray attenuation, information can be fused from

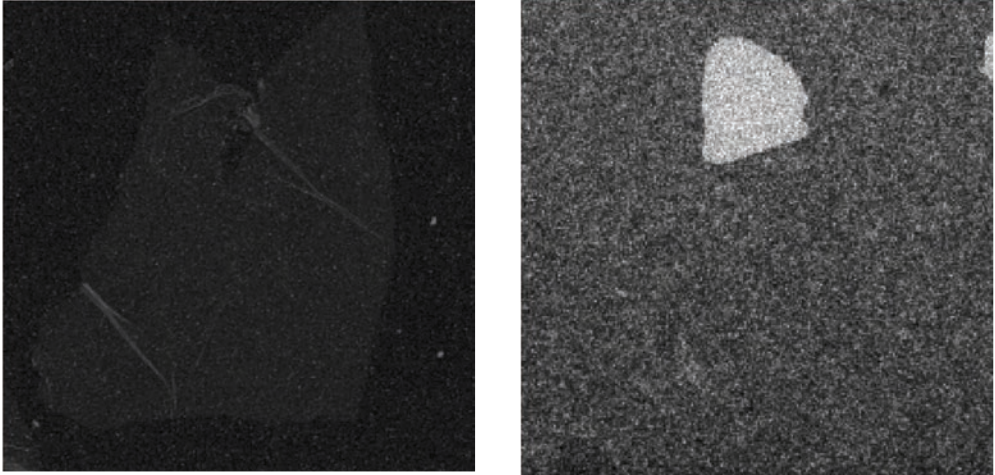


Figure 2. Two images showing the resolution of the Medipix technology with a silicon matrix detector array; 7mm by 7mm views. Left: very thin leaf gold glued on 0.1 mm sticky tape. The slightly lighter area corresponds to the gold leaf, which at less than 500 nm is much thinner than the plating typically used in electronics connectors. Right: a small gold nugget imaged behind 1 cm layer of sand. The images do not show the planned specific energy discrimination, but merely show the high spatial and density resolution achievable. The support of Juha Kalliopuska from Advacam Oy and Jan Jakobek from the Institute of Experimental and Applied Physics of the Czech Technical University, Prague, in preparing the X-ray images is gratefully acknowledged.

various sources, including 3D machine vision, for more reliable material recognition. This principle can be used when sorting scrap that has clear material density differences even without XRF spectra, e.g. when sorting lead-containing glass from ordinary glass. The imaging resolution can be very high, especially if a microfocus X-ray tube is used.

Figure 2 shows some preliminary images using Medipix-equipped sensor arrays. The images are ordinary transmission X-ray images – without the planned energy measurement – demonstrating the detectors' very fine X-ray intensity resolution and good potential for energy discriminating, imaging X-ray spectrometry.

The EU raw material strategy

The European Commission estimates that currently only about 20% of waste

from recyclable electronics and electrical equipment (WEEE) generated in the EU is collected. Enforced by the new WEEE Directive, this figure will reach 85% by 2020. The new EC Raw Material Initiative calls for cost-effective and environmentally-sound innovation to meet the future resource needs of the EU [3]. A further boost comes from the recent rise in Chinese import duties on unsorted waste material. This has spurred demand for manual sorting in China to be replaced by automated sorting in the waste producing countries, in turn accelerating demand for new automated waste analysis and sorting methods.

WEEE is the most rapidly growing urban waste fraction in Europe. It also contains many of the elements that are considered of strategic importance to our economy. As microelectronic devices become ever smaller, waste material recognition and separation



Figure 3. Hammermill shredding in large-scale operation at Kuusakoski's Heinola recycling plant. Shredded recovered metal is graded and sorted according to its elemental composition. Image courtesy of Kuusakoski Oy (Hanna Pynnönen).

methods need to achieve better resolution and sensitivity. As an example, a mobile phone today contains more than 40 different raw materials, including rare earth metals and precious metals, yet the recycling of rare earth metals currently remains technologically and economically challenging. According to the European Commission [4], additional separation steps in the collection and pre-sorting of small WEEE have the potential to increase gold recovery from the current 26% to some 43%, and to increase tantalum recovery to as high as 48% and gallium recovery to up to 30%. The described new X-ray based methods offer the best potential for reaching the targeted improvements.

VTT and Kuusakoski improve recycling of strategic metals

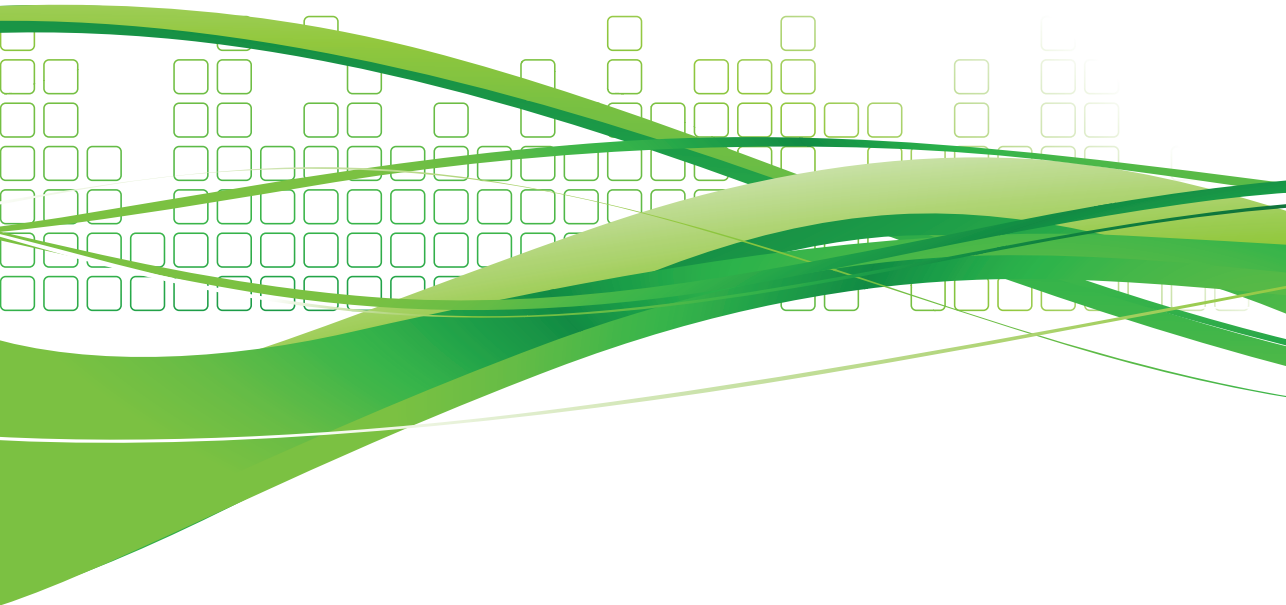
VTT and Kuusakoski Oy have cooperated for over 10 years in the development of high-tech solutions for the recycling of valuable materials. A recycling plant includes complex multi-technology systems for shredding, analysing and automatic sorting of recyclable materials (see Figure 3). For important strategic metals, on-line analysis requires sensitive detection of different elements at very low concentrations. In addition to being the leading recycler of metal-based products in Northern Europe, Kuusakoski is also recognized as one of the largest suppliers and refiners of recycled metals in the world, having over 100 service

locations in Finland, the Baltic countries, China, Denmark, Great Britain, Poland, Russia, Sweden, Taiwan and the United States.

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Waste



... to extracting proteins
from food oil production
by-products ...



Rapeseed press cake – a by-product as a source of multiple valuable components



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The processing of fish and oil plants generates abundant material co-streams rich in protein, essential amino acids, oils containing omega fatty acids, vitamins and other health-promoting substances and minerals. These valuable co-streams are excessively overlooked for human use and utilized mainly as animal feed.

VTT is currently working to find novel solutions for utilizing these substances and minerals for human nutrition¹. The goal is to develop novel eco-efficient bio-mechanical processing solutions for enriching intermediate fractions from industrial process residues originating from oil plant cultivation and fisheries.

Rapeseed press cake is an excellent source of high-value nutritional components. Vegetable oil manufacturers in Europe produce 12 million tonnes of rapeseed press cake annually, primarily for the feed market. A cold-pressed rapeseed press cake, for example, consists of one-third protein [1], which could be enriched and upgraded for human consumption by the oil producers themselves or by food ingredient companies. **Rapeseed protein would provide an interesting GMO-free alternative to the plant-based proteins currently on the market.**

Nutritionally, rapeseed proteins are equivalent to egg or milk protein and have shown good foaming properties due to their viscosity, giving them high potential for use in different food and non-food applications such as detergents, cosmetics or pharmaceuticals [2]. Another potentially valuable group of components in rapeseed press cake are

Acknowledgements

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antioxidative compounds such as phenolic acids [3].

VTT's work on the topic is focused on enzyme-aided analysis and fractionation of rapeseed press cake. The raw materials are press cakes derived from cold pressing of rapeseed either with or without dehulling of the seed [1]. In dehulling, rapeseed hulls are partially removed before oil pressing to produce mild-tasting premium quality food oil. In this process, the rapeseed cell walls remain partially intact during pressing, hindering the release of proteins from the rapeseed structure. By combining mechanical and enzymatic treatments, protein release can be enhanced and this and other valuable press cake components enriched as high-value fractions (Figure 1).

¹ The work is being carried out under the EU-APROPOS project coordinated by VTT (www.euapropos.eu, project number 289170), The project has 7 academic and 10 SME partners from Finland, Norway, Germany, Lithuania, India, Kenya, Uganda and Canada.

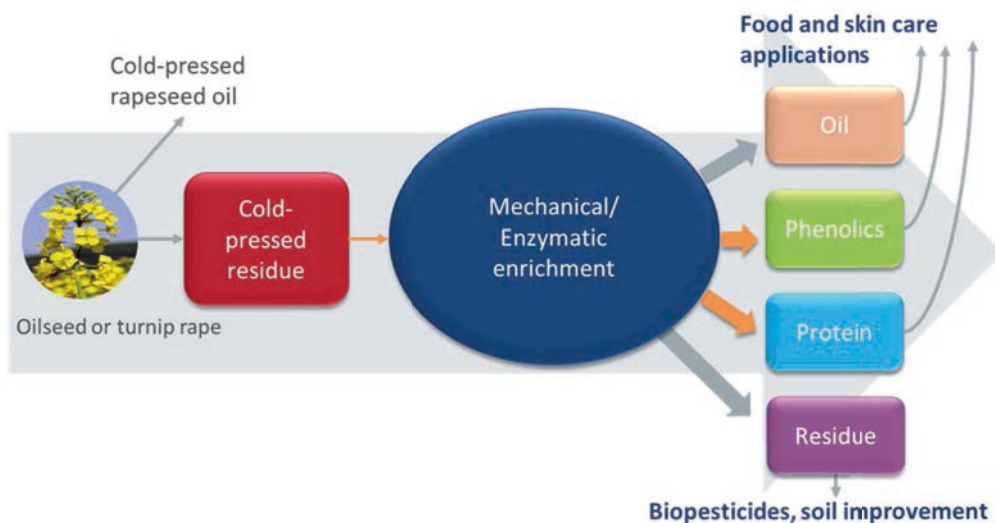


Figure 1. Combined mechanical and enzymatic enrichment to obtain high-value fractions from rapeseed press cake.

Rapeseed:

- Rapeseed is the dominant oilseed crop in the EU
- Global annual production ~62 million tonnes*
- Main producers Canada, India, China and Germany

Rapeseed press cake:

- Co-stream from rapeseed processing for oil production
- Annual production in Europe 12 million tonnes*
- Protein content ~30%
- Currently used as feed

Dehulling:

- Removal of hulls prior to pressing to obtain high quality rapeseed oil

Cold pressing:

- Rapeseed oil is extracted by physical pressing at ~50-60 °C without added heat or solvents

* Data from FAOSTAT The Statistic Division of the FAO, Food and Agriculture Organization of the United Nations

Valuable components of rapeseed press cake

Comprehensive analysis of the chemical composition of dehulled and non-dehulled rapeseed press cakes revealed the main valuable component of rapeseed press cake to be protein, accounting for more than one third of the cake dry weight (Figure 2). The oil and protein content of dehulled press cakes from Germany were found to be slightly higher compared to non-dehulled press cakes from Finland [4].

The key to liberating protein from rapeseed cells is degradation of the lignocellulosic cell wall. To achieve this, the water soluble and insoluble carbohydrates present in the rapeseed press cakes were determined in order to select enzymes for hydrolysis of the cell wall components. The main carbohydrates present in water insoluble polysaccharides were glucose, galactose, arabinose and fructose. Consistent with our results, rapeseed press cake has been previously reported to contain cellulose, arabinogalactans, arabinan and pectins with galacturonan chains containing rhamnose side units [5].

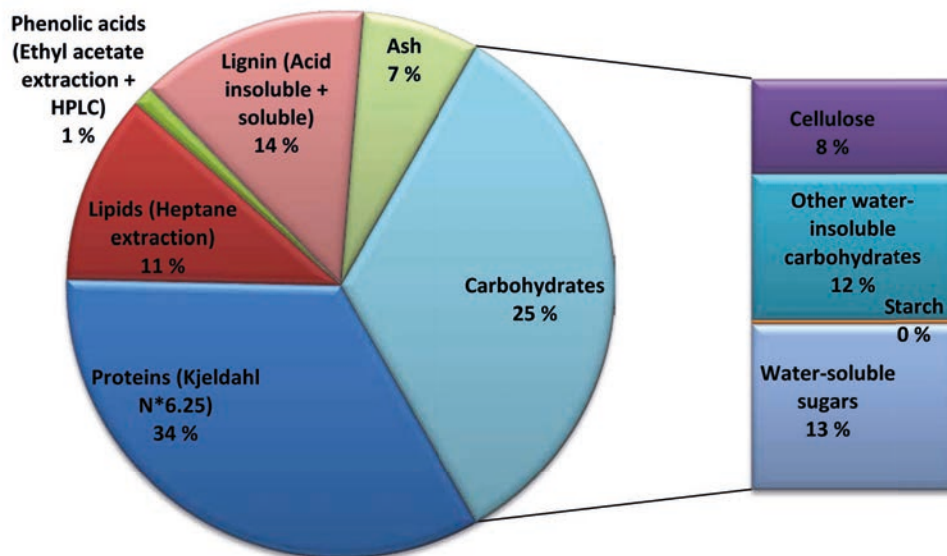


Figure 2. Composition of press cake obtained from cold pressing of rapeseed.

The analysed rapeseed press cakes contained over 1% phenolic acids, mainly sinapic acid and its choline ester sinapine. These compounds are highly antioxidative. However, they also have unpleasant taste and are easily co-enriched with rapeseed protein, thus hindering the utilization of rapeseed protein for food.

When dehulling is carried out prior to oil pressing, the remaining press cake contains higher amounts of protein and oil compared to non-dehulled press cake. The hull fraction obtained in dehulling, on the other hand, is rich in cell wall structural polysaccharides and lignin-like material. In this study, enzyme treatments are utilized in the processing of rapeseed press cake in order to enhance the liberation of protein in subsequent processing steps. Based on the analysed carbohydrate composition, three different enzyme tools for bioprocessing rapeseed press cake were chosen. The chosen enzymes were cellulase, xylanase and pectinase-rich commercial enzyme products.

Enzymes can be used to loosen the cell wall structure of rapeseed press cake

In order to release the rapeseed proteins from the press cake, the cell wall structure needs to be deconstructed. In Figure 3, microscopy images of rapeseed press cake after different processing steps are presented. The samples have been dual stained, with the sample protein stained red (acid fuchsin) and cellulose blue (Calcofluor). In the image on the left, it can be seen that the rapeseed cell wall structure has been partly broken down by oil pressing and protein has been partially released from the cells. As the middle image shows, subsequent milling of the rapeseed press cake breaks down the cell walls further. Finally, enzymatic treatment strongly affects the cell walls, disintegrating them to large extent (Figure 3, right). VTT and partners aim with this research to combine mechanical and enzymatic treatments to enhance the release of protein from the press cake in the subsequent extraction stage.

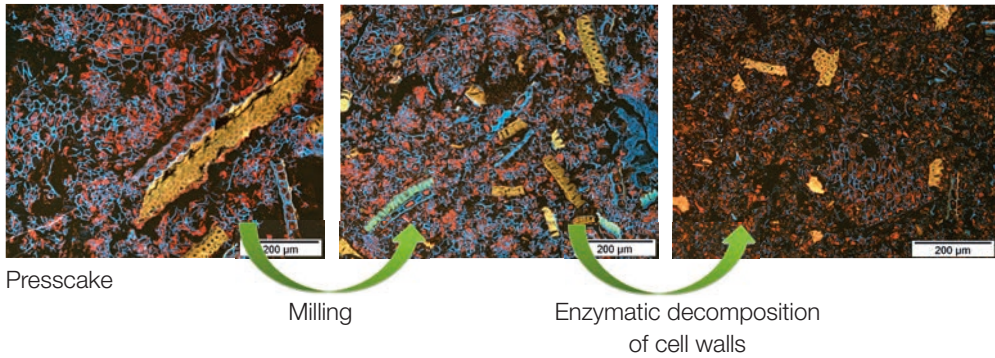


Figure 3. Epifluorescence micrographs of rapeseed press cake after milling and enzymatic treatment. Samples have been stained to visualize protein in red (acid fuchsin) and cellulose in blue (Calcofluor). Cell walls rich in cellulose are stained blue, the protein-rich cell contents are red, and the remaining recalcitrant rapeseed hulls with thick cell walls are stained yellow.

The effect of enzyme treatment on protein release from the press cakes was analysed based on the nitrogen content in the hydrolysates. Three enzyme products affecting different carbohydrates present in rapeseed cell wall structures were used. All three were shown to have a positive effect on protein release (Figure 4). **The most effective**

enzyme (Enzyme 3) increased protein release by 70% in comparison to the reference with no enzyme addition. One of the challenges in enriching rapeseed protein for human use is the water intensiveness of the processes. This will be tackled by carrying out enzymatic treatments at high consistency.

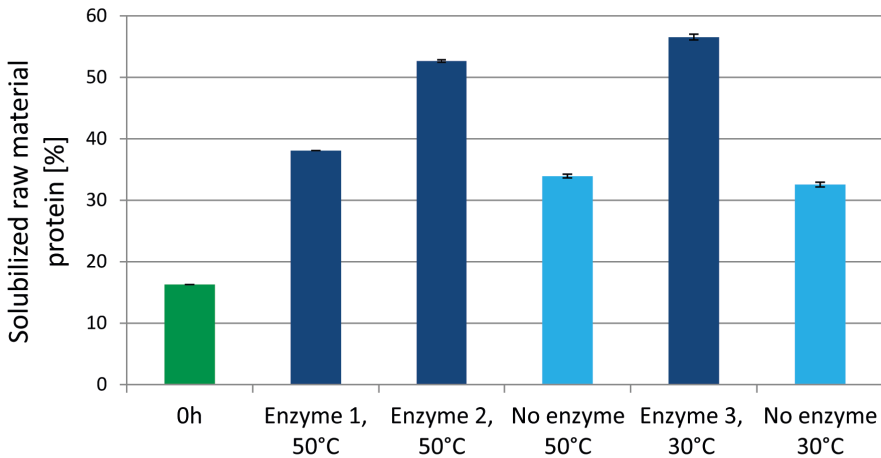


Figure 4. Enhanced protein solubilization during 48 hour enzymatic treatment.

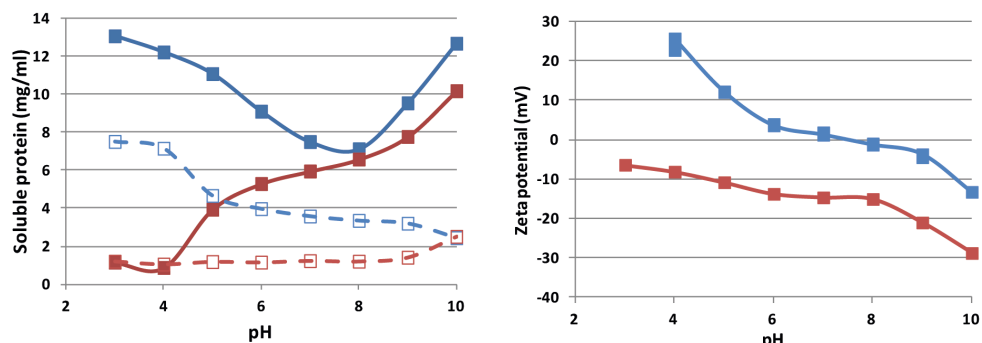


Figure 5. Solubility and zeta potential of native canola protein (blue) and partially denatured rapeseed press cake concentrate (red) before (solid line) and after (dash line) heating.

Functional properties of rapeseed proteins

The aim of this research is to identify the critical parameters for preserving the functional properties of rapeseed proteins in order to define the requirements for manufacturing a functional rapeseed protein fraction. The functional properties of plant storage proteins are generally associated with their solubility, which affects their ingredient properties such as foaming, emulsifying and network formation. Solubility is reduced by extensive heat treatment due to irreversible aggregation. But is conserving the native protein structure a prerequisite for dissolution? Another equally important question is whether purification is needed to obtain protein isolates, or whether the naturally occurring cell wall carbohydrates could be exploited as hydrocolloids in structure formation in foods and cosmetics.

The work has focused on clarifying the effect of protein denaturation and the presence of cell wall carbohydrates by comparing a pure, native canola protein isolate and partially denatured rapeseed press cake protein concentrate (Figure 5). The results indicate that the high solubility of protein isolate as compared with the concentrate at low pH (4–5) may relate to its electrostatic stabilization. In the case of protein concentrate, the

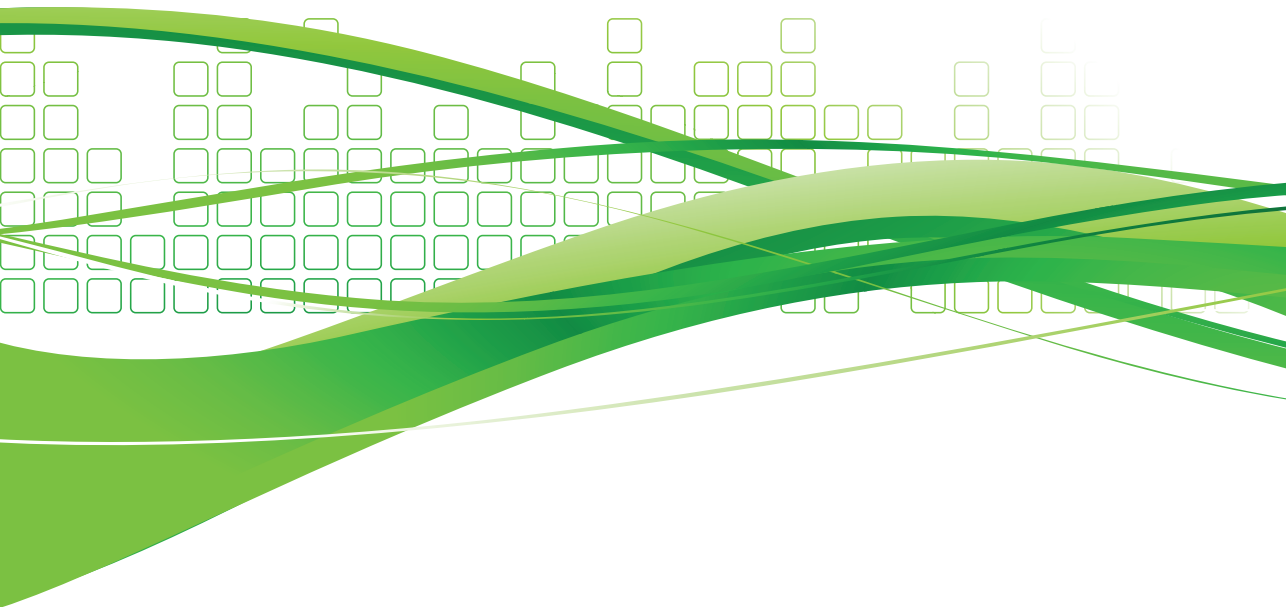
net charge of the dispersed phase remains close to 0 up to pH 8, and thus provides no stabilization. The partially denatured protein loses its dissolution ability upon further heating, indicating that denaturation itself may not be the main factor contributing to solubility, but rather, aggregation due to heat treatment. Based on our results, rapeseed protein enrichment should be carried out with minimal heat treatment to maintain functional properties. In addition, the development of concepts for exploiting colloidal protein particles rather than soluble protein in structure formation with plant proteins is also targeted.

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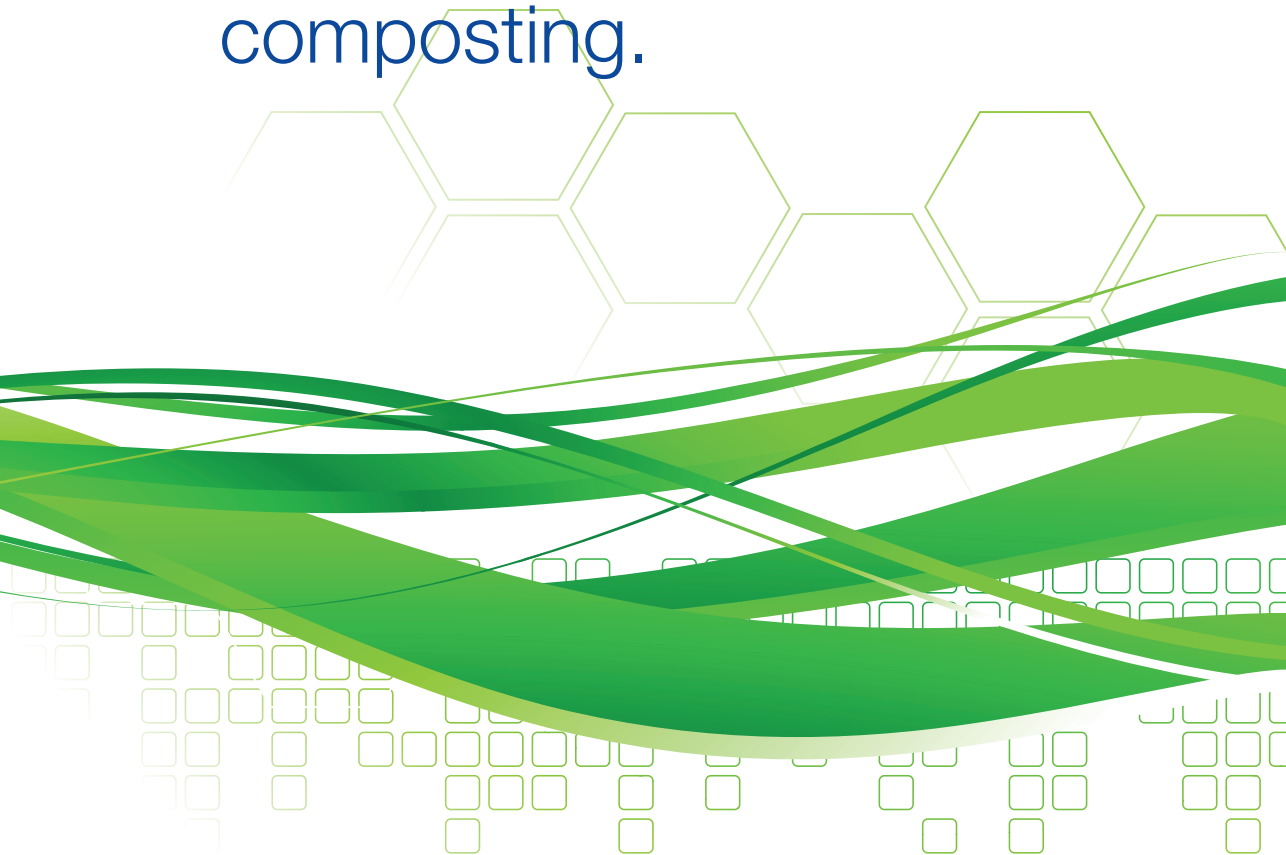
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Waste



... and to exploring the possibilities of nanowaste composting.



Is nanowaste a threat to the environment?



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The properties and behaviour of materials at the nanoscale can be very different compared to larger scales. Nanoproducts can be defined as manufactured products containing nanomaterials, such as textiles containing nano-silver, sunscreens with nano-TiO₂ or packaging materials containing nanofibrillated cellulose. The application areas for nanomaterials are very wide, including healthcare, electronics, material technology, cosmetics, textiles, fuel cells and environmental technology.

As more and more nanoproducts come on the market there is growing concern about their potential environmental and human health impacts. The risk of exposure to nanomaterials is present at all stages of the product life cycle, from production and use through to final disposal. As the volume and variety of nanoproducts produced continues to expand, the amount of products reaching the end of their life cycle as 'nanowaste' is also rising. **There is therefore an important need to identify the possible risks associated with the disposal of nanoproducts.**

Nanomaterials can take different forms

Nanomaterials are natural, incidental or manufactured materials with a size range of 1–100 nm in at least one dimension (EU definition). They can also be classed according to their shape as either nanoparticles with all three dimensions in the nanoscale; flat nanoplates; or rod-, tube- or wire-shaped nanofibres. Nanofibrillated cellulose is a versatile nanomaterial with multiple potential application

Acknowledgements

UPM-Kymmene is acknowledged for supplying the UPM Biofibrils used in the tests. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement no 247989 (NanoSustain – Development of sustainable solutions for nanotechnology-based products based on hazard characterization and LCA).

areas, such as composites for construction, vehicles, furniture, cosmetics and pharmaceutical applications. These nanofibrils have a nanoscale width and a total length of several micrometres.

At the nanoscale, materials have a bigger surface area to volume ratio than in their bulk form. This can give them unique properties, for example with respect to strength, colour or ability to conduct electricity or heat. It has been claimed that these unique properties can also generate undesirable effects, including toxicity. On the other hand, possible toxicological risks associated with nano-properties may be masked when free nanoparticles become embedded, bound or

¹ The work is being carried out in the NanoSustain project (www.nanosustain.eu). The project has 12 partners from Finland, Sweden, Germany, Denmark, UK, Italy, Lithuania, and Romania.

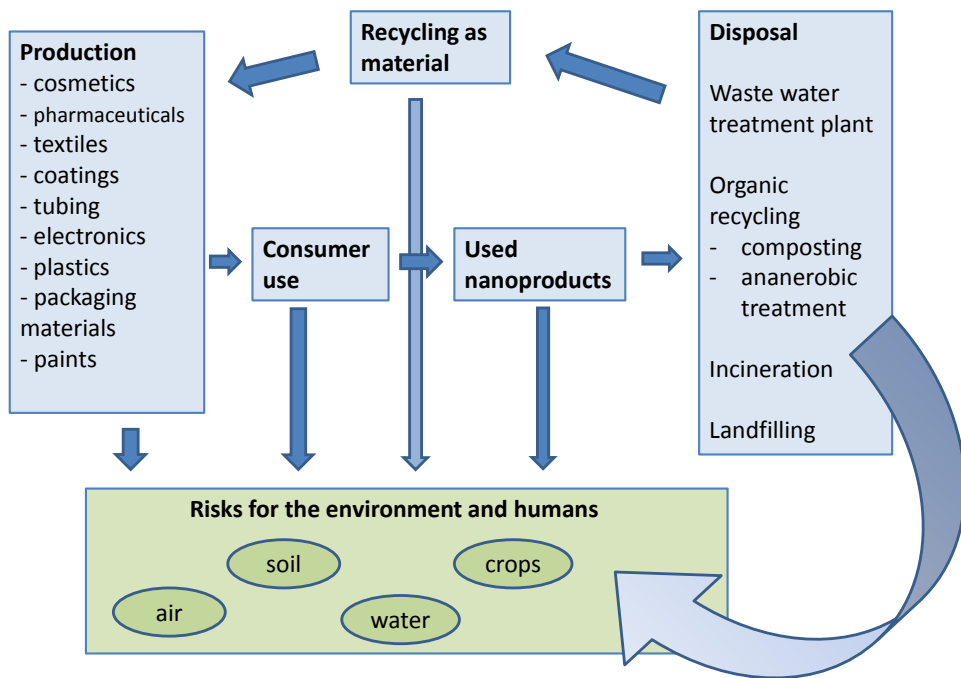


Figure 1. Environmental fate of nanoproducts. Risks of environmental and human exposure are present at each stage of the product life cycle, from production and use through to final disposal.

incorporated in the solid matrix of a product or environmental substrate [1, 2].

At the end of its life cycle, a nanoproduct is destined either for a material recycling facility, incineration plant, waste water treatment plant, composting plant or landfill site. The most suitable disposal option depends on the type of nanoproduct, EU and national legislation, and the waste management options available in the location in question. For example, packaging materials can be recycled, composted or incinerated, whereas personal care products and cosmetics typically end up at a wastewater treatment plant (Figure 1).

The end-of-life aspects of nanoproducts were specifically examined in a European collaboration¹. The aim was to explore and develop new solutions for the sustainable design, use, re-use, recycling and final

treatment and/or disposal of specific nanomaterials and associated products. **VTT's major task in this work related to the stages after disposal, including the treatment methods used in composting, incineration and land-filling.**

Can nanofibrillated cellulose products be composted?

Composting is a recognized valuable method of organic waste treatment and can be considered an effective option for recycling. According to the European Bioplastics Association [3], large-scale composting is currently the most widespread organic recovery method in Europe, although the amounts of organic material collected and treated differ widely among EU countries. Typical input materials for composting are garden and kitchen waste from households.

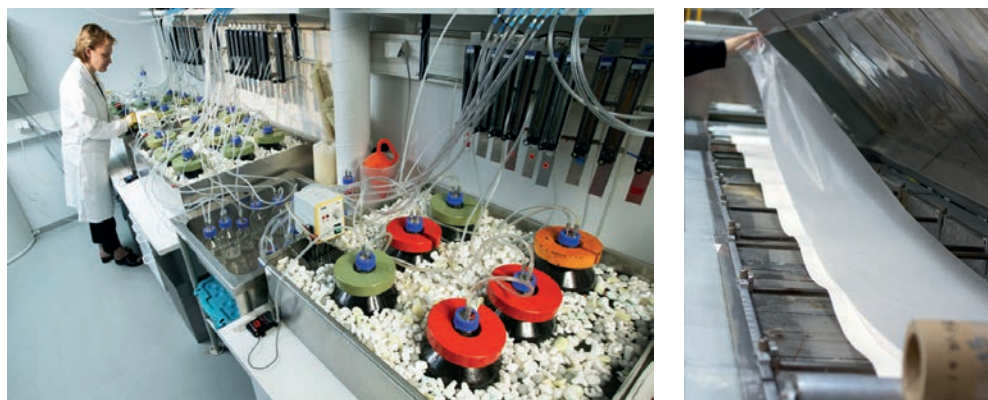


Figure 2. a) Testing equipment used to evaluate the biodegradability of nanoproducts. All samples contained nanofibrillated cellulose. The test is designed to replicate typical aerobic composting conditions for organic municipal waste. Biodegradability testing is part of the testing system used to evaluate compostability according to the European norm EN 13432 [4]. b) Film manufactured from nanofibrillated cellulose.

Manufactured products, such as packaging materials, have to meet certain European norms in order to be suitable for composting, the key requirements being biodegradability and environmental safety. As the resulting compost may be used as a soil improver, nanoproducts must not have any negative impact on the composting process or the quality of the compost.

VTT's testing systems were used to evaluate different nanoproducts containing nanofibrillated cellulose (Figure 2). All of the products tested were found to be biodegradable in compost conditions, and they also degraded in pilot-scale composting experiments. The compost quality was verified using the kinetic *Vibrio fischeri* bioluminescence inhibition assay (Flash assay).

Incineration of CNT-containing composites

With the growing use of nanomaterials in products such as construction materials, paints and cosmetics, nanoparticles are increasingly finding their way into waste incineration plants. To simulate the end-of-life treatment of carbon nanotube (CNT) -containing compos-

ites, a sample composite was incinerated in a solid fuel furnace together with wood chips as a supporting fuel ([5]; Figure 3a, 3b). The total release of nanoparticles and CNTs during the experiment were evaluated to determine the possible risks related to the incineration of CNT-containing composites.

The CNT composite consisted of electrical grade glass fibre with an epoxy hardener, of which 52.2 wt.% was Amroy Hybtonite multiwall CNT composite containing approximately 0.5 wt.% Bayer C 150 P multiwall CNT [6, 7]. Three different fuel compositions were used: wood chips with 20 wt.%, 5 wt.% and 0 wt.% of CNT-containing composite. The average combustion temperatures 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, mass concentration and size distribution were measured, and individual particle morphology and composition were studied by electron microscopy (EM). Raman spectroscopy was carried out on deposit and particle samples to detect the possible presence of CNT structures.



Figure 3a. 40 kW combustion chamber with mechanical grate used in the experiments.



Figure 3b. CNT-containing composite and wood chips used as a supporting fuel for combustion.

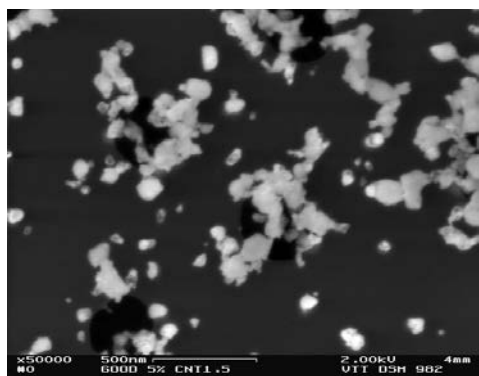


Figure 3c. Particles collected during good combustion of wood chips and 5 wt.% CNT composite. The diameter of the primary particles is larger than approximately 50 nm.

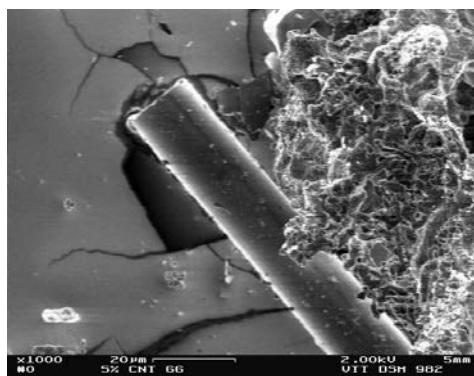


Figure 3d. Bottom ash deposit for good combustion of wood chips and 5 wt.% E-glass rods together with wood ash and molten epoxy are observed.

Nanoparticles were observed in all combustion test cases, independent of the fuel composition, in accordance with the new nanoparticle definition by the EU [8]. However, the fraction of the nanoparticles of the measured ones varied depending on the composition of the fuel being highest for the good combustion of wood chips only in case when nanoparticles were ‘counted’ as individual particles and not aggregates/agglomerates.

It should be noted, however, that the combustion conditions in the furnace were not always optimal in the CNT composite

mixture cases due to the formation of a large, hard bottom deposit on the burner grate. The formation of the deposit severely deteriorated the operation of the furnace, thus directly influencing combustion and the formation of ash and emitted particles. As an example, the morphology of the emitted particles during 5 wt.% CNT-containing composite combustion is presented in Figure 3c. The particles were almost spherical and approximately 50 nm in diameter, together with aggregates of different sizes (approx. 200 nm and larger) consisting of the primary particles.

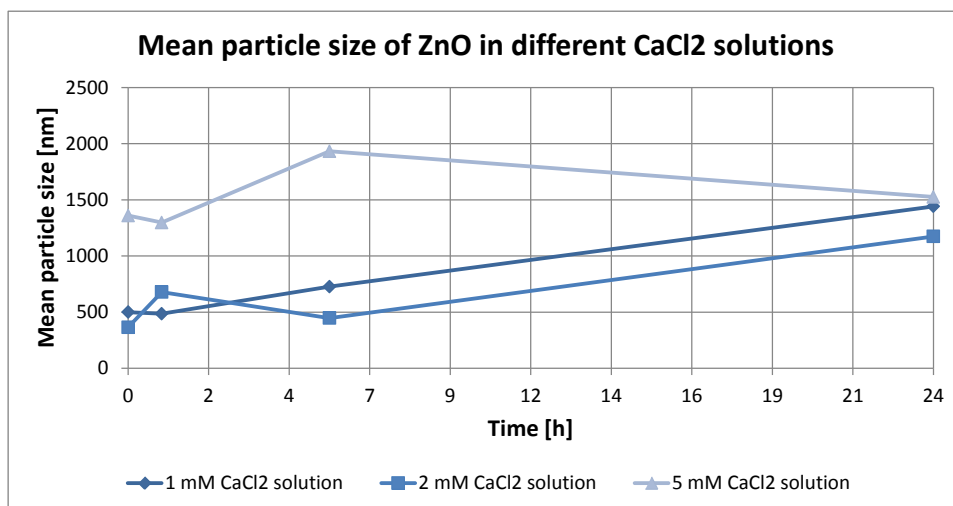


Figure 4. Influence of salt concentration on mean particle size in leaching test.

None of the combustion cases showed evidence of CNT-like tubular structures in the emitted particles. This finding was also confirmed by RAMAN spectroscopy. This was probably due to the low amount of CNT-containing composite in the fuel mixture and the formation of the large and hard, highly sintered bottom ash deposit (Figure 3d), which might 'bind' or immobilize the CNT composite species in a non-volatile matrix. The results may therefore be different for fuel mixtures with higher amounts of CNTs, or depending on the type of matrix in which the CNTs are 'bound'.

Do nanoparticles leach from landfill?

The final option for nanoproducts is landfill disposal. In the development of acceptance criteria for landfilling, the focus has been on eliminating the risk to the surrounding environment, in particular groundwater and surface water. Other key acceptance criteria include the protection of environmental protection systems (e.g. liners and leachate treatment systems), protection of the desired waste-stabilization processes within the

landfill, and protection against human health hazards. The main questions in evaluating the potential risk from nanoparticles in landfill conditions concern the level of nanoparticle release to water and the fate of the released nanoparticles.

The aim of the study was to evaluate the applicability of developed standardized test procedures for waste materials containing nanoparticles. For this purpose, **different test conditions were also examined in order to identify the critical conditions for nanoparticle release.** In particular, the conditions influencing the agglomeration of nanoparticles in aquatic phase were evaluated in order to support understanding of the leaching test results. The agglomeration of nanoparticles strongly influences the fate (e.g. mobility and retardation) of nanoparticles in landfill leachates.

The focus of the experimental study was on the release of zinc (Zn) from glass coated with nano-zinc oxide (nano-ZnO). Test series were also carried out with nano-ZnO powder mixed with glass beads. Due to the hydrophobic nature of nano-ZnO it is recommended that all test equipment should be made of

glass or possibly Teflon, even though not all test experiments showed a loss of nanoparticles during testing. Special attention should also be given to the separation of eluates from the waste water solutions.

Based on the results from the leaching test studies it can be concluded that nanoparticle release is strongly influenced by solution pH. Furthermore, the leaching test results indicated that increased salt concentration of the leachate resulted in decreased nanoparticle release (Figure 4). An interesting observation was that the release of nano-ZnO was lower than micro-ZnO in demineralized water and higher in tests with addition of dissolved organic carbon (DOC).

The strong influence of salt concentration on agglomeration indicates that in landfill conditions nanoparticle release might be lower compared to the laboratory tests with demineralized water. However, the leaching tests do not provide any indication of long-term behaviour of the formed agglomerates.

Future challenges

As the production of nanoproducts continues to increase, more and more nanowaste will enter our waste management systems. Where re-use and material recycling are not viable, the other nanowaste treatment options of organic recycling and incineration for energy recovery must be used, with landfill reserved as an option. The potential risks related to nanoproducts are greatly influenced by the type of nanoproduct and by the environmental conditions at the end of the product life cycle. The challenges related to the treatment of nanoproducts in aquatic environments (e.g. waste water treatment plants) are considerably different compared, for example, to composting.

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Water



From low-fouling
membranes ...





Low-fouling membranes for water treatment



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During the 20th century the world's population has tripled, and it is estimated to further increase by 40–50% within the next fifty years. This population growth together with booming industrialization, particularly in the developing countries, is leading to ever-increasing demand for water.

Membrane filtration is used in the water industry to provide purified water by means of ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) processes. These methods have been applied in water and wastewater treatment, desalination and water reuse since the late 1960s [1]. However, use of these techniques in industrial processes is limited by one common challenge – fouling.

To solve the critical challenge of membrane fouling, VTT is actively applying its strong know-how in material science, surface engineering and separation technology to develop low-fouling membranes for water treatment. This work is expected to generate new markets for membrane filtration water purification methods. **The new anti-fouling membranes are expected to increase membrane service life and thus decrease maintenance costs.** VTT's experimental membranes have already shown superior performance compared to commercial uncoated or coated anti-fouling membranes, and these advanced membranes are also expected to decrease the use of biocides such as chlorine, thus reducing environmental burden and process costs.

Acknowledgements

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Membrane filtration technology is key

Membrane filtration is a key water treatment method used in advanced UF, MF, NF and RO processes for the production of drinking water and in industrial processes. Various polymeric materials are used as membranes. In particular, the membranes used in UF and

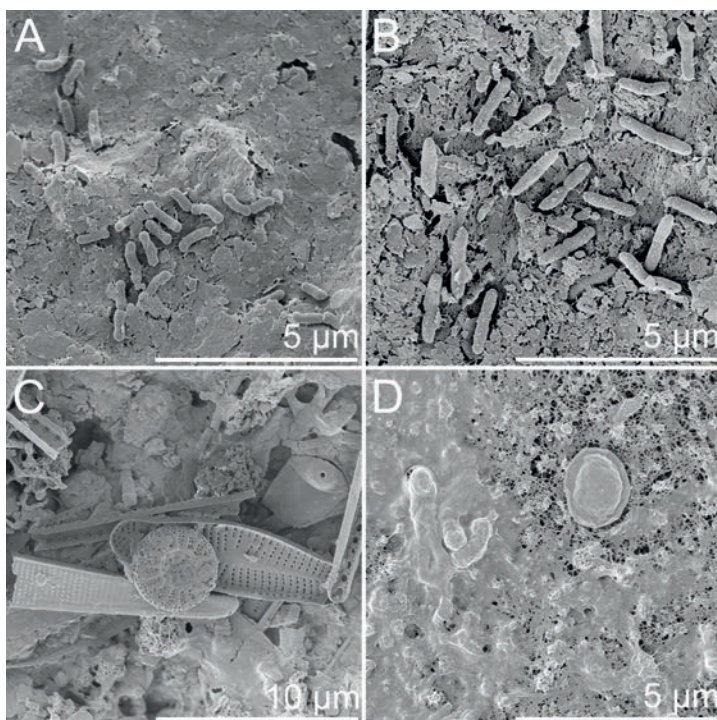


Figure 1. SEM micrographs showing biofouling layer on RO membranes. Panel A shows fouling layer consisting of inorganic scaling and bacterial cells. Extracellular substances *i.e.s* Slime produced by bacteria is forming a net-like structure on a membrane surface in Panel B, whereas panel C reveals a fouling layer consisting of inorganic substances and of diatoms. Panel D shows that slime produced by bacteria is covering large areas of a membrane surface. Images by Mari Raulio, VTT.

MF processes are typically based on nano- or microporous polymeric films that reject particles and pollutants with a size range 0.01–10 μm . For example, polypropylene (PP) and polyvinylidene fluoride (PVDF) are used as UF and MF membranes due to their mechanical and chemical resistance as well as low-fouling properties [2]. In contrast, RO and NF membranes are non-porous systems that retain particles less than 10nm in size and low molar mass species such as salt ions, micropollutants, pesticides, pharmaceuticals and organics. Traditional RO and NF membranes were based on cellulose acetate (CA). Currently, CA membrane has been replaced by thin-film composite (TFC) membrane, which

consists of polyamide (PA) as a selective layer and polysulfone as a support layer [2]. Fouling has nevertheless remained a universal problem for both CA and TFC PA membranes, especially in seawater desalination and wastewater treatment. VTT is actively developing solutions to the membrane fouling problem in these key areas by developing new UF, MF and RO membrane materials and surface modifications with improved anti-fouling performance.

Fouling – the major challenge in industrial processes

Fouling is the single most limiting factor restricting efficient use of membrane tech-

Development of anti-fouling RO membranes

Polyamide thin-film composite membranes (TFC PA), first introduced in the late 1970s, offer several advantages over traditional cellulose acetate (CA) membranes. These include improved rejection of dissolved solids and organics, increased productivity at lower operating pressures, and high structural stability, enabling them to produce two to three times more purified water per unit area than CA membranes [7].

Membrane surface properties have recently been shown to play a key role in controlling biofilm formation, and the development of anti-fouling RO membranes has gained increasing attention [8]. Several studies on the effects of membrane surface properties on long-term fouling tendency have shown that membrane surface properties such as hydrophobicity, surface roughness and surface charge play a key role in reducing fouling [9,10].

Anti-fouling membranes can be achieved through a combination of surface physicochemical properties, such as increased hydrophilicity, lowered surface roughness and neutralized surface charge [11]. For example, some commercial thin-film composite (TFC) polyamide (PA) membranes are coated with an additional thin PVA layer to introduce a hydrophilic and smooth surface [12]. These physicochemical anti-fouling properties are commonly referred to as anti-adhesion surfaces.

In addition, antimicrobial surfaces have been presented as an active anti-fouling approach. Lab-scale development routes for active anti-fouling membranes include new polymer blends, nanoparticle incorporation, surface coating by chemical or physical methods and incorporation of antimicrobial agents [11]. Optimal surface properties have, however, remained undetermined. Further research is therefore needed to identify the connection between membrane surface properties and the accumulation of biofilm.

nology. Membrane fouling can be divided into colloidal, scaling, organic and biofouling. In particular, biofouling of RO membranes remains a critical challenge in industrial water treatment applications. Figure 1 presents scanning electron microscope (SEM) images, describing the biofouled RO membrane with severe attachment of microorganisms on the membrane surface.

Biofouling is initiated by the adhesion and accumulation of planktonic microorganisms followed by their primary colonization and growth [3]. A number of microorganisms have been detected in RO and NF trains, including bacteria, fungi and yeast,

within the network of extracellular polymer substances (EPS). **The attachment of microorganisms together with their EPSs decreases membrane permeability and therefore increases the energy consumption of RO processes [4].** Biofouling can be affected by various factors, including feed water characteristics, hydrodynamic conditions, and membrane surface properties. Feed water can be pre-treated by disinfection, coagulation, filtration and/or adsorption to remove or inactivate microorganisms and to reduce organic and nutrient loading [4,5]. In addition, operating at moderate flux level seems to be effective in preventing severe

biofouling at the initial fouling stage [6]. However, controlling the growth and colonization of micro-organisms on membranes after initial attachment has remained an unsolved issue [5].

Development of anti-fouling membranes at VTT

Membrane research at VTT focuses on preventing membrane surface fouling by combining understanding of materials science, surface chemistry and processing. A current study¹ aims to develop, compare and test different surface treatment methods and modifications for typical membrane materials used in the RO process and to improve understanding of the relationship between the membrane surface and fouling.

The technological approach in the study includes surface modification of TFC PA membrane using thin coating technologies such as atomic layer deposition (ALD) and polymeric coating based on polyvinyl alcohol (PVA). The applied coatings aim to increase hydrophilicity and to decrease surface roughness.

Comparison of commercial and VTT experimental membranes

In the study, VTT has developed new inorganic and organic surface modification methods based on Al_2O_3 ALD technology and PVA polymer coating. TFC-PA membrane was used as the substrate for surface modification. In addition, two commercial brackish water treatment membranes, a low-energy membrane (LE-TFC-PA) and an anti-fouling membrane (BW30-TFC-PA), were used as references.

Various surface analysis methods and separation performance tests were performed to detect the properties of commercial and experimental membranes. Water contact angle (WCA) measurements were used to determine surface hydrophobicity, atomic force microscopy (AFM) was used to characterize surface roughness (root-mean-square (R_{RMS}) roughness), and water flux and NaCl rejection were used to describe the RO performance of the membranes.

Table 1 summarizes the surface properties and RO performance of the commercial and experimental membranes. Of the studied membranes, the coated membrane revealed

Table 1. Surface properties and RO performance of the commercial and experimental membranes. The results are summarized from Nikkola et al. [14,15].

Membrane	Coating	Provider	WCA ^a (°)	R_{RMS} ^b (nm)	Water flux (LMH/Bar) ^c	NaCl rejection (%) ^c
LE-TFC	uncoated	Commercial	53 ± 9	72 ± 7	4.3 ± 0.5	97.2 ± 1.2
BW30-TFC	PVA	Commercial	43 ± 4	56 ± 5	0.9 ± 0.07	99.4 ± 0.9
PVA-TFC	PVA	Experimental (VTT)	24 ± 2	43 ± 6	3.7 ± 0.3	98.5 ± 3.1
ALD-TFC	ALD	Experimental (VTT)	35 ± 11	56 ± 4	4.5 ± 0.4	89.7 ± 4.6

^aWater contact angle (WCA) determines the surface hydrophilicity;

^bRoot-mean-square (R_{RMS}) roughness describes the surface roughness ; ^cWater flux and NaCl rejection describe the ability of the membranes to pass water through the membrane while rejecting salt. These were evaluated using 10 mM sodium chloride (NaCl) feed solution and an applied pressure of 27.6 bar (400 psi) at 23 °C.

¹ FRONTWATER project Frontline Membrane, reuse and desalination technologies for sustainable water management, funded by Tekes and VTT.

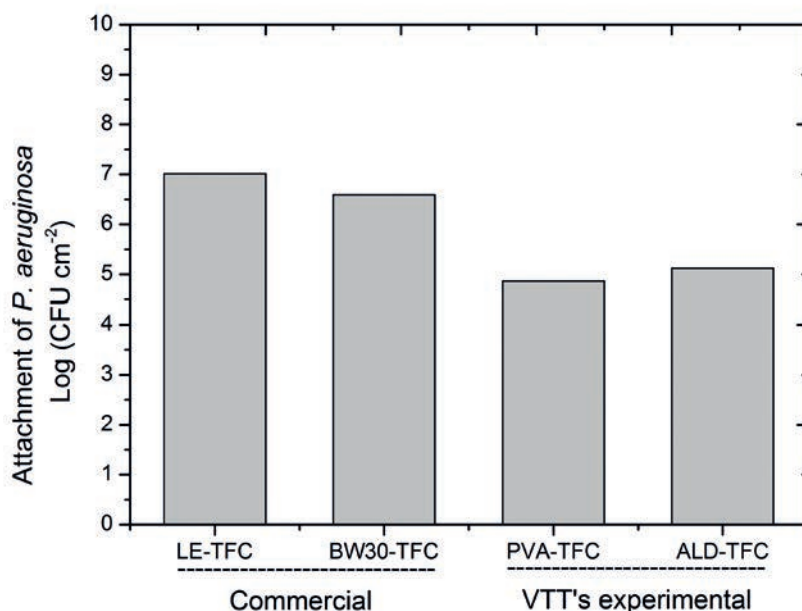


Figure 2. Attachment of *P. aeruginosa* on commercial and experimental membranes. VTT's experimental membranes attracted the lowest number of bacteria. The results are summarized from Nikkola et al. [13,14].

lower water contact angle and R_{RMS} roughness value. VTT's experimental coatings PVA-TFC and ALD-TFC showed the highest hydrophilicity and the lowest surface roughness. The VTT's experimental coatings were shown to enhance anti-fouling performance through physiochemical anti-adhesion.

Water flux and NaCl rejection describe the RO performance of a membrane. Coating layers, as a post-treatment of membrane, generally increase the hydraulic resistance of membranes, thus decreasing water flux and increasing solute retention. A decrease in water flux would decrease the efficiency of the RO process. The RO test results show that the RO performance was affected by the additional coating layers. Moreover, **the results show that VTT's experimental membranes PVA-TFC and ALD-TFC achieved relatively good water flux compared to the currently commercially available BW30-TFC reference product.** Of the coated membranes,

VTT's experimental coatings reduced water flux by 0–13% compared to uncoated LE-TFC membrane. Furthermore, the commercial BW30-TFC membrane decreased water flux by 80%.

Membrane biofouling tendency

In the study biofilm formation was demonstrated by analysing the attachment of *Pseudomonas aeruginosa* (*P. aeruginosa*) bacteria on membranes. *P. aeruginosa* is a Gram-negative bacterium widely used as a model microbe for biofilm formation studies. A bacteria attachment test was conducted by submerging the membranes in bacterial suspension for 24 hours and determining the number of adhered cells on the membranes. The results are presented as colony-forming units per membrane area (CFU cm⁻²).

Figure 2 presents the attachment of viable *P. aeruginosa* cells on commercial and VTT experimental membrane surfaces

after 24-hour exposure. Attachment of *P. aeruginosa* differed significantly between the uncoated and coated membranes. **Lowest bacterial attachment was achieved with VTT's experimental PVA-TFC and ALD-TFC membranes.** The attachment test revealed that bacterial adherence decreased with increased hydrophilicity. Furthermore, decreased surface roughness contributed to bacterial repellence.

Functional surfaces to control biofouling of RO membranes

As described above, very promising results have been achieved. ALD thin films and polymeric PVA coating have been successfully applied on uncoated RO membrane resulting in improved anti-fouling properties. In addition, VTT's experimental membranes showed better bacterial repellence compared to commercial anti-fouling membranes. It was shown that the biofouling tendency of RO membranes can be affected by decreasing surface hydrophobicity and lowering surface roughness. Moreover, VTT's experimental membranes showed better RO performance in comparison to the commercial uncoated and anti-fouling membranes.

The new anti-fouling membranes are expected to increase the service life of membranes and thus decrease maintenance costs. Moreover, the advanced membranes would decrease the use of biocides (e.g. chlorine), which is expected to decrease environmental load and process costs.

Our further investigations aim to demonstrate the membrane anti-fouling performance and its durability in long-term RO trials. Furthermore, we will investigate the up-scaling and implementation of the coating processes for industrial-scale membrane production.

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Water



... to removing arsenic
using by-product material
as a sorbent ...





Arsenic removal from mine waters using sorption techniques



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Finland is experiencing a mining boom and new methods and approaches need to be developed to reach environmental standards and sustainable production. **Mine waste water is often characterized by high mineral content (Mg, Ca, Sulphate), low organic content, potential toxic substances, varying composition and pH, and, especially in arctic regions, varying and low temperature.** These characteristics pose key challenges for the use of traditional waste water treatment methods such as biological processes, wetland treatment or membrane technologies.

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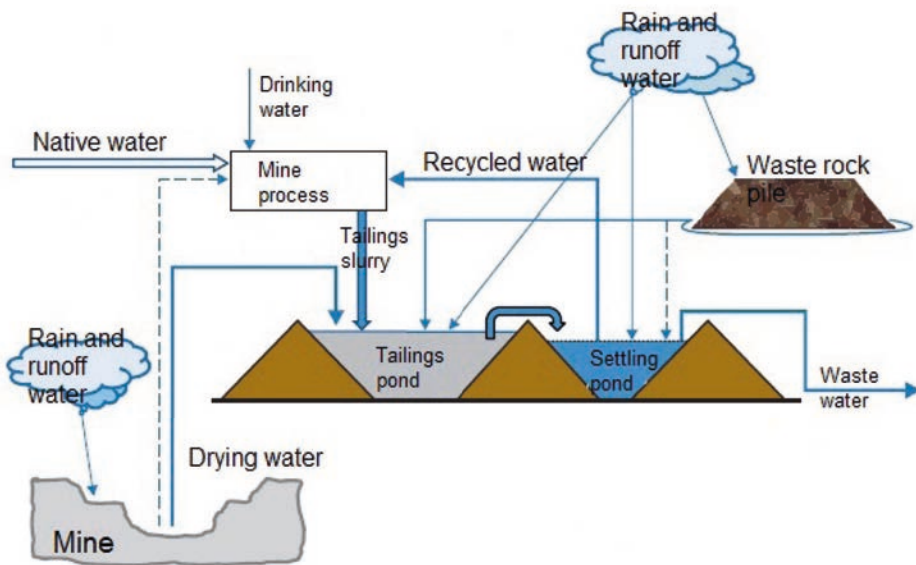


Figure 1. Typical water flows in a mine [1].

Arsenic exposure is a major concern with respect to drinking water in many parts of the world, and is a key problem with respect to effluents from the mining industry. An illustration of a typical mine water scheme is shown in Figure 1. Arsenic, commonly associated with metal ores such as gold, copper or lead, is often solubilized in the mining process, thus creating the need to treat mine effluents for its removal.

The treatment of arsenic-containing waters by precipitation with ferric or aluminium salts is a well-established and widely applied method. In the research¹ conducted at VTT, the main focus was on the treatment of trace arsenic concentrations in mine waters, where sorption techniques may offer a viable alternative to the conventional precipitation-clarification process. Sorption techniques can be applied, for example, by means of reactive barriers, where water flows through a bed of sorption material and the contaminant to be removed attaches to the sorption material by physical or chemical processes. No actual treatment process is required, which may favour the use of sorption as a final treatment

step for mine water before discharge to the environment.

The volumes of water treated in mining are often vast. This creates a need to find cost-effective sorption materials for the treatment of arsenic-containing waste waters. Previously, industrial side stream materials have been shown to have potential for arsenic removal [2, 3]. In the present research these materials are further examined based on their properties and applicability to the treatment of mine waters for arsenic removal. **The capacities of by-product materials to remove arsenic are compared to a commercial sorption material with good known arsenic sorption capacity.** The following step-wise approach was applied in identifying and analysing suitable sorption materials:

- Screening of industrial by-products and waste materials with previously reported ability to remove arsenic from water
- Kinetic testing of most promising materials in order to scale simulation tests
- Simulation of end-use application with the most promising materials

Table 1. Sorption materials included in the study.

Material	Origin	Remarks
Granulated steel slag	By-product of steel making	Original particle size 0-32 mm. Sieved and crushed to particle size of 1-2 mm
Cast iron chips	By-product from dressing of iron products	Original particle size of chip approximately 0.5x20 mm. Crushed to particle size of 1-2 mm.
Granulated ferric oxo-hydroxide (CFH 12)	Commercial iron-based sorption material	Particle size 1-2 mm
Ash pellet	Pellet made from ash of unknown origin	Cylindrical pellets with diameter of approx. 5 mm and height of 10 mm
Waste rock	Waste rock from a gold mine	Crushed to particle size of 1-2 mm.

¹ VTT has been a partner in jointly funded research project called ARSENAL Arsenic Control in Mining Processes and Extractive Industry.

Table 2. Maximum arsenic sorption capacities of the studied materials.

Material	Maximum As sorption capacity, mg As/g
Waste rock	0,02
Granulated steel slag	2,3
Ash pellet	7,9
Granulated ferric oxo-hydroxide (CFH 12)	14
Cast iron chip	46

Screening for potential sorption materials

In the first-stage sorption tests, four industrial by-product or waste materials were examined for their maximum arsenic sorption potential. A commercial sorption material developed for arsenic removal from drinking water was used as a reference material (granulated ferric oxo-hydroxide CFH12). (See Table 1.)

The first-stage sorption tests were performed as batch tests in which varying amounts of sorption material were mixed with

arsenic-containing water for 24 hours, after which the eluate was filtered and analysed for arsenic concentration. The amount of sorption material in the mixture varied between 1 and 200 g/l. As a result, the maximum capacity of a material to remove arsenic from solution was obtained as mg arsenic per gram of sorption material. Table 2 summarizes the core results from these first-stage tests.

Surprisingly, the cast iron chip by-product showed high arsenic removal capacity, even in comparison to the commercial adsorption

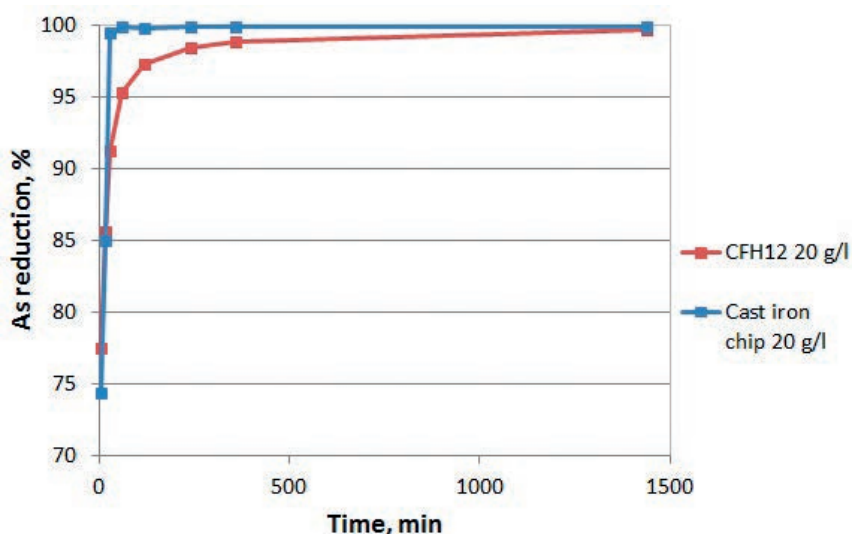


Figure 2. Arsenic removal kinetics with granulated ferric oxo-hydroxide and cast iron chips.

material CFH12. Based on the results from the first-stage sorption studies, these two materials were selected for further arsenic removal studies.

Testing the most promising materials

In the next phase, the two selected materials were further analysed for arsenic (As) removal kinetics with real mine water. The tests were conducted as 24 h batch tests with varying sorption material concentrations. The test water contained mine-sourced As (V) (0.8 mg/l) spiked with standard As (V) solution to reach an As concentration of approx. 1.5 mg/l. The test water had a pH of 8.1, Ca concentration of 550 mg/l and sulphate concentration of 5 000 mg/l.

Intermediate samples were taken during the tests to assess the reaction kinetics. An example of the test results is shown in Figure 2.

Cast iron chip removed almost all of the arsenic (99%) from the mine water in 30 minutes. The reaction kinetics of the commercial adsorption material, CFH12, were slightly slower.

Based on the findings from kinetic testing, in the next, still on-going phase, column tests simulating the end-use application were scaled to achieve a retention time of one hour (Figure 3). Water with similar characteristics to the previous stage is used in the column tests and, for comparison, laboratory deionized water spiked with similar arsenic concentration is used in parallel column tests for both materials.

Discussion

The column testing phase is currently on-going. The results from column testing will provide an estimate of the sorption material behaviour in close to real conditions with respect to arsenic removal efficiency and capacity. Also of interest are observations relating to technical behaviour (e.g. evolution of water permeability and pressure increase)



Figure 3. Column testing of sorption materials for the removal of arsenic from mine water.

of, in particular, the by-product material in the water treatment application, of which no previous experiences exist.

The research has also included experiments using conventional precipitation techniques to remove arsenic from the same water. This enables comparisons regarding, e.g., the efficiencies and economics of different arsenic removal techniques for mine waters.

Promising results have been obtained with the cast iron chip industrial by-product in the removal of arsenic from mine water. The on-going studies and comparison with other available water treatment techniques will help further evaluate the applicability of the chosen method and materials in the treatment of arsenic-bearing mine waters. Tightening environmental regulations may in the near future force mining companies to start treating mine effluents for the removal of

arsenic. For at least trace level arsenic concentrations, sorption techniques may offer an attractive alternative to chemical precipitation. **However, special attention should be paid to substances possibly leaching from the material itself, especially when dealing with waste- and by-product sorption materials.**

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Water



... to exploiting fungal
films to clean up mine
waters ...





Living fungal films clean up mine waters



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In the search for more efficient water treatment technologies, inspiration can be drawn from natural systems that depend on water. All organisms need water for life-giving chemical reactions to take place, and water is, consequently, a vital constituent of all living things. Biological systems interact with water with extraordinary levels of control at both the molecular and macroscopic level – as demonstrated by water filtration through the cell membrane, kidney function, and filter-feeding animals such as bivalves and blue whales. Biosorption is one such process in which contaminants are passively bound to biomass [1]. Fungi, in particular, are highly attractive as potential biosorbents due to their ability to effectively bind metallic ions [2].

The work presented in this article is an initial investigation into how the control of biomass structure and cell communities can influence the biosorption properties and feasibility of biological materials as biosorbents. The results show that the heavy metal concentration of treated mine process water were significantly reduced by filtration through fungal films. This demonstrates that fungal films can be used as a highly effective setup for heavy metal sorption. Furthermore, the disc-shaped films developed can be easily handled, thus contributing to their feasibility as biofilters. The possibility for recovery of metals from the films is a key area of interest and will be addressed in future research. The interdisciplinary project¹ combined the efforts of experts in biotechnology and environmental engineering.

The aim of the study was to determine whether controlling the structure of a cellular community can lead to more feasible biosorption processes. Inspired by filter-feeders, which obtain nutrients by processing large amounts of water, we devised fungal films that readily allow water to pass through them and, in the process, adsorb pollutants (Figure 1). Mine process water samples were chosen as model systems due to their high metal ion concentrations. **The results show that the fungal films were able to remove more than 90% of most metallic species from the water samples.**

Fungal films grown as entangled filamentous networks

Fungal mycelia consist of a network of entangled thin filaments. We took advantage of this network structure to produce films grown with or without solid scaffold (Figure 1). The fungi were grown on nutrient media resulting in a cohesive film less than a millimetre in thickness. The strength of the films varied according to the fungal species used, probably reflecting the mycelial structure and amount of bound water. All of the films could be easily moved and manipulated when grown on various sieve-like solid scaffolds.

We then conducted simple tests to measure the water flux through the films. Water flowed through the films easily by gravity at a rate of around 50 ml per minute. Applying vacuum suction on the filtrate side significantly increased the flow speed.

¹ BioMimWater project funded by VTT.

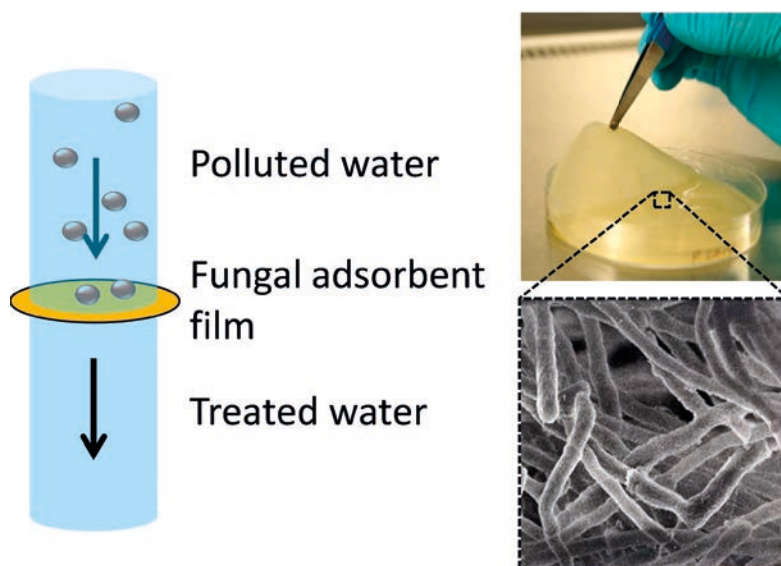


Figure 1. A thin mat of fungal biomass can effectively bind heavy metals from process waters (left). The mats are bare fungal films or films grown on a solid scaffold (right). A scanning electron microscope image of the fungal material shows a network of mycelial filaments (bottom right, image courtesy of I. Salovuori, VTT).

Biosorption using fungal films is fast and effective

Biosorption tests were carried out using defined metal solutions and the treated water samples after biosorption were analysed by inductively coupled plasma optical emission spectrometry. In comparison with fungal biomass grown in shake flasks, the fungal films performed faster in the biosorption process (Figure 2, left). This is likely due to the entangled mycelial network and higher available surface area of the fungal mats. The fast sorption process is beneficial in water treatment processes where water flux can be high.

Metal binding ability of the fungal films under equilibrium conditions is unlikely to be significantly different to conventional fungal biomass biosorbents because the material is essentially the same. In our studies we achieved at least 0.1 mmol per gram of biomass for e.g. Cd and Pb at up to 40 mg/L feed concentrations (Figure 2, right). How-

ever, the data shown in Figure 2 suggests that the maximum binding capacity could not be reached with the concentrations used.

Next, the fungal films were tested in a filtration setup with acidic mine process water samples. The concentrations of metal species in the samples ranged up to 1 g/L. In each test a fungal film with a typical dry weight between 50–80 mg was used as an adsorbent filter sheet. After passing the sample through the film the treated water was analysed. The metal concentration in the filtrate was dramatically reduced and most metals were removed by at least 90% (Figure 3). For example, Cd concentration was reduced from 0.3 mg/L to 0.03 mg/L. Removal of negative ions was more selective. Sulfates were removed by more than 90%, while phosphate by only 36%.

Discussion

Materials made of living cells are drawing increasing attention as complex, self-healing,

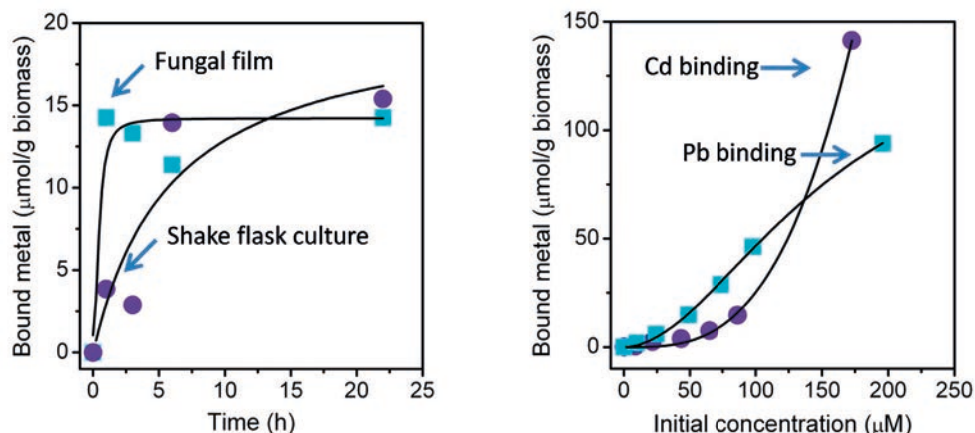


Figure 2. Biosorption of heavy metals using fungal mats is fast and effective. Comparison of biosorption kinetics between the fungal films and shake-flask grown control samples shows that the fungal films bind metals faster (left). The metal binding curves of the fungal films show that using a higher concentration of metal increases the amount of bound metal and that maximum binding capacity was not reached with the metal concentrations tested (up to 40 mg/L Pb^{2+}) (right).

and adaptive systems [3]. Similar attributes can be envisioned for the presented fungal films, such as the ability to self-heal upon crack formation. In the future we will explore how combining the control of cell community structure with genetic engineering tools can enable innovative biomimetic solutions in environmental technology.

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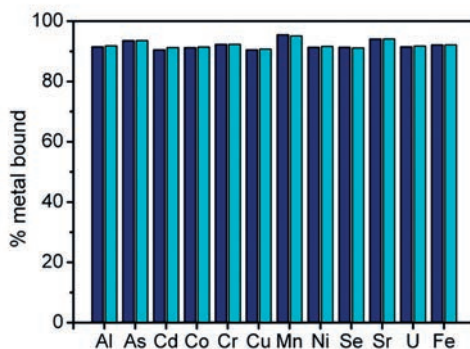


Figure 3. The fungal films bound metal ions remarkably well in the filtration setup. More than 90% of all tested metals were bound from the real mine process water samples. The analysis results for selected metals are shown in the graph.

Water



... and collecting water
from air humidity in arid
areas.





Water from the air



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Water scarcity – a giant obstacle to improving living conditions in developing countries

Availability of water is one of the most severe developmental challenges of the world. Water scarcity affects every continent and more than 40% of people on the planet. By 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world's population could be living under water stressed conditions [1]. Most countries in the near East and North Africa suffer from acute water scarcity, along with countries such as Mexico, Pakistan, South Africa, and large parts of China and India. To keep pace with the growing demand for food, it is esti-

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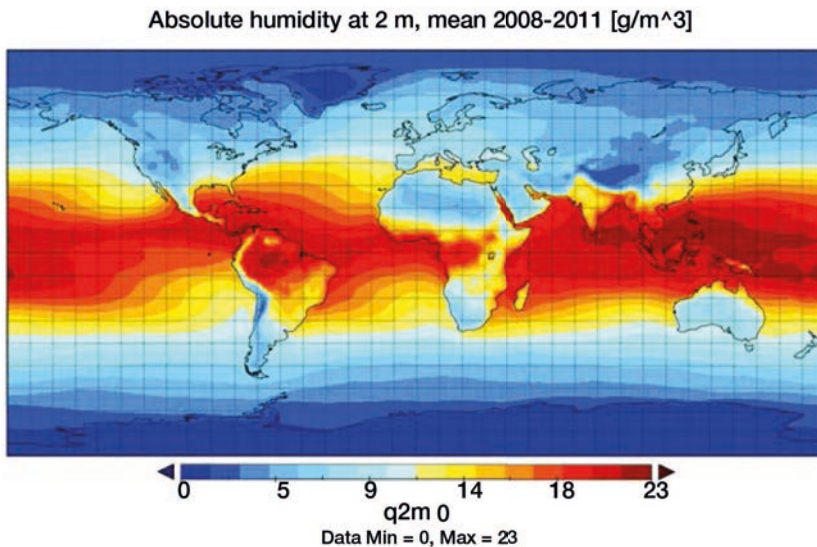


Figure 1. Absolute mean air humidity (H. Vuollekoski, UHEL-Atm, 2013).

¹ Development of cost-efficient dew and fog collectors for water management in semiarid and arid regions of developing countries (DF-Trap). The four-year project is funded by the Development research of Academy of Finland.



Dew forms as water droplets on exposed surfaces, such as blades of grass, especially during early morning hours (Figure 2). As the exposed surfaces cool by radiating their heat, moisture in the surrounding air condenses on them, resulting in the formation of dew droplets. Fog is essentially a cloud of moisture lying or moving close to the ground. Fog occurs when the temperature of humid air approaches the dew point, causing the nucleation of water molecules and resulting in the formation of suspended water droplets. Dew can be collected by large, near-horizontal plates, while fog harvesting is carried out using large vertical screens.

Figure 2. Dewfall in an arid environment.

mated that 14% more freshwater will need to be withdrawn for agricultural purposes in the next 30 years [2]. Facilitating availability to clean water for agricultural and domestic use will vastly improve quality of life in developing countries susceptible to water shortage and drought.

VTT is currently developing novel solutions to combat water scarcity in developing countries. Targeted research in this area is being carried out in cooperation¹ with the University of Helsinki (Departments of Physics and Agricultural Sciences). The goal of the project is to provide practical solutions to water shortages in arid and semiarid areas by developing simple low-cost, easy-to-use and environmentally safe materials and devices for air-water harvesting. This article presents the key elements needed to produce fresh water from the air.

Air humidity as a potential fresh water resource

Many of the world's semi-arid and arid regions with scarce rainfall have large amounts of potentially exploitable water in

the air (Figure 1). It has been proposed that production of fresh water using air humidity collectors could be a viable option for the acquisition of good quality water [3, 4, 5]. Availability of low-cost, efficient and environmentally safe fog and dew collectors would benefit communities, agriculture and reforestation in large areas of the world where lack of access to clean water is a critical concern. Conditions especially favourable to fog and dew collection can be found in the semi-arid and arid coastal regions and mountain ranges of Africa, South-America and Asia [6].

Fundamental understanding of the structural and environmental factors affecting the performance of air humidity collectors is currently being developed. This knowledge will be used for the **design and preparation of a pilot dew and fog collector setup** that will be optimized in the laboratory with respect to the collector material, physical construction and cost-effective large-scale production. (See Figure 3.)

VTT's input in the cooperation is the manufacture of experimental dew and fog

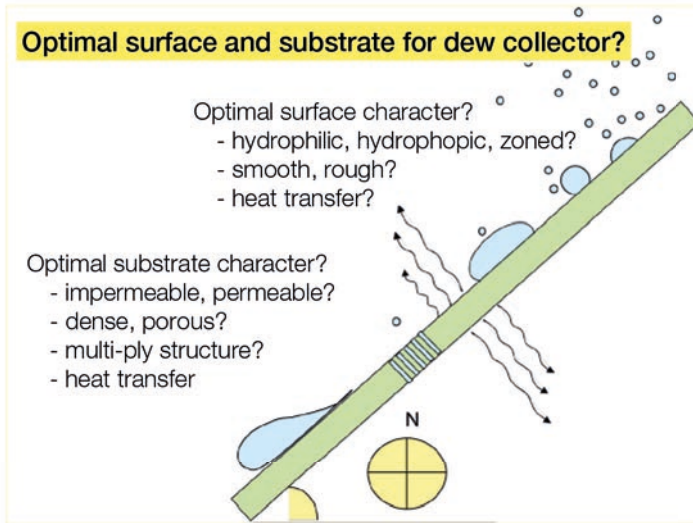


Figure 3. Air moisture collectors need to be effective, low-cost and maintenance-free. Potential production materials include specialty papers and plastics.

collectors. In order to be feasible in developing countries, the collectors must be effective, easy to use, low-cost and environmentally safe. The University of Helsinki will field test the experimental dew and fog collectors in arid or semi-arid environments in developing countries having favourable conditions for fog and dew collection and for testing of the experimental devices. In the testing, the participating parties' previous contacts with local governance in East Africa (Kenya, Ethiopia), Southern Africa (Namibia, South-Africa) and Asia (Nepal, Mongolia) will be utilized.

The basic research questions are:

- What are the governing material properties that enable optimized collection of dew and fog from ambient air?
- What is the global geographical distribution of atmospheric water that can be collected using fog and dew collectors?
- How can improved dew and fog collection infrastructures be sustainably implemented in developing countries?

Understanding the structural and environmental factors affecting the performance of air humidity collection is key to developing low-cost, effective and environmentally safe collectors. The operation of dew and fog collectors is based on the condensation of water vapour on solid surfaces, from which the liquid water is led to reservoirs for collection or direct to the roots of plants for irrigation.

Experimental fog collectors presented in literature, such as the DropNet [7], consist primarily of large vertical plastic screens that allow moving air to pass through them. Typical dew collectors consist of large plastic films placed near-horizontally close to the ground [8]. Smaller plastic plates can be placed directly above the roots of cultivated plants and saplings to collect precipitated dew for irrigation. Such dew collectors also perform a similar function to mulch in preventing weed growth and the evaporation of moisture from the soil.

The fog and dew collectors presented above are, however, costly in relation to achieved water yields. In order to be feasible

Plastic mulch films (see Figure 4) are used in agriculture for weed suppression, to control soil temperature and moisture, and to prevent rain and wind erosion. Globally, more than 80,000 km² of cultivated land was covered by plastic mulch films in 2012. The added ability of mulch films to



collect air moisture would be of invaluable benefit in arid and semiarid areas. A key focus of the research presented here is the development of such second-generation mulches for agriculture. Potential production materials include plastic, bioplastic and paper.

Figure 4. Conventional plastic mulch films in Turkey (J. Ahokas, UHEL-Agr., 2012).

in developing countries the cost of the collectors must be brought down and water yields increased. In another research project² VTT together with the University of Helsinki are developing paper mulches for agriculture. This work is of great service to the development of low-cost dew-collecting mulches.

Low-cost high technology

Novel solutions for dew and fog harvesting are also being sought from natural systems such as the superhydrophobic microstructures on plant leaves or animal skin. In all cases, surface properties and heat transfer capability seem to be the dominant factors determining a material's ability to collect water from the air.

VTT is applying its world-class expertise in modern coating techniques to explore unique opportunities for tailoring the surface properties of collector materials, such as hydrophobicity, roughness and porosity, in cost-effective and optimal ways to meet the end-use requirements of collectors in challenging environmental conditions. Hot-embossing and 3D-printing are examples of special techniques that may be used for

functionalizing the surfaces of dew and fog collecting materials.

High potential low-cost, environmentally friendly structural materials for dew and fog collectors include paperboard, non-woven fabrics, biodegradable plastics and various composite materials. An essential part of the development process is the testing of dew and fog collectors and their materials in laboratory conditions prior to costly field trials. Ideally, test environments should be capable of accurately simulating actual end-use conditions with respect to humidity, temperature, wind, and heat radiation.

VTT, in cooperation with the University of Helsinki, is currently examining suitable test environments in Finland and abroad. If viable, the project test environment will be built at VTT and made available to industrial partners for subsequent product development work.

In addition to extensive testing in laboratory and climate room environments, the developed air humidity collectors will be rigorously field tested in semiarid and arid regions. **The objective is to develop new fog and dew collectors that are simple and inexpensive to manufacture, thus enabling**

² Agripap, Tekes, 2010–2013.

them to be produced locally in the developing countries where they are needed.

VTT and research partners will cooperate closely with national and international scientific institutes in testing the collectors and controlling their functionality in areas where water scarcity is an acute problem and the climate is suitable for dew collection. Many such areas exist throughout Africa, Asia and South America. Besides water collecting ability, further research is also needed with respect to the installation, durability and mechanization of the collectors in normal use. Also of big importance is the analysis of the quality of the collected water and its suitability for irrigation or animal and human consumption.

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Title	Green solutions for water and waste — science brought into action
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Abstract	<p>The development of society towards sustainability has traditionally been driven by legislation. Today, systemic strategies for sustainable development in which environmental, social and economic dimensions are held in balance are being increasingly adopted.</p> <p>At the same time, the societal and economic importance of clean technologies is growing. Water- and mineral-intensive industries face increasing challenges in meeting their demand for mineral and water resources. More efficient methods of reuse and withdrawal need to be developed using cross-technological approaches. New opportunities within sustainable development are emerging as environmental issues gain a strategic role in business. We are in a transition from separate single-plant raw material and waste treatment solutions towards industrial symbiosis in which environmental impacts are minimized throughout the product life cycle.</p> <p>VTT's spearhead programme Green Solutions for Water and Waste (GWW, 2011–2013) targeted two important goals vital to tomorrow's society – efficient water treatment and waste management. This work is continued in VTT's follow-up programmes "Bioeconomy Transformation" and "Mineral Economy".</p> <p>The core technologies developed include energy-efficient membrane solutions for industrial water reuse, methods for the recovery of valuable compounds from waste and side streams, and novel water quality sensors. This edition of Research Highlights showcases the excellent advances VTT has made in these areas within the GWW programme.</p>
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