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Recovery of valuable raw materials and decontamination of highly complex waste products

Multi-purpose On-site Phase Separator

MUDP Report

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Contents

1.	Executive summary	5
1.1	Summary in English	5
1.2	Dansk resumé	6
2.	Background for the project	7
2.1	Scope and objectives	7
2.2	Selected test materials	7
2.2.1	Contaminated soil	7
2.2.2	Waste ashes	8
2.2.3	Industrial sludge	9
2.3	Previous experience	10
3.	Process description	11
3.1	Feeding system	11
3.2	Size separation	11
3.3	Attrition cell	12
3.4	MOPS reactor	12
3.5	Water treatment	12
4.	Reclamation of polluted soil	14
4.1	Plant configuration	14
4.1.1	Size separation	14
4.1.2	Extraction	14
4.1.3	Water treatment	15
4.2	Challenges	16
4.3	Results	16
4.3.1	Mercury	16
4.3.2	Pesticides	17
4.3.3	Water treatment	18
4.3.4	Implications of obtained results	19
5.	Extraction of metals from fly ash	20
5.1	Plant configuration	20
5.1.1	Extraction	21
5.1.2	Sludge handling	21
5.1.3	Metal recovery	21
5.2	Challenges	21
5.3	Results	21
5.3.1	Extraction	21
5.3.2	Metal recovery	22
5.3.3	Implications of obtained results	25
6.	Recovery of phosphorus from industrial sludge	26
6.1	Plant configuration	26
6.1.1	Extraction	26
6.1.2	Sludge handling	26

6.1.3	Phosphorus recovery	26
6.2	Challenges	26
6.3	Results	27
6.3.1	Extraction	27
6.3.2	Recovery	27
6.3.3	Implications of obtained results	29
7.	Future prospects and economics	30
7.1	Project's results	30
7.1.1	Follow-up on success criteria	31
7.1.2	Environmental impact	32
7.1.3	HSE experiences gained	32
7.2	Full-scale MOPS plant design for contaminated soil	33
7.2.1	Overview of streams leaving full scale plant	34
7.2.2	Indicative treatment prices	35
	References	36

1. Executive summary

1.1 Summary in English

This MUDP project have resulted in the development and successful demonstration of the MOPS-technology (Multi-purpose Onsite Phase Separator) through the construction and operation of a pilot plant, located at FMC Cheminova's Rønland Site. MOPS is a novel and competitive technology for removal of contaminants from contaminated soil and the potential for recovery of valuables from waste materials otherwise destined for landfill. This novelty is achieved through the combination of mechanical and chemical treatment, with unit operations, such as washing and filtering processes, selected and combined specifically towards these goals.

For soil remediation, the technology has reached sufficient maturity for full scale installation, thereby presenting a competitive and environmentally friendly alternative to high temperature incineration. For recovery of valuable salts and metals from other waste fractions, the technology shows promise, but will still need further development within Fortum Recycling and Waste's ash refinery program.

Three different materials were included in this study. The first material investigated consisted of highly contaminated soil from the generational pollution at Groyne 42, with the aim to reduce the concentrations of mercury and pesticides to levels consistent with the requirements for free or restricted use. The results from these tests show that the concentration of mercury could be decreased from 600-800 mg/kg dry mass (DM) to <1 mg/kg DM. Simultaneously, the concentrations of investigated pesticides were successfully decreased to near or below detection limit in the sand, thus making free or restricted utilization a distinct possibility. The released contaminants were successfully removed from the produced wastewater and accumulated in a sludge fraction, corresponding to <5% of the initial mass of the untreated sand. Treatment of the water fraction resulted in qualities consistent with requirements for re-use in the plant. For the most polluted fractions, two subsequent MOPS washing cycles, connected in series, were needed to reach these stringent requirements. This is one example of how this pilot project has helped to inform better decision making, and shape the suggested design for a full scale process.

The remaining two materials investigated using the pilot plant were ashes from high-temperature incineration of waste and sludge from the internal wastewater treatment at FMC Cheminova. For these fractions, otherwise destined for landfill, the aim was to recover and purify metals and phosphorus, respectively. The results from these tests indicate that the technology shows great promise in its ability to extract valuables from both of these materials. Removal rates for selected metals (Copper, Nickel and Zinc) ranged from 40-95% for the ashes, while 45% of the phosphorus was removed from the sludge. Lab-scale tests on the recovery potential from the produced leachates indicate that recovery rates in excess of 90% can be achieved in an optimized process for both phosphorus and selected metals.

1.2 Dansk resumé

Dette MUDP project har resulteret i udvikling og succesfuld demonstration af MOPS teknologien gennem konstruktion og drift af et pilotanlæg opført hos FMC Cheminovas Rønland lokation. MOPS er et engelsk akronym, der står for Multi-purpose Onsite Phase Separator, og kan løseligt oversættes til "Fler-formåls, På-stedet Fase-Separator". MOPS er en nyskabende og konkurrencedygtig teknologi til fjernelse af kontamineringer fra forurenet jord, og har også potentialet for at genvinde værdifulde materialer fra affaldsfraktioner, der ellers ville ende på deponi. Nyhedsværdien ved MOPS opnås gennem en kombination af mekanisk og kemisk behandling, med enhedsoperationer som eksempelvis vaske- og filtreringsprocesser, udvalgt og kombineret specifikt for at opnå disse oprensingsmål.

Til jordoprensning har teknologien opnået så meget modenhed at den nu er klar til anvendelse inden for større oprensingsprojekter, hvor den kan udgøre et konkurrencedygtigt og miljøvenligt alternativ til høj-temperatur forbrændingen. Til genvinding af værdifulde salte og metaller fra andre affaldsfraktioner har teknologien vist sig lovende, men der er stadig behov for yderligere udvikling inden for Fortum Recycling and Wastes aske-raffineringsprogram.

Dette projekt omfatter tre forskellige materialer. Det første undersøgte materiale var stærkt forurenet jord fra generationsforureningen på Høfde 42. Formålet med behandlingen her var at reducere indholdet af kviksølv og pesticider til niveauer, der ville tillade fri eller begrænset anvendelse/nyttiggørelse af sandet. Resultaterne fra disse tests viser at koncentrationen af kviksølv kunne reduceres fra 600-800 mg/kg tørstof (TS) til <1 mg/kg TS. Samtidigt lykkedes det at reducere koncentrationen af de undersøgte pesticider til tæt på eller under detektionsgrænsen, hvilket muliggør fri eller begrænset nyttiggørelse af sandet. De frigivne forureningsstoffer blev med succes fjernet fra det producerede spildevand, og overført til en slamfraktion, der mængdemæssigt svarer til under 5% af den oprindelige mængde sand. Behandling af spildevandet resulterede i en kvalitet, der muliggør genanvendelse af vandet i oprensningsprocessen. Når det kom til de mest forurenede fraktioner, viste det sig nødvendigt at benytte to MOPS vaske-processer i serie for at kunne imødekomme de opsatte krav. Dette er et eksempel på hvorledes læring fra dette pilotprojekt har bidraget til bedre beslutningstagen, og været med til at forme det foreslåede design til en fuldskala proces.

De resterende to andre materialer, der er blevet undersøgt ved brug af pilotanlægget er aske fra højtemperaturforbrænding af affald, og slam fra FMC Cheminovas interne spildevandsanlæg. For disse fraktioner, som ellers i dag blot deponeres, var formålet at udvinde og efterfølgende oprense hhv. metaller og fosfor. Resultater fra denne serie af tests viser gode indikationer af at den benyttede teknologi kan benyttes til at trække værdifulde materialer ud af disse fraktioner. Fjernelses-rater for de udvalgte metaller (kobber, nikkel, zink) lå på mellem 40-95% for asken, mens op mod 45% af fosfor-mængden kunne fjernes fra slammet. For at afdække i hvilken grad de opløste værdestoffer kunne oparbejdes, udførtes efterfølgende laboratorietests. Disse viste en udfældningsgrad på over 90% for både de udvalgte metaller, samt for fosfor.

2. Background for the project

2.1 Scope and objectives

Contaminated soils and other hazardous waste materials contain large amounts of valuable resources that can replace virgin minerals and salts. Recirculation of such materials will offer a significant contribution to the aspiration towards a society with reduced resource consumption. The main challenge is to find technologies that offer an efficient decontamination, while being resource reasonable and safe, and allow for recirculation of any valuable materials.

The scope of this project is to demonstrate:

- Use of an innovative high pressure, phase extraction recovery technology called MOPS (Multi-purpose On-site Phase Separator) to remediate waste products of high complexity.
- Feasibility of selective harvesting of valuable materials from the resulting phases, and
- Possibility to establish this as an on-site solution

The high pressure, phase extraction recovery technology has already been tested in Fortum Recycling and Waste (FRW) for washing of ash, and the resulting brines has been used for de-icing purposes. Therefore, a potential solution to concurrent remediation and circulation of more complex waste materials, such as contaminated soils and hazardous waste, would be an adjustment of the technology to fit these matrixes. Strong complexation of desired substances to solid phases will demand a solution harsh enough to release the component from the waste material, and flexible and easy adjustable for separation of resulting treated fractions. This need can be met by the high-pressure phase extraction technology. Furthermore, the concept of an on-site solution will minimize the use of long-distance transportations, which is often a major hurdle in larger remediation projects.

2.2 Selected test materials

2.2.1 Contaminated soil

The pollution at Groyne 42 is one of three generational pollutions at Harboøre Tange, which is currently managed by the Region Midtjylland. The pollution was generated throughout the 1950s and 1960s, when a depot for chemical waste was established. The depot was located on the beach at Groyne 42 with permission from the Danish state, which also used the repository for storage of pesticides from all over the country. Groyne 42 is, like other generational pollutions, a product of the knowledge and prioritization of the time, in relation to the handling of hazardous waste, and should thus not be viewed with modern eyes only.

Over time, various solutions for containing or cleaning up the depot have been tried and tested, but none have been sufficiently cost-effective. It is estimated that the depot today contains 100 tons of chemicals, which are divided between the following main components: 70 tons of parathion, 10 tons of malathion, 4 tons of methyl parathion, 6 tons of E-sulfotep, 7 tons of mercury (Rambøll, 2013). The complexity of the pollution makes soil from the depot a suitable testing material for FRW's soil reclamation technology. Based on soil analysis, no components of value for recirculation have been identified.

Under the supervision of Region Midtjylland, during the summer 2018 approximately 90 tons of highly polluted soil were excavated and transported to the newly constructed MOPS pilot plant, situated on FMC Cheminova's factory ground. A close-up photo of the polluted soil can be seen in FIGURE 3 on page 14.

2.2.1.1 Mercury contamination

The material from Groyne 42 is physically well-defined, mainly consisting of beach sand, with only traces of silt and clay fractions. The contamination, as previously described, consists of a mixture of mercury, large amount of pesticides, solvents and, to some extent, also elemental sulfur (Afgrænsning af nedvigningsområde ved Høfde 42, 2013). This complexity creates an environment within the depot which allows for several different species of mercury to co-exist. In addition, extensive periods of fluctuating sea level in the depot has over time created both aerobic and anaerobic conditions. Before encapsulation in 2005, the Groyne 42 depot had been exposed to free penetration of sea water for over 40 years. Any remaining contaminants in the depot would therefore be firmly attached to sand particles, possibly encapsulated in secondary precipitates, deeply embedded into sand grain cavities, or have strong hydrophobic properties.

With this knowledge, it is expected that the mercury in the sand is tightly bound to different types of active reduced sulfur group (thiols) as stable and insoluble substances. To confirm this hypothesis, FRW has performed sequential extraction tests. These tests showed that only a minor part of the mercury contamination could be transferred into liquid phase when the sand was exposed to water or weak acid, indicating that the mercury is not bioavailable. Exposure to strong oxidating conditions will under most conditions enable increased mobilization of mercury (Ramsey et al., 2014). In some samples a high proportion of the mercury became soluble in high pH (approx. 12). Metals mobilized at high pH are often associated with organic matter. In this case, the increased solubility of mercury at pH is most likely due to association to pesticides, which start to hydrolyze, thereby releasing the mercury. Mercury incorporated at secondary precipitates of iron- or aluminum oxide/hydroxides could also be liberated since high pH usually enhance solubilization of oxides/hydroxides.

2.2.1.2 Pesticide contamination

Besides mercury, the primary contaminations of Groyne 42 consist of organophosphorus pesticides (OPs); toxic chemicals that have been utilized as pesticides in agriculture since the 1950s. They are characterized by their high persistence and pervasiveness in the environment, and can, along with products of their biotransformation, interact with the environment and living organisms in multiple ways (Lushchak *et al.*, 2018).

Agrochemical companies have used alkaline hydrolysis for many years to neutralize and pre-treat streams containing organophosphate insecticides before biological treatment. (NorthPestClean, 2013). A pilot test study on in-situ treatment of OPs in the Groyne 42 depot has been performed by Region Midtjylland in Denmark, together with partners, from which the results came out very promising, although this process had limited effect on mercury contamination (NorthPestClean, 2013).

Along with mercury, concentrations of the organic pesticides listed in section 2.2.1 will be measured and used to show treatment efficiency. The goal for FRW is that the final sand meets criteria allowing for utilization in some form, rather than requiring a landfill.

2.2.2 Waste ashes

Ashes produced in combustion of non-hazardous and hazardous waste are usually considered to be environmental threats, and large sums are invested to ensure safe handling of them. Finding a solution that allowed for recycling or safe utilization of these ashes would be of great environmental and commercial interest.

In accordance with introduction of the landfill directive (Council Directive 1999/31/EC), sorted combustible and organic waste are no longer landfillable. This resulted in an immediate need for regional incineration solutions that could handle industrial, construction and residual waste

from households. This led to many new waste to energy plants (WtE) being taken into operation, whereby waste is converted into useful electricity and district heating. However, this process also generates ashes corresponding to roughly 20% of incoming waste mass, which needs a disposal solution. Fly ashes often contain enough toxic metals to be classified as hazardous waste, and while they might be valuable, reclamation is difficult and costly. Salts based on chloride or sulfate are often readily soluble, resulting in leaching properties that require expensive chemical stabilisation before landfill. As a consequence, many WtE plants have chosen final disposal solutions that are not covered by the Landfill Directive (1999/31/EC), such as salt mines and lime pit in the Oslo Fjord. Therefore, a more long term and sustainable solution of ash handling has to be developed in the near future.

By utilizing the MOPS pilot plant to treat waste ashes, FRW aims to achieve the following goals:

- Residue from ash washing should fulfil requirements for non-hazardous landfill.
- Total amount of waste to landfill should be reduced by 30-40%.
- Purified washing solution would contain high concentration of chloride salts, allowing for use in dust prevention or de-icing purposes.
- Valuable metals could be selectively precipitated and of such purity that recycling through refining processes is possible.

The net effect of these aspects would be an overall reduction in costs and need for transport, while also displacing the need to extract virgin materials from mines. Should some or all of these goals prove possible, the net environmental benefit will be substantial.

Two different waste ashes are tested in this project:

- An alkaline ash rich in lime, sourced from a WtE plant utilizing dry or semi-dry flue gas cleaning process
- A neutral ash rich in chlorides, sourced from FRW's Hazardous-Waste-to-Energy (HWtE) plant located in Nyborg, Denmark.

2.2.3 Industrial sludge

Treating industrial waste water before discharge to municipal sewers or recipient, in order to comply with regulations, is a common challenge among industrial actors. This is often done through precipitation of contaminants into a sludge phase, which is then dewatered and incinerated or landfilled. If the industrial process in question uses phosphorus as an ingredient, the sludge from the connected waste water treatment plant is likely to also contain a high concentration of phosphorus, making it an interesting target for recovery efforts due to its scarcity.

2.2.3.1 Phosphorus

Phosphorus is an essential component in all living organisms; it is one of the components of DNA, and the key element in the energy-supply chain in our cells. Today fertilizer production is dependent on mining and extraction of naturally occurring calcium phosphate (e.g. phosphate rock), which mainly takes place in China, the U.S., Morocco and Russia. The resources are, however, limited and phosphate rock has therefore been included in the list of critical raw materials, composed by the European Commission (EC, 2018).

FRW has, in the past, worked on methods of extracting phosphorus from sludge from municipal waste water treatment plants with limited success.

The sludge trialled in this project is a waste product from the internal wastewater treatment at FMC Cheminova. It is characterized by high concentrations of phosphorus and sulfur, and has previously been used as a direct fertilizer on agricultural land. However, due to high concentrations of pesticides, and their degradation products, this is no longer a viable option, and the

sludge is instead sent to a landfill for hazardous waste. By treating the sludge in the MOPS pilot plant, the aim is to extract the phosphorus and to recover it in such form and purity that it is useful as input material in the fertilizer industry.

2.3 Previous experience

The technical concept of the MOPS technology used in this project is based on developments at the research and development facilities at FRW AB in Kumla, Sweden. Here, leaching and washing tests have been performed on several different materials, in order to select suitable candidates, and to identify optimal operational conditions, including reactor design and operation parameters.

These tests were followed by up-scaled tests using a small-scale pilot plant (approximate capacity of up to 1 ton solid material per hour) for proof-of-concept, and to obtain important design parameters for the industrial scale pilot. In addition, these tests have provided invaluable experience and knowledge on the behaviour of the materials under the extraction conditions, which have been of great importance for the treatment in the industrial scale pilot.

The section for research and development at FRW AB has also worked with the use of selective precipitation and adsorbents to recover mobilized metals and other elements of interest (e.g. phosphorus) from leachates. Different materials have been tested in laboratory scale for their ability to remove metals from different kinds of leachates in order to treat effluents prior to release and/or to recover elements of interests. These experiences are expected to prove useful in precipitating and purifying metals extracted in the MOPS pilot plant.



FIGURE 1: Photo of pilot plant installed at FMC Rønland site.

3. Process description

The Multi-purpose On-site Phase Separator utilizes a concept called accelerated solvent extraction, which combines a straight counter-current flow and a high degree of control over reaction time. This combination makes the MOPS technology unique and different from other scrubbing systems using pressurized liquid. A visualization of the MOPS pilot plant design is shown in FIGURE 2, with critical parts of the process being described in the figure's legend. FIGURE 1 shows a photo of the constructed pilot plant, situated at FMCs factory site in Rønland. A schematic view of the plant configuration used for treatment of the sand is shown in FIGURE 4.

3.1 Feeding system

The pilot plant is constructed with a feeding hopper, meant to be loaded by tipping the special soil containers using a front loader. In order to minimize smell, the inlet shut is equipped with a lid and connected to the ventilation system. The material is transported to the process using screw conveyors.

3.2 Size separation

The pilot plant was built to handle a large variety of materials, from light ashes to the gravel contained within polluted soil. In order to avoid damage to the equipment, the process starts with pre-screening and classification of material. By separating out the material into different size fractions, the treatment for each can be tailored to its needs, in order to obtain sufficient treatment of all material.

Large objects (>60 mm) are removed by passing the material through a screen. These large objects have not been the focus of this pilot project, as they comprise only a tiny fraction of the total mass, and designing for their treatment would have increased costs significantly. After removal of oversized objects, the material is taken by the conveyor screws to the washing drum and a rinsing deck. The interior section of the drum is composed by a mesh, with a specific pore size (16 mm), and by rotating this, a highly efficient separation of the material is achieved. After the washing drum, the fine fraction (<16 mm) is transported to a rinsing deck with an even finer mesh (2 mm). The final fraction, consisting of fine particles (< 2 mm) and

water, is transferred to a hydro cyclone in which the water is removed before the material is fed to the attrition cell.

3.3 Attrition cell

This is the first stage of the actual MOPS process, also referred to as phase 1 in the MOPS treatment. During this phase, the solid matrix is blended with an extraction liquid, which is customized for the specific bulk material. The liquid is blended with the bulk material in closed cells equipped with heavy duty stirrers, causing very intensive attrition of the material. This results in liberation and softening of coatings, cracking of agglomerates etc., while allowing the extraction liquid to penetrate deep into the bulk material. Altogether, a large fraction of metals and contaminants weakly attached to the bulk material will be transferred into the liquid phase during this attrition phase. When the slurry leaves the attrition cell, hydro cyclones are used to separate the liquid from the solid material, resulting in a liquid phase which is heavily enriched with metals/contaminants. After separation, the solids are further treated in the reactor, while the liquid is collected and treated (see section 3.5).

3.4 MOPS reactor

After separation from the liquid, the bulk material-slurry enters the final treatment step of the process; the high-pressure wash. Any metals or contaminants still attached to the material are so firmly attached that liberation of these requires high amounts of energy. The previous step in the attrition cell has prepared the material by exposing the firmly attached metals/contaminants, thereby enabling removal of these using the high-pressure wash.

The technical concept of this step consists of a free flow reactor where the solid material meets a highly pressurized counter-current flow of liquid. This high-pressure liquid secures an intensive scrubbing of the material and reaction between the solid and liquid phases. The system has several advantages, compared to other commercially available scrubbing systems:

- Very low liquid/solid ratios (2:1) and accelerated reaction.
- High flexibility terms of temperature and chemistry of the extraction liquid.
- Robust and simple design, which enables for treatment of sludges and solids by direct introduction to the reactor.

Following treatment in the reactor, the liquid is removed and treated (see section 3.5). The solid material is rinsed and dewatered, before being transferred to the container for treated material. Repeated treatment in the MOPS reactor can be necessary in cases of severe contamination of the original material.

3.5 Water treatment

While the MOPS process uses a rather low L/S ratio overall, there are still several significant streams of waste water being produced. By cascading less polluted water streams, and utilizing state-of-the-art water treatment processes, it is however possible to purify and reuse the vast majority of this water, leading to a very low consumption of water overall. A low consumption also means a low rate of discharge to external water treatment facilities, saving costs and environmental impact.

Depending on the material being treated, and the extraction liquid used, the water treatment process can differ significantly. For the pilot plant, water treatment was done in cooperation with a partner through an electro-chemical process utilizing flotation to separate the solids.

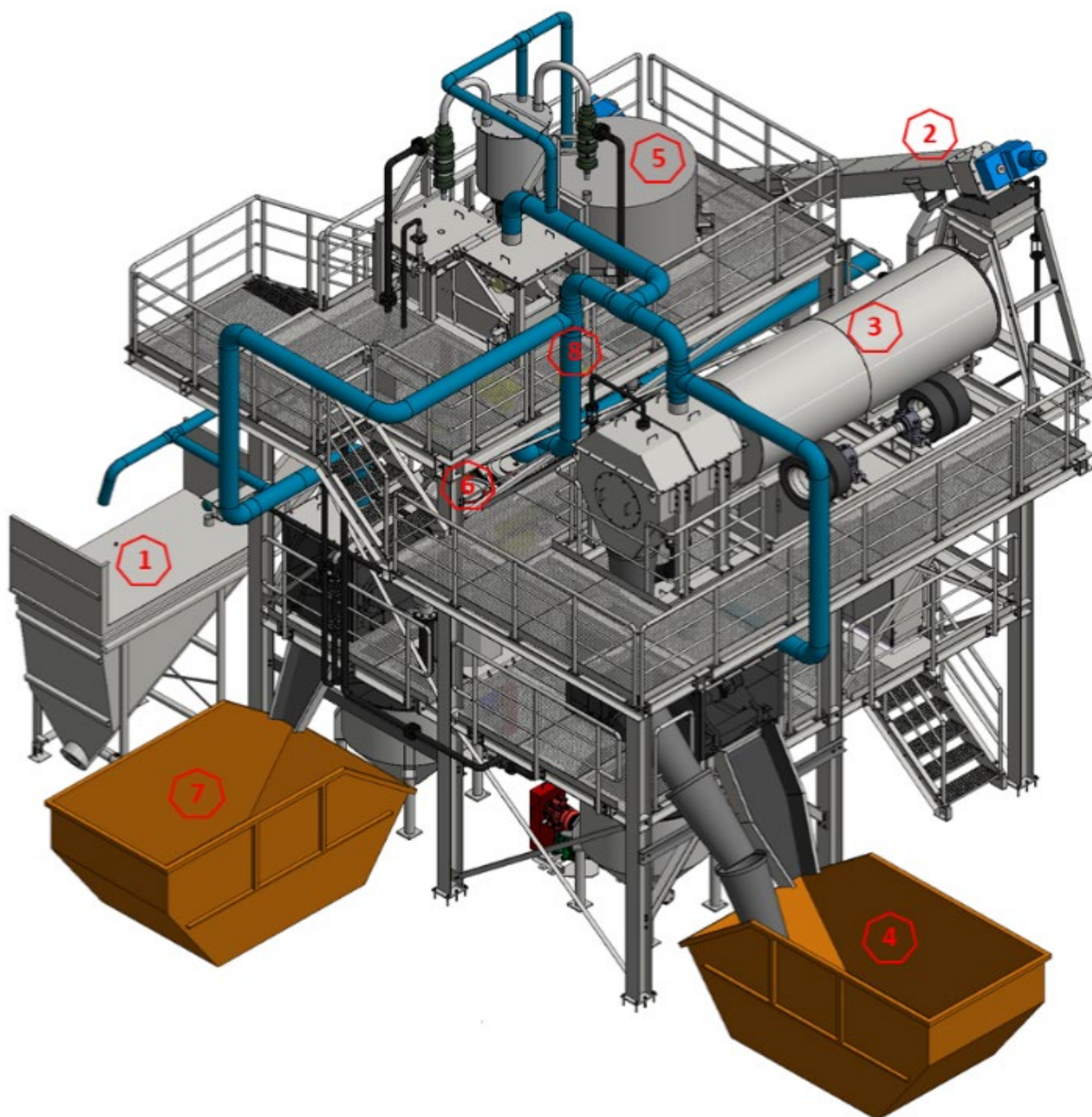


FIGURE 2: Visualization of the MOPS pilot plant design, including ventilation system (in blue) and outlets for treated fractions. Important parts of the design, highlighted in the figure with numbers in red.

1. **Inlet chute** for untreated material

2. **Transportation screws**

Rotary washing drum

3. **Container** for 2-60 mm fraction

4. **Silo** for keeping of material before entering the high-pressure reactor

5. **High-pressure reactor**

6. **Container** for treated fraction (0.06-2 mm)

7. **Ventilation system**, (blue). All parts of the system is under vacuum, which can be adjusted. Exhaust gases are treated through a demister and carbon filter before being released through a chimney. For safety reasons, the MOPS plant cannot be operated without active ventilation.



FIGURE 3. Visual appearance of untreated sand from Groyne 42 hot spot.

4. Reclamation of polluted soil

4.1 Plant configuration

The polluted soil from Groyne 42 was from the very start expected to be the biggest challenge for the MOPS process. As such, the design of the plant was tailored to this fraction by addition of specially designed feeding and pre-screening system in which bigger objects, such as wood, asphalt and stones are removed from the sand body. Furthermore, measurements were taken to minimize release of odour throughout the process; from the use of lid-equipped containers for the excavated material and enclosed feeding hopper, to the fully ventilated plant. A schematic outline of the entire process can be seen in FIGURE 4

4.1.1 Size separation

The physical structure of the sand in Groyne 42 makes it very well suited for liquid extraction of contaminants. It contains hardly any silt or clay particles, which helps limit the amount of sludge, that needs to be incinerated. With just 5% of the material being classified as oversized (> 2 mm), the material is also unlikely to clog up screens and separators. The material is therefore well suited to be used as a proof of concept for the MOPS technology.

The oversized fraction has a low ratio of surface area to mass, and as such, contaminants are expected to be loosely bound to the material. This fraction is expected to be sufficiently purified by attrition and alkaline hydrolysis in the washing drum. The remaining sand (< 2 mm) is expected to require harsher treatment, based on knowledge obtained in the laboratory scale pilot tests. The visual appearance of the untreated sand can be seen in FIGURE 3 and FIGURE 5.

4.1.2 Extraction

Several iterations on water chemistry and plant setup were performed on sand from Groyne 42, with mercury removal being the predominant goal. These iterations involved steadily increasing the concentration of active chemicals in the extraction liquid, improving rinsing of post-treatment sand, and improving size separation. The pH of the extraction liquids was fixed at 12-12.5 for all extractions, in order to enhance the mobilization of mercury and pesticides.

In addition, tests were also made to evaluate the effect of repeated treatment of the sand, in order to simulate two sequential MOPS processes running in series. For this, already treated sand was re-introduced to the plant, and treated according to the outlined procedure (FIGURE

4). Improved size separation was achieved by utilizing a bench-scale up-stream classifier to further fractionate the treated sand by grain size (< 0.063-0.25 mm; 0.25-2 mm).

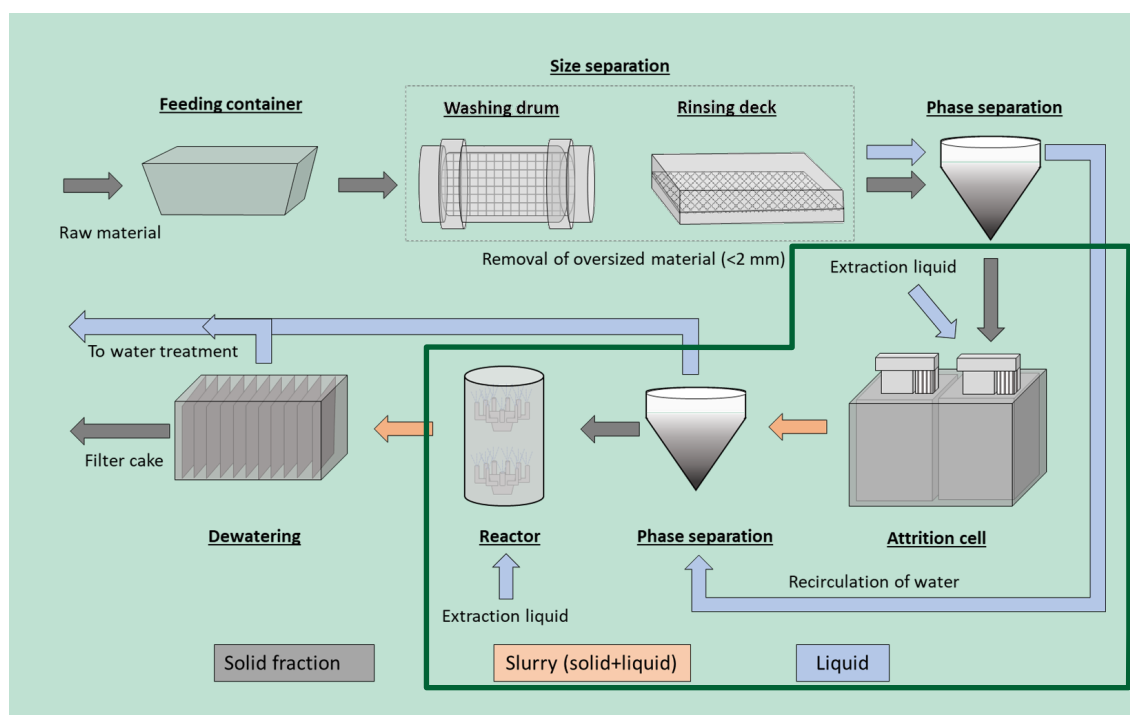


FIGURE 4. Schematic overview of the MOPS pilot plant. The flow of different materials (sand, liquid and slurry) are indicated with arrows. The area highlighted in the figure shows the core part of the plant, which is used in ash and sludge tests further described in sections 5 and 6.

4.1.3 Water treatment

Water was collected from several parts of the MOPS process and subsequently treated in order to fulfil two different objectives: ¹⁾ enable recirculation back to the process, and ²⁾ enable release to recipient. These two objectives entails different target levels in terms of quality of the water which, together with the expected variation in level of contamination within the wastewaters, put high demands on the flexibility of the wastewater treatment.

The treatment targets are much more stringent for release of the water to recipient compared to re-use in the process. However, the washing effect is dependent on the degree of contamination of the water. In order to re-use the water, low levels of mercury are necessary, but requirements for level of organics are not as high. It may therefore be sufficient to remove these when needed, as opposed to continuous treatment.

To test and evaluate different concepts for treatment of the water, a third party supplier was contracted. A modular pilot-scale system was installed and connected to the MOPS plant to enable direct feeding of produced wastewater to the water treatment. The plant used an electro-chemical process to create flocs from pesticides, mercury and small debris. These flocs were then separated in a flotation tank, followed by a clarifier, before the water was fed back into the process water tank.

The water treatment plant was not of sufficient scale to keep up with the MOPS pilot, but was partially able to catch up during breaks between batch testing. This allowed for test runs with the majority of water having been used before. Tests with treatment target in accordance with that for final discharged were performed in laboratory scale.

4.2 Challenges

Several challenges were encountered during the pilot test runs on sand from Groyne 42, the most prominent being accurate simulation of sequential processes due to cross-contamination. Although the plant was emptied and cleaned between the test runs, fractions of highly contaminated, un-treated, sand could still be found in hard-to-access areas (pipes, screws, cells in the attrition cell, etc.). When the once-treated sand was fed back into the process, this was mixed with the residues of un-treated sand, resulting in a mixture of the two and thereby hindering proper evaluation of the effect of repeated treatment. Because of this, the effect of repeated MOPS treatment is not fully reflected in the obtained results. In order to avoid this problem in a full scale plant, it could be constructed to include two MOPS processes connected in series.

The target OPs were successfully removed from the sand through alkaline hydrolysis, independent of the high initial variations in the un-treated sand. This process results in the presence of degradation products, which also have to be removed in order to ensure a good quality of the treated sand. Close monitoring of these by-products require analytical methods which were not available during this project. However, since the chemical structure of the target OPs (and their degradation products) contain both sulphur and phosphorus, these easily-monitored elements were used as indicators to evaluate the efficiency of the treatment. Although this approach was applicable in the pilot plant, a full scale treatment plant would probably require more accurate quality assurance.

Even after full treatment in the MOPS-plant, a faint smell could be detected from the final sand. Although this was completely removed after drying of the material, the nature and composition, as well as proper handling of it should be investigated.

4.3 Results

The visual appearance of the sand before MOPS treatment, as well as after attrition cell and full treatment, is shown in FIGURE 5.

4.3.1 Mercury

Initial Hg concentrations, determined by ICP-MS analysis, are consistent throughout the tests, ranging between 600-800 mg Hg/kg DM (Dry Mass). From the different test runs it is clear that although approximately 80% of the Hg contamination can be liberated from the sand quite easily, the remaining 20% require the harsh treatment of the attrition cell and the high-pressure reactor.

The tests performed in the MOPS pilot plant have shown that >99.5 % of the Hg contamination can be liberated within one MOPS washing cycle. This confirms that the primary target of reducing Hg down to < 3 mg Hg/kg DM is possible, and have also demonstrated that the goal is within reach in one single MOPS washing cycle.

A comparison of the mercury concentration in sand after different number of treatments in the pilot plant, with and without addition of complexing agent in the extraction liquid, is presented in FIGURE 6. Sand having been treated with complexing agent contain only a minor fraction of Hg, which is most likely so firmly bound that release into liquid phase is far more depending on the “aggressivity” of liquid, compared to physical impact.



FIGURE 5: Visual appearance of untreated sand (top), after attrition cell (middle), and full MOPS treatment (bottom)

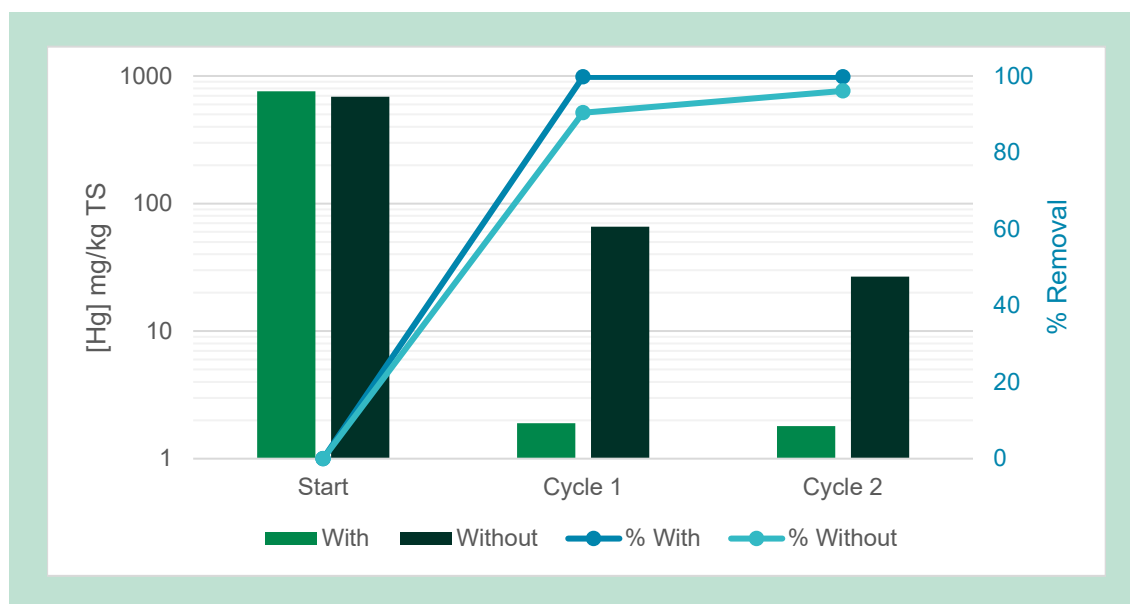


FIGURE 6. Concentration of Hg, given as log mg/kg TS, in untreated sand, as well as after 1 and 2 cycles in the MOPS pilot plant. Comparison between removal rates with and without the addition of Na_2S .

Results from complementary laboratory scale tests on the effect of further size separation of sand indicate that 70-80% of the sand could be brought to meet criteria for free use (<1 mg Hg/kg DM) after one MOPS cycle. As a consequence, the use of a wet classifier would entail that only 20-30% of the sand would require repeated treatment in the MOPS plant, which would pose as a more cost efficient alternative, compared to repeat treatment for the entire sand body.

Standardized leaching tests, commonly used for characterization of waste materials, were performed on the sand after treatment. The results from these indicated leaching properties correlating to concentrations of 0.02-0.14 mg Hg/kg DM.

4.3.2 Pesticides

The fact box on the right shows the measured range of organic pesticides in inlet samples during the tests. In addition to this, a complementary bench scale study reported a top notation of E-Parathion to be 2200 mg/kg DM, indicating even wider ranges. Following one cycle in the MOPS treatment, the target OPs were decreased with at least 95%, and in several cases the final concentrations were below the detection limit. However, for batches with high concentrations of OPs, in particular related to Parathions, one MOPS washing cycle is not enough in order to meet treatment target down to detection limit or alternatively to low sub ppm level of OPs.

Several tests were performed in which the treated sand was fed to the MOPS plant once more (wash cycle 2), results from some of these are shown in FIGURE 7. These results demonstrate that target OP:s are further reduced following this re-treatment of the sand. Addition of Na_2S does not appear to have any significant effect on the removal of target OPs. Alkaline hydrolysis seems to be effective also for the part of OP contamination which is hard bound to the sand grains or inaccessible for mechanical liberation.

Organic pesticides (OPs)	
Initial concentrations	
(mg/kg DM):	
E-parathion	3 – 930
M-parathion	97 – 236
Malation	24 – 68
E-sulfotep	6 – 146

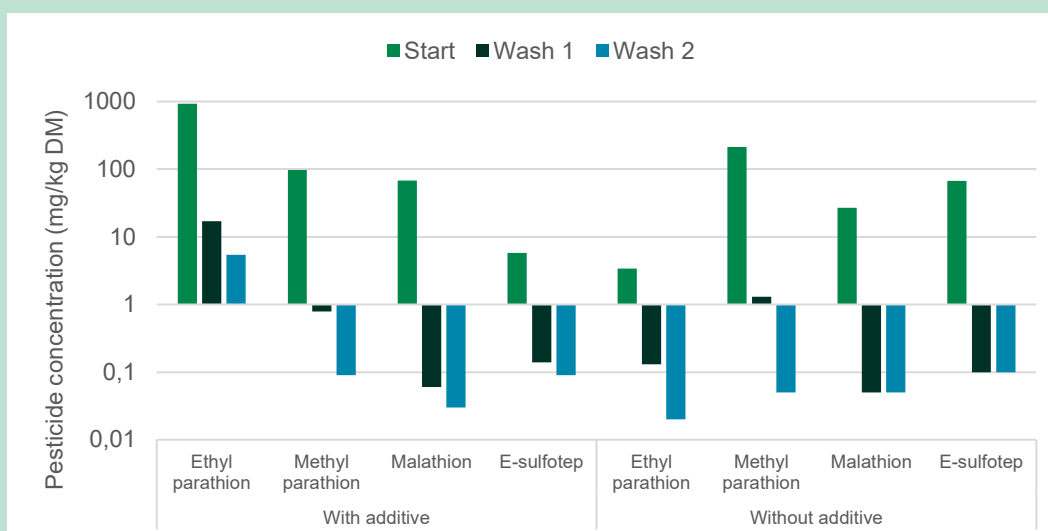


FIGURE 7. Concentrations of target OP-s (mg/kg DM) before MOPS-treatment and after one and two cycles (Wash 1 and 2, respectively), both with and without addition of Na₂S. Data obtained from tests on pilot plant.

In spite of the net gain by repeated treatment of the sand, the obtained final concentrations are still too high to allow for release of the treated sand. This is related to cross-contamination of the sample (see section 4.2) which hindered evaluation of the full effect of repeated washing of the sand. Therefore, a laboratory bench-scale pilot was constructed to evaluate the effect of repeated MOPS treatment, as described in section 4.1.2. The results from these tests showed that increased extraction time and proper rinsing of the sand, with the option to increase the temperature, will result in complete removal of target OPs.

4.3.3 Water treatment

Initial concentration of mercury in the waste water ranged from 7,7 to 50 g/L, with an average of 13,26 g/L. After treatment (electrocoagulation + floatation + clarifier) the concentration decreased significantly, resulting in levels in the range of 20-130 µg/L. The initially low concentrations of target OP-s in the wastewater hampered the monitoring of these through the treatment process, and thus also the evaluation of its efficiency. However, since a large fraction of the target OP-s (as for the Hg) were associated with suspended solids, this could be used as an indicator to estimate the treatment efficiency, together with measurements of dissolved organic carbon (DOC). Initial values for suspended solids and DOC ranged between from 4-8 g L⁻¹ and 88-336 mg/L, respectively. After treatment, all suspended solids were effectively accumulated in the sludge, while the DOC was reduced to 20-30 mg/L. Several tests were done in which the treated water was recirculated back to the MOPS process, with no negative effects on the treatment efficiency.

Although the initial process removes the turbidity from the water and produces a liquid which is useful for recirculation, the treated water still holds a strong yellow color and a distinct smell. Both the appearance and the smell of the water are related to degradation products from the hydrolyzed pesticides, and further treatment is required in order to remove these and reach target levels for discharge.

A polishing step was tested in laboratory scale, using water from the pilot scale water treatment. The visual appearance of the water before, during, and after the polishing step is shown in FIGURE 8.

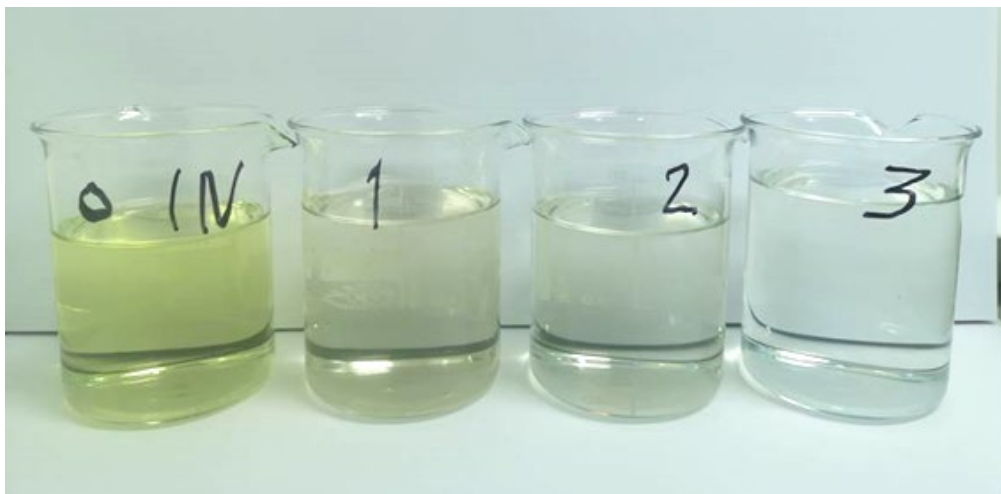


FIGURE 8. Visual appearance of water before (far to the left) during, and after (far to the right) the polishing step.

4.3.4 Implications of obtained results

The pilot tests have shown that the MOPS treatment is well suited for treating the sand from Groyne 42. Treatment goals for Hg is in reach within the first washing cycle, while a repeated treatment is necessary to reach the goal for the target OPs in parts of the material. Performed pilot tests together with complementary bench scale tests have provided good operational data and analytical results, which are necessary for designing a full scale treatment plant.



FIGURE 9. Bagging station for fly ash at FRW, Nyborg. These are the ashes referred to as “high-chloride” in the following chapter.

5. Extraction of metals from fly ash

5.1 Plant configuration

The fly-ashes used were characterized by a very uniform, fine-grained structure, eliminating the need for size separation before treatment. Instead, the ashes were fed directly to the mixer tank and treated according to the outline in FIGURE 10. After treatment in the reactor, the resulting slurry was collected and further treated in laboratory batch scale.

Tests were done in the MOPS plant on two different types of ashes, as mentioned in section 2.2.2.

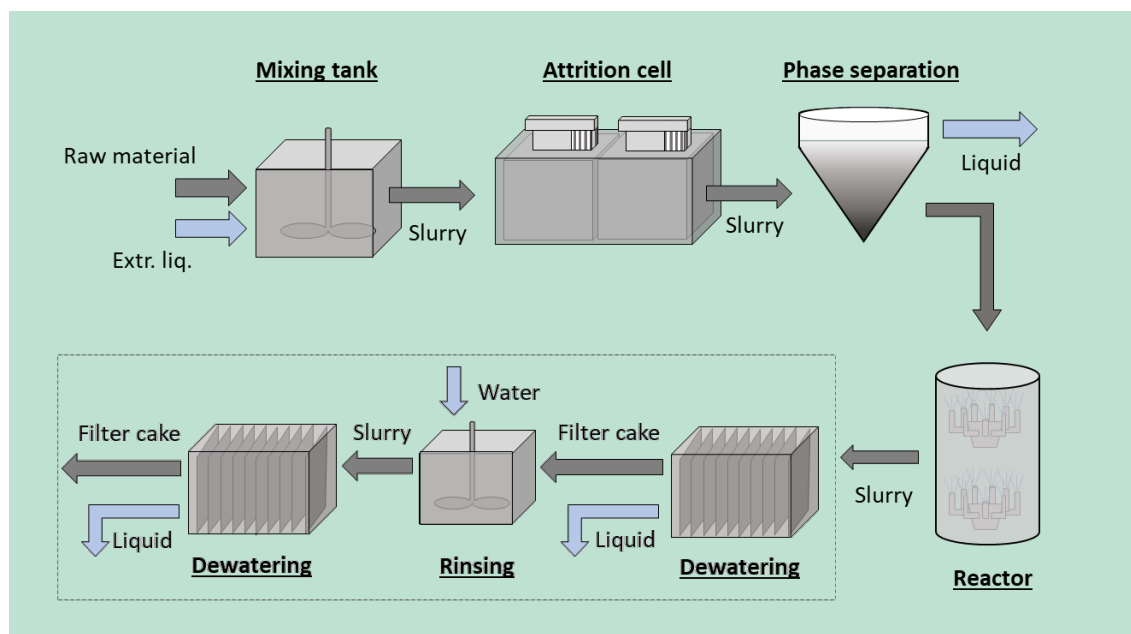


FIGURE 10. Schematic overview of the pilot plant configuration used for treating ashes and sludge. The initial screening system used in treatment of sand from Groyne 42 was excluded and prepared ash or sludge was fed directly into attrition step. The grey box in the lower left part of the figure contains parts of the process which were not included in the pilot set up and therefore simulated in laboratory scale.

5.1.1 Extraction

Since the two ashes included in here differ in terms of origin and chemical composition, different parameters were used for extraction of metals, the most prominent difference being the pH of the extraction liquids; The alkaline ashes were extracted at pH 10.5, while the high chloride ashes were extracted at pH 2. Apart from this, the overall procedure was the same for the two materials: Ashes and extraction liquid was added to the mixer tank where pH and RedOx was adjusted (RedOx value was set to +400 and +550 mV for alkaline and high chloride ashes, respectively). After stabilization of these parameters, the mixture was transferred to the attrition cell where it was treated for 10 minutes before it was transferred to the phase separation where it was allowed to settle and the liquid phase was removed. The solid residue was thereafter fed to the reactor using screw conveyors. After the reactor, the material was collected in tanks for further treatment in laboratory scale.

5.1.2 Sludge handling

After the treatment process, the residual material has to be dewatered in such way that ensures removal of all liquids, including exchange of the pore-liquid (e.g. the material has to be properly rinsed and pressed). This part of the process was performed in lab-scale. Both liquid and solid residue were then analyzed for metal content.

5.1.3 Metal recovery

Two different approaches were evaluated in terms of recovery of metals from the produced leachates; selective precipitation and sorption.

The selective precipitation was based on chemical equilibration modelling. For this, the pH of the leachate was gradually altered in order to achieve specific precipitation of the target metals. When precipitation occurred, this was separated from the liquid phase before pH was further adjusted. Sampling was done on initial samples and at the specified pH-values.

Sorption is based on the use of filter materials with high specific surface areas, which allows for adsorption of a variety of elements, based on their physical and chemical properties. Two different materials were included in these tests; ¹⁾ *Activated carbon* – A well-known, widely used, material for removal of contaminants from both liquids and air, and ²⁾ *ORE filter* – a commercially available filter material, specifically designed to treat different kinds of water.

5.2 Challenges

The main challenge encountered during these tests was the extensive foaming associated with the extraction of the alkaline ashes, most likely caused by release of CO₂. This foaming also led to slow sedimentation of the solid residues by causing a “flotation” effect of the material. In order to avoid this, the rate of pH adjustment was decreased, as the material was closely observed to detect any foaming tendencies at an early stage.

5.3 Results

5.3.1 Extraction

Results from chemical analysis of selected metals in high chloride and alkaline ash, together with calculated percentage removal rates, are presented in FIGURE 11 and FIGURE 12, respectively.

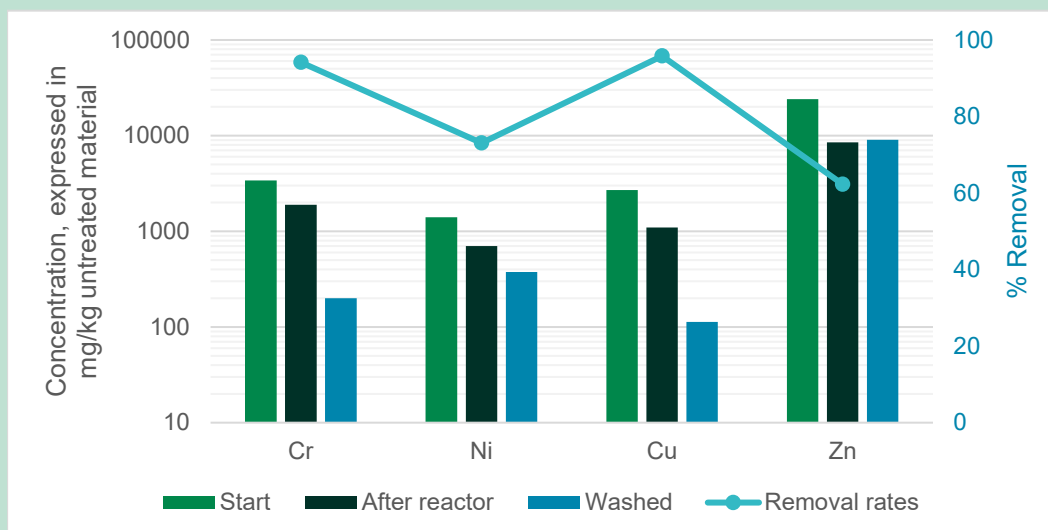


FIGURE 11. Concentrations of selected metals in untreated high-chloride ash (start), after reactor and after conditioning, given as log mg/kg TS. Calculated percentage removal rates on secondary y-axis.



FIGURE 12. Concentrations of selected metals in untreated alkaline ash (start), after reactor and after conditioning, given as log mg/kg DM. Calculated percentage removal rates on secondary y-axis

The figures show that removal rates are >60% for all metals in both ashes, despite the moderately decreased concentrations. This is related to the rather high amount degree of mass-loss, associated to the treatment process of the MOPS plant. The harsh mechanical treatment in the attrition cell and the reactor, together with the chemical conditions result in very efficient dissolution process, leaving less than half the material in the solid phase.

5.3.2 Metal recovery

The outcome of the lab-scale test on selective precipitation for recovery of metals from leachate showed decreased concentrations of metals in the leachate, as a function of pH for both high chloride (FIGURE 13) and alkaline ashes (FIGURE 14).

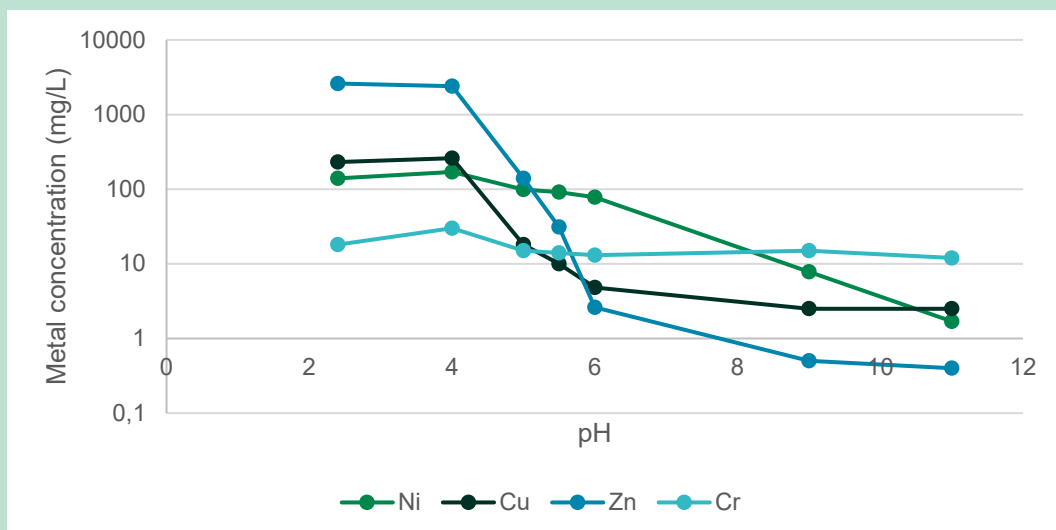


FIGURE 13. Concentration of selected metals in leachate from high chloride ashes, given in mg/L as a function of pH.

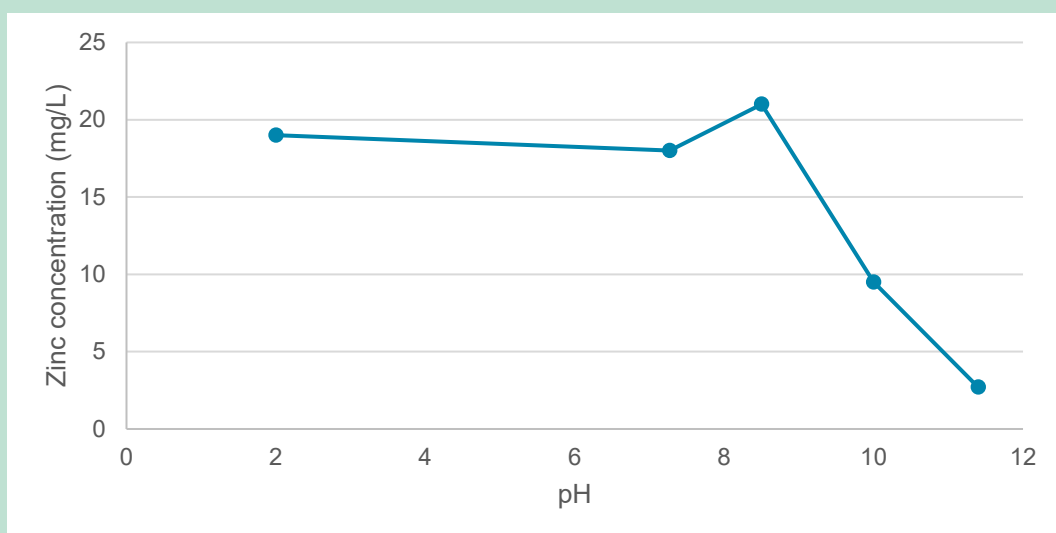


FIGURE 14. Concentration of Zn in leachate from alkaline ashes, given in mg/L as a function of pH.

There is a distinct decrease in the concentration of Zinc in leachate from high chloride ashes between pH 4 and 5. This is in accordance with expectations, which suggest that Zinc should precipitate at pH 4, most likely due to increased formation of ZnHPO_4 and different zinc oxides. The same pattern can also be seen for Copper, although not as pronounced as for Zinc due to the much lower concentration. This is also in accordance with expectations and can, as for Zinc, be ascribed to formation of CuHPO_4 and different oxides.

For the leachate rendering from alkaline ashes, the only pattern that could be distinguished was the decreased concentration of Zn at pH 10 (FIGURE 14), which is ascribed to the precipitation of $\text{Zn}(\text{OH})_2$.

The results from tests on removal of metals from the leachate by the means of two different filter materials, given as % removal rates, are given in FIGURE 15 (high chloride ashes) and FIGURE 16 (alkaline ashes). The results differ between the two types of leachates; for the high chloride leachate, both filter materials seems to work rather good in terms of removing Zn, while the removal efficiencies differ for the rest of the elements. From the alkaline leachates, however, the results indicate the two materials to be equal in performance regarding metal removal.

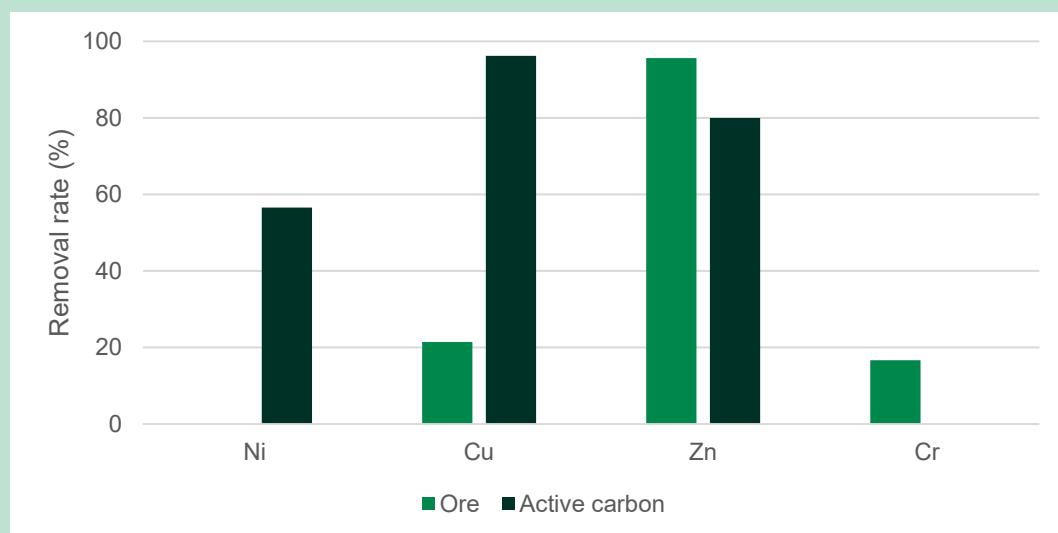


FIGURE 15. Percentage removal rates of selected metals from leachate rendering from high chloride ashes by the use of ORE-filter and Active carbon.

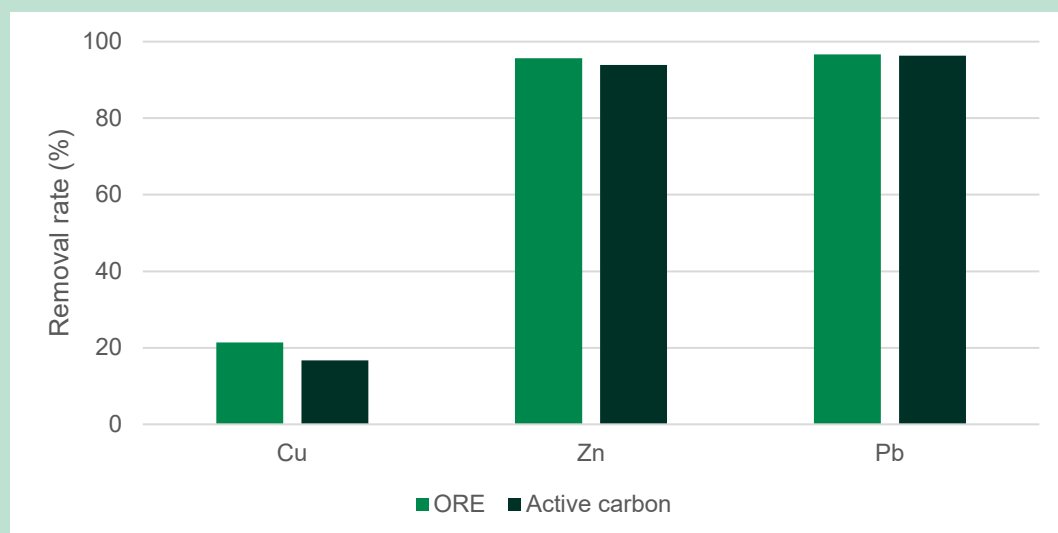


FIGURE 16. Percentage removal rates of selected metals from leachate rendering from alkaline ashes by the use of ORE-filter and Active carbon.

5.3.3 Implications of obtained results

Based on the results obtained in this study, the design of future planned ash refinery plants will go in the direction of continuous flow, compared to batch flow processes. Utilization of a continuous process with a combination of heavy attrition and high pressure extraction (e.g. MOPS technology), enable shortening in retention time as well as decreased liquid:solid ratio, compared to conventional batch processes, such as FRW's own ash refinery plant in Pori, Finland. The MOPS pilot utilizes a simpler, more compact setup, while achieving a greater degree of ash dissolving than the current process utilized in the commercial scale plant.

The tests on recovery of metals from the leachates show that chemical precipitation is a viable option; a clear decrease in especially Zinc could be seen for both leachates. It should, however, be stated that mere removal of metals from the liquid does not fulfil the goal to recover these in a useful state, and the prerequisites for metal recovery are depending on the different kinds of ashes. Therefore, FRW has started a program for development of electrolytic processes for selective metal recovery. In addition, numerous ashes contain high amounts of chlorides, which are released in the extraction process. Full scale experiments on utilization of such brines for de-icing are ongoing in Pori, with very promising results. Chemical analyses of the brines obtained in this study show similar properties and degrees of purity, which proves their applicability for de-icing purposes.



FIGURE 17: Visual appearance of industrial sludge before treatment.

6. Recovery of phosphorus from industrial sludge

6.1 Plant configuration

The same configuration was used for treatment of industrial sludge as for extraction of metals from ashes (FIGURE 10).

6.1.1 Extraction

The extraction process was initiated by feeding of sludge to the mixing tank, where water was added. pH was adjusted to 4.5, while the RedOx potential was kept un-adjusted in order to avoid problems with foaming. After stabilization, the mixture was transferred to the attrition cell where it was treated for 10 minutes before it was transferred to the phase separation and allowed to settle before removal of the liquid phase. The solid residue was thereafter fed to the reactor using screw conveyors. After the reactor, the material was collected in tanks for further treatment in laboratory scale.

6.1.2 Sludge handling

After the treatment process, the residual material has to be dewatered in such way that ensures removal of all liquids, including exchange of the pore-liquid (e.g. the material has to be properly rinsed and pressed). This part of the process was performed in lab-scale.

6.1.3 Phosphorus recovery

Two different approaches were evaluated in terms of recovery of phosphorus from the produced leachates; selective precipitation and sorption, both were performed according to the outlined procedure in 5.1.3

6.2 Challenges

The initial recipe for extraction of the sludge, based on lab-scale experiments, entailed a decrease of pH to approximately 2. However, because of the high degree of foaming obtained in the lab-scale, together with the gained experience from extraction of alkaline ashes, the parameters for the pilot plant test were altered to avoid extensive foaming in the facility. This decision did entail decreased efficiency in the extraction process, but enabled the test to be completed. Final treatment of the sludge, and precipitation of phosphorus-containing product

were also hindered by equipment issues, causing delays and preventing repeat measurements within allotted time.

6.3 Results

The results from extraction of phosphorus from industrial sludge, given as percentage removal after the MOPS treatment, as well as after conditioning of the sludge, is given in FIGURE 18. In addition to phosphorus, Ca and Fe are also included since these are the principal elements associated to phosphorus within this matrix. As can be seen from the graph, approximately 40% of the phosphorus is removed in the MOPS treatment, and a small increase can be seen after rinsing of the residues.

6.3.1 Extraction

Based on results from chemical analysis of un-treated sludge, and the fractions obtained during and after the treatment process, percentage removal rates of principal elements (P, Ca and Fe) were calculated, these are presented in Figure 18.

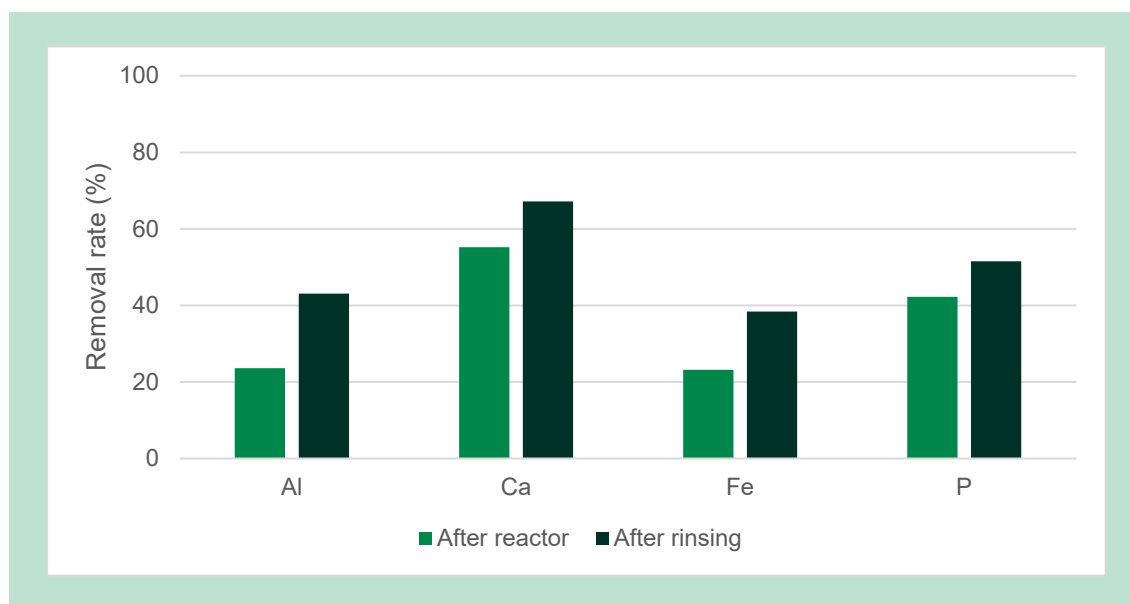


FIGURE 18. Extraction efficiency of phosphorus and other principal elements from sludge.

The figure shows modest removal rates for all principal elements obtained after treatment in the reactor, with a small additional increase following rinsing of the material. Iron and calcium is added in the industrial water treatment plant to precipitate phosphorus, because these phosphates bond strongly and have a very poor solubility. Often, strong acids are needed to liberate the phosphorus for fertilizer production. Considering this, these results show a great amount of promise.

6.3.2 Recovery

Following the lab scale tests of selective precipitation as means to recover extracted phosphorus, a strong decrease (92%) in the concentration in the extraction liquid could be seen between pH 7 and 11, see FIGURE 19, most likely caused by precipitation of calcium phosphate. This is in agreement with the theoretical model, which indicates increased amounts of Ca-associated phosphorus following increased pH. This was also supported by a measured 20% decrease in Ca concentration in the extraction liquid in the same interval.

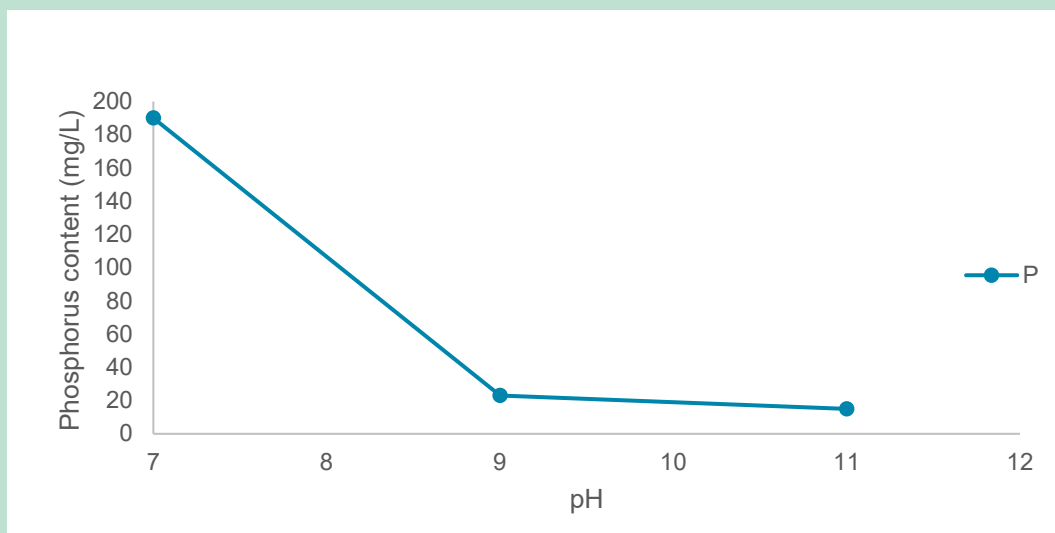


FIGURE 19. Precipitation of calcium phosphate at elevated pH.

Results from tests on removal of phosphorus from the leachate using filter materials indicated removal rates of 49 and 51% for ORE filter and active carbon, respectively. Although the removal rates for the two filter materials are virtually the same with regards to phosphorus, they differ greatly in terms of removal efficiency of Calcium and Sulfur, as can be seen in FIGURE 20. This difference suggests that there are different mechanisms responsible for the removal in the two materials, which could be of importance for future optimization of the application.

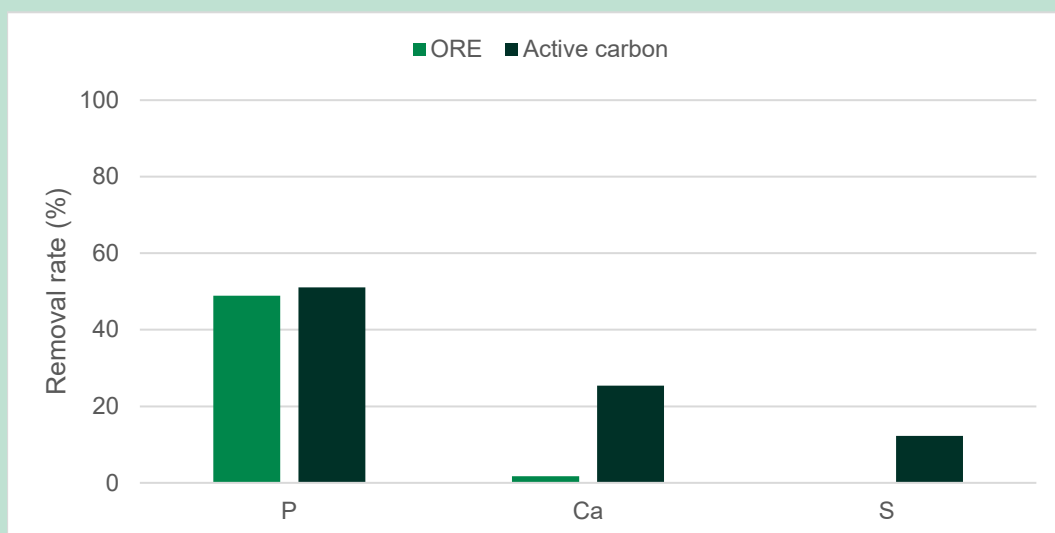


FIGURE 20. Removal rates of phosphorus, calcium and sulfur using two different filter materials.

6.3.3 Implications of obtained results

Although the performed tests have shown that the MOPS plant is a promising option for treatment of sludge with the aim to recover phosphorus, several different aspects have to be addressed before a full-scale solution can be realized:

- The removal-rate needs improvement, which entails a need for further development of the extraction procedure and evaluation of the possibility for repeated treatment.
- Results indicate that the recovered phosphorus is in the form of calcium phosphate, which should make it interesting as a replace for virgin phosphate rock that is mined for fertilizer production. However, the chemical form of the recovered phosphorus has to be determined.
- The end-product has to be tested and characterized to ensure that it does not contain any pesticides, or degradation products thereof.

7. Future prospects and economics

7.1 Project's results

As stated the scope of the project is to demonstrate the following objectives:

1. Use of an innovative high pressure, phase extraction recovery technology called MOPS (Multi-purpose On-site Phase Separator) to remediate waste products of high complexity.
2. Feasibility of selective harvesting of valuable materials from the resulting phases, and
3. Possibility to establish this as an on-site solution

The first objective has been achieved in full, as the MOPS technology has been successfully used to treat three different waste fractions, obtaining the following results:

- Highly contaminated sand, rendering from the dump site of Groyne 42, characterized by high concentrations of Hg and pesticides. The treatment has resulted in residual levels of Hg and pesticides near or below detection limit in the sand, thus making free or restricted utilization a distinct possibility. Lab scale tests performed following the pilot tests suggest, that cross contamination was a key factor in not achieving the target level of pesticide removal in all samples, as presented in FIGURE 7.
- Ashes from incineration of hazardous and non-hazardous waste, characterized by high concentration of chlorides or calcium, as well as metals of interest for recovery. The levels of both target (eg. Zn, Cu, Ni, Cl) and other elements, contributing towards hazardous waste classification for the residue (Pb, Hg, As, Cd), have been significantly decreased. This suggests that mobilization and further purification of these elements is possible. The ash residue was, after treatment, still classified as hazardous waste, but with a significant mass reduction, thus limiting need for landfilling.
- Sludge from the internal wastewater treatment at FMC Cheminova, characterized by high concentration of phosphorus, which is of interest for recovery and recirculation. The concentration of phosphorus decreased with approximately 45% following the MOPS treatment, suggesting that mobilization and thus further purification is possible.

The second objective have been partly achieved, as outlined above. While valuable components have successfully been harvested from contaminated materials, no marketable product has so far been obtained. Further tests are needed to enhance the purity of the obtained products. Since sufficient degree of purity were not reached, this has not been further investigated in this study.

The third objective has been fully implemented based on the installation of the MOPS pilot plant on-site at FMC Cheminova, Thyborøn. The plant has now been dismantled and transported to Sweden for further remediation and extraction tests at FRW's facility in Kumla.

7.1.1 Follow-up on success criteria

A range of criterium for success was listed in the MUDP application. The achievement of these criteria of the project are evaluated in the table below.

TABLE 1. Project results compared to criteria outlined in MUDP application.

Purpose	Criterium for success	Project result
Design and construction of pilot plant (Work package 1+2)	Gained experience from earlier tests utilized efficiently in set up of design parameters of pilot plant. Design and construction group will include diverse competences (R&D to operators)	Achieved A pilot plant was commissioned and ready for operation in beginning of August 2019.
Recovery of valuables in Hazardous Waste fractions (ash and sludge). (Work package 4+5)	Cost effective and environmental friendly recovery/isolation of metals/contaminants as well as recovery of salt solutions.	Achieved Liquid extraction of ashes/sludges using a minimized liquid-solid ratio compared to commercial batch processes. Partly achieved Successful enrichment of target metals based on chemical precipitation. As an alternative, capturing of metals on adsorbents were tested with promising results for isolation of contaminants. In parallel, simultaneous purification of salt solutions was accomplished.
Decontamination of soils (Work package 3)	Cost effective and environmental friendly isolation of contaminants as well as purification and recirculation of wash liquids.	Achieved. The technology has been proven to clean contaminated soils to meet stringent treatment goals. The process has been successfully operated with usage of recirculated liquids.
Dissemination and networking (Work package 6)	Project and achievement of goals visualized to important target groups through usage of several information tools	Achieved Project results and MOPS technology was widely shared to our stakeholders via press releases, radio and TV interviews, and videos. Project results were also concluded in the final report. Partly achieved Final seminar could not be organized in the planned extent.

7.1.2 Environmental impact

As stated in the MUDP application, the Multi-purpose On-site Phase Separator (MOPS) technology will address a multitude of environmental issues. The following is an evaluation of the mitigation of environmental impacts achieved or indicated by the project:

TABLE 2. Environmental impacts achieved or indicated by the project.

Impact	Result
Decontamination of highly complex waste products, such as contaminated soil, slag and ash from waste incineration plants, sludge from sewerage and other hazardous waste products from industries.	Yes, demonstrated for all materials included in this study.
Recovery and recirculation of valuable raw minerals and salts from waste products.	Yes, but more work is needed, in particular related to increased purity of harvested products.
Reducing the need for handling, containment, storage and transport of hazardous materials.	Yes. The possibility to use on-site treatment decreases the need for transportation of big quantities. Conversion of waste into values constitutes a big benefit compared to traditional disposal routes for hazardous waste.
Potential recovery of surplus heat to maintain the decontamination and recovery process	The MOPS plant is designed to allow for usage of heated washing liquids. This study has however, achieved far-reaching goals without need of input of extra heat, thereby minimizing energy consumption in the first place.
Potential recirculation of waste water from industrial processes	Yes. In particular demonstrated in treatment of contaminated sand from Groyne 42.

7.1.3 HSE experiences gained

In addition to data on the efficiency of the MOPS treatment and the overall operation of the plant, this pilot project has also delivered highly valuable knowledge on safe handling of hazardous materials, both in terms of environmental and health risks. The following precautions were taken in construction and operation of the MOPS pilot plant:

- Tested materials emit foul odour and potentially toxic gas emissions. Therefore, the whole plant was encapsulated and equipped with forced ventilation system with exhaust piping at all critical locations. The off-gases were treated by removing of aerosols and thereafter polished using activated carbon filtration.
- Regular measurements of air quality in the plant area showed no sign of elevated concentrations of toxic indicators like Hg, VOC, H₂S, CO, NH₃, thus proving the efficiency of the ventilation system. Normal personal safety equipment could therefore be used by operators
- Closed containers were used in order to prevent risks related to dust and release of volatile substances. Feeding of the materials was done using closed screw system or pumping.
- All process chemicals were injected using closed automated pump systems, thereby avoiding direct handling of material.

- All tanks, together with treatment plant, were placed in embankments in order to prevent any environmental harm in case of leakages.
- Produced process water was continuously monitored to ensure quality standards before recirculation.
- All personnel on site took part in a health control program to assure that no one had been exposed to toxic substances such as Hg and VOC. All tests taken throughout operation of the plant were negative.

7.2 Full-scale MOPS plant design for contaminated soil

Based on the experiences and conclusions contained within this report, there can be no doubt that treatment of polluted soil is the most mature and immediately market-applicable use of the MOPS technology.

Because the polluted soil is so much closer to market than metals and phosphorus recovery, this chapter is dedicated to highlighting the challenges MOPS will face on its way to market as a large-scale solution for this waste fraction.

The following main aspects will be taken into account when it comes to design, construction and operation of full-scale MOPS treatment plant:

- A wet pre-screening of the material has to be done before the treatment process, in order to separate the sand from stones, gravel and other over-sized material, which otherwise could inflict damage to the equipment or decrease the efficiency of the process.
- An efficient treatment of target OPs in hot spot sand from the Groyne 42 depot will demand a pH around 12 in the washing fluid. Mobilization of Hg will, in addition to high pH, also require addition of a complexing agent. Disodium sulfide will be added into the fluid at the attrition step.
- More than one wash cycle might be essential before quality of treated sand fulfil target criteria. Therefore, the plant will comprise of two complete MOPS washing steps connected in series. This will keep problems regarding cross contamination to a minimum, and will also stabilize the results, ensuring that most of the sand body will meet very stringent treatment goals.
- An up-stream classifier will be installed in the flow directly after the first MOPS reactor, which will allow for simultaneous fractionation and rinsing of the sand. This will stabilize the quality to such extent that a large part of the coarse-grained sand can be released for discharge already after MOPS washing sequence nr 1. It is expected that classified sand will fulfil target criteria.
- Heavy and unhealthy smell poses a serious issue regarding untreated sand from the hot spot of the Groyne 42 depot. The plant has to be constructed so fumes and aerosols are kept isolated as far as possible from free exposure to operators and nearby surroundings. Precautions of fumes in water treatment have to be taken in account in equal relevance.
- Faint smell in final sand could require a gentle, thermal treatment.
- Intermediate storage of untreated batches of hot spot sand has to be protected from exposure of rain to prevent undesired leaching and possible fumes have to be taken care of.

Overall, the basic flow will match that presented in FIGURE 4, with two main exceptions. One is the addition of a second MOPS reactor, and the other is the installation of an upstream classifier between MOPS washing sequence 1 and 2. This will allow for fine grained material (<0.25 mm) to be treated twice as default, whereas the coarse grained fraction are taken out after one washing sequence, with the option for re-treatment if needed.

7.2.1 Overview of streams leaving full scale plant

Size fractioning has been a very important part of the laboratory and pilot scale tests to avoid blockages, equipment damage and other production upsets. This will likely continue with a full scale plant, resulting in a size fractioned output as well. Depending on the specifics of the tender, this material could be utilized in different ways, or remixed and returned to the beach, should that be the desired outcome.

TABLE 3. Expected quality of treated fractions

Fraction	% of feed amount	Expected Hg content (mg/kg DM)	Expected residual OPs (mg/kg DM)	Expected exit for material
Gravel 2-200 mm	5-10%	<1	<0,02	Classification free use, local exit.
Sand 0.25-2 mm	60-80%	<1	<0,02	Classification free use, local exit.
Sand 0.125-0.25 mm	10-15%	<3	<1	Classification non-hazardous landfill.
Sludge from water treatment	2-4%	>100	>100	High temperature incineration at FRW (Nyborg)
Purified water	100%	<1	<0,02	Discharge to sewer

Each stream leaving the plant will be subject to a quality control procedure in accordance with specifications from the tender.

7.2.2 Indicative treatment prices

Based on studies performed in the industrial MOPS pilot, some preliminary cost calculations have been made regarding treatment prices of highly contaminated sand from Groyne 42. These prices have been recalculated to indicative treatment price applicable to treatment of the whole Groyne 42 depot, i.e. the total amount of high and low contaminated sand, equivalent to approx. 150 000 tons or 87 000m³ of sand (27 000 highly contaminated and 60 000m³ lightly contaminated). Approximately 20% of the sand is expected to require retreatment, which has been taken into account in the pricing. Planned capacity of the plant is estimated to 30 tons of solid material per hour, annual capacity is approx. 60-120 000 tons, depending on means of operation (e.g. day shift or two shift).

Following categories are included in the cost structure behind the pricing:

- Direct costs, such as electricity, water, chemicals, front loaders, consumables, analytical control etc.
- Transportation of sand from the Groyne depot to the plant area. Distance up to 10km. All internal transportations of sand fractions within the plant area.
- Basic infrastructure costs like storage tents, treatment building, surface coatings, electrical installations, necessary pipe works etc.
- Investment cost of MOPS plant, including demanded water treatment.
- Final transport and treatment of contaminated sludge, approx. 2-4% of feed. Discharge cost of purified water.
- Fixed costs like salaries (operators and supervisors, in total 10 persons) and maintenance costs.
- All support functions needed, like project management, handling of health- quality- safety and environment (HQSE) topics.

Indicative treatment prices do not contain any type of costs related to:

- Excavation, possible reinforcement, water treatment, project management in order to isolate and collect contaminated sand from the Groyne 42 depot.
- Transportation and disposal costs of cleaned sand due to, at this stage, unknown exits.

A density of the sand correlative to 1,8 ton/m³ has been used for the calculations, and the indicative prices are:

- Treatment of highly contaminated sand from Groyne 42 to price of 5100 DKK/m³, total volume 27 000 m³.
- Treatment of all sand inside the Groyne 42 depot to price of 2800 DKK/m³, total volume 87 000 m³.

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Recovery of valuable raw materials and decontamination of highly complex waste products - Multi-purpose On-site Phase Separator

Dette MUDP projekt har resulteret i udvikling og succesfuld demonstration af MOPS teknologien gennem konstruktion og drift af et pilotanlæg opført hos FMC Cheminova Rønland. MOPS er et engelsk akronym, der står for Multi-purpose Onsite Phase Separator, og kan løseligt oversættes til "Fler-formåls, På-stedet Fase-Separator".

MOPS er en nyskabende og konkurrencedygtig teknologi til fjernelse af kontaminerer fra forurenet jord, og har også potentialet for at genvinde værdifulde materialer fra affaldsfraktioner, der ellers ville ende på deponi. Effekten ved MOPS opnås gennem en kombination af mekanisk og kemisk behandling, med enhedsoperationer, eksempelvis vaske- og filtreringsprocesser, udvalgt og kombineret specifikt for at opnå disse oprensningsmål.

Til jordoprensning har teknologien opnået så meget modenhed at den nu er klar til anvendelse inden for større oprensningsprojekter, hvor den kan udgøre et konkurrencedygtigt og miljøvenligt alternativ til høj-temperatur forbrændingen. Til genvinding af værdifulde salte og metaller fra andre affaldsfraktioner har teknologien vist sig lovende, men der er stadig behov for yderligere udvikling.



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