



Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency



Project supported by the European Commission within the Seventh
Framework Programme Grant agreement No. 308645



Revision track

Author	Content	Date of issue
Hannes Herzel	V1	17.03.2015
Hannes Herzel	V2	24.04.2015
Hannes Herzel	V3	30.04.2015

Deliverable D 4.1

Comparative review of ash processes

Work package	WP4 Comparative review of ash processes
Deliverable number	D 4.1
Deliverable title	Technical comparison on the design, operation and performances of ash processes
Due date	Month 24
Actual submission date	04.05.2015
Start date of project	01.09.2012
Participants (Partner short names)	BAM (editor), OTC, FHNW, BSH, ING
Authors in alphabetic order	Christian Adam, Nina Eicher, Ludwig Hermann, Hannes Herzel, Joachim Mallon, Michael Schaaf, Jan Stemann,
Contact for queries	Hannes Herzel Richard-Willstätter-Straße 11, G-12489 Berlin Phone: +49 30 8104 5680 Email: hannes.herzel@bam.de
Dissemination level: (P ublic, R estricted to other P rogrammes P articipants, R estricted to a group specified by the consortium, C onfidential- only for members of the consortium)	PU
Deliverable Status:	Version 3.0

Table of content

Table of content.....	3
List of figures	4
List of tables	4
List of abbreviations.....	4
1 Introduction.....	5
1.1 Objective.....	5
1.2 Sewage sludge ash streams in Europe	5
1.3 P-recovery technologies from sewage sludge ashes	7
2 Background.....	8
2.1 ASH DEC	8
2.2 Leachphos	9
2.3 Mephrec	10
3 Process description.....	11
3.1 ASH DEC	11
3.2 Leachphos	13
3.3 Mephrec	15
4 Mass- und energy balance for ash processes.....	17
4.1 Mass- and energy balance for ASH DEC process	17
4.2 Mass- and energy balance for Leachphos process	19
4.3 Mass- and energy balance for Mephrec process with ash as input material	20
4.4 Mass- and energy balance for Mephrec with dried sludge as input material.....	21
4.5 Product quality	23
5 Comparison of energy demand	25
6 Conclusion	27
7 Reference	30

List of figures

Figure 1: Sludge valorization and disposal routes in Europe 2010	6
Figure 2: Classification of the Phosphorus Recovery Processes from sewage sludge or supernatant	7
Figure 3: ASH DEC reactor scheme	8
Figure 4: Theoretical scheme of the Leachphos process including the main treatment steps.	9
Figure 5: Mephrec reactor scheme and the shaft furnace from the pilot trial 2008 in Freiberg	10
Figure 6: Flow chart for the ASH DEC process	12
Figure 7: Flow chart for the Leachphos process	14
Figure 8: Flow chart for the Mephrec.....	17

List of tables

Table 1: Mass- and energy balance for the ASH DEC process	18
Table 2: Mass- and energy balance for the Leachphos process	19
Table 3: Mass- and energy balance for the Mephrec process with ash as input material.....	20
Table 4: Mass balance for Mephrec process with dried sludge as input material	22
Table 5: Energy balance for Mephrec process with dewatered sludge as input material	22
Table 6: Product quality for ASH DEC, Leachphos and Mephrec process.....	24
Table 7: P _{NAC} -solubility for ASH DEC, Leachphos and Mephrec process.	24
Table 8: Comparison of energy demand for equal conditions.....	26
Table 9: Process specification, benefits and remarks for the processes	29

List of abbreviations

BAT	Best available techniques
DM	Dry matter
LCA	Life cycle assessment
LCC	Life cycle cost
SS	Sewage sludge
SSA	Sewage sludge ash
WWTP	Wastewater treatment plant
MSWI	Municipal Solid Waste Incineration
ESP	Electrostatic precipitator

1 Introduction

1.1 Objective

This report gives technological information about processes for the recovery of phosphorus from sewage sludge ash including mass- and energy balance, process conditions and product quality.

The information in this report aim at giving an overview on different concepts for the recovery of phosphorus from sewage sludge ash and are intended to allow a general qualitative comparison between the different technical approaches. This report also describes the technological backgrounds of the processes that were furthermore investigated by life cycle assessment (LCA) and life cycle cost (LCC) analysis. However, most process data stated in this report are site specific data. The LCA/LCC study includes the definition of a common base line for all processes, detailed process modeling and plausibility assessments. Results of the LCA/LCC-studies are reported in deliverables D9.2 und D10.1.

1.2 Sewage sludge ash streams in Europe

According to figures reported in the Milieu Ltd, WRc and RPA (2010) the total amount of municipal sewage sludge annually produced in Europe is 11,570,000 t dry matter (DM), not providing clear information about data base and a possible share of industrial sewage sludge. For example, an amount of 2,000,000 t sewage sludge is published in this Milieu report for Germany but the German Statistisches Bundesamt (2013) reports 1,751,586 t industrial and 1,887,408 t municipal sewage sludge. In the Netherlands 560,000 t sewage sludge accrue according to Milieu Ltd, WRc and RPA (2010) but cbs Statistics Netherlands (2013) report an amount of 320,000 t municipal sewage sludge.

The utilization of the different disposal pathways for sewage sludge differs strongly from country to country depending on the status of discussions and regional differences in infrastructure. Even in the EU-27 and Switzerland the differences are substantial with Greece landfilling more than 90 % of the sludge, United Kingdom, France and Spain using above 65 % of the sludge in agriculture and the Netherlands and Switzerland incinerating 100 % of the sludge (Figure 1). Germany is one of the countries with a relatively high proportion of incineration with more than 50 %. In average 27 % of the sludge is incinerated in Europe (Milieu Ltd, WRc and RPA 2010). About half of the incineration takes place in Germany and the Netherlands and nearly the complete incineration capacity is located in the EU-15 member states (Germany, Netherlands, United Kingdom, Italy, France, Belgium, Spain, Portugal, and Austria).

The displayed percentage for incineration includes mono-incineration and co-incineration (e.g. Cement Industry, Municipal Waste Incineration, Power Plants). Only ashes from mono-incineration are relevant for the phosphorus recovery strategies because of the high P content. The P content in sewage sludge ashes from municipal sewage sludge have high P content with 10.8 % (mean value) in the Netherlands (CBS Statistics Netherlands 2015) and 8.9 % (mean value) in Germany (Krüger and Adam 2015) but most mono-incineration plants (51 % of total ash amount) incinerate a mixture of municipal and industrial sludge (mean P content 4.9 %) in Germany. Those mono-incineration plants that incinerate municipal sewage sludge only produce 41 % of German total ash amount (Krüger and

Adam 2015). A total amount of ashes in Europe cannot be reported because no reliable data are available and calculations would base on many uncertainties but the ash amount can be calculated for the main sewage sludge ash producers in Europe. The fraction of mono-incineration in the disposal route is 23 % for municipal sludge (Lehrmann 2013), 70 % of municipal sludge amount in the Netherlands (CBS Statistics Netherlands 2015) and 50 % for total sludge amount in Switzerland (Nättrop 2015). These countries have an estimated total ash production about 760,000 t per year from predominantly municipal sewage sludge.

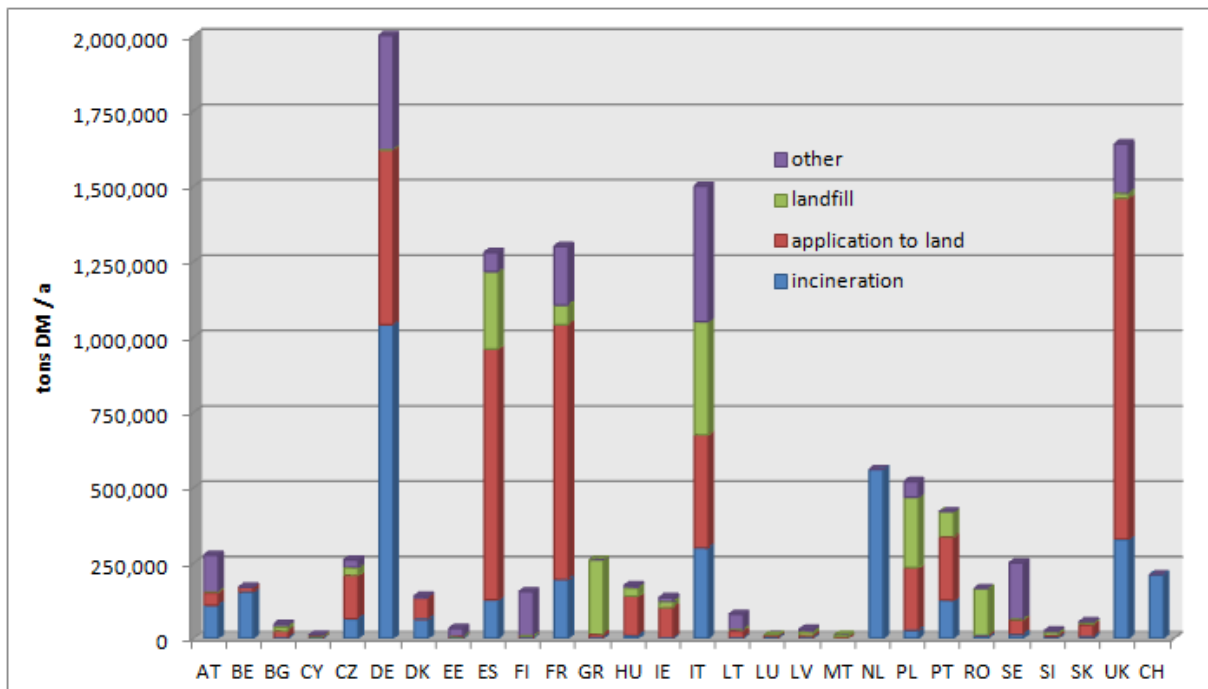


Figure 1: Sludge valorization and disposal routes in Europe 2010 (Milieu Ltd, WRc and RPA 2010)

1.3 P-recovery technologies from sewage sludge ashes

The direct utilization of the sewage sludge ash in agriculture is limited due to heavy metal contents that exceed the limit values of fertilizer regulations (e.g. national fertilizer ordinances). Furthermore, the plant availability of phosphorus in SSA is low and the direct utilization as a fertilizer is questionable. Therefore different P-recovery processes have been developed in Europe. An overview is displayed in Figure 2. Principally, technologies for P-recovery from SSA are based on two different approaches: wet-chemical and thermo-chemical treatment. The P-REX project includes two thermo-chemical processes ASH DEC and Mephrec and two wet-chemical processes Leachphos and EcoPhos. The EcoPhos process is not part of this deliverable as EcoPhos is an associated partner but not part of the P-REX consortium. However, EcoPhos provided their process data and the technology is included in the LCA and LCC studies in separate deliverables D9.2 und D10.1.

An alternative route for P-recovery could be the direct application of sewage sludge ash in the fertilizer industry to substitute the fossil resource phosphate rock. In this way, the available infrastructure and technologies could be used for P-recovery from sewage sludge ashes but the usability depends on the components of the ashes, e.g. the iron content. Until now, P-recovery in the fertilizer industry has been only tested but is not yet established. A positive impulse gave the European company ICL Fertilizers. The company committed to include 15% of phosphorus from secondary sources to their raw-materials until 2015 (Langeveld and ten Wolde 2013).

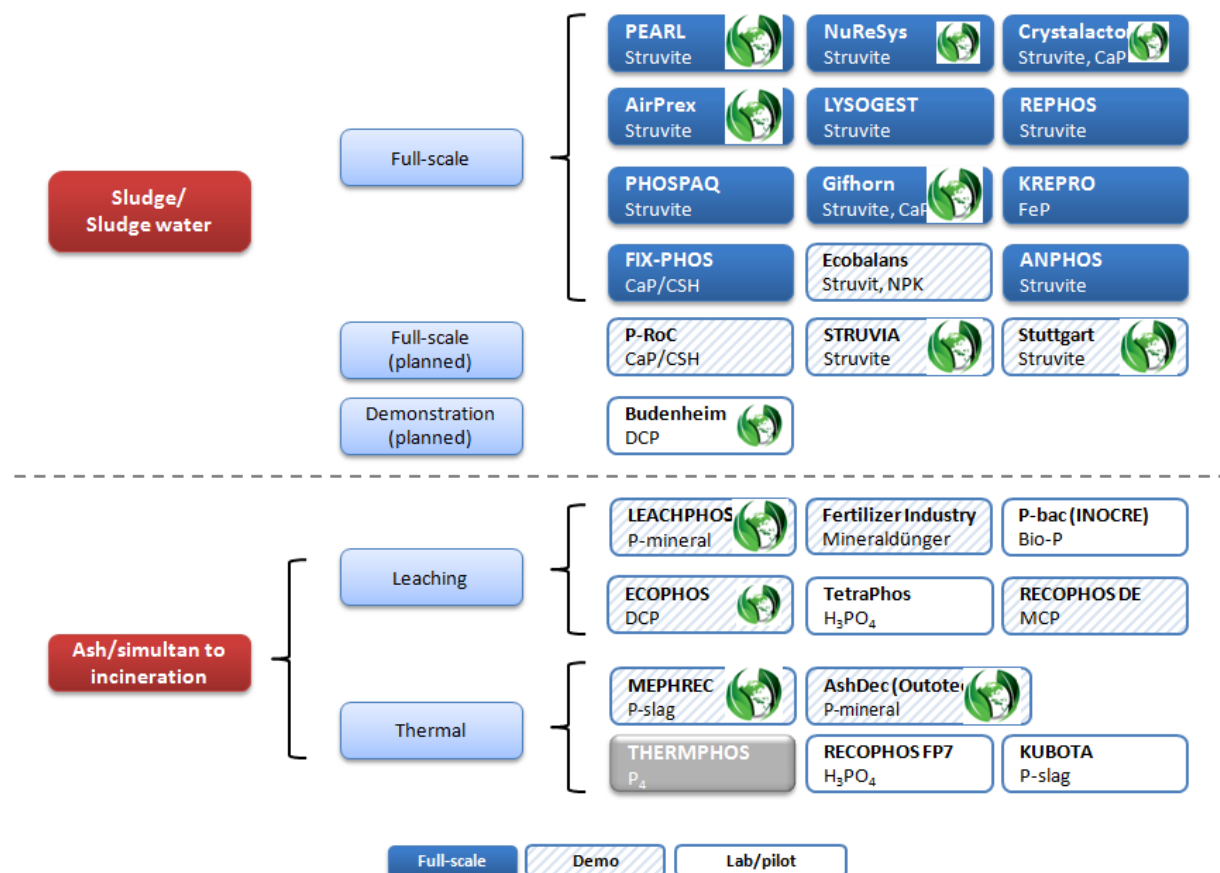


Figure 2: Classification of the Phosphorus Recovery Processes from sewage sludge or supernatant (blue = full scale operation, hatched = demo scale operation, white = lab scale operation)

2 Background

2.1 ASH DEC

The thermochemical treatment of sewage sludge ash (SSA) was mainly developed during the EU-FP6 project SUSAN in the time frame 2005-2008 (contract no. 016079). The thermochemical processing of ash has two main targets: i) heavy metals removal and ii) increase of plant availability of P in the product. The first approach for process design was based on the addition of chlorine donors to SSA and thermal treatment of the mixture at temperatures of 800-1000 °C in a rotary kiln. Volatile heavy metal chlorides and -oxichlorides are formed under these conditions and can be separated from the solid phase via the gas phase. Phosphorus remains in the solid product which is thus purified from volatilized heavy metals such as Cd, Cu, Hg, Pb, Mo, Sn and Zn. Depending on the type of chloride product dosed into the process, the phosphate phases are transformed during the process. The most favourable additive was found to be magnesium chloride as it forms magnesium- and magnesium calcium phosphates that are characterized by higher plant availability than tri-calcium phosphate (whitlockite) and aluminium phosphate (AlPO_4) present in the ashes before treatment. Greenhouse pot- and field experiments with the recycling fertilizers to test their fertilizing effect showed that the MgCl_2 -treated ashes have a good fertilization performance on acidic, but a bad performance on neutral and alkaline soils. New approaches in process design were investigated after the SUSAN project to overcome those drawbacks.

Experiments with sodium bearing additives were carried out in analogy to the known Rhenania-phosphate process that was used for thermal fertilizer production from 1918 until 1982 (Werner 1967). In the Rhenania process soda is used as additive to digest phosphate rock and produce CaNaPO_4 as the major P-bearing mineral phase which is plant available. The same process was successfully tested for sewage sludge ashes. Experiments were carried out under both oxidizing and reducing conditions in order to evaporate some volatile heavy metals such as Cd, Pb and Hg. Because of high price and carbon footprint of soda an alternative additive was found to be sodium sulphate. Several experiments showed that sodium sulphate reacts under reducing conditions with the phosphate phases and forms the targeted CaNaPO_4 . This process was jointly patented by Outotec and BAM (DE 10 2014 108 199.4) and is now the ASH DEC process that is foreseen for industrial application.

The ASH DEC process with sodium sulphate was tested in a 2 week continuous industrial demonstration trial in 2013 with the external company IBU-tec Advanced Material AG in Weimar, Germany. The available kiln was adapted to the requirements for the ASH DEC process. The facilities were suitable for producing fertilizers for field tests and for analysis in compliance with P-REX requirements. A transfer of process parameters (e.g. gas and energy consumption) to an industrial plant is not possible due to the kiln dimension (7000x300 mm) and small capacity (< 40 kg/h).

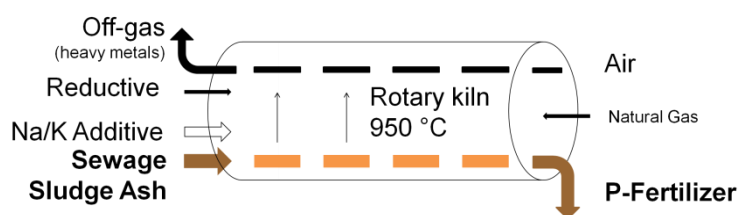


Figure 3: ASH DEC reactor scheme

2.2 Leachphos

The technical feasibility of recovering phosphorous from SSA with the Leachphos Process was tested at industrial scale in winter 2012 in Bern. The process is based on the FLUWA process, a technique to treat fly ash from Municipal Solid Waste Incineration (MSWI) to recover the heavy metals contained in the ash. BSH is experienced with that process at industrial scale for more than 15 years and has implemented this process in twelve MSWI in Switzerland and Europe.

One of the first FLUWA plants was implemented in MSWI Warmbächli in Bern. This MSWI plant was taken out of service as a new MSWI plant has been built at a more suitable location in 2012. The old plant was therefore available for the industrial scale pilot testing of the Leachphos process for a few months. As the Leachphos process is technically similar to the FLUWA process, only a few adjustments and modifications of the existing plant were necessary in order to perform the pilot testing of the Leachphos process on the existing FLUWA plant.

The sewage sludge ash was provided by the mono-incineration plant SVA Hard in Winterthur, Zürich. Between 300 and 400 kg/h of sewage sludge ash were treated and about 80 % of the contained phosphorous was recovered, so that the industrial feasibility of Leachphos was successfully demonstrated and proved. Engineering experience in constructing FLUWA plants is very valuable when planning and constructing a new Leachphos plant. From tests of the technical feasibility, important experiences for the planning and engineering of a Leachphos plant can be derived: I.e. which materials should be used and which filtration, mixing and drying techniques serve best. The main process steps of the Leachphos process are shown in Figure 4.

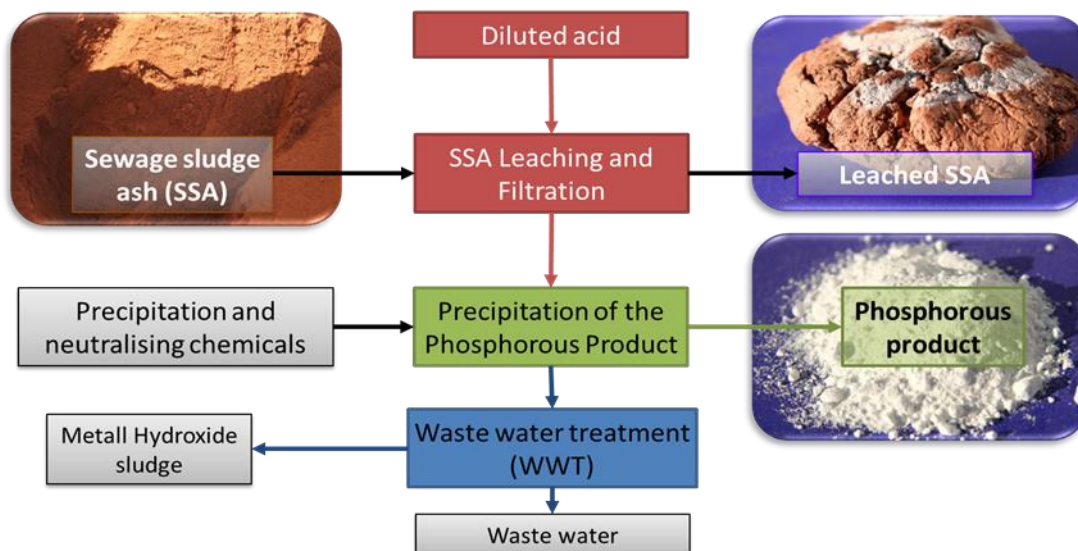


Figure 4: Theoretical scheme of the Leachphos process including the main treatment steps.

2.3 Mephrec

Based on previous experience with “Thomasmehl” production, (calcium-silico-phosphate), produced from slag of the “Thomasstahl” process, a first Mephrec process test with a modified small cupola furnace was executed in 2002 by the company Ingitec. The cupola furnace was fed with briquettes of sewage sludge (SS). The products of the metallurgical process were an raw off-gas with high-calorific value, an iron metallic phase and a liquid phosphorus slag. Analyses showed that the liquid slag (Mephrec slag) has a high solubility of phosphorus in citric acid and a very low content of heavy metals.

The successful first tests were the basic for a project funded by the DBU (AZ 24557; 05.10.2007 - 31.03.2010) for process engineering and cost estimations in laboratory scale. During this project a pilot trial with a modified cupola furnace in Freiberg (Figure 1) used briquetted sewage sludge and sewage sludge ashes as input, producing phosphate slag and a raw off-gas for power generation. The trials proved the feasibility of the principle of smelting gasification technology for integrated recovery of the material and energy from sewage sludge in a single process step. Consequently, the Mephrec process was integrated into the German fertilizer guidelines as “smelting gasification technology” for the production of recycling phosphates.

In general three main concepts for the Mephrec process were developed for process integration:

- 1) Mephrec process located at the site of the WWTP for simultaneous material- and energy utilization from sewage sludge. The energy recovery from high-calorific raw off-gas can be realized either by directly combusting and using the heat in an Organic Rankine Cycle (ORC) process, or multi-stage gas cleaning and use in a combined heat and power (CHP) plant.
- 2) Mephrec process located at the site of a refuse-derived fuel (RDF) plant. The raw off-gas is directly burned in the RDF plant for energy recovery and sub-sequent off-gas cleaning.
- 3) Mephrec process located at the site of a mono-incineration facility for material recovery from the incineration ashes. The raw off-gas of the Mephrec process is directly injected into the mono-incineration facility for off-gas cleaning.

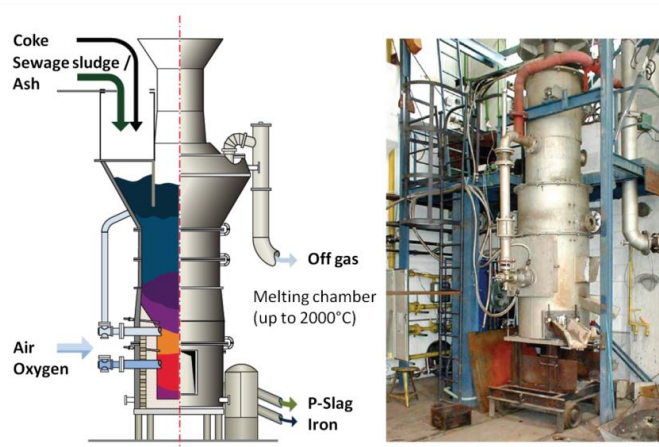


Figure 5: Mephrec reactor scheme and the shaft furnace from the pilot trial 2008 in Freiberg

3 Process description

3.1 ASH DEC

The ash treatment in the ASH DEC plant includes different process steps with thermal treatment at about 900-950 °C in a rotary kiln being the core process. The thermochemical treatment removes heavy metals and increases the plant availability of phosphorus. Finish of the calcined material to marketable fertilizers includes granulation and – preferably – additional nutrients to produce complex fertilizers. Fertilizer finish will not be further explored because of not being a necessary part of the P-recovery process and depending on the actual market requirements in the region where the plant will be built and operated.

An ASH DEC plant could stand alone and being operated as greenfield facility. For economic and ecological reasons it is planned to combine the ASH DEC plant with mono-incineration. The main advantage of the combination is the possibility of feeding hot ash directly from the mono-incineration plant to the ASH DEC facility, thus saving energy and equipment. The ASH DEC off-gas could be integrated with the off-gas treatment in the mono-incineration plant. A potential mono-incineration which could be combined with the ASH DEC plant is the facility in Zurich, currently under construction by Outotec. The energy balance in the report takes into account the benefits of the combined facility.

Three raw materials are used in the ASH DEC process: sewage sludge ash, dried sewage sludge as reducing agent and sodium sulphate. The sewage sludge ash contains 8.5 % phosphorus in the simulation and has a dry matter content of about 99 %. The sodium from the additive sodium sulphate is the reaction partner for the production of CaNaPO_4 in the thermally treated ash. Fresh sodium sulphate input could be partly replaced by recycled sodium sulphate from the mono-incineration. The dried sewage sludge (> 80 % dry matter) is charged in granules and is used as reducing agent in the ASH DEC process for the reduction of sulphate in the sodium sulphate and metal compounds. Without the addition of a reduction agent like sewage sludge or another reducing agent (e.g. coke), sodium sulphate does not react with phosphorus phases in the ash.

The process description takes into account that ash is directly charged as hot ash (>850 °C) from the combined mono-incineration. If the ash is not directly charged from the mono-incineration the used stored ash (100 °C) is pre-heated. The preheated ash and the dried sludge are directly charged to the rotary kiln. The sodium sulphate is preheated by feeding it to the hot kiln off-gas (450 °C) which was purified before in an electrostatic precipitator (ESP). The heated sodium sulphate is separated from the off-gas stream by a cyclone and charged together with sludge and hot ash to the rotary kiln.

The thermal reaction is performed in a directly heated rotary kiln in counter flow. The kiln size depends on the desired throughput. The retention time and transport rate of materials through the kiln can be controlled by varying its slope and speed of rotation. The hottest zone with 900-950 °C is in the last part of the kiln where the burner is installed. The temperature profile in the kiln supports first the decomposition of the cold sludge for reduction and in the hottest part the phase transformation to the desired phosphorus phase. The air input is adjusted for a reducing atmosphere in the material bed and an oxidising atmosphere above the bed. The off-gas is exhausted at the material input side. The air stream in the kiln is adjusted to the required reducing atmosphere.

After cooling, the thermal product is in the form of small granules (formed in the kiln) and may be finished on site or in cooperation with a customer at his site. Because of NP, PK or NPK fertilizers being EU fertilizers in compliance with the current fertilizer Regulation (EC) 2003/2003, complex fertilizers will be the preferred type for placing the ASH DEC product on the market.

The rotary kiln off-gas is cooled to about 450°C and purified in an electrostatic precipitator (ESP). Entrained particles (dust) and removed (now condensed) heavy metals are retained in the filter and discharged to a waste bin. The purified gas is used to pre-heat sodium sulphate and funnelled to the main air pollution control system of the sludge incinerator where remaining pollutants, mainly chlorides and sulphates are removed from the gas. The calculated amount of $\text{Ca}(\text{OH})_2$ is the amount to clean ASH DEC off-gas in the mono-incineration.

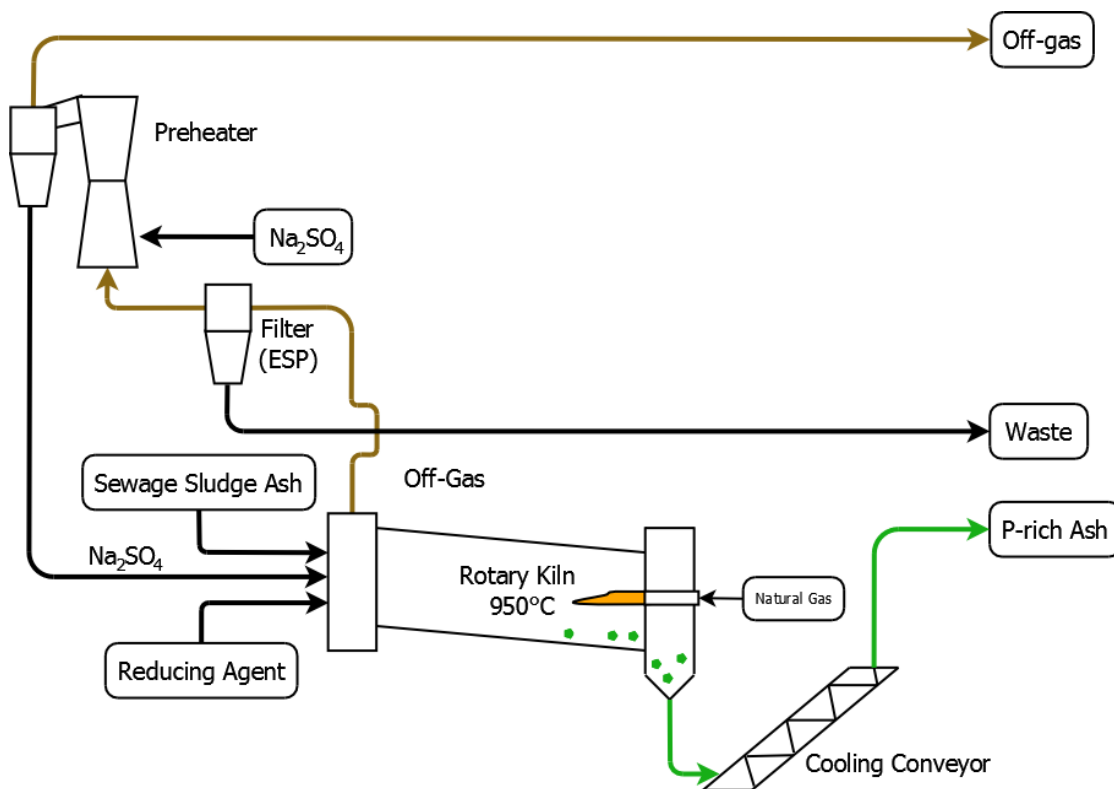


Figure 6: Flow chart for the ASH DEC process

3.2 Leachphos

The Leachphos process is a sequential process with a leaching and a precipitation step. In addition, a decontamination step for removal of selected heavy metals can be included as well, but is not discussed in detail and not included in the process description. The general flow chart of the process is depicted in Figure 7 and the different process steps are discussed below.

The first step is leaching of sewage sludge ash with dilute sulphuric acid. Leaching takes place in a stirred batch reactor for 30-120 minutes. By adjusting the concentration of sulphuric acid and the solid/liquid ratio, the amount of dissolved phosphorus and metals can be varied. Depending on these parameters, about 70-90 % of the phosphorus in the ash is dissolved into the leachate.

The leaching is followed by a solid/liquid separation step. Solid/liquid separation can be carried out on a vacuum belt filter or in a filter press. Vacuum belt filters are operated continuously and generally allow a higher degree of automation. The filter presses, on the other hand, achieve a higher dry matter content and are thus chosen for dewatering in this assessment.

The leached sewage sludge ash filter cake is withdrawn from the process and must be disposed. As the ash cake contains approximately 50 wt-% water, in comparison to the raw ash, the mass of the solid residue increases. If the ash cake contains considerable heavy metal or soluble salt fractions, it is regarded as a waste material and requires landfilling. As landfill gate fees generally are calculated based on the total mass of the material to be landfilled, disposal of wet ash cake residue is unfavourable for process economics.

One potential option is secondary leaching of residual ash cake at higher temperatures and with higher concentrated sulphuric acid. With this additional process step, a material can be produced which fulfils Swiss "inert" and "½-inert" material classification. Thus the material may be disposed at considerably lower cost at dedicated inert landfills or may be even used in cement works. This may enhance the overall process economy considerably. Secondary leaching, however, produces a heavy metal containing diluted acid. In Switzerland such spent acid may be used by the FLUWA process. A disposal route for the spent acid in other locations needs to be established in order to carry out this process step economically.

After solid/liquid separation the phosphorus containing liquid is pumped into a second stirred reactor. In this reactor the dissolved phosphorus is precipitated. This is achieved by dosing of lime (CaO) or caustic soda (NaOH). A higher pH towards the end of the precipitation process results in a higher phosphorus precipitation yield but also in precipitation of dissolved heavy metals. In general lime is considerably cheaper than caustic soda. Formation of gypsum during lime dosing, however, considerably dilutes the product. On the other hand, gypsum forms a distinct filter cake which can be easily dewatered. A product with relatively high phosphorus content (30 % P₂O₅), considerable metal depletion and sufficient dewaterability is thereby produced. The same constraints for solid/liquid separation apply as for ash cake dewatering.

Depending on the precipitation agent, phosphorus is present in different mineral phases. If precipitated mainly with lime, phosphorus is present in the form of calcium phosphate next to aluminium phosphate. First results indicate that phosphate compounds are present in an amorphous form.

After precipitation and separation of the phosphorus product, the liquid waste stream requires additional treatment. Treatment consists of pH elevation to a pH of 9 by dosing of additional lime and

of sulphidic precipitation of metals by an organosulphide precipitation agent, e.g. TMT 15. This is carried out in a third reactor followed by an additional solid/liquid separation step by a filter press. Thus the metals in the wastewater are removed almost completely. Thereafter, the pH in the wastewater is adjusted to a pH of 7 and is discharged either to a WWTP or directly to a receiving water body.

Basic engineering for the Leachphos process was carried out by BSH for a plant with a throughput of 15,000 t of sewage sludge ash per year.

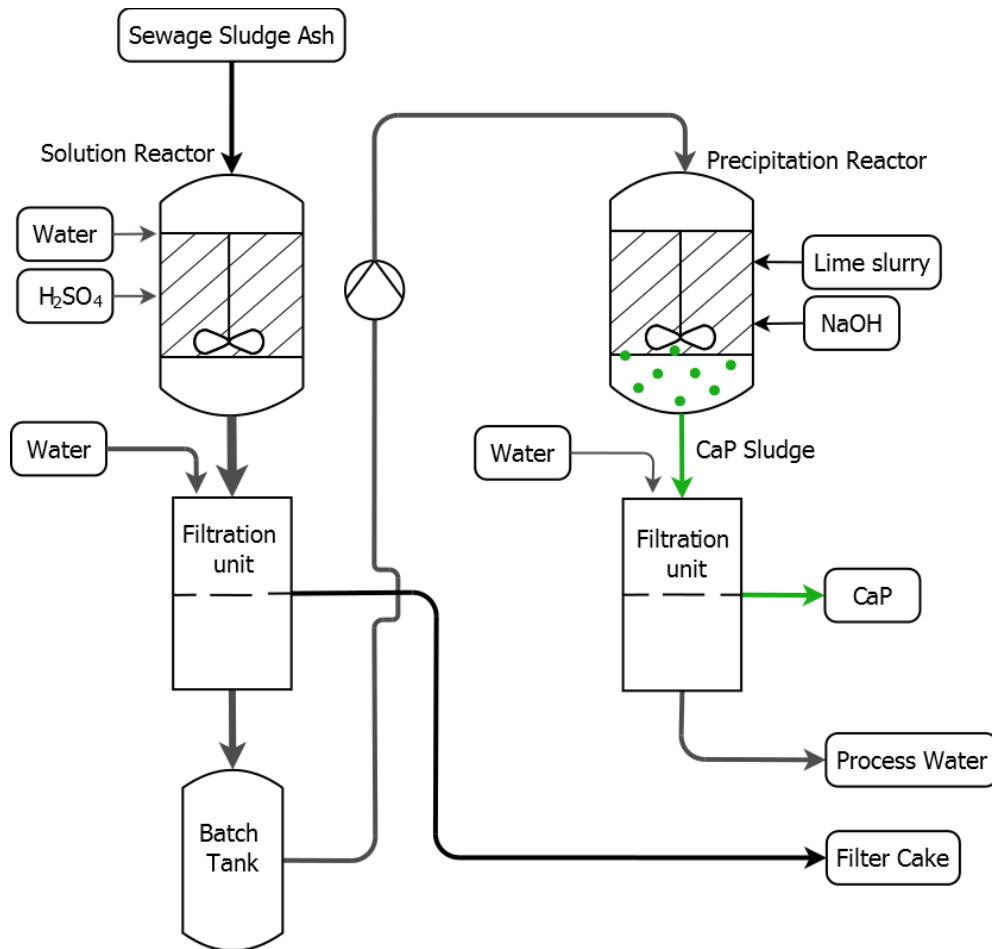


Figure 7: Flow chart for the Leachphos process

3.3 Mephrec

The input materials for the Mephrec process are dried sewage sludge, sewage sludge ash, coke and optionally further additives as slag former (e.g. limestone, cement). The Mephrec process can treat either dried sludge or ash, as well as a mixture of sludge and ash. The composition of the SS and SSA in the Mephrec process model is adapted to the defined composition of SS and SSA which were used in Life Cycle Assessment (LCA) in P-REX. The dewatered SS from the WWTP has a dry matter (DM) content of 25 %. The DM of SS has a volatile solid content of 54 % and contains 4.4 % phosphorus. The SSA contains 9.4 % phosphorus. Further additives, like limestone, could be added in the Mephrec process to modify the smelting process and the product quality.

The Mephrec process works with dried sludge. Therefore dewatered SS (25 % DM) is dried to 80 % DM. The favoured dryers are low-temperature dryer or screw dryer depending on available heat medium. The high heat consumption for drying SS could be partly or completely covered by the raw off-gas energy recovery after the Mephrec process. In general, synergies with combined plants play an important role for the overall energy balance of the Mephrec process. It is planned to cover the total heat consumption of drying SS in case the Mephrec reactor is combined with an RDF plant. The heat production after ORC process and CHP plant (off-gas and cooling water) partly covers the heat demand of drying SS. The energy balance for the drying step is an important factor for the economic feasibility.

The dried SS (80 % DM) is compacted to briquettes with a high pressure press. In case of using SSA as raw material it is mixed with 10 % water in a compulsory mixer before briquetting. During briquetting the raw materials lose about 5 % moisture. Thus the resulting final moisture is 15 % in the sludge briquettes and 5 % in the ash briquettes. The briquettes are then stored in a silo. The briquettes, coke and further additives (e.g. limestone, cement) are balanced and charged in a mixture to the Mephrec reactor via a bucket system. Thus, a quasi-continuously charging of the reactor is guaranteed. The material is charged to the top of the Mephrec reactor. The filling moves from top of the furnace down to the bottom where the liquid metal melt and slag melt separate due to different densities. The furnace inlet is designed to prevent false air getting into the reactor. The filling heats up in the furnace to > 1450 °C. The hottest part is in the nozzle area where the hot air and oxygen are injected. The temperature increases there up to 2000 °C. Below the nozzle area is the hearth zone. Due to the counter-flow set-up, the rising air heats up the filling. Thus, the raw off-gas temperature is cooled down to 200 °C at the raw off-gas outlet. The high density liquid metal melt separates from the slag melt and is on the hearth bottom of the tapping zone where the liquid metal melt is tapped discontinuously. The slag melt continuously flows out of the siphon directly into a water basin. A uniform grain size is produced due to a scraper in the water basin.

The slag contents minimal toxic trace element mass fraction because volatile toxic trace elements (As, Cd, Hg, Pb, Zn) are evaporated and separated via gas phase whereas non-volatile heavy metals (Cr, Cu, Fe, Ni) are separated from the slag in form of a liquid metal phase by density separation. The process step to finish the P-rich slag preparation to marketable fertilizers is not part of this report because it varies by the desired fertiliser quality. It includes granulation and – preferably – additional nutrients to produce complex fertilisers. The metal melt is discontinuously tapped in a mould coquille. The produced iron alloy is enriched in phosphorus and could be sold to metal trader.

The dust could be returned to the Mephrec reactor or should be disposed in case it is enriched with toxic trace elements (Cd, Hg, Pb, Zn). Furthermore, a minor part of the phosphorus transfers into the gas phase because of the reducing condition and high temperature in the kiln. Presumably, phosphorus acid forms in the gas pipelines and could lead to corrosion problems. The amount of gaseous phosphorus and toxic trace elements and a suitable method to separate these compounds will be verified in the pilot plant in Nuremberg, built within the project “KRN-Mephrec” (www.nuernberg.de/internet/krn_mephrec; 11-03-2015).

The raw off-gas from the Mephrec reactor is sucked via a suction chamber. The raw gas utilization depends on the respective raw material input (sludge or ash). The raw gas of the Mephrec process with ash is low caloric. Therefore it is injected directly into the burning chamber of the nearby mono-incineration. Thus, a separate off-gas cleaning facility in the Mephrec process is not necessary.

In case the Mephrec process works with sludge as input material and is equipped with an ORC process, the raw gas is burned in a burning chamber (post-combustion) above the Mephrec reactor, delivering heat to the ORC process. The advantage of the ORC process is that the raw off-gas can be directly used without requiring further treatment to synthesis gas quality, and variation in the raw off-gas composition does not interfere with the ORC process. The heat transfer medium from burned raw off-gas to the ORC process could be thermo-oil or air depending on the type of sludge dryer used and its requirements for heat input.

In case the Mephrec process works with a CHP plant, the raw off-gas is treated in a multi-stage gas cleaning to reach synthesis gas quality. The raw off-gas (200 °C) is cooled down in three steps to 5 °C. The first cooling step is integrated in the suction chamber of the Mephrec reactor. The condensate of dust and hydrocarbons returns to the Mephrec reactor. The condensates of the second and third cooling step are treated as wastewater and disposed into the WWTP. Afterwards the dried and dust free off-gas is cleaned from gaseous toxic substances, such as sulphuric compounds. The synthesis gas needs a well defined and constant quality to fulfil the requirements of a CHP plant.

In case the Mephrec process is connected with an RDF plant, the dust from raw off-gas is separated in a cyclone. The dust-free raw off-gas could be used directly as fuel in the RDF plant. RDF plants have the potential to produce enough heat for the drying process upstream of Mephrec if a heat exchanger is integrated in the off-gas cleaning step.

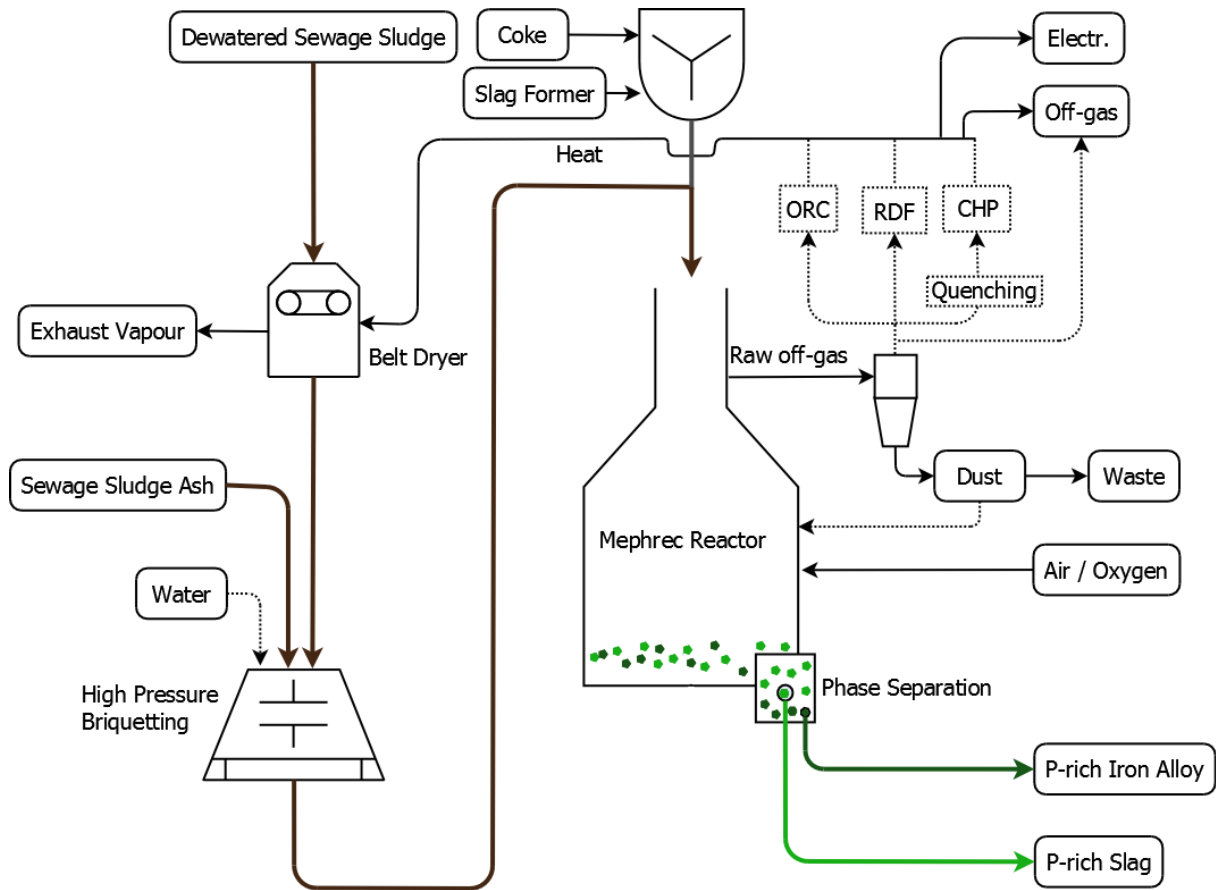


Figure 8: Flow chart for the Mephrec process including different input materials (sludge and ash) and raw off-gas utilization. The raw gas utilization (ORC, RDF and CHP) are relevant sludge is used.

4 Mass- und energy balance for ash processes

4.1 Mass- and energy balance for ASH DEC process

Data for mass- and energy flows given in Table 1 were calculated using Outotec's proprietary thermodynamic simulation software HSC Chemistry® and ASPEN Plus®. Results from laboratory and demonstration trials were used as input parameters for the simulations. The Na_2SO_4 consumption depends on the amount of P and Si in the ash because Si presumably reacts with Na to Na-silicates before CaNaPO_4 will be formed. The three starting materials (ash, sludge and Na_2SO_4) are predominately transferred into a single solid P-bearing product. The resulting overall recovery of phosphorus into the product is 98 %. The amount of P which is not recovered in the product is collected in the filter dust of the off-gas treatment system. The filter residual is contaminated by re-condensed heavy metals and is considered as waste. The calculated input amount of $\text{Ca}(\text{OH})_2$ is required to remove the acidic components of the ASH DEC off-gas which is discharged into the off-gas system of the mono-incineration.

For energy consumption of the ASH DEC process in terms of natural gas and electricity, two scenarios are calculated. Energy consumption of an ASH DEC plant depends on the optional integration into a mono-incineration plant. In case of its integration into mono-incineration, the energy consumption is minimized when hot ash is directly fed into the rotary kiln. Regardless of its integration, an ASH DEC

plant makes use of internal energy cycles to preheat materials, combustion air and – if installed – the dryer for drying fertilizer granules. Energy consumption is given in Table 1 for an integrated plant and a “stand-alone plant” (with ash heating step) representing the lower and upper limits for an ASH DEC plant with an ash flow rate of 1725 kg/h. The energy balance takes into account that the required reducing agent (sewage sludge) is delivered as dried sludge (80 % DM), therefore no energy consumption for drying is considered here.

Table 1: Mass- and energy balance for the ASH DEC process (Energy consumption for integrated and stand-alone option represents the lower and upper limits for energy consumption).

	P content	unit	unit/h		unit/kg ash		unit/kg P _{recovered}	
Input:								
Ash input	8.6 %	kg	1725		-		11.2	
Sludge input (100 % DM)	3.7 %	kg	237		0.14		1.5	
Na₂SO₄		kg	640		0.37		4.2	
Ca(OH)₂		kg	26		0.02		0.2	
Product:								
Output material	6.8 %	kg	2273		1.32		14.8	
P_{recovered}	98 % *	kg	154		0.09		-	
Waste:								
Filter residuum:		kg	43		0.03		0.3	
Energy:			integr.	alone	integr.	alone	integr.	alone
Electricity		kWh	150	180	0.09	0.10	1.0	1.2
Natural gas		Nm ³	67	99	0.04	0.06	0.4	0.6
		kWh	670	990	0.39	0.58	4.4	6.5

* recovery rate of P

4.2 Mass- and energy balance for Leachphos process

Mass flows were derived from lab scale experiments with ash from Winterthur and are stated in Table 2. Experiments were carried out in triplicate at FHNW labs in bench scale (100 g ash per trial). The process was also successfully tested in the demonstration trials from BSH with 40 t ash and further optimized in pilot trials in the pilot plant located at the FHNW. The displayed mass balance cannot be directly transferred to other ashes because the P_{recovery} , acid and base consumptions and product purity depend ash composition. In general, an overall P_{recovery} rate of 70-80 % is targeted. An additional drying of the wet product depends on the further utilization of the product and is not included in the present energy balance. The displayed electricity consumptions were up-scaled from the demonstration trial from BSH and include all relevant aggregates in the Leachphos process. The total wet waste (residual ash cake and precipitate of WWT) should be disposed. BSH developed an inertization step including leaching of residual ash cake at higher temperatures and with higher concentrated sulphuric acid to reduce the metal concentration in the waste and potential disposal costs. This step is not considered in the balance presented in Table 2.

Table 2: Mass- and energy balance for the Leachphos process

	P content	unit	unit/h	unit/kg ash	unit/kg $P_{\text{recovered}}$
Input:					
Ash input	6.3 %	kg	2000	-	22.7
H₂SO₄ (98 %)		kg	760	0.38	8.6
NaOH (50 %)		kg	160	0.08	1.8
Ca(OH)₂ (20 %)		kg	1160	0.58	13.1
TMT 15		kg	0.12	-	-
Water		L	15600	7.80	177.3
Product:					
P-product (40-50 % DM)	5-7 %	kg	1500	0.7	16.9
P-product (100 % DM)	13.1 %	kg	670	0.34	7.6
$P_{\text{recovered}}$	70 % *	kg	88	0.04	-
Waste:					
Residual ash cake (60 % DM)	0.9 %	kg	3380	1.7	38.4
Precipitate of WWT (25 % DM)	3.0 %	kg	250	0.1	2.8
Wastewater		L	16600	8.3	188
Energy:					
Electricity		kWh	212	0.11	2.4

* recovery rate of P

4.3 Mass- and energy balance for Mephrec process with ash as input material

The mass- and energy balances presented in Table 3 are based on trials carried out with the pilot plant in Freiberg, thermodynamic simulation with HSC Chemistry® and assumptions and calculations for planned industrial Mephrec plant. All this input data is taken as basis for an MS Excel-based calculation tool for process engineering. Operation and monitoring of the planned Mephrec plant in Nuremberg is important to verify the assumptions made so far. The theoretical composition of the SSA is based on the reference values defined in LCA of P-REX. The amount of limestone depends on the mass fraction of calcium in the raw material and was not considered in the simulation for the Mephrec process with ash. In contrast to the other ash processes, the Mephrec process has two product streams. The additional produced P-rich iron alloy could be sold to metal traders. The phosphorus distribution in the products is assumed as 80 % in the slag, 15 % in the iron alloy and 4.5 % in the dust. This P distribution is deduced from trials in 2008 in Freiberg, Germany. A proved P distribution can be aspect from the pilot plant in Nuremberg. The electricity consumption is without raw off-gas cleaning because it takes into account the benefits of the combination with a mono-incineration where the raw off-gas could be cleaned in the existing off-gas cleaning system.

Table 3: Mass- and energy balance for the Mephrec process with ash as input material

	P	unit	unit/h	unit/kg ash	unit/kg P _{recovered}
Input:					
Ash input	9.4 %	kg	5000	-	13.4
Coke		kg	830	0.17	2.2
		kWh	7400	1.41	19.9
Dolomite		kg	0	0	0
Pure oxygen		Nm ³	120	0.02	0.3
Product:					
Slag	9.5 %	kg	3960	0.79	10.6
P_{recovered}	80 % *	kg	373	0.07	-
Other Product:					
Iron alloy	9.7 %	kg	710	0.14	1.9
Waste:					
Filter residuum:		kg	100	0.02	0.3
Energy:					
Electricity consumption		kWh	450	0.08	1.2

* recovery rate of P

4.4 Mass- and energy balance for Mephrec with dried sludge as input material

The simulation basis is the same as for the Mephrec process with ash. The Mephrec process with dried sludge as input material is more complex compared to the ash processes because of the additional steps of sludge drying and energy recovery from the raw off-gas. The simulation takes into account that 870 kWh/t H₂O thermal energy and 90 kWh/t H₂O electricity are necessary for drying dewatered sludge (25 % DM) to dried sludge (80 % DM). The sludge briquettes for metallurgical treatment have 85 % dry substance.

Three different systems for energy recovery were considered and compared to each other. The details of integration of ORC process, CHP plant und RDF plant are described in chapter 3.2. The total electricity consumption includes drying, briquetting, Mephrec reactor and off-gas cleaning step. The off-gas cleaning step is not considered for the combination with an RDF plant, because the off-gas is cleaned in the RDF plant. The amount of limestone or dolomite depends on the mass fraction of calcium in the raw material and was considered as 0.04 kg/kg briquette.

The three considered concepts for energy recovery have different benefits in terms of electricity and heat production. The displayed recovery potential was deducted from estimated efficiency factors for each technology. The ORC process has an energy output of 13 % for electricity and 60 % for thermal energy, related to the input heat of the burned raw off-gas. The thermal energy output of the ORC process can then be used for sludge drying. The energy output for CHP plant is 37 % for electricity generation and 46 % for thermal energy related to the total heating value of the raw off-gas. However, realization of a CHP plant for burning Mephrec raw off-gas will involve a multi-stage gas cleaning to fulfil the specific requirements of CHP plants in terms of constant gas quality. The RDF plant generates 20 % electricity from the heating value of the raw off-gas. In addition, the calculation takes into account that RDF plants have the potential to produce enough heat for the sludge drying if a suitable heat exchanger is integrated in the off-gas cleaning step.

For the concepts with ORC process or CHP plant, the produced heat output does not cover the entire heat demand for sludge drying to 80 % DM. The additional heat demand could be covered by the generated heat in the connected WWTP (e.g. CHP plant). The calculated energy balance for the Mephrec plant integrated into an RDF plant has a positive energy balance because the high heat demand of the dryer could be potentially covered by heat from the off-gas system.

Table 4: Mass balance for Mephrec process with dried sludge as input material

	P	unit	unit/h	unit/kg briquette	unit/kg P _{recovered}
Input for drying step:					
Sludge (25 % DM)	1.1 %	kg	9450		
Input for Mephrec process:					
Briquette (85 % DM)	3.7 %	kg	2780	-	33.1
Coke		kg	230	0.08	2.8
		kWh	1900	0.68	22.8
Dolomite		kg	110	0.04	1.3
Pure oxygen		Nm ³	50	0.02	0.6
Product:					
Slag	9.0 %	kg	930	0.33	11.1
P_{recovered}	80 %*	kg	84	0.03	-
Other Product:					
Iron alloy	9.7 %	kg	160	0.06	1.9
Waste:					
Filter residuum:		kg	40	0.01	0.5
Water vapours		Nm ³	6.5		

* Recovery rate of P is deducted from pre-trials 2008.

Table 5: Energy balance for Mephrec process with dewatered sludge as input material

	MWh/h			MWh/kg briquette			MWh/kg P _{recovered}		
	ORC	CHP	RDF	ORC	CHP	RDF	ORC	CHP	RDF
Electricity consumption	1000	1000	820	0.36	0.36	0.29	12.0	12.0	9.8
Electricity production	-900	-2500	-1260	0.32	-0.90	-0.45	-10.8	-30.0	15.1
Net electricity	100	-1500	-440	0.03	-0.54	-0.16	1.2	-18.0	-5.3
Heat consumption	5700	5700	5700	2.05	2.05	2.05	67.9	67.9	67.9
Heat production	-4000	-3100	-5700*	-1.44	-1.12	-2.05	-47.6	-36.9	-67.9
Net heat consumption	1700	2600	0	0.60	0.94	0	19.9	31.2	0

* Heat demand of drying covered by heat recovery in total off-gas of RDF

4.5 Product quality

All analyses were done with delivered milled material according to the German fertilizer guideline. ICP-OES and ICP-MS analyses were done by a robust analysis method which was developed at BAM in the context of a monitoring program for sewage sludge ash (Krüger and Adam 2014). The method comprises microwave digestion of sewage sludge ash with nitric-, fluoric- and perchloric acid. This way the complete solids can be solubilized. The composition of the analysed ashes and products are displayed in Table 6. The P_{NAC} -solubility in Table 7 is the ratio of soluble P in neutral ammonium citrate solution according to DIN EN 15957:2011 and total amount of P.

The product quality and P_{NAC} -solubility for the ASH DEC and Leachphos were analysed from samples ($n=7$) during 40 h production time of the respective demonstration trials for ASH DEC and from samples of the lab scale experiment ($n=3$) for Leachphos, respectively

For the Mephrec process, no product samples are available from the current stage of development. The available samples from the pilot trial of 2008 in Freiberg were strongly diluted by cement input. Thus, the matrix composition given in Table 6 is based on simulation only, but not on real samples from pilot trial. In contrast, the displayed trace elements were analysed from samples taken during the pilot trials in 2008 and give an orientation for the process. However, mass fractions of heavy metals could probably be further reduced in an optimized Mephrec reactor. The samples from the pilot trial 2008 were also used for determination of P_{NAC} -solubility. The low P_{NAC} -solubility of 4 samples from various trials with different input material composition indicates low plant availability of the Mephrec product (Table 7). The P_{NAC} -solubility for one sample could be increased to 80 % by re-melting at 1500 °C and cooling to room temperature at a cooling rate of 200 K/h. This indicates that a slow cooling rate of the P-slag in the Mephrec process could increase the plant availability significantly and thus improve the product quality.

Generally, the sewage sludge ash treated by the ASH DEC process is diluted by the additive sodium sulphate. Thus, all element mass fractions except Na and S are slightly lower (~20 %) in the product compared to the original ash. Additionally, As, Cd, Hg, Pb, Tl and Zn are removed from the solid phase due to transfer to the gas phase under reducing condition. The efficiency of removal of these elements was calculated by the element recovery based on mass balances. Element recovery is defined as the mass flow of an element in the product divided by its mass flow in the input raw ash. Average removal rates of 39 % As, 20 % Cd, 32 % Hg, 61 % Pb, 34 % Tl and 91 % Zn via the gas phase were calculated for the production time. In the same production period the P_{NAC} -solubility was in average 81 % (Table 7). However, in muffle furnace trials for process optimization also P_{NAC} -solubility >90 % were achieved. It can be assumed that this can also be achieved in an industrial process.

The product quality and P_{NAC} -solubility for Leachphos is based on the same lab scale trials as the mass- and energy balances presented in Table 2. Due to the leaching and re-crystallisation step the product quality is not directly comparable to the composition in the ash. It can be noted that for matrix elements especially phosphorus and to a lesser extent also aluminium are transferred to the product. The Ca and S content in the product depends on the amount of added $\text{Ca}(\text{OH})_2$ and H_2SO_4 . The element transfer to the Leachphos product could be evaluated by the element recovery. The recovery rates for Fe, K, Mg and Si are < 15 %, as these elements remain in the ash. Concentrations of the toxicologically relevant trace elements (Cr, Hg, Ni, Tl and Pb) decrease in the range of 5-15 %. U and

Cd are exceptions with recoveries higher than 50 % but it must be noted that concentrations of specifically these elements in the raw ash are approximately one magnitude lower than in conventional fertilizers and thus should not be regarded as critical. Zn, Cu and As recoveries are in the range of 20-40 %.

Table 6: Product quality for ASH DEC, Leachphos and Mephrec process (Product composition is displayed in comparison with the input ashes for ASH DEC- and Leachphos process. Assumed data for Mephrec is shown because no reliable data are available. All analyses were done with dry material.)

	Ash Dec			Leachphos			Mephrec	
	Product quality for demonstration trial (n=7)			Product quality for trials in laboratory scale (n=3)				
	Ash	Product	R ¹⁾	Ash	Product	R ¹⁾	Product	Simulated composition
	%	%	%	%	%	%	%	
Al	6.7	5.2 ± 0.1	-	3.3	3.3 ± 0.2	33	4	
Ca	11.4	9.3 ± 0.1	-	11.9	14.9 ± 0.6	-	12	
Fe	5.9	6.2 ± 0.2	-	12.2	2.5 ± 0.2	7	4	
K	1.5	1.2 ± <0.1	-	0.8	0.3 ± <0.1	12	<1	
Mg	1.6	1.3 ± <0.1	-	1.6	0.8 ± <0.1	15	3	
Na	0.5	12.5 ± 0.8	-	0.5	1.1 ± 0.2	-	<1	
P	9.4	7.7 ± 0.2	98	6.3	13.1 ± 0.6	70	9	
S	0.9	2.6 ± 0.6	-	1.4	4.7 ± 0.3	-	3	
Si	11.4	10.9 ± 0.6	-	11.8	1.9 ± 0.1	5	10	
Ti	0.3	0.3 ± <0.1	-	0.4	0.1 ± <0.1	5	<1	
	mg/kg	mg/kg		mg/kg	mg/kg		mg/kg	Assumed concentration based on pre-trials 2008
As	11	3.6 ± 1.7	39	12	10.1 ± 0.3	29	3	
Cd	2.1	0.3 ± 0.3	20	2.6	3.8 ± 0.2	51	<0.1	
Cr	159	127 ± 5.3	-	109	34 ± 2	11	83	
Cu	767	601 ± 8	-	756	851 ± 28	38	97	
Hg	1.1	0.3 ± 0.1	32	0.4	0.2 ± <0.1	17	<0.1	
Mn	1190	971 ± 18	-	1169	1700 ± 82	49	720	
Ni	73	56.4 ± 3	-	63	13.8 ± <0.1	7	20	
Pb	123	60.1 ± 5	61	142	25 ± 1	6	20	
Tl	0.6	0.2 ± <0.1	34	< 0.1	< 0.1 ± <0.1	-	<0.1	
U	11	7.2 ± 0.1	-	4.9	10.5 ± 0.3	72	5	
Zn	2330	1710 ± 84	91	1980	1390 ± 63	24	79	

¹⁾ Element recovery rate (mass flow of an element in the product divided by its mass flow in the input raw ash)

Table 7: P_{NAC}-solubility for ASH DEC, Leachphos and Mephrec process. Same samples as in Table 6 for ASH DEC and Leachphos. Mephrec samples from pre-trials 2008.

	ASH DEC	Leachphos	Mephrec
P _{NAC} -solubility	81 %	95 %	15 - 45 % (80 %)*

* 15-45 % for 4 samples with different input material (sludge, ash); 80 % after extra heating to 1500° C (cooling rate 200 K/h) for one sample

5 Comparison of energy demand

For comparing the energy balances of the P-recovery processes, the energy consumption was calculated on the basis of the same sludge input, drying parameters and energy output of the mono-incineration (data shown in Table 8). The displayed data are related to the dried sludge (1.5 t dried sludge at 85% DM) or ash produced from its mono-incineration (0.69 t). Data for mono-incineration and P recycling processes are also reported in P-REX work packages for Life Cycle Assessment (LCA) and life cycle costing (LCC) in separate deliverables.

The considered mono-incineration produces heat in form of high pressure steam. The positive heat credit for selected P-recovery processes with energy recovery is balanced against the heat consumption in the P-recovery processes, calculating a net heat balance.

In general, the energy balance of the Leachphos process is insignificant for the economic evaluation. For the ASH DEC process, the overall heat balance is influenced by the energy demand for drying of sludge used as reducing agent. The contemplate concept for the ASH DEC process with an integration into a mono-incineration facility and delivery of dried sludge without surplus energy consumption would reduce the total heat demand up to 50% due to the savings in sludge drying. Overall, the mono-incineration process produces more usable heat than the rotary kiln consumes heat in form of natural gas, giving the combination of ASH DEC and mono-incineration an overall positive heat balance.

The impact of the sludge drying is remarkable for the Mephrec process with dewatered sludge as input material. The produced heat and electricity is consumed by the required sludge drying. The extra demand of energy for sludge drying could probably be reduced or even covered by the combination of Mephrec with a WWTP plant (excess heat of CHP plant) or RDF plant. In case the input sludge could already be received as dried sludge, the drying step could be skipped, and the Mephrec process would profit from selling the produced heat and electricity.

Table 8: Comparison of energy demand for equal conditions. Positive net balances are bold.

		Leachphos	ASH DEC		Mephrec (ash)	Mephrec (sludge)	
			integrated	standalone		ORC	RDF
Input material for P recovery:							
Dry Sludge	kg/h	-	90	90	-	1500	1500
Ash	kg/h	690	650	650	690	-	-
Mono-incineration (BAT):							
Net electricity	kWh/h	190	180	180	190	-	-
Heat production	kWh/h	-800	-750	-750	-800	-	-
Electricity balance in process:							
Electricity production	kWh/h	-	-	-	-	-570	-800
Electricity for process	kWh/h	80	60	70	60	260	150
Electricity for drying	kWh/h	-	20	20	-	370	370
Heat balance in process:							
Heat production	kWh/h	-	-	-	-	-2540	-3620
Heat for drying	kWh/h	-	230	230	-	3620	3620
Natural gas	kWh/h	-	270	400	-	-	-
Coke	kWh/h	-	-	-	1030	1220	1210
Net balance:							
Electricity	kWh/h	80	60	70	60	260	150
Heat	kWh/h	0	270	400	1030	1220	1210
Electricity (incl. sludge drying)	kWh/h	-	80	90	-	60	-280
Heat (incl. sludge drying)	kWh/h	-	500	630	-	2300	1210
Electricity (incl. mono-incineration)	kWh/h	270	240	250	250	-	-
Heat (incl. mono-incineration)	kWh/h	-800	-480	-350	230	-	-

6 Conclusion

The P-recovery processes ASH DEC, Leachphos and Mephrec using ash as starting material are considered in the P-REX assessment of this report. The processes convert the waste product sewage sludge ash to products which could be used as raw materials for P fertilizer. Until now, no industrial plant is in operation of any of the processes. The listed process parameters and data were delivered by the P-REX partners/companies representing the processes ASH DEC (Outotec), Leachphos (BSH Umweltservice) and Mephrec (Ingitec). The process parameters are based on different conditions (e.g. quality of input material, process size) and were partly generated by simulation and/or results of pilot trials. ASH DEC, Leachphos and Mephrec are based on very different types of processes (thermochemical, wet-chemical and metallurgical). Nevertheless, the processes are described in this report on a fairly comparable basis regarding mass- and energy flows. The comparison of the processes in a standardized format will be reported in the P-REX work packages life cycle assessment (LCA) and life cycle costing (LCC) in separate deliverables.

Benefits and remarks for the processes are summarized in Table 9. Process parameters and product quality were secured in pilot studies for the processes ASH DEC and Leachphos. The ASH DEC and Leachphos products are characterized by high P_{NAC} -solubilities (>80 %). This suggests a high plant availability of phosphorus in these products, which was verified by pot experiments, reported on in a separate deliverable (Deliverable D 8.1). The product samples of the Mephrec process used for the agronomic investigations in the P-REX project did not represent the current status of process development. The investigated samples originated from pilot trials carried out in 2008. At that time the quality of the slag product was not in the focus of the investigations. It was shown that a thermal post treatment of the samples with slow cooling is suitable to improve the P-solubility of the samples significantly. The product quality for the Mephrec process will be optimized and evaluated in the planned pilot plant in Nuremberg.

The following conclusions can be drawn for the processes:

- 1) The thermochemical process ASH DEC transfers the input materials predominately into a single solid P-bearing product. Consequently, the process has a high P recovery rate > 95 % and produces only a low amount of waste. The toxic trace elements are removed via gas for elements that form volatile compounds under reducing atmosphere (As, Cd, Hg, Pb, Tl, partly Zn), however Cr, Cu, Ni and predominately Zn remain in the ash and thus in the final output material. The energy demand will be significantly reduced if the ASH DEC process is integrated into a sludge mono-incineration plant. The total energy balance for the ASH DEC process combined with mono-incineration is positive, in case of a sludge incineration with BAT technology for energy recovery.
- 2) The wet-chemical Leachphos process is flexible because the leaching and re-crystallisation step can be adapted to the desired product specification. In general, a higher P recovery rate leads to higher mass fractions of toxic elements in the product, higher waste amount and higher chemical demand. Thus, the mass balance in chapter 4.2 represents an optimum balance between P recovery rate and chemical demand. The Leachphos product accumulates P in the product and has therefore the highest P content in the output material compared to the ASH DEC and Mephrec processes. One critical point is the wet residual filter cake (1.7 kg wet waste/kg ash) which requires disposal or additional treatment.
- 3) The Mephrec process can recover P from sewage sludge and/or ash. The P-bearing slag contains minimal mass fractions of toxic trace elements because volatile toxic trace elements (As, Cd, Hg, Pb, Zn) are evaporated and separated via gas phase, whereas non-volatile heavy metals (e.g. Fe, Cu, Cr, Ni) are separated from the slag in form of a liquid metal phase by density separation. In case of using sludge as input material the Mephrec process includes a sludge drying step and an energy recovery step. An optimal energy recovery minimizes or avoids the import of external energy for sludge drying. Validation and optimization of process parameters is planned in a pilot plant within the project “KRN-Mephrec” (www.nuernberg.de/internet/krn_mephrec; 11-03-2015).

Table 9: Process specification, benefits and remarks for the processes ASH DEC, Leachphos and Mephrec

	ASH DEC	Leachphos	Mephrec
P product:			
P recovery	> 95 %	70-80 %	80 % assumed
P content	5 - 10 %	10 - 20 %	5 - 10 %
P_{NAC}-solubility¹⁾ (plant availability)	High	High	No representative product
Reducing of toxic trace elements	As, Cd, Hg, Pb, Tl	As, Cr, Cu, Hg, Ni, Pb, Tl, Zn	all toxic trace elements
Process:			
Preferred quality of input material	<ul style="list-style-type: none"> • Low toxic trace elements • Low Si • High P 	<ul style="list-style-type: none"> • Low toxic trace elements • Ash with low P content possible 	<ul style="list-style-type: none"> • High P, Fe and Ca • High level of toxic trace elements tolerable
Special benefits	<ul style="list-style-type: none"> • Low waste amount • Acid free fertilizer 	<ul style="list-style-type: none"> • Flexible process • P accumulation in product 	<ul style="list-style-type: none"> • For sludge and ash • Toxic element removal • Iron alloy as by-product • Energy recovery for sludge as input material
Remarks	<ul style="list-style-type: none"> • No removal of Cr, Cu, Ni • Positive energy balance if integrated into sludge incineration plant 	<ul style="list-style-type: none"> • High waste stream or additional treatment of waste 	<ul style="list-style-type: none"> • No actual proved process data and product quality²⁾ • High heat consumption for sludge drying
Status of development	<ul style="list-style-type: none"> • Pilot plant 2008-2010 with MgCl₂-additive (about 1500 t ash) • Pilot study 2014 with Na₂SO₄-additive (4 t ash) 	<ul style="list-style-type: none"> • Pilot study 2012/13 (40 t ash) 	<ul style="list-style-type: none"> • Simulation + pre-pilot trial 2008
Planned operation	<ul style="list-style-type: none"> • Several conceptual studies completed • Implementation pending 	<ul style="list-style-type: none"> • Implementation pending 	<ul style="list-style-type: none"> • Pilot plant 2015/16 (500 t sludge + ash)

¹⁾ P_{NAC}-solubility > 80 %

²⁾ no pilot trial data for energy recovery, P distribution, plant availability

7 Reference

CBS Statistics Netherlands (2015). Urban waste water treatment per province and river basin district, 1981-2013 Statistics Netherlands (CBS), Date Published: 17-03-2015, Date Accessed: 20-04-2015

DE 10 2014 108 199.4. Process for citrate soluble phosphates by calcination of secondary phosphate sources with a sodium-sulfuric compound

Krüger, O., Adam, C. (2014). Monitoring von Klärschlammmonoverbrennungaschen hinsichtlich ihrer Zusammensetzung zur Ermittlung ihrer Rohstoffrückgewinnungspotentiale und zur Erstellung von Referenzmaterial für die Überwachungsanalytik, Forschungskennzahl (UFO-PLAN) 37 11 33 321. Umweltbundesamt.

Krüger, O., Adam, C. (2015). Recovery Potential of German Sewage Sludge Ash. Waste Management; corrected proof, in press.

Langeveld, C.P., ten Wolde, K.W. (2013). Phosphate Recycling in Mineral Fertiliser Production. Proceeding 727, International Fertiliser Society.

Lehrmann, F. (2013). Überblick über die thermische Klärschlammbehandlung – Trocknung, Monoverbrennung und Mitverbrennung. In: Thomé-Kozmiensky, K. J. and Beckmann, M.: Energie aus Abfall, Vol. 10, Neuruppin.

Milieu Ltd, WRc and RPA (2010). Study on the environmental, economic and social impacts of the use of sewage sludge on land, Contract DG ENV.G.4/ETU/2008/0076r.

Nättrop, A. (2015). Regions implementing sustainable phosphorus management Switzerland - Phosphorus flows, policy and perspectives, presentation, Second European Suitable Phosphorus Conference 2015.

Statistisches Bundesamt (2013). Umwelt, Abwasserbehandlung – Klärschlamm – Ergebnisbericht, Erhebungsjahr 2010. Statistisches Bundesamt, Wiesbaden.

Werner, W. (1967). Die Rhenania-Dünger. Monographie über Herstellung, Eigenschaften und Wirkung der Rhenania-Dünger., Verlag M. u. H. Schaper, Hannover, Germany.