

BALTIC 21



Phosphorus Recycling and Good Agricultural Management Practice



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Techniques for P-recovery from waste water, sewage sludge und sewage sludge ashes - an overview

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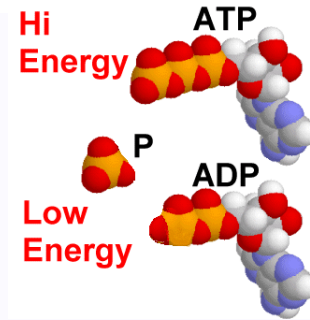
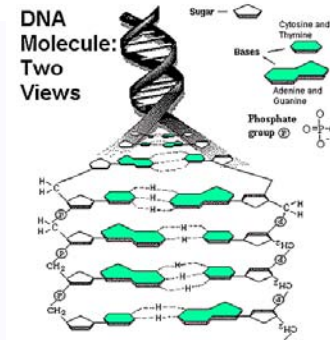


Federal Institute for Materials Research and Testing
Division IV.3 „Waste Treatment and Remedial Engineering“

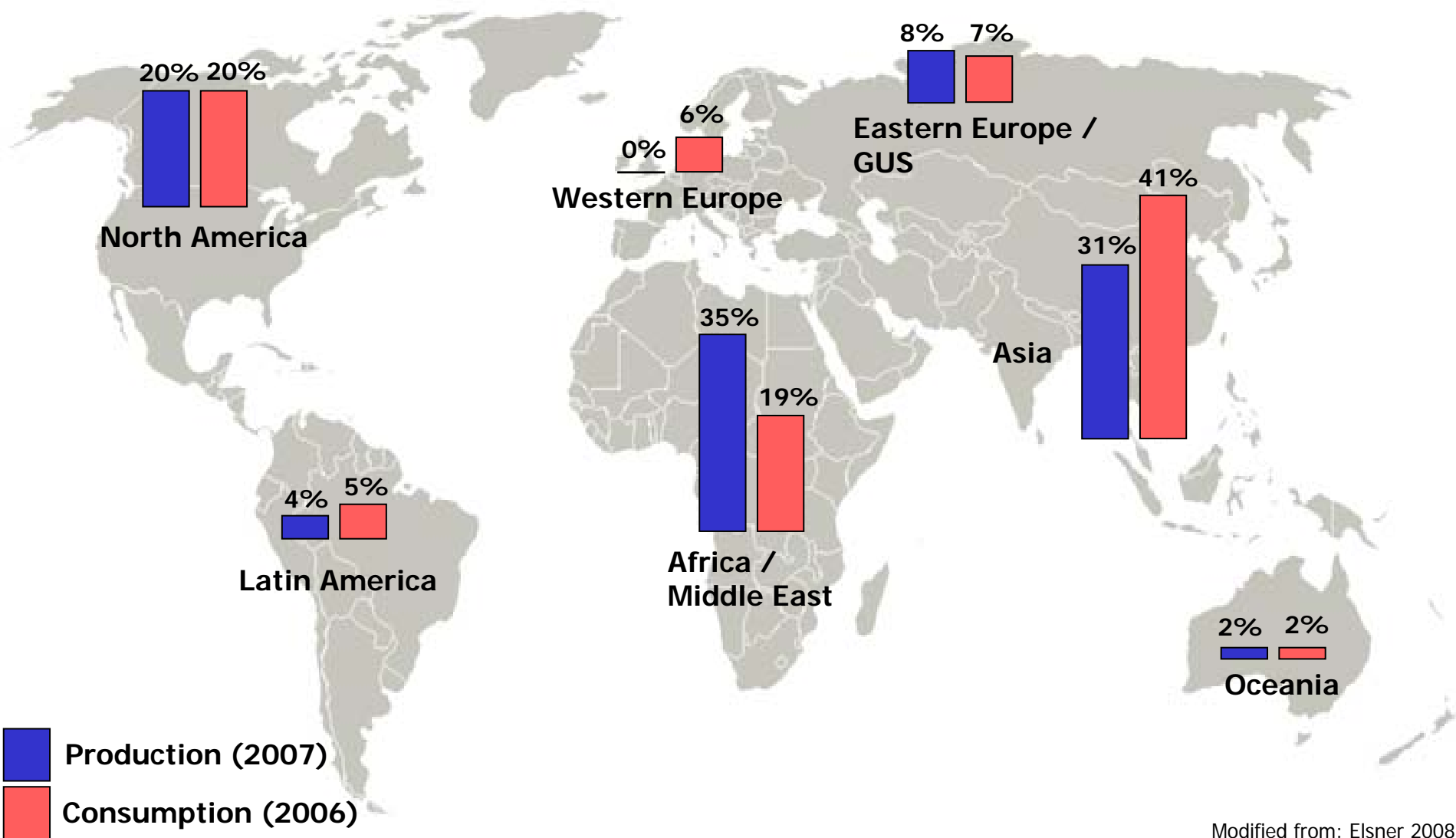
- About Phosphorus
- Possible locations for P-recovery at the WWTP
- Processes for P-recovery from
 - waste water
 - sewage sludge
 - sewage sludge ash
- Characterisation of technologies and recycling products
- Summary

About phosphorus (P)

- P is essential for all living organisms due to its important functions (DNA, RNA, ATP,...,bones,...)
- P is a main element for plant nutrition and essential for crop production
- P is taken up by plants and removed from the fields by harvest. It is required for plant and animal production. Around 150,000 Mg P/a leave the agricultural sector in form of market products (Germany)
- Phosphate rock is a non-renewable resource and its utilisation for fertiliser production bears some environmental disadvantages (current global reserves depleted in 50-100 years)
- Phosphate rock often contains toxic elements like cadmium and uranium
- Waste water is the municipal waste flow with the highest potential for P-recovery (Germany: approx. 60,000 Mg P/a)

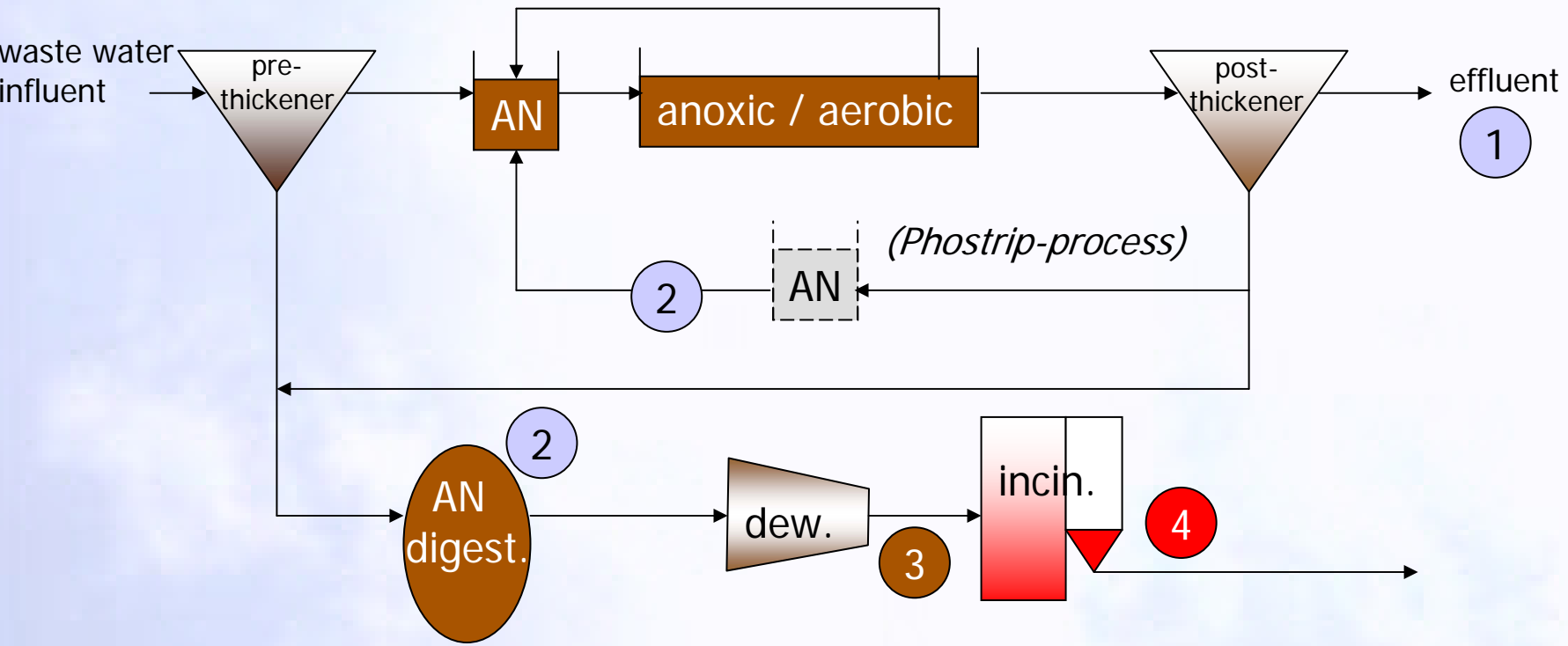


About phosphorus (P) – Production and Consumption



Modified from: Elsner 2008

Possible locations for P-recovery at the WWTP



- ① effluent of WWTP (main stream)
- ② process water / sludge liquor (side stream)
- ③ dewatered sewage sludge
- ④ sewage sludge ash

Characterisation of the different locations for P-recovery

Location	volume-/ mass- flow	relative volume-/ mass-flow	P-conc.	conc. Factor	type of chemical bond	P-recovery potential related to P- influent
1 WWTP effluent (main stream)	200 l/(C·d)	100%	< 5 mg/l	1	Dissolved	max. 55 %
2 sludge liquor (side stream)	1-10 l/(C·d)	0.5-5%	20-100 mg/l	4-20	Dissolved	max. 50 %
3 dewatered excess sludge	0.15 l/(C·d)	0.075%	~ 10 g/kg DM	2,000	biologically -/ chemically bound	~ 90 %
4 sewage sludge ash	0.03 (kg/C·d)	0.015%	64 g/kg	12,800	chemically bound	~ 90 %

Modified from: David Montag 2008, Dissertation, RWTH Aachen

Processes for P-recovery

Watery phase: wastewater (treated) or process water (e.g. sludge liquor)

- Crystallisation**
 - DHV-Crystalactor[®] (*Giesen und De Boer, 2003*)
 - Unitika PHOSNIX[®] (*Ueno und Fujii, 2001*)
 - Ostara PEARL[™] (*Esemag, 2006*)
 - CSH-process Darmstadt (*Petzet, 2009*), P-ROC-process (*Berg, 2005*)
- Precipitation**
 - Process of Berliner Wasserbetriebe / AirPrex (*Heinzmann, 2008*)
 - PRISA-process (*Pinnekamp and Montag, 2007*)

Dewatered (or dried) sewage sludge

- Wet chemical**
 - Seaborne-process or Gifhorn-process (*Versterager, 2003; Müller, 2005*)
- Thermal**
 - Mephrec-process, (dried sludge) (*Scheidig et al., 2009*)

Sewage sludge ash

- Wet chemical**
 - BioCon-process (*Hultman et al., 2003*)
 - SEPHOS-process (*Cornel and Schaum, 2005*)
 - PASCH-process (*Montag et al., 2005; Pinnekamp et al., 2007*)
- Thermal**
 - BAM-/ASH DEC-process (EU-project SUSAN) (*Adam, 2009; Hermann, 2009*)
 - Electro thermal P (Thermphos/SNB) (*Cornel, 2002; Korving and Schipper, 2009*)

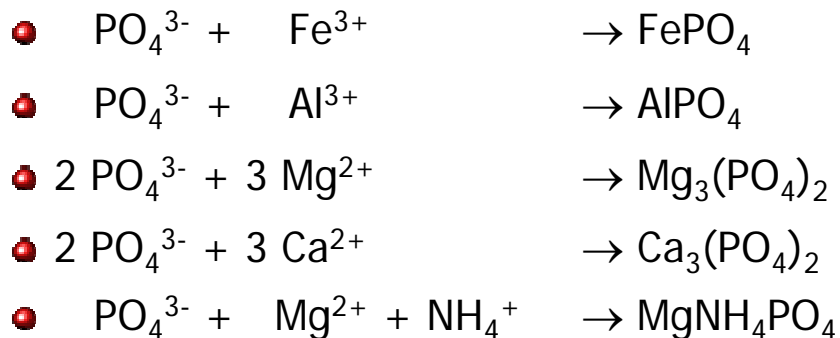
Recovery of dissolved phosphate

Dissolved phosphate ions can be transferred into solid form by

- precipitation
- crystallisation

(crystallisation products generally better defined in composition and less polluted)

Possible (basic) reactions



- FePO_4 not suitable for fertiliser application or electro thermal phosphorus production
- AlPO_4 suitable for electro thermal phosphorus production
- $\text{Mg}_3(\text{PO}_4)_2$ suitable for fertiliser production ?
- $\text{Ca}_3(\text{PO}_4)_2$ low bioavailability; but suitable for electro thermal phosphorus production
- MgNH_4PO_4 suitable as fertiliser; not suitable for electro thermal phosphorus production

Crystallisation of phosphates in industrial scale



Unitika PHOSNIX®

(Ueno und Fujii, 2001)

- fluidised pellet reactor
- seed material generated from recycled pellets (small)
- reference plant
Lake Shinji Eastern
Clarification Center
 - 21 m³/h
 - MgNH₄PO₄ route
utilisation as fertiliser



DHV-Crystalactor®

(Giesen und De Boer, 2003)

- since 1985 P-recovery from wastewater
- fluidised pellet reactor
- seed material is sand
- reference plant Geestmerambacht
 - 250 m³/h
 - Ca₃(PO₄)₂ route
utilisation for electro thermal
phosphorus production at Thermphos



Ostara PEARL™

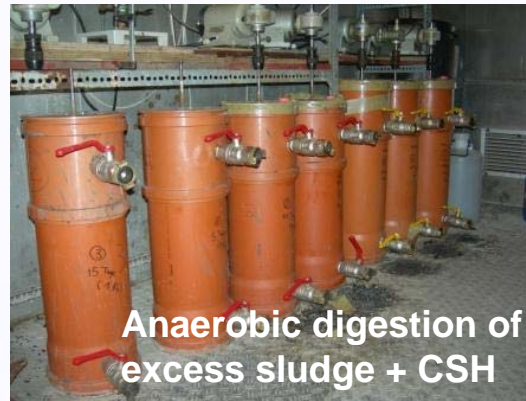
(Esemag, 2006)

- Fluidised pellet reactor
- seed material generated from recycled pellets (small)
- reference plant
Edmonton Gold Bar WWTP
 - 21 m³/h
 - MgNH₄PO₄ route
utilisation as fertiliser Crystal Green™

- Combination with EBPR-plant favourable \Rightarrow side stream processes were established treating highly concentrated process water with 60-100 ppm P
- Separation of sludge and P-loaded sludge liquor before treatment in the crystallisation reactor (except Unitika-PHOSNIX[®])
- Adjustment of **pH** and dosing of **MgCl₂** in the case of **MAP**-crystallisation and addition of **lime** in the case of **Ca₃(PO₄)₂**-crystallisation

Current research on crystallisation processes

Calcium-Silicate-Hydrate (CSH)



Separation of P-loaded CSH from the sludge



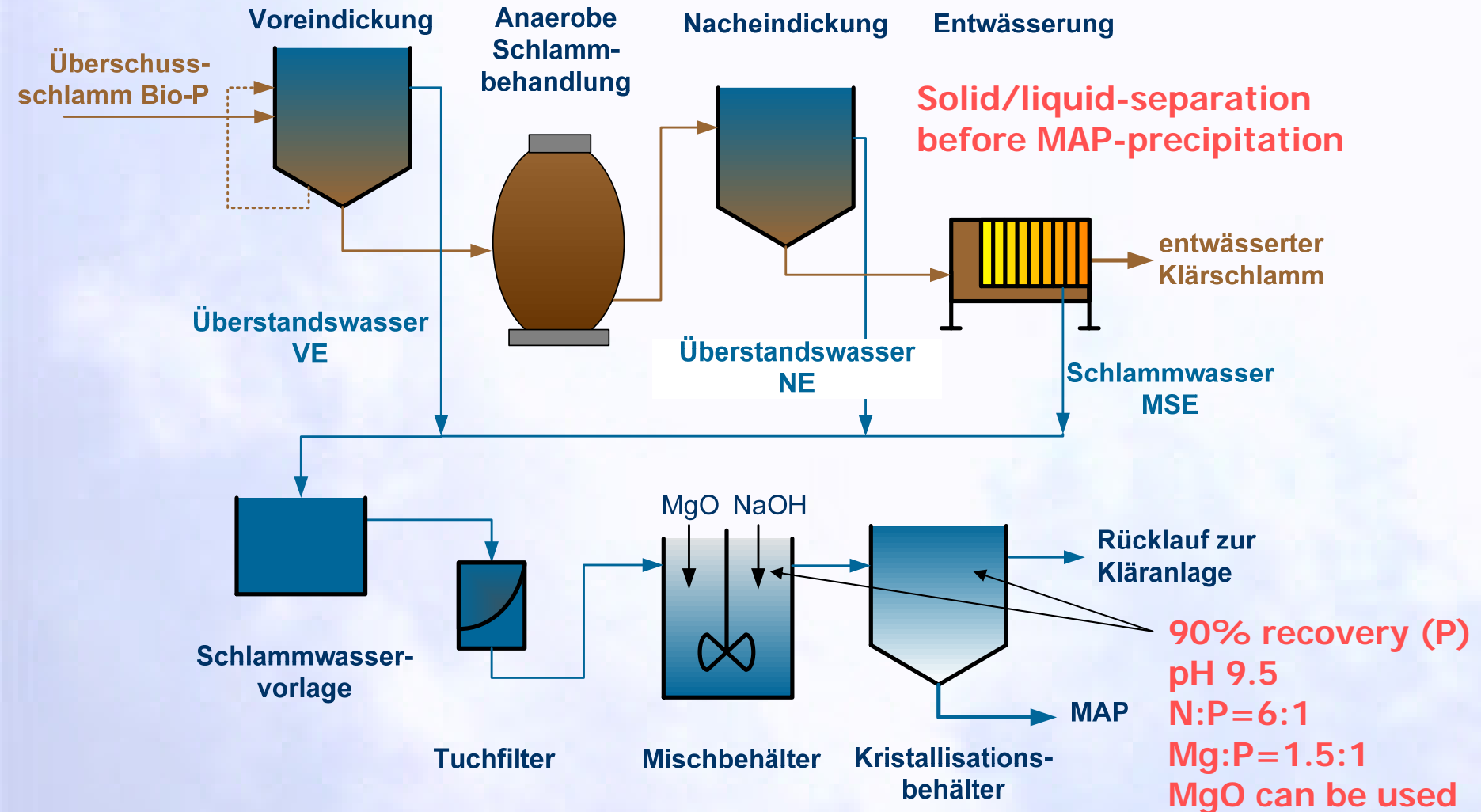
- Basic process P-ROC[©] was developed at Forschungszentrum Karlsruhe (*Berg, 2005*)
- CSH releases Ca^{2+} \Rightarrow crystallisation of hydroxyapatite or brushite on the surface of the CSH pellets (which is kinetically inhibited)
- TU Darmstadt: P-release during anaerobic digestion of excess sludge and in situ crystallisation of Ca-P compounds on CSH pellets
- P-loaded CSH pellets can be removed and used as a raw material for fertiliser production or they remain in the sludge that is subsequently incinerated



TECHNISCHE
UNIVERSITÄT
DARMSTADT

source: *Petzet and Cornel, 2009*

Anaerobic P-release optimised



source: David Montag, 2009

- P is fixed in the sludge in diverse forms (cell material, poly phosphates, Ca-phosphates, Fe-phosphates, Al-phosphates, adsorbed at Fe-oxides and zeolites...)
- Destruction, extraction or transformation of P-compounds required
- Furthermore, P must be separated from pollutants such as heavy metals

Wet-chemical destruction with

(acid, pressure, heat, oxidising agents)

- CAMBI-process (Sievers et al., 2005)
- Aqua Reci process (Stendahl und Jäferström, 2002)
- KREPRO-process, KEMICOND-process (Karlsson, 2001)
- Seaborne-process or Gifhorn-process (Versterager, 2003; Müller, 2005)
- LOPROX-process with subsequent nanofiltration (Blöcher, 2005)

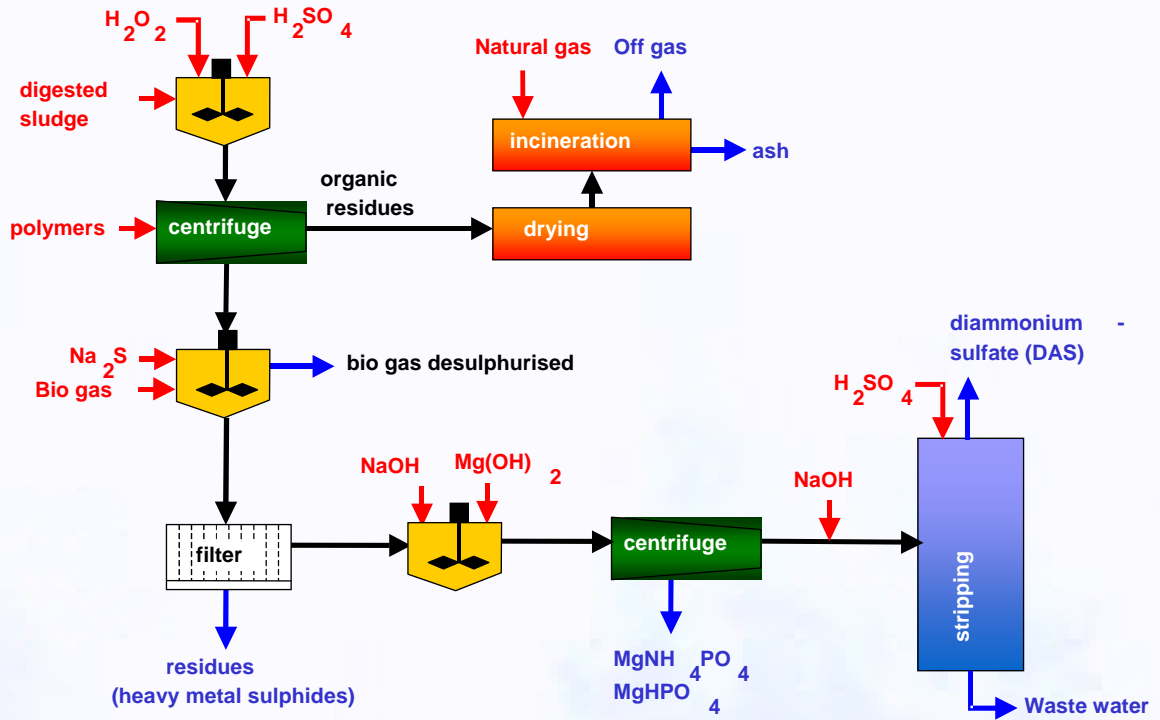
presentation

Thermal destruction

- ATZ-process in a molten iron bath (Mocker and Faulstich, 2005)
- Mephrec-process in a shaft furnace (Scheidig et al., 2007)

poster

"Seaborne-process" – demonstration plant at WWTP Gifhorn



Output of the plant: ca. 1.3 Mg/d mineral./org. N-P-fertiliser
 ca. 1.8 Mg/d liquid N-fertiliser

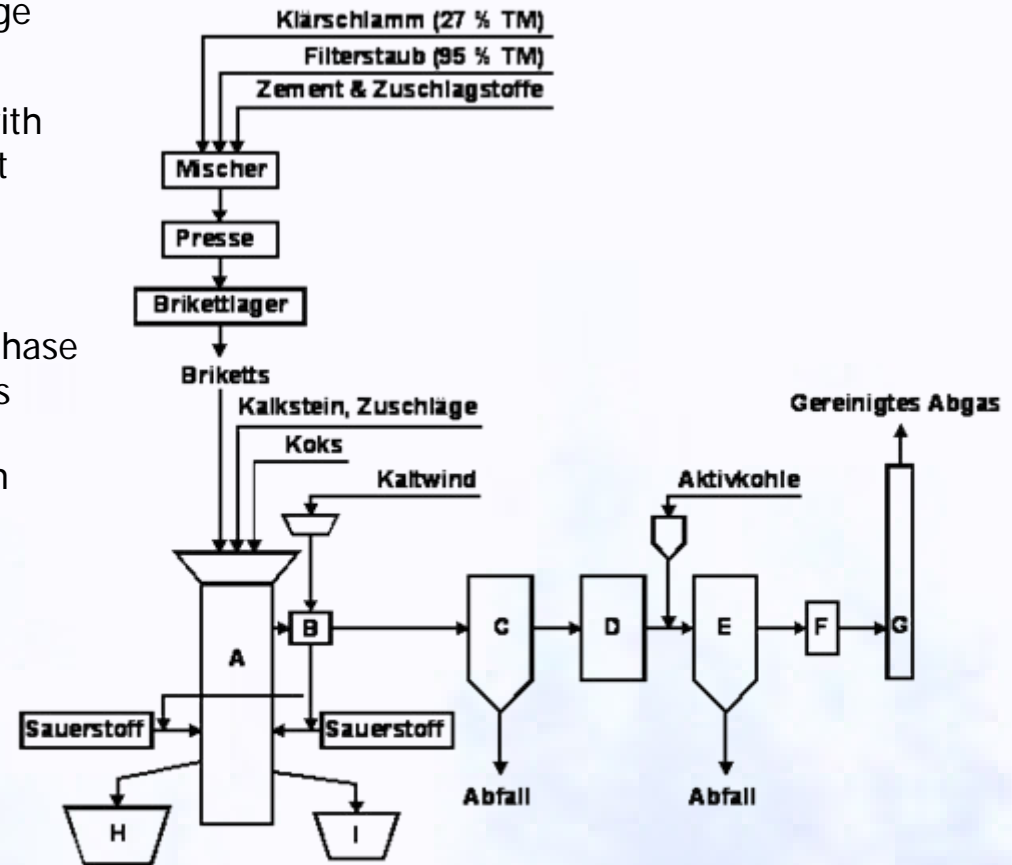
Total cost 7.557 Mio EUR (50% funding)

The demonstration plant is continuously operated since 2007

source: Bayerle, 2008

Mephrec-process, Ingitec (Poster presentation by Dr. Klaus Scheidig)

- **Input:** sewage sludge (dry), sewage sludge ash, meat and bone meal (dry)
- **Process:** briquetting of waste materials with additives and subsequent melting in a shaft furnace (reducing conditions)
 - T up to 2000 °C
 - P-slag tapped at around 1450 °C
 - Fe, Cu, Cr, Ni transferred into metal phase
 - Zn, Cd, Hg, Pb transferred into off gas
- **Product:** 4.6-12 % P₂O₅ (>90% soluble in citric acid); analogy to "Thomasmehl"
mineral phases: Silico-phosphates



Legende

A	Schachtofen	F	Abgasanalyse - Abgaskontrolle
B	vollständige Nachverbrennung / Rekuperator	G	Abgasschornstein
C	Gaswäsche / Sprühabsorber	H	flüssige Schlacke / Granulierung im Wasserbad
D	Nacherwärmung	I	Flüssigmetall / Kokille
E	Gewebefilter		



BAM

IV.3 Waste Treatment and Remedial Engineering

- P is fixed in the sewage sludge ashes mainly in form of $\text{Ca}_3(\text{PO}_4)_2$ and **aluminium phosphates**
- Destruction, extraction or transformation of P-compounds required
- Furthermore, P must be separated from pollutants such as heavy metals

Wet-chemical destruction

acid leaching is a suitable way >90%
However, heavy metals are also dissolved

leaching with water is not possible <1%
leaching with bases is not sufficient <30%

- BioCon-process (Hultmann et al., 2003)

- SEPHOS-process
(Cornel and Schaum, 2005)

- PASCH-process (Montag et al., 2005;
Pinnekamp et al., 2007)

Thermal destruction

- Production of white phosphorus at Thermphos (Korving and Schipper, 2009)

- BAM-/ASH DEC-process (Adam, 2009;
Hermann, 2009)

presentation

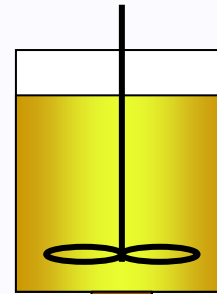
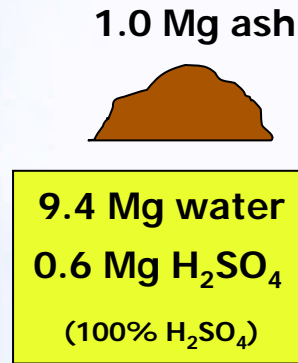
presentations

Acid leaching of phosphates from sewage sludge ashes

Mass flows in the SEPHOS-process

Acid leaching

- also possible with HCl (PASCH)
- >90% P dissolved
- heavy metal precipitation with Na_2S possible (Cu, Cd at pH 1)



2.8 Mg residues
(67% water)
~0.92 Mg dry matter

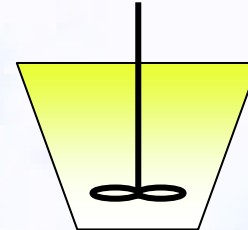
Solid-/liquid-separation



Precipitation of phosphates

- pH 3.5, precipitation of AlPO_4
- AlPO_4 -product can be re-dissolved in NaOH at pH 12-14, heavy metals would be removed as solids, P would be precipitated as Ca-phosphates (extended SEPHOS)

0.3 Mg NaOH
(100% NaOH)



4.0 Mg " AlPO_4 " product
(80% water, 20% SO_3 , 10% Na_2O)
~0.8 Mg dry matter

12% P

4.8 Mg waste water



Source: Christian Schaum, PhD Thesis, TU Darmstadt, 2007

Thermochemical treatment of sewage sludge ashes

BAM- / ASH DEC-process, EU-project



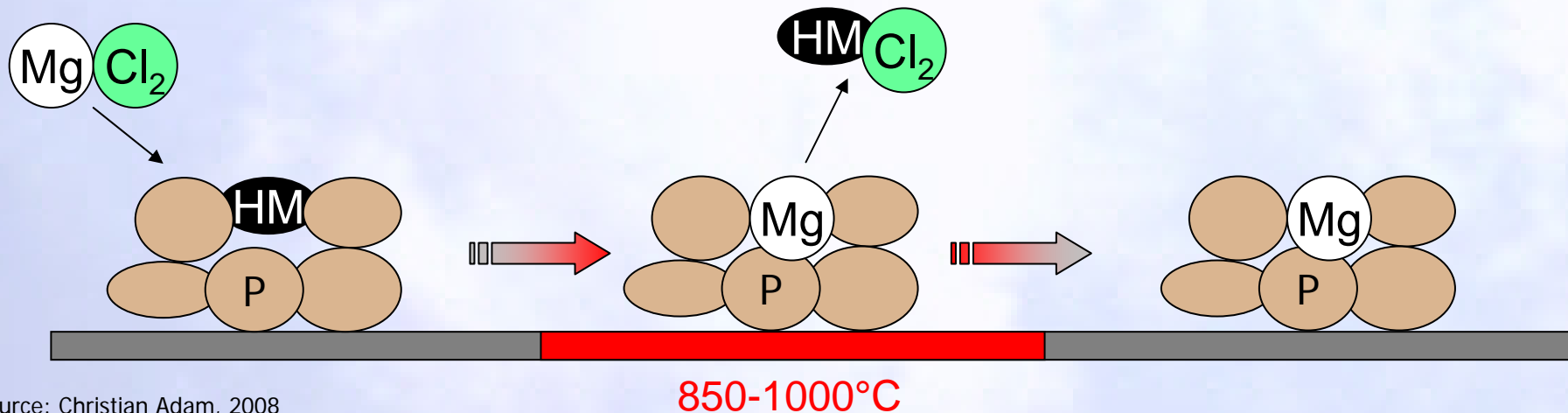
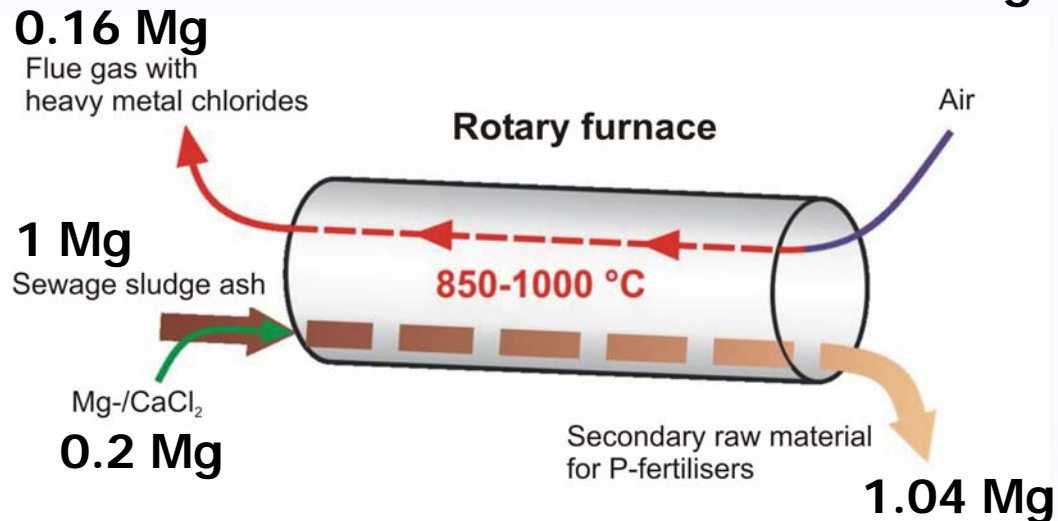
energy demand
600-800 kWh/Mg

- Addition of a Cl-donor
($MgCl_2$ / $CaCl_2$)

- Thermochemical Treatment
at 850-1000°C

1. Formation and evaporation of
volatile heavy metal chlorides

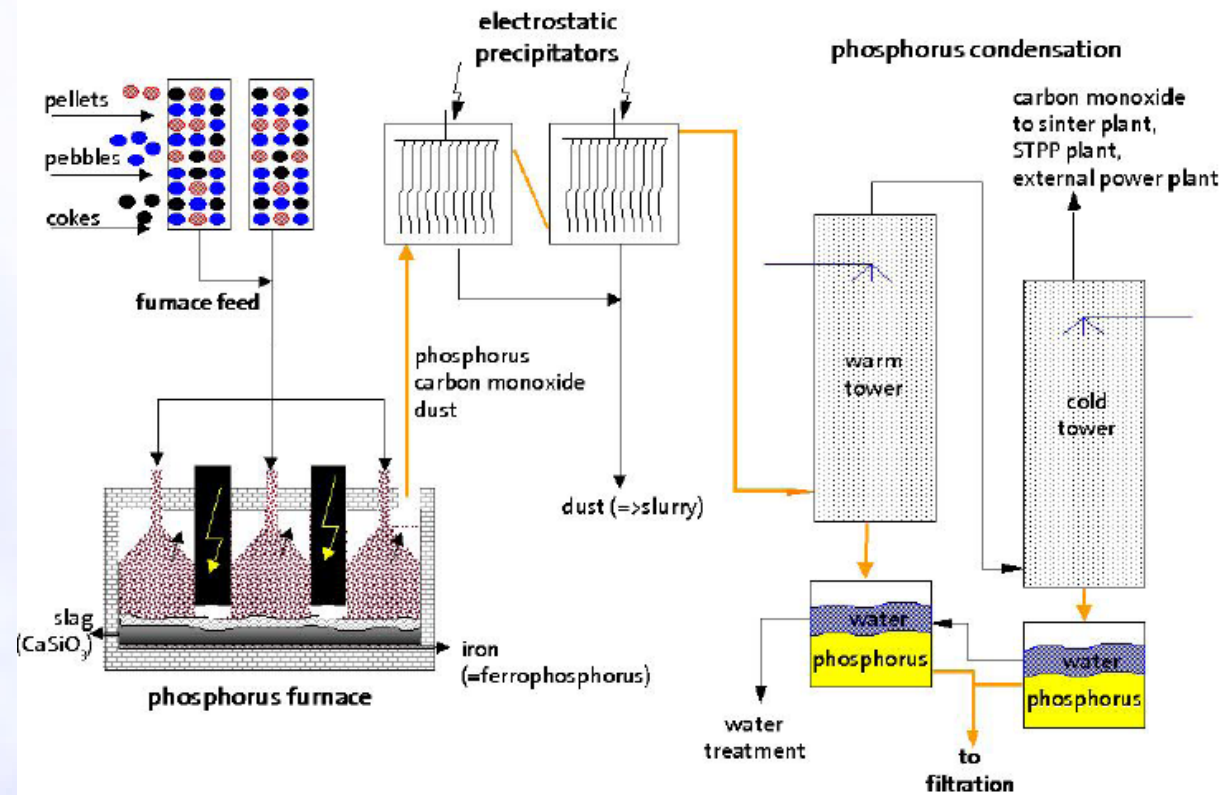
2. Formation of new bioavailable P-bearing
mineral phases such as
 $Mg_3(PO_4)_2$ and $Ca_4Mg_5(PO_4)_6$



Source: Christian Adam, 2008

Electrothermal production of white phosphorus (Thermphos/SNB)

- The company Thermphos (NL) produces white phosphorus from rock phosphate
- Rock phosphate is intended to be partly substituted by sewage sludge ashes
- Problem: Fe, Cu and Zn in the ashes decrease the efficiency of the process (FeP/Fe₂P formation, Cu accumulation in FeP, Zn in filter dust)
- Fe/P < 0.2
- SNB incinerates sewage sludge in separate lines in order to produce ashes with Fe/P < 0.2
- Already 6,400 Mg Fe-low ashes from SNB were used at Thermphos for P-production (630 Mg P)
- Continuation of this cooperation planned



PROCESS	STATUS	PRODUCTS
Watery Phase: waste water (treated) or process water (sludge liquor)		
Crystallisation DHV-Crystalactor® Unitika PHOSNIX® Ostara PEARL™ CSH-process	<ul style="list-style-type: none"> Processes already in industrial scale Operational experience Side stream processing in combination with EBPR-plant (Bio-P) favourable 	<ul style="list-style-type: none"> MgNH₄PO₄ (MAP), or Ca₃(PO₄)₂ High purity by crystallisation possible MAP: not water soluble but bio-available Ca₃(PO₄)₂ suitable for P-industry (Thermphos)
Precipitation BWB/AirPrex, PRISA	<ul style="list-style-type: none"> Demonstration plant (BWB) Applicable in combination with an EBPR-plant (Bio-P) only 	<ul style="list-style-type: none"> MgNH₄PO₄ (MAP) Not as pure as crystallisation products Not water soluble but bio-available
Dewatered (or dried) sewage sludge		
Wet chemical Seaborne/Gifhorn	<ul style="list-style-type: none"> Demonstration plant at WWTP Gifhorn (1.3 Mg NP-fertiliser/d) Seaborne-process had to be simplified 	<ul style="list-style-type: none"> NH₄MgPO₄ / MgHPO₄ and (NH₄)₂SO₄ (DAS) Sold as organic NP-fertiliser Not water soluble but bio-available
Thermal Mephrec	<ul style="list-style-type: none"> Technical-scale trials (300 kg/h) 	<ul style="list-style-type: none"> Calcium-silico-phosphates Not water soluble but bio-available Analogy to the well known "Thomasphosphat"
Sewage sludge ash		
Wet chemical BioCon, SEPHOS, PASCH	<ul style="list-style-type: none"> Lab- and pilot-scale trials 	<ul style="list-style-type: none"> BioCon: phosphoric acid Calcium-, calcium-aluminium-phosphate or magnesium-phosphate Ca- and Mg-phosphates not water soluble but bio-available
Thermal BAM / ASH DEC Thermphos/SNB	<ul style="list-style-type: none"> Pilot-plant in operation (7 Mg/d) Demonstration plant 2010 with a capacity of approx. 15,000 Mg/a Industrial application 	<ul style="list-style-type: none"> Calcium- and magnesium phosphates Not water soluble but bio-available White phosphorus (diverse phosphorus compounds)

Summary

- P-recovery from watery phase by precipitation or crystallisation already implemented in industrial scale (z.B. Crystalactor[®], UNITIKA PHOSNIX[®], OSTARA PEARL[™] etc.)
- Struvite (MAP) is the favoured product with satisfying bio-availability
- The P-recovery potential is limited to 50% of the total P-freight (actual~30%).
Higher recovery rates >90% can only be achieved from sewage sludge or -ashes
- Thermal and wet chemical processes for P-recovery from sewage sludge are currently investigated in technical scale (Mephrec) and in a demonstration facility (Gifhorn)
- The highest P-concentrations are present in the ashes
Wet chemical processes and a thermochemical process were developed
Electro thermal production of white phosphorus is already tested in industrial scale
- Wet chemical processes are tested in lab- und small-scale
- The thermochemical process is tested by ASH DEC Umwelt AG in a pilot plant (7 Mg/d)
An industrial plant (ca. 15,000 Mg/a) is in the planning phase

A sunset scene with a bright sun low on the horizon, casting a golden glow across the sky and reflecting on the water below. A dark horizontal band, possibly a shadow or a design element, runs across the middle of the image.

**Thank you very much
for your attention!**

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