Overview
of process engineering approaches to phosphorus recovery

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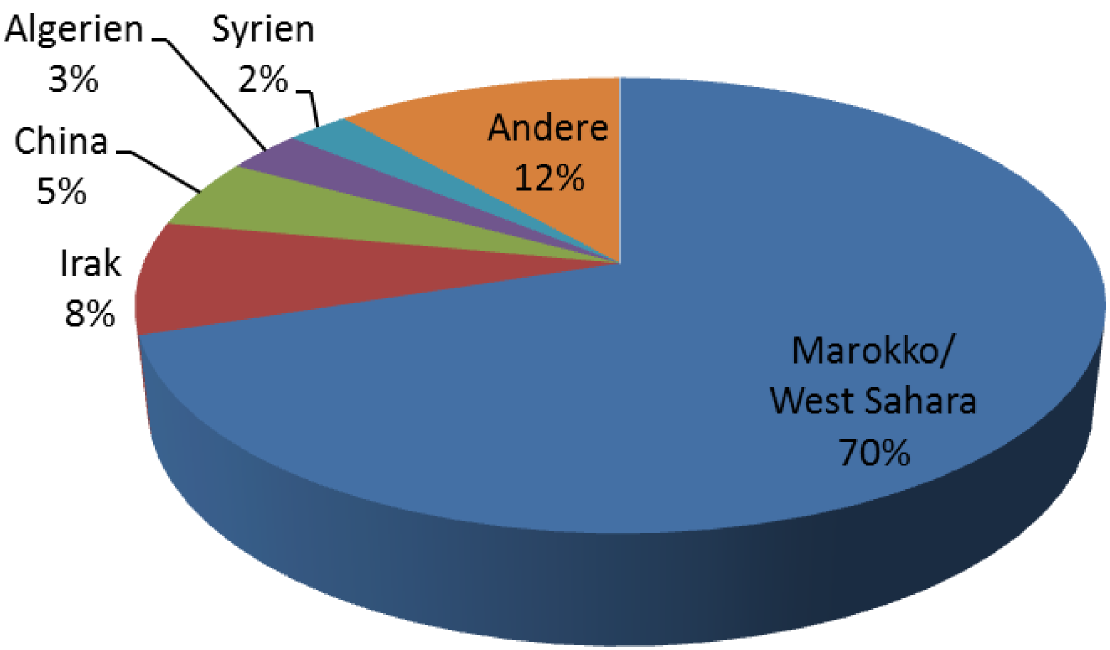
Relevance of phosphorus
Blessing and curse

- Phosphorus: 12th most common element in Earth's crust.
  Bottleneck of life, limits the biomass potential on earth! *Asimov 1959*
- Discovered in 1669 by Hennig Brand, German pharmacist and alchemist
- Phosphorous is essential, not synthesizable, not substitutable
  - ➡ Most important plant nutrient and significant plant fertilisers
- But also a curse!
  - ➡ Esters of phosphorous acids are neurotoxins/ chemical warfare agents (e.g. Sarin)
  - ➡ White phosphorus inserted in lethal gas and fire/incendiary bombs, 1st & 2nd World War and actually?
- Import dependency rate for Germany 100%
- Index of substitutability 0.91
- End-of-life-recycling utilization rate) 0 %

The resource phosphorus



Discussion on range of coverage?
P-mine reserves 2011: 71 billion t
Annual output 2011: ca. 0.2 billion t
Statistical range: 150 - 350 years

- Excavation of geogenic deposits not sustainable
- Actually costs
  - 83,73 €/t P_2O_5 (+8,95%)
- Quality of ores decreases (contaminations Cd, U)

Source: according Kabbe, Kompetenzzentrum Wasser, Berlin

Phosphorus consumption

- **Europe**
  - 90% of phosphorus as fertiliser in agriculture
- **Germany**

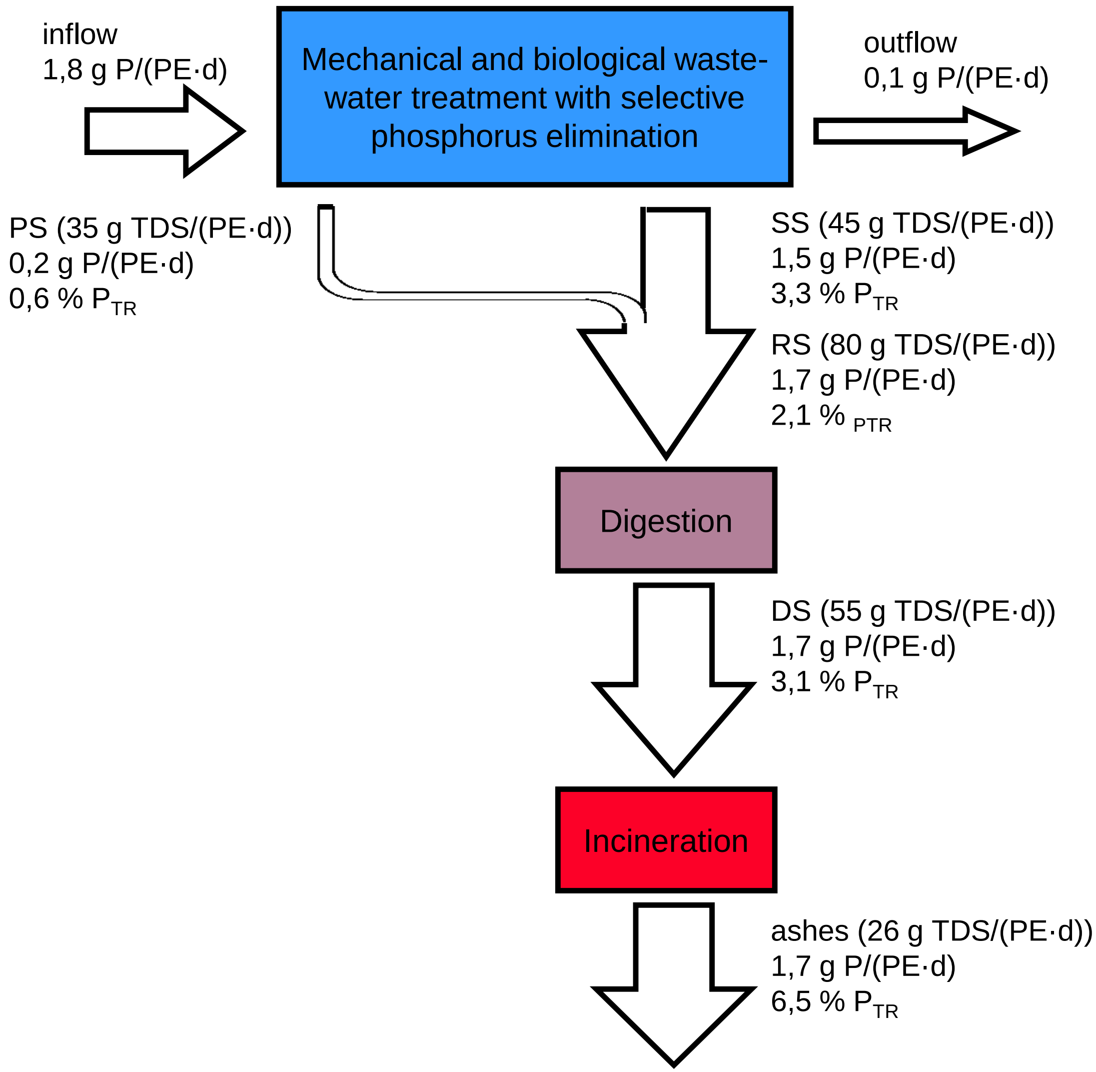
115.000 t P/a as mineral fertiliser	**(ca. 58%)**
50.000 - 37.490 t P/a as animal feedstuff	**(ca. 25%)**
10.000 - 20.000 t P/a as soaps and detergents	**(ca. 8%)**
10.000 - 3.200 t P/a foodstuff and beverages	**(ca. 3,5%)**
Up to 7.750 t P/a metal treatment	**(ca. 3,5%)**
4.300 - 2.230 t P/a water treatment	**(ca. 1,5%)**
4.000 - 1.120 t P/a flame retardants, plasticisers	**(ca. 1,5%)**

- **Recovery potential in Germany**
  - Potential of recovery from WTTP's : 71.714 t/a
  - Theoretically up to ca. 60% of raw phosphate imports substitutable
  - Recycling P by agricultural utilisation of sewage sludge problematical (harmful substances, bioavailability for plants)

Destatis

P-balance model plant (Baltic region Germany)

spec. resultant wastewater 100 l/(PE·d)

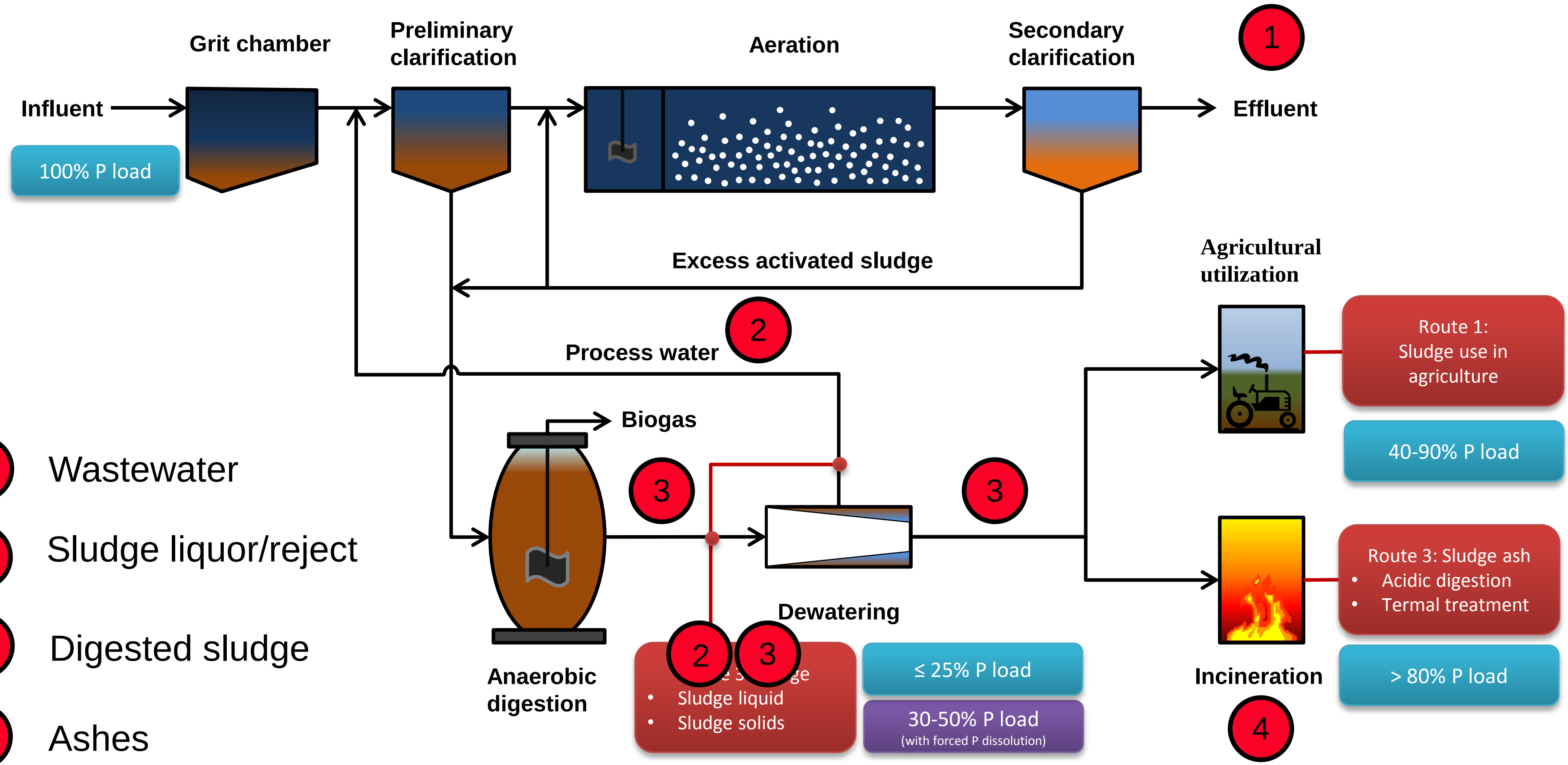


German new sludge strategy for P-Recovery„Klärschlammverordnung“

- WWTPs with a capacity > 100.000 PE
  - ➡ have to recover phosphorus after a transition period of 12 years
- WWTPs with a capacity > 50.000 PE
  - ➡ have to recover phosphorus after a transition period of 15 years
- Direct use of sewage sludge as fertilizer is not allowed after the transition period of 12/15 years
  - ➡ Exemptions for small and medium WWTP ➔ agricultural use possible
- Objectives for phosphorus recovery:
  - ➡ At least 50 % extraction efficiency
  - ➡ Lowering the P-Content < 20 g P/TDS
  - ➡ No co-incineration of sludges containing > 20 g P/TDS

Bergs 2018

Hot spots for P-recovery from municipal wastewater



1 Wastewater

2 Sludge liquor/reject

3 Digested sludge

4 Ashes

Kabbe, 2017

Processes for P-recovery

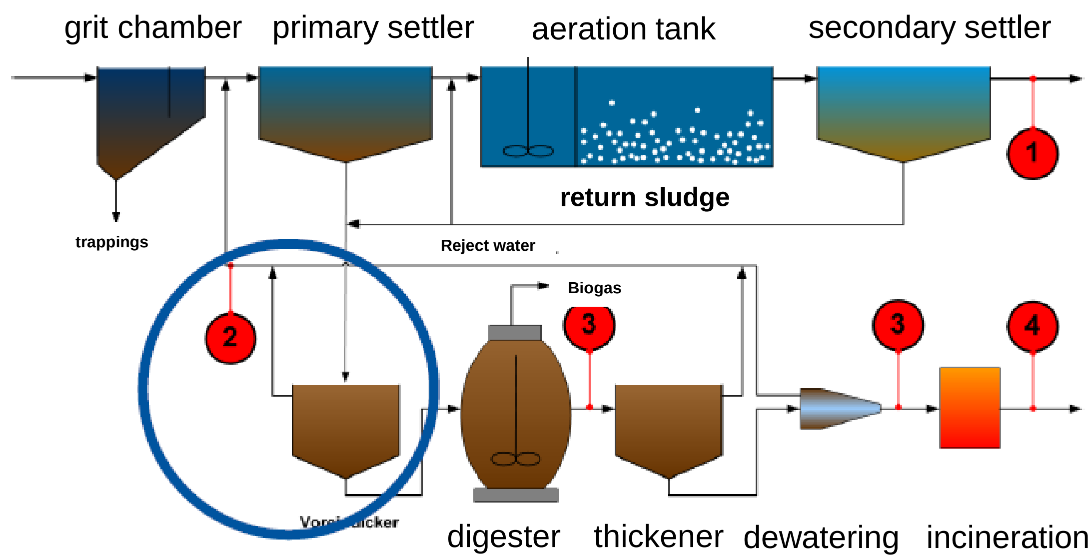
Full-scale | Demo / Pilot | Lab

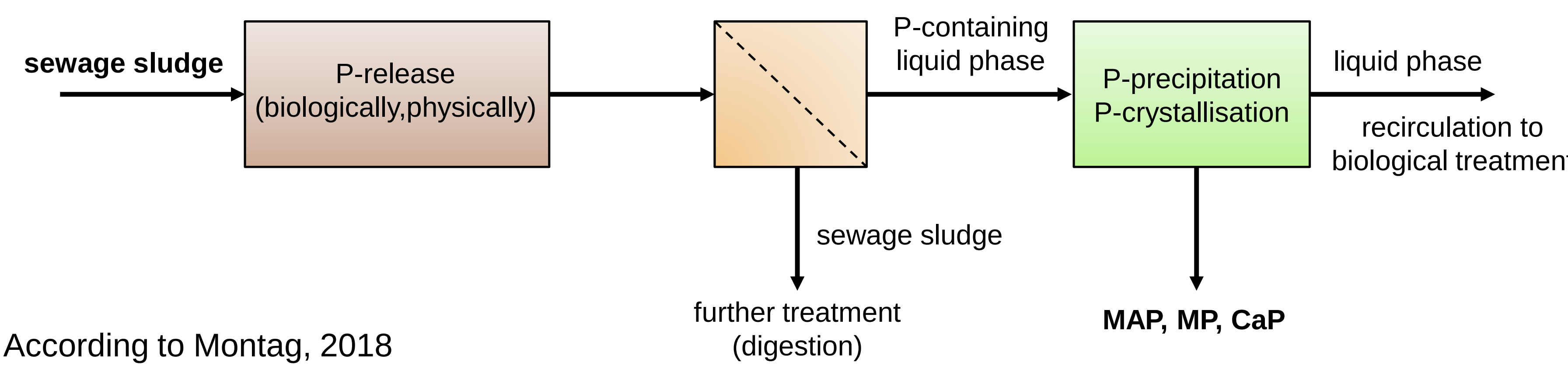
- **Wet sludge/ process water at WWTP site**
  - Liquid phase (ortho-P dissolved)
    - PEARL – Struvit
    - AirPrex – Struvit
    - NuReSys – Struvit
    - PHOSPAQ – Struvit
    - ANPHOS – Struvit
    - REPHOS – Struvit
    - PhosphoGreen – Struvit
    - STRUVIA – Struvit
    - NutriTec – Struvit, DAS
    - Naskeo – Struvit
    - PHORWater – Struvit
    - P-RoC – Struvit, CSH
  - After accelerated P-release
    - Budenheim – EXTRAPHOS® DCP
    - Gifhorn – Struvit/CaP
    - Stuttgart – Struvit
    - LYSOGEST
    - WASSTRIP
    - TDH (allgemein)
- **Thermal after WWTP Sludge and ash**
  - Wet-chemical ash disintegration
    - DüM-Industrie – Mineraldünger
    - Elektrodialyse – H_3PO_4
    - LEACHPHOS – H_3PO_4
    - ECOPHOS – H_3PO_4/DCP
    - TetraPhos – H_3PO_4
    - RECOPHOS DE – MCP
  - Thermal (pre-) treatment
    - MEPHREC – P-Schlacke
    - AshDec (Outotec) – $CaNaPO_4$
    - PYREG – P-reiches Pyrolysat
    - THERMPHOS – P_4 †
    - RecoPhos FP7/ICL – H_3PO_4/P_4
    - KUBOTA – P-Schlacke

According to Kabbe 2017

P-recovery from sewage sludge
Sludge liquor/sewage sludge

- Examples for processes
  - Parforce
  - PEARL
  - PRISA
  - P-RoC
  - PhosphoGreen



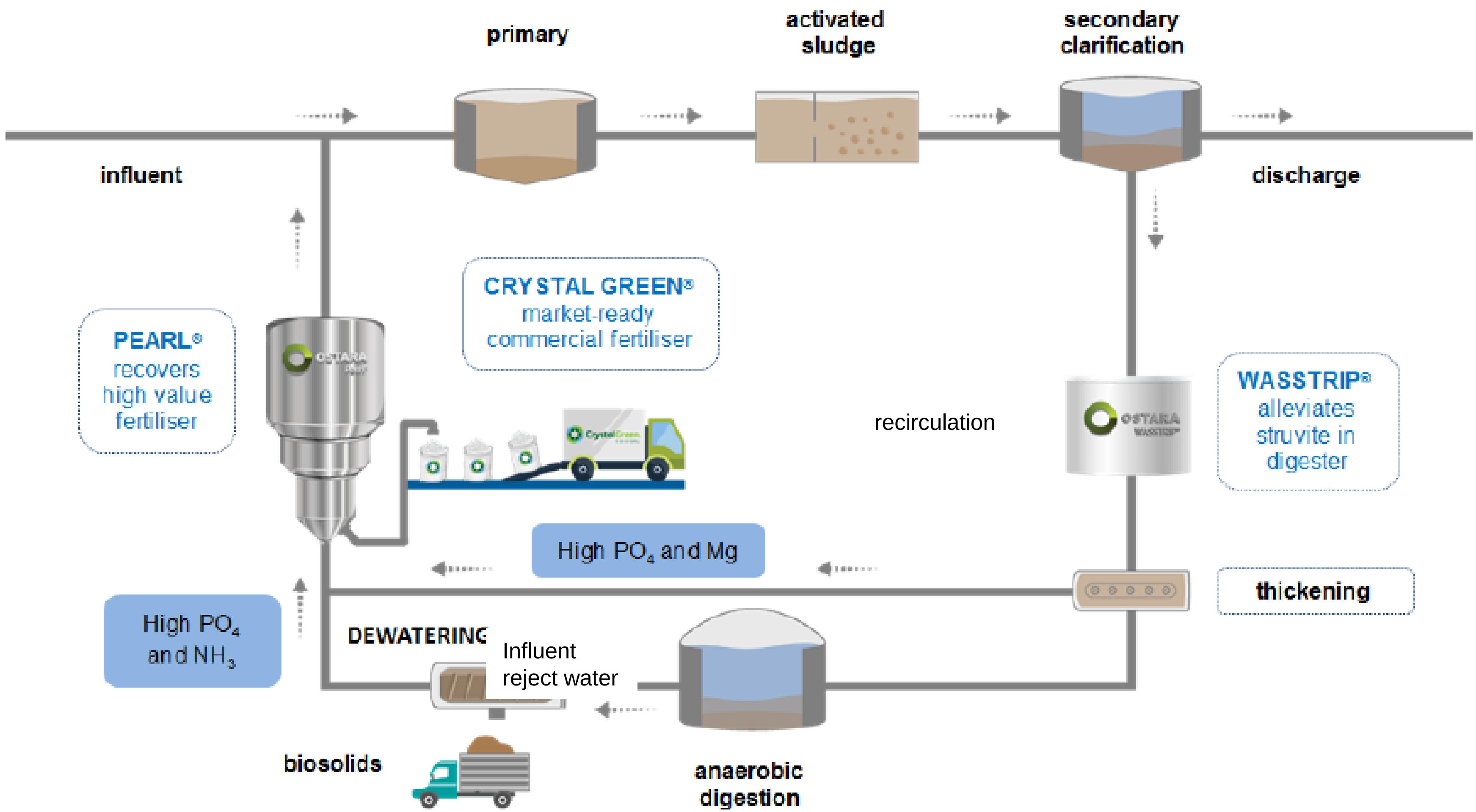


According to Montag, 2018

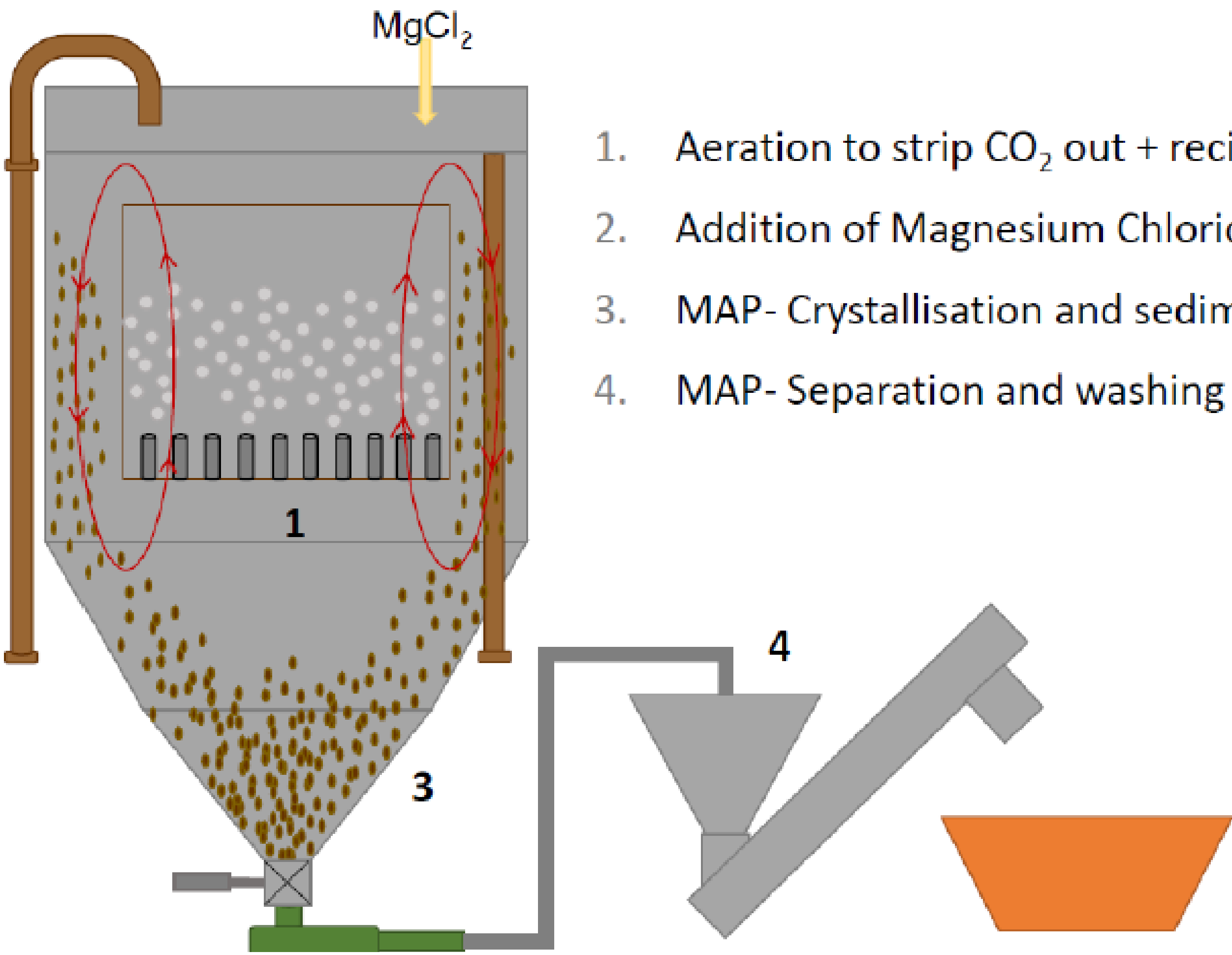
Pearl and Wasstrip process

$Mg_2^+ + NH_4^+ + PO_4^{3-} + 6\ H_2O \rightarrow MgNH_4PO_4 \bullet 6\ H_2O$

Recovery potential 30%

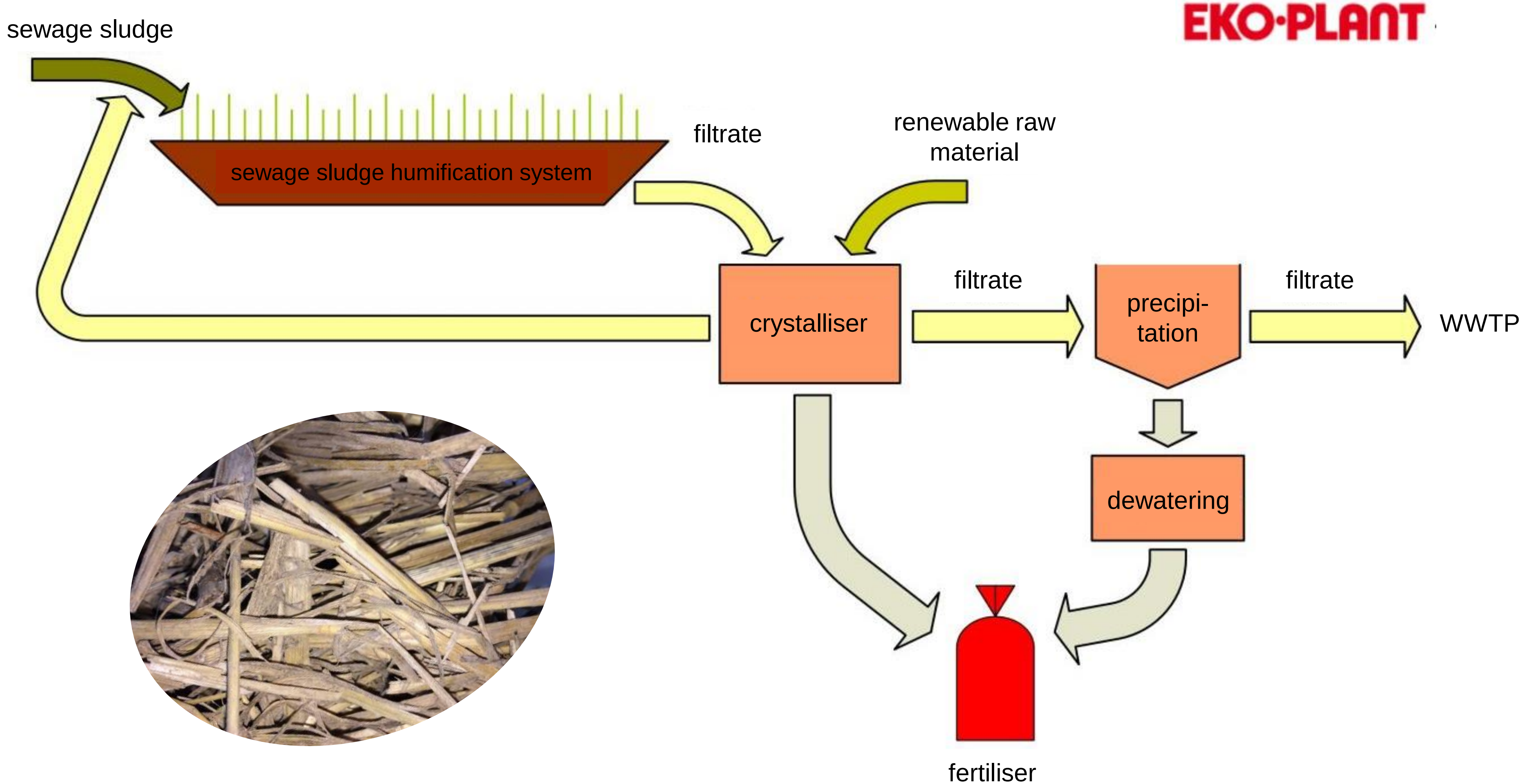


AirPrex process



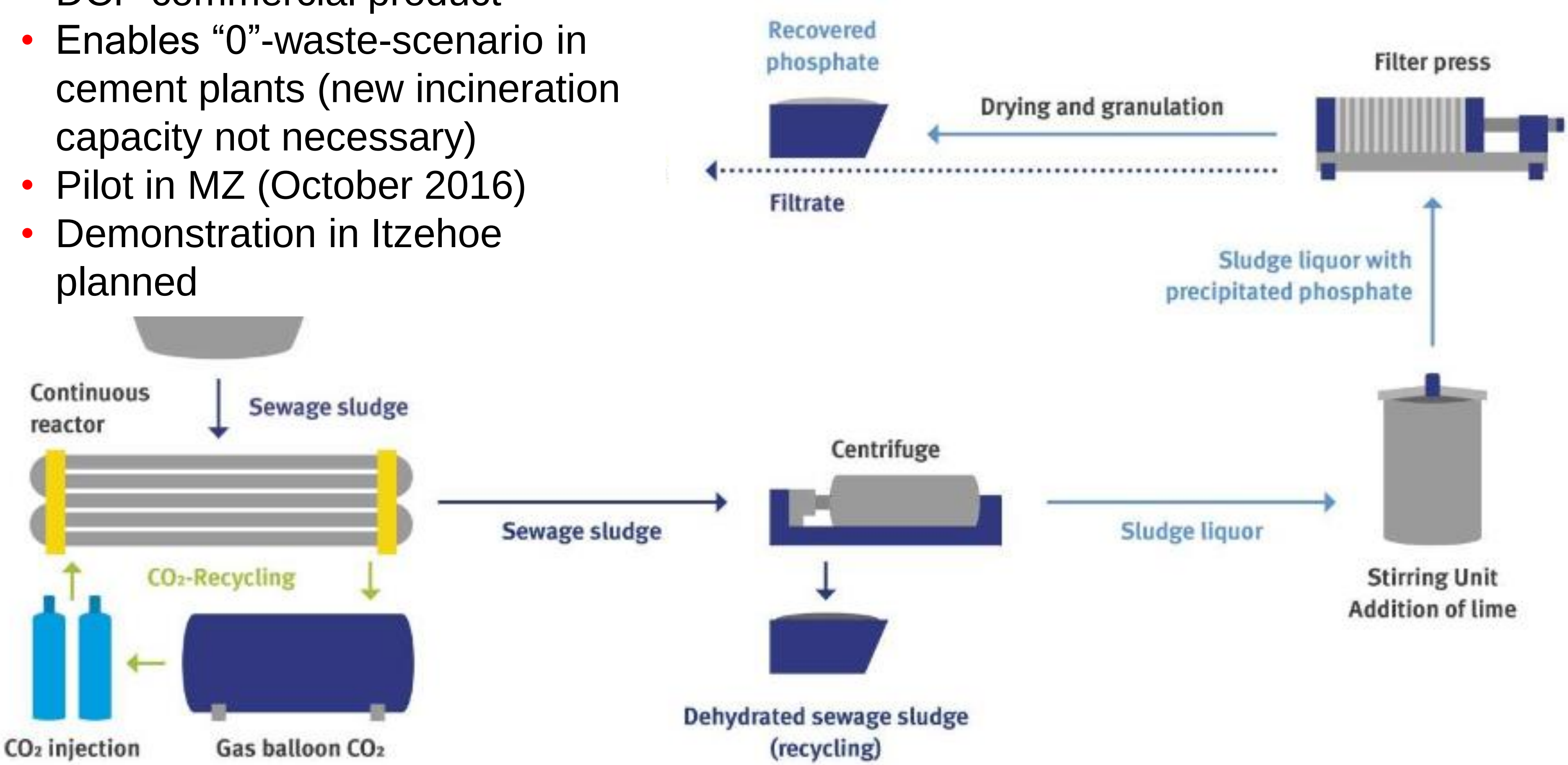
1. Aeration to strip CO_2 out + recirculate sludge
2. Addition of Magnesium Chloride ($MgCl_2$)
3. MAP- Crystallisation and sedimentation
4. MAP- Separation and washing

Huminification red beds
P-recovery at small WTTP'S:

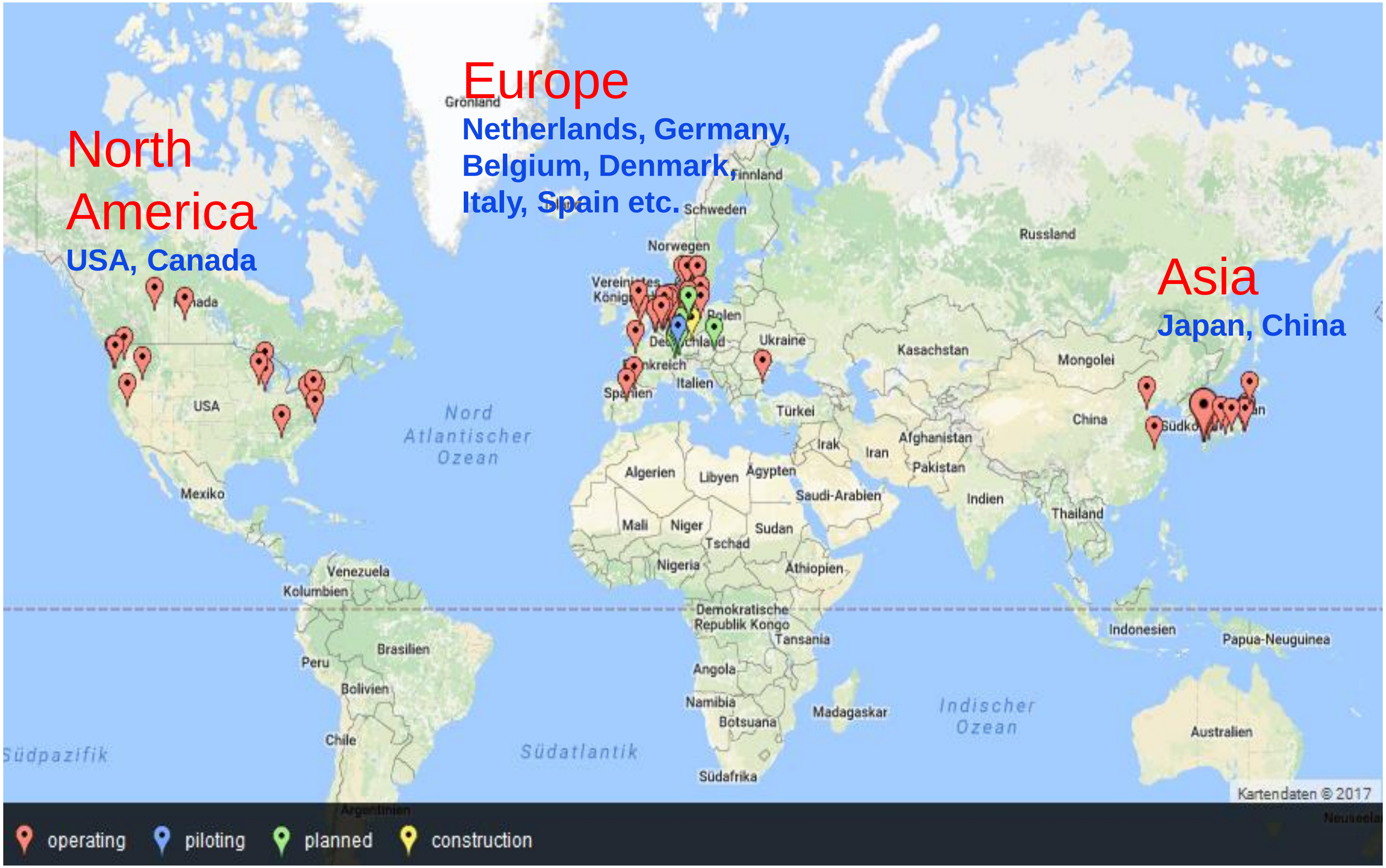


Budenheim process (ExtraPhos)

- Only CO_2 as solvent
- DCP commercial product
- Enables "0"-waste-scenario in cement plants (new incineration capacity not necessary)
- Pilot in MZ (October 2016)
- Demonstration in Itzehoe planned



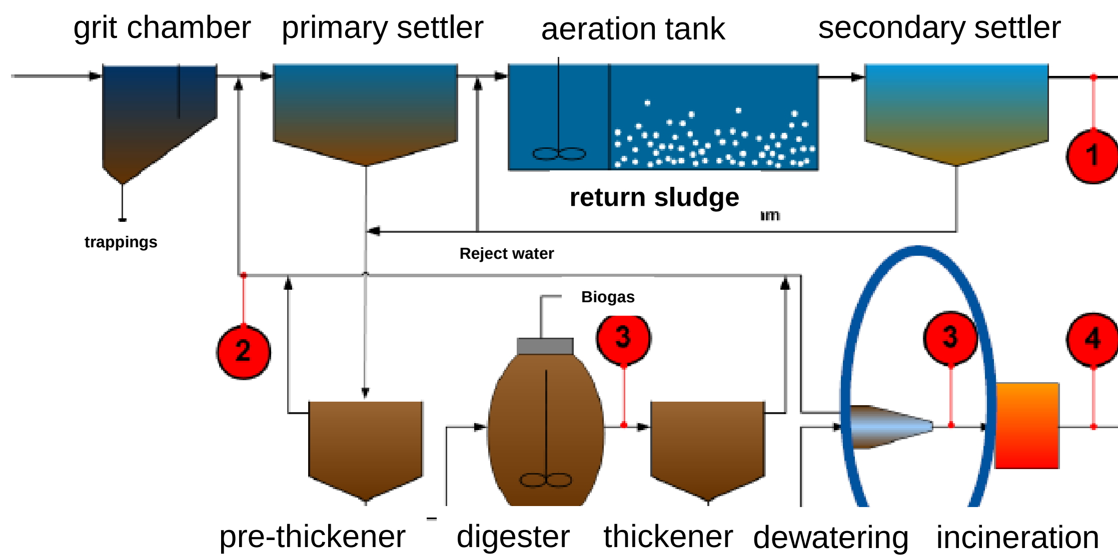
Worldwide operation of P-recovery plants from wastewater path (sludge rejects water)

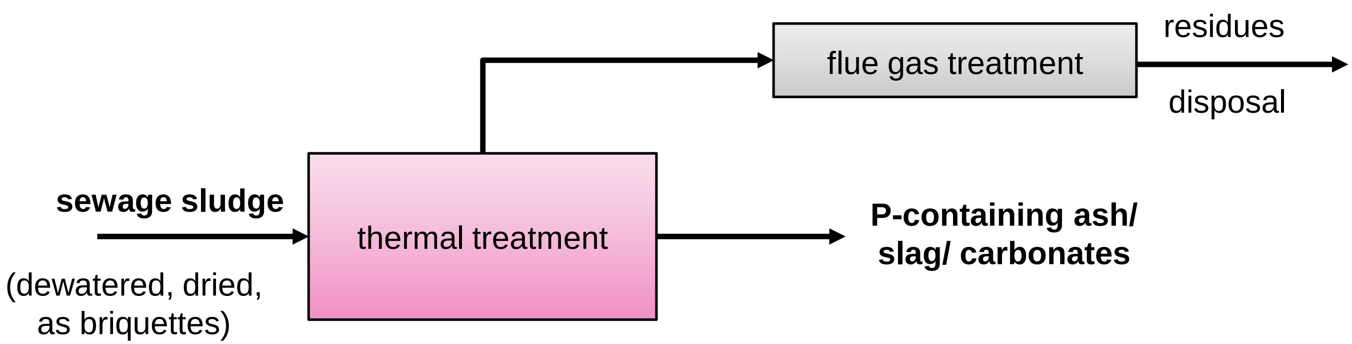


Source: Kabbe, P recovery from wastewater path in 2017 BatchGeo, https://de.batchgeo.com/map/0f9d56a3aa57a51379a3cb23af27d202

P-recovery from sewage sludge
Thermal

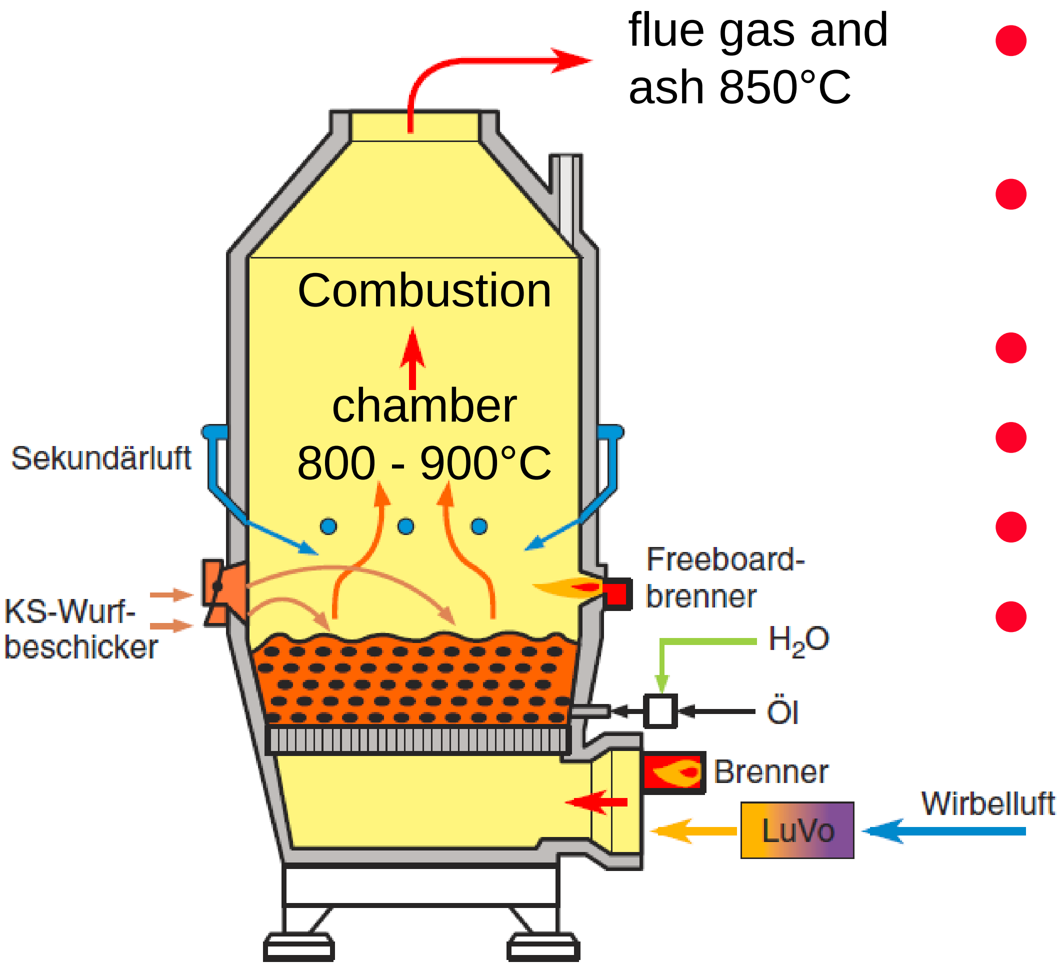
- Examples for processes
  - EuPhoRe
  - Mephrec
  - Pyreg





According to Montag, 2018

(Mono)-Incineration
Example fluidised bed

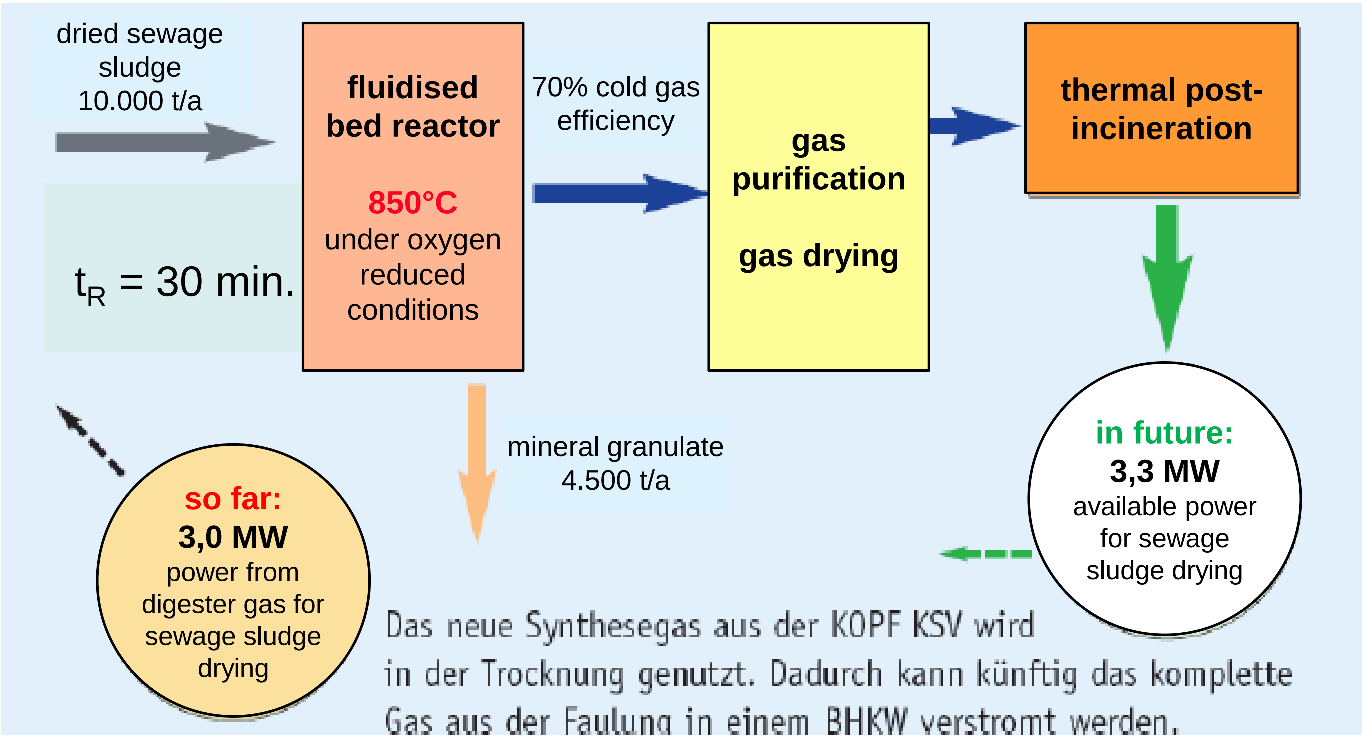


- Net calorific value of sewage sludge might be < 4.000 kJ/kg TS
- For autothermic incineration (dewatering/drying is necessary)
- Temperatures 850 to 950°C
- Ash discharge by flue gas path
- Plant sizes: 2.000 to 4 · 45.000 t_{TS}
- Costs: 180 to 400 €/t_{TS} ….640 €/t_{TS}

Ermel 2014, adjusted

Sewage sludge gasification

SynGas plant in Mannheim (5.000 t_{TS}/a)

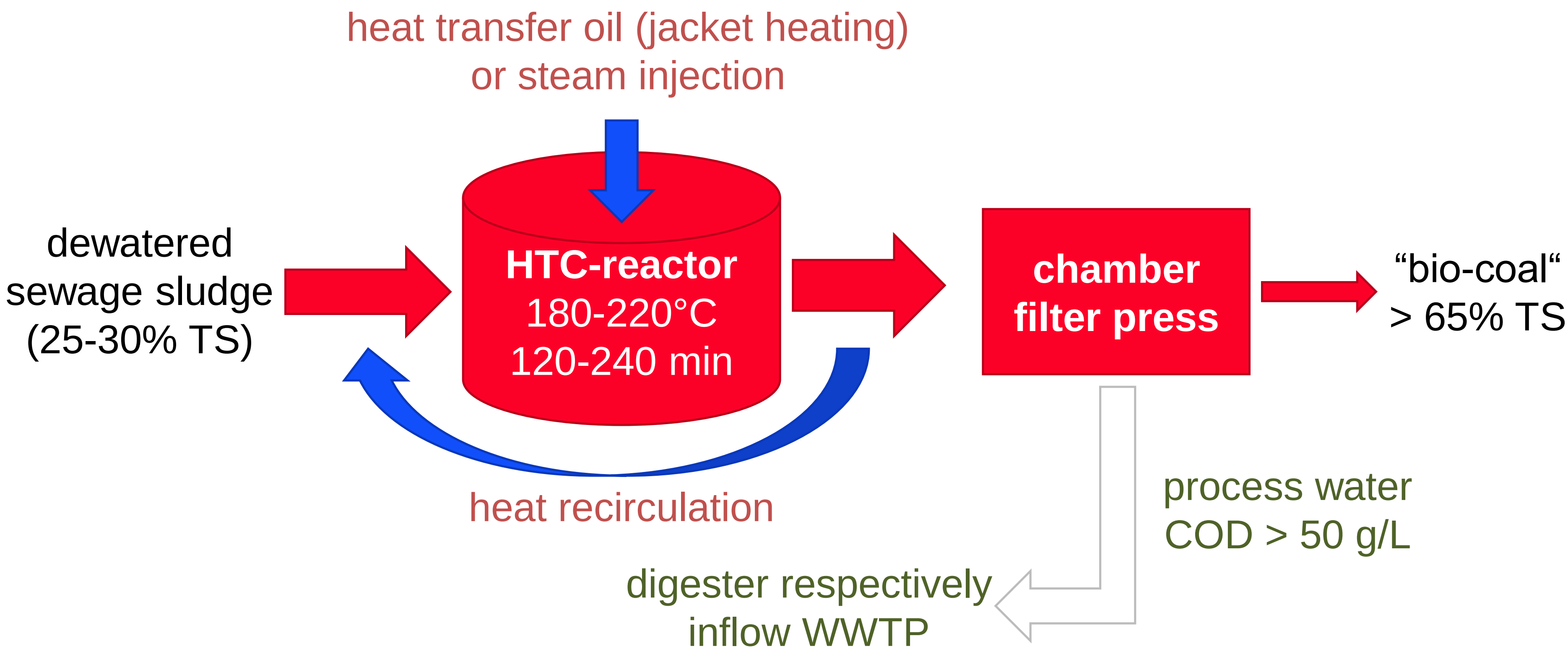


Gaiffi 2013

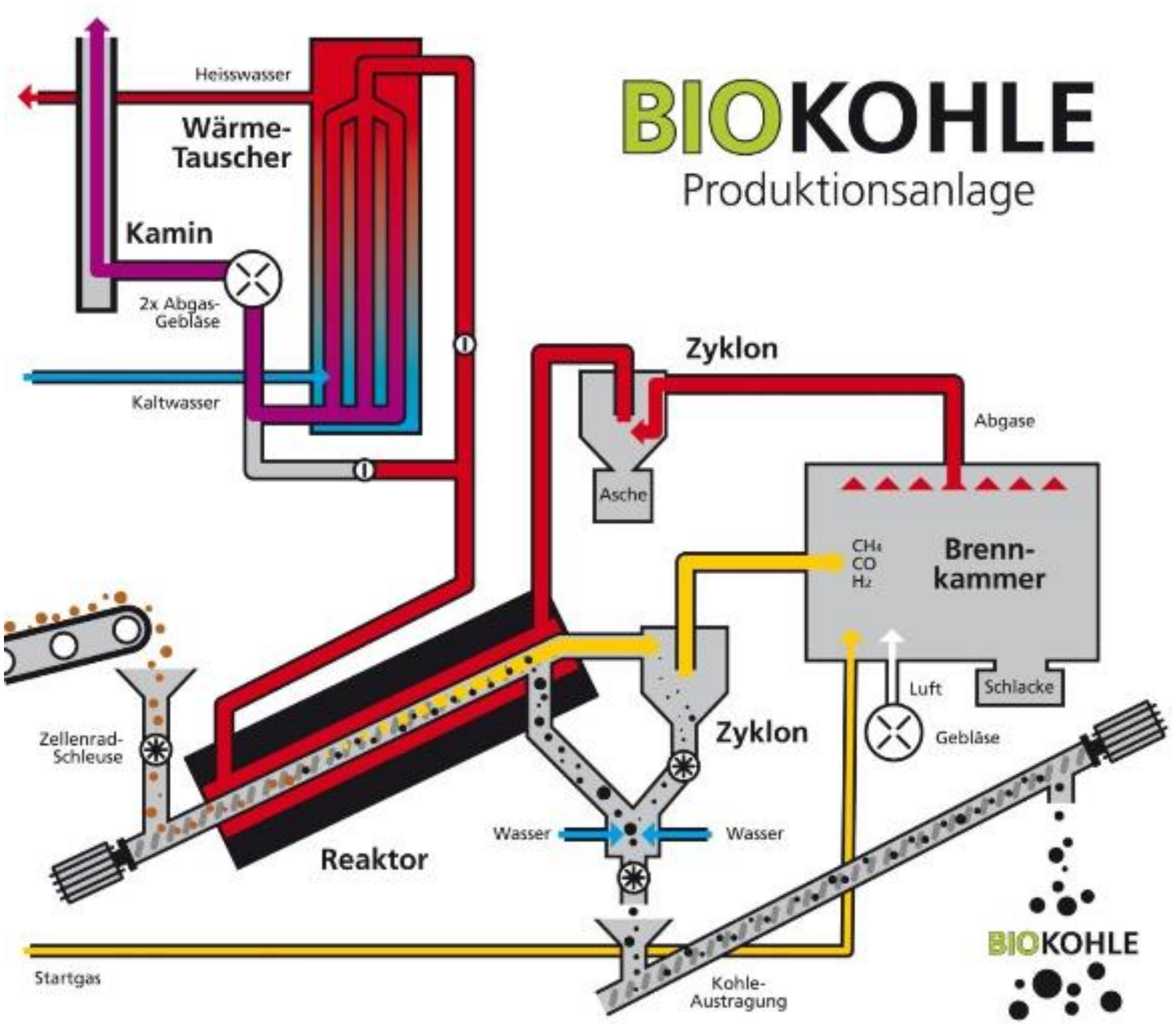
- Sewage sludge has to be dried to < 90% TS
- Gas mixture of CO_2, CH_4, N → energy-rich
- Organic pollutants get burned
- Sewage sludge pellets (heavy metal precipitation by ceramic filter)
- Application as additive to asphalt respectively mono deposit

Hydrothermal carbonation (HTC) of sewage sludge

- Thermal treatment of dewatered sewage sludge
- Goal: high-efficient dewatering to up to > 65% TS
- Mass reduction and high net calorific value ("bio-coal")



Pyrolysis (e.g. Fa. GreenLife)



Technical data e.g.

- Capacity: 4.000 t TS/a with 25%
- Up to 50.000 PE
- Bio-coal production:
  up to 70 kg/h resp. 500 t/a
- Engine output:
  up to 500 kW per unit
- Operational limits:
  net calorific value > 6 MJ/kg
  humidity < 50%
- Thermal heat output:
  up to 150 kW (heat of gas exhaust)
- Installation as 20-feet-container

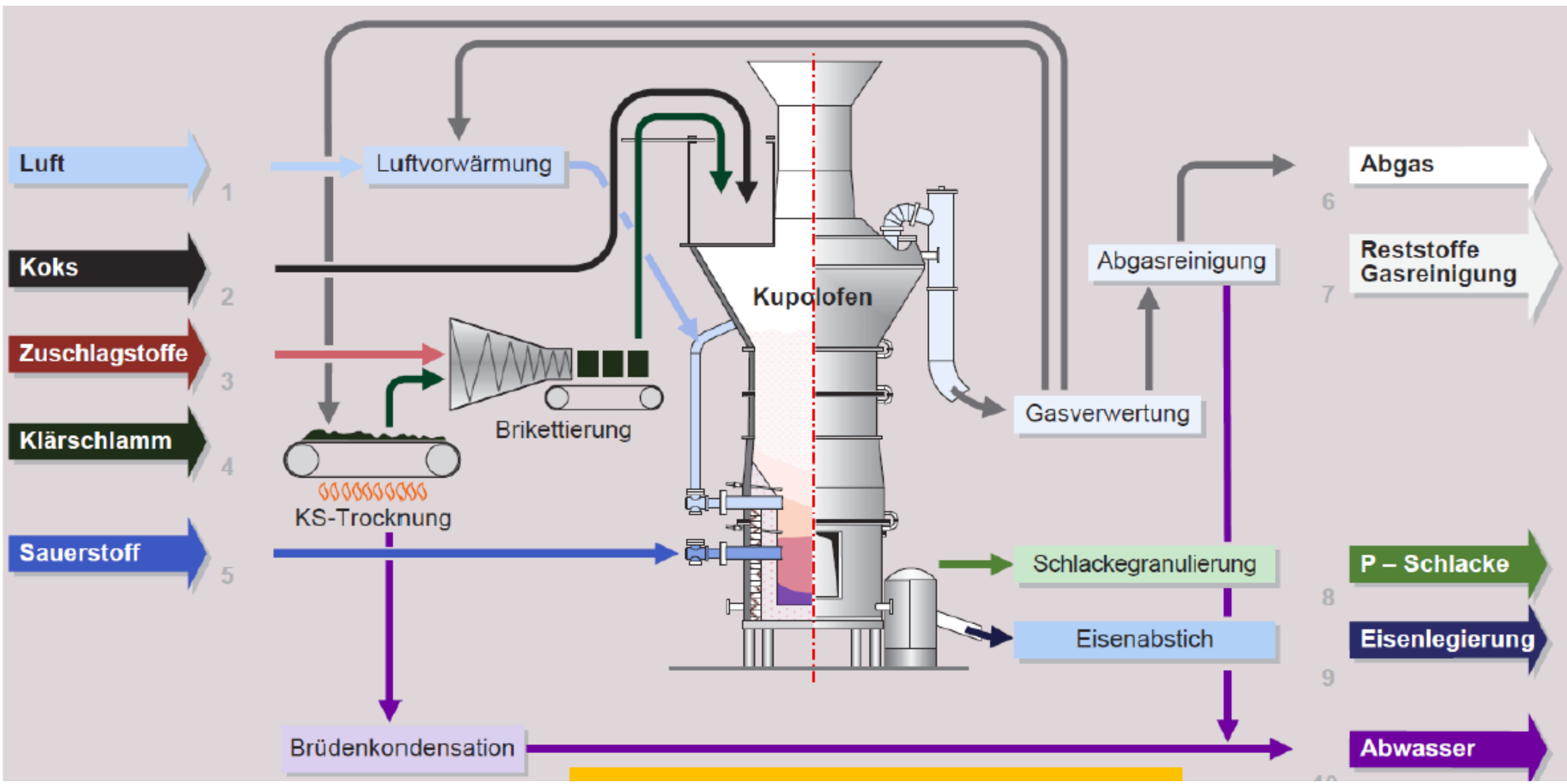
Future energetic usage of sewage sludge

	Gasification	Incineration	Pyrolysis	Hydrothermal carbonation (HTC)
Electricity generation	+++ (30%)	+ (15%)	+ (-)	-
Heat generation	+++ (40-80%)	++ (50-70%)	+(35%-50%)	- (fuel)
Nutrient recovery	+++	++	++	++
Economic feasibility	+++	+	-	-

Mey 2014

MePhRec process

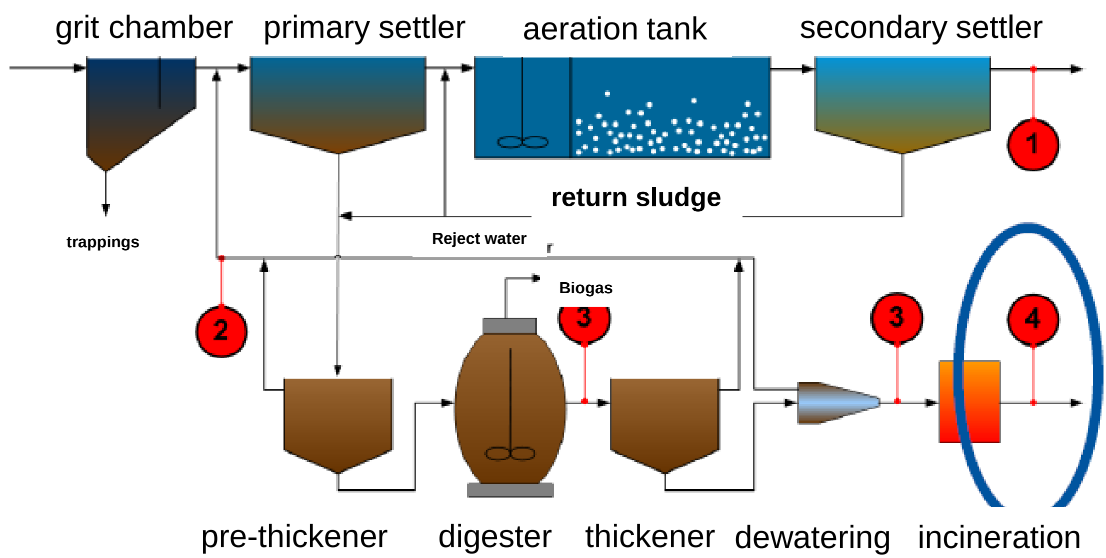
- Pilot plant in Nuremberg (Nürnberg)
- Start-up in progress
- P-rich slag
- Metal deposition (recovery)

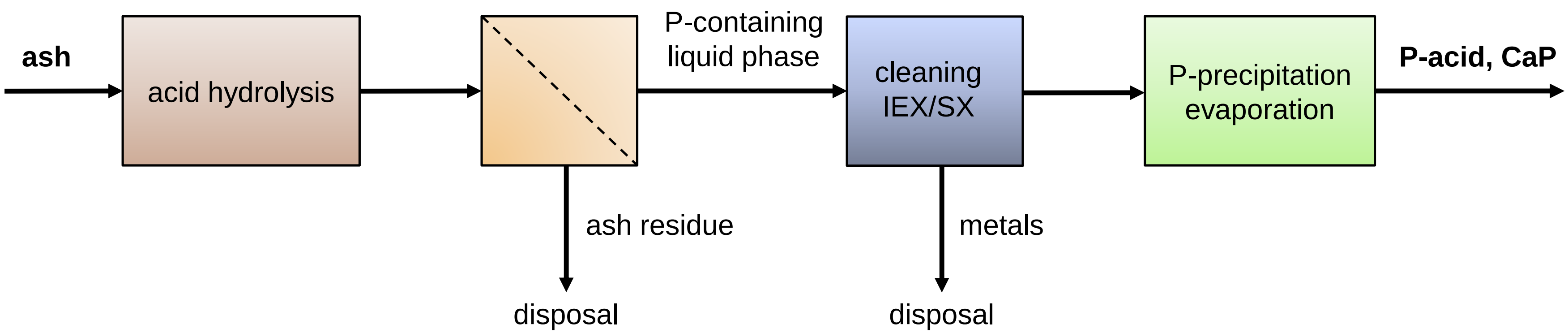


Source: www.sun.nuernberg.de

P-recovery from sewage sludge
Wet-chemical

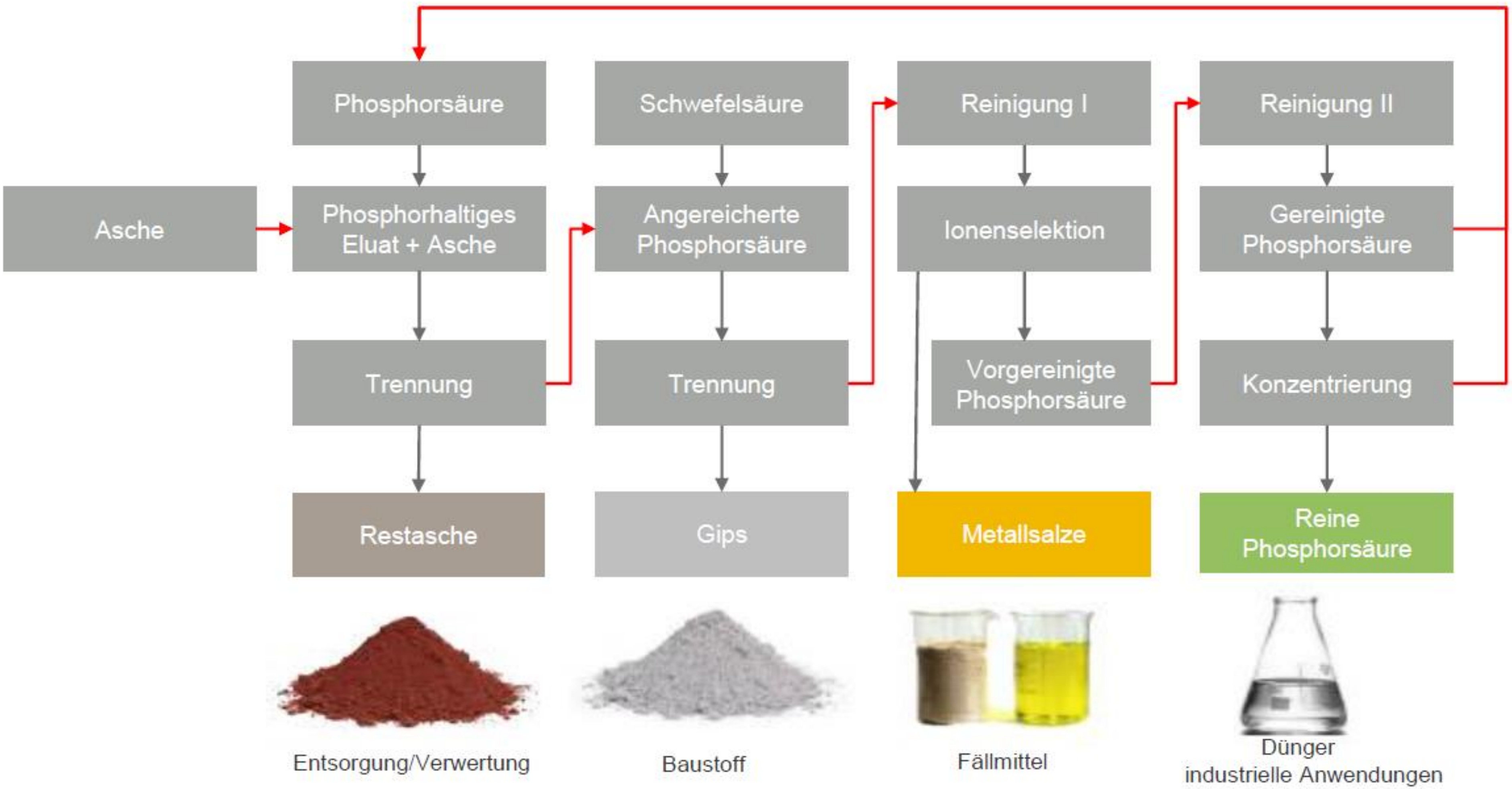
- Examples for processes
  - EcoPhos
  - Leach-Phos
  - PASCH
  - Phos4Life
  - SEWAPHOS
  - TertaPhos





According to Montag, 2018

TetraPhos process (Remondis)

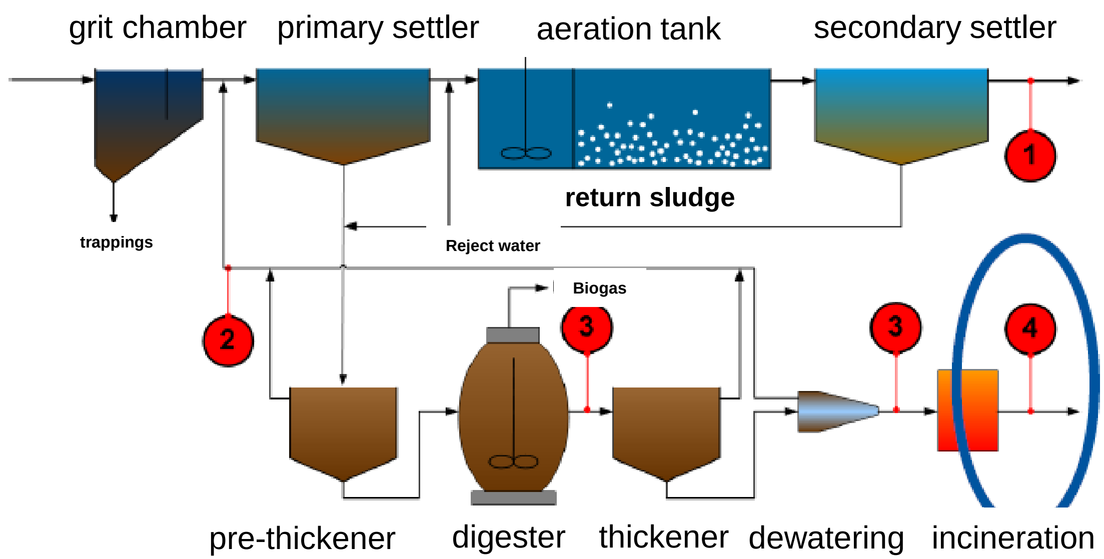


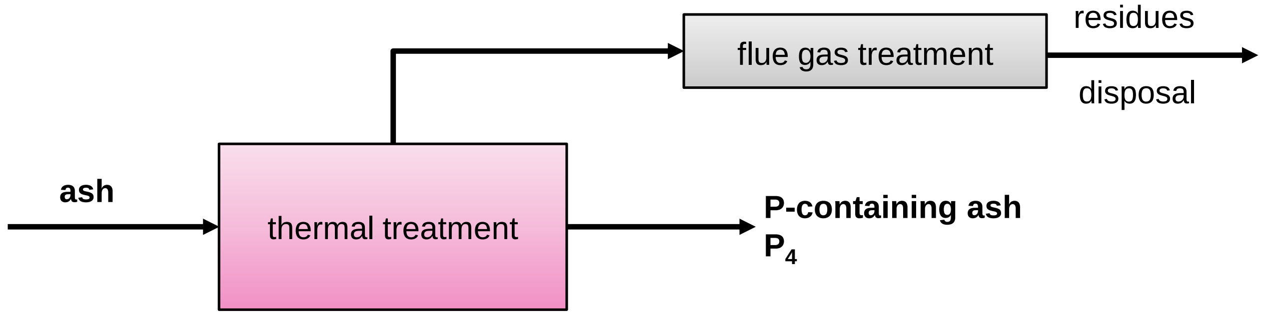
Quelle: Remondis Aqua Industrie GmbH

P-recovery from sewage sludge

Thermal, chemical

- Examples for processes
  - AshDec
  - RecoPhos-ICL

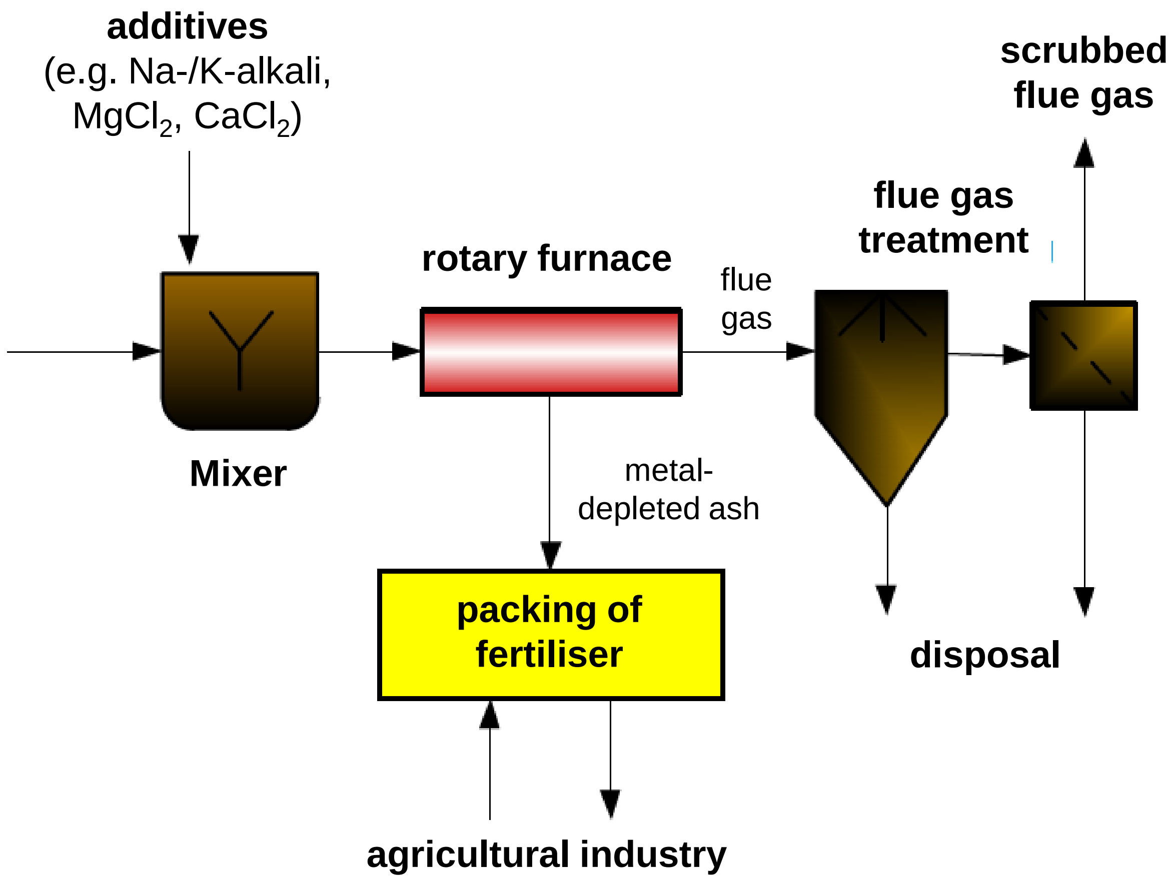




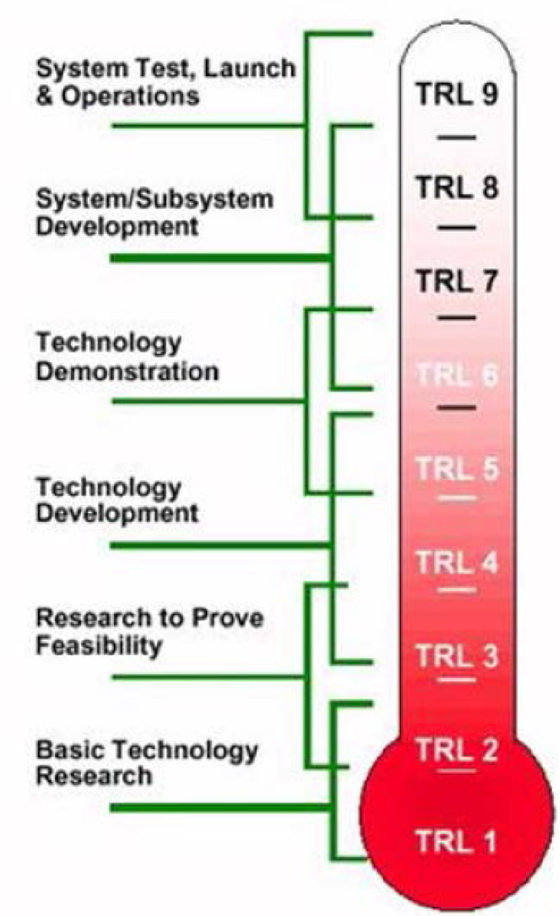
According to Montag, 2018

Schematic diagram of AshDec process

- Recycled material: fertiliser from ash
- Efficiency of recovery referring to WWTP inflow: 90%



Technology Readiness Level (TRL)(TRL)



TRL 9: Intensive proof of successful application at plant site, inclusively full documentation

TRL 7: Prototype well integrated into plant site, nearly true to scale, technical feasibility proven

TRL 5: Experimental set-up in operational environment, not integrated into existing systems

TRL 4: Experimental set-up at laboratory

TRL 3: Operational reliability proven, not integrated

TRL 1: Observation and description of basic principle

Quelle: www. fz-juelich.de/iek/iek-3/DE/Forschung/BGE/Brennstoffzellenseiten/Systementwicklung/Bild 30

Evaluation of degrees of mature technology

2

Sewage water/sludge

Air-Prex	TRL 9
OSTARA PEARL	TRL 9
Parforce	TRL 4-8 (je nach Komponente)
P-Roc	TRL 5-9 (Mittel TRL 6)

3

Sewage sludge

ExtraPhos	TRL 5
KRN Mephrec	TRL 5
PYREG	TRL 8
Stuttgarter Verfahren	TRL 7
TerraNova Ultra	TRL 4-5
EuPhoRe	TRL 7 (bei Nutzung vorhandener RGR)

4

Sewage sludge ash

ASHDEC	TRL 6
PASCH	TRL 4
TetraPhos	TRL 5-6

According to Montag, 2018

Future prospects

- Legal regulations are set finite in Germany
  - ➡ **Report on assurance of phosphorus recovery**, § 3a (till 31.12.2023)
  - ➡ Prohibition of soil-related utilisation after 12 years (1.1.2029/1.1.2032 [100.000/50.000 PE])
  - ➡ Sewage sludge interim storage?
- Is it in the responsibilities of sewage sludge producers?
  → phosphorus recovery
- Practicability of P-recovery processes has to be examined and developed further on
- Recovered P-compounds have to be suitable for recycling
- Profounded evaluation of economic feasibility and sustainability is still missing
- **P-recovery isn't P-recycling yet!!**
  - ➡ Market has to be developed