POLITECNICO MILANO 1863 | DIPARTIMENTO DI INGEGNERIA CIVILE E AMBIENTALE

CNR ISSMC
Istituto di Scienza, Tecnologia e Sostenibilità per lo Sviluppo dei Materiali Ceramici

WORKSHOP
Geopolymer for Environmental Remediation

February 14th 2025, Faenza, Italy

Phosphorus recovery from wastewater, sludge and sewage sludge ashes – a short overview

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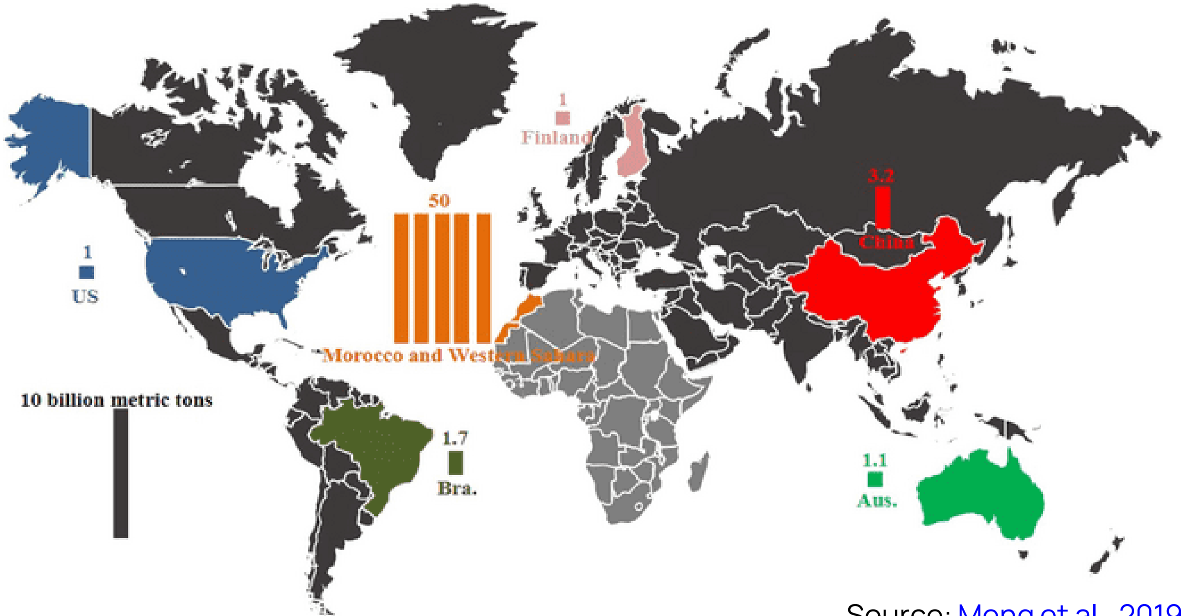
Contents

1. Phosphorus - overview

- Plant **macronutrient** (N, P, K)
    - 2023: 20×10^6 tonne/y P for fertilizers (USGS)
- Many **applications**:
    - Fertilizers, animal feed
    - Pesticides, herbicides
    - Detergents
    - Li-Fe-P batteries



Source: Meng et al., 2019

- **Non-renewable** (phosphate rocks - PR)
    - Depletion time: **100 – 400 years**
    - **Uneven distribution** of PR reserves (Morocco, China)
- PR (2014), P (2017): **EU Critical Raw Materials**
- Excessive use of fertilizers (**P losses** and **eutrophication**)

Recover P from **secondary** sources !

2.1 Phosphorus secondary sources - overview

P content

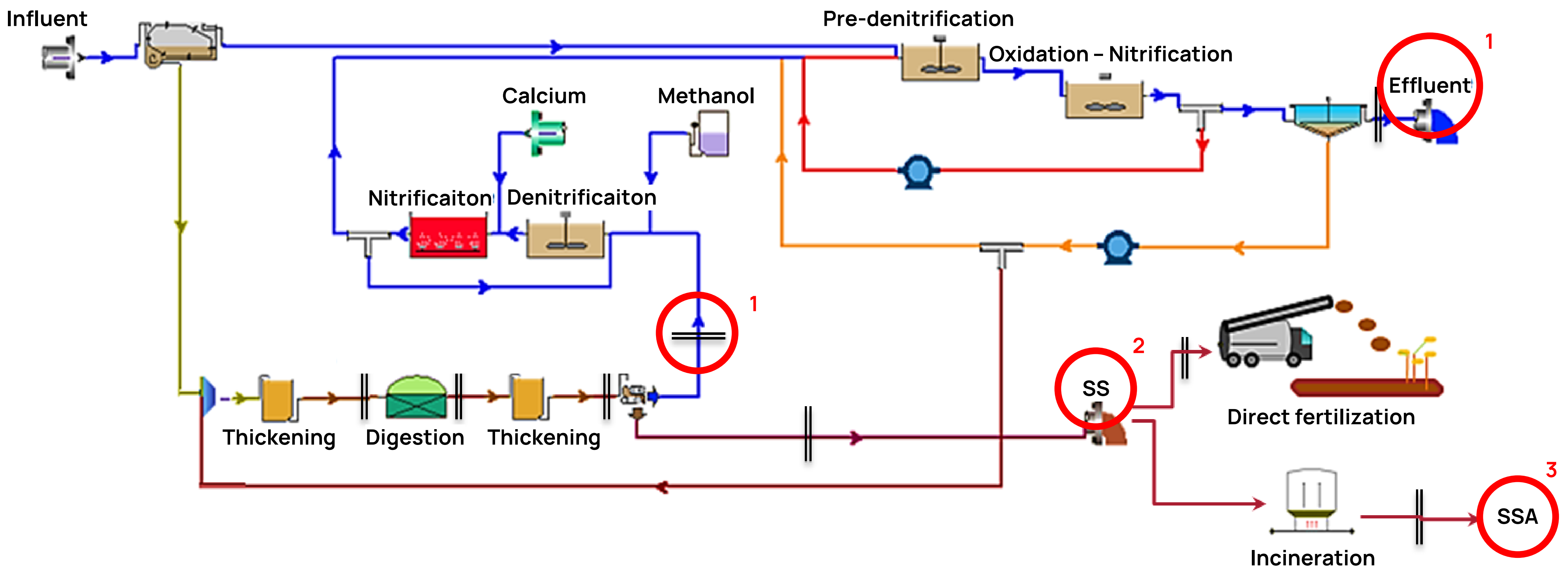
Production volume

Table 1. Phosphorus content in selected biowaste.

Biomass and biowaste	P content	References
Liquid fraction swine manure	0.203 g/L	[148]
Dairy manure	4.10 g/kg – 18.3 g/kg DM	[131]
Dairy manure slurry	67.5–101.0 mg/L	[131]
Pig manure	1.9 g/kg	[152]
Poultry litter	13.6 g/kg	[30]
Slaughter waste	1.79 g/kg DM	[31]
Cattle bones	104 g/kg DM	[55]
Pig bones	93.6 g/kg DM	[55]
Poultry bones	85.2 g/kg DM	[55]
Fish bone ash	172 g/kg	[32]
Chicken bone ash	155 g/kg	[32]
Beef bone ash	142 g/kg	[32]
Sewage sludge ash	80 g/kg	[44]
Sewage sludge ash	88.4 g/kg	[33]
Sewage sludge	25.68 g/kg	[34]
Sugarcane waste	5.30 g/kg	[30]
Cabbage waste	0.26 g/kg	[30]
Food waste	4.2 g/kg	[35]

Source: Witek-Krowiak et al., 2022

2.2 Phosphorus secondary sources - WWTP



1. **Aqueous phases**: WWT effluent, sludge liquor
2. **Sewage sludge** (SS): digested sludge, dewatered/dried sludge
3. **Sewage sludge ash** (SSA)

3. Phosphorus recovery processes and recovered products

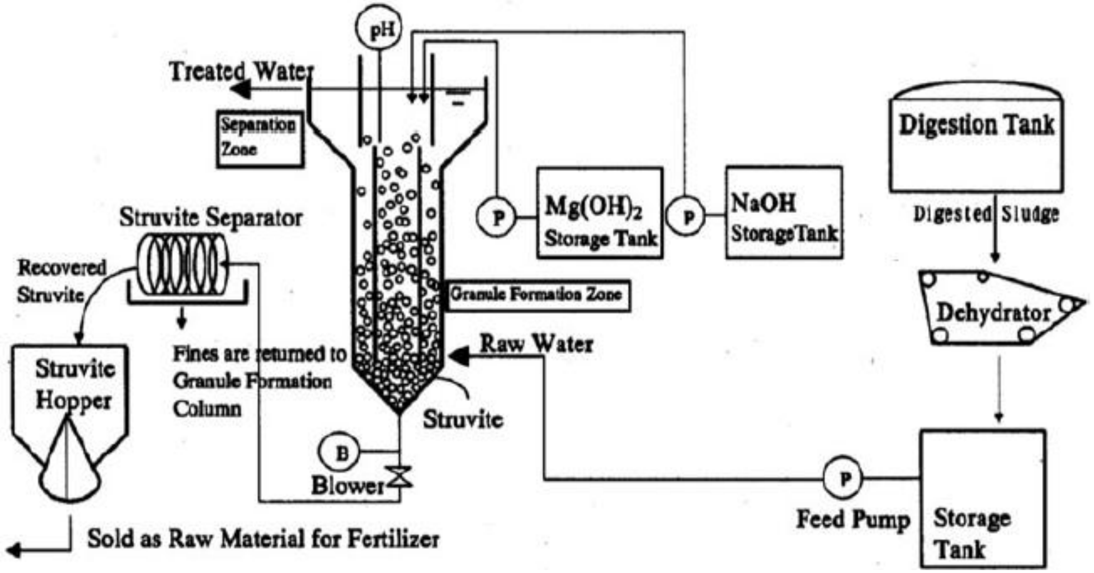
Recovery processes

- Precipitation/crystallization
- Chemical extraction
- Thermochemical treatment
- Adsorption

Recovered products

- Ca-P (e.g., hydroxyapatite)
- Mg/NH_4-P (e.g., struvite)
- H_3PO_4
- P_4

4.1 Phosphorus recovery processes – precipitation/crystallization



PHOSNIX process. Source: [Ueno and Fuji, 2001]

Principle

Ca/Mg salts + Na(OH)/CO_2 stripping = struvite

- ($MgCl_2$)
- (pH 8 – 10)
- ($NH_4MgPO_4 \cdot 6(H_2O)$)

Applications

SS liquors

- Ostara (PEARL), PHOSNIX, DHV Crystalactor
- High maturity (TRL 9, > 40 operating plants)
- Recovery efficiency = 10-50%
- 6-10 €/kg $_{\text{P recovered}}$

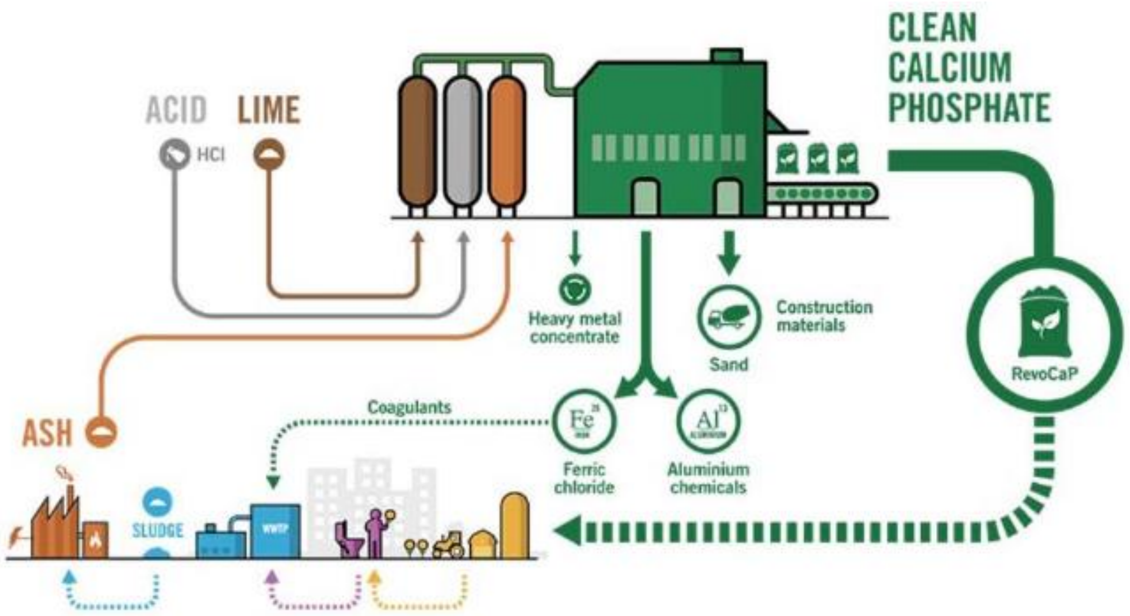
Pros

- Reduced scaling in anaerobic digestion
- Improved SS dewatering properties

Cons

- Limited applicability: > 50 – 60 mg/L P-PO_4^{3-}
- High investment costs
- Struvite competitivity in the fertilizer market

4.2 Phosphorus recovery processes – chemical extraction



ASh2Phos process. Source: https://www.easymining.com/

Principle

Extraction + S/L sep. + Precipitation = Ca-P

- Inorganic acids (H_2SO_4, HCl)
- Organic acids (oxalic),
- Alkaline (NaOH)
- Chelants (EDTA)

- Alkalines (NaOH, $Ca(OH)_2$, CaO, MgO)

- Hydroxyapatite ($Ca_5(PO_4)_3OH$)
- Brushite ($CaHPO_4 \cdot 2\,H_2O$)

Application

SS (2 – 3% P); SSA (4 – 15% P)

- Seaborne (Gifhorn); Ash2Phos, Flashphos
- TRL: 7 – 8
- Recovery efficiency = 40 – 70%; 70 – 90%
- 12 – 16 €/kg $_{\text{P recovered}}$; 2 – 6 €/kg $_{\text{P recovered}}$

Pros

- Similar to current P extraction from PR
- Flexible and scalable
- Low energy requirement

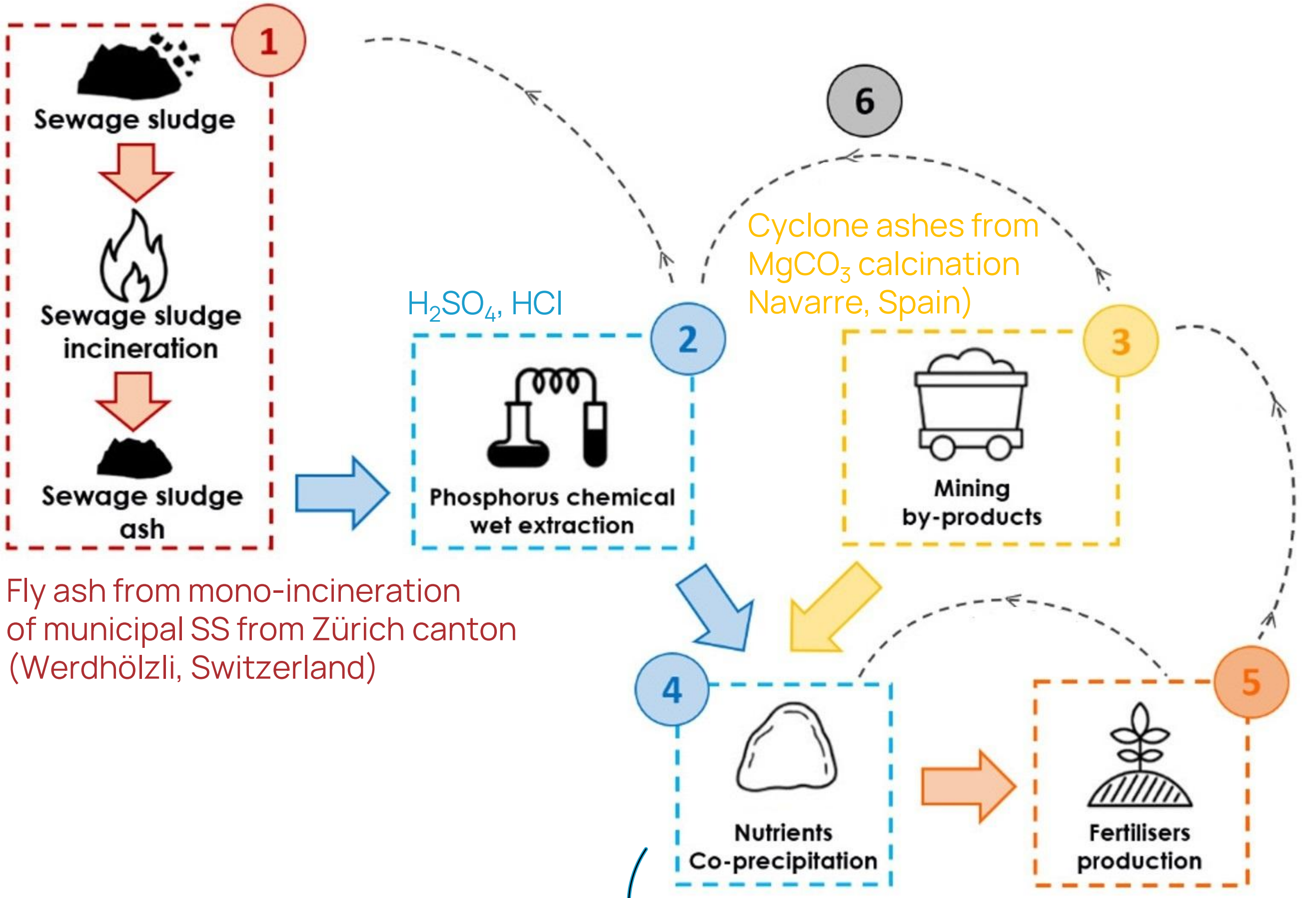
Cons

- Disposal of undissolved SS/SSA
- Selective decontamination/precipitation of HMs

4.2.1 Phosphorus recovery processes – chemical extraction – PHOSTER project

Phoster ERA-MIN

Phosphorus and magnesium recovery from waste streams for production of high-value renewable fertilizers



- P (4 – 8%)
- Mg (2 – 16%)
- K (0.1 – 0.3%)

POLITECNICO MILANO 1863 | MM | University of Ljubljana Faculty of Mechanical Engineering | GREENTHESIS GROUP | MAGNA MAGNESITAS NAVARRAS | Timac AGRO Italia

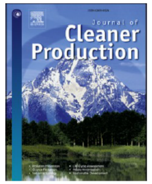
PHOSTER process. Source: https://phoster-project.eu/

4.2.1 Phosphorus recovery processes – chemical extraction – PHOSTER project

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



Optimization of phosphorus wet acid extraction from sewage sludge ashes: Detailed process insight via multi-variate statistical techniques

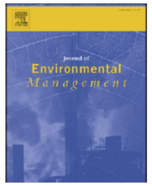
Gaia Boniardi [a], Elia Paini [a], Tine Seljak [b], Arianna Azzellino [a], Alessandro Volonterio [c], Roberto Canziani [a], Andrea Turolla [a,*]

Source: https://doi.org/10.1016/j.jclepro.2024.142491

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman



Research article

Optimizing phosphorus precipitation from acidic sewage sludge ash leachate: Use of Mg-rich mining by-products for enhanced nutrient recovery

Gaia Boniardi [a], Lorenzo Esposito [a], Marco Pesenti [a], Arianna Catenacci [a], Maitane Guembe [b], Inigo X. Garcia-Zubiri [b], Daniel El Chami [c], Roberto Canziani [a], Andrea Turolla [a,*]

Source: https://doi.org/10.1016/j.jenvman.2024.122943

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Journal of Cleaner Production

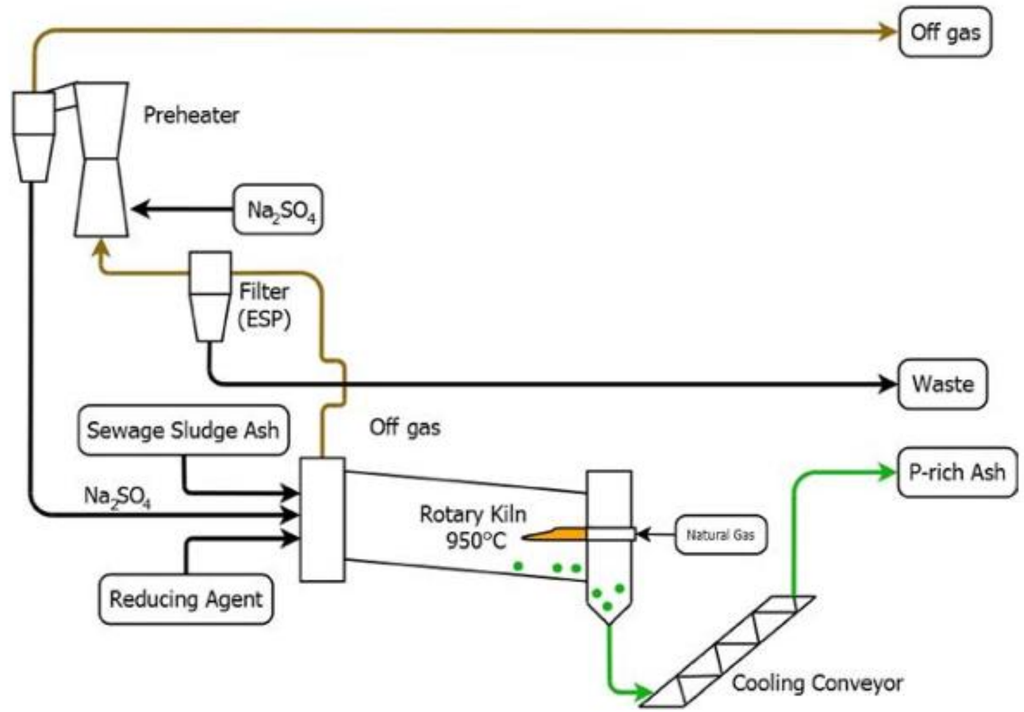
journal homepage: www.elsevier.com/locate/jclepro

Development of a multi-objective support tool for optimizing phosphorus recovery from sewage sludge ash: A step towards process feasibility

Lorenzo Esposito [a], Gaia Boniardi [a], Marco Frigerio [b], Maitane Guembe [c], Íñigo X. García-Zubiri [c], Daniel El Chami [d], Roberto Canziani [a], Andrea Turolla [a,*]

Source: https://doi.org/10.1016/j.jclepro.2024.144378

4.3 Phosphorus recovery processes – thermochemical treatments



AshDec® process. Source: [Schaum et al., 2018]

Pros

- Enhanced P bioavailability
- HMs volatilization (~ 90% of Pb, Cd, Cu and Zn)

Principle

- Rotary kiln + Cl/Na donors → P_4/ P-rich slag
  - (1000 – 1600°C, 40 – 120 min)
  - ($MgCl_2$, $CaCl_2$, Na_2SO_4)
  - Buchwaldite ($CaNaPO_4$)
  - Chlorapatite ($Ca_5(PO_4)_3Cl$)

Application

SS; SSA

- EuPhoRe, Kubota; AshDec
- TRL: 7 – 8
- Recovery efficiency: >90%
- 2 – 5 €/kg $_{\text{P recovered}}$

Cons

- High energy requirement
- Equipment lifetime
- High concentration of non-volatile HMs (Ni, Cr)
- ~ 30% P lost with flue gases

4.4 Phosphorus recovery processes – adsorption

Principle

+ regeneration + precipitation → Struvite

↓

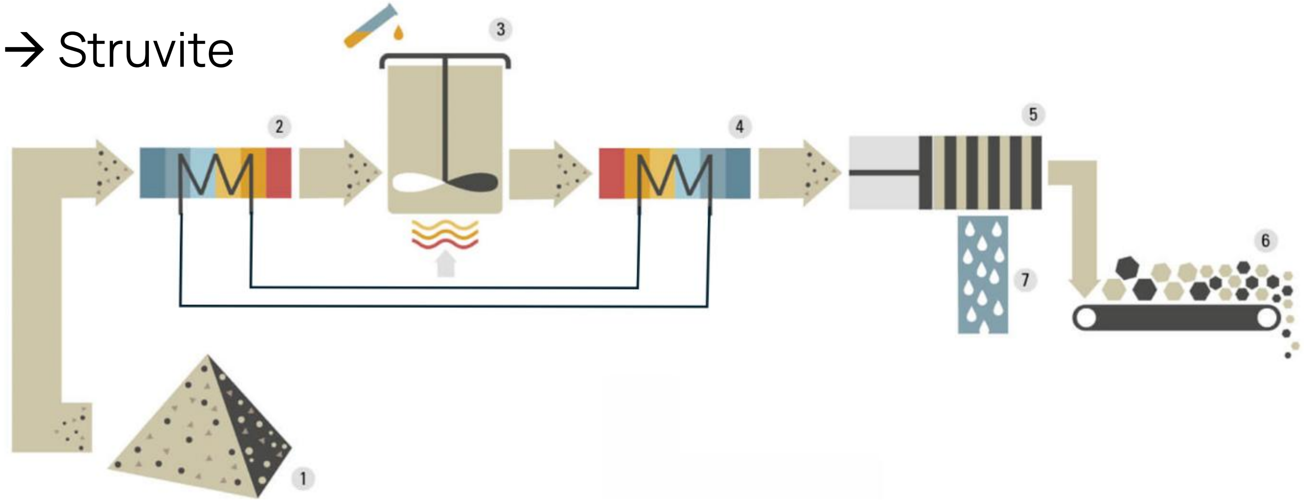
- (NaOH)

- Adsorbent

↓

Direct use as fertilizer

- C-based materials: activated carbon, biochar
- Metal oxides/hydroxides (Al, Fe, Ca, Mg)
- Ion-exchange resins
  - Bio-based products (Posidonia, P-binding proteins from E.Coli)
  - Industrial by-products (red mud, furnace slags)



Terranova process. Source: https://www.terranova-energy.com/en/

Application

WWT effluent; SS/SSA leachate

- TerraNova
- Full-scale (2 tonne/h SS, China); Demonstration (250 kg/h SS, Duisburg – Germany)
- Recovery efficiency = 60 – 70%
- 3 – 4 €/kg $_{\text{P recovered}}$

Pros

- Cheaper operation
- Selectivity
- Effective also at low P concentration

Cons

- Ionic competition (Cl^-, SO_4^{2-}, CO_3^{2-})
- Waste management (spent adsorbents / regenerants)

4.5 Phosphorus recovery processes – Literature

- Egle et al., 2015:
  Overview and description of technologies for recovering phosphorus from municipal wastewater
- Jupp et al, 2021:
  Phosphorus recovery and recycling – closing the loop
- Witek-Krowiak et al., 2022:
  Phosphorus recovery from wastewater and bio-based waste: an overview
- Usman et al., 2022:
  A review of adsorption techniques for removal of phosphates from wastewater
- Zheng et al., 2022:
  Recovery of phosphorus from wastewater: A review based on current phosphorous removal technologies
- Canziani et al., 2023:
  Phosphorus recovery—recent developments and case studies

5. Technology inventories

Catalogue of Nutrient Recovery Technologies – European Sustainable Phosphorus Platform

- The ESPP Catalogue of Nutrient Recovery Technologies summarises processes for recovery of nutrients from sewage, manure or other sources, covering nutrient recovery technologies that are operational or demonstrated at full-scale or pilot scale
- https://www.phosphorusplatform.eu/activities/p-recovery-technology-inventory

European Sustainable Phosphorus Platform Catalogue of Nutrient Recovery Technologies

Italian Phosphorus Platform (Piattaforma Italiana del Fosforo)

- La presenza di tecnologie ed esperienze per il recupero del fosforo a livello nazionale è stata verificata tramite compilazione da parte dei singoli partecipanti alla Piattaforma di un questionario
- https://www.piattaformaitalianafosforo.it/it/tecnologie.html

PIATTAFORMA ITALIANA DEL FOSFORO Tecnologie e buone pratiche di gestione circolare del fosforo

6. Global distribution of P recovery plants (2019)

In operation

- Central Europe: >20
- North America: 16
- Far East: 13

Under construction

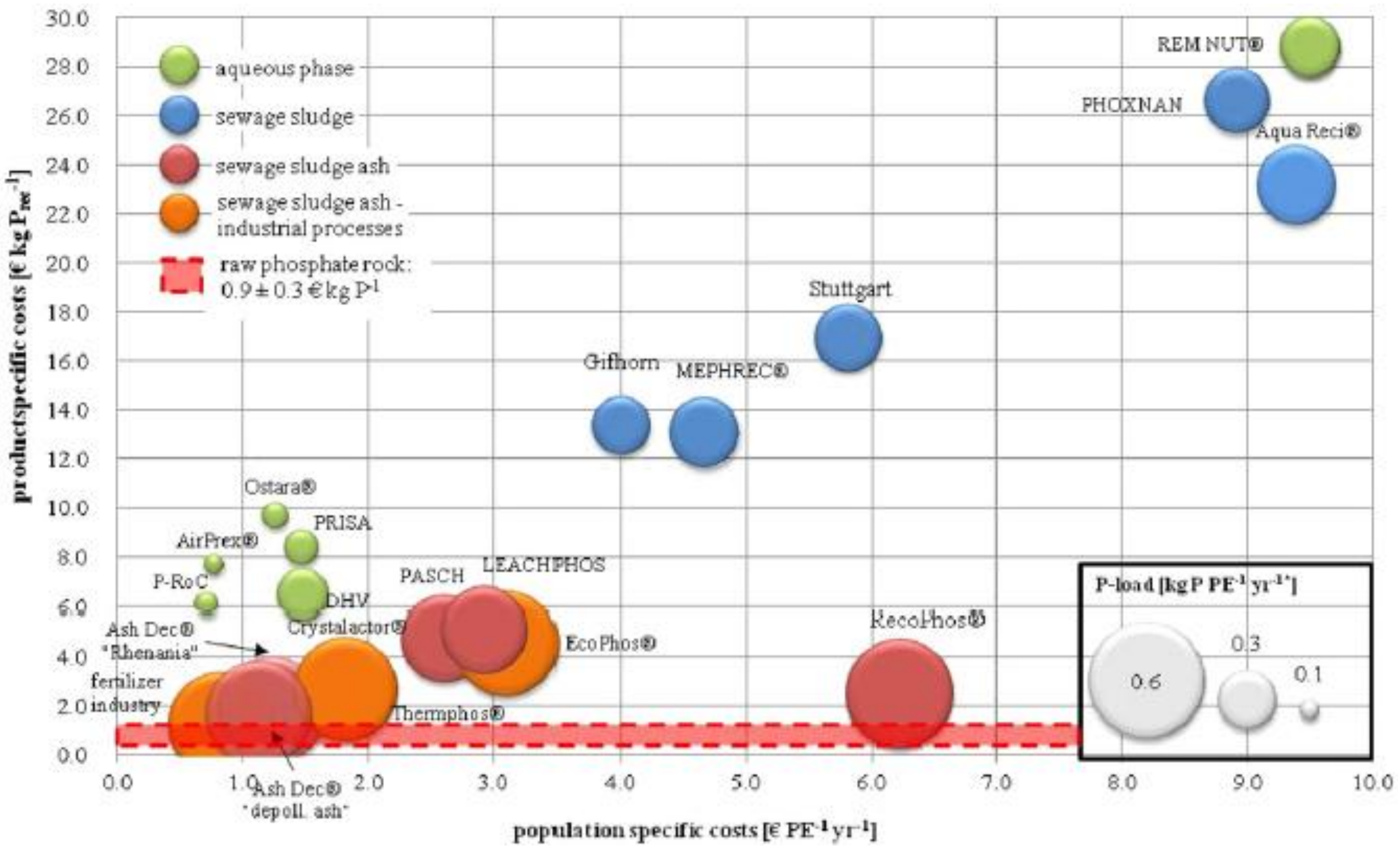
- Central Europe: 2
- North America: 0
- Far East: 0

Planned

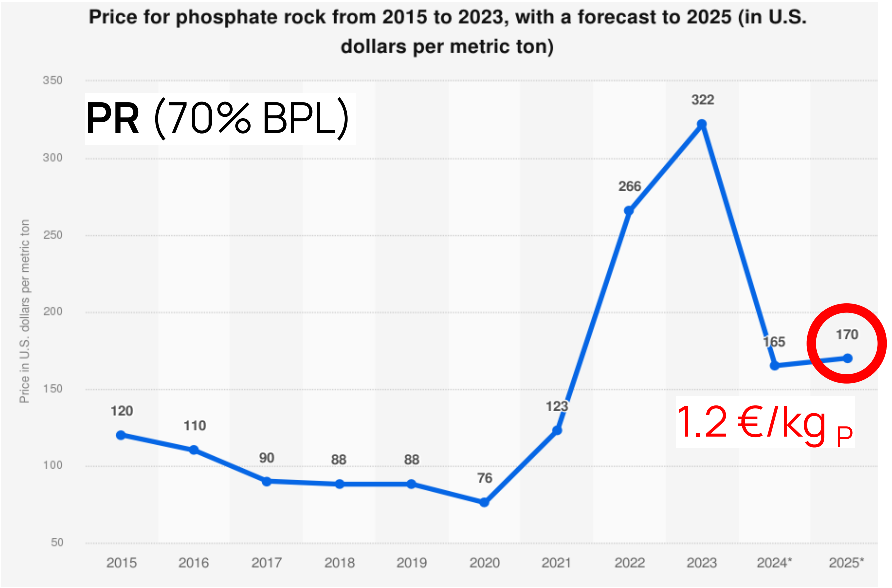
- Central Europe: 5
- North America: 1
- Far East: 0

Source: [Shaddel et al., 2019]

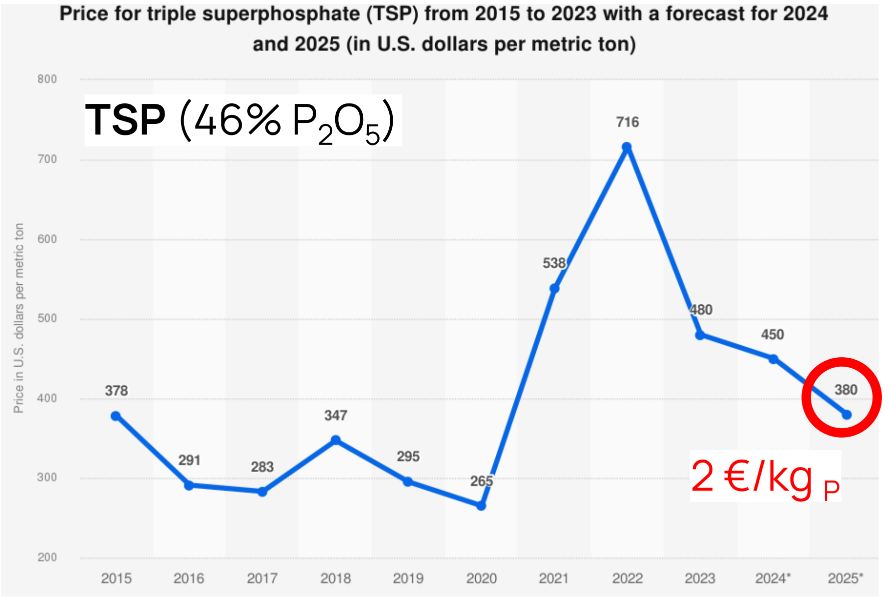
7. Economics



Source: Egle et al., 2016



Source: Statista



Source: Statista

8. EU regulations

Switzerland (Waste Avoidance and Disposal Act, VVEA, **2015**)

- P recovery from 2026 from SS, bones and bone meal

Germany (Sewage Sludge Ordinance, AbfKlärV, **2017**). P recovery mandatory for:

- WWTP > 100.000 PE & P in SS > 20 g/kg from 2029.
- WWTP > 50.000 PE, by 2032.
- Optional for WWTP < 50.000 PE.

Austria (Waste Incineration Ordinance, AVV, **2022**):

- WWTP > 20.000 PE, P recovery by 2030 (Recovery efficiency 60-80%)

Sources: VVEA; AbfKlärV;AVV

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Thank you for your attention

Any question?

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