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Wastewater Technology

P-recovery from sewage sludge and sewage sludge ashes

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Introduction

Investigation at TU-Darmstadt

- Wet chemical phosphorus recovery from sewage sludge ashes (**SSA**)
- Phosphorus recovery from Bio-P sludges with calciumsilicate hydrate (CSH)

Which ways of phosphorus recovery are feasible right now?

1) Use of **SSA** raw material in the phosphorus industry

- Requirements for **SSA**
- Description of the Thermphos process
- Recovery potential

2) Direct use of **SSA** as fertilizer

- Requirements for **SSA**
- Treatment of **SSA** with sulphuric acid for digestion and heavy metal removal

Introduction

- P-recovery investigation in Germany was initiated around 2000
- TU-Darmstadt concentrated research on **SSA**:
- **SSA** contain 90% of the P-inflow of a WWTP (in cases of P-removal)
and 100% of removed P
- **SSA** are hygienically safe, organic contaminants are destroyed
- The waste stream is small and concentrated
- Less chemicals are required for P-dissolution (if wet chemical recovery is envisaged) as compared to *sewage sludge*
- **SSA** contain same ratio of P and heavy metals as sewage sludge

P-Recovery from ashes

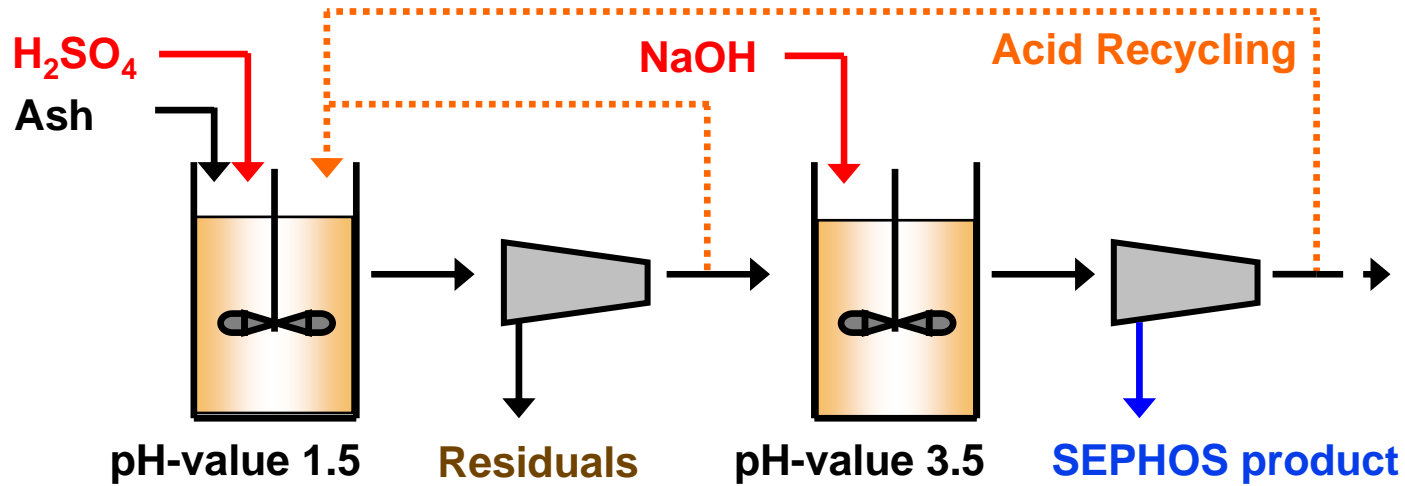
- But:
 - Only applicable for **mono-incineration-ashes** Currently **approx. 25%** of the municipal sewage sludge in Germany (2,3 Mio. t/a) goes to mono incineration
 - **P** in the ashes is not plant available and ashes could legally not be used as fertilizers at the time
→ **The situation changed in the meantime!!**
 - The phosphorus industry was initially not interested to substitute phosphate rock with **SSA** due to differing composition (to much Fe and heavy metals)
→ **The situation changed in the meantime!!**
- **Investigation in separation of heavy metals and P was initiated**

Investigation at TU-Darmstadt

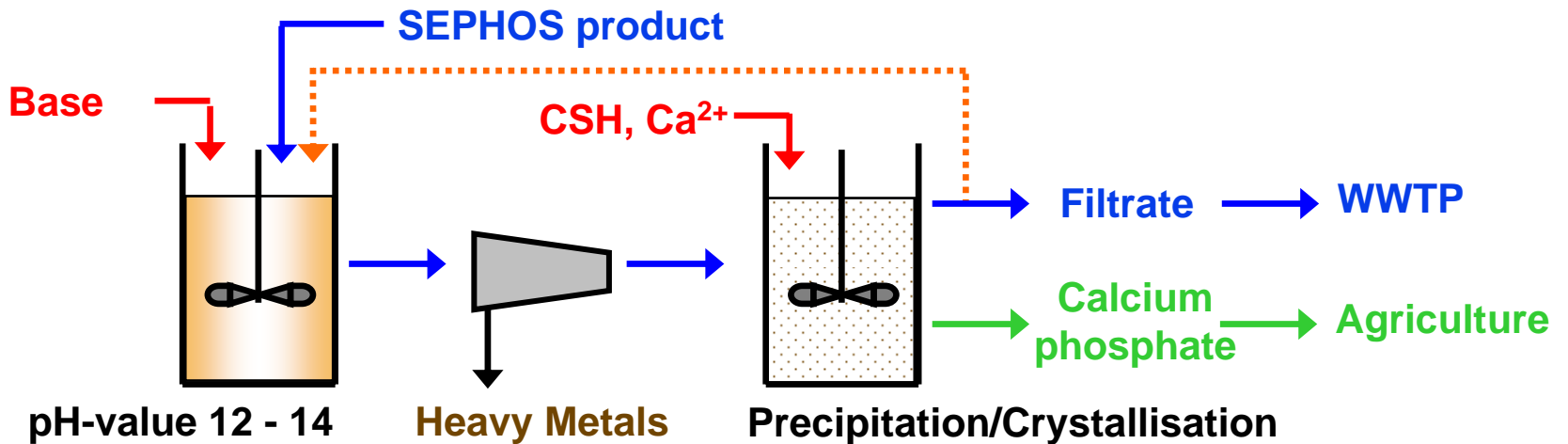
Wet chemical phosphorus recovery from Al-sewage sludge ashes

SEPHOS Process

SEPHOS Process



Advanced SEPHOS Process



Investigation at TU-Darmstadt

Phosphorus recovery and removal from waste activated sludge from Bio-P process

Addition of CSH to waste activated Bio-P sludge for P-removal and recovery



1. Fresh CSH



2. Addition of CSH to waste activated sludge



3. Reaction within anaerobic reactor



4. Separation of P-loaded CSH and P-depleted sewage sludge



5. Washing of the CSH



6. Recycling product: CSH after drying

- Crystallisation of calcium phosphate on particle surface
- Removal of dissolved $\text{PO}_4\text{-P}$ that is released during anaerobic sludge treatment
- Reuse as P-fertilizer (very low content of heavy metals)

Which ways of phosphorus recovery are feasible right now?

Sewage sludge ashes are a good starting point for direct P-recycling

- In the meantime the situation has changed since direct recycling of **SSA** is possible in two ways:
 - The phosphate industry (Thermphos) is ready to take suitable **SSA** ($\text{Fe/P} < 0,2$)
 - Since 2008 German fertilizer legislation allow the recycling of **SSA** as fertilizer
- The mono incinerators can sell their ashes (if suitable...)

Use of sewage sludge ashes as raw material in the phosphorus industry

Requirements for the recycling of ashes

- **Low iron content: (Fe/P Ratio < 0.2 [mol/mol])**
 - Iron increases the energy demand and reduces the output of P₄ more ferro-phosphorus is formed which has a lower value
- **Other metals are a problem:**
 - Volatile metals as Zn, Cd or Pb accumulate in the dust fraction of the furnace
 - Cu present at quite high concentrations in SSA ends up in the ferro-phosphorus and reduces the value
- **What can be done to change the composition of ashes?**
 - Change to Al-precipitation for phosphorous removal (WWTP)
 - Incinerate iron rich and iron poor sludges separately (Incinerators)

Potential for this recycling route:

- Thermphos aims to replace as a first step 20% of its phosphate rock input of 600.000 t/a with **SSA**
→ 120.000 t/a of **SSA** → 8400 t P/a → 11 Mio. population equivalent (PE)
- The percentage could increase in the future!
- The theoretical capacity of Thermphos if operated only with **SSA** would be 600.000 t/a → 55 Mio. PE
- Comparison of size:
 - Netherlands incineration capacity: ca. 150.000 t/a ashes → 14 Mio. PE (56 % of sewage sludge in NL (550.000 t TS/a))
 - German incineration capacity: ca. 300.000 t/a ashes → 27 Mio. PE (24 % of sewage sludge in Germany (2,3 Mio t TS/a))

Thermphos cooperation with SNB

- Slibverwerking Noord-Brabant (SNB) Europe's biggest mono incineration plant delivers ashes to Thermphos
- SNB supplies 6000 t/a → 18.000 t/a in 2013 are planned
- Currently 20% of the sludge incinerated at SNB is iron-poor - SNB plans to increase this to 50% within 5 years

How?

- Eventually SNB aims at differentiating sludge processing tariffs for Fe rich and Fe poor sludges, thus providing an incentive towards Al dosage
- water boards are converting WWTP to biological phosphorus removal plants

→The recycling of ashes is already under way !!!

Advantages of P-recovery at Thermphos



- 90 % P-recovery from ashes is possible without major changes in the sewage sludge infrastructure (most other recycling technologies recover only 30-40%)
- Other recycling routes require investment and operational costs (5 €/kgP) (energy/chemical demand)
- The energy demand for processing **SSA** is only slightly higher compared to phosphate rock
- Change to Al-precipitation and separate incineration is technically feasible
- **Extra cost:** higher costs for Al- precipitants and mono incineration are low compared to other options
- A high theoretical recovery potential of 55 Mio. PE in the future
- Phosphate rock is directly substituted
- Money can be saved → Win Win for both sides

Direct use of sewage sludge ashes as fertilizer

Recycling of sewage sludge ashes as fertilizer



- Direct recycling of **SSA** as fertilizer is legal in Germany if concentration limits for pollutants are met (**As, Pb, Hg, Cd**) (DüMV 2008)
 - No threshold values for Cu and Zn - they are considered micronutrients
- Declaration as “**fertilizer with micronutrients**” if
200 mg/kg > **Cu** < 700mg/kg / 200mg/kg > **Zn** < 5g/kg
- Most **SSA** contain more than 700 mg/kg Cu
 - The P in **SSA** is not water soluble (Whitlockite Ca-P and Al-P)

Recycling of sewage sludge ashes as fertilizer



Solutions:

- 1) Digestion of **SSA** with H_2SO_4 (following the process for super phosphate). 50-80% of P water soluble depending on sludge type (Fe/Al) and amount of acid
- 2) “Dilution” of Zn and Cu by mixing the **SSA** with other P-fertilizer (with low Zn and Cu concentration) in order to meet requirements

→ **Mixing of fertilizers in order to meet threshold values of contaminants is not legal**

Direct use of ashes as fertilizer

- **SSA** contain less Cd (19 mg/kg P_2O_5) and U (50 mg/kg P_2O_5) than phosphate rock but far more Pb and Ni per kg P_2O_5
 - Phosphate rock: 86-569 mg U /kg P_2O_5 and 5-290 mg Cd /kg P_2O_5 , depending on origin of the rock
- The high concentrations of Zn and Cu can be reduced by mixing with other P-fertilizers (P-rock)
- Direct use of ashes as fertilizer is limited; mostly due to high contents of Ni and Pb and low P content (only 6 of 15 testes ashes were suitable)

Summary direct use of ashes

For both recycling options “Thermphos” and “direct use as fertilizer” it will be necessary...

→to switch to Al-precipitation (Fe-Ashes poor P-solubility)

→ to incinerate

“**good sludge**” (high P content, low Fe content, low ratio of heavy metals/P) and
“**bad sludge**” (low P content, high Fe content high ratio of heavy metals/P)
separately!

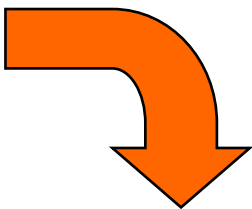
→to further reduce the heavy metals in waste water (only 40% of ashes recyclable)

What could happen to the 9 out of 15 tested ashes that are not suitable for Thermphos or fertilizer use....?

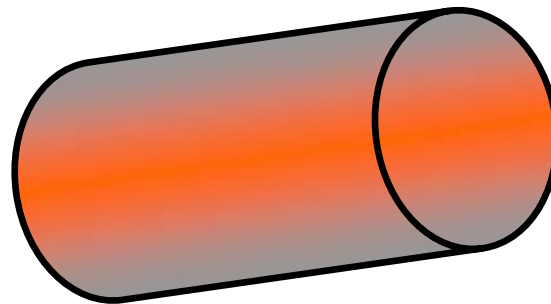
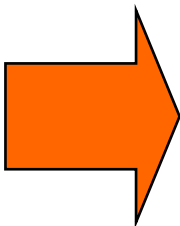
Phosphorus recovery from ash by thermo chemical treatment



$MgCl_2$,
KCl

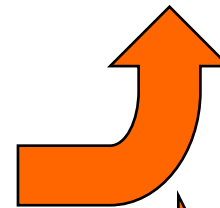


ash

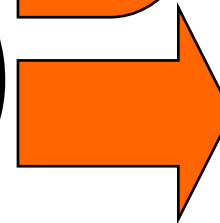


$T > 1,000^\circ C$

gas scrubbing
separation of heavy metal sulfides
(Cd, Hg, Pb, Cu, Zn)



K-/Mg-
phosphate



Conclusions

- **SSA** offer the best starting point for P-recovery as they contain 90% of the incoming P. The following options are at hand:
- **P-recovery in the phosphate industry Thermphos**
 - is technically feasible, high potential for P-recovery
- **P-recovery in the fertilizer industry**
 - direct recycling of ashes that meet requirements for fertilizer
 - **SSA** contain less Cd and U than phosphate rock
 - further reduction of heavy metals (Pb, Ni) necessary at the source
- **Thermochemical P- recovery by ASHDEC © Process**
 - **SSA** that are neither suitable for Thermphos nor as fertilizer could be treated with the ASHDEC ® process

→ Political incentives are necessary to support mono incinerators and waterboards

P-recovery from sewage sludge and sewage sludge ashes

Thank you for your attention!

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