SÜLZLE KOPF SynGas

P-recovery potential from thermal gasified sludge

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Workshop "Phosphorus recovery from wastewater, with a focus on the potential of thermochemical sludge treatment"

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Content

- Company profile
- Motivation
- Alternatives for P-recovery from sewage sludge
- Evaluation of gasification ashes as P-fertiliser
- Summary

Company Profile

- About us
  - Design and construction of turnkey plants
  - Thermal treatment of sewage sludge via gasification
  - Operational basis
    - It belongs 100% to private shareholders
    - Part of the SÜLZLE Group (> 1000 employees)

- Regarding phosphorous recovery
  - Primary approach: Production of high quality ashes to be used directly as fertilisers
  - Alternative: Cooperation with partners offering the best technology in market

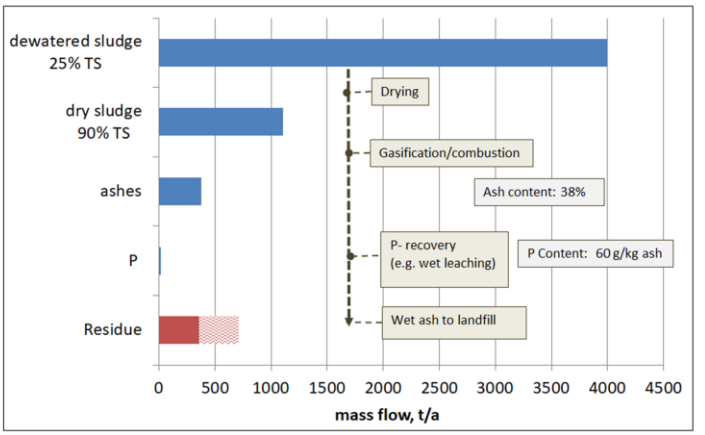
- The primary approach of Kopf Syngas is to produce ashes that fullfill the quality requirements to be used directly as fertiliser.

- The composition of the ashes depends on the quality of the sewage sludge. Because of this, in some cases the expected quality cannot be achieved without post-treatment. In this case look for the cooperation with partners that offer a suitable technology for the treatment of the ashes.

Motivation

- Sewage sludge treatment and transportation generates operational costs to be minimised
- Thermal treatment → Mass reduction, heat/electricity production, elimination of organic pollutants
- P content in ashes is only about 6-8% of the total mass
- The residue has to be disposed (50-100 €/tonne) in landfills
- Other elements are not recycled

→ It is reasonable to extract only P or use the complete ash as fertiliser?

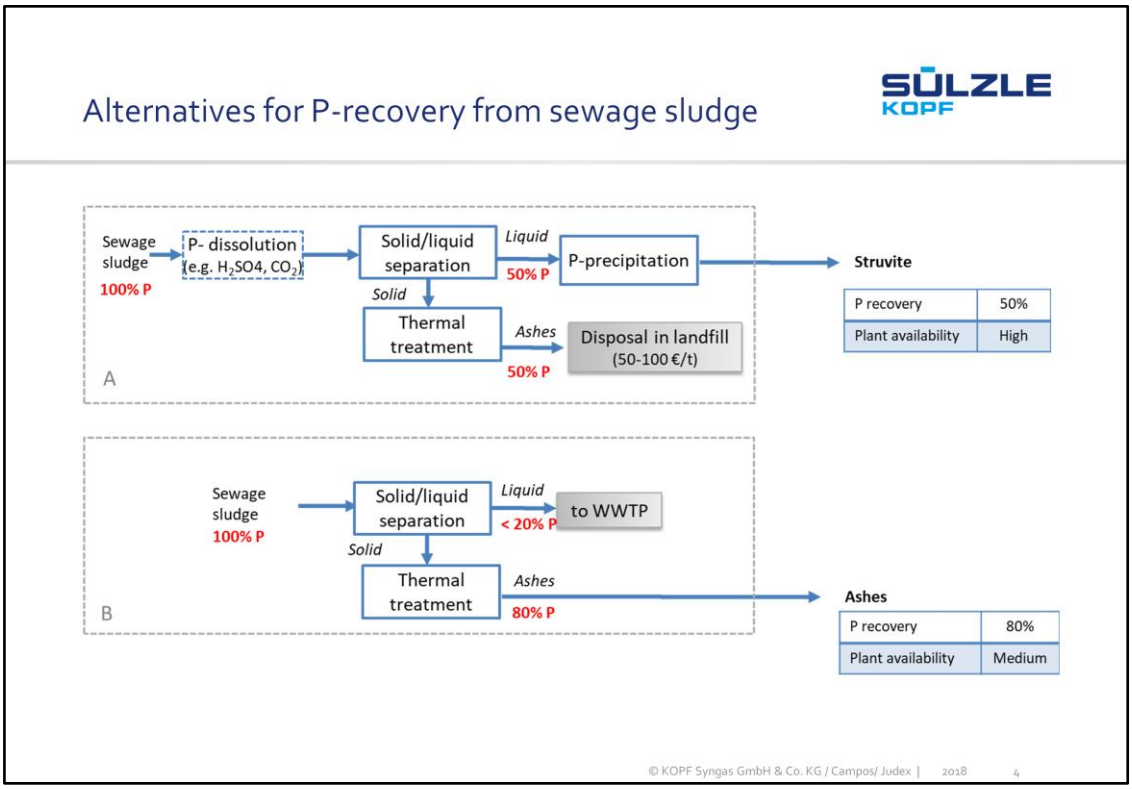


- In Germany: Since 2017 P recovery from sewage sludge is mandatory

 3

- Drying and gasification of sewage sludge reduces the sewage sludge volume considerable.

- Processes for P extraction from ashes produce residues. These residues (for instance wet ashes after P leaching) have to be disposed at high costs



There are three alternatives for the P recovery from sewage sludge:

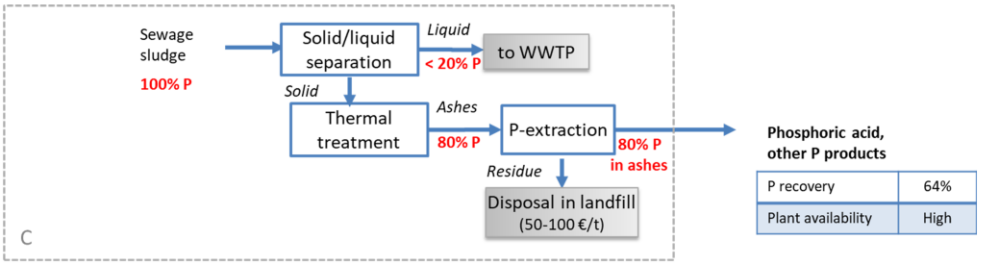
<u>Alternative A: P recovery only from the liquid fraction of sewage sludge</u>

- Disadvantage: Only a small part of P is dissolved in the liquid fraction. It is reported that some technologies have a P recovery of only about 10% .
- To increase the P solubility to max. 50% some processes include an acidication step, which results in more operational costs.
- The solid fraction have still to be treated and the residues disposed
- The advantage of this approach is that the P salts recovered (mainly struvite) have a high plant availability

<u>Alternative B: P recovery from ashes</u>

- Because most of P is in the solid fraction more than 80% can be recovered as ashes
- There is no residues to be disposed because the complete ashes are used as fertiliser
- The plant availability of the ashes is medium, comparable to phosphate rock

Alternatives for P-recovery from sewage sludge



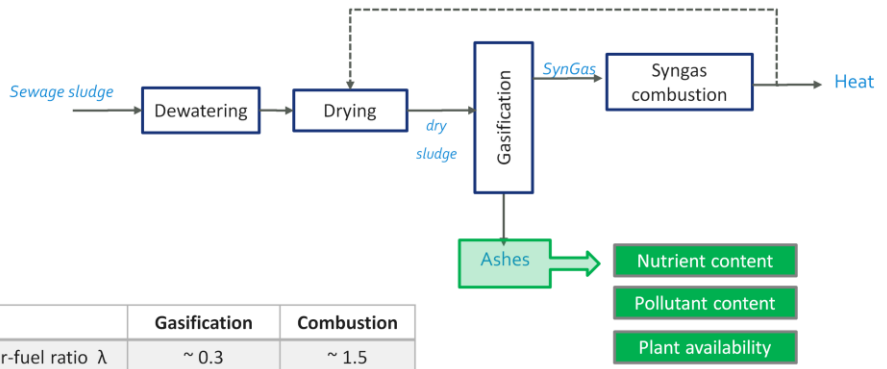
- Direct use as fertiliser → minimise costs (capital, operation,disposal) of further treatments
- If quality requirements cannot be fulfilled (for example high heavy metal concentration in sewage sludge) → post-treatment necessary

<u>Alternative C: P-extraction of the sewage sludge ashes</u>

- This is an alternative in case the the ashes cannot be directly used as fertiliser (for example due to poor quality of sewage sluge with high heavy metals concentration)
- P can be extracted as phosphoric acid or other fertiliser products
- Disadvantage: Residues to be disposed are produced

Evaluation of gasification ashes as P-fertiliser

Gasification technology



	Gasification	Combustion
Air-fuel ratio λ	~ 0.3	~ 1.5
Atmosphere	Reducing	Oxidising
Power density	~ 1.5 MW/m²	< 0.9 MW/m²
Output	Syngas	Flue gas
Ashes type	Carbonaceous	Oxidised

- The main important parameters for the determination of the ash quality as fertiliser are: Nutrient content, pollutant content and plant availability.

Evaluation of gasification ashes as P-fertiliser

Nutrient content

Ash samples	• Ash-BA : WWTP Balingen, Germany • Ash-KO: WWTP Koblenz, Germany

Total nutrient (%)

	Ash-BA	Ash-KO
P	7.5	8.0
K	0.6	0.5
Ca	4.4	1.9
Mg	1.1	1.1
Fe	13.2	18.9

Soluble P (% from P_{total})

	Ash-BA	Ash-KO
Water	<3	<4
Citric acid 2%	47	44
Neutral ammonium citrate	57	31

 7

- The P content of the ashes is high enough to be used as fertilizer according to the German fertiliser regulation

- As expected from this type of material the water soluble P content was low. However, this does not mean that the ashes do not have a fertilising effect in plants. This was proved by the plant tests

Evaluation of gasification ashes as P-fertiliser

Heavy metal content

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Heavy metal content (mg/kg)

	Ash-BA	Ash-KO	Threshold German Fertiliser Regulation
Cd	1.7	<0.2	50
Cr	241	131	300
Hg	0.3	<0.05	1
Ni	129	51.6	80
Tl	<0.1	<0.4	1
Pb	73	20.4	150
As	10.1	3.2	40

- The heavy metal concentration in the two ashes was below the threshold of the German Fertiliser regulation

- The only exception was the nickel concentration in Ash-Ba sample. However, this high value was not found in other ash samples from the WWTP Balingen.

    - The approach in this case is to monitor the concentration over time (several weeks) to determine if the nickel concentration consistently exceed the threshold. If this occurs, the ashes will need a post treatment before they can be used as fertilisers.

Evaluation of gasification ashes as P-fertiliser

Determination of mineral phases

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- **Method**: X-ray diffraction

	$Ca_{2.6}Mg_{0.4}(PO_4)_2$	$(Ca,Mg)_3(PO_4)_2$	$Ca_3Mg_3(PO_4)_4$	Fe_2O_3	Fe_3O_4	$CaSO_4$
	Calcium-Magnesium-Phosphat	Whitlockite, magnesian	Calcium-Magnesium-Phosphat	Haematite	Magnetite	Calcium Sulfate
Ash-BA	✓	✓	✓	✓	✗	✗
Ash-KO	✓	✗	✓	✓	✗	✗
Combustion ashes	✓	✗	✗	✗	✓	✓

- Only qualitative analysis of crystalline forms possible
- Phosphorus as Mg and Ca phosphates
- Depending on thermal treatment conditions (e.g. temperature, oxygen content) Fe is oxidised as haematite or magnetite

→ Correlation between crystalline form and plant solubility ? How can be influenced by the thermal process parameters?

 9

- Aim of this analysis: to determine the phosphorus mineral phases in the ashes after thermal treatment (gasification and combustion)

- Future work: to determine the correlation between the thermal process parameteres (e.g. temperature, oxygen content) and the mineral P phases formation and the relation with the P solubility and plant availability

Evaluation of gasification ashes as P-fertiliser

Plant growth tests at the University of Hohenheim

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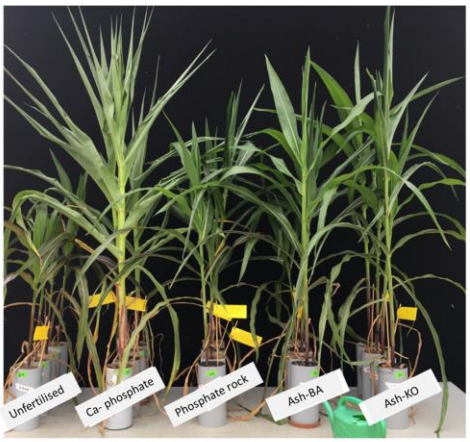
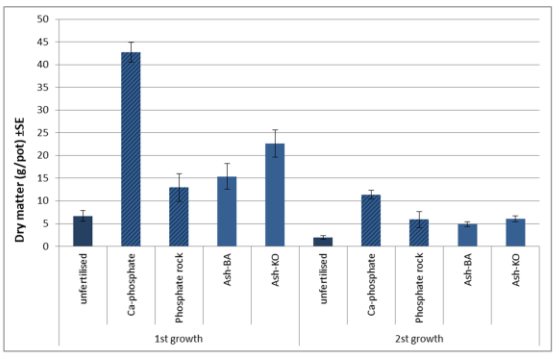
Ash samples	• Ash-BA • Ash-KO
Controls	• Unfertilised • Calcium dihydrogen phosphate (completely soluble P/ traditional agriculture use) • Ground phosphate rock (moderate soluble P / organic agriculture use)
Test plant	• Maize
Substrate	• Mixture of a silty clay soil pH 6.1 and quartz sand • P-fertilisation: 150 mg P/ kg soil
Harvesting	• First growth : 7 weeks • Second growth : 6 weeks



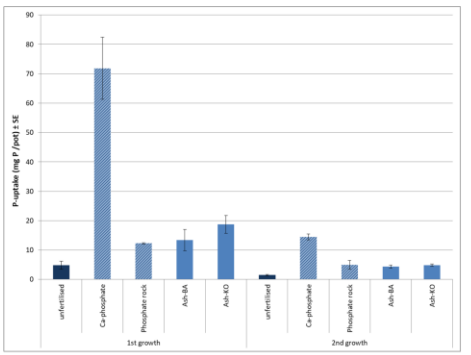
- The plant growth test was carried out by the Institute of Crop Science of the Unviersity of Hohenheim.

Evaluation of gasification ashes as P-fertiliser

Plant growth tests: Dry matter yield and P-Uptake



Maize dry matter yield (g/pot)



P-Uptake of maize (mg P/pot)

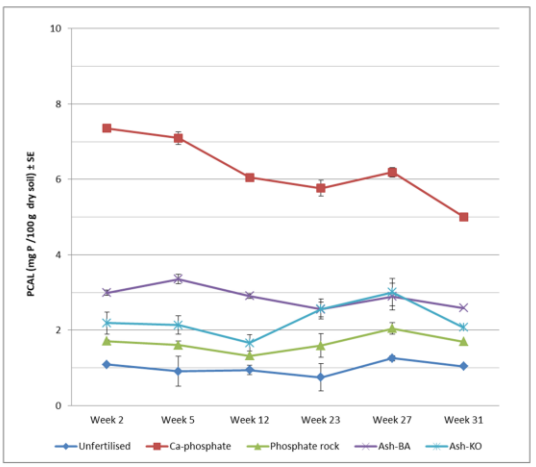
- Dry matter yield and P-uptake of the ashes samples are comparable to phosphate rock in both growths

- The performance of the gasification ashes in comparison with phosphate rock was very positive

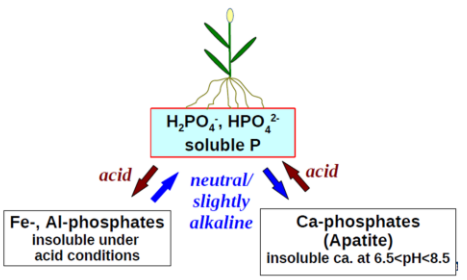
- The higher yield was obtained with calcium phosphate but this was expected because it is a complete water soluble fertiliser. Respect to this, we find that is not adequate to compare one-to-one the performance of fertiliser products from secondary materials (such as ashes) with synthetic soluble products.

Evaluation of gasification ashes as P-fertiliser

Soil P extraction



Soil $P_{CAL\ (calcium\ acetate\ lactate)}$ after incubation at 20°C



Source: Müller, Hohenheim University

- The long term P solubility of the P fertilisers in soil was tested with a P_{CAL} extraction method. This is a standard method for soil analysis.
    - A sample of the soil-fertiliser mixture was dissolved in a calcium-acetate-lactate solution and the dissolved phosphorus in the liquid was measured.
- The P_{CAL} concentration of the calcium phosphate sample clearly decresed with time. This can be explained by the sorption reactions that take place in soil, which immobilised the phosphate ions.
- The P_{CAL} concentration of the other samples (ashes and rock phosphate) was constant with time.
- Conclusion: The gasification ashes can be used as long-term P reservoirs. In this case the P solubility can be comparable with calcium phosphate.

Summary

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- Approach: Direct use of gasification ashes as P-fertiliser → Quality requirements should be fulfilled
- Evaluation of gasification ashes as P-fertiliser
  - High total P-content : 7.5 - 8 % P (16.5 - 17.6 P_2O_5)
  - Low water (<4 % of total P) and medium citric acid/citrate solubility (31-57 % of total P) solubility
  - Plant growth tests showed that availability of gasification ashes is similar to phosphate rock → Direct use as fertiliser in the organic farming for example
- Soil P measurements necessary to determine long term effect of ashes as P deposit
- Further studies of mineral phases and plant tests are planned
  - Effect of thermal process parameters (e.g. oxygen content, temperature, reactor type)
  - Effect of use of additives
  - Effect of the P- elimination process in the WWTP (e.g. Fe/Al precipitation, Bio-P)
- Governmental support
  - Regulations that support the direct use of gasification ashes
    - Revision of the EU Fertiliser regulation in progress
  - Stricter control of heavy metal discharges entering the WWTP → Quality of ashes

Thank you
for your attention

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