Why P-recycling?

- Raw materials securing
  - P-resources > 300 years
  - Dependency on supplier countries (Morocco, China, Russia, Syria)
  - Influence from geopolitical uncertainties

- Environmental protection
  - Nutrient are taken away from the nutrient circular (co-combustion, cement) or are recycled with huge environmental impact (eutrophication)
  - Heavy metal content in P-fertilizer; mainly Uranium (no limit in D), Cd (5-50 mg/kg DM*)

- Legal regulation in Germany
  - “Klärschlammverordnung”: P-recycling is mandatory from 2030 (for P>20g/kg DM)
  - Concepts for P-recycling needs to be provided until 2023

*dry matter
Sewage sludge potential in Europe (Kabbe, 2017)
green, blue and orange = new potential; red = replacement
Resources & nutrient recovery processes

I. Anaerobic Digestion
Manure
140 Mt DM
5 Mt P$_2$O$_5$
Sewage sludge
12.5 Mt DM
750,000 t P$_2$O$_5$
Animal by-products
cat. 1
1.5 Mt DM
450,000 t P$_2$O$_5$

II. De-watering
Biogas (SNG/LNG)
N
Ammonium-sulfate
N+K struvite
5-8% DM

III. Drying
25-30% DM
Landfill

IV. Thermal conversion
45-90% DM
Ash from WHB

V. Ash processing
ASH DEC Process
Secondary residues
Raw material P(K)Fertilizer

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April 2018
AshDec Process - IWA Sweden Seminar - Phosphorus recovery from wastewater
Dryer – pilot plant Sweden

Sewage sludge incineration plant Switzerland
# P-rich ash vs. rock phosphate concentrate

<table>
<thead>
<tr>
<th>Substance</th>
<th>Khouribga rock MA</th>
<th>D&lt;sup&gt;1&lt;/sup&gt; Animal by-products</th>
<th>NL&lt;sup&gt;2&lt;/sup&gt; Poultry manure</th>
<th>NL Pig manure 1</th>
<th>NL Pig manure 2</th>
<th>NL WWTP Sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P}_2\text{O}_5$ %</td>
<td>32.97</td>
<td>32.50</td>
<td>22.71</td>
<td>23.60</td>
<td>22.00</td>
<td>21.30</td>
</tr>
<tr>
<td>CaO %</td>
<td>51.34</td>
<td>44.10</td>
<td>37.19</td>
<td>17.90</td>
<td>16.80</td>
<td>15.70</td>
</tr>
<tr>
<td>SiO$_2$ %</td>
<td>2.35</td>
<td>1.80</td>
<td>3.19</td>
<td>15.70</td>
<td>10.90</td>
<td>21.60</td>
</tr>
<tr>
<td>Al$_2$O$_3$ %</td>
<td>0.40</td>
<td>1.10</td>
<td>0.79</td>
<td>1.70</td>
<td>1.00</td>
<td>10.80</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ %</td>
<td>0.20</td>
<td>1.00</td>
<td>1.05</td>
<td>2.10</td>
<td>11.90</td>
<td>16.30</td>
</tr>
<tr>
<td>MgO %</td>
<td>0.30</td>
<td>3.00</td>
<td>6.67</td>
<td>13.10</td>
<td>11.00</td>
<td>2.90</td>
</tr>
<tr>
<td>Na$_2$O %</td>
<td>0.80</td>
<td>7.90</td>
<td>3.59</td>
<td>1.60</td>
<td>1.80</td>
<td>1.00</td>
</tr>
<tr>
<td>K$_2$O %</td>
<td>0.10</td>
<td>2.90</td>
<td>17.17</td>
<td>6.80</td>
<td>7.70</td>
<td>1.00</td>
</tr>
<tr>
<td>SO$_3$ %</td>
<td>1.70</td>
<td>4.30</td>
<td>6.71</td>
<td>6.10</td>
<td>11.70</td>
<td>5.00</td>
</tr>
<tr>
<td>Cd mg/kg $\text{P}_2\text{O}_5$</td>
<td>51.60</td>
<td>0.92</td>
<td>21.09</td>
<td>10.17</td>
<td>12.72</td>
<td>13.76</td>
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<tr>
<td>Pb mg/kg $\text{P}_2\text{O}_5$</td>
<td>9.10</td>
<td>26.77</td>
<td>475.56</td>
<td>33.89</td>
<td>36.36</td>
<td>943.67</td>
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<tr>
<td>Zn mg/kg $\text{P}_2\text{O}_5$</td>
<td>700.00</td>
<td>1’415.38</td>
<td>12’091.59</td>
<td>31’355.93</td>
<td>25’000.00</td>
<td>10’239.43</td>
</tr>
</tbody>
</table>
AshDec process

Na\textsubscript{2}SO\textsubscript{4}

As, Cd, Pb, (Zn)

CaNaPO\textsubscript{4}

ASH  PROCESS  FERTILIZER

1000°C
AshDec – basic flowsheet without heat recovery
Consumption figures and residues

• Na$_2$SO$_4$ consumption depends on P and Si content in ash
  • Na : P $\approx$ 1,3 – 1,6 mol ratio
  • Na : Si $\approx$ 0,3 – 0,5 mol ratio
  • Example: For one ton of fertilizer produced 0.26 t of Na$_2$SO$_4$ are needed (typical sludge composition assumed)

• Reduction agent – containing P and C – consumption depends on the level of heavy metal removal (Pb, Cd, Hg)
  • 10 – 20 wt.% - HM removal in range of 30 – 50 %
  • 25 – 75 wt.% - HM removal in range of 40 – 70 %

• Fuel consumption depends on the ash temperature and heat recovery within the process
• Residue: Typical amount is 3 - 5 % of ash feed; residue contains removed heavy metals
AshDec® product bioavailability from gasification compared to superphosphate (Ylivainio, K., 2017)

- Solubility tests don’t give always the „correct“ conclusion regarding the fertilizer quality
- AshDec product has much lower P solubility as superphosphate
- P-Bioavailability in AshDec product is 2.4-time higher than in superphosphate
- Pot test showed stronger growth of barley grain with AshDec product than with the same amount of superphosphate
Corn pot test (M. Severin et al. 2014)

Sandy soil 1.14 mg P/100g soil, pH 7.0 after neutralization with lime, Mitscherlich-pot 6 kg/pot, 9 corn crops.

Fertilizing in 3 steps (0.176; 0.352 and 0.528 g P per pot)
CLOOP* – developing NextGen Fertilisers
*Closing the global nutrient Loop

Duration: 01.11.2017-31.10.2020

Summary:
CLOOP aims at developing a market for recycled fertilizers (AshDec and struvite) by gradually changing the perception of a quality fertilizer, i.e. products that release nutrients in synchrony with crop uptake in compliance with the NextGen Fertiliser concept of University Queensland.

Partners: Bundesanstalt für Materialforschung und -prüfung (BAM) Kompetenz Zentrum Wasser Berlin (KWB) Rheinischen Friedrich-Wilhelms-Universität Bonn University of Queensland and Universidad de Sao Paulo
CLOOP - Objectives

• Increasing the phosphorus use efficiency in comparison to conventional
• Reducing phosphate losses to aquatic bodies, eutrophication and algae blooms. (This is especially important at the Great Barrier Reef where the critical state is demanding fast action and real solutions to the problem of nutrient losses but applies generally to all water bodies. Globally, the levels of reactive phosphorus in the biosphere are now 3-fold above natural background (and higher in many water bodies) which demands urgent action and real innovation.)
• Eliminating the contribution of free acids in fertilizers to the acidification of soils.
• Reduce the demand for the critical raw material (CRM) rock phosphate
• Reducing or almost eliminating the waste flows of conventional fertilizer processes.
Outotec  Sustainable use of Earth’s natural resources