PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE – IDEAS FOR FURTHER STUDIES TO IMPROVE LEACHING

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ABSTRACT
Development of methods to recover phosphorus will make handling of sewage sludge more sustainable. In earlier studies sludge incineration ash and SCWO-residues have been leached with acid and base. Acid leaching gives a high degree of recovery but releases besides phosphate also the main part of other metals (including heavy metals). This gives a large separation problem and gives a complicated process technology. Leaching with base (NaOH) gives a lower degree of recovery (up to about 50 %) however with less dissolution of metals. When leaching with base, the calcium content in the sludge probably binds phosphorus as calcium phosphate.

To improve leaching different possibilities can be studied such as use of a two-step leaching process. In a first step acid leaching dissolves calcium and magnesium. Treating the leachate with sulphuric acid, calcium sulphate (gypsum) is precipitated and phosphoric acid is obtained. Remaining ash or SCWO-residual product can afterwards be treated by alkaline leaching. Another alternative is to study leaching at anaerobic conditions. Since ferrous iron(II) phosphate is more soluble than ferric iron(III) phosphate the phosphate is more easily dissolved and the heavy metal contamination will be lower.

KEYWORDS
Acid, Base, Leaching, Phosphorus recovery, Sewage sludge

BACKGROUND
Sustainable handling of municipal organic waste and sewage sludge has as an important goal to recycle resources without supply of harmful substances to humans or the environment (Levlin 1999, Hultman and Levlin, 1997). Another important goal is to avoid deposition of waste and sludge on landfill. In Sweden a tax of 250 SEK/ton on all deposited solid waste was introduced year 2000 (SFS 1999:673). Deposition of incinerable waste has been prohibited and in year 2005 there will be a ban on deposition of all organic material on landfill (SFS 2001:512). Incineration (ATV, 1997) and SCWO, Super Critical Water Oxidation (Stendahl and Jäfverström, 2003), are methods that eliminate all organic content and the potential energy of the organic material can be utilised. SCWO occurs in water of a supercritical phase at a temperature above 374 °C and a pressure higher than 22 Mpa. Sludge incineration requires that the sludge have to be dried to 40 % dry substance. The energy produced from the incineration is consumed in the drying process and there is therefore normally no net energy recovery from sludge incineration. With use of SCWO, energy can be recovered also from sewage sludge and organic waste with too low dry substance for incineration. Anaerobic digestion eliminates half of the organic content and half of the energy can be utilised as
methane gas. Increasing the energy recovery from sewage sludge and organic waste decreases the need of fossil fuel and makes the society more sustainable. Handling of sludge and organic waste can be integrated by use of food waste disposers and transporting the organic waste to the wastewater treatment plant with the sewer net (Karlberg and Norin, 1999). The resources in sludge and solid organic waste remaining after SCWO or incineration are nutrients such as phosphorus. Sludge incineration and SCWO are processes that may be introduced in Sweden to be able to fulfill the requirements for deposition. This may be followed with requirement that phosphorus shall be recovered from the ash or the residual product.

Development of methods to recover phosphorus will make handling of municipal organic waste and sewage sludge more sustainable. The motives for phosphorus recovery are summarised in table 1. Since phosphorus is needed as a fertilizer in the agriculture, a requirement for getting sustainable wastewater treatment is to create a method to recover the phosphorus from the wastewater. Most of the phosphorus used in the agriculture originates from mining of phosphate ores, which thus is a limited resource. Phosphorus recovery by spreading sludge on agricultural land has been stopped to a high extent due to resistance from the farmers’ organisation (LRF) and food industries. The pollution content in sewage sludge (Levlin et al., 2001) makes direct use of sludge as fertilizer difficult. An alternative to phosphorus recovery is to pure sludge from toxic contaminants (Levlin et al., 1996). However, phosphorus recovery reduces the amount of materials and thereby the transport cost.

Table 1. Motives for phosphorus recovery from sewage water, sludge and ash.

<table>
<thead>
<tr>
<th>Motive</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus as a limited resource</td>
<td>Minable resources of estimated 12 000 million tonnes is estimated to last for a period up to 100 years. The reserves of estimated 47 000 million tonnes is estimated to last for a period up to 370 years (ATV, 2003) (Large differences between estimations).</td>
</tr>
<tr>
<td>Phosphorus as a diffuse pollutant</td>
<td>Phosphorus release can be 20 % at aerobic conditions during 10 years for sludge used as soil cover (higher release at anaerobic conditions) (Rydin et al., 1999). In some soils there are already phosphorus saturation.</td>
</tr>
<tr>
<td>Pollutants in sludge for use in agriculture and green areas</td>
<td>Difficulties to fulfill requirements by authorities and to gain public acceptance</td>
</tr>
<tr>
<td>Income from phosphorus products</td>
<td>Low compared to the cost for phosphorus recovery</td>
</tr>
<tr>
<td>Influence on sludge volumes and sludge properties</td>
<td>Decreased sludge volume for deposition. Dewatering properties are often improved at recovery from sludge</td>
</tr>
</tbody>
</table>

Recently, Swedish policy recommends phosphorus to be recycled and, because agricultural sewage sludge re-use is increasingly limited, this is putting pressure on cities to develop phosphorus recovery systems. In a number of cases, authorisation to construct sludge incinerators is being given condition that phosphorus must be recovered. A national goal has been proposed to the Swedish government that at least 75 % of phosphorus from wastewater and other biological wastes should be recovered at latest by 2010 without risks for health and environment (Miljömålskommittén, 2000). The Swedish Environment Protection Agency (SEPA) has been given a commission from the government to better evaluate possibilities to implement the goal and propose modifications. A draft "state-of-the-art" report on phosphorus recovery has been worked out (Balmér et al., 2002, Balmér, 2003). The new goal of SEPA was 60 % recovery of phosphorus from sewage.
Precipitation of phosphorus into the sewage sludge decreases emission of phosphorus from wastewater treatment plants. Phosphorus removal from municipal wastewater has a long tradition in Sweden to protect receiving waters from eutrophication with the first plant for phosphorus removal in Åker municipality in 1961. Since that time phosphorus removal in Sweden has mainly been based on chemical precipitation with iron salts as dominating precipitation agent. Only a few plants are operated with biological phosphorus removal in Sweden, although this process technology is widely used internationally. However, phosphorus precipitated in sludge can be released at sludge disposal (Rydin, 1996) and thus contribute to eutrophication. Release of phosphorus to marine environment favours growth of nitrogen fixation algae, thus decreasing the effect of reducing nitrogen emissions (Naturvårdsverket, 2003). Recovery of phosphorus from sludge and organic waste thereby reduces phosphorus release from disposal sites and thereby the risk for eutrophication.

Leaching with acid and base is a promising method for phosphorus recovery from waste water treatment of sewage sludge. Phosphorus recovery from SCWO, Super Critical Water Oxidation, residues by leaching with acid and base in order to recover phosphorus from sludge has been studied in experimental works (Hultman et al, 2002, Hultman and Löwen, 2001, Levlin et al., 2002, 2004a, 2004b, Stark, 2002a, 2002b and 2002c, Stark and Hultman, 2003) at the department of Land and Water resources Engineering, KTH.

Samples of ash taken from the co-incineration of sludge with municipal waste, sludge incineration plant and SCWO residues have been leached with acid, hydrochloric acid and base, sodium hydroxide. The metal and phosphorus content before leaching has been analyzed as well as the metal and phosphorus content in the leachate. Leaching with acid gives a higher release of phosphorus compared to leaching with base. The largest degree of leached phosphorus (80 – 100 % at acid concentrations below 0.5 M) was obtained by leaching SCWO residue with acid. Acid leaching of sludge incineration ash gave 75 – 90 % leached phosphorus at the concentration 1 M. Alkaline leaching of sludge incineration ash and SCWO-residue gave 50 – 70 % leached phosphorus at the concentration 1 M. When leaching with base, the calcium content in the sludge binds phosphorus as calcium phosphate. On leaching with acid it is difficult to recover phosphorus as other products than iron phosphate. However, iron phosphate has no commercial value as raw material for the phosphate industry, and the low solubility makes it less favorable to use as fertilizer. For the production methods used in phosphate the industry iron phosphate is a pollutant, which binds phosphorus and reduces the amount of produced phosphorus.

POSSIBILITIES FOR IMPROVING LEACHING

Two stage leaching
A solubility diagram for aluminum phosphate, calcium phosphate (apatite) and iron phosphate is shown by figure 1. According to the figure it should be possible to leach selectively with increasing acid addition, first release of calcium phosphate, thereafter aluminum phosphate and finally iron phosphate. Leaching ash from Mora with 0.25 mol/l gave a content in the leachate of 814 mg Ca/l, 85.6 mg Fe/l, 56.6 g Mg/l, 836 mg Al/l and 1134 mg P/l. Dominating ions in the leachate were Ca$^{2+}$ and Al$^{3+}$ and dissolved H$_3$PO$_4$. At lower acid concentration the quota Ca/Al increases and the amount of released phosphorus becomes lower.
Differences in compositions of sludge depend mainly on the choice of precipitation chemicals. Use of iron as precipitation chemicals gives high iron content and use of aluminium as in Mora gives high iron aluminium content in the ash. The chemical composition of Mora ash is 41.1 % Al₂O₃, 6.91 % CaO, 11.9 % Fe₂O₃, 0.99 % MgO, 18.5 % P₂O₅ and 20.1% SiO₂. The chemical need for dissolving different inorganic components (table 2) can be calculated. Mainly phosphate and aluminate are dissolved at alkaline leaching. Leaching Mora ash with 0.5 mol/l NaOH gave a leachate with 2 mg Ca/l, 1.1 mg Fe/l, 970 mg Al/l and 930 mg P/l (Levlin et al., 2004a and 2004b). The phosphorus release was 60 %. It is possible that leaching have been prohibited by precipitation of insoluble calcium aluminium compounds for instance Ca₂AlOH (compare with Farrell et al., 1968).

Table 2. Chemical need for leaching inorganic sludge components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Leaching reaction</th>
<th>g HCl or NaOH for component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching with acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>Fe(OH)₂ + 2H⁺ → Fe²⁺ + 2H₂O</td>
<td>0.811</td>
</tr>
<tr>
<td>Fe₃(PO₄)₂</td>
<td>Fe₃(PO₄)₂ + 4H⁺ → 3Fe²⁺ + 2H₂PO₄⁻ (pH&gt;2.2)</td>
<td>0.408</td>
</tr>
<tr>
<td>Fe₃(PO₄)₂</td>
<td>Fe₃(PO₄)₂ + 6H⁺ → 3Fe²⁺ + 2H₃PO₄⁻ (pH&lt;2.2)</td>
<td>0.612</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>Fe(OH)₃ + 3H⁺ → Fe³⁺ + 3H₂O</td>
<td>1.024</td>
</tr>
<tr>
<td>FePO₄</td>
<td>FePO₄ + 2H⁺ → Fe³⁺ + H₂PO₄⁻ (pH&gt;2.2)</td>
<td>0.484</td>
</tr>
<tr>
<td>FePO₄</td>
<td>FePO₄ + 3H⁺ → Fe³⁺ + H₃PO₄⁻ (pH&lt;2.2)</td>
<td>0.725</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>Al(OH)₃ + 3H⁺ → Al³⁺ + 3H₂O</td>
<td>1.402</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>AlPO₄ + 2H⁺ → Al³⁺ + H₂PO₄⁻ (pH&gt;2.2)</td>
<td>0.598</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>AlPO₄ + 3H⁺ → Al³⁺ + H₃PO₄⁻ (pH&lt;2.2)</td>
<td>0.897</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>CaCO₃ + 2H⁺ → Ca²⁺ + CO₂ + H₂O</td>
<td>0.729</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>MgCO₃ + 2H⁺ → Mg²⁺ + CO₂ + H₂O</td>
<td>0.865</td>
</tr>
<tr>
<td>Leaching with base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePO₄</td>
<td>FePO₄ + 3OH⁻ → PO₄³⁻ + Fe(OH)₃</td>
<td>0.796</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>Al(OH)₃ + OH⁻ → Al(OH)₄⁻</td>
<td>0.513</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>AlPO₄ + 4OH⁻ → Al(OH)₄ + PO₄³⁻</td>
<td>1.312</td>
</tr>
</tbody>
</table>
A process system for phosphorus recovery from ash or SCWO-residual product is illustrated in figure 2. In a first step the solid products is leached with hydrochloric acid (HCl). Since it is a rather expensive chemical the main purpose is to dissolve calcium and magnesium ions and a part of the phosphorus. For this step sulfuric acid (H₂SO₄) cannot be used since calcium sulfate has a very low solubility. If the leachate after this step is treated with sulfuric acid, calcium sulfate (gypsum) is precipitated and phosphoric acid is obtained together with some ions, which have a value as fertilizer (potassium, magnesium). If the phosphorus recovery at the leaching is required to be high (more than 60 %) some aluminum will also be leached. It may then be necessary to separate dissolved aluminum ions from the leachate before production of phosphoric acid or calcium phosphate. Separation of aluminum can be made with ion exchange according to the process proposed by Petruzzelli et al. (2000) with alkaline regeneration of the ion exchanger. Alternatively dihydrogen phosphate may be removed by ion exchange or by selective adsorption material. Remaining ash or SCWO-residual product from the acid leaching can afterwards be treated by alkaline leaching. Also sodium hydroxide is an expensive chemical but since part of the phosphorus and eventually aluminum already has been leached, is the chemical need for the complementary alkaline leaching rather low. Sodium hydroxide can be recovered through precipitation of phosphate with lime and removal of aluminate (precipitation or ion exchange). For the precipitation that is obtained as calcium phosphate at addition of lime and eventual calcium aluminum compound there are possibilities to further processing by addition of acid in the same way as by the acid leaching in step 1.

**Figure 2.** Illustration of system for recovery of phosphorus from ash or SCWO-residual product.
Leaching at anaerobic conditions
A technology for recovery of phosphate from iron phosphate may be using natural reactions occurring in see sediment (Hultman, 1998). At oxygen rich conditions iron is precipitated as ferric (III)phosphate (figure 3). At oxygen free conditions iron is reduced to ferrous ions and the more soluble ferrous phosphate is dissolved. If both ferrous iron and phosphate is released from the sediment, the iron is oxidized to ferric iron and the phosphate is precipitated as ferric phosphate. However if hydrogen sulfide is present in the sediment the ferrous iron is precipitated as ferrous sulfide and the phosphate can be released from the sediment.

Figure 3. Different reactions between phosphate, sulfide and iron in lake sediment at which phosphate can be released (Klee, 1985).

Rydin (1996) found at leaching sludge with rainwater at pH-level=5, that about 95 % of the phosphorus could be released at anaerobic conditions, while leaching at aerobic conditions only dissolved about 20 % - 30 %. If sulphide in the sediments reacts with divalent iron to ferrous sulphide and phosphate can be released from the sediment. Without sulphide the iron is oxidised then the ions reach oxygen rich water and ferric phosphate is precipitated. The use of sulphide for phosphorus recovery has been studied by Suschka et al. (2001). At addition of sulphate by anaerobic conditions the sulphate was reduced by sulphate reducing bacteria to hydrogen sulphide. The ferrous phosphate was thereby dissolved and the iron was precipitated as ferrous sulphide.

\[
\text{Fe}_3(\text{PO}_4)_2 (s) + 3 \text{H}_2\text{SO}_4 \rightarrow 3 \text{FeS} (s) + 2 \text{H}_3\text{PO}_4 + 2 \text{O}_2
\]

Solubilities of ferrous and ferric phosphate
Ferrous phosphate is more soluble than ferric phosphate and the solubility is higher at acid conditions. Since the concentration of phosphate ions decreases at lower pH-values, phosphate compounds are soluble in acids and can thus be leached and recovered from incineration ashes by use of acid.

\[
\begin{align*}
\text{H}_3\text{PO}_4^0 & \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+ \\
\text{H}_2\text{PO}_4^- & \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+ \quad \text{pK}_1=2.148 \\
\text{HPO}_4^{2-} & \leftrightarrow \text{PO}_4^{3-} + \text{H}^+ \quad \text{pK}_2=7.198 \\
\end{align*}
\]
The equilibrium concentration of phosphate is calculated by the formula:

\[ [\text{PO}_4^{3-}] = K' \times [\Sigma \text{PO}_4] \]

there: \([\Sigma \text{PO}_4]\) = total concentration of phosphate in the solution

\[ K' = \frac{1}{1 + 10^{(-pH + 12.023)} + 10^{(-2*pH + 12.023 + 7.198)} + 10^{(-3*pH + 12.023 + 7.198 + 2.148)}} \]

From this relationship the solubility of phosphorus compounds can be calculated. The solubility for ferric and ferrous phosphates are:

- \(\text{FePO}_4 \cdot 2\text{H}_2\text{O} (s) \rightarrow \text{Fe}^{3+} + \text{PO}_4^{3-} + 2 \text{H}_2\text{O}\) Stumm and Morgan (1981): \(K = 10^{-26}\)
- \(\text{FePO}_4 (s) \rightarrow \text{Fe}^{3+} + \text{PO}_4^{3-}\) Corbridge (1995): \(K = 1.3 \times 10^{-22}\)
- \(\text{Fe}_3(\text{PO}_4)_2 (s) \rightarrow 3 \text{Fe}^{2+} + 2 \text{PO}_4^{3-}\) Stumm and Morgan (1981): \(K = 10^{-32}\)

The concentration of for instance ferrous iron(II) phosphate in a solution in equilibrium with iron and phosphate ions can be calculated from that dissolution of \(X\) mole phosphate and gives a dissolution of \(1.5X\) mole iron(II):

\[ [\text{PO}_4^{3-}]^2 \times [\text{Fe}^{2+}]^3 = (K' \times [\Sigma \text{PO}_4])^2 \times [1.5X]^3 = (K')^2 \times (1.5)^3 \times [X]^2 \times [X]^3 = 10^{-32} \]

Which gives:

\[ X = \sqrt[5]{\frac{10^{-32}}{(1.5)^3 \times (K')^2}} \text{ mole/litre} \]

The concentration of for instance ferric iron(III) phosphate in a solution in equilibrium with iron and phosphate ions can be calculated from that dissolution of \(X\) mole phosphate and gives a dissolution of \(X\) mole iron(III):

\[ [\text{PO}_4^{3-}] \times [\text{Fe}^{3+}] = (K' \times [\Sigma \text{PO}_4]) \times [X] = (K') \times [X] \times [X] = 10^{-22} \]

Which gives:

\[ X = \sqrt[2]{\frac{10^{-22}}{K'}} \text{ mole/litre} \]

From these formulas a diagram of solubility versus pH can be made (figure 4). In this diagram the dissolution of ferric phosphate at higher pH-levels due to precipitation of ferric hydroxide have not been considered.

\[ \text{FePO}_4 (s) + 3 \text{OH}^- \rightarrow \text{Fe(OH)}_3 (s) + \text{PO}_4^{3-} \]
However the diagram shows that the solubility of ferric phosphate is high enough at low pH-level to allow leaching of phosphate with a weaker acid than with ferrous phosphate. Since heavy metals such as mercury and cadmium are more insoluble at anaerobic conditions than at aerobic (Levlin, 1993) and the leaching can be made at higher pH-level, the dissolution of heavy metals will be lower. A phosphorus product less contaminated by heavy metals can therefore be obtained. To obtain a phosphate product the dissolved iron has to be separated from the leachate. This may be done with ion exchange or with hydrogen sulfide.

\[
\begin{align*}
\text{Fe(II)}_3(\text{PO}_4)_2 & \quad K_s=10^{-32} \\
\text{Fe(III)PO}_4 & \quad K_s=1.3\times10^{-22} \\
\text{Fe(III)PO}_4 & \quad K_s=10^{-26}
\end{align*}
\]

(Stumm and Morgan, 1981; Corbridge, 1995)

Figure 4. Calculated solubility for ferrous and ferric phosphates versus pH.

CONCLUSIONS

The results achieved in earlier studies of leaching sludge incineration ash and SCWO-residues with acid and base pointed on following problems:

- Acid leaching of sludge or ash releases besides phosphate also the main part of other metals (including heavy metals). This gives a large separation problem and gives a complicated process technology.
- Leaching with base (NaOH) gives a rather low degree of recovery (up to about 50 %).

To improve leaching phosphorus with a lower heavy metal contamination different possibilities can be studied:

- Use of two-step leaching process. In a first step acid leaching dissolve calcium and magnesium. Treating the leachate with sulfuric acid, calcium sulfate (gypsum) is precipitated and phosphoric acid is obtained. Remaining ash or SCWO-residual product can afterwards be treated by alkaline leaching.
- Leaching at anaerobic conditions makes the iron phosphate more soluble. A phosphorus product less contaminated by heavy metals can therefore be obtained.
ACKNOWLEDGEMENT
Gratitude is given to VA-Forsk for financing further studies to improve leaching sludge incineration ash and SCWO-residues.

REFERENCES


