

SUSTAINABLE SLUDGE HANDLING – METAL REMOVAL AND PHOSPHORUS RECOVERY

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ABSTRACT

Sustainable sludge handling means recycling of resources without supply of harmful substances to humans or the environment. An important resource is nutrients which can be utilised through using sludge as fertiliser in the agriculture. Thus, the harmful substances such as heavy metals in the sludge must be minimised through source control. Otherwise, harmful metals such as chromium can be removed from the sludge by leaching methods. Alternatively, the nutrients can be recovered and used as fertiliser. Phosphate fertiliser is produced by mining of phosphate ores, and the supply may become crucial. Phosphate removed biologically from the wastewater can be recovered from the supernatant after digestion by precipitation as struvite $MgNH_4PO_4$. Phosphate removed chemically as metal phosphate must be leached from the sludge. Thermal hydrolyse is in the KREPRO project used to fractionate the sludge and in the Cambi process used to increase the efficiency in the digestion. To avoid waste disposal, the inorganic content of the sludge can be used for production of building material.

KEYWORDS

Sludge handling, metal removal, chromium, phosphorus recovery

INTRODUCTION

Wastewater sludge may be regarded both as a resource which should be recycled in a proper way and a threat to the environment (Hultman and Levlin, 1997). Sustainable sludge handling may therefore be defined as a method that meets requirements of efficient recycling of resources without supply of harmful substances to humans or the environment. The sludge handling should be performed in an energy and resource efficient way. The sludge handling scheme should consider most of the sludge components as resources suitable for manufacturing of products, while the pollutants should be separated into a small stream or be destructed.

SOURCE CONTROL

An important resource in the sludge is nutrients which can be utilised through using sludge as fertiliser in the agriculture. Agricultural use is regarded as the best alternative if the pollutants in the sludge is below limiting and guidance values. The policy of Stockholm Water (Mossakowska et al. 1998) is to regard sludge as a resource that should be recirculated in an eco-cycle. The use in agriculture has therefore been considered as the main alternative.

The use of sludge in agriculture has, however, not been accepted from the food industry, certain interest organisations and part of the public even if the sludge quality is better than the stringent requirements from the authorities. Many metals accumulate to high concentrations in the surface layer of soil treated with sewage sludge (Alloway, 1995). The depth of the contaminated soil depends on the depth to which sludge is

physically incorporated by ploughing or other cultivation. After addition there is little evidence of significant downward movement of the metals in the soil.

Source control of pollutants to the sewer net has a key role for the sludge quality. Every Swedish municipality may state restrictions on what substances that may be supplied to the sewer net for example limiting values or prohibition of certain substances. These restrictions are valid both for connected industries and households. In general, there has been a decrease in the metal contents in the sewage sludge due to less metal use in society. Examples include a change to lead free gasoline, a stop in use of mercury thermometers, and ban on cadmium in paints and in finishing. A guarantee of the sludge quality may be secured by use of an intensive control of the dewatered sludge. Stockholm Water has produced routines for the control of the sludge quality to be able to determine final disposal method for the sludge so that no sludge that is not approved will be supplied to agricultural land.

METAL REMOVAL

Leaching with acid

If the metal content of the sludge is too high, the metal can be removed from the sludge by leaching with acid (Levlin et al., 1996). Figure 0 shows solubility for pure metal hydroxide as a function of pH (Nilsson 1971). After the acid metal solution has been separated from the sludge, the acid is neutralised and the metals are precipitated as a metal hydroxide sludge.

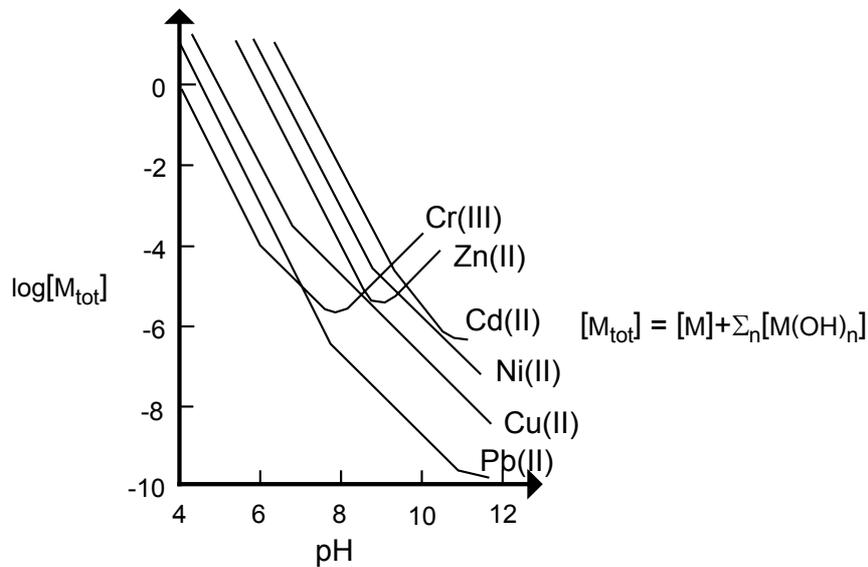
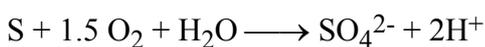


Figure 1. Solubility for pure metal hydroxide as a function of pH (Nilsson 1971).

Table 0 shows metal solubilization in a comparison between chemical and microbial leaching (Blais et al., 1992). The three alternatives there:

- Chemical leaching with sulphuric acid at pH-level 1.5.
- Microbial leaching with addition of sulphur, which by the action of sulphide oxidising bacteria is transformed to sulphuric acid.



- Microbial leaching with addition ferrous sulphate. The ferrous ions are by iron bacteria oxidised to ferric ions, which oxidises the metal sulphide to soluble sulphate. An acid solution is obtained by addition of sulphuric acid and precipitation of ferric hydroxide.

The largest solubilization was obtained with microbial leaching through addition of sulphur. Biological leaching reduces the costs for chemicals, but the sludge has to be aerated, which increases the capital cost. However, the aeration oxidises the metal sulphides to soluble sulphate, which increases the metal solubilization.

Table 2. Metal solubilization in per cent in a comparison between chemical and microbial leaching (Blais et al., 1992).

Leaching method		Chemical	Microbial	Microbial
Addition		Sulphuric acid	Sulphur	Iron sulphate
pH-value after leaching		1.49 ± 0.03	1.90 ± 0,38	2.92 ± 0,55
ORP (mV) after leaching		392 ± 56	371 ± 49	503 ± 96
Aluminium	Al	26	30	11
Cadmium	Cd	59	82	74
Chromium	Cr	27	31	7
Copper	Cu	41	75	60
Manganese	Mn	83	92	89
Nickel	Ni	68	79	63
Lead	Pb	22	27	9
Zinc	Zn	66	85	82

If an ion exchanger is used the metal ions can be transferred from the sludge to the ion exchanger, and a high degree of solubilization can be reached at a higher pH-level. However, the ion exchanger has to be separated from the sludge, which can be achieved if a magnetic ion exchanger is used, which is separated from the sludge with use of a magnetic drum (Swinton et al., 1989).

Removal of chromium

In Novy Targ, Poland, there is a high content of chromium in the sludge. The leaching experiment in table 0 gives 30 % solubilization of chromium, which is the same as lead. In figure 0 the solubility of chromium and lead is the same at low pH-values and lower than for the other metals. Since chromium is reduced by organic matter in the treatment work, chromium in sewage sludge is in the form of chromium (III) (Alloway, 1995). The solubility of chromium (III) is limited by precipitation of Cr₂O₃ or Cr(OH)₃ (Nriagu and Nieboer, 1988). Above pH-level 4 the chromium concentration in equilibrium with Cr₂O₃ is less than 0.005 mg/l, while the chromium concentration in equilibrium with Cr(OH)₃ vary from 0.05 to 500 mg/l between a pH of 5 and 9 (see figure 0). Figure 1 shows the solubility in water of Cr₂O₃ depending on pH-level and redox potential and figure 2 shows areas of dominance of dissolved chromium species at equilibrium in the system Cr, H₂O and O₂. The redox potential depends on the oxygen concentration and at aerated conditions it lies at the oxygen line and at anaerobic conditions down near the hydrogen line. Since chromium is not precipitated as sulphide at anaerobic conditions, chromium can be leached with acids also at anaerobic conditions. Chromium is soluble at low pH-levels as chromium (III) ions and at high redox potential as chromate ions. Chromate ions may, however, be precipitated as chromate salt with other metal ions present in the sludge (see table 1). Alkali, ammonium and magnesium chromate are soluble while lead chromate is insoluble.

Oxidised chromium (IV) is also more toxic than chromium (III). A complication in recovery of chromium from sludges is that chromium is to a significant extent bound as organic complexes.

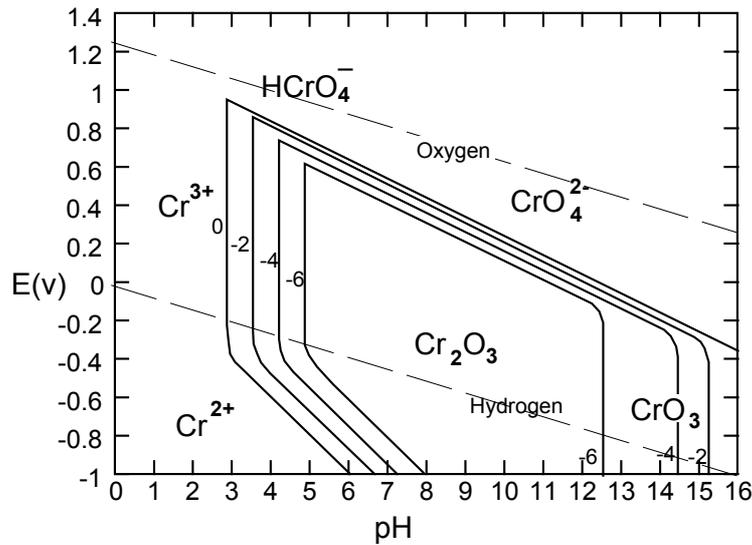


Figure 1. Isoconcentration lines for solubility of Cr₂O₃ in log ion activity; 0, -2, -4 and -6, depending on pH-level and redox potential (after Jones, 1992).

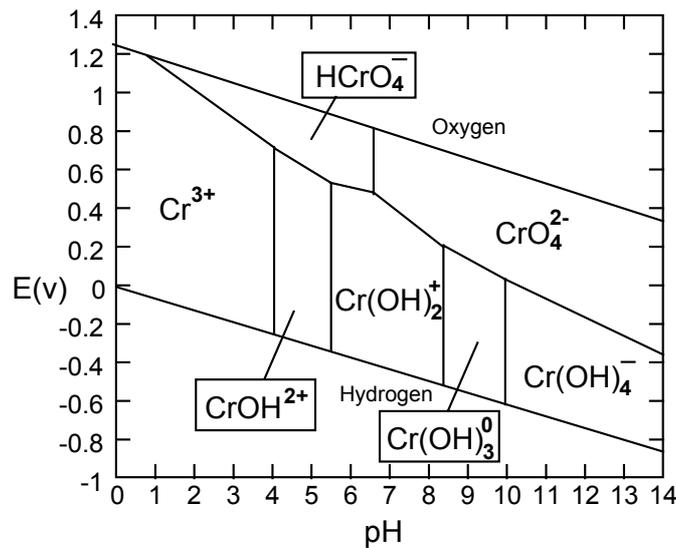


Figure 2. Areas of dominance of dissolved chromium species at equilibrium in the system Cr, H₂O and O₂ at 25 °C and 1 atm depending on pH-level and redox potential (Nriagu and Nieboer, 1988).

Table 1. Solubility of some chromium compounds (Stephen and Stephen, 1963).

Compound	Na ₂ CrO ₄	MgCrO ₄	BaCrO ₄	PbCrO ₄	CrSO ₄	Cr ₂ (SO ₄) ₃
Solubility g/l	466	420	0.01	0.0001	110	545

PHOSPHORUS RECOVERY

Instead of removing the impurities as metals from the sludge the nutrient in the sludge can be recovered and used as fertiliser in the agriculture. The nutrients in the sludge are potassium, calcium, phosphate and nitrogen. Of these nutrients phosphate is most important to recover. Phosphate fertiliser is produced by mining of phosphate ores. More than 300 different phosphate minerals are available, but only apatite (calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$) is used for production of fertiliser (Corbridge 1995). In 1995 the world phosphate rock production was 160 000 ton per year (as P_2O_5), having tripled over the last 40 years. About 90% of this is used as fertiliser. At this rate of consumption the known apatite reserves have been estimated to last for a period up to 1000 years. However, if the present increase in world population and the increasing need for fertiliser for food production is taken into account, the supply of phosphate may well be crucial within a century. Since nitrogen is the main part of the atmosphere the supply for nitrate is unlimited. Recovery of nitrogen shall be done if the energy required for recovery is less than the energy consumed by producing from nitrogen gas.

In the studies to find solutions for a sustainable sludge handling at centralised municipal wastewater treatment plants phosphorus recovery has been the main issue (Hultman et al., 1997). In the wastewater treatment process phosphorus is precipitated and transferred to the sludge phase (Rybicki, 1997). This process can be both chemical with addition of iron or aluminium salts and biological. In the chemical process is phosphorus precipitated as ferrous or aluminium phosphate. In the biological process is phosphorus at aerobic conditions taken up by the micro-organisms. Also without salt addition some chemical precipitation will occur with metal ions in the wastewater. The phosphate in the sludge will therefore be present as both metal phosphate precipitations and incorporated in the biomass. During anaerobic digestion the biomass will be converted to methane gas and the phosphate will be released to the supernatant. The degree of phosphate release during digestion will thus depend on the degree of biological phosphorus removal in the treatment process. The phosphate released during digestion can be recovered from the supernatant by precipitation. Possible phosphate precipitations are listed in table 2. One promising alternative, struvite precipitation, was studied in the laboratory (Hultman et al., 1997). Depending on pH-level struvite is precipitated according to the reactions given in table 3. According to these reactions optimal precipitation is achieved between pH 9.2 and 12. The experiments showed that the precipitation increased with increasing pH-level. However, at the pH-levels for optimum precipitation, the concentrations in the solutions was 10 to 100 times higher than given by the equilibrium with the pK-values. Only at a low pH-level the precipitation was in equilibrium with the pK-values with the difference increasing with increasing pH-value.

Table 2. Possible phosphate precipitations (Mamais et al., 1994, *Stumm and Morgan, 1981).

Precipitation	Name	pKs	Precipitation rate	Optimum at pH
MgNH_4PO_4	MAP or struvite, magnesium ammonium phosphate	12.6*	Medium	7-8
$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	HAP or hydroxide apatite	57*	Very low	9.5-11
$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Bobierite		Very low	
CaHPO_4	Calcium hydrogen phosphate	6,6		
$\text{Ca}_3(\text{PO}_4)_2$	Tricalcium phosphate	24		

Table 3. Reactions for precipitation of struvite depending on pH (Hultman et al., 1997).

Chemical reaction	pH-interval	pK
$\text{MgNH}_4\text{PO}_4 + 2\text{H}^+ \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{H}_2\text{PO}_4^-$	< 7.2	6.5
$\text{MgNH}_4\text{PO}_4 + \text{H}^+ \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-}$	> 7.2 and <9.2	0.6
$\text{MgNH}_4\text{PO}_4 \leftrightarrow \text{Mg}^{2+} + \text{NH}_3 + \text{HPO}_4^{2-}$	> 9.2 and <12	9.85
$\text{MgNH}_4\text{PO}_4 \leftrightarrow \text{Mg}^{2+} + \text{NH}_3 + \text{PO}_4^{3-} + \text{H}^+$	> 12	21.85

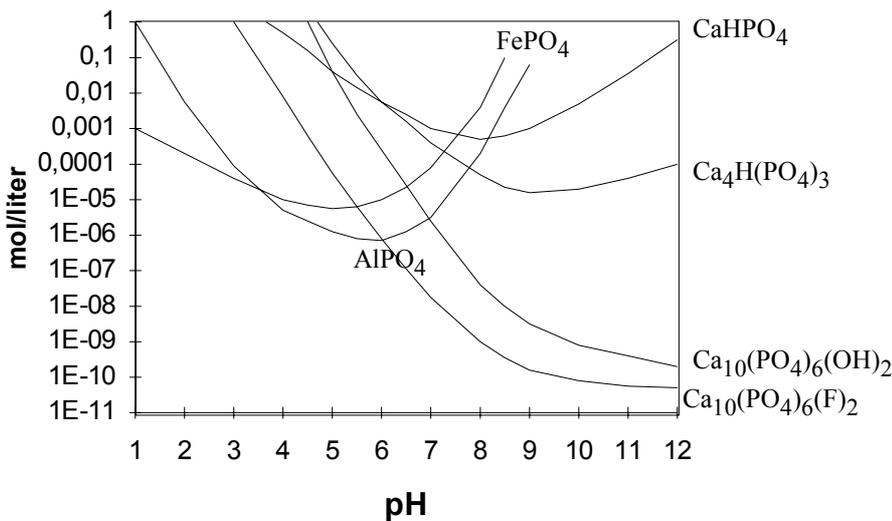
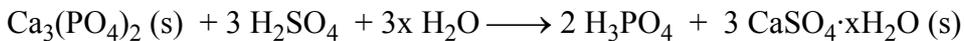
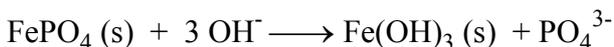


Figure 3. The solubility of metal phosphates (Stumm and Morgan, 1981).

The possibility of dissolving precipitated metal phosphate is also being studied. The phosphate can be leached from the digested sludge or leached from the ash after incinerating the sludge. Figure 3 shows the solubility of some metal phosphates (Stumm and Morgan, 1981). The solubility increases with decreasing pH-value which indicate that phosphate can be recovered by leaching with acid. Phosphate fertiliser is produced by leaching apatite with sulphuric acid (McKetta and Cunningham 1990):



The precipitation of calcium sulphate makes the reaction to continue until all sulphuric acid is consumed. For leaching aluminium or ferrous phosphate the pH-value must be lower. However, aluminium or ferrous phosphate can also be dissolved at high pH-values. At a high pH-value aluminium and iron are converted to metal hydroxide thus dissolving the phosphate (Stumm and Morgan, 1981):



Another possibility to recover phosphate from ferrous phosphate is to use hydrogen sulphide.

THERMAL HYDROLYSIS PROCESSES

The KREPRO process

The KREPRO project has been initiated with the aim to fractionate the sludge and recover the sludge components. One subproject is a sludge hydrolysis plant at Öresundsverket in Helsingborg, Sweden. In the plant is digested sludge treated in a reactor with sulphuric acid (pH-level 1) at a temperature of 160°C. The sludge is fragmented and heavy metals and phosphorus are dissolved. The organic sludge residue has a to high content of mercury and copper and too low content of nutrients to be used as fertiliser. The hydrolysed sludge is dewatered and the acid solution is neutralised and an inorganic hydroxide sludge is precipitated. Another subproject is to process the inorganic sludge to recover phosphorus and precipitation chemicals. The sludge is dissolved in sulphuric acid and oxidised to get an iron phosphate precipitation which can be separated from an acid solution with the heavy metals. The heavy metals are precipitated as a hydroxide sludge.

The Cambi process

In the Cambi process (Gotthardsson, 1997) is the sludge thermally hydrolysed before the digestion. A plant has been built at the WWTP in Hamar, Norway. Figure 4 shows a sketch of the process. The sludge is in a batch process treated with steam of a temperature of 180 °C. Larger organic molecules are in the process fragmented and thereby more accessible for the micro-organisms. The reduction of organic material by the digestion is increased from 45-50% to 65-70% and the methane gas production is increased with 30%. Future development works are directed to recover resources as precipitation chemicals.

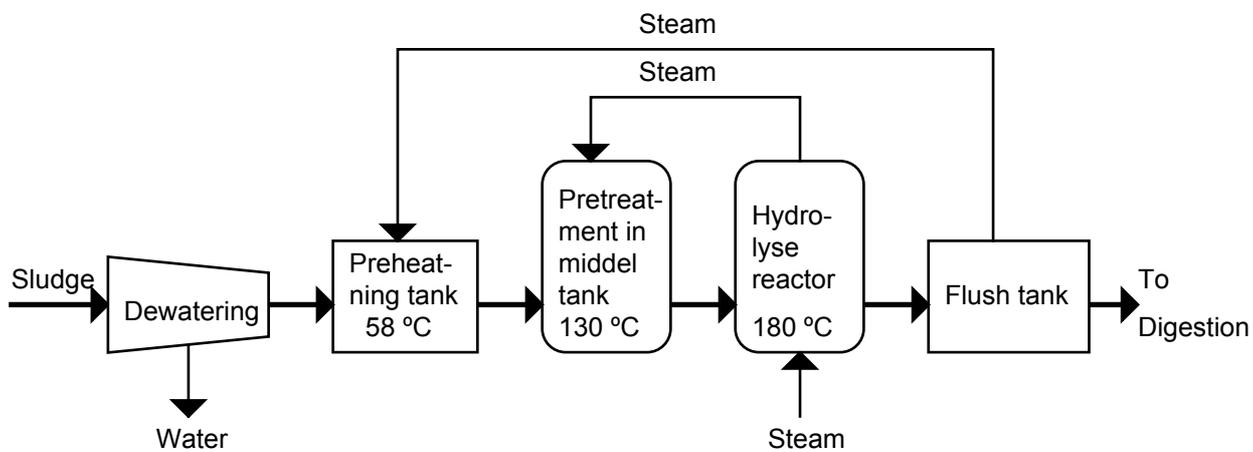


Figure 4. Thermal hydrolysis with the Cambi process. (Gotthardsson, 1997)

UTILISATION FOR BUILDING MATERIAL

One resource in sludge is the inorganic materials that can be used for production of building materials. Any environmental hazardous contaminants are bound as mineral to the material and utilisation of sludge reduces mining of raw material for production of building material. If the nutrients are recovered the sludge must otherwise be deposited for instance on a waste disposal site.

The content of sludge from water treatment plants depends mainly on the chemicals used for coagulation of suspended particles in the raw water (Cornwell and Westerhoff, 1981). The high aluminium content of a sludge produced at water treatment with aluminium salts makes it useful for production of aluminous cement (Lubarski et al., 1996).

Sludge from waste water treatment has been used for production of:

- Bricks (Alleman and Berman, 1984, Tay and Show, 1997).
- Lightweight aggregates in concrete (Tay and Show, 1997).
- Cementitious material (Tay and Show, 1997).

The inorganic content in wastewater sludge is more diversified. In incinerated and melted slag the main oxides are; SiO₂ 26-42%, P₂O₅ 12-27%, Fe₂O₃ 5-25%, Al₂O₃ 11-21% and CaO 8-14% (Ozaki et al., 1997). The inorganic content is about half of the sludge weight. When sludge is used for brick manufacturing, the organic content in the sludge is incinerated, which makes the brick porous and of lower compression strength. This can be avoided by incinerating the sludge and use of the inorganic ash for brick manufacture.

CONCLUSIONS

An important resource is nutrients which can be utilised through using sludge as fertiliser in the agriculture. This requires that harmful substances such as heavy metals must be minimised through source control or that metals such as chromium can be removed from the sludge by leaching methods.

Alternatively, nutrients can be recovered from the sludge and used as fertiliser. Phosphate fertiliser is produced by mining of phosphate ores, and the supply may be crucial within a century. Phosphate removed biologically from the wastewater can be recovered from the supernatant after digestion by precipitation as struvite MgNH₄PO₄. Phosphate removed chemically as metal phosphate must be leached from the sludge.

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To avoid waste disposal the inorganic content of the sludge can be used for production of building material.

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