## ForskEL project no. 2008-1-0111:

# Working up phosphate from ashes

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# Content

# Summary

In the last 5 years an increasing awareness of the phosphate issue has arisen. Intensive agriculture is highly dependent on phosphate fertilizers that are produced from easily accessible phosphate rock. The phosphate rock is a limited, unrenewable resource; reserves are predicted to last for 25-250 years. Once scarcity sets in global food production will for a long period depend on China and Morocco, since these two countries control more than two thirds of the known reserves. Without phosphate fertilizer the currently high crop yields cannot be maintained. To avoid a future food crisis of unforeseeable dimensions, it is therefore imperative that phosphate recycling be developed and put into practice.

The aim of this project has been to develop processes for the recycling of phosphate from ashes. Phosphorus rich ashes are the residual product when waste fractions of animal origin are combusted. Ashes from three such waste fractions are considered, namely meat and bone meal, manure fibre and sewage sludge. Without some kind of industrial pretreatment the ashes have limited fertilizer value due to their poor plant accessibility.

Meat and bone meal (MBM) was until 2001 used in feed production, but a general EU ban of this use was imposed to prevent spread of the mad cow disease. The 2001 ban left European renderers with an enormous waste problem, which has been solved by utilization of the meals as fuels, primarily in cement production. Since the MBM ash ends up as part of the cement clinkers, phosphate recycling is not an option in this context. However a few English mono-incineration facilities exist, producing an MBM ash suitable for recycling. The amount of ash from these facilities is estimated to be 30.000ton per year. A fertilizer production scheme has been set up based on the MBM ash, comprising acid addition followed by drying and pelletizing. The work with this process is continued in a project termed “Tørring og pelletering af gødning fra fosforholdige asker”, which is supported by the Environmental Protection Board.

Manure fibre is separated from manure in order to minimize the phosphorus surplus being applied to fields with manure. No general limitations have been imposed on the phosphorus surplus applied by Danish animal producers, but if a farmer wishes to expand or start up new production facilities, there are demands regarding the phosphorus surplus that need to be fulfilled in order for the farmer to get environmental approval. Thus about 3% of the Danish manure is currently being separated. Most fibre is used directly as fertilizer, mixed in compost or used in anaerobic digestion plants. Almost no manure fibre is incinerated at present, so ashes are not available in large amounts. The potential of separating manure, drying and incinerating the manure fibre and producing a fertilizer product from the ash has been assessed in this project, based on a representative sampling of manure fibre produced on Danish farms. Generally ashes can be used for fertilizer production using an acid addition/drying/pelletizing process, but ashes produced using polymer contained cupper and zink in concentrations exceeding the threshold values stated in “Slambekendtgørelsen”.

Sewage sludge incineration is becoming a more and more widespread solution, so ash production is quite sufficient to sustain a production facility. Around 6000ton of ash per year is produced from two Copenhagen wastewater treatment plants alone. Ashes from sewage sludge contain aluminium, iron and heavy metals, making it a technically difficult task to obtain a usable product from this ash. Producing a fertilizer by simple acid addition is not an option, since the phosphoric acid thus obtained will be polluted by aluminium and heavy metals, which are not easily removed. Basic leaching provides poor yields with

most sewage sludge ashes due to the calcium phosphate not being soluble in base. A solution may be the production of trisodium phosphate from sludge ash. Due to the easy crystallization of this salt a high purity product can be obtained. The process comprises pretreatment with sulfuric acid, precipitation of heavy metals at high pH and finally crystallization of trisodium phosphate from a basic aluminate liquor. The price of such treatment will exceed 1000kr per ton ash, but this may still be the cheapest way of recycling phosphate from sewage sludge ash. Unfortunately the market of industrial grade trisodium phosphate has become limited since phosphates are no longer used in laundry detergents.

# Introduction of project background

In the following the project background is presented. The experimental work with the ashes is presented in three separate reports:

- Appendix 1: Working up phosphate from meat and bone meal ash, written by Anita Rye Ottosen
- Appendix 2: Potential of manure fibre combustion with ash based fertilizer production, written by Ole Thygesen and Tina Johnsen
- Appendix 3: Recycling phosphate from sewage sludge ashes, written by Tina Johnsen

## Phosphate scarcity makes recycling imperative

The world will be facing phosphate scarcity within the next century or two. Some scientist believe that phosphate production will peak within the next three decades (Global Phosphorus Research Initiative, 2010), other experts believe that known reserves will last longer (IFDC). Anyhow, everyone agrees that phosphorus cannot be replaced, that global food production is dependent on phosphate fertilizers and that phosphate resources are limited. This makes efficient phosphate management imperative, including the recycling of phosphorus rich waste fractions.

This report concerns recycling of phosphate from the ashes obtained, when combusting specified risk material meat and bone meal (SRM MBM), manure fibre and sewage sludge. Besides high phosphorus content, these wastes share their animal origin, and will in common be referred to as animal waste.  As fuels regarded, all three waste fractions have the disadvantage of being wet, meaning that they can hardly burn without being dried, and when dried and combusted the net energy gain is moderate.

## Drying of wet waste as a means of energy storage

As the world moves towards less dependence on fossil fuels, engineering practical energy storage solutions will become increasingly important. Although wind mills may supply 100% of the electricity consumption on a windy day, power plants will still have to deliver the electricity on less windy days. In order to obtain the high temperatures needed for efficient electricity production all non-fossil materials that can burn will be needed in future power plants; straw, wood and other dry biomasses will of course be the first choice, but wet waste fractions like SRM MBM, manure fibre and sewage sludge may also become important as “buffers” in future energy infrastructure.

Wet waste fractions may have little direct value as fuels, but the opportunity exists to dry the waste, thus creating solid fuels with a high calorific value, which can be moved or stored to best fit the purpose. The main advantage lies in the opportunity to utilize the wet waste for energy storage. When surplus energy from industrial processes can be stored in a dried fuel for use in a power plant, a more efficient way of administering energy can be obtained. Drying may take place at waste incineration facilities during summer periods when district heat consumption is low, whereas combustion can take place at large, highly efficient power plants.

## Untreated ashes have limited fertilizer value

Phosphate rich ashes can perhaps be used as slow release fertilizers, but the fertilizer value is low due to poor plant accessibility. Intensive agriculture demands efficient fertilization with water soluble phosphate. Moreover fertilizer products need to be spreadable, in practice meaning that the physical form is preferably 1-4mm round balls with high compressible strength. To meet these demands industrial ash pretreatment is necessary.

## Parameters influencing ash quality

Different fuels characteristics make power plants mix different fuels in order to achieve a variety of technical goals. For instance the combination of coal and straw has gained some acceptance as a means of overcoming the corrosion problems associated with the combustion of straw. The down side of this combination is that the fertilizer value of the straw ash is lost. The straw/coal combi-ash is used as filler in asphalt and concrete, where the potassium derived from the straw does not come to its best use.

In order to avoid waste of fertilizer value, co-firing should be planned with caution. Ash free fuels like gas or biodiesel can probably be used in co-firing without negative consequences on the ash quality. Co-firing with ash rich fuels like straw, wood or coal should probably be avoided, since the phosphate content of the mixed ash will be diluted compared to the mono-incinerated animal waste ash. The practical experience regarding co-firing of dried animal waste is limited, so new combinations will need to be tested in order to investigate the implications on the ash quality.

Another way of co-firing animal waste without mixing the ashes may be by gasification of the animal waste in a separate unit, followed by co-combustion of the gasification gas with other fuels. DONG is presently testing this concept and up scaling an add-on gasification unit designed by Peter Stoholm at the Asnæs power plant (coal fired) in Kalundborg, Denmark. Straw is the first fuel being tested, since it is readily available in large amounts, but within a foreseeable future dried sewage sludge may offer a feasible fuel, since Kommunekemi is planning to build a large sludge drying facility in Nyborg.

## MBM

The mad cow disease pandemic that roared in UK in the late eighties and thoughout the century is largely over, as illustrated by the graph below. Around 150 people infected with variant Creutzfeldt-Jakobs disease, the human version of mad cow disease, have died since the pandemic set in.

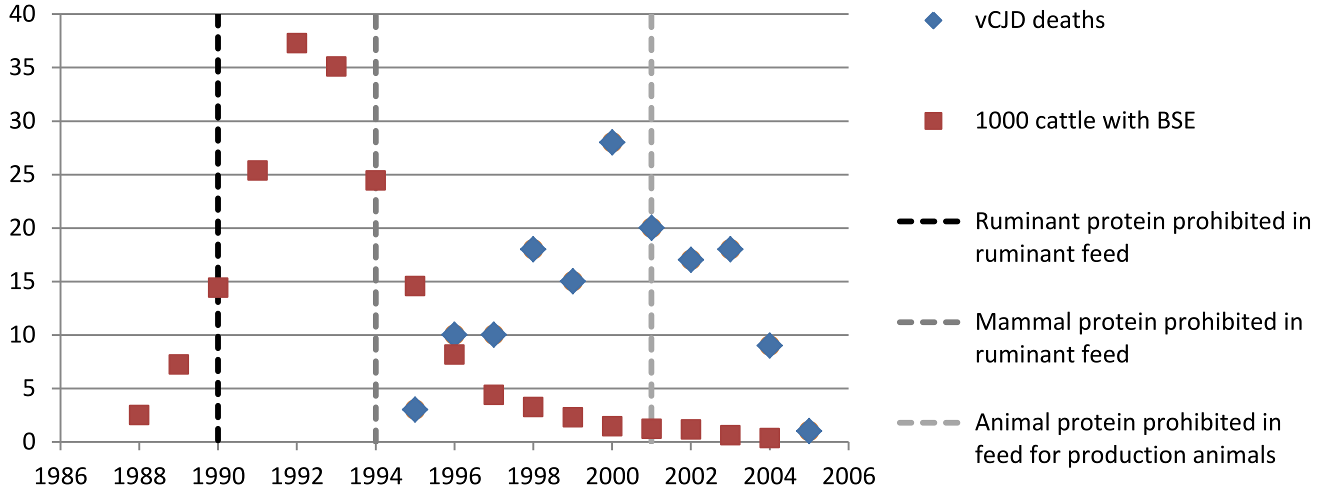

**Figure 1: Cases of mad cow disease and variant Creutzfeldt-Jakobs diseases in the United Kingdom. New cases are becoming seldom.**

Fear of a new pandemic caused by some inter-species transmissible agent has lead to the 2001 EU ban of using processed animal protein (PAP, meaning any kind of slaughterhouse byproduct based meal) in the feed for food production animals (Council decision 2000/766/EC). This restriction left European renderers with an enormous waste problem, since previously the major outlet for processed animal protein was the feed industry. In 2009 the production of category 1 and 2 processed animal protein was 1.5 million tons in EU19, of which 1.1million ton was incinerated, according to EFPRA, the European organization of renderers. Most incineration takes place in cement ovens, since this practice saves the costs of depositing the ashes, which are incorporated in the cement clinker. England is thus the only place, where MBM ash is produced.

In England four incineration plants dedicated for SRM MBM are in use. These are a plant in Widnes and the Goosey Lodge Power Plant in Wymington, both owned by Prosper de Mulder group, the Fawley Waste to Energy Plant in Southhampton, run by Tradebe (previously Pyros – MBM plant seemingly mothballed) and the Glanford Power Station (designed for poultry litter, since 2000 MBM has been used as fuel), owned by Fibrogen. The two biggest of these are the power plants Glanford and Goosey Lodge, both generated app. 80.000MWh in 2006, whereas the Fawley and Widnes plants generated app. 33.000MWh and 34.000MWh, respectively, in 2006. The MBM ash used in the laboratory work is obtained from the Prosper de Mulder plant in Widnes.

The Danish production of SRM MBM is approximately 100.000tons, which is used as fuel in the production of Leca in Randers and of cement in Aalborg. Danish non-SRM MBM is exported to Russian pet food producers and to Swedish and German ecological farmers as a fertilizer (Communication with DAKA).

## Manure fibre

Since the eighties awareness about the negative environmental consequences of applying excessive amounts of phosphorus to agricultural soils have made most European countries minimize the P surplus. However, in 2000-2004 Denmark still applied unusual high amounts of phosphorus to agricultural soils as illustrated by Table 1.

| Country | Average P surplus 2000-2004 [kg/ha/year] |
|---|---:|
| Poland | 2,2 |
| Greece | 4,0 |
| France | 4,5 |
| Germany | 4,6 |
| Ireland | 6,6 |
| Denmark | 11,4 |

Table 1: Average surplus of P applied to agricultural soils for some EU countries from 2000-2004 (both years included). Whereas other EU countries have managed to minimize the P surplus since the eighties, Denmark still applied an unusual high amount of surplus P. (Data from OECD Statistics used to calculate average values).

According to Danmarks Miljø Undersøgelser (DMU), the Danish phosphorus surplus has decreased to about 4kg P/ha/year in 2005-2008 and further to 0,6kg P/ha/year in 2009 (DMU: Vandmiljø og Natur 2009). In 2005 a tax was imposed on mineral feed phosphates, which may have had an effect on the phosphorus surplus. Whether or not the marked decrease from 2008 to 2009 is an artifact caused by high fertilizer prices in 2008 and 2009 remains to be seen in future phosphorus balances.

Comparison of the data from DMU and OECD should be done with care, since the P surplus calculated by OECD is generally higher than the surplus from DMU. Figure 2 illustrates the difference.

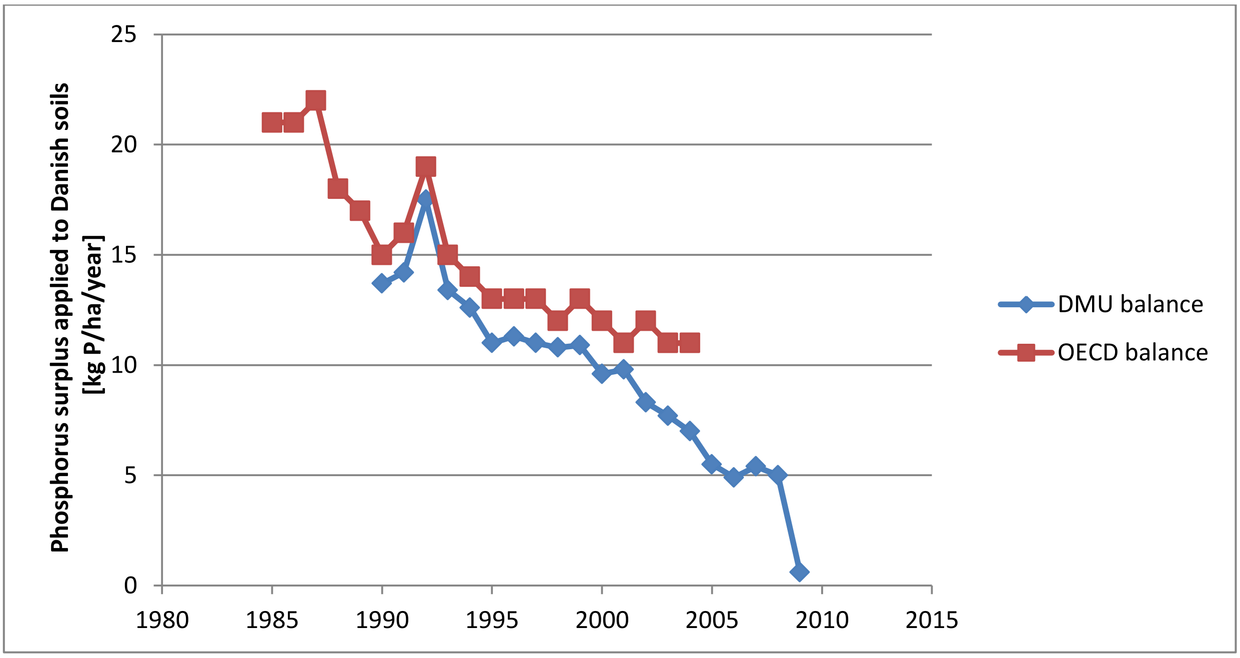

Figure 2: Phosphorus balances from DMU and OECD.

In relation to surplus phosphorus application via manure it is important, what kind of animal production is taking place. As shown in the below table diary production is very P intensive due to the possibility of spreading  manure equal to 230kg N/ha, which is open to cattle farmers using more than 70% of their land for fodder production (grass, beets). Danish diary production is more than three times larger than domestic consumption, placing Denmark among the top 5 diary export countries in the world (Danish Dairy Board, 2010). Production of piglets and weaners yields a larger P application with manure than production of finishers. Danish export of weaners to Germany has exploded over the last 10 years, from approximately 1 to 7.5 million weaners per year in 2010. On this background it seems reasonable to assume that phosphorus is still applied in a massive surplus in animal dense regions.

| | **Yearly nutrient excretion** | | **P application according to harmony rules** | |
|---|---|---|---|---|
| | *kg N* | *kg P* | *kg P/ha at 140kgN/ha* | |
| **Sow with 25 piglets to 7.3kg** | 26,5 | 6,04 | 31,9 | |
| **25 weaners 7.3-31kg** | 16,0 | 3,25 | 28,4 | |
| **25 finishers 31-104kg** | 79,5 | 13,5 | 23,8 | |
| | | | *kg P/ha at 170kg N/ha* | *kg P/ha at 230kgN/ha* |
| **Diary cow, heavy breed** | 136,3 | 21,8 | 27,2 | 36,8 |
| **Diary cow, jersey** | 112,5 | 18,5 | 28,0 | 37,8 |
| **Nursing cow** | 72,0 | 6,8 | 16,1 | 21,7 |
| **Calf 0-6months, heavy breed** | 27,0 | 2,4 | 15,1 | 20,4 |
| **Calf 0-6months, jersey** | 20,4 | 1,8 | 15,0 | 20,3 |

**Table 2: Yearly nutrient excretion from different animals according to Danish norm figures and P application according to EU harmony rules (calculated from the norm figures).**

According to an article on the status of separation of manure approximately 880.000 ton of manure per year was separated in Denmark, 2010. (Status over anvendelsen af gylleseparering i Danmark, maj 2010). This constitutes approximately 3% of the entire Danish manure produced, so utilization of the energy potential will require massive investments in manure separation equipment. The figure below illustrates how the number of separation units grew fast from 9 to 47 units in 2006, driven by the possibility to have a larger animal production with the same land. After 2007 the development stagnated, probably due to the lacking possibilities to get rid of the manure fibre. Since then land prices have dropped and the expansive development in animal production has vanished due to the global recession that hit in autumn 2008. Installation of more separation units therefore cannot be expected without a new driving force.

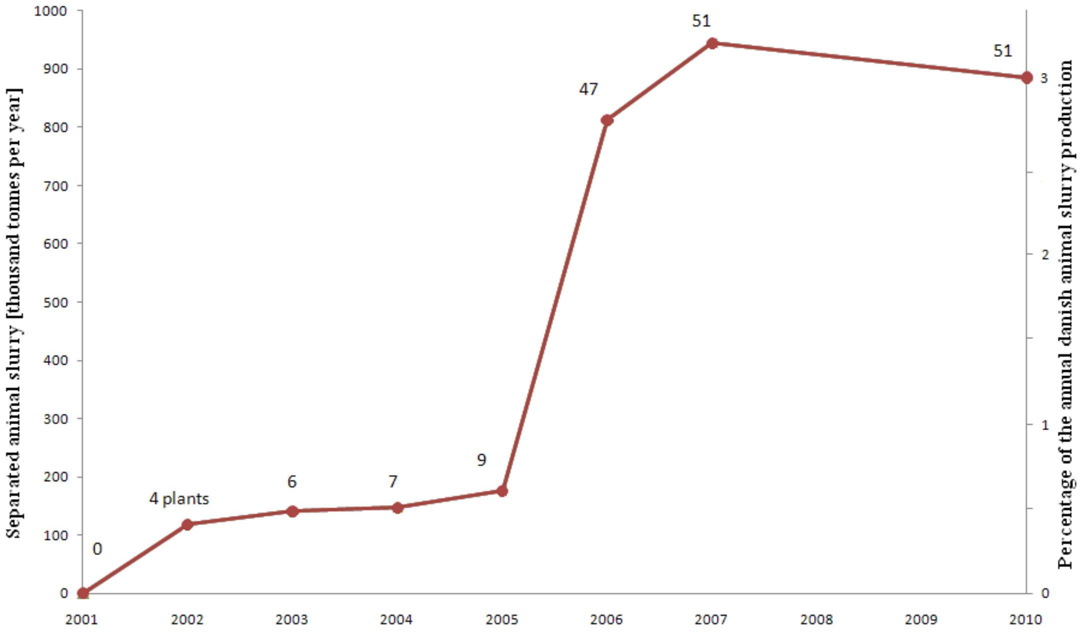

Figure 3: Separation units were installed at a fast rate in 2006, but this development stagnated in 2007. 3% of the Danish manure is currently being separated.

## Sewage sludge

A great deal of attention has been paid to the recycling of phosphate from sewage. Several approaches has been proposed, among these the crystallization of fertilizer salts like struvite or apatite directly from the sewage. None of these processes have really had great success, although they have been implemented in full scale at a wastewater treatment plant (WWTP). One disadvantage is that the fertilizer salts produced do not meet the agricultural demands for high performance fertilizers.

Sewage sludge is to an increasing degree being incinerated throughout the European Union. The reason for this is most importantly the general uncertainty about the possible negative consequences of field application regarding both food safety and environment. Other factors like logistics, uncertainty about future limitations on field application, taxes imposed on land filling prices etc. also makes incineration of sewage sludge the more attractive solution for WWTPs.

Sewage sludge ashes fall mainly into two categories depending on the metal used for phosphate precipitation at the WWTP. Some WWTPs use primarily aluminium salts, yielding ultimately an aluminium rich sludge ash, termed aluminium ash, whereas others use primarily iron salts, yielding iron ashes. A typical WWTP use iron salts, so the work has been concentrated on iron ashes. Specifically most work with sewage sludge ash has been conducted using the ash from Spildevandscenter Avedøre. At Spildevandscenter Avedøre the sludge produced is dried to 32% DM and combusted in a fluidized bed incinerator. Another major WWTP in Copenhagen called Lynetten is building a similar fluid bed facility. Together Spildevandscenter Avedøre and Lynetten produce around 6000 tons of sludge ash per year.

## Project dilemma

A dilemma in this project has been that the only ash presently available in large amounts is the sewage sludge ash, which is from a technical point of view is the worst quality ash to work with.

Meat and bone meal ashes in large amounts would make up a perfect basis for fertilizer production, but unfortunately meat end bone meal typically ends up in cement ovens. The English mono-incineration plants may however supply sufficient ash to sustain a fertilizer production plant.

Manure fibre ashes could likewise provide the basis for fertilizer production, if only someone would combust the manure fiber on a large scale. Manure fibre ashes holds a great potential, since anaerobic digestion plants may in future function as manure collection stations facilitating manure separation and fibre combustion with ash utilization on a large scale.

We chose to work on all three ash types, since none of the ashes could be ruled out as not having potential. The experimental work is presented in the three appendices:

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In addition, theoretical thermodynamical calculations using a extended Uniquac model have been performed for the system H2O – ($K^+$, $Na^+$, $H^+$, $Ca^{2+}$, $Fe^{3+}$, $Cu^{2+}$) – ($Cl^-$, $HSO_4^-$, $SO_4^{2-}$, $OH^-$, $CO_2$, $HCO_3^-$, $CO_3^{2-}$, $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$, $PO_4^{3-}$, $F^-$). Reports covering the work are given in enclosure A, B, C and D. During the investigations the calculations have been instrumental for verification and explanation of experimental results. They have furtner been an inspiration for further investigations.

## References

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