

# Environmental Footprint of Thermo-Chemical Phosphate Recycling

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Received: October 15, 2013 / Accepted: October 30, 2013 / Published: November 25, 2013.

**Abstract:** Three phosphate fertilizers from fossil and secondary starting materials have been assessed for their accumulated environmental footprint. Fertiliser types have been selected for their similarity in terms of phosphate and secondary nutrient concentrations and small waste flows, although significant and unavoidable differences in terms of phosphate solubility remain. Input data were taken from literature and from process simulations in Aspen Plus and HSC Chemistry, being based on evaluations of plants in operation or under construction. It was tested and confirmed that HSC Chemistry data can be directly exported to GaBi as an LCA evaluation tool. The paper shows in two cases a positive energy balance and a rather low environmental footprint of all three assessed processes.

**Key words:** Phosphates, fertilisers, P-recovery, environmental footprint, life cycle assessment.

## 1. Introduction

In response to recent discussions about the medium and long term security of mineral P (phosphorus) supplies to European farmers, a number of recycling technologies have been developed. While the technical viability and economic feasibility have been in the focus of developers, little attention has been paid to the comparative environmental footprint of these technologies.

The thermo-chemical ASH DEC process has particularly been frequently criticized for its allegedly high energy consumption and CO<sub>2</sub> footprint.

The present paper aims at comparing two P-recovery pathways: a thermo-chemical technique and a wet chemical approach. The comparison includes the production of the closest conventional fertiliser; single superphosphate, in terms of the total

environmental footprint of each technique.

## 2. Materials and Methods

### 2.1 From Phosphate Mining to Single Superphosphate

SSP (single superphosphate) was selected as benchmark product because of its relative similarity with the two selected renewable products from sewage sludge. SSP contains 20wt% of largely water soluble P<sub>2</sub>O<sub>5</sub>, as well as all impurities from rock phosphate concentrate and all reaction products after acidulation of the starting material with concentrated sulphuric acid. The comparatively simple acidulation process leaves only a small waste fraction from wet air pollution control systems scrubbers.

The system boundaries include: mining (usually open pit mining), beneficiation (production of a tradable concentrate) and reaction with sulphuric acid. Sulphur being largely recovered from desulphurization of fossil fuels and produced by the BAT (best available technology).

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### 2.2 From Sewage Sludge to Acidulated Phosphates with 11% $P_2O_5$

An alternative to calcining ash is acidulation with acid. For the comparative assessment, sulphuric acid has been chosen because of it being the most accessible and most frequently used compound for fertiliser production.

The process starts with ash from sludge incineration and shares the first building block with the calcining process. The ash is, however, treated in the same way as rock phosphate concentrate to produce SSP, by mixing with sulphuric acid. If aiming at the same high degree of solubility—in this case again water or citrate solubility—more acid is needed than for producing SSP and a lower phosphate concentration of 11% in the product is obtained. Removal of pollutants would be possible but requires additional process steps which are not likely to be performed in conventional phosphate fertiliser plants, where this process will be introduced in the near future. Consequently, all pollutants from sludge ash are transferred to the final product. An additional drawback is that the largest ash fraction in the market, containing 10%-15% iron, cannot be used for this process because of producing a sticky, non drying product [1].

### 2.3 From Sewage Sludge to Calcined Phosphates (ASH DEC) with 15% $P_2O_5$

In contrast to a comparative LCA performed as a master thesis by Martin Steiger [2], boundaries for recovered phosphates were extended to sludge incineration. This decision is motivated by the fact that the original starting material for this P-recovery pathway is sludge; a solid (wet) waste product from wastewater treatment. Operators of WWTPs (wastewater treatment plants) have several options for disposing sludge: re-use on cropland, processing to compost or incineration. Incineration is the only one producing ash as a starting material for efficient thermo- or wet chemical processing to fertilisers. Incineration may be considered to produce a

phosphate concentrate, analogue to the beneficiation processes performed in phosphate mines.

The incineration ash is processed to a calcined fertiliser, preferably in a vertically integrated plant downstream of sludge incineration. This setup allows hot ash to be fed to the treatment reactor minimizing the consumption of fossil fuels. In addition, emissions from the incinerator are used to produce a dry sodium-sulphur compound which is used to replace about one third of sodium carbonate; the standard material for solubilization of calcined phosphates. The calcined phosphate fertiliser is largely (> 90%) citrate soluble in full compliance with the European Fertiliser Act (EC) 2003/2003. 70%-90% of toxic compounds such as arsenic, cadmium and lead are removed by the process and retained as filter dust in the last filtration unit shared with the sludge incinerator. Lead is, however, the only pollutant present in considerable concentrations in the final product.

### 2.4 Methodical Approach

The master thesis of Martin Steiger [2] (which was based on the data base supported comparative assessment of three P-recovery processes including ASH DEC) did not produce clear results in terms of the environmental footprint of the investigated technologies. This paper started from scratch by collecting and directly evaluating available process data on the basis also of Aspen Plus simulations of ASH DEC.

For the conventional fertiliser (SSP) manufacturing process, data were retrieved from booklets of Fertilisers Europe, former EFMA (European Fertilizer Manufacturers' Association) [3], depicting BAT technologies for the production of most popular fertilisers as well as from environmental reviews of the European Commission [4] and the Dutch Ministry of Housing, Spatial Planning and the Environment [5]. The fertiliser industry is the original source behind all evaluated data sources, assuring a benevolent interpretation of potentially controversial issues.

Energy consumption for manufacturing single superphosphates—from phosphate rock and sulphuric acid—are mainly based on a 1998 paper of Kongshaug, reviewed and updated by Jenssen [6]. The average European energy consumption is considered, except for mining, as it is a factor of nine larger in terms of energy intensity than mining sedimentary phosphates in northern Africa and thus much less representative. Consequently, typical energy consumption for sedimentary phosphate mining was selected for assessment.

The energy balance of phosphate recovery techniques considers state-of-the-art sludge incineration plants as currently under construction in Zürich. These plants produce energy and do not need fossil fuels except for start-up. Both investigated recovery processes having ash as a starting material are equally benefiting from significant energy generation by sludge incineration.

An updated review of impurity and pollutant concentrations in rock phosphates are based on data from thirty sedimentary rock phosphates from nine regions, collected and analyzed by Mamdoh Sattouf for his Ph.D. thesis [7]. It shows that industry reports tend to underestimate the real pollutant concentrations in rock phosphate, possibly because of referring to samples having been taken and analyzed thirty or 40 years ago.

For the assessment of pollutant concentration of sewage sludge ashes, analysis of eighteen ash samples have been reviewed from; Germany, the Netherlands,

Switzerland, France and Austria, performed by BAM in the SUSAN FP7 research project [8].

From both, rock phosphates and ashes, minimum, maximum and median pollutant concentrations, transfer coefficients and chemical reactions have been calculated by Excel and HSC Chemistry to predict realistic and representative pollutant concentrations in starting materials and end products, waste materials and emissions to air and water.

### 3. Results

#### 3.1 Energy Balance

As Fig. 1 shows two out of three integrated processes exhibit a positive energy balance—They produce more energy than they consume. Even the third, conventional fertiliser process can achieve a positive energy balance with the most energy efficient sulphuric acid plants currently available (e.g., from Outotec).

The energy balances are a consequence of exothermic upstream processes of the final fertiliser process. The production of sulphuric acid from elemental sulphur releases energy as steam, which can be converted to electricity or used for downstream manufacturing of phosphoric acid. State-of-the-art sludge incineration releases even more energy to be used for similar purposes; generation of electricity, preheating the chemicals being used for fertiliser acidulation and district heating. Most sludge incinerators are in the vicinity of large population density,

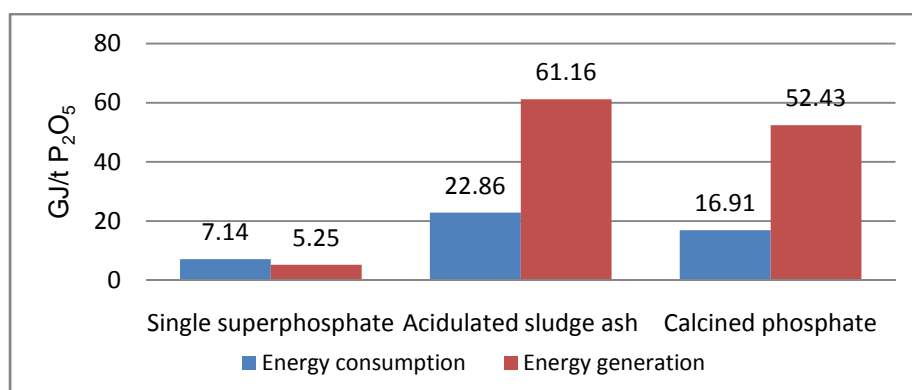


Fig. 1 Cumulated energy balance of the processes.

sometimes also having access to a district heating network. In an integrated ASH DEC plant, hot ash is fed to the reactor, thus saving most of the energy needed for heating up the starting material. This advantage cannot be used if the ash is acidulated. In this case, however, both upstream processes are exothermic and are accumulated for the energy balance of the final product.

### 3.2 Material Balance

The conventional single superphosphate has only two relevant input streams: rock phosphate concentrate and sulphuric acid, mainly produced from elemental sulphur (Table 1). The process is inducing a reaction between these components whereby the insoluble phosphate compounds of rock phosphate are largely converted to water soluble mono-calcium-phosphates.

If ashes are used for the same reaction, a number of unwanted side reactions cause an increased acid consumption and the product contains iron-, aluminium and mono-calcium-phosphates. Relevant iron mass fractions in the starting material must be avoided because of producing insoluble iron phosphates turning the product into a permanently humid and sticky material. Because of the lower P-concentration in ash (compared to rock phosphate) and the higher acid consumption, only 11%  $P_2O_5$  are attained in the product (Table 2).

Because of the current scarcity of suitable ashes, Outotec decided to invest in an alternative process

whereby phosphate compounds are solubilized by thermal-chemical reactions between phosphate and sodium compounds, producing citrate soluble sodium-calcium-phosphates. The big advantage of this process is not being sensitive to impurities such as iron, aluminium, magnesium in the form of carbonates and many others usually present in sludge ashes and in an increasing number of phosphate ores (Table 3).

All three processes have a small waste flow because of keeping the impurities and the reaction products in the fertiliser, and this is essentially not a problem because many impurities are secondary or trace nutrients (sulphur, calcium, sodium, magnesium, etc.).

### 3.3 Pollutant Concentrations in Products

Toxic heavy metals are, however, of concern because of accumulation in soils and transfer to the food and feed chain. Consequently, the thermo-chemical process is conceived to largely remove the toxic substances: arsenic, cadmium and lead. A similar effect may be achieved by sequential acidulation of ash, increasing the number of process steps and the waste flow of this process. No relevant pollutant removal is yet foreseeable in the super phosphate production process whereby all pollutants present in rock that are quantitatively transferred to the fertiliser product (Fig. 2).

## 4. Conclusions

An environmental footprint assessment of three plant available phosphate fertilisers; single superphosphate,

**Table 1** Material and energy flows of single superphosphate production.

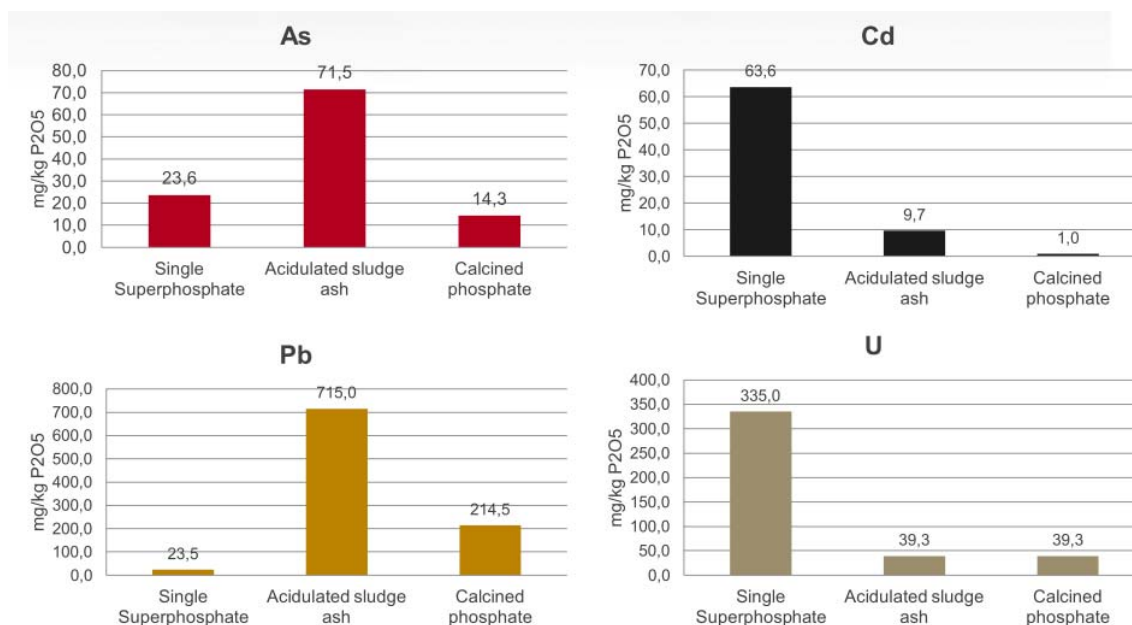
Input streams	Unit	Reference value
Raw phosphate ore from sedimentary mine body	t/t $P_2O_5$	15.63
Sulphur, largely from $SO_2$ recovery	t/t $P_2O_5$	0.58
Energy	GJ/t $P_2O_5$	7.14
Output streams	Unit	Reference value
Single superphosphate, 20%	t/t $P_2O_5$	5
Tailings (+ clay ponds, spent solvents, flotation wastewater)	t/t $P_2O_5$	12.50
Solid emissions and waste	t/t $P_2O_5$	0.05
Energy from sulphur burning	GJ/t $P_2O_5$	5.25

**Table 2 Material and energy flows of acidulated ash production.**

Input streams	Unit	Reference value
Sewage sludge as delivered, 100% dry matter	t/t P <sub>2</sub> O <sub>5</sub>	10.87
Sodium hydro-carbonate NaHCO <sub>3</sub> as Sorbens	t/t P <sub>2</sub> O <sub>5</sub>	0.96
Ammonia NH <sub>4</sub> OH 25% for NO <sub>x</sub> abatement	t/t P <sub>2</sub> O <sub>5</sub>	0.11
Calcium hydrate Ca(OH) <sub>2</sub> as sorbent	t/t P <sub>2</sub> O <sub>5</sub>	0.11
Coke (furnace coke) as sorbent	t/t P <sub>2</sub> O <sub>5</sub>	0.004
Sand as bed material	t/t P <sub>2</sub> O <sub>5</sub>	0.008
Concentrated sulphuric acid for acidulation	t/t P <sub>2</sub> O <sub>5</sub>	4.50
Water as boiler feed and cooling water	t/t P <sub>2</sub> O <sub>5</sub>	3.48
Natural gas as fuel	GJ/t P <sub>2</sub> O <sub>5</sub>	0.55
Electricity consumed	GJ/t P <sub>2</sub> O <sub>5</sub>	15.66
Steam	GJ/t P <sub>2</sub> O <sub>5</sub>	6.65
Output streams	Unit	Reference value
Acidulated sludge ash, 11% P <sub>2</sub> O <sub>5</sub>	t/t P <sub>2</sub> O <sub>5</sub>	9.5
Emissions/waste	t/t P <sub>2</sub> O <sub>5</sub>	0.1
Energy		
Electricity—energy delivered	GJ/t P <sub>2</sub> O <sub>5</sub>	9.13
Steam/heat—energy delivered	GJ/t P <sub>2</sub> O <sub>5</sub>	52.03
Flue gas		
CO <sub>2</sub> (> 90% from organic part of sewage sludge)	t/t P <sub>2</sub> O <sub>5</sub>	9.64
CO (legal emission limit—not to be exceeded)	t/t P <sub>2</sub> O <sub>5</sub>	0.003
NO <sub>x</sub> (legal emission limit—not to be exceeded)	t/t P <sub>2</sub> O <sub>5</sub>	0.005

**Table 3 Material and energy flows of ASH DEC.**

Input streams	Unit	Reference value
Sewage sludge as delivered, 100% dry matter	t/t P <sub>2</sub> O <sub>5</sub>	10.28
Sodium hydro-carbonate NaHCO <sub>3</sub> as sorbent	t/t P <sub>2</sub> O <sub>5</sub>	0.91
Ammonia NH <sub>4</sub> OH 25% for NO <sub>x</sub> abatement	t/t P <sub>2</sub> O <sub>5</sub>	0.10
Calcium hydrate Ca(OH) <sub>2</sub> as sorbent	t/t P <sub>2</sub> O <sub>5</sub>	0.18
Coke (furnace coke) as sorbent	t/t P <sub>2</sub> O <sub>5</sub>	0.004
Sand as bed material	t/t P <sub>2</sub> O <sub>5</sub>	0.007
Sodium sulfate Na <sub>2</sub> SO <sub>4</sub> as reactant	t/t P <sub>2</sub> O <sub>5</sub>	1.18
Dry sludge (waste from third parties) as reducing agent	t/t P <sub>2</sub> O <sub>5</sub>	0.65
Water as boiler feed and cooling water	t/t P <sub>2</sub> O <sub>5</sub>	4.58
Natural gas as fuel	t/t P <sub>2</sub> O <sub>5</sub>	0.16
Natural gas as fuel	GJ/t P <sub>2</sub> O <sub>5</sub>	7.17
Electricity consumed (> 85% from own generation)	GJ/t P <sub>2</sub> O <sub>5</sub>	9.75
Output streams	Unit	Reference value
Calcined fertilizer	t/t P <sub>2</sub> O <sub>5</sub>	6.70
Waste	t/t P <sub>2</sub> O <sub>5</sub>	0.12
Energy		
Electricity—energy delivered	GJ/t P <sub>2</sub> O <sub>5</sub>	8.63
Steam/heat —energy delivered	GJ/t P <sub>2</sub> O <sub>5</sub>	43.80
Flue gas		
CO <sub>2</sub> (> 75% from organic part of sewage sludge)	t/t P <sub>2</sub> O <sub>5</sub>	10.13
CO (max. amount)	t/t P <sub>2</sub> O <sub>5</sub>	0.003
NO <sub>x</sub> (max. amount)	t/t P <sub>2</sub> O <sub>5</sub>	0.004



**Fig. 2** Pollutant concentrations in the final products of the wet and thermo-chemical processes.

acidulated sludge ash and calcined ASH DEC phosphates, using fossil rock phosphate or sewage sludge as starting material exhibit an acceptable footprint for all three processes.

Contrary to frequently uttered concerns, the energy footprint remains low even for the calcined phosphates, mainly because of the excess energy delivered by state-of-the-art sludge incineration.

Depending on the starting materials, we see either elevated concentrations of cadmium and uranium or lead in the product, to which all raw material borne pollutants are transferred. Analyses confirm that heavy metal removal from calcined phosphates can effectively prevent pollutants from being transferred to the food and feed cycle.

While an environmental footprint could be performed from the data presented in Tables 1-3, some key footprint data are not available in the GaBi database. Hence an evaluation is not presented here as it can at most only be indicative.

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