RECOPHOS: FULL-SCALE RECOVERY OF PHOSPHATE FROM SEWAGE SLUDGE ASH

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SUMMARY: The substitution potential of sewage sludge for German primary phosphate imports has been estimated as 40 %. Yet, a marketable option for the full scale recovery has been lacking. This study focuses on a novel process for the manufacture of a P-fertilizer from sewage sludge ash (SSA) adapted from the production of Triple Superphosphate. Given (i) conformity of the input with phosphate ores mined from sedimentary deposits, (ii) comparability of the product with a commercially available P-fertilizer regarding contaminant levels, P fractionation and yield effects, (iii) compliance of the output with the German Fertilizer Ordinance, and (iv) physical product characteristics suited for bradcast application by spreader disk the RecoPhos P 38 fertilizer was discharged from the waste legislation regime. The fertilizer is currently being produced at a rate of 1,000 tonnes per month and sold at a competitive price.

1. INTRODUCTION

In response to current population growth rates the worldwide demand for staple foods, livestock products, biofuels etc. is increasing. To meet this demand, nutrient levels of agricultural soils need to be replenished by application of soil fertilisers. One indispensable nutrient for plant growth is phosphate. This element is primarily provided by mining and processing of igneous or sedimentary phosphate rock deposits.

The static lifetime of primary P stocks, defined as economically minable phosphate rock deposits divided by actual annual consumption, is estimated as roughly one century (Steen, 1998) and the peak in global phosphorus production has been projected to occur around 2030 (Cordell et al. 2009). Asides scarcity, the mined raw material is characterized by increasing contamination with geogenic uranium and cadmium (Romero Guzmán et al, 2002; Chien et al. 2011). During phosphate rock processing these elements are transferred to either the P-fertilizer or its most prominent by-product phosphogypsum (Keyzer, 2009; Chien et al., 2011).

In view of the above, the use of phosphate from secondary raw materials has turned into focus. One possible source of high availability is municipal sewage sludge. Its substitution potential for German primary phosphate imports has been estimated as 40 % (Cornel and Schaum, 2003). In many industrial countries sewage sludge is used in agriculture by direct application to the soil. However, awareness of sewage sludge contamination by persistent organic compounds (Harrison et al., 2006) has caused doubt on the sustainability of this practice (Sartorius and von Horn, 2010). Among the organic contaminants endocrine disrupting chemicals (EDCs) pose a major problem through bioaccumulation in the food chain. Therefore, in some countries, the agricultural use has been banned and sewage sludge incineration with concomitant destruction of organic contaminants is regarded as a superior option (Franz, 2008).

A recent review by Herman (2009) has summarized the status of phosphate recovery technologies. These may be classified according to the matrix addressed, i.e., the waste water stream, sewage sludge or the ash generated by mono incineration of sewage sludge (SSA). Options for the recovery of phosphate from SSA include, among others, sequential acid leaching procedures to release phosphate from low solubility phases (Levlin, 2007), metallurgic/ thermochemical treatment of SSA to produce a metal-depleted solid residue (Mattenberger et al., 2008; Adam et al., 2009) or the application of direct current electric fields to selectively enrich SSA-borne phosphate in the anolyte (Sturm et al. 2010).

Although some of the technologies have already been implemented on a larger scale their maturity and cost-effectiveness has been questioned (Levlin, et al. 2002; Levlin, 2007; Franz, 2008). Since phosphate rock and phosphate fertilizers are both commodities on the international market, cost-effectiveness of a P recovery process directly depends on the marketability of the product. Costs for secondary Magnesium Ammonium Phosphate (MAP) fertilizer have been reported to be around 1 € per kg P (Montag et al, 2008). This is about three times the current market price for primary fertilizer and would require subsidization or a drastic price increase to be competitive.

In this study we evaluate a novel technique for the full-scale treatment of sewage sludge ash. The proprietary process (patent pending) aims at the production of a readily marketable phosphate fertilizer which may either be directly applied in agriculture or further customized to yield a polynutrient soil amendment. A comparison of input qualities was undertaken on the basis of phosphorous contents and contaminant levels in phosphate rock and in SSA. Similarly, phosphorus availability and metal content were compared in a commercially available P-fertilizer and the output of the RecoPhos process.

2. MATERIALS AND METHODS

2.1 The RecoPhos process

Phosphate contents of sewage sludge ash (SSA) have been reported to be as high as 26 % P_2O_5. This value is comparable to medium to high-grade ores (Aydin, 2010) highlighting the substitution potential of this waste stream. Similar to the primary material, P in SSA is present in the sparingly soluble minerals, e.g. Whitlockite, Enstatite, Brushite, and Hilgenstockite (Sturm et al. 2010) rendering it unavailable to plants. In the RecoPhos process, the plant-available phosphate fraction is increased by reacting the SSA with phosphoric acid (eq. 1).

$$Ca_4Mg_5(PO_4)_6 + 12\ H_3PO4 \cdot 2H_2O \rightarrow 4Ca(H_2PO_4)_2 + 5Mg(H_2PO_4)_2 + 12H_2O \qquad (1)$$

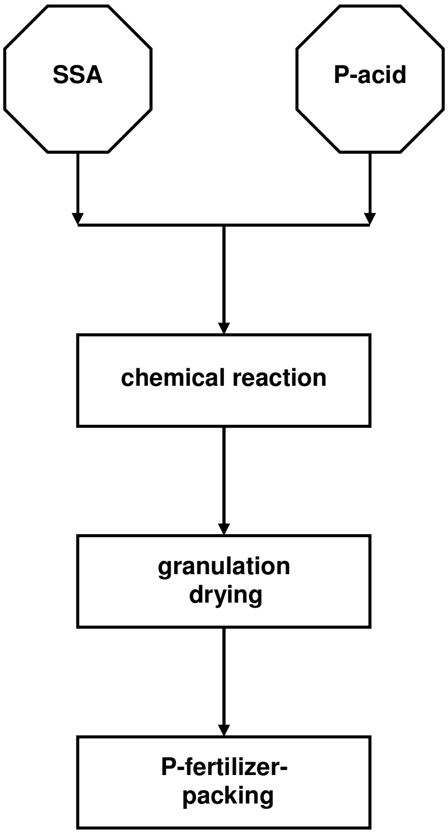

Figure 1. Scheme of the RecoPhos process for the production of the P 38 fertilizer from sewage sludge ash

Thereby, the primary minerals are transformed into soluble Calcium and Magnesium dihydrogenphosphate, the primary nutrient component of the RecoPhos P 38 fertilizer. This process conforms to the industrial production of Triple Superphosphate, with phosphate rock being substituted by SSA (cf. Figure 1).

2.2 Framework for the discharge of RecoPhos P 38 from the waste legislation regime

Typically, the SSA from mono combustion of municipal sewage sludge in fluidized bed incinerators is classified by the waste code 190112 {non-hazardous waste from incineration or pyrolysis of waste, specifically bottom (and boiler) ash and slag} of the German Waste Catalogue Ordinance (Anonymous, 2001). Plant operators accepting such waste for further processing are committed to keep a register of the proper waste management according to the German Ordinance on Waste Recovery and Disposal Records (Anonymous, 2006). In case of a fertilizer produced from SSA this commitment includes tracking and locating the disposition until the fertilizer is ultimately used.

For practicability reasons, Chemische Fabrik Tangermünde GmbH applied for discharging RecoPhos P 38 from the waste legislation regime. Therefore, the authorities of the Federal State of Saxonia-Anhalt (Landesverwaltungsamt Sachsen-Anhalt) requested to demonstrate (i) that SSA conforms to phosphate rock regarding the input quality and (ii) that the RecoPhos P 38 product conforms to conventional P-fertilizers regarding the output quality. This gave rise to the evaluation scheme presented in Figure 2.

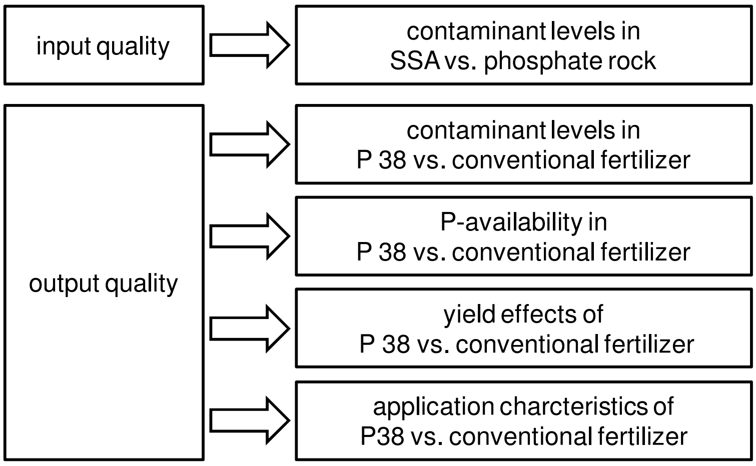

Figure 2. Evaluation scheme for the discharge of the RecoPhos P 38 fertilizer from the waste legislation regime

2.3 Evaluation of input quality

Inorganic contaminants in SSA were determined in samples obtained from the operators of 3 mono incineration plants for municipal sewage sludge. Analyses were performed by accredited laboratories according to standard methods. For comparison and process control, inhouse X-ray fluorescence (XRF) analyses were carried out by Chemische Fabrik Tangermünde GmbH (SPECTRO Xepos, SPECTRO Analytical Instruments GmbH, Kleve, Germany). Samples were dried at 105 °C for 30 minutes and ground in a ball mill for 5 minutes. Four g of the powder a placed into autosampler cups for XRF analysis under He atmosphere.

Information on the metals content in phosphate rock depending on the mining region was obtained by reviewing available literature (Pantelica et al., 1997, Kratz and Schnug, 2005; Sabiha-Javied et al., 2009).

2.4 Evaluation of output quality

Testing for product quality was performed under full-scale conditions. As outlined in Figure 2, this included (i) the comparison of contaminant levels in RecoPhos P 38 vs. a commercially available P fertilizer from primary P-sources against the limit values of the German Fertilizer Ordinance (Anonymous, 2008), (ii) a comparison of total, extractable, and water soluble P_2O_5 as above, (iii) comparative growth tests with rapeseed and maize as well as (iv) testing for fertilizer grain strength and broadcast radius.

During the full-scale test, 100 metric tonnes of the RecoPhos P 38 fertilizer were produced from the SSA of three mono incinerators (fluidized bed) and stored in Big Bags. A total of 61 product samples were taken by an independent contractor and combined to a collective sample. Sealed aliquots of the collective sample were sent to three certified laboratories specialized in fertilizer testing.

Analyses comprised the quantification of major and trace elements, perfluorinated compounds and phosphate fractions by standardized extraction procedures. The analytical spectrum as well as the methods conformed to the German Fertilizer Ordinance. Phosphate availability was studied by differentiation of total P, the fraction extractable by neutral ammonium citrate and the fraction of water-soluble P. For comparison with P-fertilizers manufactured from primary P-sources, a commercially available P-fertilizer with a similar phosphate level (Yara International

ASA) was included in the analyses. For quality control, additional analyses were undertaken at three institutes at Freiberg University of Mining and Technology, each using different analytical techniques (ion chromatography, ICP/AES, XRF).

For agricultural applications, the RecoPhos P38 fertilizer needs not only to conform to the fertilizer ordinance but also to correspond to handling and plant nutrition requirements. In modern agriculture, fertilizers are applied using machine tracks with working widths of 12, 18, 24 and 32 m. Therfore, RecoPhos P 38 was tested for mechanical streghth of grains. Throw width and spread areas achievable by spreader plate systems were evaluated on test stands of two agricultural equipment manufacturers (Amazonen-Werke H. Dreyer GmbH & Co. KG, Maschinen- und Antriebstechnik Güstrow GmbH & Co.KG). Yield effects of RecoPhos P 38 were studied in comparative pot experiments using a P-deficient soil. Replicates of maize (var. Lukas) and rapeseed (var. Ability) planted in 5 L Mitscherlich pots were amended with incremental levels of RecoPhos P 38 and the Yara fertilizer. Nitrogen and potassium levels were identical (1.5 g N and K per pot) in all variants. The Mitscherlich pots were kept at 60% water holding capacity for 77 (rapeseed) and 83 days (maize) at 12 h illumination and a temperature of 20 °C. Evaluation was based on the aboveground biomass and P fractionation in the soil.

3. RESULTS AND DISCUSSION

3.1 Input quality

A comparison of the metal contents in rock phosphate and the SSA samples included in this study is given in Table 1.

The data show a considerable spread of contaminant levels in the phosphate ores both within and among the mining regions. Substantially lower metal levels of phosphate rock from Russia are due to the magmatic origin of the ores.

Table 1. Comparison of selected metals and metalloids in phosphate ores from different mining regions and sewage sludge ash (SSA). Data in $mg/kg_{dry\ matter}$. Phosphate rock data compiled from Pantelica et al. (1997), Kratz and Schnug (2005) and Sabiha-Javied et al. (2009); n.a.: not available

Element	*USA*		*Morocco*		*China*		*Middle East*		*Russia*		*SSA*	
	min	*max*	*min*	*max*	*min*	*max*	*min*	*max*	*min*	*max*	*min*	*max*
As	7	14	9.2	13	9	26	2.4	35	1	10	<5	19
Cd	6.1	92	15	38	<2	2.5	1.5	35	0.1	1.3	2.1	2.9
Cr	60	637	75	291	18	33	25	230	13	23	54.6	79.8
Cu	9.6	23	1	22	n.a.	n.a.	5	31	15	30	619	864
Hg	0.05	0.29	0.04	0.86	0.005	0.21	0.002	0.02	0.004	0.01	0.08	0.47
Ni	17	37	n.a.	26	n.a.	n.a.	20	80	2	15	58.6	72.2
Pb	4.6	17	7	14	1.5	6	1	33	1.8	33	96.2	124
V	23	769	87	200	8	80	29	630	n.a	100	28	82
Zn	204	403	261	345	n.a.	n.a.	29	630	19	23	2320	2780
U	65	180	75	155	23	31	40	170	10	85	4	32

For a comparison of metal contents in SSA and primary P sources the ratio of mean contaminant levels in SSA and phosphate rock from Morocco was calculated. This region was chosen for having the largest share of the global phosphate reserves (Jasinski, 2009). According to the data in Table 1, the elements Cd, Cr, Hg, V and U have lower levels in the SSA compared to Moroccan phosphate rock (concentration ratios SSA / phosphate rock 0.81, 0.09, 0.37, 0.61, 0.38 and 0.15, respectively), whereas the elements Cu, Ni, Pb and Zn have higher levels (concentration ratios SSA / phosphate rock of 64, 2.51, 10.5 and 8.41, respectively). The enrichment of certain elements in SSA is balanced out by the depletion of others. Thus, the input quality of SSA conforms to phosphate rock of sedimentary origin.

3.2 Output quality

The results obtained by the three independent laboratories and the inhouse analyses were highly consistent with variation coefficients of 0.1 for metals/metalloid and 0.06 for phosphate fractions.

3.2.1 Contaminant levels

The contaminant levels observed in RecoPhos P 38 and the conventional fertilizer are summarized in Table 2. Relative to the latter, RecoPhos P 38 exhibits lower Ca and higher Mg levels (not shown). Regarding the micro nutrients Cu and Zn, the SSA-derived fertilizer has higher contents. With respect to heavy metals, the levels are partly comparable (As, Cr), partly higher (Pb, Hg) and partly lower (Cd, Ni, Tl).

Table 2. Metals and metalloids in RecoPhos P 38 and conventional P-fertilizer (Yara). Data in $mg/kg_{dry\ matter}$

Element	*Recophos P 38*	*Yara*	*Element*	*Recophos P 38*	*Yara*
As	9.10	8.30	Ni	47.4	55.1
Cd	2.16	20.0	Pb	51.4	1.82
Cr	118	120	Se	3.83	5.40
Cu	664	36.5	Tl	0.20	0.42
Hg	0.70	< 0.054	Zn	1600	439

Regardless the comparability between RecoPhos P 38 and the conventional P-fertilizer, compliance with the German Fertilizer Ordinance is a prerequisite for marketability. As shown in Table 3 all relevant elements as well as perflourinated compounds {PFC = perfluorooctane sulfonate (PFOS) + perfluorooctanoate (PFOA)} are below the legal limit. The pertinent limit value for Cd is 50 mg/(kg P_2O_5) given the high P content. Regarding Ni and Hg a labelling obligation needs to be observed since the values are above 40 mg/kg and 0.5 mg/kg, respectively.

Table 3. Compliance of RecoPhos P 38 with limit values for soil fertilizers according to the German Fertilizer Ordinance (Anonymous, 2008)

Parameter	Limit value	RecoPhos P38
As	40	9.10
Pb	150	51.4
Cd	1.5[1)]	2.16
Cr_{total}	300 (indication)	118
Cr(VI)	2	< 0.01
Ni	80	47.4
Hg	1	0.70
Tl	1	0.20
PFC	0.1	< 0.01

[1)] at $P_2O_5 > 5\%\text{-wt}_{dry\ matter}$: 50 mg Cd/kg P_2O_5

3.2.2 Phosphate availability

Average P-fractionation data obtained for the RecoPhos P 38 and the Yara fertilizers are summarized in Table 4. The P_2O_5 levels in the ammonium citrate-extractable and the water-soluble fractions are proxies for the share of plant-available P. The results show that processing significantly increases P-availability relative to the native SSA. The ratio of water-soluble to ammonium citrate-extractable phosphate is 80 %. This is below the value of 85 % indicative of a Triple Superphosphate fertilizer according to the commission regulation (EC) No 2076/2004 (Anonymous, 2004). Comparison of total P and ammonia citrate-soluble plus water-soluble fraction between RecoPhos and the Yara product shows, that regarding phosphate fractionation the P-fertilizer produced from SSA conforms to fertilizers from primary P-sources.

Table 4. Phosphate fractionation in RecoPhos P 38 and conventional P-fertilizer (Yara). Data in $P_2O_5\ \%_{dry\ matter}$

Phosphate fraction	*RecoPhos P 38*	*Yara*
Total	40.35	39.80
NH_4 citrate plus H_2O-soluble	38.07	38.50
H_2O-soluble	30.30	36.30

3.2.4 Yield effects

Results of the pot experiments conducted with respect to the fertilizing properties of RecoPhos P 38 are shown in Figure 3. Rapeseed yields of the RecoPhos-amended pots were comparble to the replicates amended with the conventional fertilizer, when the yield differences of the corresponding blank are considered. Surprisingly, after harvesting P fractionation in the soil of the RecoPhos treatments showed no depletion of the water-soluble fraction over the other fractions. This may indicate that biomass yields profited evenly from the different P-pools.

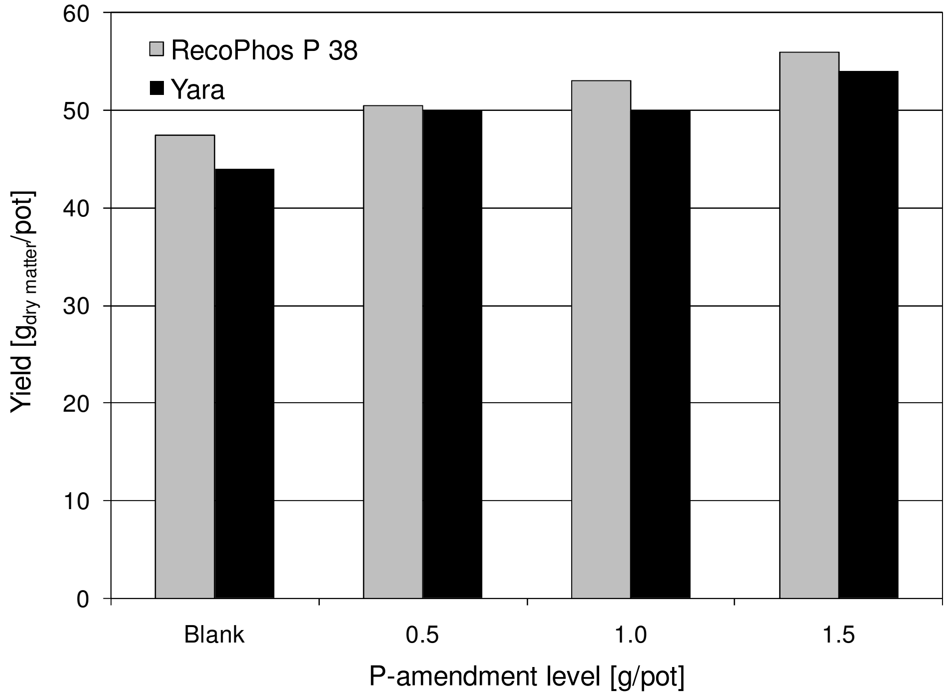

Figure 3. Rapeseed yield in a comparative pot experiment with incremental fertilization using RecoPhos P 38 and a conventional P-fertilizer

3.2.4 Application characteristics

To meet the throw and spread requirements of modern fertilizer application practices grain stabilities must be between 20 Nm and 30 Nm. The grain stability of RecoPhos P 38 lies in the range of 20 to 25 Nm. This confirms test stand results according to which working widths of 24 m can be achieved at a spreading precision equivalent to conventional fertilizers.

4. CONCLUSION

The evaluation of SSA regarding its input quality for the production of a P-fertilizer showed that this waste stream conforms to primary phosphate sources obtained from the mining of sedimentary phosphate rock deposits. RecoPhos P 38 proved comparable to a commercially available product manufactured from primary P-sources both with regard to nutrient fractionation and heavy metal content. RecoPhos P 38 complies with all limit values of the German Fertilizer Ordinance, has comparable fertilization effects on crops and is suited for broadcast application. Based on these findings obtained with the output of a pilot test under full-scale conditions the product was officially discharged from the waste legislation regime. Currently, 1,000 metric tonnes of fertilizer per month are being produced at a marketable price.

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