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## Waste Management

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# Thermochemical treatment of sewage sludge ash with sodium salt additives for phosphorus fertilizer production – Analysis of underlying chemical reactions

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## ARTICLE INFO

## Article history:

Received 27 May 2015

Revised 14 July 2015

Accepted 17 July 2015

Available online xxxxx

## Keywords:

Phosphorus recovery

Plant availability

Solubility in ammonium citrate

Whitlockite-to-buchwaldite transformation

## ABSTRACT

Stocks of high grade phosphate rock are becoming scarce, and there is growing concern about potentially harmful impurities in conventional phosphorus fertilizers. Sewage sludge ash is a promising secondary phosphorus source. However, to remove heavy metals and convert the phosphorus contained in sewage sludge ash into mineral phases available to plants, an after-treatment is required. Laboratory-scale calcination experiments of sewage sludge ash blended with sodium salts using dried sewage sludge as a reducing agent were carried out at 1000 °C. Thus, the  $\text{Ca}_3(\text{PO}_4)_2$  or whitlockite component of raw sewage sludge ash, which is not readily plant available, was converted to  $\text{CaNaPO}_4$  (buchwaldite). Consequently, nearly complete phosphorus solubility in ammonium citrate (a well-established indicator for plant availability) was achieved. Moreover, it was shown that  $\text{Na}_2\text{CO}_3$  may be replaced by moderately priced  $\text{Na}_2\text{SO}_4$ . However, molar ratios of  $\text{Na/P} > 2$  were required to achieve >80% phosphorus solubility. Such over-stoichiometric Na consumption is largely caused by side reactions with the  $\text{SiO}_2$  component of the sewage sludge ash – an explanation for which clear evidence is provided for the first time.

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## 1. Introduction

Phosphate rock is a non-renewable resource that is commonly used as a raw material for P-fertilizer production (USGS, 2013). Moreover, reserves that are low in impurities and easily accessible will likely become scarce in the near future (Gilbert, 2009). A number of technologies are emerging for phosphorus recovery from sewage sludge (SS)<sup>1</sup> or sewage sludge ash (SSA)<sup>2</sup> (Donatello and Cheeseman, 2013). Among them are thermochemical treatment processes, which intend to increase the plant availability of P via the formation of soluble P-bearing mineral phases. Simultaneously, these processes reduce the heavy metal load by partial separation of heavy metals via the gas phase. In the past, thermochemical treatment processes have often been associated with high specific energy demands. However, recent advances in process integration, which facilitate the direct transfer of hot SSA from the incinerator to the subsequent calcination and advanced heat recovery, promise a

reduction of energy consumption to levels comparable to wet chemical processes. It has been shown that the thermochemical treatment of SSA with  $\text{MgCl}_2$  hydrate at approx. 1000 °C results in a very effective heavy metal removal (Adam et al., 2009). However, the ammonium citrate solubility of phosphates in the treated SSA remains limited and does not exceed 30% (Vogel et al., 2013). Pot experiments revealed that products from the thermochemical treatment of SSA with  $\text{MgCl}_2$  work well on acidic soils, but the fertilization performance is drastically reduced on neutral or alkaline soils (Nanzer et al., 2014). A new approach was investigated in this study to achieve high plant availability on neutral or alkaline soils (Werner, 1967; Severin et al., 2014; Wilken et al., 2015). This method involves the blending of calcium phosphate-rich SSA with sodium salts, followed by calcination under reducing conditions. This approach bears some similarity to the Rhenania process which, however, used raw materials different from SSA and did not apply reducing conditions for heavy metal removal.

In the Rhenania process, rock phosphate was fused with  $\text{Na}_2\text{CO}_3$  and  $\text{SiO}_2$  at 1100–1300 °C. The main P-bearing component of the product is buchwaldite, the low-temperature modification of  $\text{CaNaPO}_4$ . This mineral phase is insoluble in water but soluble in alkaline and neutral ammonium citrate. It exhibits excellent plant availability. Presumably,  $\text{Ca}_3(\text{PO}_4)_2$  is the main P-bearing mineral

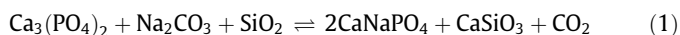
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<sup>1</sup> SS = sewage sludge.

<sup>2</sup> SSA = sewage sludge ash.

phase in most sewage sludge ashes. Based on experiments with model substances carried out under reaction conditions close to those used in the Rhenania process (i.e., at 1100–1300 °C), the following reaction equation was suggested to describe the formation of  $\text{CaNaPO}_4$  from  $\text{Ca}_3(\text{PO}_4)_2$  (Messerschmitt, 1938):



Eq. (1) suggests that a molar ratio of  $\text{Na/P} = 1$  is sufficient to produce fully citrate-soluble P. To the best of the present authors' knowledge, only one study has been published to date aimed at increasing the plant availability of P in SSA by calcination with  $\text{Na}_2\text{CO}_3$  (Hauschild and Werner, 1981). Interestingly, that study reports that  $\text{Na/P}$  molar ratios of 1.3–2.7 were necessary to achieve 80–90% alkaline ammonium citrate-soluble phosphorus. However, it did not investigate why the  $\text{Na/P}$  ratio needed to be that high. A possible explanation proposed for the increased Na consumption is that P and Si may compete for Na. Consequently, side reactions of Na with Si might be responsible for the increased Na consumption, as well as for the reduced P solubility, if the molar ratio of Si/P exceeds 0.5 (Gunawardane and Glasser, 1979).

Preliminary experiments on the calcination of SSA blended with  $\text{Na}_2\text{CO}_3$  were carried out by the present authors and yielded products with a high plant availability. However, accompanying process simulations revealed two drawbacks: the cost for  $\text{Na}_2\text{CO}_3$  alone would make up 50% of the operating costs of a large-scale plant, and in addition, a high carbon and environmental footprint is associated with  $\text{Na}_2\text{CO}_3$ . Hence, alternative alkaline salts, such as  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{K}_2\text{SO}_4$ , were tested as possible substitutes for  $\text{Na}_2\text{CO}_3$ . In these preliminary experiments, all Na-based substances yielded good ammonium citrate solubility when being calcined under reducing conditions. However,  $\text{Na}_2\text{SO}_4$  turned out to be the most attractive substance, as it has two additional advantages. It is the most abundantly available of these alternative substances and costs approximately half as much as  $\text{Na}_2\text{CO}_3$ . Moreover,  $\text{Na}_2\text{SO}_4$  is a by-product of rayon fiber production. Therefore, depending on its origin, it may have a small environmental footprint. Consequently, the present paper is focused on three main scopes: First, on the investigation of the feasibility of substituting  $\text{Na}_2\text{SO}_4$  for  $\text{Na}_2\text{CO}_3$  under reducing calcination conditions for producing P-fertilizers from SSA rich in calcium phosphate. Second, on the quantification of the  $\text{Na/P}$  and  $\text{Na/Si}$  ratios which are necessary to achieve products with high phosphorus solubility using an alkaline ammonium citrate test. Third, on the analysis of the Na-consuming side reactions occurring under the applied calcination conditions through an X-ray diffraction (XRD) investigation of a selected number of the product samples used for the solubility tests.

## 2. Materials and methods

### 2.1. Materials

The sewage sludge ash (SSA) used throughout the present investigation was produced at the incineration facility of the municipal wastewater treatment plant in Winterthur, Switzerland. Dried sewage sludge (SS), which was used as a reducing additive in the experiments, was acquired from the waste water treatment plant in Berlin-Wassmannsdorf, Germany. Two characteristics of this SS were revealed by thermogravimetric analysis carried out from 20 to 1000 °C at a heating rate of 5 K/min. First, at up to 150 °C, a mass loss of 8% was observed, which can be mainly attributed to physisorbed water. Second, at the end temperature, just 29% of the original mass of the SS was not volatilized and can thus be defined as its ash content. The chemical compositions of both raw materials are given in Table 1. Sodium carbonate

**Table 1**  
Elemental compositions of sewage sludge ash, sewage sludge and product samples.

	Sewage sludge ash		Sewage sludge		Product samples	
	Mean	SD	Mean	SD	Mean	SD
	mg/kg					
Al	29,000	1000	7550	80	27,290	700
Ca	109,300	3200	34,210	820	101,200	2100
Fe	133,600	2200	10,330	280	119,400	4500
K	6800	300	3614	22	7150	840
Mg	14,070	440	19,309	93	12,660	750
Na	3300	280	1640	60	82,500	2600
P	70,510	910	38,360	480	69,850	1800
S	13,900	81	12,850	180	31,100	1800
Si	115,500	6700	22,510	790	110,300	9100
As	12.8	0.5	12.0	0.6	11.0	0.6
Cd	7.35	0.05	0.90	0.04	3.8	0.5
Cr	121.4	5.2	33.5	1.9	103.8	1.5
Cu	820.9	3.8	889.4	8.8	827	16
Mn	1305	11	120.6	0.2	1281	27
Ni	63.8	3.4	21.1	0.1	59.5	2.3
Pb	248.4	3.5	32.5	2.1	112	17
Zn	2535	25	957	27	2120	60

SD = standard deviation; sewage sludge ash:  $n = 3$ , sewage sludge:  $n = 3$ , product samples:  $n = 4$  (repeated experiment S13–S16).

anhydrous GR for analysis and sodium sulfate anhydrous fine powder analytical reagent grade were supplied by Merck, Darmstadt, Germany, and by Fischer Scientific, Loughborough, UK, respectively.

### 2.2. Calcination experiments

A detailed overview of the design of the experiments carried out in the present study is given in Table 2. For each experiment, excluding S1, 10.00 g of SSA was mixed with 2.00 g of dry SS, which was used as a reducing agent. The amount of added  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  was systematically varied. The ratios of  $\text{Na/P}$  and  $\text{Na/Si}$  used in Table 2 and Fig. 1 are defined as the molar ratio of the total Na content in a sample to its P content or Si content, respectively. Here, the total Na content takes into account the weighed amounts of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$ , as well as the Na content of the raw SSA and the dried SS. In total, 32 experiments were carried out (S1–S32), including the two blank experiments (S1 and S2), which had no Na salt addition. To determine the reproducibility of the procedure, a repeated experiment with 4 replicates (S13–S16) was included. This repeated experiment lies close to the center of the design of experiments. For each experiment, the starting materials were mixed for 30 min in an overhead mixer at 40 rpm and subsequently transferred into a corundum crucible with a volume of 85 mL. Corundum was used because of the high ferric content of this SSA, which, together with the reducing conditions, might be damaging for Pt crucibles. The crucibles were calcined in a pre-heated muffle furnace at 1000 °C for 30 min. After calcination, the crucibles were removed from the furnace and were allowed to cool under ambient conditions. During calcination and cooling, the crucibles were covered with a corundum lid to maintain reducing conditions. The crucible filled with the sample was weighed before and after each calcination. Thus, the mass yield was determined based on the ratio of the net sample weight after calcination to that before calcination.

### 2.3. Analytics

#### 2.3.1. Sample preparation

Each sample was removed from the crucible after the thermochemical treatment and pulverized and homogenized for 15 s in a vibratory disc mill (Pulverisette 9, Fritsch, Germany), which

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