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## Modelling thermal phosphorus recovery from sewage sludge ash

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## ABSTRACT

Phosphorus is an essential and irreplaceable element for life, and its growing production is mainly based on the processing of non-renewable phosphate ores, often extracted in regions with political instability risks, making it a critical element. An alternative phosphorus source, explored in the RecoPhos project, is found in sewage sludge ash. In this project, an inductively heated packed carbon bed reactor has been developed to treat the ashes at high temperature. Phosphorus is recovered by reduction and vaporization, and can be recovered as white phosphorus or phosphoric acid. In order to describe the chemistry and predict the potential outputs and yields, InsPyro has developed thermodynamic models for the system and the reactor. The results for the reduction behavior of slag, ferrophosphorus formation, and overall P recovery show good agreement with lab and pilot scale tests. Using the model, optimal reduction and fluxing parameters can be determined.

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### 1. Introduction

Phosphorus is an essential element in the molecules with genetic and energetic functions in all life forms. It therefore plays a vital and irreplaceable role in agriculture and food production, with the largest amounts being used as a fertilizer. Its production relies mainly on phosphate rock, a limited natural resource. Rising consumption is expected, which has led several authors to emphasize the need for phosphorus stewardship [1,2]. Also, because of its economic importance and the fact that Europe has to import it from politically instable regions, the European Commission has classified phosphate rock as a critical raw material [3], alongside with rare earths, antimony, etc.

The phosphorus flows in Europe have recently been assessed [4], from which it is clear that the largest losses are from human consumption – end-of-life in classical recycling terms – and from food processing. Whereas manure is recycled since ages as a fertilizer, human waste is less easy to recycle, due to its scattered and diluted production. In developed areas, human excrements are collected in sewage systems, and pollutants are subsequently removed from the municipal wastewater. Phosphorus is removed with iron or aluminum salts, or through biological processes, to avoid eutrophication of waterways. The phosphate precipitate forms a fraction of the sewage sludge. Due to heavy metals contents and limited plant availability, sewage sludge is often not a suitable or legal fertilizer. Different recycling and reuse

possibilities have been investigated [5]. Modifications to the wastewater treatment process are also possible, and the precipitation of a separate P-rich struvite precipitate, suitable as a fertilizer has started industrially [6,7]. Many other options to recover fertilizers are under investigation [7–10].

Nevertheless, end-of-life recycling of phosphorus remains very limited, and large quantities of sewage sludge ash are available from recovery of thermal energy from the organic fraction in the sludge, e.g. in Germany [8,9,11,12]. Whereas the conversion to a fertilizer is a common research topic, the RecoPhos project aims at the production of thermal phosphorus. Indeed, certain high quality products and specific chemicals need to be produced from elemental phosphorus rather than phosphoric acid. Elemental phosphorus is classically produced in a submerged arc furnace [13] from phosphate rock. The use of secondary raw materials in such a process had started at the Dutch producer ThermPhos [14] but the company has filed bankruptcy in 2013 [15].

The RecoPhos project aimed at the use of a flexible innovative reactor [16] to produce thermal phosphorus from in first instance sewage sludge ash [9,17]. A schematic process overview is shown in Fig. 1. The core of the process is an inductively heated packed carbon bed reactor (InduCarb). A mix of sewage sludge, reductant, and fluxes is fed to the top, and flows over the bed. P is reduced and evaporates as elemental phosphorus, which can be condensed as white phosphorus, or converted to oxide or phosphoric acid in an afterburner and washer (as in Fig. 1). The reduced slag can be used to produce building materials [18].

This paper discusses the thermodynamic modelling of the process, performed by InsPyro in the framework of the RecoPhos

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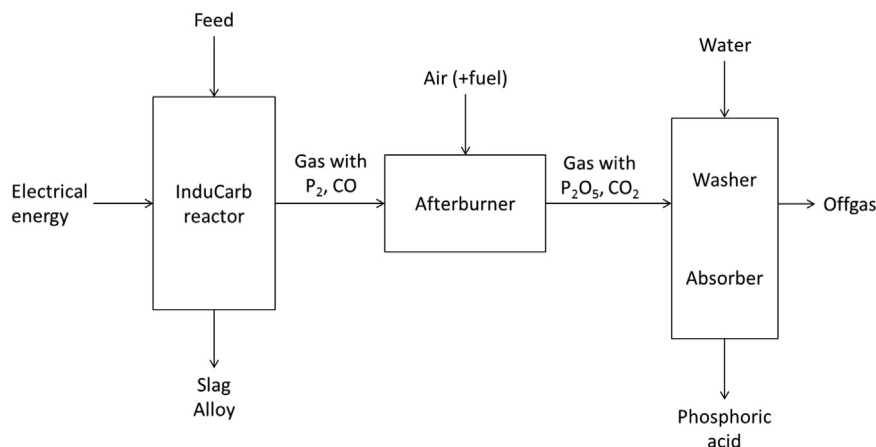


Fig. 1. Scheme of the RecoPhos process with phosphoric acid recovery (after [19]).

project. Other partners in the project focused on a.o. CFD modelling [20], experimental work [21], and the construction of a small scale continuous demonstration plant, which was presented in 2015 [19].

## 2. Methods

### 2.1. Input material composition

The sewage sludge ash used within the RecoPhos project was recovered from the Stuttgart incinerator, mixed, and sampled. Its composition was determined by ICP, XRF, and XRD. The main phases in the ash detected by XRD were  $\text{SiO}_2$ ,  $\text{Ca}_9\text{AlP}_7\text{O}_{28}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FePO}_4$ . The ash contains minor amounts of heavy metals, which are not all taken into account for the calculations in the present article. The composition used for the calculations is given in Table 1 below (assuming the S content as CaS). At high temperature, the material can be considered rather acidic, with a basicity  $\text{CaO}(\text{total Ca})/\text{SiO}_2$  of 0.55.

As a reductant, different carbon-rich materials can be added. For the calculations the reductant is assumed to be 100% C. Similarly, fluxes are assumed to be pure CaO or  $\text{SiO}_2$ .

### 2.2. Thermodynamic modelling

All calculations are performed with FactSage 6.3 [22]. The databases used were partially state-of-the-art databases, available in FactSage, and internally developed. From our evaluation, commercial databases were suitable for the gas phase (FactPS incl.  $(\text{P}_2\text{O}_3)_2$ , PO,  $\text{PO}_2$ ,  $\text{P}_2$  and  $\text{P}_4$  species) and liquid metal phase (FSStel), also at high phosphorus contents. However, the oxide database in FactSage (FTOxid) was only suitable for calculating melts with  $\text{P}_2\text{O}_5$  in the dilute species regime, and would show unrealistic solubilities and melting points for the high  $\text{P}_2\text{O}_5$  levels in the input material. Also in literature, only a limited number of subsystems have been assessed and described thermodynamically. The system  $\text{CaO}-\text{P}_2\text{O}_5$  has been described with both quasichemical [23] and ionic liquid [24] models for the melt. The system  $\text{SiO}_2-\text{P}_2\text{O}_5$  has been described in the quasichemical framework [25]. The published systems [23] and [25] are part of a more complete but not

yet commercially available database for dephosphorization in steel [26]. Therefore, several subsystems were studied in detail and modelled in the framework of the RecoPhos project [27]. For the melt, the associate liquid model was used, such that the models could be integrated with the GTT oxide database GTXO [28–30]. This allows calculating the behavior of oxide melts with various components over the full composition range. As an example, the liquidus projection for the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{Al}_2\text{O}_3$  is shown in Fig. 2. At temperatures above 1600 °C, this result deviates strongly from the estimated results in the standard experimental reference for the ternary system [31], but is more realistic due to the use of fully assessed data on the binary systems.

The process model is based on full equilibrium with a stepwise addition of reductant. Although the process concept is continuous, it is assumed that it can be approximated more correctly by an open model, in which the gas phase produced in every step is removed from the calculation for the subsequent steps. This type of model is classically used for batch processes (e.g. the AOD [32] or EAF [33] process for steelmaking). The assumption is based on the quick removal of hot gases from the reactor, which is not expected to enable reactions between the gases formed at the top of the reactor and the condensed phases at the bottom.

### 2.3. Experimental work

To verify the thermodynamically expected behavior, a limited number of lab scale experiments were set up. Small quantities of sewage sludge (4–8 g) were mixed with a 20% addition of pet coke or graphite, in graphite crucibles. The cylindrical crucibles were made to measure by SGL Carbon and had an inner diameter of 20 mm and a rather tall usable height of 45 mm, which allowed the direct use of the very fine and voluminous sewage sludge ash. For every experiment, a crucible was suspended on a 2 mm thick Mo wire in the top cold zone of a 5 cm diameter  $\text{Al}_2\text{O}_3$  tube furnace. The furnace was then flushed with Ar and heated to the desired temperature started. The crucible was then lowered into the hot zone of the furnace, where it was held for 4 h. In a single test, the crucible was kept at high temperature only for 5 min. Finally, the crucible was quenched by lowering it to the bottom cold zone of the furnace. After further cooling and flushing with Ar, the furnace was flushed with air. This closed furnace quenching procedure was followed in order to avoid the ignition of potential phosphorus depositions on colder surfaces in the furnace. Throughout the experiment, the exit gas was led through a water bottle for basic scrubbing. The crucibles were cut, and polished surfaces were investigated and analyzed by SEM-EDX on a Philips XL40 LaB6 instrument with Noran System Six software.

Table 1  
Composition of the RecoPhos ash (wt%).

$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$	FeO	CaO	CaS	$\text{Al}_2\text{O}_3$	ZnO	MnO
30.2	21.8	16.2	0.9	15	1.9	13.8	0.3	0.1

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