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Phosphorus recovery alternatives for sludge from chemical phosphorus removal processes – Technology comparison and system limitations

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ABSTRACT

Several approaches have recently been proposed in the literature for P recovery after metal precipitation, but a robust comparison of these approaches in a techno-economic framework is still lacking. Five phosphorus recovery methods using sewage sludge or sludge ash as feed material were compared based on their specific operational recovery cost by scaling the processes to unified size and operational conditions. The selected technologies were (1) wet leaching + struvite precipitation, (2) magnetic vivianite separation, (3) sludge melt gasification, (4) the thermochemical sodium sulfate process, and (5) white phosphorus recovery. The analyses were based on the literature values in addition to a plant-wide model used to estimate chemical consumption and phosphorus and metal-related sludge properties. The technologies were assessed by operational cost, end-product quality, recovery efficiency, and technology maturity. The choice of the recovery process is dependent on the precipitant used in the wastewater treatment processes. Technologies using sewage sludge ash, (4) and (5), had the highest recovery efficiency, technical maturity, and product quality, but they require mono-incineration. Technology (2) had the lowest recovery efficiency among all the compared technologies, however, it produced an end-product with the second highest P content. The operational costs were calculated for energy and chemical costs for same scale and operational conditions. The specific recovery cost ranges from 6 to $38 \notin/kgP_{recoverged}$

1. Introduction

Phosphorus (P) is a vital element for life on Earth. Its role in biological systems is irreplaceable as phosphorus is part of DNA and essential for growth and sustaining life [1]. However, excess phosphorus is also a detrimental contaminant, especially in aquatic environments [2,3]. Primary productivity in most freshwater systems is P-limited [3–5], and the agriculture-induced increase in global P use has made P more available than ever in recent time [6]. The abundant P availability in a natural environment that used to be P-limited results in ecological disorder, which is typically termed as eutrophication [4]. The severe negative environmental consequences of excess P pollution are accompanied by the paradoxical challenge of dwindling conventional P stocks critical to global food production. Current sources of P are non-renewable phosphate rock with finite reserves that are found only in a limited number of locations around the world [7–10]. P depletion is a global challenge and utilizing municipal waste flows rich in nutrients is expected to become a major pathway to recover P products that are vital for the human population—especially in the EU, where P is a critical raw material [11] since 83% of P is imported [12].

The purpose of wastewater treatment plants (WWTPs) has traditionally been pollution prevention, but recently it has been in transition

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Abbreviations: AD, Anaerobic digestions; Al, Aluminum; °C, Celsius temperature unit; Ca, Calcium; CO₂eq, Carbon dioxide equivalent; CPR, Chemical phosphorus removal; DNA, Deoxyribonucleic acid; EBPR, Enhanced biological phosphorus removal; EU, European Union; Fe, Iron; HAP, Calcium phosphates; kgP, Kilogram phosphorus; kWh, Kilo watt hour; MAP, Magnesium ammonium phosphate; MJ, Mega Joule; m_n^3 , Normal Cubic Meter, the quantity of Natural Gas which, at a temperature of 0° C and 1.01325 bar, occupies the volume of 1 cubic meter.; MWh/y, Mega Watt hour per year; P, Phosphorus; PE, Population equivalent; SS, Sewage sludge; SSA, Sewage sludge ash; TSP, Triple superphosphate; WAS, Waste-activated sludge; WRRF, Water resource recovery facility; WWTP, Wastewater treatment plant.

to resource recovery [13], as nutrients are recognized as a valuable resource. There is a significant amount of P available in wastewater flows. Most wastewater in Europe is treated at WWTPs, and 310 Gg of P/ year flows in sludge while fertilizers applied to European agriculture contain 1080 Gg P/year [14]. However, utilizing precipitated P sludge as direct fertilizer is not accepted everywhere due to concerns related to the presence of heavy metals, organic pollutants, and other trace elements in the sludge [15]. An increasing amount of research is focused on developing techniques to recover P from wastewater flows in a purer and bioavailable form. Comprehensive reviews have been published by Egle et al. [16] and Melia et al. [17], among others. However, these reviews have not examined the connection between the wastewater treatment process characteristics and the P recovery technologies. Also, their focus is generally on biological P recovery technologies. This study aims to fill knowledge gaps by including the wastewater treatment process into the cost calculation and focusing on chemically precipitated P.

WWTPs have two primary P removal methods: enhanced biological P removal (EBPR) and chemical P removal (CPR). These methods can be combined [18]. Investment costs are lower for CPR plants compared to EBPR plants, and it is possible to reach a lower effluent concentration with a chemical process [19]. P recovery from EBPR sludge has been researched more thoroughly than P recovery from CPR: brushite and struvite precipitation are already commercial pathways to recycle P, although the recovery efficiency is between 10% and 40% [13,20]. In addition, calcium phosphate precipitates are another attractive recovery pathway [21]. According to data collected by Korving et al. [13], CPR is the dominant treatment method in most of Europe. Their study examined Germany (CPR: 61%, combined: 31%, [22]), the Netherlands (CPR: 32%, combined: 51%, [23]), the United Kingdom (CPR: 77%, combined: 18.3%, [24]), and Sweden (CPR: 97%, combined: 3%, [25]). Overall, the choice of technology seems to vary across the world [26]. Furthermore, even if EBPR is the dominant method, many plants use CPR as a backup or additional treatment step [13] to reach effluent limits defined by their environmental permit. P effluent limits are predicted to become stricter in the future, especially in vulnerable areas such as the Baltic Sea [27], thus increasing the need to implement CPR because it is relatively difficult to reach low P effluent concentrations with EBPR. Furthermore, many papers discuss the effect of adding metal coagulants to digesters treating sludge from an EBPR process to prevent P release [28-31].

CPR can occur through chemical precipitation, selective adsorption, and flocculation and co-precipitation [32]. Aluminum, iron, or calcium can be used to precipitate P [33]. These metals form various compounds with phosphate, depending on the process conditions. The general formula for these is $Me_r \bullet H_2PO_4(OH)_{3r-1}(s)$ [34]. Iron(III) compounds, such as Fe(OH)₂, Fe_rPO₄(OH)_{3r-3}, and FePO₄, are reduced to iron(II) in anaerobic digestion (AD) [35]. The presence of iron(II) in digestate decreases the soluble phosphate [28,29], as Fe(II) precipitates as different species. Mamais et al. [36] suggested that Fe₃(PO₄)₂ leads to a low soluble PO₄³⁻ concentration, but Korving et al. [13] concluded that the chemistry of iron is not entirely understood. Recent studies have highlighted vivianite (Fe₃(PO₄)₂·8H₂O) as the main compound for ferrous phosphates [37], alongside various ferrous-(hydroxyl)-phosphate compounds [35]. High sulfur content inhibits ferrous phosphate formation [35].

Aluminum-based coagulants are commonly used to precipitate phosphorus [30]. These coagulants form amorphous hydroxides, where P can be adsorbed or form insoluble salts, AlPO₄ [38]. Novak & Park [39] concluded that the effect of aluminum is minor on the AD process. Calcium precipitation processes result in several compounds, hydroxy-apatite (HAP, $Ca_5(PO_4)_3$ •OH) being the most stable compound and most likely to precipitate through precursors [38,40]. Similarly, a magnesium presence leads to different precipitates, struvite (MgNH₄PO₄•6H2O) being the most common one [38,40]. Other metals inhibit the struvite crystallization process [31].

This study focuses on analyzing and comparing the possibilities of P recovery methods from sludge originating from treatment facilities

where only chemical P removal processes are used. While several approaches have been proposed recently in the literature to recover P after metal-precipitation, a robust comparison of these approaches in a techno-economic framework is lacking. The interest in P recovery from WWTPs is increasing, and since recovery processes from CPR are in their infancy [16], a comprehensive comparison is useful for experts in the field. Also, the benefit and requirements of the technologies are considered along with the local operators' preferred chemicals since their availability and price vary greatly. The evaluated parameters for the technologies are operational costs, end-product quality, recovery efficiency, technology maturity, and limitations set by the water and sludge process choices. Furthermore, laboratory scale P recovery processes are presented. This work relies on data compiled from the literature complimented by modeling of the digested sludge characteristics and linear scaling of the processes' operational costs. A decision flowchart is presented for readers to clarify the selection of P recovery process.

2. Material and methods

2.1. Comparison of recovery options

To compare P recovery reliably, the methods are applied to a representative $50,000 \text{ m}^3/\text{d}(13.2 \text{ MGD})$ water resource recovery facility (WRRF). The purpose of the wastewater treatment process model was to produce sludge characteristics and chemical consumption estimate and thus the model was only developed to fulfil this purpose. The recovery methods included in this study focus on sewage sludge (SS) or sewage sludge ash (SSA) mainly containing (1) vivianite, (2) aluminum phosphate, or (3) hydroxyapatite, corresponding to the precipitation metal used in the mainstream process (iron, aluminum, or calcium). Treating SSA is an interesting option due to its high P content [41,42]. Also, mono-incineration is a fairly common practice in some European countries [43].

2.2. Characterization of influent wastewater and sludge

SUMO process simulation software (Dynamita Ltd., version 19.3.0) was used to simulate wastewater treatment process chemical consumption and digested and dewatered sludge qualities for the typical WWTP (Fig. 1). The principles of P precipitation in wastewater treatment are elaborated on general level in [44]. Furthermore, the developers at Dynamita have published papers detailing SUMO models, for example [45]. Hauduc et al. in [45] recommend further investigation on competing substances for phosphate removal. The Gujer matrix of the model uses rate values of 0.1 g.m⁻³.d⁻¹ for calcium carbonate, 5 g.m⁻³. d⁻¹ for amorphous calcium phosphate, for 10 g.m⁻³.d⁻¹ struvite and 0.01 g.m⁻³.d⁻¹ for vivianite precipitation. This represents the current understanding of the precipitation processes, granted that it is only an approximation.

The sludge characteristics were modeled to ensure their comparability. Influent characteristics in the model reflect Viikinmäki WWTP (Helsinki, Finland) values, which were 50,000 m³/d, 600 gCOD/m³, 50 gN/m³, 6 gP/m³ (58% as PO₄), and 15 °C with influent fractions set as Sumo1 concentration-based influent. The influent also contains 150 gCa/m³ but no Fe or Al. The Viikinmäki WWTP uses only CPR and is therefore used as a standard to ensure the model results are within the correct range. The model uses the Sumo1 full plant model: (1) primary sedimentation with metal coagulant dosing for P removal and aerobic activated sludge process, (2) a mesophilic anaerobic digester fed with both waste-activated sludge (WAS) and primary sludge, and (3) monoincineration. Thermal drying is typically done before incineration; but to simplify the model, it is not included in this model. The costs related to dewatering are not included in this study, but the cost of thermal drying is included when incinerator is involved (Sections 3.2.4 and 3.2.5). Detailed model settings are presented in the supplementary



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Fig. 1. Sludge characteristics production model schematic captured from SUMO. Incinerator was not a part of the SUMO model.

materials (SM). The wastewater treatment process performance was optimized for approximately 95% P removal. Chemical consumption is based on the metal/P molar ratios of 3.7, 6.1 and 20.7 for Fe, Al and Ca, respectively.

2.3. Process scaling

A comparison of different phosphorus recovery technologies was conducted by linearly scaling the recovery processes (presented in Section 3) to an equal size. The literature values reported are subject to their respective operational settings and process scale. Using the annual P load, recovery efficiency, or sludge mass feed as the scaling factor, we scaled the selected technologies up or down to an equal scale. The values marked as "reported" are extracted from the literature, and those marked with "scaled" are obtained from the authors' own calculations.

For energy and chemical cost-scaling calculations, a linear relationship between literary values and representative plant values is assumed as they are based on molar ratios [37]. The equation for scaling is shown in Eq. (1).

$$C_{scaled} = P_{m}/P_{r^*}C_{reported}$$
(1)

where P_m is the modeled P load from SUMO, P_r is the reported P load value from the literature, C_{scaled} is the scaled specific consumption value for a chemical or energy, and $C_{reported}$ is the reported specific consumption value for a chemical or energy. Larger plants typically have lower specific energy and chemical consumption costs [46,47]. However, upscaling studies generally do not mention the specific chemical or energy consumption for various scales. Thus, the authors feel that linear estimation is valid. This highlights the research needs for complicated mathematical dependencies between pilot and full-scale chemical process applications.

2.4. Energy and chemical prices

Table 1 lists the prices of chemicals and energy used in this study. Prices gathered in May 2022 are used in the analysis, as the prices form October 2022 (also shown in Table 1) are much higher (and volatile) due to the volatile political situation in the world. To provide an equal comparison, most of the chemical prices were extracted from Alibaba. com in bulk orders of several tons. Energy and natural gas prices are based on European Union statistics. It is noteworthy that the chemical prices vary significantly based on location and time, and readers are encouraged to use their own expertise to evaluate their respective situation. The ultimate goal of this study is to develop a simplified framework for assessing the feasibility of the available P recovery technologies and help decision-makers select the most suitable choice for their needs.

3. Results

3.1. Modeled sludge characteristics

The wastewater treatment process model yielded characteristics for the sludge, presented in Table 2. The P removal efficiencies vary slightly depending on the precipitation metal used (Fe: 96%, Al: 95% and Ca: 94%) and this leads to small variation in the characteristics of the different sludges. Ca sludge has the highest P mass concentration, although the differences are small. Al sludge produced the highest sludge flow rate (both mass and volumetric flow) and Ca sludge lowest. SUMO model yields different Al and Ca species but not Fe species, and there are distinct differences between these species. Precipitated Al has a high mass concentration but Al—P compounds much lower mass concentration, indicating that most P has is bound on the precipitate rather than directly with Al. Calcium species have dominantly amorphous phosphates.

Table 3 shows the costs related to mainstream precipitation chemicals. The values were calculated as a product of metal consumption in the model and the price of that chemical.

Table 2

Modeled sludge qualities after digestion and dewatering. Coagulant dosing was chosen so that the plant had 94–96% P removal between the effluent and influent.

| Coagulant | Fe | Al | Ca |
|---|--------|----------|--------|
| Coagulant consumption ^a [t/d] | 2 | 0.45 | 0.54 |
| Total solids (TSS) [kgTS/m ³] | 290.0 | 290.0 | 290.0 |
| Total phosphorus (TP) [gP/kgTS] | 27.3 | 26.1 | 27.9 |
| Total iron [gFe/ kgTS] | 53.6 | 0.0 | 0.0 |
| Aluminum precipitates in TSS [g/kgTS] | 0.0 | 164.9 | 0.0 |
| Aluminum phosphate compounds [g/kgTS] | 0.0 | 15.6 | 0.0 |
| Aluminum hydroxide compounds [g/kgTS] | 0.0 | 24.2 | 0.0 |
| Calcium [gCa/kgTS] | 0.5 | 0.5 | 0.3 |
| Amorphous calcium phosphate [g/kgTS] | 5.4 | 0.7 | 117.8 |
| Calcium carbonate [g/kgTS] | 2.8 | 0.0 | 0.0 |
| Magnesium [gMg/kgTS] | 0.1 | 0.1 | 0.1 |
| Sludge flow rate [m ³ /d] | 34.4 | 35.8 | 32.62 |
| Solids load [kgTS/d] | 9972.6 | 10,385.8 | 9460.3 |
| P load [kgP/d] | 272.6 | 271.3 | 264.2 |

^a Model setting for Ca feeding is in Ca(OH)₂ with a value of 1 t/d.

Table 1

Energy and chemical prices used in this study. The prices are presented in both ϵ /ton and ϵ /mol to serve both academic and practical application attuned audiences. Prices from October 2022 are added as a background information to support discussion.

| | Chemical formula | Prices from May 2022 | | Prices from October 2022 | Reference | |
|-------------------------------|--|---|--------------------|---|--------------------|-----------|
| | | Value (ϵ/kWh or ϵ/tn) | Value (€-cent/mol) | Value (ϵ/kWh or ϵ/tn) | Value (€-cent/mol) | Reference |
| Electricity | | 0.1 | | 0.2 | | [a] |
| Ferric chloride ¹ | FeCl ₃ | 284 | 1.6 | 852 | 4.8 | [b] |
| Aluminum chloride | AlCl ₃ | 332 | 0.9 | 542 | 1.5 | [b, e] |
| Calcium hydroxide | Ca(OH) ₂ | 244 | 1.0 | 192 | 0.8 | [b, e] |
| Sulfuric acid ² | H_2SO_4 | 202 | 2.0 | 263 | 2.6 | [c] |
| Citric acid ² | HOC(CO ₂ H)(CH ₂ CO ₂ H) ₂ | 540 | 10.3 | 659 | 12.5 | [b] |
| Magnesium oxide ¹ | MgO | 176 | 0.4 | 267 | 0.6 | [b] |
| Sodium hydroxide ² | NaOH | 568 | 2.3 | 568 | 2.3 | [d, b] |
| Sodium sulfate ² | Na ₂ SO ₄ | 132 | 1.6 | 80 | 0.9 | [c] |
| Chlorine ¹ | Cl ₂ | 1540 | 16.2 | 1540 | 16.2 | [b] |
| Limestone | | 60 | | 398 | | [b] |
| Foundry coke | | 250 | | 102 | | [b] |
| Natural gas | | 0.03 | | 0.13 | | [b] |

[a] EU statistical service [b] Alibaba.com [c] Chemanalyst.com [d] Echemi.com [e] Intratec.com.

¹ Price per mole is based on only relevant element of the molecule (Fe, Al, Ca, Mg and Cl).

² Price per mole is based on the entire molecule.

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Table 3

Specific cost of P removal with different precipitation chemicals in the modeled representative treatment facility. The unit cost is the product of the price (May 2022) and the modeled consumption.

| Precipitation chemical | Unit cost [€/kgP _{removed}] | | |
|------------------------|---------------------------------------|--|--|
| FeCl ₃ | 10.8 | | |
| AlCl ₃ | 8.2 | | |
| Ca(OH) ₂ | 4 | | |

3.2. Phosphorus recovery methods

The methods discussed in this study are (1) wet leaching and struvite precipitation, (2) magnetic vivianite recovery, (3) white phosphorus production, (4) sludge melting, and (5) thermal sodium sulfate treatment. These methods were chosen to represent a wide array of techniques available, including both chemical and thermal processes. The availability of accurate information was also an important factor in choosing the technologies.

3.2.1. Wet leaching and struvite precipitation

3.2.1.1. Process description. Wet leaching of phosphorus with acidic or alkaline chemicals is a well-established process. A simplified schematic is shown in Fig. 2. The dissolution of phosphorus and metals is applicable to both digested SS and SSA. Dissolved phosphorus can be recovered in a secondary precipitation step. Heavy metal precipitation is controlled with the addition of citric acid for metal complexation [48]. Phosphorus recovery efficiency depends on leaching pH. Meyer et al. [48] report that the economically best pH range is 3–5, although recovery efficiency increases significantly towards pH 2 [42].

Meyer et al. [48] also reported that dissolution is preferable with sludges containing iron phosphates compared to aluminum phosphates due to their higher dissolution rate with sulfuric acid. Additionally, aluminum is not preferable due to its persistence in the dissolution phase. Ion exchange resin can be used to remove aluminum ions [49], but it was deemed economically unfeasible [42]. Furthermore, aluminum phosphate dissolution is more efficient with alkali than acidic chemicals [50]. Wet leaching of sludge containing calcium phosphates produces dissolved Ca, which requires more citric acid for complexation compared to iron salt sludge. It is noteworthy that excess citric acid feeding will lead to magnesium complexation and decreased struvite precipitation [48]. Precipitation to slow-release fertilizers like struvite (magnesium ammonium phosphate, MAP), calcium phosphates (HAP), or brushite is commonly reported in the literature [20,51]. The processing costs of waste streams of this process are not included in the economical evaluation.

3.2.1.2. Inputs and assumptions. The authors performed a more detailed techno-economic analysis on P recovery from SS by wet leaching followed by struvite precipitation based on the Meyer et al. [48] study. The SS treatment process consists of acidic wet leaching, ultra-filtration, citric acid metal complexation, and struvite precipitation. The P load they reported was unclear, so the authors used the size of the plant (5000 population equivalent (PE)) and P load per capita (1.8 gP/cap/d) to estimate the P load, which is 2957 kgP/year. Reported chemicals required are 11.9 L of sulfuric acid (78%) / $kgP_{recovered}$ for leaching, 29.3 L citric acid (50%) / $kgP_{recovered}$ for metal complexation, 3.3 kgmagnesium oxide (95%) / $kgP_{recovered}\!\!\!\!\!$ and 43.4 L sodium hydroxide (20%) / kgPrecovered for the struvite precipitation reaction [48]. The SS in their process has a more diverse metal composition than the iron-based sludge in Table 1. Thus, the authors estimate that to reach the same recovery efficiency of 67%, less sulfuric and citric acids would be required. They report an energy consumption of 27.7 kWh/kgP_{recovered}. Fe is used as the precipitation chemical for the overall economic calculation.

3.2.1.3. Wet leaching and struvite precipitation results. The scaled-up consumption values are presented in Table 4 along with original values reported by Meyer et al. [48]. The SS used by Meyer et al. [48] contained higher concentrations of Fe, Al, and Ca than the SS in Table 1, column 2. Thus, citric acid consumption would be reduced, but it is not included in the calculation as the exact value is difficult to determine. The chemical and energy cost sum is $23 \text{ } \text{€/kgP}_{recovered}$, which is a bit higher than what Meyer et al. [48] reported but this is likely caused by an increase in chemical prices over the COVID pandemic. The authors applied 10% (min. 60% and max. 74%) variance to the recovery efficiency (while assuming that the chemical and energy consumption

Table 4

Reported and scaled values for the acid leaching and struvite precipitation process.

| Parameters | Reported value [48] | Scaled value |
|--|------------------------|---|
| P load [kgP/y] | 2957 | 99,500 |
| P recovered [kgP/y] | 1981 | 66,300 |
| Recovery efficiency [%] @ pH 3 | 67 | $67\pm10\%$ |
| Sulfuric acid (78%) [m ³ /y] | 24 | 790 |
| Citric acid (50%) $[m^3/y]$ | 58 | 1950 |
| Magnesium oxide (95%) [t/y] | 6.5 | 220 |
| Sodium hydroxide (20%) [m ³ /y] | 86 | 2900 |
| Energy [MWh/y] | 55 | 1850 |
| Product | Struvite, 12.3% P (w/v | w), 26.5% P ₂ O ₅ (w/w) |
| Cost sum ^a [$\ell/kgP_{recovered}$] | 20 | 23 ± 2 |
| | | |

^a Chemical and energy cost.



Fig. 2. Simplified process schematic for wet leaching and struvite precipitation process.

remains the same). This variance contributes to ± 2 $€/kgP_{recovered}$ to the sum of the chemical and energy costs.

Franz [42] studied P leaching from SSA and concluded that using 14% (w/w) sulfuric acid with a liquid-to-solid ratio of 2 L/kg yields the best leaching result. Keeping the process mentioned above the same for the other steps, the sulfuric acid (78%) consumption would be 48 m^3/y (down from 790 m^3/y) while energy consumption would increase to 3038 MWh/y (up from 1850 MWh/y). Furthermore, adding a similar fuel cost for supplementary fuel (natural gas) brings the process operational cost down from 23 to 18 ${\rm €/kgP_{recovered}}.$ However, this analysis has great uncertainty and thus is closer to an interesting detail for the reader rather than a proper P recovery pathway that is comprehensively analyzed. The scale of Franz's experiment [42] was too small to place industrial calculations on them. The low leaching pH of 2 also dissolves higher concentrations of other metals and this in turn increases citric acid and magnesium oxide feeds. Unfortunately, industrial processes such as TetraPhos or Easy Mining have not published sufficient amount of data for comparison. Nevertheless, the recovery cost is lower P recovery from ash due to the large decrease in sulfuric acid consumption.

3.2.2. Magnetic vivianite separation

3.2.2.1. Process description. Sufficient Fe dosing promotes vivianite formation after anaerobic digestion [13,52]. Based on the estimation by Wilfert [53] up to 80–90% of P in sludge is bound in vivianite if sufficient amount of iron is dosed in the wastewater treatment process. The work for magnetic vivianite recovery is very recent and pushed forward by a research team in Wetsus, Neatherlands [52,54]. At the current stage, the process can recover 80% of P from sludge and 60% of the P in the wastewater treatment process influent [55]. The magnetic vivianite separation method utilizes a Jones-type low energy magnetic separator used in the mining industry, followed by optional alkaline leaching to separate P from potential heavy metals. A simplified schematic is shown in Fig. 3.

3.2.2.2. Analysis inputs and assumptions. Wijdeveld et al. [55] recorded 80% magnetic vivianite recovery efficiency, which is used here despite not being a production-optimized value. We assume that 85% of the P is bound in vivianite in the sludge [53]. With vivianite recovery efficiency of 80%, the total P recovery efficiency from sludge is 68%. A commercial Jones Wet High Intensity Magnetic Separator [56] appropriate for the size of the model plant was used in this study (0.4 dry tons per hour). The authors selected a one-step higher capacity device—a DP 71 with 21 kW energy consumption— that is deemed more suitable for this application [56]. Another manufacturer's fact sheet shows the same range of energy consumption [57] for a similar device. Higher iron dosing promotes vivianite formation [37,52,54]. Prot et al. [52] increased iron dosing from 0.46 to 0.85 Fe/P molar ratio to promote vivianite formation. Considering that iron dosing for the SUMO model is already at a 3.7 Fe/P molar ratio, the authors did not consider increasing iron dosing for the

vivianite scenario. Alkaline consumption for P dissolution is not yet on a scale that can be compared and thus it is left out of the analysis. However, the separated vivianite structures have 9.8% P (22.4% $P_{2}O_{5}$ equivalent) content. There are impurities in the material, represented by 10% carbon content and acceptable levels of heavy metals [55]. An additional benefit of vivianite precipitation is reduction in sludge volume, similar benefit as struvite precipitation in EBPR systems [58]. However, this benefit is not quantified in this study.

3.2.2.3. Magnetic vivianite recovery results. The scaled-up costs for recovery as vivianite are shown in Table 5. The operational cost for the recovered vivianite is very low, only 0.3 €/kgP_{recovered}. A 10% margin was also applied to the recovery efficiency while assuming that the energy consumption remains the same. This applies 10% variance to the cost sum as well. However, the quality of the end-product containing vivianite depends on the source material qualities, which is problematic due to the presence of heavy metals and other potential contaminants. Vivianite itself has been reported to have qualities as a slow-release fertilizer [59,60], so purifying it by another process step seems necessary for legislative requirement in agriculture applications and/or a positive image as a fertilizer. Vivianite can also have other uses, such as art pigments [61]. This assessment highlights the potential and the need for further studies in vivianite recovery. However, the scale of the study was small, and therefore extrapolating the results to economic feasibility is uncertain.

3.2.3. Sludge melt gasification

The purpose of sludge gasification is to produce synthesis gas as an energy source [62]. However, Hagspiel et al. [63] have amended the technology for primarily P recovery. The behavior of P in gasification processes has been investigated in several studies [64,65]. Organic P is converted to inorganic P [65], and an increasing fraction of P is volatilized when the total P_2O_5 (wt%) mass fraction and temperature increase in the sludge [62]. Heavy metals still present in the sludge are retained in the slag [66], although Abanades et al. [67] also showed that

Table 5

Scaled costs for vivianite separation.

| | - | |
|--------------------------------------|----------------------------------|--|
| Parameters | Reported value [52,54] | Scaled value |
| P load [kgP/y] | | 99,500 |
| P recovered [kgP/y] | | 67,700 |
| Recovery efficiency [%] ^a | 68 | $68\pm10\%$ |
| Energy [MWh/y] | | 184 |
| Product | 9.8–12.3% P, or 22.4% P; content | ₂ O ₅ equivalent, 10% carbon |
| Cost sum [$\ell/kgP_{recovered}$] | | 0.27 ± 0.03 |

^a In regard to P in SS.



Fig. 3. Simplified process schematic for magnetic vivianite recovery.

they can volatilize during incineration. The sludge melt gasification system is a different application than what is presented in Bourgel et al. [62] as the temperatures are higher.

3.2.3.1. Process description. A melt-gasification system, shown in Fig. 4, claims to solve the heavy metal issue [63]. The data from the publication of Hagspiel et al. [63] is extrapolated in this study. Drying and briquetting steps are required to convert sludge into 4% moisture and 8% P_2O_5 content briquettes. Along with those, foundry coke and limestone are heated to 1800–2000 °C. Hagspiel et al. [63] did not report any P volatilization. It might be insignificant due to the low P_2O_5 content of 25 wt% or higher. However, the results in Zhang et al. [64] refute this by showing that volatilization 15–30% of P (wt%) occurs in much lower P_2O_5 mass fractions (0.5–3% (wt%)) at 1300 °C. The thermal reactor separates flue gases, P-rich slag, and melted metals (including heavy metal traces) in separate fractions. P-rich slag is the granulated end-product. Some volatilized P is recovered from flue gas cleaning filter dust.

3.2.3.2. Analysis inputs and assumptions. This process seems viable for any precipitant used. The process was downscaled using sludge mass feed as the scaling parameter. Hagspiel et al. [63] used SS containing a high concentration of Fe, which has the highest melting point of the coagulants compared in this study. For the economic calculation, Ca is used to present best case scenario. Fe or Al do not offer significant advantages for this process. To compare this process with Fe-containing sludge, Fig. 2 in the discussion shows a side-by-side comparison for the technologies.

3.2.3.3. Sludge melt gasification results. The scaled costs are shown in Table 6. The cost of the energy and chemicals is $21 \pm 2 \text{ (}_{kgPrecovered}$ with the 10% margin that was also applied to the recovery efficiency while assuming that the specific consumption for chemicals and energy remain the same. The drying energy consumption dominates the energy consumption (140/210 kWh/kgP_{recovered}). However, syngas is produced, which could offset the process costs if utilized: the syngas emanating from biomass or sludge sources that has a gross calorific value (GCV) of 4–7 MJ/m_n³ [68,69]. Estimating with 4 MJ/m_n³, the energy value of produced syngas is 30,300 MWh/y, which is almost twice as much as the process energy consumption. However, Hagspiel et al. [63] did not report this or the flue gas composition. It is assumed that the flue gases have a low energy value and are recycled for free.

3.2.4. Thermochemical sodium sulphate process

Thermochemical sodium sulphate process and white P recovery process (Section 3.2.5) treat sewage sludge ash (SSA). For this reason, an inclusion of mono-incineration to the cost calculation is needed. Yang et al., [71] published an assessment of WWTP energy balance, including an incinerator. According to their data, an incinerator consumes 0.0058 to 0.0473 kWh/m³, meaning it is close to but not exactly zero energy solution. With the model of this study, the annual energy consumption

Table 6

| Reported and scaled | l values for the m | elt gasification process. |
|---------------------|--------------------|---------------------------|
|---------------------|--------------------|---------------------------|

| Parameters | Reported value [63] | Scaled value |
|--|------------------------------|--------------|
| Sludge input [tn-TS/d] | 14.4 | 10 |
| P load [kgP/y] | | 96,400 |
| P recovered [kgP/y] | | 79,200 |
| Recovery efficiency [%] | 80 | $80\pm10\%$ |
| | | |
| Foundry coke [tn/y] | 298 | 200 |
| Limestone [tn/y] | 526 | 360 |
| Specific energy [kWh/kgP _{recovered}] ^a | 143 | 210 |
| Energy [MWh/y] | | 15,900 |
| Product | P-rich (2.5%) pollutant-free | e slag |
| Cost sum [€/kgP _{recovered}] | | 21 ± 2 |
| Other benefits | | |
| Syngas production [MWh/y] | 43,800 | 30,300 |

^a Hagspiel et al. [63] did not report sludge drying to 92% TS content energy consumption. [70] was used to calculate drying energy consumption (900 kWh/ tn-sludge was used).

for the incinerator is approximately 250 kWh. This value is small compared to the P recovery process' energy consumption.

3.2.4.1. Process description. A rotary kiln–type process, shown in Fig. 5, has been developed to form Rhenania phosphates (CaNaPO₄) in the product material, with sodium sulphate acting as a reaction catalyst to achieve the desired process conditions and end-product [72]. The process temperature is 950 °C. Heavy metals are removed during the process by chlorine-aided evaporation, reported in detail by Mattenberger et al. [41,73].

3.2.4.2. Analysis inputs and assumptions. The operational costs of the process are calculated using the specific energy and chemical consumption values reported by Hermann and Schaaf [72], shown in Table 7, and scaled using the ash mass feed. Hermann and Schaaf [72] did not mention chlorine consumption, excluding it from the examination. However, Mattenberger et al. [41] used 100 gCl/kgAsh. This is included in the calculation but has insignificant role in the overall cost. Ca is used for economic calculation since the formation of Rhenania phosphates requires the presence of Ca.

3.2.4.3. Thermochemical sodium sulphate results. The scaled-down values are shown in Table 7. Hermann and Schaaf [72] reported specific values, and these are translated to annual values for consistency. The operational cost is exceptionally low, $0.76 \notin /kgP_{recovered}$. Comparing 90% and 100% recovery efficiency yields small variation to the cost, but the recovery cost remains very low. In addition, the recovery efficiency efficiency efficiency the end-product has high P content as well. Rhenania phosphates are an old fertilizer product and there are only few recent publications that discuss it [69,quoting Werner,1967].



Fig. 4. Simplified sludge melt gasification process schematic.



Fig. 5. Simplified schematic for Thermochemical sodium sulphate process.

Table 7

| Reported | and | scaled | values | for | the | thermochemics | l sodium | sulphate | nrocess |
|----------|-----|--------|--------|-----|-----|----------------|----------|-----------|---------|
| reporteu | and | scarca | varues | 101 | unc | uncrimochemice | i sourum | Surpliate | process |

| Parameters | Reported value [72] | Scaled value | |
|-------------------------------------|--|------------------|--|
| Ash input [tn/y] | 13,500 | 4.3 | |
| P load [kgP/y] | _ | 96,300 | |
| P recovered [kgP/y] | _ | 94,400 | |
| Recovery efficiency [%] | 98 | 98 (90%–100%) | |
| | | | |
| Natural gas [MWh/y] | 5.2 ^a | 500 | |
| Sodium sulphate [tn/y] | 3.3 ^a | 320 | |
| Calcium hydroxide [tn/y] | 0.1 ^a | 10 | |
| Sodium hydroxide [tn/y] | 0.1 ^a | 10 | |
| Chlorine ^b [tn/y] | | 0,4 | |
| Energy [MWh/y] | 0.85 ^a | 80 | |
| | | | |
| Product | CaNaPO ₄ material, 15–25% P ₂ O ₅ content | | |
| Cost sum [$\ell/kgP_{recovered}$] | - | 0.76 (0.83–0.75) | |
| | | | |

 $^a\,$ Value is reported as specific consumption per kgP_{recovered} (kWh/kgP_{recovered} or kg/kgP_{recovered}).

^b Chlorine calculation is based on Mattenberger et al. [41].

3.2.5. White phosphorus recovery

Incinerator and ash mass flow is conducted in a similar manner, as presented in Section 3.2.4.

3.2.5.1. Process description. Recovering P in pure form, P₄, is another recovery path [75–77]. P₄ is also called white phosphorus and it is the most reactive P allotrope [78]. It is the precursor to many synthetic P compounds used by different industries [79]. Using the electric arc process, the SSA with coke can be heated to 1600 °C, where gaseous P separates from the liquid phase. Typically, also silica is present in the reaction [78]. A simplified schematic is shown in Fig. 6.

3.2.5.2. Analysis inputs and assumptions. The economic evaluation is based on information reported by Langeveld [80]. Iron inhibits P recovery [75,81], making aluminum or calcium-based sludge a preferable precipitation chemical. Al is used for calculations since it was used by

Langeveld [80]. The iron that is present forms ferrophos, $C_{44}H_{48}FeP_2$ [82] which remains in slag [80]. Syngas is produced in this process, but its potential benefits are not included, similar to the process in Section 3.2.3. Furthermore, unlike the process in 3.3, the syngas amount and the energy content are fairly low.

3.2.5.3. White *P* results. The down-scaled results are presented in Table 8. The recovery cost is also low, with the 10% margin around 3 $\epsilon/kgP_{recovered}$, but the end-product quality is very high. Furthermore, it can be converted to phosphoric acid, but this is not included in the evaluation since accurate costs for that tertiary process are not available.

4. Comparison and discussion

4.1. Recovery cost

The choice of recovery method is influenced by the characteristics of the sludge, which are determined by the precipitation chemicals used. The overall costs for chemicals and energy for recovering P are combined in Fig. 7, consisting of the precipitation chemical cost in the mainstream wastewater treatment process, the respective chemical and energy costs for each recovery process (marked with different pattern),

Table 8

Reported and scaled values for the white phosphorus recovery process.

| Parameters | Reported value [80] | Scaled value |
|------------------------------------|---------------------------|--------------|
| P load [kgP/y] | 16,8539 | 99,000 |
| P recovered [kgP/y] | 150,000 | 88,100 |
| Recovery efficiency [%] | 89 | $89\pm10\%$ |
| Energy [MWh/y] | 26 ^a | 2291 |
| Coke [tn/y] | 1.45 ^a | 128 |
| Product | 99.9% pure P ₄ | |
| OPEX [€/kgP _{recovered}] | _ | 3.2 ± 0.3 |
| Other benefits | | |
| Syngas production [MWh/y] | 9.7 ^a | 855 |

^a Value is reported as specific consumption per kgP_{recovered} (kWh/kgP_{recovered} or kg coke/kgP_{recovered})



Fig. 6. Simplified schematic for white phosphorus process.



Fig. 7. Operational chemical and energy cost comparison for the combined cost of main process removal and end P recovery (using May 2022 prices). The sections in the bars with single set of stripes leaning right is incineration cost, single set of stripes leaning left are chemical costs and crossing stripes are energy costs. The precipitant Fe/Al/Ca cost (no stripes) is based on the P input to the wastewater treatment process rather than the quantity of P recovered.

and the incineration cost (using the May 2022 prices). The values vary from 6 to 38 $\epsilon/kgP_{recovered}$. Fe is the most expensive precipitation chemical (15 $\epsilon/kgP_{influent}$), despite its price being cheaper than Al, since the dose quantity needed to reach 95% P removal in the mainstream process is higher than Al. Al dosing costs 9 $\epsilon/kgP_{influent}$. Ca is the cheapest option on paper with 5 $\epsilon/kgP_{influent}$. However, Ca is known to be prone to practical issues, such as clogging, which might affect the choice of precipitation chemical.

The prices for chemicals have a significant impact on the recovery costs. Wet leaching + struvite precipitation process is impacted by the cost of citric acid and sodium hydroxide. Vivianite recovery cost consists mainly of the wastewater treatment process chemical, while sludge melt gasification cost is dominated by the high energy demand. Thermochemical sodium sulphate and white P process costs are lower and the largest part is the wastewater treatment process metal. These SSA utilizing processes require mono-incineration, which is a drawback if no incinerator is available as it is the case in Finland. Other technologies can be applied anywhere, and sludge melt gasification and the thermochemical sodium sulfate process can utilize sludge containing all three metal phosphates. The overall cost for these processes increases by $4 \notin /kgP_{recovered}$ if Al is used and by 10 $\notin /kgP_{recovered}$ if Fe is used instead of Ca.

Specific operational cost for recovery is considerably higher for methods utilizing SS compared to SSA excluding vivianite. Incineration increases operative costs slightly in the form of energy and fuel [71], although it depends on the heating value of the sludge [83]. It is possible to increase the plant energy efficiency by heat recovery, for instance, by using heat from an incinerator to benefit a digester [84]. However, incineration has a major impact on the global warming effect (GWE) [85]. Piippo et al. [86] compared the net carbon emissions from sludge incineration and other sludge treatment methods. The emission values vary between few hundred and several thousand t-CO₂eq/t-sludge. The sludge characteristics, fuel material and sludge drying method affect the emissions significantly.

However, generally the recovery cost, even for the SSA based methods, is too high to be competitive purely on economic basis. The global triple superphosphate (TSP) price is $1.7 \ \epsilon/kgP$ [87]. Although, when compared to the TSP, the coagulation chemical (Fe, Al or Ca) should be excluded from the comparison since the metal is used in the wastewater treatment process to meet the environmental performance

goals of the treatment plant. Only vivianite and thermochemical sodium sulphate recovery paths are in the same range as TSP price.

4.2. Sensitivity analysis

The recovery cost calculation has uncertainties related to it. The price trends of second half of 2022 showcase this well. The assumptions for prices of chemicals and the chemical and energy use of the recovery technologies may not be accurate in the selected scale. To work around the uncertainties, the sensitivity for the recovery cost was analyzed by varying the recovery efficiency by 10% while keeping the specific energy and chemical consumption constant. The variance in recovery efficiency has an impact on the recovery cost. However, the differences in the recovery cost between technologies are greater than the variance of individual technology, thus the variance does not change the order of the recovery technologies in cost comparison. On the other hand, the initial assumption of chemical or energy price has a greater potential impact on the recovery cost. Especially magnetic vivianite recovery, thermochemical sodium process and white P process are sensitive to coagulant prices since they are selective for specific coagulant and sludge melt gasification is more sensitive to the price of energy. Similar situation applies to the chemicals used by each technology as chemical prices may change significantly based on location and potential industrial synergies present. Fig. 7 stacked bar sections are directly proportional to the sensitivity of each stack and give a visual indication which chemical or energy cost is the most impactful for each recovery technology.

We selected to use May 2022 prices since they represent more stable state of economy. Creating Fig. 7 using October 2022 prices would have practically doubled the recovery cost for all technologies except for Thermochemical sodium sulphate process (which stayed almost the same). However, this would be misleading information since availability of chemicals and prices for them and energy are volatile during the later half of 2022.

Recovery processes should be considered in a wider context and evaluated by other parameters besides the price. This cost comparison is limited to operational energy and chemical consumption, but potentially lacking infrastructure sets a financial limitation to certain technologies. These interdependencies are highlighted later in Table 9. In addition, environmental performance and desired end product quality affect the

Table 9

Suitable precipitation chemical, recovery efficiency, end-product, technological maturity, and possible requirements for the technologies. The information in this table is based on the same sources as presented in the chapter 3 for each technology. The TRL values were determined by us based on the process descriptions and by talking to the process developers when possible.

| | Wet leaching + Struvite | Vivianite | Sludge melt gasification | Thermochemical sodium sulphate process | White phosphorus |
|---|---------------------------------------|--|---------------------------------------|--|--|
| Precipitation chemical | Fe ^a , Ca | Fe | Ca ^a , Fe, Al | Ca ^a , Fe, Al | Al ^a , Ca |
| Recovery efficiency compared to sludge (%) | 67 | 68 | 80 | 98 | 89 |
| Recovery efficiency compared to influent (%) | 61 | 62 | 70 | 86 | 80 |
| End-product quality (P content%) | 12.3 ^a | 9.8–12.3 | 2.5 | 6.5–11 | 99.9 |
| End-product and applications | Struvite: slow- release fertilizer | Vivianite: slow-release fertilizer and pigment | P-rich slag: narrow sector for use | Rhenania phosphates (CaNaPO ₄): fast release fertilizer | Elemental P ₄ : Versatile product for refinement |
| Technical maturity (EU TRL) | 6–7 | 6 | 8–9 | 9 | 7–8 |
| Additional requirement(s) | - | Excess iron feeding to wastewater treatment process | - | Incinerator exists already | Incinerator exists already |
| Other benefits | Lower sludge disposal costs | Lower sludge disposal costs | - | - | - |

^a Metal was used in the calculation.

choice of recovery technologies.

4.3. Other considerations & further research need

Wet leaching and magnetic vivianite recovery have a positive effect on sludge disposal costs since they decrease the sludge volume [88]. Furthermore, as these processes recover P before sludge disposal, the post-recovery sludge can be co-incinerated to produce energy. This makes these processes more favorable for locations where coincineration has presence. Vivianite is not directly comparable with other technologies because the costs do not include heavy metal removal or hygienization steps. Separating P from vivianite sludge to produce pure vivianite also requires high alkaline conditions [52], which would increase the process costs. More research is required to better understand this promising P recovery pathway and to improve the magnetic separation efficiency of vivianite and sludge.

The end-product quality in terms of P content varies greatly as presented in Table 9. White P is the most pure and versatile product, followed by struvite and Rhenania phosphates. Fertilizers are the most important end-product for recycled P as most of the mined phosphate rock is used for fertilizers [10,89]. However, detailed considerations regarding the end-product fertilizing potential fall outside of the scope of this study. Still, a brief discussion is presented. Struvite and vivianite, if used as fertilizer, release P slowly [60,90]. Commercially available fertilizers manufactured from phosphate rock have high solubility to maximize the instantaneous P release and plant availability [91]. The bioavailability of P in soil is measured through various extraction methods [92], typically with ammonium citrate solution [91,93]. However, a simple solubility test does not simulate the fertilizers' effect on plant growth [93,94], and a great portion of water-soluble P may leach off from the soil into adjacent water bodies [95,96]. P from CPR is not generally deemed to be readily usable for plants [17] or fertilizer production [97]. However, the situation is more complex. Phosphorus in soils is mostly insoluble, and the transfer of P to soil depends on the buffering capacity of the soil [98]. Furthermore, many other characteristics affect the release of water-soluble P: soil characteristics (sorption properties, pH, porosity, P compound type, organic matter type), fertilizer or biosolid properties (particle size, P content and speciation, pH, electrical conductivity, carbon chemistry, nitrogen content), and management of soil and environmental variables (placement and mixing, climate, crop type, and agronomy) [94].

As such, struvite and vivianite would be suitable for fertilizing purposes in agricultural locations which have vulnerable water bodies nearby and/or are prone to nutrient leaching. Vivianite has also nonfertilizer use as a pigment [61]. P-rich slag from sludge melt gasification could have similar use as struvite and vivianite, but the P content in the slag is low compared to other products and thus would not likely be selected for fertilizer purposes. Rhenania phosphates have been used as fertilizers during the 20th century already [69, quoting Werner, 1967] and thus seem suitable for that purpose. The P release rate of Rhenania phosphates is higher than concentrated superphosphate in acidic soil [99], so it should be classified as fast release fertilizer (as opposed to slow-release fertilizer). The most versatile product is the elemental P produced by white P process since it can be oxidized to phosphoric acid, which in turn can be used for industrial purposes, including fertilizer production.

Increasingly relevant is also the environmental performance of the recovery technology. As mentioned above, incinerators produce greenhouse gas emissions in significant amounts [85,86]. Wastewater treatment plants have started to analyze their environmental impacts over the past decade using a life cycle assessment tool (LCA) [100]. Further research should focus on applying the same mindset to recovery technologies that will augment the current treatment system, since there is a clear knowledge gap related to environmental impacts of recovery technologies. In similar fashion, more relevance should be paid on waste streams that are generated as they are crucial part of cost profile and environmental impact.

Table 9 shows the summary for non-economic-related parameters for the technologies. This highlights the maturity of SSA methods: they have higher recovery efficiency and the EU technological readiness level (TRL) [101]. Other technologies need further research to bring their cost in line with the SSA based technologies. The additional requirement for vivianite forming is the use of Fe in the wastewater treatment process and mono-incineration has to be available thermochemical sodium sulphate and white P processes. Wet leaching and vivianite recovery paths have an additional benefit (that is not quantified in this study) of reducing the sludge volume. This decreases the disposal cost of the P depleted sludge.

4.4. Decision-making flow chart

Selecting a recovery technology for specific conditions is complicated. The authors attempted to simplify the decision making into a flow chart that the reader can utilize, shown in Fig. 8. It considers the noneconomic aspects of the technology selection, as those are dependent on the operational environment. The reader is recommended to start from the top and follow the paths according to their own preference and/or operational environment. The five technologies compared in this



Fig. 8. Decision-making flow chart for the most suitable P recovery technology. * Metal fed to the wastewater treatment process.

study are the endpoints of the paths, highlighted as boxes in the flow chart.

It seems clear that where mono-incineration is readily available, it is more beneficial to recover phosphorus from SSA, at least when environmental impacts are not considered. If there is no access to monoincineration, sludge melt gasification is still more feasible than wet leaching + struvite precipitation since it has higher recovery efficiency and slightly lower cost. However, the lower cost comes down to the choice of precipitation chemical. If Fe or Al is used instead of Ca, sludge melt gasification recovery route costs increase to roughly the same level as wet leaching + struvite precipitation. Furthermore, struvite might be a more desirable end-product than 2.5% P-content slag from sludge melt gasification.

This approach has few shortcomings. The system is simplified and thus information is lost. In addition, these processes were examined as if they were in a vacuum, which means potential industrial synergies were not considered. Furthermore, literary data was not completely available, forcing the authors to make assumptions or combine pieces of information from different sources, which increases the uncertainty of the results. However, the analysis presented here can serve as a useful tool for performing a reasonable comparison between P recovery technologies.

5. Small-scale P recovery technologies with promising potential

Some recovery methods are still in their early development, so it is not possible or meaningful to extrapolate their costs as above. These recovery pathways were collected in this section and briefly discussed.

5.1. Sludge pyrolysis

Sludge pyrolysis serves as a method to reduce sludge volume while valorizing it [102]. Pyrolysis conditions remove organic pollutants and can restrain heavy metals release from the resulting char [103,104]. Pyrolysis also stabilizes P to the char, decreasing its mobility but increasing the P pool for long-term benefits should the char be applied especially to P-deficient soils [104,105].

5.2. Tertiary P recovery – metal coagulation and wet leaching

While this paper is focused on P recovery from sludge and ash, the authors agree with Mo and Zhang [106], Puchongkawarin et al. [107], and Mihelcic et al. [108] that the wastewater sector should move towards resource recovery facilities. Recovering P directly from the mainstream has the potential to avoid the quality issue of concentrated heavy metals and/or organic pollutants being present in sludge or sludge ash. Rossi et al. [109] have approached this by developing a method to let P flow through a conventional treatment process and coagulating it as a tertiary process. Precipitated P is leached with phosphoric acid to yield more phosphoric acid, similar to Lebek et al. [110], except that they leached P from sludge ash.

5.3. Phosphate binding proteins

Few studies have investigated the possibility to recover P with phosphate-binding proteins (PBPs) [111,112] with *E. coli*. They high-lighted the very low P concentration in the effluent indicating that the focus of this recovery technique is to complement mainstream P removal with a tertiary process. Research regarding this technique is still in its early phase. However, high P specificity [112] and the phosphate of PBPs would make it a suitable mainstream recovery path—provided further research is invested in this technology to increase recovery efficiency and optimize conditions in non-synthetic wastewaters.

5.4. Ion exchange

Another possible way to recover P from the WWTP effluent is ion exchange. Guida et al. [113] reported a hybrid ion exchanger (HAIX) system that can reduce PO_4 -P concentration from 6 mg/L to 0.3 mg/L. The system allows regeneration of the exchange resin and allows P to be recovered as hydroxyapatite. This study was conducted in lab scale but with real wastewater. Huang et al. [114] analyzed this process in greater context, showing that it can be comparable economically feasible process in full scale either as secondary or tertiary treatment option.

6. Conclusions

Five common P recovery methods using SS or SSA were compared by scaling the processes to the same size and environment. The analysis is based on the literature values in addition to a mathematical process model used to estimate precipitation chemical consumption and metal content in the sludge. The technologies are assessed by operational cost, end-product quality, recovery efficiency, and technology maturity. A decision-making flow chart was developed to help professional and researchers to choose the most appropriate P recovery technology among the compared ones. The decision as to which recovery process is deemed suitable depends on the operational environment and materials and infrastructure availability.

The specific recovery cost related to chemical and energy consumption, including mainstream precipitation and a possible incineration step, ranges from 6 to $36 \notin /kgP_{recovered}$, with technologies using SSA having an advantage over the others. Based on costs alone, recovering P through the thermochemical sodium sulfate process is most favorable if an incinerator is available. If not, wet leaching + struvite precipitation costs are comparable to sludge melt gasification costs, and the desired end-product and recovery efficiency dictate which process is better.

The end-product value varies with the market and potential utilization. White P is the most pure and versatile end-product, followed by Rhenania phosphates from the thermochemical sodium sulfate process and struvite from wet leaching + struvite precipitation. The technologies using SSA also have a higher maturity rating. Their primary downside is that they require mono-incineration. In a location where a mono-incinerator does not exist (for example, Finland or the US), the capital costs related to building an new incinerator may make the ash processing technologies completely unfeasible.

Comparing P recovery technologies is challenging. A "one solution fits all" mentality is not viable in the complicated wastewater industry and better tools are needed to solve the complexity of the situation. The authors feel that it is necessary to develop more sophisticated tools for the industry to support informed decision-making. These tools could be, for example, a LCA analysis on the environmental "hotspots" for the processes or more comprehensive cost analysis tools that include capital investment cost estimations. In addition to the analysis tools, the recovery technologies need further development to reach feasibility.

CRediT authorship contribution statement

J. Uzkurt Kaljunen: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. R.A. Al-Juboori: Resources, Supervision. W. Khunjar: Conceptualization. A. Mikola: Funding acquisition, Project administration, Supervision. G. Wells: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

- V. Smil, Phosphorus in the environment: natural flows and human interferences, Annu. Rev. Energy Environ. 25 (1) (Nov. 2000) 53–88, https://doi.org/10.1146/ annurev.energy.25.1.53.
- [2] M.R. Hart, B.F. Quin, M.L. Nguyen, Phosphorus runoff from agricultural land and direct fertilizer effects: a review, J. Environ. Qual. 33 (6) (Dec. 2004) 1954–1972, https://doi.org/10.2134/jeq2004.1954.
- [3] D.L. Correll, The role of phosphorus in the eutrophication of receiving waters: a review, J. Environ. Qual. 27 (2) (1998) 261–266, https://doi.org/10.2134/ jeq1998.00472425002700020004x.
- [4] Y.G. Yang, Z.L. He, Y. Lin, P.J. Stoffella, Phosphorus availability in sediments from a tidal river receiving runoff water from agricultural fields, Agric. Water Manag. 97 (11) (Nov. 2010) 1722–1730, https://doi.org/10.1016/j. agwat.2010.06.003.
- [5] D.W. Schindler, et al., Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment, Proc. Natl. Acad. Sci. 105 (32) (Aug. 2008) 11254–11258, https://doi.org/10.1073/ pnas.0805108105.
- [6] F. Hashemi, J.E. Olesen, T. Dalgaard, C.D. Børgesen, Review of scenario analyses to reduce agricultural nitrogen and phosphorus loading to the aquatic environment, Sci. Total Environ. 573 (Dec. 2016) 608–626, https://doi.org/ 10.1016/j.scitotenv.2016.08.141.
- [7] J.D. Edixhoven, J. Gupta, H.H.G. Savenije, Recent revisions of phosphate rock reserves and resources: a critique, Earth Syst. Dyn. 5 (2) (Dec. 2014) 491–507, https://doi.org/10.5194/esd-5-491-2014.
- [8] R.W. Scholz, F.-W. Wellmer, Comment on: Recent revisions of phosphate rock reserves and resources: a critique; by Edixhoven et al. (2014) – clarifying comments and thoughts on key conceptions, conclusions and interpretation to allow for sustainable action, Earth Syst. Dyn. 7 (1) (Feb. 2016) 103–117, https:// doi.org/10.5194/esd-7-103-2016.
- [9] P. Walan, S. Davidsson, S. Johansson, M. Höök, Phosphate rock production and depletion: regional disaggregated modeling and global implications, Resour. Conserv. Recycl. 93 (Dec. 2014) 178–187, https://doi.org/10.1016/j. resconrec.2014.10.011.
- [10] J.J. Schroder, D. Cordell, A.L. Smit, A. Rosemarin, Sustainable use of phosphorus: EU tender ENV.B1/ETU/2009/0025 357, Plant Research International, Wageningen, 2010. Accessed: May 04, 2022. [Online]. Available: https://library. wur.nl/WebQuery/wurpubs/404463.
- [11] EC, Communication from the Commission to the European Parliament, the Council the European economic and social Committee and the Committee of the regions (On the review of the list of critical raw materials for the EU), in: EUR-Lex - 52017DC0490 - EN - EUR-Lex, 2017. Accessed: Apr. 06, 2020. [Online]. Available, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52 017DC0490.
- [12] IFASTAT, IFASTAT. https://www.ifastat.org/databases/graph/2_1, 2022 (accessed May 04, 2022).
- [13] L. Korving, M. Van Loosdrecht, P. Wilfert, Effect of iron on phosphate recovery from sewage sludge, in: H. Ohtake, S. Tsuneda (Eds.), Phosphorus Recovery and Recycling, Springer Singapore, Singapore, 2019, pp. 303–326, https://doi.org/ 10.1007/978-981-10-8031-9 21.
- [14] C. Ott, H. Rechberger, The European phosphorus balance, Resour. Conserv. Recycl. 60 (Mar. 2012) 159–172, https://doi.org/10.1016/j. resconrec.2011.12.007.
- [15] G. Mininni, A.R. Blanch, F. Lucena, S. Berselli, EU policy on sewage sludge utilization and perspectives on new approaches of sludge management, Environ. Sci. Pollut. Res. 22 (10) (May 2015) 7361–7374, https://doi.org/10.1007/ s11356-014-3132-0.
- [16] L. Egle, H. Rechberger, J. Krampe, M. Zessner, Phosphorus recovery from municipal wastewater: an integrated comparative technological, environmental and economic assessment of P recovery technologies, Sci. Total Environ. 571 (Nov. 2016) 522–542, https://doi.org/10.1016/j.scitotenv.2016.07.019.
- [17] P.M. Melia, A.B. Cundy, S.P. Sohi, P.S. Hooda, R. Busquets, Trends in the recovery of phosphorus in bioavailable forms from wastewater, Chemosphere 186 (Nov. 2017) 381–395, https://doi.org/10.1016/j.chemosphere.2017.07.089.
- [18] M.C. Tomei, V. Stazi, S. Daneshgar, A.G. Capodaglio, Holistic approach to phosphorus recovery from urban wastewater: enhanced biological removal combined with precipitation, Sustainability 12 (2) (Jan. 2020), https://doi.org/ 10.3390/su12020575. Art. no. 2.
- [19] S.J. Kang, K. Olmstead, K. Takacs, J. Collins, Municipal nutrient removal technologies reference document, US Environmental Protection Agency (EPA), 2008.
- [20] Z. Li, M. Tabanpour, G. Forstner, Comparison of phosphorus recovery through pre-anaerobic-digestion brushite precipitation and post-anaerobic-digestion struvite crystallization, Proc. Water Environ. Fed. 2018 (5) (Jan. 2018) 499–507, https://doi.org/10.2175/193864718824940259.
- [21] S. Daneshgar, D. Cecconet, D. Capsoni, A.G. Capodaglio, Side-stream phosphorus recovery in activated sludge processes, Water 14 (12) (Jan. 2022), https://doi. org/10.3390/w14121861. Art. no. 12.

- [22] DWA, Stand der Klarschlammbehandlung und Entsorgung in Deutschland, Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall, 2005.
- [23] L. Korving, Trends in slibontwatering, STOWA 2011–46 (2012) [Online]. Available: ISBN 978.90.5773.577.6.
- [24] J. Cooper, Managing Phosphorus in the UK Water Industry to Increase National Resource Security, d.ph, University of Birmingham, 2015. Accessed: May 04, 2022. [Online]. Available, https://etheses.bham.ac.uk/id/eprint/5764/.
- [25] SCB, Utsläpp till vatten och slamproduktion 2016. Sveriges officiella statistik statistiska meddelanden MI 22 SM 1081, 2016, pp. 1–2. https://www.scb.se/ contentassets/4d4d22ee07cf4baa9f47e5bab805c00c/mi0106_2016a01_s m mi22sm1801.pdf.
- [26] J.A. Oleszkiewicz, J.L. Barnard, Nutrient removal technology in North America and the European Union: a review, Water Qual. Res. J. 41 (4) (Nov. 2006) 449–462, https://doi.org/10.2166/wqrj.2006.048.
- [27] HELCOM, Baltic Sea Action Plan, 2007.
- [28] S. Ofverstrom, R. Dauknys, I. Sapkaitė, The effect of iron salt on anaerobic digestion and phosphate release to sludge liquor / GELEŽIES DRUSKOS [TAKA ANAEROBINIO DUMBLO PŪDYMO PROCESUI IR FOSFATŲ IŠSISKYRIMUI Į DUMBLO VANDENĮ, Moksl. - Liet. Ateitis 3 (5) (Dec. 2011) 123–126, https://doi. org/10.3846/mla.2011.097.
- [29] X. Cheng, J. Wang, B. Chen, Y. Wang, J. Liu, L. Liu, Effectiveness of phosphate removal during anaerobic digestion of waste activated sludge by dosing iron(III), J. Environ. Manag. 193 (May 2017) 32–39, https://doi.org/10.1016/j. jenvman.2017.02.009.
- [30] D.A. Georgantas, H.P. Grigoropoulou, Orthophosphate and metaphosphate ion removal from aqueous solution using alum and aluminum hydroxide, J. Colloid Interface Sci. 315 (1) (Nov. 2007) 70–79, https://doi.org/10.1016/j. jcis.2007.06.058.
- [31] S. Petzet, P. Cornel, Prevention of struvite scaling in digesters combined with phosphorus removal and recovery—the FIX-Phos process, Water Environ. Res. 84 (3) (Mar. 2012) 220–226, https://doi.org/10.2175/ 106143012X13347678384125.
- [32] J. Bratby, Phosphorus removal in wastewater treatment plants, in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, International Water Association, 2018, pp. 109–131, https:// doi.org/10.2166/9781780408361_109.
- [33] L.E. de Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38 (19) (Nov. 2004) 4222–4246, https://doi.org/10.1016/j.watres.2004.07.014.
- [34] Metcalf and Eddy, Wastewater Engineering: Treatment and Resource Recovery, 5th ed., McGraw Hill, 2013.
- [35] J. Roussel, C. Carliell-Marquet, Significance of vivianite precipitation on the mobility of iron in anaerobically digested sludge, Front. Environ. Sci. 4 (Sep. 2016), https://doi.org/10.3389/fenvs.2016.00060.
- [36] D. Mamais, P. Pitt, Y. Cheng, J. Loiacono, D. Jenkins, Determination of Ferric Chloride Dose to Control Struvite Precipitation in Anaerobic Sludge Digesters, 1994, https://doi.org/10.2175/WER.66.7.8.
- [37] P. Wilfert, A.I. Dugulan, K. Goubitz, L. Korving, G.J. Witkamp, M.C.M. Van Loosdrecht, Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery, Water Res. 144 (Nov. 2018) 312–321, https://doi.org/10.1016/j.watres.2018.07.020.
- [38] H. Huang, J. Liu, L. Ding, Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation, J. Clean. Prod. 102 (Sep. 2015) 437–446, https://doi.org/10.1016/j. jclepro.2015.04.117.
- [39] J.T. Novak, C.M. Park, The effect of iron and aluminium for phosphorus removal on anaerobic digestion and organic sulfur generation, Water Sci. Technol. 62 (2) (Jul. 2010) 419–426, https://doi.org/10.2166/wst.2010.300.
- [40] E. Musvoto, Integrated chemical-physical processes modelling—II. Simulating aeration treatment of anaerobic digester supernatants, Water Res. 34 (6) (Apr. 2000) 1868–1880, https://doi.org/10.1016/S0043-1354(99)00335-8.
- [41] H. Mattenberger, et al., Sewage sludge ash to phosphorus fertiliser (II): influences of ash and granulate type on heavy metal removal, Waste Manag. 30 (8–9) (Aug. 2010) 1622–1633, https://doi.org/10.1016/j.wasman.2010.03.037.
- [42] M. Franz, Phosphate fertilizer from sewage sludge ash (SSA), Waste Manag. 28 (10) (2008) 1809–1818, https://doi.org/10.1016/j.wasman.2007.08.011.
- [43] M.C. Samolada, A.A. Zabaniotou, Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece, Waste Manag. 34 (2) (Feb. 2014) 411–420, https://doi. org/10.1016/j.wasman.2013.11.003.
- [44] D. Batstone, X. Flores-Alsina, H. Hauduc, Modeling the phosphorus cycle in the wastewater treatment process, in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future: Motivations, Technologies and Assessment of the Elimination and Recovery of Phosphorus from Wastewater, IWA Publishing, 2018, pp. 219–238.
- [45] H. Hauduc, et al., A dynamic physicochemical model for chemical phosphorus removal, Water Res. 73 (Apr. 2015) 157–170, https://doi.org/10.1016/j. watres.2014.12.053.
- [46] E. Vaiopoulou, P. Melidis, A. Aivasidis, Process control, energy recovery and cost savings in acetic acid wastewater treatment, J. Hazard. Mater. 186 (2–3) (Feb. 2011) 1141–1146, https://doi.org/10.1016/j.jhazmat.2010.11.115.
- [47] R. Singh, T. Babadagli, Mechanics and upscaling of heavy oil bitumen recovery by steam-over-solvent injection in fractured reservoirs method, J. Can. Pet. Technol. 50 (01) (Jan. 2011) 33–42, https://doi.org/10.2118/132459-PA.

- [48] C. Meyer, et al., Chapter 21: the Stuttgart process (Germany), in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, IWA Publishing, 2018, pp. 375–390.
- [49] S. Donatello, D. Tong, C.R. Cheeseman, Production of technical grade phosphoric acid from incinerator sewage sludge ash (ISSA), Waste Manag. 30 (8–9) (Aug. 2010) 1634–1642, https://doi.org/10.1016/j.wasman.2010.04.009.
- [50] T.U. Ali, D.-J. Kim, Phosphorus extraction and sludge dissolution by acid and alkali treatments of polyaluminum chloride (PAC) treated wastewater sludge, Bioresour. Technol. 217 (Oct. 2016) 233–238, https://doi.org/10.1016/j. biortech.2016.02.017.
- [51] E. Desmidt, et al., Global phosphorus scarcity and full-scale P-recovery techniques: a review, Crit. Rev. Environ. Sci. Technol. 45 (4) (Feb. 2015) 336–384, https://doi.org/10.1080/10643389.2013.866531.
- [52] T. Prot, et al., Magnetic separation and characterization of vivianite from digested sewage sludge, Sep. Purif. Technol. 224 (Oct. 2019) 564–579, https://doi.org/ 10.1016/j.seppur.2019.05.057.
- [53] P. Wilfert, Phosphate Recovery From Sewage Sludge Containing Iron Phosphate, Dissertation (TU Delft), 2018, https://doi.org/10.4233/uuid:f3729790-0cfe-4f92-866b-eca3f2f2df24.
- [54] T. Prot, et al., Full-scale increased iron dosage to stimulate the formation of vivianite and its recovery from digested sewage sludge, Water Res. 182 (Sep. 2020), 115911, https://doi.org/10.1016/j.watres.2020.115911.
- [55] W.K. Wijdeveld, T. Prot, G. Sudintas, P. Kuntke, L. Korving, M.C.M. van Loosdrecht, Pilot-scale magnetic recovery of vivianite from digested sewage sludge, Water Res. 212 (Apr. 2022), 118131, https://doi.org/10.1016/j. watres.2022.118131.
- [56] MBE, MBE. https://www.mbecoalandmineral.in/magnetic_separator.php (accessed May 04, 2022).
- [57] Outotec, Vertically Pulsating High Gradient Magnetic Separator, Metso Outotec, 2022. https://www.mogroup.com/portfolio/vertically-pulsating-high-gradientmagnetic-separator/ (accessed May 04, 2022).
- [58] R. Kumar, P. Pal, Assessing the feasibility of N and P recovery by struvite precipitation from nutrient-rich wastewater: a review, Environ. Sci. Pollut. Res. 22 (22) (Nov. 2015) 17453–17464, https://doi.org/10.1007/s11356-015-5450-2.
- [59] A. Domenico Rombolà, et al., Prevention of Iron-deficiency induced chlorosis in kiwifruit (*Actinidia deliciosa*) through soil application of synthetic vivianite in a calcareous soil, J. Plant Nutr. 26 (10–11) (Sep. 2003) 2031–2041, https://doi. org/10.1081/PLN-120024262.
- [60] Y. Fodoué, R. Tchameni, J. Pénaye, Assessment of the fertilizing effect of vivianite on the growth and yield of the bean "phaseolus vulgaris" on oxisoils from Ngaoundere (Central North Cameroon), in: undefined, 2015. Accessed: May 04, 2022. [Online]. Available: https://www.semanticscholar.org/paper/Assess ment-of-the-Fertilizing-effect-of-Vivianite-Fodou%C3%A9-Tchameni/7dfa36d6 de681e46e93d39973170a03c1d23ad39.
- [61] M.O. Figueiredo, T.P. Silva, J.P. Veiga, The blue of iron in mineral pigments: a Fe K-edge XANES study of vivianite, Appl. Phys. A Mater. Sci. Process. 99 (2) (May 2010) 357–361, https://doi.org/10.1007/s00339-010-5637-9.
- [62] C. Bourgel, E. Véron, J. Poirier, F. Defoort, J.-M. Seiler, C. Peregrina, Behavior of phosphorus and other inorganics during the gasification of sewage sludge, Energy Fuel 25 (12) (Dec. 2011) 5707–5717, https://doi.org/10.1021/ef201308v.
- [63] B. Hagspiel, O. Schwarzmann, V. Demmelbauer, Chapter 23: KRN-Memphrec (Germany), in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, IWA Publishing, 2018, pp. 395–400.
- [64] Q. Zhang, H. Liu, W. Li, J. Xu, Q. Liang, Behavior of phosphorus during cogasification of sewage sludge and coal, Energy Fuel 26 (5) (May 2012) 2830–2836, https://doi.org/10.1021/ef300006d.
- [65] A. Amrullah, Y. Matsumura, Sewage sludge gasification under a hydrothermal condition: phosphorus behavior and its kinetics, Energy Fuel 33 (3) (Mar. 2019) 2301–2307, https://doi.org/10.1021/acs.energyfuels.8b04289.
 [66] H. Saveyn, J.-H. Ferrasse, A.-B. Hernandez, J. Rose, P. Van der Meeren, N. Roche,
- [66] H. Saveyn, J.-H. Ferrasse, A.-B. Hernandez, J. Rose, P. Van der Meeren, N. Roche, The distribution of heavy metals following sewage sludge gasification, J. Residuals Sci. Technol. 8 (Jan. 2011) 61–66.
- [67] S. Abanades, G. Flamant, B. Gagnepain, D. Gauthier, Fate of heavy metals during municipal solid waste incineration, Waste Manag. Res. J. Sustain. Circ. Econ. 20 (1) (Feb. 2002) 55–68, https://doi.org/10.1177/0734242X0202000107.
- [68] J.C. Solarte-Toro, Y. Chacón-Pérez, C.A. Cardona-Alzate, Evaluation of biogas and syngas as energy vectors for heat and power generation using lignocellulosic biomass as raw material, Electron. J. Biotechnol. 33 (May 2018) 52–62, https:// doi.org/10.1016/j.ejbt.2018.03.005.
- [69] M. Dogru, A. Midilli, C.R. Howarth, Gasification of sewage sludge using a throated downdraft gasifier and uncertainty analysis, Fuel Process. Technol. 75 (1) (Jan. 2002) 55–82, https://doi.org/10.1016/S0378-3820(01)00234-X.
- [70] L. Bennamoun, P. Arlabosse, A. Léonard, Review on fundamental aspect of application of drying process to wastewater sludge, Renew. Sust. Energ. Rev. 28 (Dec. 2013) 29–43, https://doi.org/10.1016/j.rser.2013.07.043.
- [71] X. Yang, et al., The correlations among wastewater internal energy, energy consumption and energy recovery/production potentials in wastewater treatment plant: an assessment of the energy balance, Sci. Total Environ. 714 (Apr. 2020), 136655, https://doi.org/10.1016/j.scitotenv.2020.136655.
- [72] L. Hermann, T. Schaaf, Chapter 27: The AshDec process Evolution from its earlier stages to current practice, in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, IWA Publishing, 2018, pp. 425–434.
- [73] H. Mattenberger, G. Fraissler, T. Brunner, P. Herk, L. Hermann, I. Obernberger, Sewage sludge ash to phosphorus fertiliser: variables influencing heavy metal

removal during thermochemical treatment, Waste Manag. 28 (12) (Dec. 2008) 2709–2722, https://doi.org/10.1016/j.wasman.2008.01.005.

- [75] W. Schipper, L. Korving, Full-scale plant test using sewage sludge ash as raw material for phosphorus production, in: K. Ashley, D. Mavinic, F. Koch (Eds.), International Conference on Nutrient Recovery from Wastewater Streams Vancouver, IWA Publishing, 2009, pp. 591–598.
- [76] S. Arnout, E. Nagels, Modelling thermal phosphorus recovery from sewage sludge ash, Calphad 55 (Dec. 2016) 26–31, https://doi.org/10.1016/j. calphad.2016.06.008.
- [77] J.-O. Jung, Fundamental study on the recovery and removal of white phosphorus from phosphorus sludge, Environ. Eng. Res. 10 (1) (2005) 38–44, https://doi.org/ 10.4491/eer.2005.10.1.038.
- [78] C.M. Hoidn, D.J. Scott, R. Wolf, Transition-metal-mediated functionalization of white phosphorus, Chem. Eur. J. 27 (6) (2021) 1886–1902, https://doi.org/ 10.1002/chem.202001854.
- [79] B.M. Cossairt, N.A. Piro, C.C. Cummins, Early-transition-metal-mediated activation and transformation of white phosphorus, Chem. Rev. 110 (7) (Jul. 2010) 4164–4177, https://doi.org/10.1021/cr9003709.
- [80] K. Langeveld, The RecoPhos/Inducarb Process (the Netherlands), Jun. 2018, https://doi.org/10.2166/9781780408361_443.
- [81] W.J. Schipper, et al., Phosphate recycling in the phosphorus industry, Environ. Technol. 22 (11) (Nov. 2001) 1337–1345, https://doi.org/10.1080/ 09593330.2001.9619173.
- [82] NCBI, "Ferrophos," National Center for Biotechnology Information. PubChem Compound Summary for CID 129651327, Ferrophos. https://pubchem.ncbi.nlm. nih.gov/compound/129651327 (accessed May 04, 2022).
- [83] B. Li, F. Wang, Y. Chi, J.-H. Yan, Study on optimal energy efficiency of a sludge drying-incineration combined system, J. Mater. Cycles Waste Manag. 16 (4) (Oct. 2014) 684–692, https://doi.org/10.1007/s10163-014-0293-3.
- [84] R.D. Thierbach, H. Hanssen, Utilisation of energy from digester gas and sludge incineration at Hamburg's Köhlbrandhöft WWTP, Water Sci. Technol. 46 (4–5) (Aug. 2002) 397–403, https://doi.org/10.2166/wst.2002.0635.
- [85] B. Khoshnevisan, P. Tsapekos, M. Alvarado-Morales, S. Rafiee, M. Tabatabaei, I. Angelidaki, Life cycle assessment of different strategies for energy and nutrient recovery from source sorted organic fraction of household waste, J. Clean. Prod. 180 (Apr. 2018) 360–374, https://doi.org/10.1016/j.jclepro.2018.01.198.
- [86] S. Pilppo, M. Lauronen, H. Postila, Greenhouse gas emissions from different sewage sludge treatment methods in north, J. Clean. Prod. 177 (Mar. 2018) 483–492, https://doi.org/10.1016/j.jclepro.2017.12.232.
- [87] "TSP fertilizer price forecast 2015–2035," Statista. https://www.statista. com/statistics/1251265/tsp-fertilizer-price-forecast/ (accessed Feb. 15, 2022).
- [88] L. Shu, P. Schneider, V. Jegatheesan, J. Johnson, An economic evaluation of phosphorus recovery as struvite from digester supernatant, Bioresour. Technol. 97 (17) (Nov. 2006) 2211–2216, https://doi.org/10.1016/j. biortech.2005.11.005.
- [89] M. Prud'homme, World phosphate rock flows, losses and uses. Presented at the International Fertilizer Industry Association, in: Phosphates 2010 International Conference, 2010.
- [90] H.-D. Ryu, C.-S. Lim, Y.-K. Kim, K.-Y. Kim, S.-I. Lee, Recovery of struvite obtained from semiconductor wastewater and reuse as a slow-release fertilizer, Environ. Eng. Sci. 29 (6) (Jun. 2012) 540–548, https://doi.org/10.1089/ees.2011.0207.
- [91] D.F. Leikam, F.P. Achorn, Phosphate fertilizers: production, characteristics, and technologies, in: Phosphorus: Agriculture and the Environment, John Wiley & Sons, Ltd, 2005, pp. 23–50, https://doi.org/10.2134/agronmonogr46.c2.
- [92] D. Beegle, Assessing soil phosphorus for crop production by soil testing, in: Phosphorus: Agriculture and the Environment, John Wiley & Sons, Ltd, 2005, pp. 123–143, https://doi.org/10.2134/agronmonogr46.c5.
- [93] S. Kratz, C. Vogel, C. Adam, Agronomic performance of P recycling fertilizers and methods to predict it: a review, Nutr. Cycl. Agroecosyst. 115 (1) (Sep. 2019) 1–39, https://doi.org/10.1007/s10705-019-10010-7.
- [94] M. Hedley, M. McLaughlin, Reactions of phosphate fertilizers and by-products in soils, in: Phosphorus: Agriculture and the Environment, John Wiley & Sons, Ltd, 2005, pp. 181–252, https://doi.org/10.2134/agronmonogr46.c7.
- [95] P.J.A. Withers, M.J. Bowes, Phosphorus the pollutant, in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, International Water Association, 2018, pp. 1–33, https://doi.org/ 10.2166/9781780408361_003.

- [96] G.C. Chen, Z.L. He, P.J. Stoffella, X.E. Yang, S. Yu, D. Calvert, Use of dolomite phosphate rock (DPR) fertilizers to reduce phosphorus leaching from sandy soil, Environ. Pollut. 139 (1) (Jan. 2006) 176–182, https://doi.org/10.1016/j. envpol.2004.12.016.
- [97] D. Donnert, M. Salecker, Elimination of phosphorus from municipal and industrial waste water, Water Sci. Technol. 40 (4–5) (Aug. 1999) 195–202, https://doi.org/10.2166/wst.1999.0592.
- [98] G.M. Pierzynski, R.W. McDowell, J. Thomas Sims, Chemistry, cycling, and potential movement of inorganic phosphorus in soils, in: Phosphorus: Agriculture and the Environment, John Wiley & Sons, Ltd, 2005, pp. 51–86, https://doi.org/ 10.2134/agronmonogr46.c3.
- [99] S.H. Chien, Reactions of phosphate rocks, rhenania phosphate, and superphosphate with an acid soil, Soil Sci. Soc. Am. J. 42 (5) (1978) 705–708, https://doi.org/10.2136/sssaj1978.03615995004200050009x.
- [100] J.C. Pasqualino, M. Meneses, M. Abella, F. Castells, LCA as a decision support tool for the environmental improvement of the operation of a municipal wastewater treatment plant, Environ. Sci. Technol. 43 (9) (May 2009) 3300–3307, https://doi.org/10.1021/es802056r.
- [101] M. Héder, From NASA to EU: the evolution of the TRL scale in public sector Innovation, Innov. J. 22 (Aug. 2017) 1.
- [102] I. Fonts, G. Gea, M. Azuara, J. Ábrego, J. Arauzo, Sewage sludge pyrolysis for liquid production: a review, Renew. Sust. Energ. Rev. 16 (5) (Jun. 2012) 2781–2805, https://doi.org/10.1016/j.rser.2012.02.070.
- [103] R.C. Kistler, F. Widmer, P.H. Brunner, Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge, Environ. Sci. Technol. 21 (7) (Jul. 1987) 704–708, https://doi.org/10.1021/es00161a012.
- [104] V. Frišták, M. Pipíška, G. Soja, Pyrolysis treatment of sewage sludge: a promising way to produce phosphorus fertilizer, J. Clean. Prod. 172 (Jan. 2018) 1772–1778, https://doi.org/10.1016/j.jclepro.2017.12.015.
- [105] E. Agrafioti, G. Bouras, D. Kalderis, E. Diamadopoulos, Biochar production by sewage sludge pyrolysis, J. Anal. Appl. Pyrolysis 101 (May 2013) 72–78, https:// doi.org/10.1016/j.jaap.2013.02.010.
- [106] W. Mo, Q. Zhang, Energy-nutrients-water nexus: integrated resource recovery in municipal wastewater treatment plants, J. Environ. Manag. 127 (Sep. 2013) 255–267, https://doi.org/10.1016/j.jenvman.2013.05.007.
- [107] C. Puchongkawarin, C. Gomez-Mont, D.C. Stuckey, B. Chachuat, Optimizationbased methodology for the development of wastewater facilities for energy and nutrient recovery, Chemosphere 140 (Dec. 2015) 150–158, https://doi.org/ 10.1016/j.chemosphere.2014.08.061.
- [108] J.R. Mihelcic, et al., Accelerating innovation that enhances resource recovery in the wastewater sector: advancing a national testbed network, Environ. Sci. Technol. 51 (14) (Jul. 2017) 7749–7758, https://doi.org/10.1021/acs. est.6b05917.
- [109] L. Rossi, S. Reuna, T. Fred, M. Heinonen, RAVITA technology new innovation for combined phosphorus and nitrogen recovery, Water Sci. Technol. 78 (12) (Dec. 2018) 2511–2517, https://doi.org/10.2166/wst.2019.011.
- [110] M. Lebek, A. Rak, H. Hanssen, Chapter 24: The REMONDIS TetraPhos process at the WWTP in Hamburg (Germany), in: C. Schaum (Ed.), Phosphorus: Polluter and Resource of the Future – Removal and Recovery from Wastewater, IWA Publishing, 2018, pp. 401–409.
- [111] K. Venkiteshwaran, N. Pokhrel, F. Hussein, E. Antony, B.K. Mayer, Phosphate removal and recovery using immobilized phosphate binding proteins, Water Res. X 1 (Dec. 2018), 100003, https://doi.org/10.1016/j.wroa.2018.09.003.
- [112] Y. Yang, W. Ballent, B.K. Mayer, High-affinity phosphate-binding protein (PBP) for phosphorous recovery: proof of concept using recombinant *Escherichia coli*, FEMS Microbiol. Lett. 363 (20) (Oct. 2016) fnw240, https://doi.org/10.1093/ femsle/fnw240.
- [113] S. Guida, G. Rubertelli, B. Jefferson, A. Soares, Demonstration of ion exchange technology for phosphorus removal and recovery from municipal wastewater, Chem. Eng. J. 420 (Sep. 2021), 129913, https://doi.org/10.1016/j. cei.2021.129913.
- [114] X. Huang, S. Guida, B. Jefferson, A. Soares, Economic evaluation of ion-exchange processes for nutrient removal and recovery from municipal wastewater, Npj Clean Water 3 (1) (Mar. 2020), https://doi.org/10.1038/s41545-020-0054-x. Art. no. 1.