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Effect of process parameters on phosphorus conversion pathways during hydrothermal treatment of sewage sludge: A review

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ABSTRACT

Sewage sludge represents a renewable source of organic carbon and nutrients such as nitrogen (N), potassium (K), and phosphorus (P) that can be valorised through the recovery of energy carriers (e.g. biofuels) and fertilizers (N, K, and P precipitates). This review analyses >60 recent studies that have investigated P recovery potential from sewage sludge by hydrothermal processes. The effect of process parameters such as temperature, residence time, pressure, solid-to-liquid ratio, and addition of additives on P conversion pathways has been investigated by a critical discussion of the results published in the literature. Results show that temperature is the most influential parameter for P speciation and repartition: the increase in temperature appears to promote the increase in solid P recovery yield, the mineralization of organic P, and the conversion of non-apatitic P into apatitic P. The increase in reaction time has similar effects as temperature, but to a lesser extent. Solid P recovery yield and apatitic P fraction can be enhanced by increasing the medium alkalinity and by adding Ca-containing reactants. Non-apatitic P fraction can be increased by lower medium alkalinity, and by the addition of Fe- and Al-containing reactants. The results of this review provide to researchers and practitioners in the field of sewage sludge management key elements for the best operation of hydrothermal reactors to improve the recovery of P and biofuels. Finally, some new research perspectives and technical challenges are proposed to improve the knowledge and the scaling up of the technology.

1. Introduction

Phosphorus (P) is an essential nutrient for modern agriculture and food production. In the last century, P-based fertilizers have been affected by a growing demand related to the world's population growth [1,2]. Nowadays, P-fertilizer production primarily depends on P extraction from natural deposits of phosphate minerals (apatite rocks) [3]. According to Liu et al. [2], >70% of the global reserves of apatite rocks in 2020 are located in Morocco and Western Sahara, while the reserves of the most populous countries are expected to run out over the next few decades at the current extraction rate [4,5]. Apatite rock scarcity and geopolitical tensions can impact P-fertilizers production and distribution, affecting agriculture product costs and threatening the global food supply. Therefore, it is necessary and of high importance to develop P recovery from P-rich waste streams at a large scale.

Sewage sludge (SS) is a heterogeneous liquid–solid suspension continuously generated in wastewater treatment plants (WWTP) that is mainly composed of water (up to 98%) [3], organic matter (dissolved and particulate organic compounds), dangerous compounds (heavy

metals, pathogens, and pollutants) [6] and important amounts of P and other nutrients such as nitrogen (N) and potassium (K) [7], which, if not recovered, can end up in rivers, lakes, water basins, and finally in the sea, contributing to eutrophication. SS global production rate is rising, due to world population growth and wastewater volumes increase. Because of these reasons, the use of SS as a resource for P recovery becomes an important tool to support the global food supply and limit eutrophication [2,8]. In some countries, SS could be the largest P waste stream source [8], making P recovery from SS a crucial step to realize the perspective of a sustainable cycle. SS composition and properties, including P amount and speciation, strongly depend on the sources and the type of processes exploited in the WWTP [6,9–13].

SS must be subjected to treatments to reduce its dangerousness to the environment and human health before being released. Currently, SS treatments for safe disposal can account for up to 60% of the total costs of WWTP [14]. In the past, raw sludge application on agricultural lands has been the most popular SS disposal method, but due to increasingly strict legislation [15,16] and the reduction of available land space [17], this application is now generally avoided.

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Several methods are available for SS treatment and disposal. Dewatering (SS water content reduction) can be realized by different techniques: solid–liquid mechanical separation[18], evaporation[19], and membrane treatments[20] are possible alternatives to reduce the SS water content and individually exploit the liquid and solid phases. Gas-liquid ammonia stripping, struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), calcium phosphate or hydroxyapatite precipitation, ion exchange and adsorption are all available processes for recovering nutrients (P, N, K) from SS[21].

Thermal treatments allow to destroy organic pollutants and to kill pathogen, while yielding valuable by-products including chars, biofuel and syngas[22]. Among the possible thermal treatments, the most applied ones are dry processes such as incineration, pyrolysis, and gasification[23–25]. These treatments differ in temperature, pressure, and oxygen conditions[21], but they are all performed at high temperatures ($>300^\circ\text{C}$) to decompose organic pollutants and reduce pathogens [26]. Most of the nutrients (especially P and K) are generally retained in the solid residues (biochars and ashes)[3], and, therefore, these by-products are directly used as fertilizers, or subjected to chemical leaching to recover the nutrients[21,27]. However, these treatments usually require an energy-intensive pre-drying step that can affect operative costs[17,28].

During the last decade, an increasing number of international studies has investigated the applicability of hydrothermal (HT) processes (HT carbonization, liquefaction, and gasification) for the treatment and valorization of various types of residual biomasses, including algae, animal manure, sewage sludge, and anaerobic digestates[29–32]. HT treatments consist in exposing the wet biomass to high temperatures and autogenous pressures[33,34] to convert the biomass into high-value by-products (biofuels and chemicals)[35,36] through energy densification, carbon concentration, and oxygen elimination[1]. The by-products' characteristics and distribution depend on various factors, including biomass composition, water content, presence or absence of a catalyst, temperature, and process duration[6]. The main advantage of HT treatments is that they do not require a pre-drying step, which makes them more economically attractive than dry processes[36]. Indeed, water has a central role in HT treatments because it acts both as a reaction medium and as a reagent, promoting the polymerization, decarboxylation, dehydration, and hydrolysis reactions that characterize the HT conversion process[28]. With increasing temperature, the water dielectric constant decreases[37], allowing water to dissolve organic molecules. Besides, a temperature increase leads to a viscosity reduction, which increases the diffusion coefficient and mass transfer coefficients, and increases the ionic product k_w , making sub-critical water an optimal medium for catalyzing acid/base reactions[38]. HT treatment of SS is the subject of numerous studies and many reviews in the literature[1–3,6,9,17,23,28,34,39]. However, to the best of our knowledge, there is no complete and comprehensive review on the effect of the main HT process parameters on P distribution and speciation in the by-products, and the main P conversion pathways during HT treatment of SS are still poorly understood. This review analyzes the results of a relevant number of recent studies that have investigated P conversion during HT treatments of SS, providing a critical reading of the collected results, and explaining the physicochemical mechanisms underlying the P conversion pathways. The influence of the main process parameters, including temperature, pressure, reaction time, liquid-to-solid ratio, acidic-basic treatment, and addition of additives, on the distribution and speciation of P in the HT by-products is also investigated by a in depth critical analysis of the literature data, providing a comprehensive overview to elucidate the main P conversion pathways.

2. Selected studies of hydrothermal treatments of sewage sludge

A critical classification and analysis of published studies in the literature allowed to select of over 60 works that investigate P conversion during HT treatments of SS. The studies were selected using Web of Science (Clarivate) by using the combination of different keywords

(hydrothermal, phosphorus, nutrients, speciation, fate, carbonization, liquefaction, gasification). All studies have been published in the last 10 years, 40 of which after 2020. Table 1 shows the selected works that provide information on the main HT process parameters and experimental results on P speciation and migration in HT treatment by-products.

2.1. Sewage sludge type and composition

The main parameters that were considered for the characterization of the SS used as feedstock in the selected studies are their geographical origin and production process, as well as physical–chemical parameters such as their pH, water content, nutrient content (P, N, and K), and metal content, in particular Ca, Fe, Al, and Mg, which are elements with high affinity for P binding.

The SS presented in Table 1 have been categorized into four main categories according to their production process: primary SS, that are generated by mechanical treatments, in which solid particles and oils are separated from wastewater; secondary SS, that result from biological treatments in which various microorganisms degrade the organic fraction; digested SS, that represent the product of anaerobic digestion in which SS is stabilized with a simultaneous biogas production[40]; and finally mix or not specified sludge, that represent mixtures of different types of sludges, or in case there was not enough information to identify the sludge nature. Among the selected works, digested SS constitutes the main SS type used as feedstock (40% of the selected studies). As shown in Table 1, most of the studies are from Europe (39%), China (31%), USA (11%), and Japan (8%).

Fig. 1a presents a statistical analysis on the contents of P, N, Fe, Ca, Al, Mg, and K among the SS used as HT feedstock in the selected studies (mg element/g dried SS). The results indicate that P content varies between 2.8 and 56.2 mg P/g SS, with an average value of 27.4 mg P/g SS and a median value of 22.7 mg P/g SS. This P distribution, obtained by combining the data of 65 different sludges, is in good agreement with the findings of Liu et al. [9]. P concentration in raw SS presents a certain variability, due to several factors, including wastewater origin and SS production process. For most studies in Table 1, SS derives from municipal WWTP, which usually treats domestic effluents. However, the treated wastewater is not always specified, and some of the SS reported in Table 1 could derive from a mixture of domestic and (agro)-industrial effluents, which can affect P content variability.

The average contents of Fe, Ca, Al, and Mg in SS used as feedstock in the selected studies were 36.5 mg Fe/g SS, 30.3 mg Ca/g SS, 19.0 mg Al/g SS, and 7.1 mg Mg/g SS, respectively. It is important to consider these elements, as under HT conditions they may form stable solid precipitates such as Ca and Mg phosphates, but also Fe and Al (hydro)-oxides which can adsorb phosphates in solution (P-ferrihydroxide, P-alumina, P-Al hydroxide)[41]. Fe, Al, Mg, and Ca-P complexes are known to be the ones with lesser solubility compared to other compounds such as K and Na-P salts[42,43]. This property together with the prevailing amounts of these elements over other metals in wastewater treatment systems[9] makes Fe, Al, Mg, and Ca-P complexes the main precipitate forms controlling P recovery in the solid product. The average contents of N and K in SS used in the selected studies are 48.6 mg N/g SS and 10.2 mg K/g SS, respectively (Fig. 1a). It is also interesting to characterize N and K contents, because they can react with P to form stable precipitates with strong practical interest (two commercialized fertilizers), namely struvite and K-struvite ($\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$). Figure S1 (Supplementary material) shows the molar ratios Fe/P, Ca/P, Al/P, Mg/P, N/P, K/P in the SS that were used as HT feedstock in the selected studies. Average molar ratios of Fe/P, Ca/P, and Al/P were 1.00, 1.47, and 0.93, respectively. These values are very close to those of the most commons Fe, Ca, and Al phosphates that can precipitate in water solutions (FePO_4 , CaHPO_4 , $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, AlPO_4)[42], suggesting that in most SS Fe, Ca, and Al contents are not limiting for phosphate precipitation. Indeed, N is nearly always present in higher stoichiometric quantities than those required

Table 1

Main results from selected studies that have investigated P conversion during hydrothermal treatment of SS. HT = hydrothermal treatment; HTC = hydrothermal carbonization; HTL = hydrothermal liquefaction; HTG = hydrothermal gasification; PSS = primary sewage sludge; SSS = secondary sewage sludge; DSS = digested sewage sludge; M/NS = mixed or not specified sludge.

Reference	Hydrothermal treatment	Type of sludge	Sludge origin	Temperature (°C)	Reaction time (min)	Solid-to-liquid ratio (Kg/L)	P content in sludge (mg P/g dry SS)	Solid product recovery yield (%)	P recovery yield in the solid product (%)	P content in the solid product (mg P/g dry char)	P concentration in the liquid product (mg P/L)
[62]	HTC	PSS	China	120–300	30–180	0.16	26.8	47.7–101	69.6–100 ^a	27.1–81	0–4570
[57]	HT	M/NS	USA	125–225	30–270	0.11	19	42.3–102	92.6–99.5 ^a	18.4–42	98–224
[57]	HT	DSS	USA	125–225	30–270	0.11	33	52.8–100	95.4–98.3 ^a	33.5–62	64–127
[87]	HT	SSS	Spain	100–200	15–210	0.035	16		80.5–97.8 ^a	12.9–15.64 ^e	
[7]	HTC	SSS	China	170–320	30	0.23	25.4		17.25–95.8	27.65–47.8	
[76]	HT	M/NS	USA	90–155	240	0.07	12.1 ^b			13.32–18.6	12.3–44.6
[76]	HT	M/NS	USA	90–155	240	0.05	12.7 ^b			13.63–21.1	12.3–38
[94]	HTC	M/NS	China	160–280	120	0.11				28.4–40.5	129–485
[72]	HTC	SSS	Australia	180–240	30–150	0.25	14	68.6–75.7	92.8–102 ^a	19	
[72]	HTC	PSS	Australia	180–240	30	0.25	7	77.4–84	96–111 ^a	8–10	
[72]	HTC	SSS	Australia	180–240	30	0.25	21	68.1–74.8	103–107 ^a	29–33	
[48]	HTC	SSS	China	200–260	60–480	0.17	43			25.8–41.3	54–72
[70]	HTC	SSS	China	150–300	120	0.31	17.9	79.7–92.8	97.9–105 ^a	19–22.5	
[77]	HT	DSS	USA	90–185	240	0.06	34.2 ^b			34.2–59	7.7–27.6 ^a
[33]	HTC	SSS	USA	225	1440	0.11	41	31.7–37.1	55.3–71.8 ^a	71–79	
[91]	HTC	DSS	China	170	30	0.18–0.23	23.1–30.5			31.5–40.9	39–415
[41]	HTC	SSS	USA	225	240–960	0.18	41	48.5–55.2	89.3–101	76–81	
[41]	HTC	DSS	USA	225	240–960	0.18	33	49.8–55.6	81.7–95.5	49–61	
[120]	HTL	PSS	Denmark	300–350	11.6–21						2.3–7.6 ^c
[103]	HTC	M/NS	Germany	200–240	120	0.11	36.1	53.8–69	93.2–99		58–326
[50]	HTC	DSS	Germany	180–260	60–240	0.11–0.25	32	64.9–80.5	87.5–100	38.6–48.5	
[58]	HT	M/NS	China	140–200	10–60	0.10	96.2			113.9–178.6	
[73]	HTC	DSS	Finland	210–250	30–120	0.17–0.34	37.2	72–88.3	83.6–101 ^a	37.4–56.7	330–1130
[89]	HT	SSS	USA	125–225	240	0.20	56.2				159–163 ^a
[63]	HTC	M/NS	UK	200–250	240	0.11	2.8	63.7–73.8	53–92	2.3–3.5	
[64]	HTC	DSS	Singapore	200–380	20	0.05–0.21	13	35–76	91.6–99.4 ^a	17–35 ^a	16–229
[29]	HT, HTC, HTL, HTG	DSS	Belgium	170–500	30–60	0.06–0.11	16.4	54–80	91.52–96.6 ^a		560–1360 ^d
[81]	HTC	DSS	China	200–260	120	0.11	13.6	61.14–70.6	76.99–99	16.18–20.8	
[59]	HTC	SSS	China	200–260	30–240	0.03	117.8	42.27–54.8	93.4–96.2 ^a	36.59–37.4 ^e	
[52]	HTC	M/NS	China	280	120	0.11	22.7	46.6–54.8	81.4–95.4 ^a	38.7–42.2	1–114
[121]	HTC	M/NS	South Korea	200	120		79.3	65.8	110 ^a	132.8 ^a	
[80]	HT	SSS	China	200–260	30	0.24	10.2	52–66.4	80.3–94.1 ^a	12.45–16.2	
[49]	HT	DSS	Japan	200–280	60	0.18	26.2			32.37–38.4	
[122]	HTC	M/NS	Italy	190	60		23	71.8 ^a	94.0 ^a	30.3 ^a	76.5
[74]	HTC	DSS	Spain	180–240	60	0.20	45.8	51.8–74.2	75.5–88.9 ^a	52.8–63	
[104]	HTC	DSS	Germany	190–220	120	0.18	31		91.3–102	42–45	74–173 ^c
[123]	HTC	DSS	Switzerland	200	240	0.25	34.1	68.0	98.6 ^a	49.5	208
[105]	HTC	DSS	Germany	220	120	0.11	34.4				180–306
[96]	HTC	M/NS	China	220	30	0.13	24.8	39.8	66.6 ^a	41.5	
[82]	HTG	M/NS	China	380–460	6–18	0.03	38.1		82.6–97.1		
[99]	HT	M/NS	China	145	120	0.11	25.4			40.1–52.9	
[66]	HTC	M/NS	China	160–280	120	0.11	27.1	41.9–58.2	78.9–91.8	38.9–57.4	
[124]	HTC	M/NS	India	200	60–480	0.09		80.8–84.2			372–632 ^c
[85,125]	HTG	SSS	Japan	300–600	0.08–1	0.26	13		6–57		
[67]	HTC	DSS	Canada	180–220	15–60	0.30	13.7	63.2–90.5	81.8–116 ^a	16.25–19	86–207 ^d
[47]	HTC	DSS	Sweden	180–250	120	0.12	45	59.5–67.1	75.5–84.6 ^a	51–64	
[75]	HTC	DSS	Germany	180–240	85–439	0.33	47	52.4–84.9	44.7–83.7 ^a	30.7–57.6	134–2410
[65]	HTC	SSS	China	150–240	30–90	0.11	12.9	26.6–59.5	36.6–91.7 ^a	13.5–34.1	

(continued on next page)

Table 1 (continued)

Reference	Hydrothermal treatment	Type of sludge	Sludge origin	Temperature (°C)	Reaction time (min)	Solid-to-liquid ratio (Kg/L)	P content in sludge (mg P/g dry SS)	Solid product recovery yield (%)	P recovery yield in the solid product (%)	P content in the solid product (mg P/g dry char)	P concentration in the liquid product (mg P/L)
[86]	HTC	DSS	Japan	120–240	30	0.02	44.9				373–580 ^c
[79]	HTC	PSS	Spain	200–260	30–180		12.3	65–87 ^a	79.1–97.9	13.9–15.4	
[79]	HTC	SSS	Spain	200–260	30–180		16.7	57–83 ^a	73.3–99.7	20–21.6	
[119]	HTG	M/NS	China	400	30	0.12			44.3–98.9 ^a		41–2215
[78]	HT	M/NS	USA	90–185	240	0.06	19.2 ^b			29.1–47.1	5.9–10.5
[100]	HTL	DSS	Denmark	300–350	20	0.20	7.8	42.2–47.2	128–132 ^a	21.16–24.4	
[90]	HTL	SSS	Denmark	350–400	15	0.27	9.6	27.3–28.1	92.6–93.9	24.2–27.2	131–186
[126]	HTL	M/NS	Qatar	350	30–120	0.14	12.3			3.3–8.9	
[97]	HTL	PSS	Denmark	350	300	0.04	21.2		46.8	99.2	15.8
[88]	HT	DSS	UK	160–250	30	0.05		56.8–73.4	11–37		73–104
[102]	HTC	DSS	UK	250	30	0.03–0.43		68–76	66.8–75.7 ^a		66–168
[83]	HT	M/NS	Japan	225–275	15–60	0.04	7		55–79		
[106]	HTC	DSS	Switzerland	205	420	0.25					14.3–17.8
[106]	HTC	PSS	Switzerland	190–220	300–420	0.10	25.2		97	28.1	72.7–159.6
[101]	HTC	M/NS	China	150–250	120	0.25	17.9	82.6–92.8	98–102 ^a	19.0–22.0	
[127]	HTC	DSS	Italy	190–250	180	0.14	22	62.9–83.3		42.0–47.0	
[128]	HTC	M/NS	Italy	190–250	30–60	0.03	5.22 ^b	49.4–77.2	87–103 ^a	6.2–10.2	11.1–38.4
[128]	HTC	DSS	Italy	190–250	30–60	0.03	5.81 ^b	64.6–82.8	75–103 ^a	6.7–7.5	12.2–22.7
[128]	HTC	DSS	Italy	190–250	30–60	0.17	9.22 ^b	66.8–88.2	79–88 ^a	9.2–10.9	0.2–0.4
[95]	HT	PSS	Japan	200	60	0.03	35	65–73.1	40.1–96.4	18.3–47.5	39.0–704
[93]	HTG	M/NS	China	350–500	5–60	0.05–0.20	14.1			19.7–22.6	43.8–70.8
[129]	HTC	DSS	Thailand	200	60–360	0.33		73.6–81.2			804–813
[130]	HTC	SSS	Italy	190–220	85–240	0.03–0.17	22.79	53.0–68.1	31.8–108.1 ^a	12.3–43.5	
[131]	HTL	M/NS	China	220	30	0.10–0.13	77.6	55.3–66.3	70–113 ^a	97.9–138.5	
[132]	HTL	SSS	Denmark	350–400	15	0.37	22.34		93–98	37.4–43.0	179–1503 ^d

^a Calculated from paper data.

^b Does not consider dissolved P.

^c PO₄³⁻ content.

^d Expressed in mg/kg.

^e Expressed on a dry raw sludge basis.

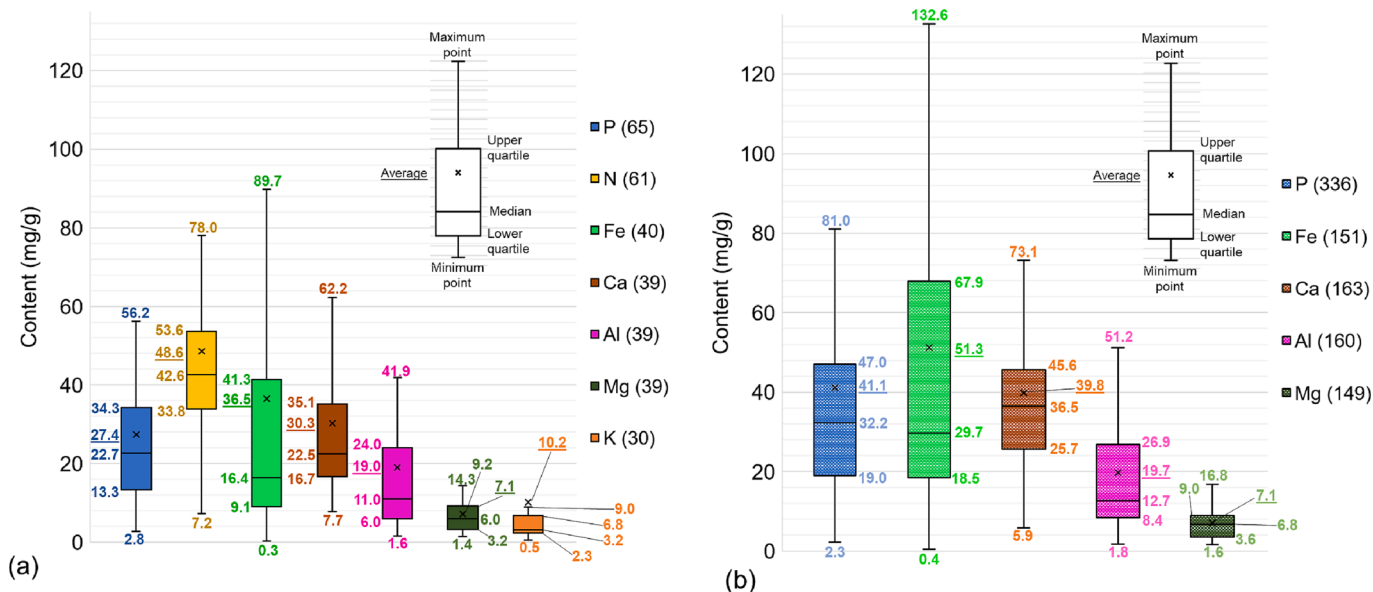


Fig. 1. Box distributions of P, N, Fe, Ca, Al, Mg, K contents in SS expressed as mg/g of dry SS (Fig. 1a) and P, Fe, Ca, Al, Mg contents in solid products of HT process expressed as mg/g of dry solid product (Fig. 1b). Average values are underlined. Data collected from works listed in Table 1. For each distribution, the number of experimental data is shown in brackets in the legend. Data from solid products include only HT treatments without pH adjustments or addition of additives.

for struvite precipitation, as shown by the average N/P molar ratio of 6.3 (Figure S1). This suggests that struvite precipitation is not an effective way for N recovering from SS, as only a small fraction of the total N in SS would be recovered. Moreover, it should also be noticed that Mg is present in stoichiometric defect (average Mg/P molar ratio in SS is 0.56), and it would be necessary to add Mg salts to allow complete P recovery by struvite precipitation. The results in Figure S1 also indicate that K is always present in stoichiometric defect (average K/P molar ratio in SS is 0.37) compared to the amounts required for K-struvite precipitation.

Fig. 2a presents a statistical analysis on the contents of non-apatite inorganic P (NAIP), apatite inorganic P (AIP), and organic P (OP) compared to the total P contents (TP) in SS used as feedstock for the selected studies. These P fractions were determined by Standard

Measurements and Testing method[44,45]. TP represents total P, which includes OP and inorganic phosphorus (IP). The latter can be further classified in AIP and NAIP. OP is referred to P present in organic compounds such as DNA, phospholipids, and ATP. AIP represents P associated with various Ca compounds, whereas NAIP is inorganic P that is not associated with Ca compounds[46]. The average values in Fig. 2a indicate that NAIP usually represents the highest P fraction in SS (57% of TP), followed by AIP (24% of TP) and OP (16% of TP)[7,47–50]. However, it should be noticed a high variability on P fractions between the different SS. Indeed, the original Ca, Al, Fe, and Mg contents in wastewater, as well as the addition of FeCl₃ or Al₂(SO₄)₃ as reagents to improve P precipitation in WWTP can affect the distribution of P fractions in SS.

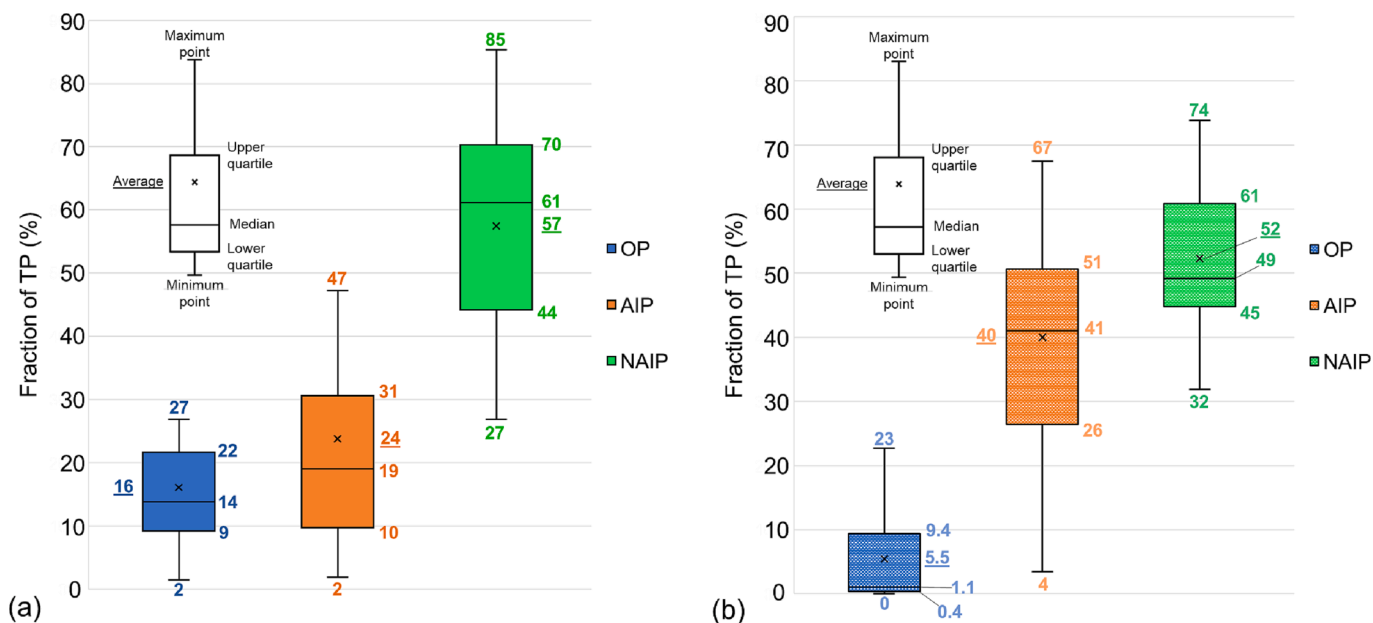


Fig. 2. Box distribution of the apatite inorganic P (AIP), non-apatite inorganic P (NAIP), and organic P (OP) relative amounts in SS (Fig. 2a) and solid products of HT process (Fig. 2b) expressed as a fraction of the total P content. Average values are underlined. Data from [7,47–50,52,57,59,62,66,74,80,81,91,93–97]. Data from hydrochar include only HT treatments without pH adjustments or addition of additives.

It has been suggested that the geographical origin could reflect some of SS physicochemical characteristics, because of local differences in people's diets and/or WWTP sizes and technologies. Nevertheless, according to the results of this study, no specific trend was observed between SS composition and P speciation and its geographic origin, probably because of the small number of selected samples and the strong variability on production processes and WWTP process parameters among the same geographical areas.

2.2. Hydrothermal process parameters

The main HT process parameters that have been investigated in the selected studies from the literature (Table 1) are the temperature and duration of the HT process, and the solid-to-liquid ratio (SLR), which is defined as the mass ratio of the total solids to water of the SS solution used as HT feedstock (equation (1)).

$$SLR = \frac{m_{TotalSolids}}{m_{water}} \quad (1)$$

HT treatments can be classified based on the nature of the product present in a higher quantity or which is the object of practical interest, as follows: HT carbonization (HTC), which produces mainly a solid product, the hydrochar, operated between 180 and 280 °C with a slow heating rate [39]; HT liquefaction (HTL), realized at 250–400 °C with a fast heating rate and a shorter residence time [39], the target product is the bio-oil; and HT gasification (HTG), at temperatures > 400 °C, in supercritical water conditions, and leads to a high H₂-rich syngas yield [35,51].

For this review, 580 experimental points (temperature and time

pairs) have been collected and analyzed from the selected studies summarized in Table 1. As shown in Fig. 3, many of the temperature–time pairs are within the temperature range associated with HTC (60%) or lower temperatures (18%), and only a small fraction is within the temperature ranges associated with HTL (12%) or HTG (10%). Moreover, data in Fig. 3 indicates that relatively longer reaction times (>120 min) are usually associated with lower temperatures (<250 °C), while at higher temperatures usually correspond shorter reaction times. Importantly, it should be also mentioned that the distinction between HTC, HTL, and HTG is not unambiguously defined, and slightly different alternative temperature ranges are often suggested in the literature. What defines whether the HT treatment is carbonization, liquefaction, or gasification, is above all the nature of the target product (solid, liquid, or gaseous). For this reason, some of the studies that carry out HTC, also apply temperatures above 280 °C, which are generally associated with HTL.

The SLR values for the different HT treatment studies summarized in Table 1 range from 0.02 to 0.34 kg/L (70 %wt to 98 %wt of water content), with a median value of 0.11 kg/L (90 %wt of water content). This large range of SLR values may indicate that solid/liquid pretreatment such as centrifugation, drying, or dilution, was applied to raw SS before performing HT experiments.

2.3. Main results of the selected studies

The main results of HT treatments, including solid product recovery yield (%), P recovery yield in the solid product (%), P content in the solid product (mg P/g dried hydrochar), and P concentration in the liquid product (mg P/L), for all the selected studies are summarized in Table 1.

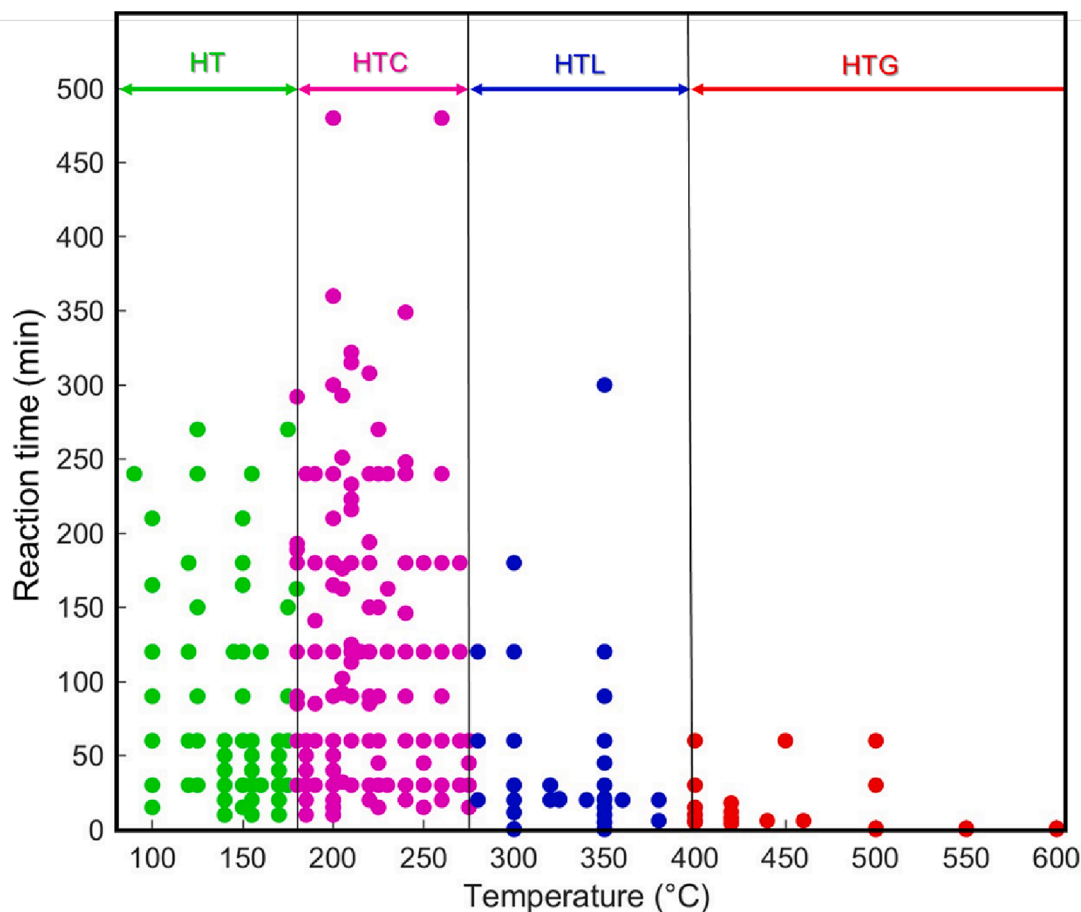


Fig. 3. Temperature and reaction time of HT studies listed in Table 1. Pink points (274) correspond to typical HTC temperatures, blue points (49) to HTL temperatures, red points (45) to HTG temperatures, and green points (90) to HT treatments at relatively low temperatures ($T < 180$ °C).

The solid product recovery yield (%) is defined by equation (2), where $m_{SP,dry}$ is the solid product dry mass (g), and $m_{SS,dry}$ is the feed SS dry mass (g). The solid product recovery yield from the selected studies varies from a minimum of 27% up to 100%, with an average value of 67%. Generally, most of the works report a solid product recovery yield between 60% and 80% (Table 1).

$$\text{Solid product recovery yield (\%)} = \frac{m_{SP,dry}}{m_{SS,dry}} \cdot 100 \quad (2)$$

The P recovery yield in the solid product (%) is defined by equation (3), where $C_{P,SP}$ and $C_{P,SS}$ are the total P content in the solid product and in the SS, respectively (mg P/g of dried mass). The P recovery yield in the solid product from the selected studies varies from a minimum of 6% up to 100%, most probably because the large range of temperature and duration of the HT treatment process among the different studies (Table 1).

$$P \text{ recovery yield in solid product (\%)} = \frac{C_{P,SP} \cdot \text{Solid product recovery yield}}{C_{P,SS}} \cdot 100 \quad (3)$$

According to the data in Table 1, total P content in the solid product vary from 3.3 to 178.6 mg P/g dried hydrochar, whereas P concentration in the liquid product (process water) varies from 0.2 mg/L up to 5160 mg P/L, with an average value of 442 mg P/L and a median value of 130 mg P/L. This high variability in P concentration could be partially explained by the large discrepancies on SLR used for HT experiments in the different studies, as higher SLR may give higher P concentrated liquid effluents.

Fig. 1b summarized the statistical distribution of total P, Fe, Ca, Al, and Mg contents in the solid products from the HT treatments (mg element/g dried hydrochar) for the selected studies in Table 1. The average contents in hydrochars were 41.1 mg P/g, 51.3 mg Fe/g, 39.8 mg Ca/g, 19.7 mg Al/g, and 7.1 mg Mg/g, respectively, thus indicating that all these elements tend to be concentrated in the HT solid product [1].

Fig. 2b summarizes the distribution of OP, AIP, and NAIP fractions (%) compared to the total P content in the solid products from the HT treatments for the selected studies in Table 1. The average values in Fig. 2b indicate that NAIP represents the highest P fraction in the HT solid products (52% of TP), followed by AIP (40% of TP) and OP (5.5% of TP). Interestingly, NAIP and OP fractions in HT solid residues are significantly lower than those of SS before HT treatment (Fig. 2a). Most probably, the high temperature of the HT process had the effect of promoting OP mineralization to phosphate[41,52,53], followed by Ca-phosphate precipitation, thus reducing OP and increasing AIP fractions.

The characterization of P species in the products from HT process is very important to predict their P bioavailability. Indeed, plants can directly sorb only inorganic P anions, such as orthophosphates[54]. Phosphorus bio-availability is a complex subject that depends on different factors, such as temperature, P distribution between OP, NAIP, and AIP fractions, presence of Fe and Al oxides, amount of CaCO_3 , P adsorption-desorption rates, pH, and humidity[55,56].

Therefore, several studies have further characterized P contents in SS and HT products by Liquid ^{31}P NMR. The most commonly analyzed compounds are orthophosphate, orthophosphate monoester and diester, pyrophosphate, and polyphosphate[7,57–59]. Orthophosphate and pyrophosphate are considered inorganic P (IP), while monoester-P and diester-P are major constituents of OP [7]. The results indicate that orthophosphate is the dominant specie in SS before HT treatment [7,57,59], with smaller proportions of monoester-P[7,57,59], diester-P [57,59] and pyrophosphate[7,59]. Indeed, OP species (monoester and diester) are usually not present in the HT products[7,57], making orthophosphate the only detectable P form in the hydrochars[33]. Shi et al.[7] observed a stronger pyrophosphate signal in hydrochars

compared to raw SS, suggesting that OP (monoester-P) is hydrolyzed and converted into pyrophosphate during the HT treatment.

3. Effect of hydrothermal process parameters on phosphorus conversion pathways

3.1. Temperature, reaction time, and pressure

Temperature and reaction time are the most investigated HT process parameters among the selected studies presented in Table 1. Temperature variation has a strong effect on the products from HT processes, directly related to the physical properties of water[60,61]. Reaction time is another important parameter that impacts product yields, properties, and nutrient migration. It has a decisive effect when physical phenomena and chemical reactions have relatively slow kinetics, thus requiring more time to reach thermodynamic equilibrium.

Most studies in Table 1 indicate that the solid product recovery yield decreases with increasing temperature, as clearly shown in Figure S2a. Indeed, temperature increase enhances organic matter dissolution and degradation by dehydration and decarboxylation reactions[47,62–65], and leads to biopolymers[29,66] and inorganic species solubilization in the liquid phase[63]. As shown by Figure S2, the effect of reaction time on solid product recovery yield is usually less straightforward than temperature[53]. Many studies in Table 1 have found that the solid product recovery yield decreases with increasing reaction time [41,57,62,67].

To better understand the combined effects of temperature and reaction time, many authors use a parameter called HT severity factor $f(T, t)$, which is function of time and temperature. According to the literature, the Ruyter coalification model [68] is the mostly used severity function to calculate the severity factor $f(T, t)$ of HT processes[9,62,69] (equation (4)), where t represent the reaction time (s) and T is the temperature (K).

$$f(T, t) = 50t^{0.2} e^{-\frac{3500}{T}} \quad (4)$$

This function has been developed by modeling experimental kinetic data from HT carbonization of various biowastes between 120 and 390 °C, and reaction time from 1 min to 6 months. This function is based on the assumption of time-temperature equivalence, according to which the same products' characteristics can be obtained with a shorter reaction time and higher temperature, or with a longer reaction time and lower temperature.

Fig. 4 shows the solid product recovery yield (%) as a function of the HT severity factor $f(T, t)$ for the studies listed in Table 1. The results indicate that higher $f(T, t)$ (>0.5) can lead to lower solid product recovery yield (<55%), with the only exception of two experimental points by Fei et al.[70] and Ekpo et al. [29]. This reduction in solid product recovery yield by increasing $f(T, t)$ has been already observed in previous studies[6,9], and it was primarily attributed to cell rupture, biopolymers degradation and solubilization into the aqueous phase at high $f(T, t)$. According to this, the minimum value for the solid product recovery yield would correspond to the ash content of the feedstock [6,71], which indicates the total conversion and/or transfer of organic carbon to the liquid and gaseous phases.

Many studies presented in Table 1 have also found that P content in the solid product increases with increasing temperature [47–49,57,62,64,66,72–78] and/or with increasing reaction time [41,48,57,62,67,73,79]. However, the results of comparative studies indicate that temperature has a more relevant effect on solid product P content rather than reaction time[50,62]. These findings suggest that, although the increase in temperature and/or reaction time process promotes solid organic matter solubilization and decrease in solid product recovery yield, P tends to remain preserved in the solid fraction, and therefore its content in the solid product increases[62,70,76,79,80].

Fig. 5 shows the P recovery yield in the solid product (%) as a

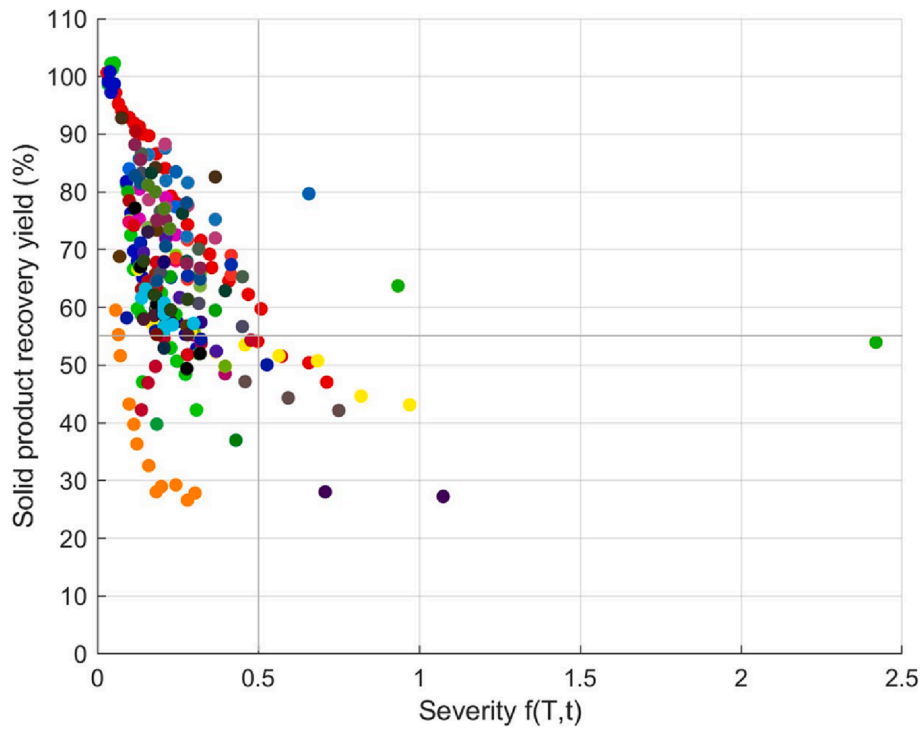


Fig. 4. Solid product recovery yield as a function of process severity expressed with the Ruyter severity factor $f(T,t)$ (equation (4)). Each color represents a different study listed in Table 1.

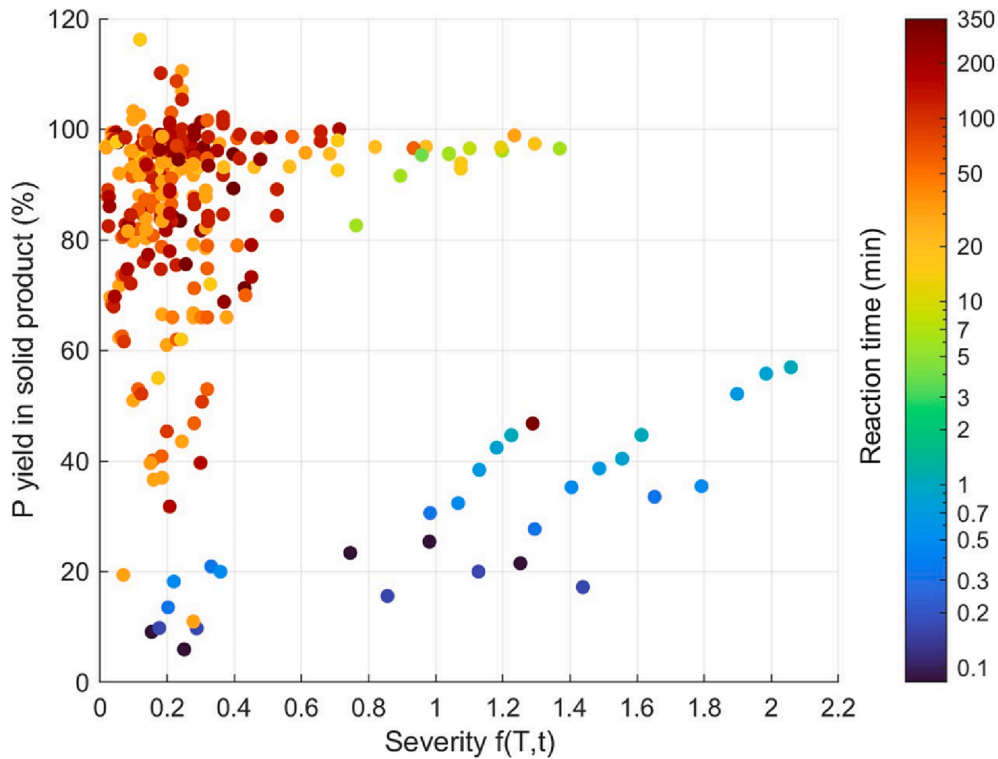


Fig. 5. P recovery yield in the solid product as a function of process severity expressed with the Ruyter severity factor $f(T,t)$ (equation (4)). The color scale represents the treatment duration expressed in minutes. Data collected from works listed in Table 1.

function of $f(T,t)$ and reaction time. A positive trend between the increase in $f(T,t)$ and the increase in P recovery yield in the solid product, has been observed for many studies [7,29,47,48,58,62,64,65,70,80–83], thus indicating that higher temperature and/or higher reaction time

usually promote P recovery in the solid product rather than in the process water. As already found for P content in solid product, temperature seems to have a more relevant effect also on P recovery yield in the solid product compared to the duration of the HT process.

The effect of HT reaction time on P recovery yield in the solid product is often more relevant when working at low temperature (<180 °C), probably because of the influence of temperature on the kinetic of OP mineralization to soluble orthophosphates. Indeed, previous studies have found that the kinetic of OP mineralization during HT processes is primarily controlled by the temperature according to a Arrhenius kinetic law[84]: lower temperature may result to slower kinetics, thus requiring a longer time to mineralize OP to orthophosphates [57]. This is in agreement with the finding of various authors who observed that OP fraction decreases with increasing reaction time [57,62,85]. The findings of several studies indicate that OP is completely mineralized to orthophosphates in <60 min, in particular at temperatures above 175 °C[7,48,50,57,85,86], whereas total mineralization of OP can occur in <10 s at temperature higher than 500 °C[85]. Then, orthophosphates can react with metal cations (e.g. Ca²⁺, Fe³⁺, Al³⁺, Mg²⁺, Mn²⁺) to form solid precipitates that are recovered in the solid product[7,48,85]. However, some studies[63,74,87,88] report a decrease in P recovery yield in solid product as temperature rises, thus suggesting that OP mineralization was not followed by orthophosphate precipitation, orthophosphate remaining dissolved in process water [39,41,47,62,89]. This was most probably due to a lack of metal cations or to pH values that were not conducive to metal phosphate precipitation. The effect of HT temperature increase on the increase in P, Ca, Fe, Al, and Mg contents of solid products has been observed in many studies [7,47,50,58,67,76,79,90], and their results appear to confirm that temperature promotes P recovery in solid product via OP mineralization to orthophosphates followed by metal phosphate precipitation. Additionally, results from X-ray photoelectron spectroscopy (XPS) analysis also indicate that OP can hydrolyze into *ortho*-P/pyro-P during HT treatment[91,92], and that Fe³⁺ ions from iron oxides and Al³⁺ ions can combine with free orthophosphates to form FePO₄ and AlPO₄[92].

Among the studies analyzed in this review, there is a general agreement that the temperature increase favors the conversion from NAIP to AIP. Fig. 6a shows the evolution of NAIP and AIP fractions as a function of the process severity expressed by the Ruyter function $f(T,t)$. Although AIP is generally the minor inorganic fraction in SS (Fig. 2a), its content increases in the solid product after HT treatment, particularly at temperatures above 220 °C[50]. On the contrary the NAIP fraction tends

to decrease with the increase in the HT severity factor $f(T,t)$ [7,47–50,52,59,62,66,74,80,81,93–97]. As shown in Figure S3, temperature effect on NAIP and AIP speciation is more evident than reaction time effect. The addition of reagents, such as FeCl₃ or the presence of high Ca relative amounts can lead to experimental points inconsistent with the general trend (Fig. 6a). High temperature promotes the precipitation of inorganic orthophosphates into the form of Ca-phosphates, but it may also promote dissolution of NAIP complexes (such as Fe- and Al-phosphates) to Fe³⁺, Al³⁺, and orthophosphate ions, which may reprecipitate under the forms of stable Fe- and Al-(hydro)-oxides, and Ca-phosphates[27]. Similarly, longer reaction time has been found to promote AIP species in the inorganic fraction[48,50,62].

Fig. 6b shows the evolutions of the sum of H₂O-P and NaHCO₃-P fractions, and the sum of NaOH-P, HCl-P and residual-P fractions in the solid products, determined by the Hedley sequential fractionation method[98], as a function of the severity factor $f(T,t)$ [41,57,70,72,76–79,89,99–101]. Figure S5 shows the individual trends of each fraction. According to the Hedley sequential fractionation method[98], H₂O-P corresponds to very weak bound P that is extracted by deionized water, NaHCO₃-P is exchangeable P that can be extracted by 0.5 M NaHCO₃, NaOH-P is generally associated with Fe- and Al-bound P that can be extracted by 0.1 M NaOH, HCl-P usually corresponds to Ca-bound P species that are extracted by 1 M HCl, while residual-P represents more stable residual P compounds that are extracted by concentrated HCl (10–12 M) at high temperature (80 °C).

The sum of H₂O-P plus NaHCO₃-P is often defined as readily available P. According to Fig. 6b, the sum of H₂O-P and NaHCO₃-P fractions decreases, while the sum of NaOH-P, HCl-P and residual-P fractions increases when increasing the severity factor $f(T,t)$. Figure S4 shows that temperature has a more influential effect on P fractionation than reaction time. According to Figure S5d, HCl-P fraction individually increases, while for the NaOH-P fraction there is no clear trend (Figure S5c). These results suggest that, when increasing $f(T,t)$, H₂O-P and NaHCO₃-P fractions are converted to the more stable NaOH-P and HCl-P fractions. However, at the same time, a fraction of NaOH-P may be converted to HCl-P by dissolution of Fe- and/or Al-phosphates followed by phosphate reprecipitation under the form of Ca phosphates. According to this hypothesis, Ca²⁺ content and pH values of the process

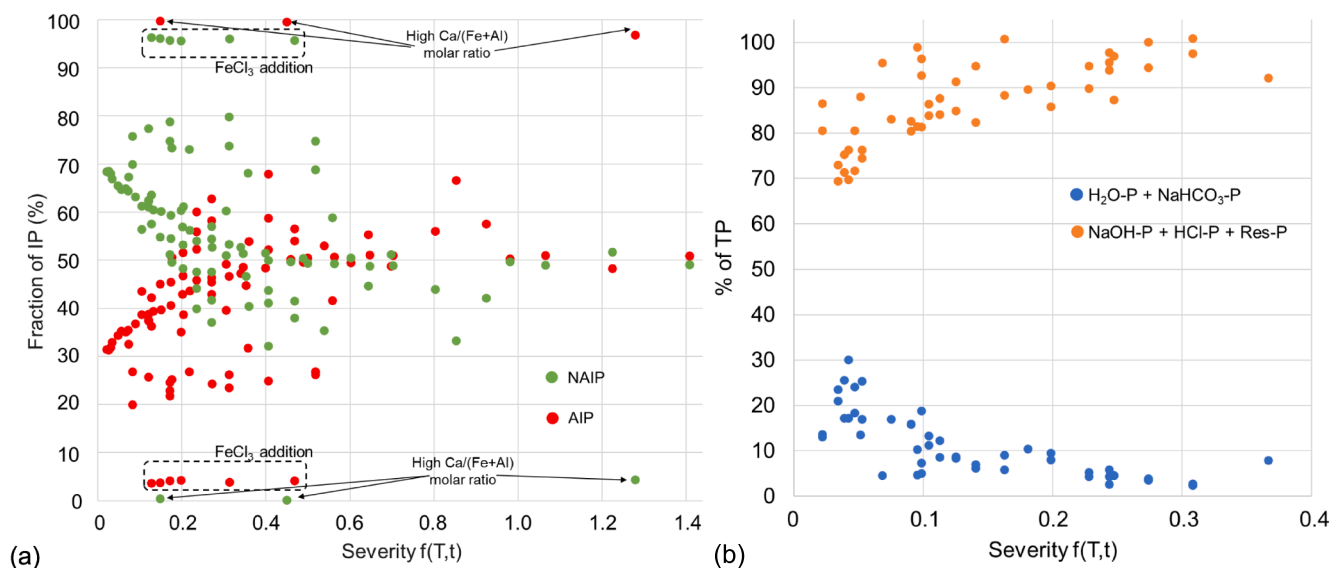


Fig. 6. (a) Non-apatitic inorganic P (NAIP) (green points) and apatitic inorganic P (AIP) (red points) fractions over total inorganic P (IP) as a function of the process severity expressed by the Ruyter severity factor $f(T,t)$ (equation (4)). Data from [7,47–50,52,59,62,66,74,80,81,93–97]. Points in dashed rectangle are related to a FeCl₃-assisted process[59]. Points marked by arrows are characterized by a relatively high Ca/(Fe + Al) molar content[49,97]. (b) Sum of the H₂O- and NaHCO₃-extracted P fractions (blue points), and the NaOH-, HCl- and residual- P fractions (orange points) as a function of the process severity expressed by the Ruyter severity factor $f(T,t)$ (equation (4)). Data from [57,72,77,78,99,101].

water can play a key role on phosphate reprecipitation, thus affecting the P speciation of solid residues. Therefore, depending on which phenomenon is predominant, the NaOH-P fraction can increase or decrease, thus explaining the fluctuating values of NaOH-P fractions according to the increase in severity factor $f(T, t)$.

Most of the studies in Table 1 were performed under autogenous pressure conditions, and no additional gas was used. As pressure increases with increasing temperature, the effect on P speciation coincides with the influence of temperature increase. Zhu et al.[93] have investigated the effect of pressure (from 20.5 up to 23.5 MPa) on HTG of SS at 400 °C for 1 h of reaction time. They observed a decrease in P recovery yield in the solid product with increasing pressure, as well as a decrease in OP fraction of solid products, while no trend was observed for NAIP and AIP fractions. They also observed that soluble P concentration in the liquid product increased with increasing pressure. These results appear to suggest a link between pressure increase and solubility increase of the main metal phosphates species. However, the scarcity of experimental results does not allow today to confirm this trend.

3.2. Solid-to-liquid ratio

The effect of different solid-to-liquid ratio (SLR) of the feed on HT treatment performance of SS was investigated by some of the studies listed in Table 1[50,64,73,102]. Several authors have found that the solid product yield increase by increasing SLR, which correspond to a higher solid content in the feed[50,64,102], whereas higher water content of the feed can promote hydrolysis of high-molecular-weight compounds and dissolution of less stable solid phases, thus decreasing the solid product recovery yield[64,102].

Moreover, a higher SLR has been found to promote P recovery yield in the solid product[50,64,102] and to decrease the P recovery yield in water[64,73,102]. Both He et al.[64] and Aragón-Briceño et al.[102] observed that a higher SLR leads to a higher P concentration in water, most probably because smaller water volumes resulted to higher P concentrated solutions. On the contrary, Hämäläinen et al.[73] found lower orthophosphate concentration in water at a higher SLR, and this was mainly attributed to a less efficient OP mineralization. Furthermore, Ovsyannikova et al.[50] observed an increase in AIP fraction recovery by increasing SLR, and this was primarily related to the high alkaline conditions of the samples which had favored Ca phosphate precipitation. Indeed, the increase in the solid content often produces a higher alkaline reaction medium, which stabilizes Ca phosphates while mobilizing Fe and Al phosphates. Nevertheless, available data were not sufficient to clearly describe a global and unequivocal tendency correlating P speciation and content to solid-to-liquid ratio, thus requiring more specific studies on the subject.

3.3. Acidic and basic treatments

A large number of studies in Table 1 have also investigated the effect of pH adjustment on P speciation and migration during HT treatments of SS[7,33,48,52,66,72,75,81,91,103–106]. Indeed, adsorption, precipitation, and other P-related chemical reactions are considerably affected by pH[107]. Different acidic or alkaline solutions can be used to adjust the pH of the feed, producing a significant effect on the product's properties and P speciation. NaOH is generally used to increase the medium pH[48,52,66,72,81,91,103]. Acid solutions used in the selected works include hydrochloric acid[7,52,66,72,91], nitric acid[33,48,104], sulfuric acid[75,103,105], formic acid[103], acetic acid[81,103], and citric acid[106].

The effect of pH on the solid product recovery yield is not clear. Some authors correlated a pH increase with a higher solid product recovery yield[33,66]. By contrast, Shettigondahalli Ekanthalu et al.[103] suggested that the solid product recovery yield decreases at higher pH. Regardless of the initial feed pH, the reaction medium after the HT process presents an approximately neutral pH[72,81,103]. Indeed, the

presence of dissolved organic compounds, carbonates, and colloids can produce a buffering effect that helps to shift the product's pH towards neutral values. The solid product can be slightly more acidic than the liquid one due to the presence of organic acids resulting from the decomposition of carbohydrates[72].

Fig. 7 shows all the collected experimental points that correlate the P recovery yield in the solid product with the feed pH, showing that the P recovery yield in the solid product increases with increasing pH, then for pH higher than 12 it decreases. This could be explained by considering that both Ca phosphate and Ca carbonate solubility decrease with increasing pH[108–110]. At pH higher than 12, CO_3^{2-} become the most prevalent carbonate specie in solution. Therefore, the precipitation of CaCO_3 could become prevalent over that of Ca phosphates, thus leading to competition with phosphates for Ca^{2+} ions, resulting in a lower relative amount of Ca phosphates in the solid product.

Several authors agree with the positive effect of the pH increase on the recovery of P in the solid product [7,33,52,66,75,81]. Higher pH promotes Ca phosphate precipitation[48], while a lower pH promotes P dissolution in water[7,105] as a more acidic medium can more easily dissolve inorganic P species as well as metal species[7], preventing their precipitation. McIntosh et al.[72] obtained the lowest P recovery yields in the solid products at the extreme range of the tested pH values (2 and 12), while the highest value is obtained at almost neutral pH. The colors in Fig. 7 represent the different acidic and basic species used to adjust the feed or feedwater pH. The use of two different acid solutions, organic and inorganic, to adjust the pH of the medium to the same value, leads to divergent results. Inorganic acids such as HCl and H_2SO_4 favor P solubilization and recovery in the liquid product to a higher extent compared to organic acids (acetic and formic acid)[103].

In general, more acidic conditions have been associated with a decrease in OP content in the solid product [7,66,81], whereas pH increase usually leads to a decrease in NAIP and an increase in AIP fraction over the total P content[7,48,52,66,81,91], most probably because higher pH favors Ca phosphate precipitation. However it should be noticed that carbonate alkalinity plays an important role in Ca phosphate equilibrium: high carbonate alkalinity could lead to CaCO_3 precipitation at $\text{pH} > 10$ [111], which can be in competition with Ca phosphate precipitation. Moreover, the concentration of both NAIP and AIP species has been observed to increase as the pH increases, probably because the inorganic P total amount in the solid product increases [7,48,52]. Regarding P speciation in the liquid product, more acidic conditions promote a higher orthophosphate content in the liquid product, because low pH prevents precipitation of orthophosphate under the form of solid metal phosphates[91,105,106].

These results are coherent with the comprehensive results related to P availability in soils as a function of pH, which show that P fixation by Ca presents a maximum around pH 8, while P fixation by Al and Fe occurs at lower pH, presenting a maximum respectively around pH 5.5 and pH 3.5[112,113].

3.4. Use of additives

Recovering P under the form of AIP from SS is interesting because it can be used to produce mineral fertilizers[114]. The Ca:P molar ratio of the solution represents one of the most important parameters to improve AIP recovery from wastewater treatment systems. Indeed, Ca:P molar ratios of the most common AIP minerals (e.g. dicalcium phosphate, tricalcium phosphate, octacalcium phosphate, hydroxyapatite) are comprised between 1 and 1.67, and often it is needed to add Ca-containing additive to have sufficient Ca^{2+} ions to convert all P into AIP. Different works investigate the effect of Ca addition on P fate and speciation during HT treatments of SS[48,52,64,80,91,94]. Free lime (CaO) represents the most used Ca-containing additive in the literature. Indeed, CaO dissolution in water results to an increase in Ca^{2+} ions and pH of the solutions, which are both two important parameters controlling Ca phosphate precipitation. To define the Ca addition effect alone,

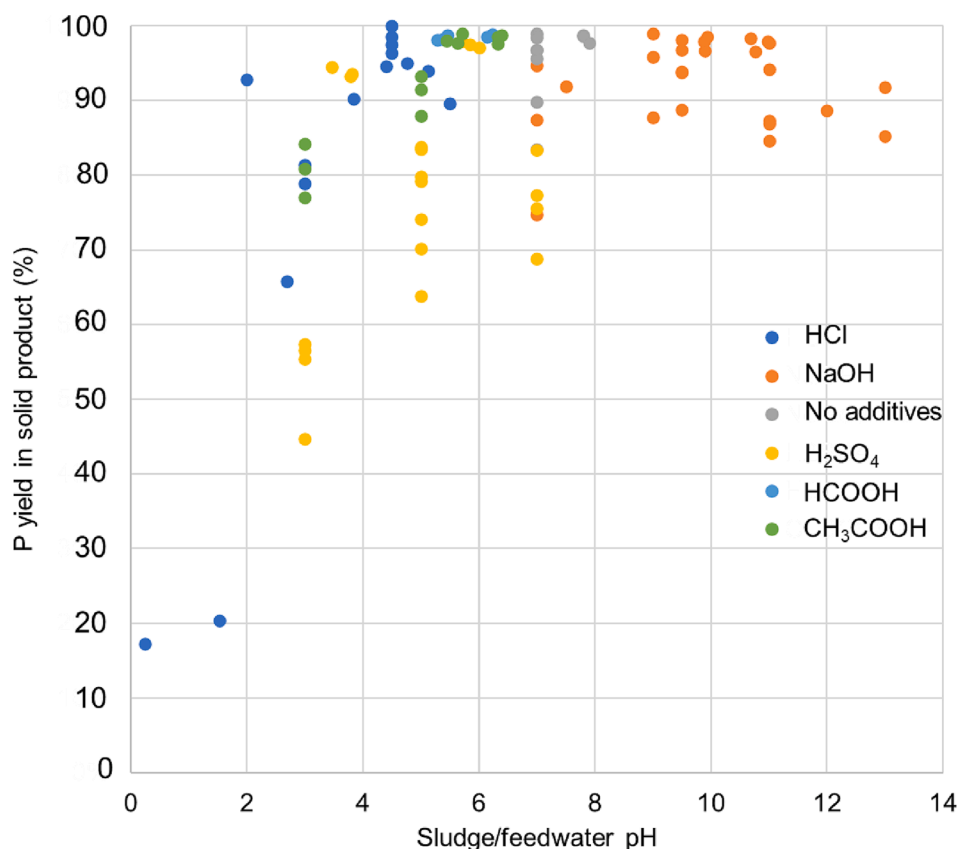


Fig. 7. P recovery yield in the solid product as a function of water process pH, each color represents a different solution. Data from [7,52,66,72,75,81,91,103].

separated from the pH increase effect, and to avoid the problem of lime low solubility in water, Zheng et al. [52] proposed CaCl_2 as an alternative, which showed the same results as CaO in terms of conversion of NAIP to AIP, and allowed to recover almost all soluble P in the solid phase by Ca phosphate precipitation.

Fig. 8 shows the collected experimental points which correlate the process severity factor $f(T,t)$ and Ca:P molar ratio with the relative amount of AIP in the hydrochar (expressed as % of total IP). The results in Fig. 8 clearly show that AIP fraction increases by increasing severity factor and by increasing Ca:P molar ratio of the feed. The results of Zheng et al. [94] have also indicated that Ca addition also promotes the increase in IP and the decrease in OP fractions in the solid products. Most probably, the alkaline conditions related to the Ca addition have promoted OP extraction from solid phase, followed by OP mineralization to orthophosphates, and then Ca phosphate precipitation. Overall, the results in the literature confirm that Ca addition leads to a significant AIP increase in the solid products, both in relative fraction and absolute concentration, which is accompanied by a NAIP decrease. Moreover, the results of some authors indicate that the NAIP conversion to AIP could be virtually complete when adding the correct amounts of CaO [48]. Indeed, the increase in pH due to CaO addition promotes Al and Fe phosphates dissolution to Al^{3+} , Fe^{3+} , and orthophosphate ions. Then, orthophosphate can react with Ca^{2+} ions and precipitate in the form of Ca phosphates at high pH [64].

Other studies have examined the addition of different substances to the sludge feed to investigate their effects on P speciation and distribution. The nature of the selected additives is disparate, and all the selected substances have an industrial application. Table 2 lists the substances used in the selected works as additives, their main purposes and practical function and their effects on P speciation during HT process of SS.

Li et al. [59] studied P migration and distribution under FeCl_3 -

assisted HTC of secondary SS. FeCl_3 is a well-known and widely used P-removal agent. Its addition improved both the solid product recovery yield and the P recovery in solid product. Besides, FeCl_3 promotes an acidic environment, allowing the dissolution of AIP in the liquid phase [44,95], releasing free orthophosphates which react with Fe^{3+} ions, and then leading to the precipitation of NAIP [115].

Yu et al. [95] investigated the effect of three different salts addition (FeCl_3 , AlCl_3 , and CaCl_2) during HTC of primary SS. The salts addition increased the P recovery yield in the solid product. Among the three salts, AlCl_3 fixed the largest P amount, followed by CaCl_2 and FeCl_3 . During hydrothermal treatment with the addition of AlCl_3 , the Al^{3+} ions concentration decreased sharply while the Fe^{3+} and Ca^{2+} ions concentration increased, indicating that P preferentially precipitated with Al under such experimental conditions [95]. Fe and Al phosphates constitute stable precipitates under slightly acid pH conditions, while at basic conditions they are replaced by Ca-containing compounds. HTC's liquid product is generally weakly acidic, and therefore Al and Fe are most effective for P fixation. FeCl_3 addition led to a NAIP concentration increase and to a AIP fraction decrease, indicating that a robust presence of Fe^{3+} ions can break the Ca-containing P species and fix P [95]. CaCl_2 addition resulted in an AIP fraction increase [95]. AlCl_3 addition led to a strong NAIP fraction increase, while the AIP fraction almost totally disappeared.

Qi et al. [65] studied the effects of different additives, namely FeCl_3 , polyacrylamide, and poly aluminum chloride. Solid product recovery yield increased following the use of all three additives, but this effect was more prominent for FeCl_3 and poly aluminum chloride, probably because Fe^{3+} and Al^{3+} ions were released into the medium and then they were available to precipitate with P. Beside the chemical effect of adding metal ions in the medium, these additives are generally used in coagulation-flocculation [116] processes, stabilizing the negative charged smaller particles and increasing the size of coagulated clumps. These

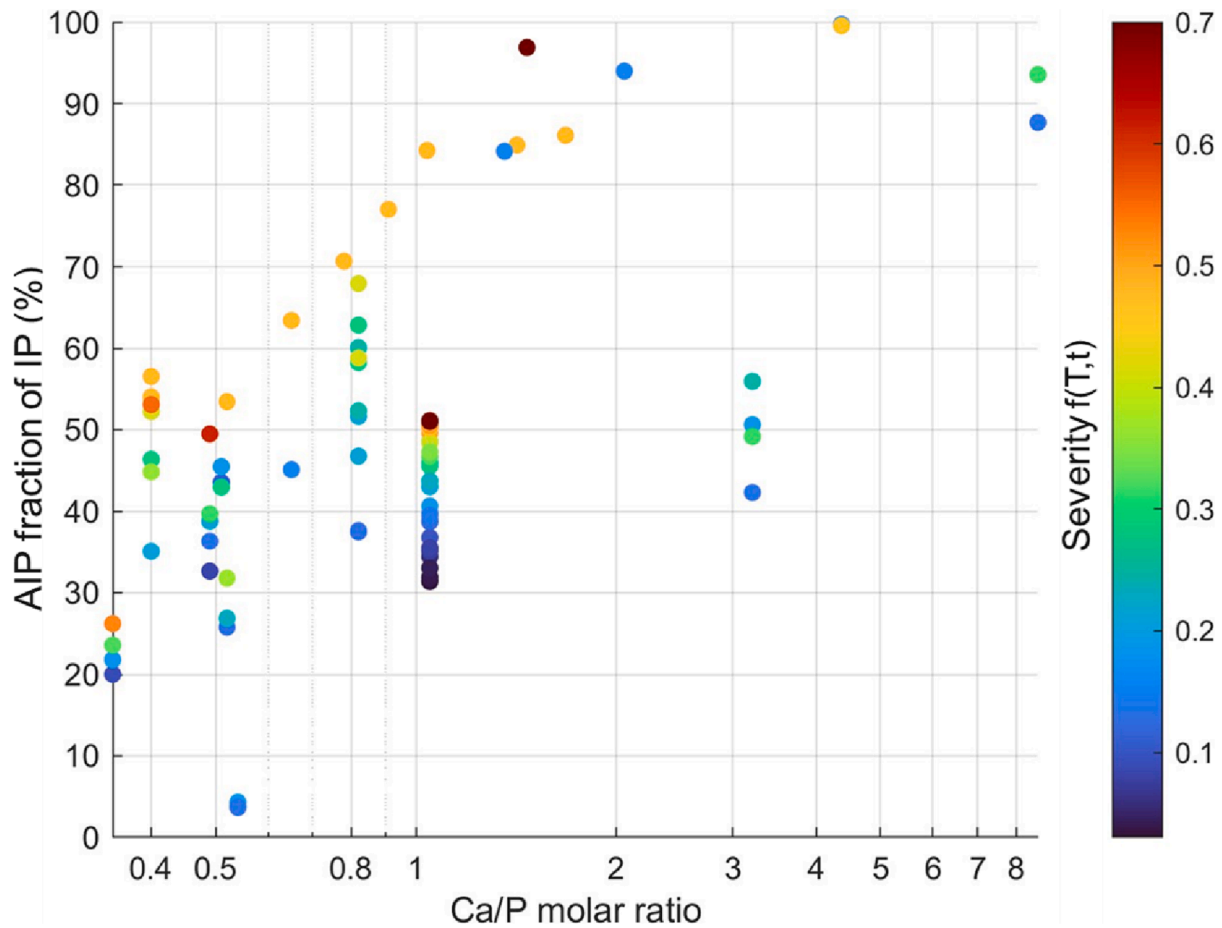


Fig. 8. Apatite inorganic P (AIP) fraction over total inorganic P (IP) as a function of the Ca:P molar ratio of the feedstock. Color represents process severity expressed by the Ruyter severity factor $f(T,t)$ (equation (4)). Data from [7,47–50,59,62,66,74,80,95,97].

Table 2
Additives used in the selected works and their effects on P speciation.

Name	Formula	Purpose	Solid product recovery yield	P recovery in solid product	P recovery in liquid product	AIP %	NAIP %	References
Ferric chloride	FeCl ₃	Fe ³⁺ ions supplier	↑	↑	↓	↓	↑	[59,65,95]
Calcium chloride	CaCl ₂	Ca ²⁺ ions supplier		↑	↓	↑	↓	[95]
Aluminum chloride	AlCl ₃	Al ³⁺ ions supplier		↑	↓	↓	↑	[95]
Sodium persulfate	Na ₂ S ₂ O ₈	Improving sludge dewaterability		↑	↓			[99]
Polyacrylamide	(C ₃ H ₅ NO) _n	Flocculating agent	↑	≈	≈			[65]
Poly aluminum chloride	[Al ₂ (OH) _n Cl _n ⁶⁻] _m	Flocculating agent	↑	↑	↓			[65]
Sodium carbonate	Na ₂ CO ₃	Improving H ₂ production in HTG		↓	↑			[119]
Potassium carbonate	K ₂ CO ₃	Improving H ₂ production in HTG, alkalinity regulator, preventing coke formation, achieving higher deoxygenation in HTL		↓	↑			[90,119]

properties can further explain the solid product recovery yield increase reported in Table 2.

Xiong et al.[99] studied the influence of sodium persulfate during a hydrothermal treatment of SS. The introduction of sodium persulfate led to a noticeable increase in P recovery in the solid product, most probably because SO₄^{•-} radicals attack OP[117] and decompose it into free orthophosphates, later fixed in the solid phase by metal species[118].

Wang et al.[119] realized a supercritical water gasification of SS, with and without the addition of two alkaline additives, Na₂CO₃ and K₂CO₃. The carbonates addition resulted in a 54-fold higher P concentration in the liquid product, disengaging Ca from phosphates to form more stable Ca carbonates. K₂CO₃ seems to be more effective to increase

the P concentration in the liquid product[90], probably because K⁺ has a higher capacity to combine with aluminum ions, releasing orthophosphates from aluminum-P species.

In summary, P precipitation in the solid product can be improved through the addition of different reagents and flocculant agents, including Fe, Al, and Ca chlorides, sodium persulfate, and poly aluminium chloride. Among the chlorides, CaCl₂ leads to an increase in the AIP fraction, while Fe and Al chlorides increase the NAIP fraction.

3.5. Proposed mechanisms of phosphorus conversion

Overall, the experimental results collected from the literature appear

to indicate three main mechanisms involving P conversion during HT treatment of SS, as summarized by Fig. 9 and in the following points:

(i) OP mineralization to soluble orthophosphates, thus leading to a decrease in OP content in the liquid and/or solid phases, and to an increase in P concentrations in the liquid phase. The kinetic of OP mineralization to orthophosphate is primarily controlled by the temperature according to a Arrhenius kinetic law[84], with longer time required for OP mineralization at lower HT temperature (<180 °C). Acidic conditions and strong oxidizers further favor OP mineralization.

(ii) Dissolution of inorganic P compounds to soluble orthophosphates, thus leading to a decrease in the inorganic P content of the solid phase, and to an increase in P concentrations of the liquid phase. Physical properties of HT water (e.g. dielectric constants, ionic product) appear to be the main parameters controlling the dissolution of the different inorganic P compounds (e.g. Fe-P, Al-P, Ca-P complexes), according to their relative temperature to dissolution dependence. High T, high pH and CaO addition favor Fe-P and Al-P species dissolution, while acidic conditions and FeCl₃ and AlCl₃ addition promote Ca-P complexes dissolution.

(iii) Orthophosphates (re)-precipitation under the form of solid metal phosphates, thus leading to a decrease in P concentration of the liquid phase, and to an increase in the P recovery yield in the solid product [58,100]. The availability of metal cations (Ca²⁺, Fe³⁺, Al³⁺, Mg²⁺, and Mn²⁺), as well as the temperature, pH, and alkalinity conditions of the water process, are the main physical-chemical parameters controlling metal phosphate precipitation and P speciation in the solid products. Slightly acidic conditions and FeCl₃ and AlCl₃ addition promote Fe-P and Al-P complexes precipitation, while basic conditions (pH ≈ 8) and CaO or CaCl₂ addition favor Ca-P species precipitation.

4. Closing remarks and perspectives

P recovery from SS is considered as a critical strategy to satisfy the growing food-production demand and to reduce eutrophication[2,8]. It is the object of increasing attention from the scientific community, trying to find new value chains for sewage sludge disposal. From this perspective, thermal treatments have been extensively studied[23]. P and N can be recovered in the solid products (ashes and biochars) from the thermal treatments, which can be used directly as soil improvers or subjected to chemical extraction or other processes to recover the nutrients or remove heavy metals[3]. SS has a high-water content (>95%), which leads to high energy costs related to pre-drying treatments [17,28]. However, hydrothermal treatments are carried out in a wet medium, and the water itself improves heat and matter diffusion and

promotes polymerization, decarboxylation, and dehydration reactions [33,34]. P migration and speciation during SS hydrothermal treatments are the subjects of different studies. Through a critical analysis of the various variables that affect P migration in HT products, it is possible to better understand the mechanisms that regulate the nutrients' fate in these processes and the interactions between organic matter, nutrients, and metals. The parameters that influence P speciation and recovery are various, but HT severity is the one that has the largest impact on P migration and that has been extensively characterized. More specifically, the HT temperature is the factor that affects P speciation the most [60]: a temperature increase leads to a higher P recovery in the solid product, a lower P concentration in process water, the decomposition of OP, and the conversion of NAIP to AIP, although these assumptions can be made only for high enough temperatures that allow organic matter breakdown and metal compounds precipitation. Reaction time also influences P speciation, but the temperature effect seems to be prevalent. The influence of temperature and reaction time are not independent: it has been observed that time influences P speciation differently at different HT temperatures. Even though it has been suggested that low temperatures with longer times may have the same effect as shorter times with higher temperatures, the collected results do not allow to build a definitive picture of reaction time impact on P speciation. Future studies should further investigate reaction time role on nutrients reaction paths, to explore P transformation kinetics, which today constitute an important knowledge gap: a relatively simple kinetic model has been proposed for organic P decomposition and orthophosphates precipitation[85], but it has been conceived for high temperatures and short durations, further efforts should be made to realize a kinetics model for other HT conditions.

Very few data are available regarding the effect of pressure on P speciation during SS hydrothermal treatments. Further investigations are expected to clarify the role of this parameter on the properties and characteristics of HT products and P migration. A pressure increase has been correlated with a water dielectric constant increase, which would improve organic matter and organic P species dissolution.

Between the other parameters that influence P speciation, a higher SLR is correlated to an increased solid product recovery yield [50,64,102] and an increased P recovery in the solid product [50,64,102]. However, collected data were not sufficient to show a definite trend correlating P pathways and distribution to solid-to-liquid ratio, thus requiring further studies on the topic.

P recovery in the solid product can be enhanced by increasing the medium alkalinity and by adding different additives, Ca-containing ones such as CaO, CaCl₂, and Ca(OH)₂[48,52,64,80,91,94], but also other

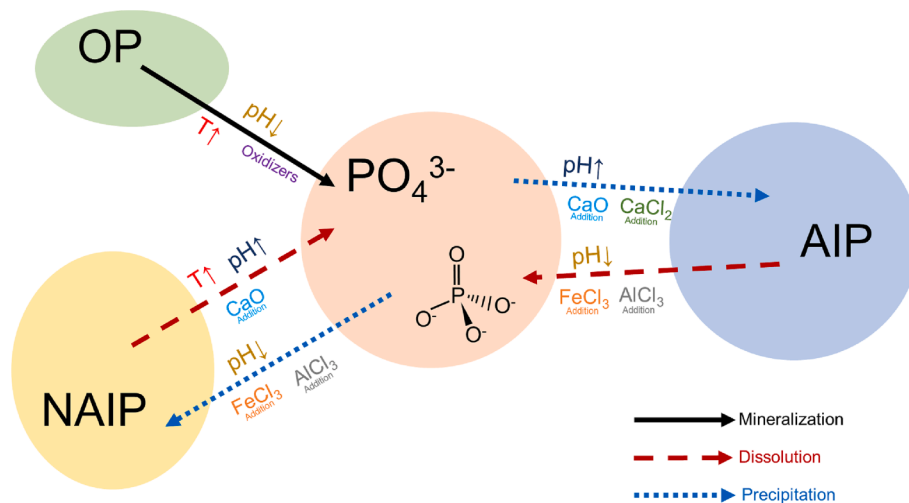


Fig. 9. Proposed main mechanisms involving P conversion during HT treatment of SS. OP = organic phosphorus; NAIP = non-apatitic inorganic phosphorus; AIP = apatitic inorganic phosphorus.

metals chlorides, namely FeCl₃ and AlCl₃, sodium persulfate, and poly aluminium chloride. By contrast, the dissolution of P in the liquid product can be promoted by lower pH[91,105,106] and the addition of Na₂CO₃ or K₂CO₃[119]. Higher pH and the addition of Ca-containing species have been associated with higher AIP yields, while the NAIP fraction can be increased by lower pH, and the addition of Fe- and Al-containing species. The AIP fraction appears to be quite interesting because it is less soluble and more thermodynamically stable than other P fractions at high temperatures. Considering HT products, P-containing species solubility needs to be fully investigated to study the viability of their valorization as fertilizers. Although a large percentage of soluble-P is interesting as it is readily available for plants, it is possible that unbalanced qualities of this nutrient are not absorbed in time and that they are lost because of erosion, runoff, weathering, and leaching. For this reason, the recovery of by-products that contain less soluble and more slow-release P is often the object of investigation, with the aim of producing high-efficiency P soil amendments. It has been shown that, since HT treatment leads to the transformation of soluble and unstable P species into more stable and less soluble species, HT solid products present reduced P leaching rate compared to raw SS[39]. In this perspective, the recovery of AIP-rich HT solid products is particularly interesting, and it could be opposed to other commonly applied P recovery processes such as struvite precipitation from SS leachates, which presents some complications including the incomplete N and P recovery and the necessary Mg addition.

Most of the reviewed studies operate at temperatures generally associated with HTC (T < 280 °C), and less experimental data are available for higher temperatures corresponding to HTL and HTG. For this reason, although the mechanisms related to P transformation during SS HT processes seem to be fundamentally the same above 300 °C, more effort is needed to better characterize P speciation during HTL and HTG.

The results of this review have allowed to describe the main tendencies and behaviors in P conversion and speciation during SS HT treatment, by proposing the main mechanisms and the most important parameters that play a role in this phenomenon. This first approach offers the basis to develop new studies that will specifically focus on the identification of the optimum parameters to maximize P recovery yield in the desired product. Then, further pilot-scale experiments will be required to elaborate an economic and environmental cost-benefit analysis that will assess the practical feasibility of the process. Indeed, HTL and HTG target products are respectively the bio-oil and the syngas, which could be used to optimize energy recovery from SS. Coupling the bio-oil and/or syngas production with nutrient recovery in the form of solid products with a practical economic value could allow reducing the costs, thus paving the way for new SS valorization routes. The cost-effectiveness of certain additives should be also the subject of further studies. For example, CaO dissolution in water is strongly exothermic, and, therefore, its use as reagent for Ca phosphate precipitation would allow to reduce the heating energy consumption of the HT process. Finally, a detailed assessment of pollutants in the HT products should be made (e.g. heavy metals, polycyclic aromatic hydrocarbon), in order to estimate the costs of their removal or the most suitable approaches to reduce their amount and hazard.

5. Conclusions

Phosphorus migration and speciation during sewage sludge hydrothermal treatments have been extensively investigated by collecting data available in the literature. Temperature is the parameter that influences P transformation the most. Results suggest that a reaction time increase has the same effect as a temperature increase, but to a lesser extent. Water content, pH, and the presence of additives also affect P migration and the relative distribution between apatitic and non-apatitic P in hydrochar. Additional investigations should be made to further explore P transformation at HTL and HTG conditions, and to fill the knowledge gap regarding the kinetics of this phenomenon.

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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