Effect of chlorination during sewage sludge thermochemical treatment: phosphorus recovery and trace metal elements vaporization

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Phosphorus (P) is a non-substitutable vital element for life and food production (Ruttenberg, 2003). It is also a strategic resource as the modern agricultural system has become highly dependent on P-based industrial fertilizers massive application on fields. These fertilizers are however mostly produced through the exploitation of non-renewable phosphate rock (PR) deposits (Cordell, 2009). Even if the scientific community is split about whether or not the reserve depletion will occur within 50 or 300 years, there is a general consensus on (i) the uneven distribution of PR deposits around the world, (ii) the remaining PR decreasing quality and (iii) the increasing extraction processing and shipping costs (Daneshgar, 2018). Consequently, finding alternative ways with circular economy approach to secure P for fertilizer applications has become one of the major challenges for the next decade.

Among several options, the P recovery from sewage sludge (SS) has gathered the interest of many scientists (Raheem, 2018). Indeed, SS contains the second greatest amounts of P after bone meal and has the main advantage of being abundantly produced worldwide. However, due to trace metal elements (TME), microbiologic and organic pollutants presence, SS are most of the time incinerated for energy production and not further valorized as a secondary P resource (Schnell, 2020). Indeed, in such thermal processes the TME (Cr, Ni, Cu, Pb, Zn…) are concentrated along with P in the solid residues. European legislation will thus evolved. In 2026 in Switzerland, it will be mandatory to recover at least 80% of the P contained in SS before final disposal, while Germany, France and the EU may follow before 2030. Simple SS incineration processes will therefore not be further possible. Finding a way to recover both P and energy during SS treatment is therefore highly desirable (Gao, 2020).

Alternative SS thermochemical treatments may be a solution. The idea is to thermally treat SS with chemical additives to produce energy and P-rich solid residues that may be directly valorized as fertilizers or soil conditioners (Meng, 2019). Cl-based compounds such as $MgCl_2$, $CaCl_2$, PVC, NaCl, KCl… are the most frequently used (Adam, 2009). The roll of these additives is to help fix P under bioavailable forms in solid residues (interaction with Mg, Ca, Na, K…) while promoting TME vaporization through the gas phase (chlorination mechanisms). Current existing thermochemical treatments can be performed either in one (Xia, 2020) or two steps (Adam, 2009). In two step processes, SS are first incinerated (energy production and waste volume reduction), then the obtained ashes are thermochemically treated with additives for P recovery (Nowak, 2010). The two step processes have been extensively studied during the last decades due to existing widespread SS incinerators (Schnell, 2020). In single step SS thermochemical processes, the sludge are directly treated with additives either by incineration, pyrolysis or gasification, with the combined aim to recover energy and P. Despite advantages of single industrial installation, only few studies focus on the single step SS thermochemical treatments. Furthermore, to our knowledge, no one-step sewage sludge gasification experiments, with the aim to recover phosphorus in the solid residues and vaporize TME were reported so far.

In the present work, thanks to the combination of (i) existing literature data compilation, (ii) thermodynamic equilibrium simulations (FactSage 8.0 software) (iii) laboratory-scale and (iv) pilot-scale experiments, the impact on TME vaporization and P availability of various operating parameters during one-step SS thermochemical treatments will be explored.

First, the following parameters were studied and discussed during SS thermochemical treatments thanks to literature and simulation data compilation: thermal treatment temperature, sludge residence time, reactor type (fixed-bed, rotary, fluidized bed), treatment gas composition (air, N_2, H_2O presence), additives nature (Cl-based) and concentration, and initial SS composition (majors). Table 1 presents the most relevant parameters influencing P bioavailability and TME vaporization properties during SS thermochemical treatment with $MgCl_2$ addition. The presented results showed that, even if Ni and Cr vaporizations are limited, $MgCl_2$ use allows removal rates higher

than 90 % for Cd, Cu, Pb and Zn combined with interesting P fixation (> 90 %) and bioavailability rates ($Mg_3(PO_4)_2$ formation). $MgCl_2$ is thus considered as one of the most efficient additives for SS thermochemical treatment (Yu, 2016). Similar compilations were also performed for other Cl-donors such as $CaCl_2$, NaCl, KCl and PVC.

Table 1 – Relevant parameters influencing P bioavailability and TME vaporization during sewage sludge thermochemical treatment with $MgCl_2$ addition

TME	$MgCl_2$ addition			Increasing temperature	Optimal T (°C)	Gas composition			Majors in SS	Maximal removal (%)
	impact	g Cl/kg	Mechanisms			N_2	Air	H_2O		
As	(+)	100-200	$Mg_3(AsO_4)_2$	(+)	≥ 700	/	/	/	++ Si	60
Cd	(+)	100-200	Low interaction	++	≥ 700	0	0	++	- Si	>95
Cr	(-)	0-150	CrO_4^{2-} formation	+	≥ 1200	-	+	- -	- - Ca	30
Cu	++	≥ 100	$(CuCl)_3$ + CuCl	++	≥ 900	-	+	/	+ Si	>95
Ni	(+)	100-200	Low interaction	+	≥ 1200	/	/	- -	- Fe	40
Pb	++	≥ 50	$PbCl_2$ formation	++	≥ 800	0	0	/	+ Ca	>95
Zn	++	≥ 150	$ZnCl_2$ formation	+	≥ 1000	0	0	(-)	(+) Si	>95
P	++	≥ 50	$Mg_3(PO_4)_2$ formation	+	≥ 900	/	/	/	- Al, Fe	Fixation >90 Solubility >80

++ strongly positive influence
+ positive influence
(+) low positive influence
0 no influence
(−) low negative influence
− negative influence
− − strongly negative influence

Then, specific SS thermochemical treatments with selected Cl-donors were performed at laboratory-scale, with the aim to understand and optimize the additives interaction pathways with TME and P. Indeed, in the literature, the Cl-donors are most of the time used in high excess during SS thermochemical treatments, leading to important unreacted chlorine loss through the gas phase. Different operating conditions were therefore studied, and all prepared mixtures were treated in a tubular furnace at 1000°C under air excess and with a 4h residence time. The obtained ashes were characterized by XRD to identify the principal crystalline forms and by ED-XRF to determine the TME vaporization rates. A special focus was also done on phosphorus. First the bioavailable P forms were extracted in water, citric acid and neutral ammonium citrate and dosed by ICP-AES. Then, P was fractioned in organic, inorganic, apatite, non-apatite and residue, thanks to Williams-Saunders method.

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