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Trace metal elements vaporization and phosphorus recovery during sewage sludge thermochemical treatment – A review

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1 **Trace metal elements vaporization and phosphorus recovery during sewage**
2 **sludge thermochemical treatment, a review**

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6 **Abstract**

7 Phosphorus (P) plays essential roles in crops growth. Natural mineral sources of phosphate are non-
8 renewable, overexploited and unevenly distributed worldwide, making P a strategic resource for
9 agricultural systems. The search for sustainable ways to secure P supply for fertilizer production has
10 therefore become a critical issue worldwide. Sewage sludge (SS) is an organic waste material
11 considered as a key alternative source of P. Switzerland and the European Union are is about to make
12 it mandatory to recover P from SS or its treatment residues. Among the many technical options to
13 achieve this objective, SS thermochemical treatments spiked with Cl-donors appear as a promising
14 approach to recover P from SS and separate it from mineral pollutants such as trace metal elements
15 (TME). The purpose of Cl-donor additives is to fix P within the mineral residues, possibly in
16 bioavailable P species forms, while promoting TME vaporization by chlorination mechanisms. This
17 review paper compares the various thermochemical treatments investigated worldwide over the
18 past two decades. The influence of process conditions and Cl-donor nature is discussed. The
19 presented results show that, except for nickel and chromium, most TME can be significantly
20 vaporized during a high temperature treatment (over 900 °C) with Cl addition. In addition, the
21 fixation rate and solubility of P is increased when a Cl-donor such as MgCl₂ is added.

22 **Key words**

23 Phosphorus recovery, trace metal elements, Sewage sludge, Thermochemical treatment,
24 Vaporization

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51 1. Introduction

52 Phosphorus (P) is a vital element for all life forms that cannot be substituted [1]. It is a component of
53 key biomolecules such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine
54 triphosphate (ATP), etc. At the cellular level, phosphate bounds biosynthesis and hydrolysis are
55 universal mechanisms for energy exchanges in all living beings' metabolism [2]. At a more
56 macroscopic level, P availability is often a limiting factor for plants growth in natural ecosystems [3].
57 Agriculture therefore uses P as a key fertilizing element to stimulate crops development and increase
58 production yields. In natural ecosystems, P fluxes occur in a quasi-closed loop, with negligible runoffs
59 [4]. Anthropogenic pressures however induce dramatic alterations of P biogeochemical cycles through
60 unbalanced inflows and outflows massive intensification. In agriculture for example, crops are
61 exported from the agricultural sites to distant food processing units, which then further distribute
62 food products to consumption places all over the world. Herbicides, fungicides and insecticides
63 massive use also strongly affects phosphorus dynamics in agricultural soils [4–6]. Consequently, P-
64 rich fertilizer continual application has become necessary, to compensate for its exportation in crops
65 and food production [1–3,5–11]. P has therefore become a strategic resource that needs to be
66 available in high amounts for industrial-scale fertilizer production [1,2,7,9,12–14].

67 P is the 11th most abundant element in the earth crust [9]. It is distributed around the world
68 mostly under mineral forms (aluminum/iron and calcium phosphate) contained in sedimentary rocks
69 [15]. Phosphate rocks (PR) deposits containing enough P to be economically exploitable (13-14wt%)
70 are however scarce and non-renewable resources [1]. Few prospects exist for new discoveries [15].
71 Even if the scientific community is split about whether or not the reserve depletion will occur within
72 50 or 300 years, there is a general consensus on (i) the uneven distribution of PR deposits around the
73 world (around 70% of the world total reserves are in Morocco and Western Sahara only), (ii) the
74 decreasing quality of remaining PR resources and (iii) the increasing extraction processing and
75 shipping costs [1,2,9,16]. Finding alternatives to secure P for fertilizer production has therefore
76 become one of the objectives for sustainable development in the next decades [2,7,10,17–20].

77 The major option to slowdown PR deposits depletion is to reduce P wastage [2,14,17,21].
78 According to Daneshgar et al. [2], only about 16% of the mined P is actually consumed by humans in
79 the current anthropogenic P cycle. Most of it is lost by leaching from cropland, improper animal
80 waste disposal and food waste production [2]. Several studies proposed solutions to limit P leaking
81 from the anthropogenic cycle [6,7,14,17,18,21–24], with highly positive environmental impacts by
82 limiting eutrophication phenomenon [2,25,26].

83 The second option is to increase P recycling from human and animal waste materials [27–32].
84 Among the waste materials of concern, sewage sludge (SS) contains the second strongest amount of
85 P, after bone meal [27,33,34]. It is a complex heterogeneous mixture of microorganisms, undigested
86 organics such as paper, plant residues, oils, fecal materials, inorganic materials and moisture [35,36].
87 It has been estimated that the sludge produced by developed countries in the world exceeds 30
88 million tons per year (dry sludge), and this amount is still rising [36]. SS is a potential resource for
89 nutrients and energy [35]. The most common treatments currently applied are (i) direct land
90 spreading applications, (ii) production by composting of an organic soil conditioner, and (iii)
91 production of heat or other energy vectors by thermochemical or anaerobic biological processes [37–
92 39].

93 SS direct (or after composting) land spreading allows to recycle P and other nutrients [33].
94 However, due to the presence of potentially toxic trace metal elements (TME), organic pollutants and
95 possibly microbial pathogens this practice is strongly regulated [27,29,34]. Thermochemical

96 processes such as incineration, gasification and pyrolysis allow to recover energy from SS while
97 neutralizing microbiologic and organic pollutants through high temperature treatment [37–40].
98 However, poorly volatile TME such as chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), etc.
99 concentrate in the solid residues, which may induce environmental limits or constraints to their use
100 or disposal [33]. In addition, high temperature thermochemical treatments can induce small amounts
101 of P and other nutrients vaporization, which are then lost from the solid residues [41,42]. Finding a
102 way to recover both nutrients and energy from SS is therefore a scientific and technical challenge
103 [8,29].

104 One of the solutions under investigation is to operate thermochemical treatments with
105 controlled additions of various additives [37,39,40], in the purpose of producing energy and
106 bioavailable P-rich solid residues that may be used in the formulation of fertilizers or soil
107 conditioners. Cl-based compounds such as MgCl₂, CaCl₂, polyvinyl chloride (PVC), NaCl and KCl are
108 the most frequently used additives [43–78]. Their role is to help fix and form bioavailable P species in
109 the solid residues (interaction with Mg, Ca, Na, K, etc.) while promoting TME vaporization through
110 the gas phase (chlorination mechanisms). The thermochemical treatments with Cl-donor can be
111 performed either in one [62,63,65] or two steps [45–47]. In the two-step processes, SS is first
112 thermochemically treated without additives for energy production and waste volume reduction
113 (classic incineration, pyrolysis or gasification processes), and the resulting ashes are further
114 thermochemically post-treated at high temperature with Cl-based additives [38].

115 In 2026 in Switzerland, it will be mandatory to recover 50 to 80% of the P contained in SS before
116 final disposal. Germany, France and the EU may follow before 2030. Along with other P recovery or
117 removal technologies, SS thermochemical treatments with Cl-donor may therefore develop strongly
118 in the coming years. In general, these processes allow almost all P to remain within the solid
119 residues. The primary scientific/industrial issue is therefore to enhance TME removal through the gas
120 phase. The impact of SS thermochemical treatments on TME vaporization properties with Cl-donors
121 [43–78] and without additives [79–94] have been extensively studied these past decades. However,
122 only small paragraphs in review papers have a special focus on both TME vaporization and P recovery
123 [8,34,94,95].

124 The objective of this synthesis article is therefore to provide an in-depth critical review aggregating
125 reported findings about TME vaporization rates improvement and bioavailable P fixation in solid
126 residues during SS or SS ashes thermochemical treatments. A focus is first made on the TME removal
127 efficiency during classic SS thermochemical treatment without additives. Then, thermochemical
128 processes with Cl-donors are extensively explored with a focus on the effects of the additive's
129 nature, processes and operating conditions on TME vaporization. It is important to note that, in this
130 review paper, only three thermochemical treatments are considered: incineration, pyrolysis and
131 gasification. The Cl-donors influence on the bioavailability of P species is finally discussed.

132 2. Sewage sludge and trace metal elements

133 2.1. Sewage sludge use and disposal

134 SS is a waste material produced in high amount all over the world [36]. It is generated all along the
135 wastewater treatment process, with various composition depending on the water origin and the
136 treatment steps [33]. According to Rulkens et al. [36], SS is a complex heterogeneous mixture
137 characterized by six groups of components:

- 138 - Water (content varying from 1-2 to more than 95%),

- 139 - Nontoxic organic carbon compounds ($\approx 60\%$ on a dry basis), mostly from biological origin,
- 140 - Nitrogen (N) and phosphorus containing components,
- 141 - Toxic inorganic and organic pollutants:
 - 142 ○ TME such as Zn, lead (Pb), Cu, Cr, Ni, cadmium (Cd), mercury (Hg), and arsenic (As)
 - 143 (contents from < 1 to > 1000 mg/kg),
 - 144 ○ Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins,
 - 145 pesticides, linear-alkyl-sulfonates, nonyl-phenols, polybrominated fire retardants, etc.
- 146 - Pathogens and other microbiological pollutants,
- 147 - Inorganic compounds, such as silicates, aluminates, calcium and magnesium containing
- 148 compounds.

149 Although SS is considered as a waste material, two components can technically and
 150 economically be recycled from SS: nutrients (primarily N and P) and energy (directly linked to carbon
 151 content) [35]. Depending on their origin and composition different recovery processes are therefore
 152 possible: agricultural spreading or composting (nutrients recovery) or thermochemical treatment
 153 (energy recovery). In 2019 in France, 30% of the SS were co-composted with green/organic waste,
 154 40% directly spread on fields, 28% incinerated and 2% buried. The disposal pathways differ strongly
 155 from country to country in the EU [78]. For example, in Germany, more than 55% of the produced
 156 sludge are incinerated, while for the Netherlands and in Switzerland 100% are thermochemically
 157 treated (incineration mostly) [38].

158 SS direct use as fertilizers or soil conditioners is highly regulated and therefore limited in EU due
 159 to TME, pathogens, microbiological and organic pollutants presence in the raw material [38]. **Table 1**
 160 presents the European, French, German and Swiss regulations concerning the maximal TME contents
 161 in recycled fertilizer products. Arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc
 162 are the 8 TME concerned by these regulations. Furthermore, SS is produced all year long while
 163 fertilizers are applied to fields only once or twice a year. Storage is therefore necessary and can be
 164 complicated due to fermentation processes [33]. To limit this issue, SS can be composted or co-
 165 composted with other organic waste materials, for further use in agricultural spreading and by
 166 nurserymen and municipalities. However, neither the TME nor all the pathogens, microbiological and
 167 organic pollutants are eliminated by composting. Only a dilution effect can occur so that co-
 168 composting processes comply with the regulations.

Table 1 – Regulations for TME threshold values in fertilizing products in EU, France, Switzerland and Germany

TME	French regulation, 2020		EU regulation, fertilizers, 2019	German regulation, fertilizers, 2017	Swiss regulation, fertilizers, 2019	
	Fertilizers	Culture carrier			mg/kg P	mg/kg dry matter*
	mg/kg dry matter	mg/kg dry matter	mg/kg dry matter	mg/kg dry matter		
As	40	40	40	40	100	5
Cd	1	1	3	1.5	25	1.25
Cr VI	/	/	2	2	/	/
Cr tot	120	150	/	/	1000	50
Cu	300	200	600	900	3000	150
Ni	50	50	100	80	500	25
Pb	120	120	120	150	500	25
Hg	1	1	1	1	2	0.1
Zn	800	500	1500	5000	10000	500

* Calculation for SS ashes containing 5wt% of P

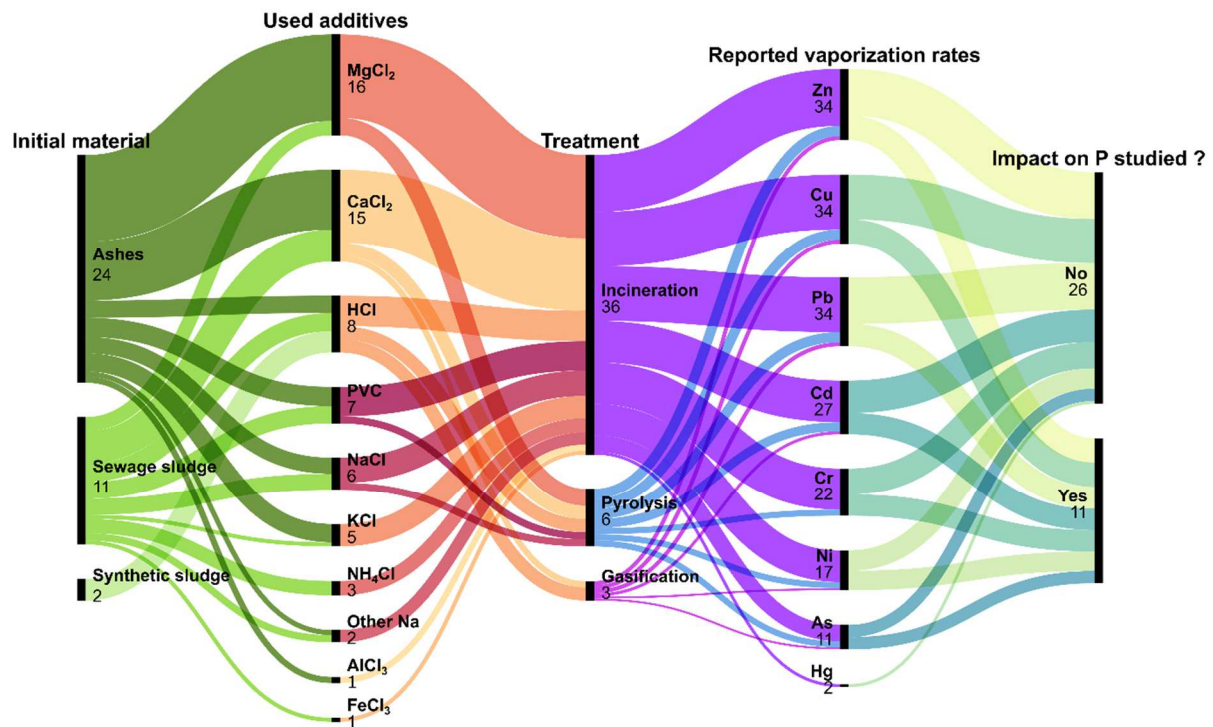
169 As explained previously, an important part of SS is energetically recovered (55% of the produced
 170 SS in Germany) [40]. Three thermochemical processes are suitable: incineration, gasification and

171 pyrolysis [39]. In addition to energy recovery, they allow to neutralize microbiologic and organic
172 pollutants through high temperature treatment. The most used is by far SS incineration [37]. Its goal
173 is to burn the organic part of SS to produce energy and significantly reduce the waste volume [38]. In
174 2020 in Germany, about half of the thermally treated sludge was mono-incinerated and the other
175 half co-incinerated with coal, in cement kilns or waste incineration plants. Pyrolysis and gasification
176 treatments are for now limited and mostly tested at the bench or pilot scale [38].

177 Ashes produced after classic thermochemical processing are difficult to further reuse. Indeed,
178 most TME are concentrated along with P and other nutrients in the solid residues [33]. To recover P,
179 thermochemical post-treatments at high temperature (800 to 1200 °C) gathered scientists' interest
180 during the last two decades [43–55,57,59,64,66,67,71–76]. They are based on various Cl-donors use
181 such as $MgCl_2$, $CaCl_2$, PVC, NaCl and KCl. Indeed, their addition help fix and form bioavailable P
182 species in the solid residues thanks to interaction with Mg, Ca, Na and K, while promoting TME
183 vaporization through the gas phase via chlorination mechanisms [45–47]. The main limitation of such
184 thermochemical post-treatments, is that the overall SS recovery process is carried out in two steps,
185 limiting the energy efficiency (energy input is required for the thermochemical post-treatment step).
186 To limit this issue, the thermochemical ash treatment step can be integrated into a waste incinerator,
187 as in the CT-Fluapur®-process [52]. The hot gases produced during incineration step can thus be
188 mixed with HCl from the incinerator's acid scrubber and used as both a heat and Cl sources for the
189 ashes post-treatment. However, according to Nowak et al. [52], the system complexity and the costly
190 equipment required currently limit the process development.

191 Single step (or direct) SS thermochemical treatments are also suitable, with the same additives
192 than for two-step processes [42,56,58,60–63,65,68–70,77,78]. In such processes, SS is directly
193 treated with $MgCl_2$, $CaCl_2$, PVC, NaCl and/or KCl, either by incineration, pyrolysis or gasification, with
194 the combined aim to recover energy and P. Despite advantages of single industrial installation, fewer
195 studies focus on the single step SS thermochemical treatments in comparison with two-step
196 processes.

197 **Fig. 1** was built thanks to literature data [43–78]. It allows to have a broad view of the works
198 investigating the impact of SS or SS ashes thermochemical treatment with Cl-donors on the TME
199 vaporization properties and/or P bioavailability. The figure (alluvial diagram) shows the number of
200 publications (for a total of 37) dealing with the following parameters: (i) the initial material form (SS,
201 SS ashes or synthetic SS), (ii) the Cl-donor used ($MgCl_2$, $CaCl_2$, (...) and/or $FeCl_3$), (iii) the
202 thermochemical treatment performed (incineration, pyrolysis or gasification), (iv) the TME
203 vaporization properties reported (As, Cu, (...) and/or Hg) and (v) whether or not the P bioavailability
204 is studied. It is important to note that multiple parameters can be studied in only one work.



205

206 **Figure 1** – Alluvial diagram built thanks to literature data [43–78] and showing the number of publications (for a total of 37)
 207 dealing with the following parameters: (i) the initial material form, (ii) the Cl-donor used, (iii) the thermochemical treatment
 208 performed, (iv) the TME vaporization properties reported and (v) whether or not the P bioavailability is studied

209 **Fig. 1** shows that, in 24 of the 37 publications selected, SS ashes are used, almost always
 210 incinerated and preferentially with MgCl₂ or CaCl₂ as Cl-donor (in 16 and 15 works respectively).
 211 Direct SS treatment with other Cl compounds by pyrolysis or gasification is only little studied.
 212 Regarding the TME, Zn, Cu and Pb are the most often studied (34 publications) while only 2 and 11
 213 works investigate Hg and As behavior respectively. Finally, only 11 of the 37 publications deal with
 214 the question of P bioavailability in the solid residues obtained after treatment. In addition to the
 215 works compiled in **Fig. 1** dealing with thermochemical treatment with Cl-donors [43–78], the TME
 216 vaporization properties also have been extensively studied during SS or SS ashes thermochemical
 217 treatment without Cl-donor [79–94] and thanks to thermodynamic simulations tools [43–
 218 45,66,68,69,74–77,96–99]. The results from these works are further discussed.

219 Either during one or two-steps SS thermochemical treatments, TME removal rates and P species
 220 formed are highly dependent on the following operating conditions that are extensively studied in
 221 the next parts of this paper:

- 222 - Initial material nature (raw SS or SS ashes) and composition (major elements contents),
- 223 - Additives nature: MgCl₂, CaCl₂, PVC, NaCl, KCl, etc. and amount added (Cl concentration),
- 224 - Type of reactor used: fixed-bed, rotary kiln, fluidized bed and material residence time,
- 225 - Treatment temperature,
- 226 - Treatment gas composition (depends on the chosen thermochemical processes, i.e.
 227 incineration, pyrolysis or gasification): oxidative or reductive atmosphere, H₂O presence, etc.

228 2.2. Trace metal elements speciation in sewage sludge

229 During SS or SS ashes thermochemical treatment and depending on the operating conditions, the
 230 TME can be vaporized through the gas phase. In this part, a special focus on the vaporization

231 properties of the 8 TME whose contents are regulated for recycled fertilizers (**Table 1**) is therefore
 232 made.

233 As detailed previously, SS is a complex heterogeneous mixture [36]. Indeed, its composition
 234 depends on various parameters such as the sludge origin (industrial and/or municipal wastewater)
 235 and pretreatments performed (biological treatment, Al or Fe based coagulants use, etc.). In addition,
 236 SS can be mixed with municipal solid waste before thermochemical treatment. It results in high
 237 variation in elemental composition and speciation for the treated materials [78]. In SS, the TME are
 238 generally not under elemental state but under various forms (oxides, chlorides, sulphates, sulphides,
 239 carbonates, organic, combined with major elements, etc.). **Table 2** thus presents the most common
 240 forms in SS for the 8 TME of interest according to Udayanga et al. [94], and their physical properties
 241 (melting and boiling points) [88,89,94].

Table 2 – Most common TME forms in SS and their physical properties [88,89,94]				
TME	Forms	Example	Normal melting point (°C)	Normal boiling point (°C)
Arsenic	Elemental	As	817 (28 bar)	615
	Chloride	AsCl ₃	-16	130
	Sulfide	As ₂ S ₃	310	707
	Oxide	As ₂ O ₃	275-313	193 (sublimation)
Cadmium	Elemental	Cd	321	767
	Chloride	CdCl ₂	564	960
	Sulfate	CdSO ₄	1000 (decomposition)	
	Sulfide	CdS	1750	980 (sublimation)
	Oxide	CdO	1540 (sublimation)	
Chromium	Elemental	Cr	1907	2671
	Chloride	CrCl ₂	815	1300
		CrCl ₃	631	945
		CrO ₂ Cl ₂	-96.5	117
	Sulfate	Cr ₂ (SO ₄) ₃	90	700 (decomposition)
	Sulfide	Cr ₂ S ₃	1350	n.a.
Oxide	Cr ₂ O ₃	2435	4000	
Copper	Elemental	Cu	1085	2562
	Chloride	CuCl	451	1212
		CuCl ₂	498	993
	Sulfate	Cu ₂ SO ₄	110	n.a.
		CuSO ₄	560 (decomposition)	
	Sulfide	CuS	500 (decomposition)	
Oxide	Cu ₂ O	1236	1800 (decomposition)	
Mercury	Elemental	Hg	-39	357
	Chloride	HgCl ₂	276	304
		Hg ₂ Cl ₂	525	383 (sublimation)
Lead	Elemental	Pb	327	1749
	Chloride	PbCl ₂	501	954
		PbCl ₄	-15	50
		Sulfide	PbS	1112
	Sulfate	PbSO ₄	1087 (decomposition)	
	Oxide	PbO	886	1470
		PbO ₂	290 (decomposition)	
Carbonate	PbCO ₃	315 (decomposition)		
Nickel	Elemental	Ni	1455	2913
	Chloride	NiCl ₂	1009	970 (sublimation)
	Sulfate	NiSO ₄	100	840 (decomposition)
	Sulfide	NiS	797	1388
	Oxide	NiO	1955	n.a.
Zinc	Elemental	Zn	420	907
	Chloride	ZnCl ₂	317	732
	Sulfate	ZnSO ₄	680 (decomposition)	
	Sulfide	ZnS	1700	1180 (sublimation)

	Oxide	ZnO	1975	2000 (sublimation)
--	-------	-----	------	--------------------

In **bold**, the predominant forms of TME in SS according to Udayanga et al. [94]

n.a.: not available

242 In elemental form, Hg has the lowest vaporization temperature under normal pressure (357 °C)
 243 followed by As and Cd (615 and 767 °C respectively). Zn vaporizes at 907 °C and Pb at 1749 °C. Cu, Cr
 244 and Ni have higher vaporization temperatures of 2562, 2671 and 2913 °C respectively (**Table 2**). The
 245 TME vaporization properties in SS can however be divided into three categories, as reported by
 246 Fraissler et al. [43]:

- 247 - Cd, Hg and Pb are “easily volatile TME”. The low Cd boiling point of 767 °C and the Pb fusion
 248 temperature of 327 °C allow removal to the gas phase at low temperature (in droplet form
 249 for Pb). Hg can also be classified as an easily volatile TME due to its low vaporization
 250 temperature of 357 °C.
- 251 - Zn, Cu and As are “semi-volatile TME”. Zn vaporizes at 907 °C and, for Cu, even if the element
 252 has a high boiling point (2562 °C), its high mobility allows the formation of more easily
 253 volatile species during thermochemical treatment (chloride, sulfide, etc.). For As, although it
 254 should vaporize “easily” at 615 °C, its strong interactions with SS major elements [77] lead to
 255 variable vaporization properties [62,77,90].
- 256 - Cr and Ni are “low-volatile TME”. Their vaporization temperatures are high (2671 and 2913
 257 °C respectively), and the two species present a low mobility.

258 Regarding the normal boiling point changes between different TME forms presented in **Table 2**, it is
 259 clear that the TME volatilities are highly impacted by their speciation. For example, Cu in elemental
 260 form vaporizes at 2562 °C while CuCl₂ normal boiling point is at 993 °C. It is interesting to note that,
 261 except for Cd, the chlorides species most of the time have the lowest vaporization temperature. It
 262 explains why the addition of Cl-compounds combined with a high temperature treatment is
 263 particularly interesting to promote TME vaporization. It is further extensively discussed.

264 3. Sewage sludge thermochemical treatment without additives

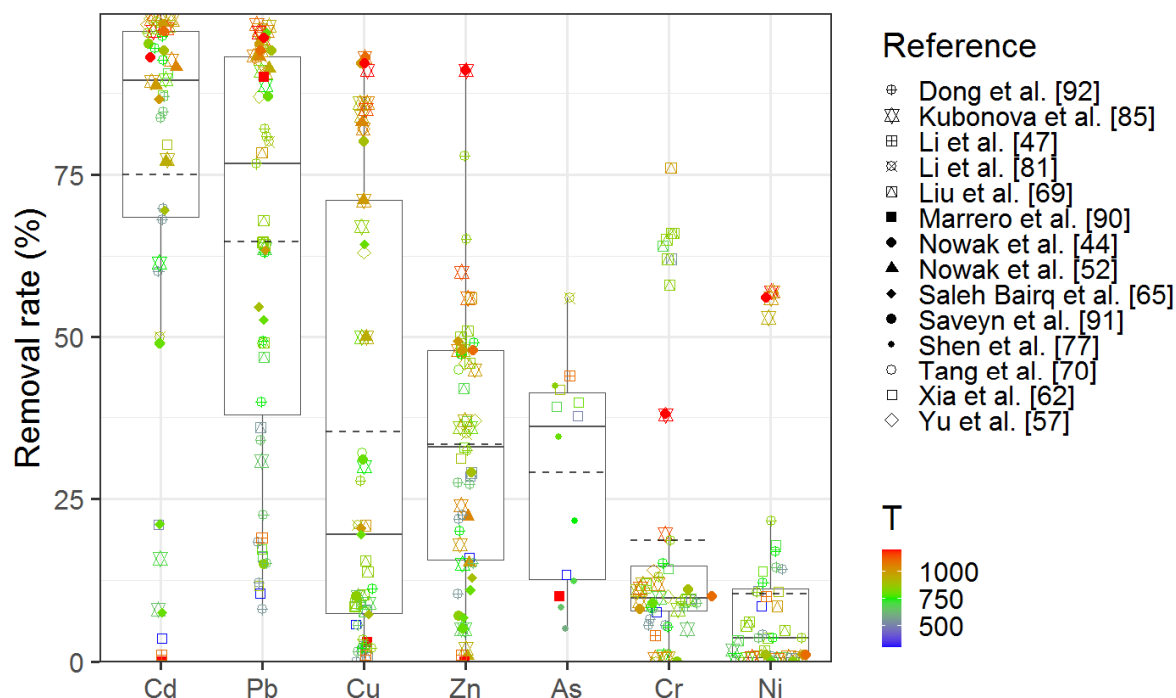
265 **Table S1** gathers results from [52,62,65,69,77,81,85,90–92] and presents the TME removal rates
 266 during classic SS thermochemical treatment without additives under various operating conditions.
 267 The TME removal rates were replicated from the various works explored (values extracted from
 268 graphs most of the time). The variations of the following parameters are reported:

- 269 - Feed material nature and composition (dried SS or ashes and CaO or SiO₂-rich),
- 270 - Residence time (1.5 to 1440 min) and reactor type (fixed-bed, fluidized bed and rotary kiln),
- 271 - Treatment gas nature (air, H₂O and N₂ – i.e. oxidative or reductive treatment conditions),
- 272 - Process temperature (300 to 1200 °C).

273 Because of its high volatility (vaporization temperature of 357 °C, **Table 2**), Hg behavior during
 274 SS thermochemical treatment is most of the time not explored. It is always considered to be
 275 vaporized significantly irrespective of treatment conditions [99]. Temperature seems to be the most
 276 important parameter for Hg removal in the gas phase [99].

277 To ease the reading and subsequent discussions, the principal results from literature concerning
 278 TME removal rates during classic SS thermochemical treatment without additives are also presented
 279 in **Fig. 2**. The figure is a box plot and was built with the results compiled in **Table S1**. It represents the
 280 removal rates for each TME. The different references studied are visible via the points shape while
 281 the treatment temperature is represented by the color scale (blue at 300, green at 750 and red at
 282 1200 °C). The mean (dotted horizontal line) and median (horizontal line) removal rates for each TME

283 are also shown, along with the first and third quartiles (black rectangles) and the 95% confidence
 284 interval (black vertical line). **Fig. 2** is widely discussed afterwards.



285
 286 **Figure 2** – Boxplots compiling data from Table S1 and representing the reported Cd, Pb, Cu, Zn, As, Cr and Ni removal rates
 287 as a function of the treatment temperature (color scale) and the reference studied (shape scale). The mean (dotted
 288 horizontal line) and median (horizontal line) removal rates for each TME are also shown, along with the first and third
 289 quartiles (black rectangles) and the 95% confidence interval (black vertical line).

290 As visible in **Fig. 2**, reported TME removal rates confirm the classification as high-volatile for Cd
 291 and Pb, semi-volatile for As, Cu and Zn, and low-volatile for Cr and Ni [43].

292 The TME removal rates compiled in **Table S1** and **Fig. 2** allow to investigate the impact of the
 293 operating conditions on their vaporization properties during SS classic thermochemical treatment
 294 without additives. The general trends and the most relevant parameters influencing TME removal are
 295 summarized in **Table 3** and are further discussed for each TME. **Table 3** was also built thanks to
 296 results from various thermodynamic simulations experiments [43–45,66,68,69,74–77,96–99]. In
 297 these works, SS thermochemical treatments under various operating conditions (temperature,
 298 atmosphere, initial composition) were explored via simulation tools such as FactSage, ChemSheet or
 299 HSC Chemistry.

Table 3 – Summary table: relevant parameters influencing TME removal during SS or SS ashes thermochemical treatment without additives

TME	Mean - median removal rates (%)	↗ temperature	↗ residence time	Reactor type	Thermochemical treatment type	Major elements predominance				Treatment gas nature		
						Al	Ca	Fe	Si	H ₂ O	O ₂	N ₂
As	29 - 36	+	(+)	/	(+) Pyrolysis	--	-	/	++	/	/	(+)
Cd	75 - 89	++	+	(+) Fixed bed	(+) Pyrolysis	0	(+)	0	-	+	0	(+)
Cr	19 - 10	+	+	(+) Fixed bed	(+) Combustion	0	(-)	0	++	--	+	(-)
Cu	35 - 20	+	++	(+) Fixed bed	+ Combustion	(+)	+	(-)	(+)	(+)	+	-
Hg	/	++	/	/	/	/	/	/	/	/	/	/
Ni	10 - 4	+	+	++ Rotary	+ Combustion	0	0	-	(-)	-	+	-
Pb	65 - 77	+	+	(+) Fixed bed	+ Combustion	0	+	0	+	-	++	--
Zn	33 - 33	++	+	- Rotary	(+) Gasification	(-)	+	(-)	+	-	-	+

++ strong positive influence		(-) low negative influence
+ positive influence	0 no influence	- negative influence
(+) low positive influence	/ not studied	-- strong negative influence

300 3.1. High-volatile TME – Cd and Pb

301 Reported Cd removal rates during SS thermochemical treatment without additives varied from 0 to
302 99%, depending on operating conditions, with a 75% mean vaporization rate (**Fig. 2**) [52,62,85,92].
303 According to Fraissler et al. [43], during thermochemical treatment, Cd vaporizes under Cd(OH)₂, CdO
304 and Cd gas forms. The authors also reported that to increase removal rate, temperature is the most
305 important parameter followed by SiO₂ absence (Si-rich sludge leads to CdSiO₃ formation which is a
306 stable compound), H₂O presence (to promote Cd(OH)₂ production) and a long treatment residence
307 time. It is confirmed in **Fig. 2** showing that the highest Cd removal rates are mostly observed for
308 treatment temperatures above 800 °C (orange and red points).

309 Lead vaporization varies from 10 to 99% depending on operating conditions, with a 65% mean
310 vaporization rate (**Fig. 2**). It is temperature dependent and promoted under oxidative conditions
311 (**Tables 3 and S1**) [92]. Indeed, Pb removal rates higher than 80% were most of the time reported
312 when the treatment temperature was above 800 °C (orange and red points, **Fig. 2**) [52,81,85,90,92].
313 The residence time also seems to be an important parameter for Pb removal with rates ranging from
314 53 to 97% when it increases from 60 to 120 min, as reported by Saleh Bairq et al. [65] (**Table S1**). On
315 the contrary, pyrolysis and H₂O gasification treatments have a strong negative impact on Pb
316 vaporization, with removal rates below 20%, as reported by Xia et al. [62] and Saveyn et al. [91] and
317 visible in **Table S1**. Indeed, in reductive conditions, lead vaporization is limited as no O₂ is available to
318 interact with Pb and form volatile oxides [43].

319 3.2. Semi-volatile TME – As, Cu and Zn

320 Reported As removal rates are most of the time below 50% (29% mean vaporization rate, **Fig. 2**)
321 [62,77]. According to the simulations performed by Shen et al. [77] and Liu et al. [98], it is due to As
322 interaction with the major inorganic elements initially present in SS. Indeed, stable As-based
323 compounds such as Ca₃(AsO₄)₂, KAsO₂ and AlAsO₄ can be formed, with decomposition temperatures
324 above 1000 °C [77]. It means that As vaporization properties are mostly controlled by the major
325 elements initial contents in treated SS. According to Liu et al. [98], SiO₂ rich SS may thus significantly
326 help for As removal. Expect for temperature, the other operating parameters seem to have low
327 impact on As vaporization properties (**Table 3**).

328 In several works, Cu vaporization properties are below 20% (median removal rate of 20%, **Fig. 2**)
329 [62,69,92]. However, Kuboňová et al. [85] and Nowak et al. [52] reported Cu removal rates above
330 80% for treatment temperatures higher than 900 °C (orange and red points in **Fig. 2**). Interestingly,
331 the same raw material was used in the two works, i.e. municipal solid waste fly ash with a high Cl
332 content as alkali (sodium and potassium) chlorides [52,85]. Furthermore, according to the
333 thermodynamic simulations performed by Fraissler et al. [43], regardless of SS initial composition, Cu
334 removal at temperatures below 1000 °C without chlorine addition is nearly impossible. Cl presence
335 may therefore explain the high Cu removal rates observed in [52,85], as well as the long residence
336 time used [65], the high treatment temperature, CaO predominance in sludge and the oxidative
337 conditions used [52,85,92]. These parameters seem therefore to have a positive impact on Cu
338 vaporization properties during classic SS thermochemical treatment (**Table 3**).

339 Zinc seems to be slightly more volatile than Cu, with equal mean and median vaporization rates of
340 33% (**Fig. 2**). The treatment temperature seems to be the most relevant parameter influencing Zn
341 vaporization properties (**Fig. 2** and **Table 3**). Removal rates above 50% are thus reported for
342 treatment temperatures higher than 1000 °C (orange and red points, **Fig. 2**) [69,85]. Below 1000 °C,
343 Zn is however hard to volatilize. Indeed, according to Fraissler et al. [43], Zn behaves similarly to Cu.
344 Its vaporization is therefore highly dependent on chlorine addition and availability. It may explain the
345 high removal rates observed by Liu et al. and Kuboňová et al. [69,85]. Two parameters seem to have
346 a negative influence on Zn vaporization properties: the use of a rotary kiln (compared to fixed-bed
347 reactors) [52,85] and oxidative combustion conditions [92] (**Table 3**).

348 3.3. Low-volatile TME – Cr and Ni

349 Except in the work of Liu et al. [69], reported Cr removal rates are below 20% (**Fig. 2**) [62,85,92]. High
350 treatment temperatures seem to enhance Cr volatility (see red points in **Fig. 2**), but even with a
351 treatment at 1200 °C, obtained removal rates are below 40% [85]. The highest vaporization rates
352 (62% at 550 °C) observed by Liu et al. [69] are difficult to explain and not commented by the authors.
353 It may be due to a high SiO₂ content (28wt%), Cl presence and the fact that the treated SS was
354 dehydrated prior to thermochemical treatment (**Table S1**). Indeed, according to Fraissler and al. [43],
355 SiO₂-rich sludge can promote Cr vaporization during thermochemical treatment as well as Cl
356 presence when no H₂O is involved during treatment (to promote volatile CrO₂Cl₂ production) (**Table**
357 **3**). Such high Cr removal rates, however, have only been reported in this study to our knowledge.

358 Reported Ni removal rates are most of the time below 10% (**Fig. 2**), except in Kuboňová et al.
359 work, where the authors reported removal rates around 50% for experiments in a rotary kiln
360 (**Table S1**) [85]. They explained the observed results by enhanced mass transfers between solid and
361 gas phase due to rotary kiln use [85]. These results are however questionable as such high removal
362 rates were not further observed, to our knowledge. The other parameters that seem to slightly
363 positively impact Ni vaporization are the treatment temperature, residence time and oxidative
364 conditions (combustion) (**Table 3**) [69,92]. Finally, according to Fraissler et al. [43], H₂O presence in
365 the flue gas may negatively impact Ni removal.

366 Regarding the results reported in **Table 3**, **S1** and **Fig. 2**, it seems that classic SS thermochemical
367 treatment without additives is not efficient to vaporize all TME for direct use of the ashes as recycled
368 fertilizers [38]. It is particularly the case for elements like Cu, Zn, As, Ni and Cr whose removal rates
369 remain most of the time below 50% during classic SS thermochemical treatment.

370 4. Sewage sludge thermochemical treatment with various Cl-donors

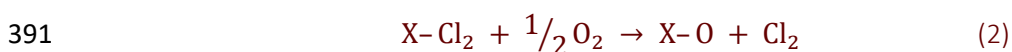
371 4.1. Chlorination mechanisms with various Cl-donors

372 To go further and enhance stable TME (Cu, Zn, As, Ni and Cr) vaporization properties, SS or SS ashes
373 thermochemical treatments with Cl-based compounds developed in the past two decades [43–78].
374 The Cl-donors lead to chlorination mechanisms. The general principle is to convert the TME initially
375 present in various forms (metallic, oxide, alloys, associated with Si, Fe, Al, S, CO₃²⁻, etc.) in raw SS or
376 SS ashes into chlorides, in order to form species with lower boiling points and higher vapor pressures
377 (**Table 2**).

378 Several reaction pathways are possible to vaporize TME by chlorination [53]. Indeed, Cl can be
379 applied during thermochemical treatment either as gaseous Cl₂ and HCl [48], or as solid chlorine-
380 donor (MgCl₂, CaCl₂, KCl, NaCl, PVC, etc.) [44,45,63]. Furthermore, each Cl-donor can react differently

381 during thermochemical treatment depending on operating conditions [44]. According to Nowak et al.
382 [52], the best Cl-donor is Cl₂, but it requires expensive equipment for safe handling and can lead to
383 the chlorination of non-hazardous elements like Ca or Fe. To our knowledge, no publication therefore
384 detailed its direct use in SS or SS ashes thermochemical treatment. Solid chlorine-donors are mostly
385 used [43–65,78,79]. For industrial processes they offer the advantages of low cost, easy availability,
386 low toxicity and trouble-free handling during the chlorination process [43].

387 Chlorination reaction steps between TME and Cl are suggested as follows by Jeon et al. [53],
388 with M: TME, MO: TME oxides, X: metals, X-Cl₂: Cl-donors, MCl₂: chlorinated TME, X-O: metal
389 oxides.



395 Depending on the operating conditions and the Cl-donor used, the TME can react with chlorine
396 either directly (“direct chlorination”, eqn. (1)) or indirectly. In this case, the Cl-donors react with O₂ or
397 H₂O to produce Cl₂ or HCl, which in turn react with TME (“indirect chlorination”, eqn. (2) to (5)).
398 According to Nowak et al. [50] and Jeon et al. [53], for indirect chlorination processes, Cl₂ or HCl
399 formation reactions are considered as the limiting step for the TME removal (eqn. (2) and (4)) and
400 not TME chlorination itself (eqn. (3) and (5)).

401 In the next parts of the review, the chlorination mechanisms and efficiency with MgCl₂, CaCl₂, NaCl,
402 HCl gas, PVC, KCl and NH₄Cl are detailed. Data from different works are compiled in **Tables S2 to S5**,
403 in order to investigate the impact of different operating conditions (feed material type and major
404 elements composition, residence time, treatment gas, reactor type, Cl-concentration and treatment
405 temperature) on the TME vaporization properties during SS or SS ashes thermochemical treatment
406 with Cl-donor. The replicated removal rates were obtained from the various works explored (values
407 extracted from graphs most of the time). In the case where no removal rates were given by the
408 authors, the TME contents in the solid residues after thermochemical treatment were instead given.

409 4.2. Magnesium chloride – MgCl₂

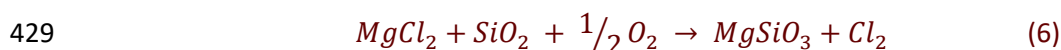
410 The most common Cl-donor used to promote TME vaporization during SS or SS ashes
411 thermochemical treatment is MgCl₂. It is an abundant, cheap, safe and non-toxic compound that has
412 been extensively studied [44,45,47,49,53,57,62,63,65,75].

413 MgCl₂ is considered as a low temperature Cl-donor and as both an indirect and direct
414 chlorination agent, the indirect pathway being kinetically and thermodynamically favored [44]. Most
415 of the time, MgCl₂ is used in powder hexahydrate form (MgCl₂·6H₂O) and milled or mixed with SS (or
416 SS ashes) prior to thermochemical treatment [44,52,57,62]. The Cl-donor can also be solubilized in
417 water before being added to SS [45,55]. The preparation methods for the mixtures are however only
418 poorly detailed in most papers.

419 According to Yu et al. [57], MgCl₂·6H₂O decomposition under air can be divided into three
420 stages:

- 421 - At a temperature lower than 150 °C, MgCl₂·6H₂O is first dehydrated, with MgCl₂·xH₂O (x = 2
 422 and 4) and H₂O as main products,
 423 - Between 150 and 500 °C, an intermediate compound, Mg(OH)Cl, is formed by hydrolysis
 424 reaction, leading to HCl production as early as 150 °C,
 425 - At a temperature higher than 500 °C, Mg(OH)Cl is converted to MgO with HCl formation.

426 Under N₂ atmosphere (pyrolysis), chlorination mechanisms are slightly different according to Xia
 427 et al. [62]. In their work, they detected both HCl (above 500 °C) and Cl₂ (as early as 100 °C)
 428 production. The proposed reactions explaining these two compounds production are as follows:



431 **Table S2** compiles the results from [44,45,47–49,53,57,62,63] and presents the TME removal rates
 432 obtained during SS or SS ashes thermochemical treatment with MgCl₂ addition. The results are
 433 discussed in the next part of the paper (section 5.).

434 4.3. Calcium chloride – CaCl₂

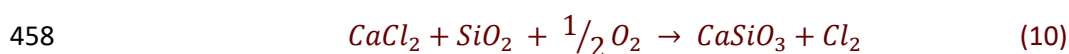
435 The second most common Cl-donor used to promote TME vaporization during SS or SS ashes
 436 thermochemical treatment is CaCl₂. As MgCl₂, it is an abundant, cheap, safe and non-toxic compound
 437 that has been extensively studied as chlorinating agent [43,44,50–53,62,63,74,75].

438 According to Fraissler et al. [43,71], CaCl₂ is both a direct and indirect chlorinating agent.
 439 However, the thermodynamic calculation performed by the authors seem to indicate that CaCl₂
 440 reaction with H₂O and O₂ is thermodynamically and kinetically favored compared to direct
 441 chlorination, which can occur as a second pathway. The authors also showed that a higher surface
 442 area leads to higher reaction rates with H₂O and/or O₂ thus, milled CaCl₂ may improve TME removal
 443 more than CaCl₂ in flake form [43]. CaCl₂ is therefore most of the time used in powder form
 444 (CaCl₂·2H₂O) and milled with SS (or SS ashes) prior to thermochemical treatment [44,50,52]

445 Vogel et al. [75] compared MgCl₂·6H₂O and CaCl₂·2H₂O thermal decomposition under O₂ thanks
 446 to thermogravimetry coupled with an infrared detector. After dehydration around 150 °C, the
 447 thermal decomposition of CaCl₂·2H₂O follows a different pathway than the one of MgCl₂·6H₂O.
 448 Indeed, no HCl gas was detected. According to the authors, only Cl₂ gas (not visible in FTIR spectra)
 449 was formed during CaCl₂·2H₂O thermal degradation in absence of gaseous H₂O, while for
 450 MgCl₂·6H₂O, both Cl₂ and HCl were formed. However, in contact with water, both Cl-donors react
 451 similarly and produce HCl during thermochemical treatment [52,71]. Depending on the presence or
 452 absence of water in the atmosphere, the two possible chlorination reactions of CaCl₂ are therefore
 453 the followings:



456 During pyrolysis under N₂ atmosphere, according to Xia et al. [62], both HCl and Cl₂ gases are
 457 produced, following the proposed reactions:

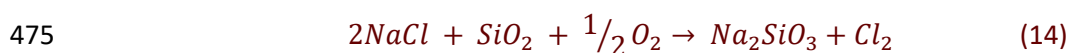
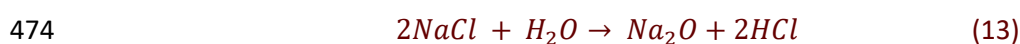


460 **Table S3** compiles the results from [43,44,48,50–53,62,63] and presents the TME removal rates
461 obtained during SS or SS ashes thermochemical treatment with CaCl₂ addition. The results are
462 discussed in the next part of the paper (section 5.).

463 4.4. Sodium chloride – NaCl

464 NaCl is another common, abundant, cheap, safe and non-toxic salt that can be used as Cl-donor
465 during SS or SS ashes thermochemical treatment. However, it has not been studied as much as CaCl₂
466 or MgCl₂, due to its high vapor pressure [44,53,62,69]. Indeed, depending on the operating
467 conditions, NaCl can evaporate in high quantities without reacting, especially when a rotary kiln or a
468 fluidized bed reactor is used [44].

469 NaCl is considered as both a direct and indirect chlorination agent. However, unlike MgCl₂ and
470 CaCl₂ and according to Nowak et al. [44], the direct pathway is thermodynamically and kinetically
471 favored over the reaction with H₂O and O₂. Under N₂ atmosphere (pyrolysis), according to Xia et al.
472 [62], the chlorination mechanisms are the followings:



476 Similar reaction pathways were also proposed by Liu et al. [69] for incineration experiments.

477 **Table S4** compiles the results from [44,53,62,69] and presents the TME removal rates obtained
478 during SS or SS ashes thermochemical treatment with NaCl addition. The results are discussed in the
479 next part of the paper (section 5.).

480 4.5. Other Cl-based compounds: KCl, PVC, HCl gas, NH₄Cl

481 KCl, NH₄Cl and FeCl₃ have also been tested as Cl-donors [49,53,68,70]. KCl is considered as a high
482 temperature Cl-donor (> 800 °C) [49] but only few information on the chlorination mechanisms are
483 available for these compounds as they have not been studied as much as MgCl₂, CaCl₂ or NaCl.

484 Gaseous hydrochloric acid (HCl) can also be used for SS or SS ashes thermochemical treatment
485 [45,48,72]. In this case, the reaction mechanisms are simple. Direct chlorination is possible as long as
486 HCl is available for reaction with the TME according to the following equation:



488 To allow a good interaction between HCl gas and SS, the thermochemical treatment needs to be
489 carried out either in a rotary kiln or in a fluidized bed reactor [48].

490 Finally, Cl-rich waste materials like polyvinyl chloride (PVC) are suitable to enhance TME
491 vaporization properties during SS or SS ashes thermochemical treatment [46,47,62,67,69,73,77]. PVC
492 is the third most produced synthetic plastic polymer in the world. About 40 million tons of PVC are
493 produced each year. Most of it can be recycled after use, but there are still streams of used PVC
494 which are not and need to be valued [46]. PVC has a high Cl content of 52-53 wt% and a high heat
495 energy of approximately 18 MJ/kg [46]. For these reasons, PVC can be used as a cheap organic
496 chlorinating agent and as an energy carrier for SS or SS ashes thermochemical treatment.

497 Vogel et al. [46] studied PVC thermal decomposition in air thanks to thermogravimetric
498 experiments coupled with infrared. The obtained results show an important mass loss (65wt%)
499 around 220 °C corresponding to HCl production from PVC. Cl₂ may also be formed at this stage but is

500 not visible in FTIR spectra [75]. PVC is therefore considered as a low temperature and indirect Cl-
 501 donor. During pyrolysis (under N₂ atmosphere), according to Xia et al. [62], both Cl₂ and HCl are
 502 produced during thermochemical treatment, according to the following equations:



505 **Table S5** compiles the results from [46–49,53,62,68–70,77] and presents the TME removal rates
 506 obtained during SS or SS ashes thermochemical treatment with PVC, HCl, NH₄Cl, FeCl₃ or KCl addition.
 507 The results are discussed in the next part of the paper (Section 5.).

508 5. Trace metal elements removal

509 The TME removal rates compiled in **Tables S2 to S5** allow to investigate the impact of various Cl-
 510 donors and operating conditions on their vaporization properties during SS or SS ashes
 511 thermochemical treatment. The general trends and the most relevant parameters influencing TME
 512 removal are compiled in **Table 4** and are further discussed for each TME.

513 It is important to note that in this part, when no additives are used (“no Cl” column in **Table 4**),
 514 the vaporization rates reported in Kubuňová et al. [85], Nowak et al. [52] and Liu et al. [69] were
 515 excluded due to high Cl contents in the raw SS and SS ashes. Indeed, the surprisingly high removal
 516 rates for Cu, Zn, Cr and/or Ni observed in these studies may be due to Cl presence. The goal of this
 517 part being to study Cl addition impact (use of Cl-donors), these works may thus interfere. It explains
 518 the differences in the calculated mean and median removal rates when no additives are used
 519 between **Tables 3 and 4**.

Table 4 – Summary table: relevant parameters influencing TME removal during SS or SS ashes thermochemical treatment with Cl-donors

TME	Mean-median removal rates (%)						Temperature (°C)		Cl content (g Cl/kg)		Vaporization forms	Best conditions
	No Cl*	MgCl ₂	CaCl ₂	NaCl	PVC	other	↗ T	Optimal	↗ C	Optimal		
As	29-36	45-45	27-38	29-32	45-48	/	(+)	≥ 800	(+)	≥ 200	AsO – AsCl ₃	Oxidative
Cd	75-89	82-96	82-93	78-94	61-93	77-78	++	≥ 700	0	0	CdO – Cd(OH) ₂	Reductive
Cr	10-9	9-6	9-6	20-17	25-26	18-16	+	≥ 1000	+	150-200	CrO ₂ Cl ₂	Oxidative
Cu	22-9	70-83	74-80	66-73	56-69	62-73	+	≥ 900	++	100-150	CuCl – CuCl ₂	Oxidative
Ni	6-3	9-2	17-11	16-15	16-16	14-14	+	≥ 1000	+	150-200	NiCl ₂	Oxidative
Pb	65-77	87-94	90-94	85-94	54-63	76-95	++	≥ 800	++	50-100	PbO – PbCl ₂	Oxidative
Zn	30-28	72-77	75-81	54-55	76-83	42-45	+	≥ 900	++	100-150	ZnCl ₂	Reductive

++ strong positive influence

+ positive influence

(+) low positive influence

0 no influence

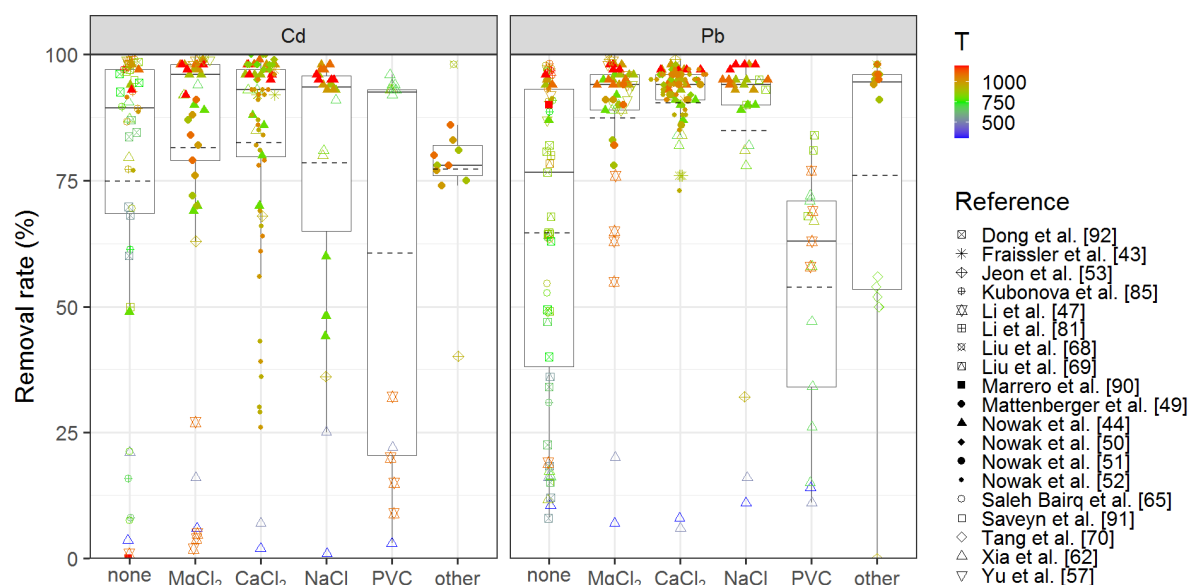
/ not studied

* the works from Kubuňová et al. [85], Nowak et al [52] and Liu et al [69] are excluded for the calculations due to high Cl contents in the raw material.

520 For ease of reading and further discussion, the main results from literature concerning TME removal
 521 rates during SS thermochemical treatment with various Cl-donors compiled in **Tables S2 to S5** are
 522 also presented in **Figs. 3 to 6** and **Figs. S1 to S4**. **Figs. 3 to 6** represent the reported removal rates (for
 523 Cd and Pb in **Fig. 3**, for Cu and Zn in **Fig. 4**, for Cr and Ni in **Fig. 5** and for As in **Fig. 6**) as a function of
 524 the treatment temperature (color scale: blue at 300, green at 750 and red at 1200 °C), the reference
 525 studied (shape scale) and the used Cl-donor (none, MgCl₂, CaCl₂, NaCl, PVC and other Cl-based). The
 526 mean (dotted horizontal line) and median (horizontal line) removal rates for each TME are also
 527 shown (and compiled in **Table 4**), along with the first and third quartiles (black rectangles) and the
 528 95% confidence interval (black vertical line). **Figs. S1 to S4** (Cd and Pb in **Fig. S1**, Cu and Zn in **Fig. S2**,
 529 Cr and Ni in **Fig. S3** and As in **Fig. S4**) present boxplots constructed with the same database but this

530 time with a color scale representing the Cl concentration (green for 0, red for 150 and black for 250 g
 531 Cl/kg raw material) instead of the treatment temperature. It therefore allows to study the impact of
 532 increasing Cl content with the various Cl-donors studied. It is important to note that only the studies
 533 reporting TME removal rates were used to build these figures. Some authors only gave TME contents
 534 in solid residues and were therefore not included (see **Tables S2 to S5**). Their results are however
 535 discussed in the text.

536 5.1. Cadmium and lead



537
 538 **Figure 3** – Boxplots compiling data from Tables S1 to S5 and representing the reported Cd and Pb removal rates as a
 539 function of the treatment temperature (color scale), the reference studied (shape scale) and the used Cl-donor (none, MgCl₂,
 540 CaCl₂, NaCl, PVC and other Cl-based). The mean (dotted horizontal line) and median (horizontal line) removal rates for each
 541 TME are also shown, along with the first and third quartiles (black rectangles) and the 95% confidence interval (black
 542 vertical line).

543 As previously discussed, Cd and Pb are easily volatile TME. Indeed, during classic SS or SS ashes
 544 thermochemical treatments (without Cl addition), these elements are most of the time vaporized at
 545 rates above 80% when the treatment temperature reaches 800 °C or higher (see section 3.1.). It is
 546 also the case during thermochemical treatment with Cl-donors as visible in **Fig. 3**. Indeed, the figure
 547 shows higher Cd and Pb removal rates for treatment temperatures above 800 °C (orange and red
 548 points in **Fig. 3**).

549 The differences in removal rates between thermochemical treatment of SS or SS ashes with and
 550 without additives (Cl-donors) are small for Cd (**Fig. 3**). The additives seem to have neither a positive
 551 nor a negative impact on Cd vaporization properties, except for PVC (negative impact due to high C
 552 and H contents according to Li et al. [47], **Fig. 3**). Therefore, Cl addition does not impact Cd removal.
 553 This result is in good agreement with the thermodynamic simulations performed by Fraissler and al.
 554 [43] and Liu et al. [68], showing neither positive nor negative interactions between Cd and Cl. It is
 555 also confirmed in **Fig. S1** with no visible correlation between Cd removal and increasing Cl content
 556 during thermochemical treatment. Cd removal is therefore controlled by the treatment temperature.

557 Low Cd vaporization rates are however observed in Li et al. [47] and Jeon et al. [53] works for
 558 treatment temperatures above 800 °C (**Fig. 3** and **Tables S2 to S5**). According to Li et al. [47], it is due
 559 to the following reaction mechanism:

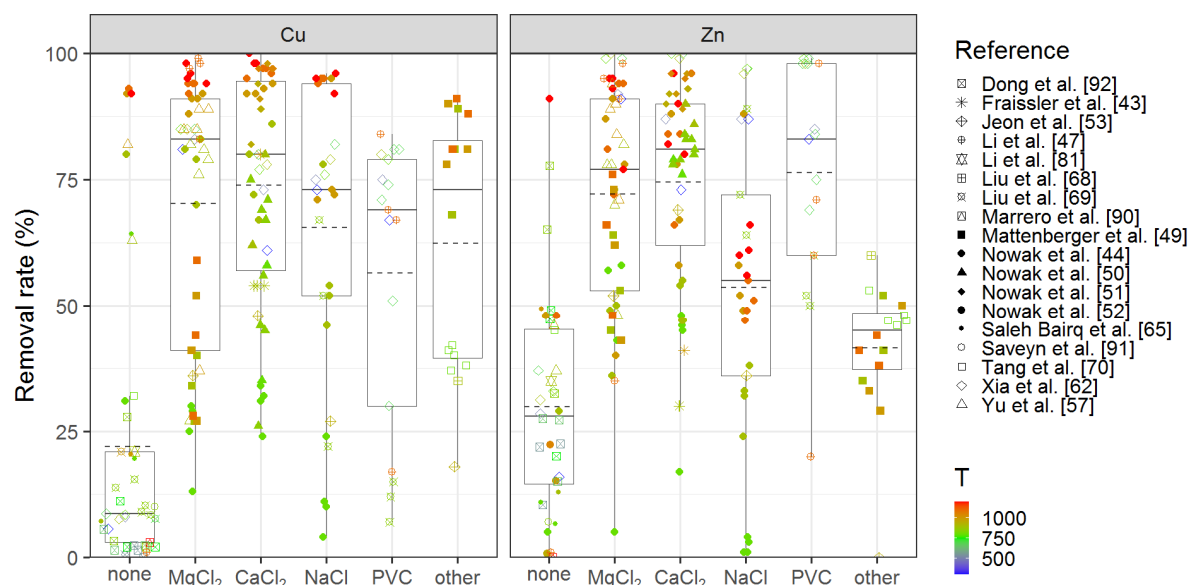


561 CdO·Al₂O₃·2SiO₂ is a stable product with a low volatility. It can be formed during SS incineration prior
562 to Cl addition due to the high Al₂O₃ content in the raw SS [47]. The absence of water (due to SS ashes
563 use) may also explain the low removal rates observed in these works. Indeed, according to Fraissler
564 et al. [43], H₂O presence promotes Cd(OH)₂ production and therefore Cd vaporization.

565 For lead, the compiled data show mean removal rates of 87, 90, 85, 54 and 76% when MgCl₂,
566 CaCl₂, NaCl, PVC or KCl are respectively used for thermochemical treatment (**Fig. 3** and **Table 4**).
567 Except with PVC, Cl addition therefore promotes Pb removal through the gas phase (**Fig. 3**). As visible
568 in **Fig. S1**, low Cl contents (from 50 g Cl/kg raw material) allow to reach high Pb removal rates.
569 Interestingly, under reductive conditions (pyrolysis), Pb vaporization rate is high when Cl is involved
570 (vaporization rate of 90% with MgCl₂ against 16% without at 700 °C according to Xia et al. [62],
571 **Tables S1 and S2**). It is due to Pb interaction with chlorine to form PbCl₂, a compound that vaporizes
572 significantly below 800 °C [69]. In comparison, without Cl addition, under reductive conditions, lead
573 vaporization is limited as no O₂ is available to interact with Pb and form volatile oxides (**Table S1**)
574 [43].

575 When PVC is used as Cl-donor, the reported Pb removal rates are slightly lower than with classic
576 salts (**Fig. 3** and **Table S5**). According to Liu et al. [69], it is due to a change in the chlorination
577 mechanisms. Indeed, the authors reported that when NaCl is used as Cl-donor, PbCl₂ is
578 predominantly produced during thermochemical treatment while when PVC is involved, PbCl₂,
579 Pb(ClO₄)₂ and PbCl₂O₄ are detected. For Li et al. [47], the reduced Pb removal rates observed with
580 PVC are related to the high C and H contents in PVC. Nevertheless, even with PVC as Cl-donor, lead
581 vaporization rates are above 60% in several cases (**Fig. 3** and **Table 4**).

582 As a conclusion for Cd and Pb, it seems that for Cd, the vaporization properties are neither positively
583 nor negatively changed when Cl-donors are involved during treatment (**Fig. 3**). For Pb, they are
584 enhanced thanks to chlorination mechanisms, except when PVC is used as additive (**Fig. 3**). Cd
585 removal is therefore temperature dependent while Pb is both temperature and Cl-donor dependent
586 (**Table 4**).



588

589 **Figure 4** – Boxplots compiling data from Tables S1 to S5 and representing the reported Cu and Zn removal rates as a
 590 function of the treatment temperature (color scale), the reference studied (shape scale) and the used Cl-donor (none, MgCl₂,
 591 CaCl₂, NaCl, PVC and other Cl-based). The mean (dotted horizontal line) and median (horizontal line) removal rates for each
 592 TME are also shown, along with the first and third quartiles (black rectangles) and the 95% confidence interval (black
 593 vertical line).

594 Copper and zinc are considered as semi-volatile TME [43]. Their vaporization properties are limited
 595 under classic thermochemical treatment conditions (no additives) but highly enhanced during
 596 thermochemical treatments with Cl addition, as presented in **Fig. 4** (as a function of temperature)
 597 and **Fig. S2** (as a function of Cl content). Indeed, these two compounds present good mobility and
 598 therefore can interact easily with the Cl-donors to form volatile species like ZnCl₂, CuCl, CuCl₂ or
 599 (CuCl)₃ [44,69]. **Fig. 4 and S2** also allow to compare the various Cl-donors impact on Cu and Zn
 600 removal rates. Thus, MgCl₂ and CaCl₂ are the most efficient Cl-donors for Cu, while for Zn, MgCl₂,
 601 CaCl₂ and PVC are better suited. It is further discussed.

602 As it can be seen in **Fig. 4, S2** and **Tables S2 to S5**, it can be generally stated that Cu vaporization
 603 properties are highly enhanced by (i) an increase in the treatment temperature (orange and red
 604 points in **Fig. 4**), (ii) Cl addition in high amounts (red and dark-red points in **Fig. S2**) and (iii) a long
 605 material residence time:

- 606 (i) Nowak et al. [44] reported Cu removal rates of 30 and 91% at 800 and 1000 °C respectively, with
 607 150 g Cl/kg SS ashes as MgCl₂ (**Table S2**). Xia et al. [62], Adam et al. [45], Yu et al. [57] and many
 608 other authors also reported significantly higher Cu vaporization rates with increasing treatment
 609 temperature (orange and red points in **Fig. 4**) [43,49,63]. In general, it can be stated that at least
 610 900 °C are required to obtain Cu removal rates higher than 80% during SS or SS ashes
 611 thermochemical treatment with Cl-donors (**Table 4**).
- 612 (ii) With CaCl₂ as Cl-donor, Yang et al. [63] detected 208 ppm of Cu in the solid residues obtained
 613 after thermochemical treatment at 900 °C with 1 wt% Ca while only 17 ppm were remaining
 614 after a treatment with 10% Ca (**Table S3**). The authors noticed the same behavior with MgCl₂
 615 addition in different amounts [63]. The same trend (Cu removal increase with increasing Cl
 616 content) is in general observed, except when PVC is used as Cl-donor (red and dark-red points in
 617 **Fig. S2**). Indeed, it seems that adding too much PVC (more than 200 g Cl/ kg SS ashes) inhibits Cu

618 vaporization [46,47]. According to Li et al. [47], it can be attributed to the C and H contents in
619 PVC, promoting Cu transformation into Cu_3P , which is a more stable compound. Classic salts like
620 MgCl_2 or CaCl_2 (indirect chlorination agents) are therefore considered as the most effective Cl-
621 donors for Cu removal [45], as confirmed in Fig. 4. It is however difficult to tell which one allows
622 to obtain the highest vaporization properties. Indeed, Xia et al. [62] and Nowak et al. [44]
623 showed that MgCl_2 use allows slightly higher Cu removal rates than CaCl_2 while Yang et al. [63]
624 and Jeon et al. [53] observed the opposite behavior. As for the other Cl-donors, NaCl, PVC and
625 KCl seem slightly less efficient to enhance Cu vaporization properties while NH_4Cl and FeCl_3
626 present low impacts (Fig. 4 and Tables S4 and S5). To understand these differences, it is
627 interesting to focus on the experiments performed with HCl gas (Table S5 and [48,56,58,72]).
628 Vogel et al. [48] detected 1093 ppm of Cu in the solid residues obtained after thermochemical
629 treatment at 1000 °C without HCl while only 39 ppm were remaining after a treatment with HCl
630 at 178 g Cl/kg SS ashes. These results mean that copper easily interacts with HCl, as also
631 reported by Fraissler et al. [43]. It may explain why indirect chlorinating agents like MgCl_2 and
632 CaCl_2 generally present the highest impact on Cu vaporization during SS or SS ashes
633 thermochemical treatments (Fig. 4).

634 (iii) Nowak et al. [52] observed that increasing the residence time during the treatment of municipal
635 solid waste fly ash with CaCl_2 at a concentration of 170 g Cl/kg raw material in a rotary kiln
636 increases significantly Cu removal rates (Table S3). The authors thus reported a Cu vaporization
637 of only 23% at 1000 °C for a 10 min residence time against 44% at the same temperature when
638 the ashes are kept 45 min in the kiln [52]. In another work, they also reported an increase from
639 26 to 67% for Cu removal rate when the residence time increases from 10 to 30 min at 850 °C
640 with a concentrations of 150 g Cl/kg raw material [50].

641 Low Cu removal rates can be observed in some works even at high temperature, with a high Cl
642 content and a long residence time (Fig. 4). For example, Jeon et al. [53] reported Cu vaporization
643 rates of 36 and 48% with MgCl_2 and CaCl_2 respectively, for fly ashes treated at 950 °C under air for 30
644 min and with 100 g Cl/kg ashes. Nowak et al. [52] also observed less than 30% removal for fly ashes
645 treatment under air at 1050 °C for 45 min with 120 and 170 g Cl/kg ashes as CaCl_2 (Table S3). The
646 authors claim that the low vaporization rates are due to the chosen operating conditions leading to
647 important HCl and Cl_2 loss in the gas phase without interaction with Cu [52]. It was subsequently
648 corrected in their works, leading to high Cu removal rates reported in [44,51]. The data from Nowak
649 et al. in [52] concerning Cu removal were therefore excluded from the box plot in Fig. 4. Finally, Yu et
650 al. [57] also reported lower Cu vaporization rates under reductive conditions than under oxidative
651 conditions (37 against 89% at 1000 °C with MgCl_2 at 150 g Cl/kg raw material, Table S2). It was
652 however not confirmed by Xia et al. [62].

653 Concerning Zn, (i) the treatment temperature (orange and red points in Fig. 4) (ii), the Cl-content
654 (red and dark-red points, Fig. S2) and donor nature (Fig. 4) (iii) and the residence time also seem to
655 be the most important parameters to promote its vaporization during SS or SS ashes thermochemical
656 treatment:

657 (i) For temperature, Nowak et al. [44] showed that, with MgCl_2 as Cl-donor, increasing the
658 temperature from 900 to 1200 °C allows Zn removal rates to shift from 36 to 93% with a
659 constant Cl content of 100 g Cl/kg ashes. Adam et al. [45] reported Zn contents in solid residues
660 of 922, 654, 391 and 85 ppm after thermochemical treatment with MgCl_2 as Cl-donor at 750,
661 800, 900 and 1000 °C respectively (Table S2). Increasing the treatment temperature therefore
662 enhances Zn vaporization properties (orange and red points in Fig. 4). In general, it can be stated
663 that at least 900 °C are required to obtain Zn removal rates higher than 80% during SS or SS

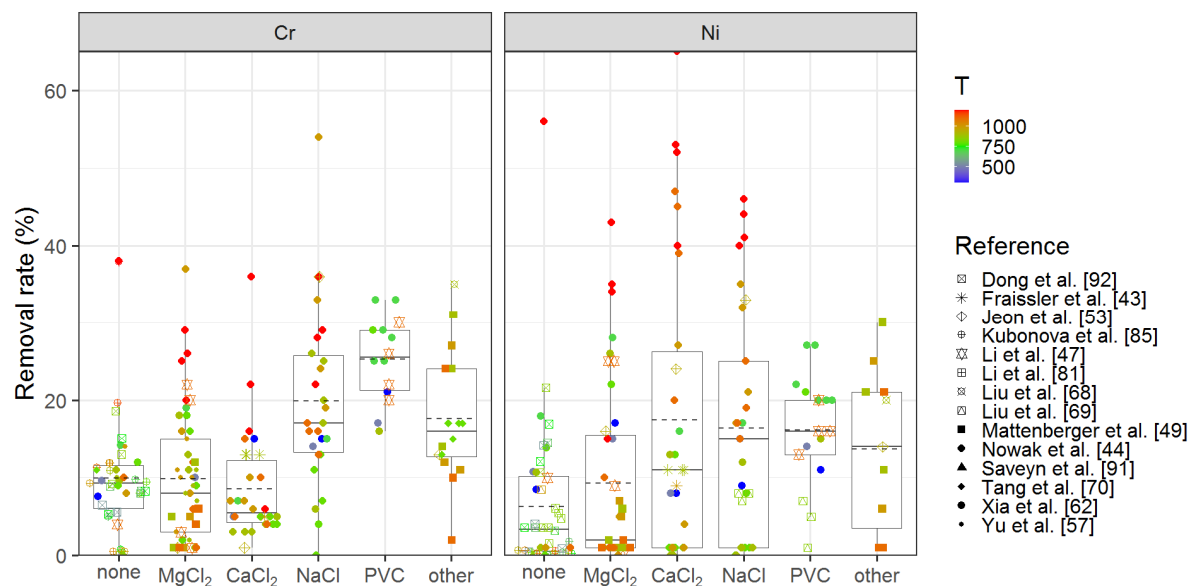
664 ashes thermochemical treatments with Cl-donors (**Table 4**). Under reductive conditions with Cl
665 addition (MgCl_2 , CaCl_2 , NaCl or PVC), 80% Zn vaporization can even be reached with a treatment
666 temperature as low as 300 °C [62]. Indeed, when no O_2 is involved during thermochemical
667 treatment, ZnCl_2 formation is favored in comparison to ZnO [46].

668 (ii) Increasing the Cl content during thermochemical treatment seems to have a highly positive
669 impact on Zn removal (red and dark-red points, **Fig. S2**). Liu et al. [69] reported vaporization
670 rates of 49, 64, 72 and 89% when respectively 0, 1, 3 and 5% of Cl is added to dehydrated SS as
671 NaCl and treated at 850 °C under air (**Table S4**). Yang et al. [63] detected Zn concentrations in
672 solid residues of 1215, 359, 109, 50 and 35 ppm after thermochemical treatment at 1000 °C with
673 0, 1, 2, 5 and 10% of Ca (as CaCl_2) respectively (**Table S3**). Concerning the different Cl-donors, as
674 visible in **Fig. 4**, it seems that CaCl_2 , PVC and MgCl_2 are more efficient to vaporize Zn than the
675 other Cl-donors. For KCl, the low removal rates reported are likely to be due to its high thermal
676 stability limiting Zn and Cl interaction [49,70].

677 (iii) Concerning the residence time, Nowak et al. [52] showed important increase in Zn removal rates
678 when the fly ashes reactor residence time goes from 10 to 45 min (**Table S3**). Indeed, in the
679 chlorination process, kinetics is the limiting step and longer residence time therefore allows
680 higher removal rates.

681 Zn removal rates below 50% can be observed in some works from Fraissler et al. [43], Jeon et al.
682 [53], Nowak et al. [44,52] and Mattenberger et al. [49] (**Fig. 4**). Different mechanisms can be
683 involved. For example, Vogel et al. [76] showed that sulfur rich SS ashes can lead to the formation of
684 the solid and stable ZnS compound, limiting zinc removal as ZnCl_2 . Oxidative conditions can also limit
685 chlorination mechanisms by favoring ZnO formation instead of ZnCl_2 [46]. Finally, operating
686 conditions leading to Cl vaporization to the gas phase without reacting with SS (high gas velocity in a
687 fluidized bed reactor or a rotary kiln and/or use of a volatile Cl-donor such as NaCl) can also limit Zn
688 removal [44,52].

689 As a general conclusion on Cu and Zn removal during SS or SS ashes thermochemical treatment, their
690 vaporization can be considered as Cl-donor dependent. Indirect chlorination agents such as MgCl_2
691 and CaCl_2 (about 100-150 g Cl/kg raw material) seem to be the best Cl-donors and treatment
692 temperatures above 900 °C are required to reach removal rates higher than 80% (**Fig.4** and **Table 4**).



694
 695 **Figure 5** – Boxplots compiling data from Tables S1 to S5 and representing the reported Cr and Ni removal rates as a function
 696 of the treatment temperature (color scale), the reference studied (shape scale) and the used Cl-donor (none, MgCl₂, CaCl₂,
 697 NaCl, PVC and other Cl-based). The mean (dotted horizontal line) and median (horizontal line) removal rates for each TME
 698 are also shown, along with the first and third quartiles (black rectangles) and the 95% confidence interval (black vertical
 699 line).

700 Chromium and nickel are considered as low-volatile TME [43]. Achieving high vaporization rates
 701 during SS or SS ashes thermochemical treatment is therefore challenging (**Fig. 5**). Indeed, with only a
 702 few exceptions, the reported Cr and Ni removal rates are most of the time below 40%, as visible in
 703 **Fig. 5** and **Tables S2 to S5**. It can however be noticed in **Fig. 5** that, for Ni, high treatment
 704 temperatures (above 1000 °C, red points) combined with CaCl₂ or NaCl use seem to slightly enhance
 705 the vaporization rates in comparison with the other Cl-donors. PVC may also be promising for
 706 treatment at lower temperatures (**Fig. 5**). For Cr, NaCl and PVC seem to be the most efficient Cl-
 707 donors (**Fig. 5**). However, due to a lack of data for these Cl-donors, **Fig. S3** does not allow to see
 708 visible correlations between Cr and Ni removal rate and increasing Cl content.

709 For Cr, the works reporting removal rates above 40% during SS or SS ashes thermochemical
 710 treatments are scarce:

- 711 - Liu et al. [69] reported removal rates above 60% without Cl addition at a temperature as low
 712 as 550 °C (**Table S1**). These results are quite surprising as Cr is considered as a low volatile
 713 element (section 3.3.). The obtained removal rates of 72 and 71% during thermochemical
 714 treatment at 850 °C with NaCl and PVC respectively are also difficult to explain and were
 715 unfortunately not much discussed by the authors (**Tables S4 and S5**) [69]. They were
 716 therefore excluded from the database used to build **Figs. 5 and S3**.
- 717 - Yang et al. [63] showed that 10% Ca addition (as CaCl₂) and a thermochemical treatment at
 718 1000 °C allows to decrease the Cr content in the obtained solid residues from 126 ppm when
 719 no CaCl₂ is involved to 70 ppm (**Table S3**). However, according to the authors, Cr cannot be
 720 removed by chlorination and the decrease in Cr content was attributed to the dilution effect
 721 by the added CaCl₂ [63].
- 722 - Nowak et al. [44] reported a 54% vaporization rate for Cr when fly ashes are treated at 1000
 723 °C with NaCl in high amounts (200 g Cl/kg fly ashes, **Table S4**). In comparison with MgCl₂ and

724 CaCl₂, NaCl and PVC seem to be the only Cl-donor slightly enhancing Cr removal (**Fig. 5 and**
725 **S3**). According to the authors, when MgCl₂ and CaCl₂ are used during thermochemical
726 treatment, CaCr₂O₄ and MgCr₂O₄ stable compounds can be formed, with a negative impact
727 on Cr vaporization properties [44]. Kurashima et al. [72,73] also observed that Mg-based
728 compounds addition during thermochemical treatment can lead to the formation of
729 (MgO)(Cr₂O₃) and limit Cr removal at high temperature.

730 - Thermodynamic simulations performed by Fraissler et al. [43] show that Cr removal at
731 temperatures lower than 1000 °C is theoretically possible in only one scenario (not verified
732 experimentally): Si predominance in the raw SS ash, H₂O absence in the flue gas and high Cl
733 content of at least 10wt%.

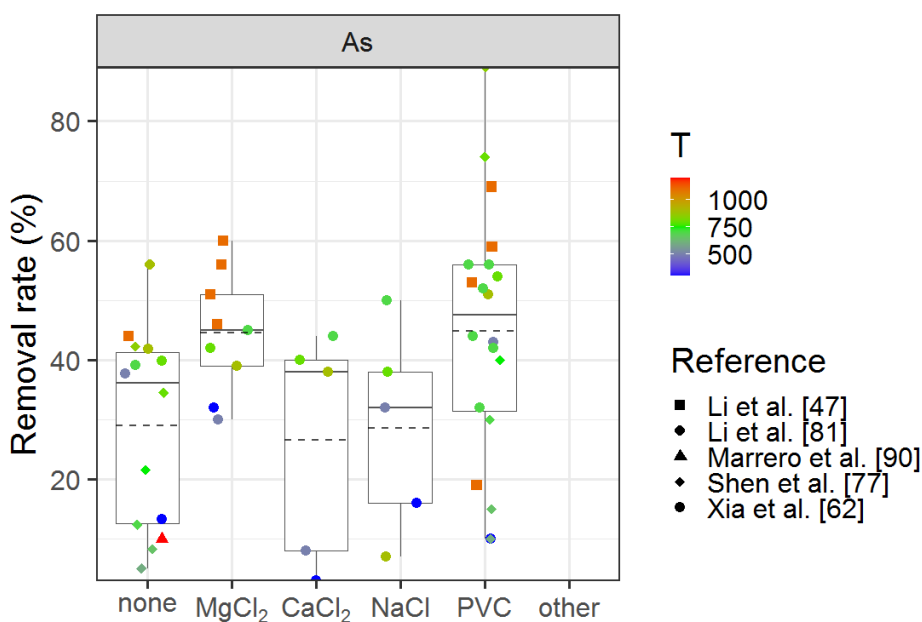
734 For Ni, the works reporting removal rates above 40% during SS or SS ashes thermochemical
735 treatments are the followings:

736 - As detailed in a previous section (section 3.3.), Kuboňová et al. [85] reported Ni removal
737 rates above 50% during thermochemical treatment in a rotary kiln without Cl addition. The
738 authors explained the observed results by enhanced mass transfers between solid and gas
739 phase due to rotary kiln use, and a high Cl content in the raw fly ashes [85]. The results are
740 however questionable and were not further confirmed for other experiments with rotary
741 kilns [43,45,48]. They were therefore excluded from the database used to build **Figs. 5 and**
742 **S3**.

743 - Nowak et al. [44] reported nickel vaporization rates of 47 and 65% for thermochemical
744 treatment with 200 and 150 g Cl/kg fly ash as CaCl₂ at 1100 and 1200 °C respectively (**Table**
745 **S3**). CaCl₂ addition in high amounts combined with a high temperature treatment therefore
746 seems to slightly enhance Ni vaporization properties, but it was not observed again.

747 - According to the thermodynamic simulations performed by Fraissler et al. [43] and Liu et al.
748 [78], nickel vaporization at temperatures below 1000 °C is challenging. Like for chromium, Cl
749 presence in amounts above 10wt% can enhance nickel vaporization, but only in H₂O absence
750 in the flue gas (Cl₂ formation rather than HCl) [43]. Fe shows a negative influence on Ni
751 volatilization because of the stable ferrite NiFe₂O₄ formation.

752 Cr and Ni removal during SS or SS ashes thermochemical treatment is difficult, even with chlorination
753 (**Table 4**). From the boxplots presented in **Fig. 5 and S3**, it can however be stated that PVC and NaCl
754 seem to be the most promising Cl-donors for Cr and Ni removal combined with high treatment
755 temperatures (≥ 1000 °C) and Cl contents (> 150 g Cl/kg raw material). Unfortunately, only few works
756 focused on these two compounds vaporization, which results in a lack of data and little information
757 on the reaction mechanisms.



759

760 **Figure 6** – Boxplots compiling data from Tables S1 to S5 and representing the reported As removal rates as a function of the
 761 treatment temperature (color scale), the reference studied (shape scale) and the used Cl-donor (none, MgCl₂, CaCl₂, NaCl,
 762 PVC and other Cl-based). The mean (dotted horizontal line) and median (horizontal line) removal rates for As are also shown,
 763 along with the first and third quartiles (black rectangles) and the 95% confidence interval (black vertical line).

764 Arsenic vaporization properties during SS or SS ashes thermochemical treatment has not been much
 765 explored in comparison with the other TME (**Figs. 6 and S4**). Only few works determined its content
 766 in the obtained solid residues [45–48,62,77,81,90]. During thermochemical treatment, the As
 767 vaporization rates remain most of the time below 60% (**Fig. 6**). Xia et al. [62] thus reported removal
 768 rates of 7, 39 and 38% for SS treatment at 900 °C with 80 g Cl/kg SS as NaCl, MgCl₂ and CaCl₂
 769 respectively (**Tables S2 to S4**). Vogel et al. [48] showed that 150 g Cl/kg SS ashes addition (as CaCl₂)
 770 and a thermochemical treatment at 1000 °C allows to slightly decrease the As content in the
 771 obtained solid residues from 34 ppm when no CaCl₂ is involved to 21 ppm (**Table S3**). The reported
 772 vaporization rates are in the same order of magnitude as those observed during simple
 773 thermochemical treatment without additives (**Fig. 6**). It therefore seems that Cl addition has no
 774 significant impact on As removal. Indeed, as reported by Shen et al. [77] and Liu et al. [98], and
 775 according to thermodynamic simulations, the interaction between As and Cl is low as arsenic
 776 preferentially interacts with the major elements present in the sludge. It is confirmed in **Fig. S4**
 777 showing no visible correlations between As removal rates and Cl addition in high amounts during
 778 thermochemical treatment.

779 Arsenic removal rates above 50% were reported in some works. Li et al. [47] reported 60 and 69%
 780 vaporization rates for As after thermochemical treatment at 1100 °C with MgCl₂ (100 g Cl/kg SS
 781 ashes) and PVC (250 g Cl/kg SS ashes) respectively (**Tables S2 and S5**). The high removal rates are
 782 likely to be due to the combination of the high treatment temperature (1100 °C) and the Si-rich SS
 783 ashes used as raw material (section 3.2.). Xia et al. [62] reported As removal rates of 56% at 700 °C
 784 when PVC is used as Cl-donor (**Table S5**). In the work of Shen et al. [77], vaporization rates as high as
 785 74 and 89% were reported for a treatment with PVC (5% Cl) at 800 and 850 °C respectively (**Table**
 786 **S5**). PVC use as Cl-donor during SS or SS ashes thermochemical treatment may therefore help for

787 arsenic removal (as also visible in **Fig. 6**). No reaction mechanisms were however suggested and the
788 lack of data for this element limits the extent of the conclusions.

789 6. Phosphorus recovery

790 So far, the focus has been on how to vaporize TME during SS or SS ashes thermochemical treatment
791 by optimizing the operating conditions and the Cl-donor nature. However, the impact on P of these
792 parameters has not yet been discussed. This part is therefore dedicated to the impact of the
793 thermochemical treatments on the forms and solubility of P (note that this has been studied in
794 relatively few papers [45–48,53,62,63,65,78]).

795 **Table 5** compiles data from literature and presents the impact of the thermochemical treatment
796 conditions on P fixation rates, P forms and P solubility in 2% citric acid (P_{cit}) and in neutral ammonium
797 citrate (P_{NAC}). P solubility is a good indicator of its bioavailability for plants. The Cl-donors investigated
798 are the followings: $MgCl_2$, $CaCl_2$, $NaCl$, KCl , PVC , $AlCl_3$ and HCl [45–48,53,62,63]. Results with other
799 additives such as $MgCO_3$, MgO , Na_2SO_4 , Na_2CO_3 , $NaOH$, K_2SO_4 , K_2CO_3 and KOH were also reported
800 [78].

801 First, it is interesting to focus on the P forms initially present in the raw SS used. During
802 wastewater treatment, P must be separated from the outflow of the treatment plant to avoid
803 eutrophication phenomena [27]. Enhanced biological P removal treatment is predominantly used
804 [26]. It is a multistep process alternating aerobic and anaerobic stages. According to Cieslik et al. [27],
805 during biological treatment, most of the P is stored in the activated sludge flora cells as organic
806 adenosine triphosphates ($C_{10}H_{16}N_5O_{13}P_3$). Al and Fe based coagulants ($AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$,
807 $Fe_2(SO_4)_3$) can also be added during wastewater treatment, resulting in the precipitation of P in iron
808 and aluminum forms [8]. In raw SS, P can therefore be found in organic but also inorganic forms,
809 depending on the sludge origin. Unfortunately, the initial forms of P were not reported in the
810 reviewed literature. Xia et al. [62] only determined a P_{NAC} of 15% for the raw SS used (**Table 5**).

811 During classic SS thermochemical treatments such as incineration, pyrolysis or gasification
812 (without Cl-donors), the organic P forms initially present in the SS are converted to inorganic forms
813 (**Table 5**). Xia et al. [62] thus detected $FePO_4$ as the predominant crystalline form of P after pyrolysis
814 treatment at 700 °C. Adam et al. [45] and Vogel et al. [46,48] showed that the ashes obtained after
815 incineration were enriched with $Ca_3(PO_4)_2$ and $AlPO_4$. Yang et al. [63] showed that with increasing
816 combustion temperature, Fe/Al-P species ($Ca_9Fe(PO_4)_7$ and $AlPO_4$) transform into Ca-P species. It is
817 confirmed by Meng et al. [8], who show that SS incineration leads to the formation of apatite
818 ($Ca_5(PO_4)_3[OH, Cl, F]$) from Al and Fe phosphates and amorphous Ca phosphate phases. Concerning P
819 fixation rates, Yang et al. [63] showed that increasing the incineration temperature from 800 to 1000
820 °C improves P fixation in solid residues from 69 to 82%, with a maximum of 89% at 950 °C (**Table 5**).
821 According to the authors, high temperature treatment stimulates the transformation of Fe/Al-P
822 species to Ca-P, which is beneficial for P fixation since Ca-P species are more stable than Fe/Al-P ones
823 [63]. An increase in P_{cit} with increasing treatment temperature was also reported by Yang et al. [63],
824 because Ca-P species are more soluble than Fe/Al-P ones (**Table 5**). Xia et al. [62] showed that
825 pyrolysis at 700 °C increases P_{NAC} from 15% (for raw SS) to 39% (**Table 5**). SS classic thermochemical
826 treatments therefore seem to enhance both P fixation rates and solubility.

Table 5 – P fixation rates, solubility and forms after thermochemical treatments under various operating conditions

Reference	Feed material		Thermochemical treatment					P				
	Type	Major elements-wt%	Residence time (min)	Treatment gas	Reactor type	T (°C)	Additive nature	Concentration	Fixation (%) [†]	Solubility (%) [†]		Forms
										Cit 2%	NAC [^]	
Xia et al. [62]	WWTP ⁺ dried SS	/	No thermochemical treatment					/	/	15	/	
			240	Pyrolysis under N ₂	Lab-scale horizontal furnace	700	No additives			39	FePO ₄	
							PVC			80 g Cl/kg	72	AlPO ₄
							NaCl				74	Ca ₅ (PO ₄) ₃ Cl
							MgCl ₂				76	Mg ₃ (PO ₄) ₂
							CaCl ₂				74	Ca ₂ PO ₄ Cl
Adam et al. [45]	SSAs ^o	SiO ₂ -21.6 P ₂ O ₅ -21.3 Fe ₂ O ₃ -16.3 CaO-15.7	60	Combustion under air	Lab scale rotary furnace	No thermochemical treatment		29	/	Ca ₃ (PO ₄) ₂ + AlPO ₄		
						450	MgCl ₂	150 g Cl/kg		44	Ca ₃ (PO ₄) ₂ + AlPO ₄	
						600				74	Ca ₂ PO ₄ Cl	
						750				79	Ca ₂ PO ₄ Cl	
						800				86	Mg ₃ (PO ₄) ₂	
						900				93	Mg ₃ (PO ₄) ₂	
						1000				97	Ca ₄ Mg ₅ (PO ₄) ₆	
Vogel et al. [48]	SSAs ^o	Ca-13.4 Fe-10.0 P-9.0 Al-5.6	30	Combustion under air	Lab scale rotary furnace	No thermochemical treatment		43	10	Ca ₃ (PO ₄) ₂ + AlPO ₄		
						1000	MgCl ₂	150 g Cl/kg	71	22	Mg ₃ (PO ₄) ₂	
							CaCl ₂		64	3	Ca ₅ (PO ₄) ₃ Cl	
							HCl		53	6	Ca ₅ (PO ₄) ₃ Cl + AlPO ₄	
							MgCO ₃ /HCl		+ 50 g Mg/kg	71	15	Mg ₃ (PO ₄) ₂
Vogel et al. [46]	SSAs ^o	Si-10.3 Fe-9.6 Ca-9.1 P-9.1	20	Combustion under air	Lab scale rotary furnace	No thermochemical treatment		14	/	Ca ₃ (PO ₄) ₂ + AlPO ₄		
						800	PVC + MgO	150 g Cl/kg + 95 g Mg/kg		25	Mg ₃ (PO ₄) ₂ + Ca ₄ Mg ₅ (PO ₄) ₆	
										850		28
										900		33
										950		37
						900	PVC + MgO	100 + 95		25		
								150 + 95		33		
200 + 95	26											
Herzel et al. [78]	SSAs ^o	Si-11 Ca-11 P-9 Al-7	30	Combustion under air	Crucible	1000	2 mol/mol P	/	/	95	/	
										Na ₂ SO ₄		90
										Na ₂ CO ₃		85
										NaOH		45
										K ₂ SO ₄		70
										K ₂ CO ₃		75

Reference	Feed material		Thermochemical treatment						P			
	Type	Major elements-wt%	Residence time (min)	Treatment gas	Reactor type	T (°C)	Additive nature	Concentration	Fixation (%) [†]	Solubility (%) [†]		Forms
										Cit 2%	NAC [^]	
Yang et al. [63]	Dewatered SS	Fe-11 P-8 Si-5	120	Combustion under air	Lab-scale muffle oven	800	No additives		69	6	/	Transformation from Fe/Al-P to Ca-P
									72	7		
									78	9		
									89	13		
									82	22		
						800	MgCl ₂	0% Mg	69	6		Ca ₉ Fe(PO ₄) ₇ + AlPO ₄
								1% Mg	87	36		
								1.6% Mg	90	50		
								2.5% Mg	95	69		
								3% Mg	94	64		
								0% Mg	78	9		
								1% Mg	92	35		
								1.6% Mg	95	49		
								2.5% Mg	98	66		
								3% Mg	99	64		
						900	MgCl ₂	0% Mg	82	22		Ca ₉ Fe(PO ₄) ₇ + AlPO ₄
								1% Mg	85	37		
								1.6% Mg	89	39		
								2.5% Mg	94	37		
								3% Mg	93	41		
						1000	MgCl ₂	0% Mg	82	22		Ca ₉ Fe(PO ₄) ₇ + AlPO ₄
								1% Mg	85	37		
								1.6% Mg	89	39		
								2.5% Mg	94	37		
								3% Mg	93	41		
						800	CaCl ₂	0% Ca	69	6		Ca ₉ Fe(PO ₄) ₇ + AlPO ₄
								1% Ca	90	13		
								3% Ca	92	31		
								5% Ca	98	49		
								10% Ca	98	56		
900	CaCl ₂	0% Ca	78	9	Ca ₉ Fe(PO ₄) ₇ + AlPO ₄							
		1% Ca	90	13								
		3% Ca	96	16								
		5% Ca	97	23								
		10% Ca	99	31								
1000	CaCl ₂	0% Ca	82	22	Ca ₉ Fe(PO ₄) ₇ + AlPO ₄							
		1% Ca	91	22								
		3% Ca	92	19								
		5% Ca	95	21								
		10% Ca	97	30								

Reference	Feed material		Thermochemical treatment					P					
	Type	Major elements-wt%	Residence time (min)	Treatment gas	Reactor type	T (°C)	Additive nature	Concentration (g Cl/kg)	Fixation (%)†	Solubility (%)†		Forms	
										Cit 2%	NAC^		
Jeon et al. [53]	SS fly ash	Ca-9 Al-9 P-9 Fe-6	No thermochemical treatment					AlPO ₄ + KH ₂ PO ₄ + Ca ₃ (PO ₄) ₂					
			30	Combustion under air	Lab-scale muffle furnace	950	No additives		100	45	Ca ₇ Mg ₂ P ₆ O ₂₄ + Fe ₃ (PO ₄) ₂		
							MgCl ₂	80	100	72	AlPO ₄ + Mg ₃ (PO ₄) ₂ + Ca ₅ (PO ₄) ₃ Cl		
							CaCl ₂		95	63	Ca ₅ (PO ₄) ₃ Cl + Ca ₃ (PO ₄) ₂		
							NaCl		95	52			
							KCl		90	28	Clod formation		
AlCl ₃	100	45											
Li et al. [47]	P-enriched SSAs°	Si-26 Ca-18 P-17 Al-14	No thermochemical treatment					Ca ₉ Al(PO ₄) ₇ + Ca ₃ (PO ₄) ₅ OH + Al(PO ₄)					
			30	Combustion under air	Lab-scale tube furnace	1100	PVC	0	83	/	/	Ca ₉ Al(PO ₄) ₇	
								50	91				
								100	92				
								150	92				
								250	92				
							MgCl ₂	0	83				
								50	93				
								100	94				
								150	98				
250	97	Ca ₅ (PO ₄) ₃ F _{0.09} Cl _{0.88} + Zn ₃ P ₂ + Ni ₂ P ₅ + Cu ₃ P											

* WWTP = wastewater treatment plant

MSW = municipal solid waste

° SSAs = sewage sludge ashes from incineration plant

† Color scales: low P solubility in red (<20%), medium in yellow (40-60%) and high in green (>80%)

^ NAC = neutral ammonium citrate

827 When Cl-donors are added to SS or SS ashes, the fixation rate and the solubility of P are in most
828 cases greatly enhanced (**Table 5**). Yang et al. [63] thus reported an improvement in P fixation rate at
829 800 °C, from 69% without additive to 94 and 98% when MgCl₂ (3% Mg) and CaCl₂ (10% Ca) are
830 respectively added (due to Mg and Ca addition and interaction with P, **Table 5**). Furthermore, the
831 authors also reported a significant increase in P_{cit}, from 6% without Cl-donor to 64 and 56% with
832 MgCl₂ (3% Mg) and CaCl₂ (10% Ca) respectively. Similar trends were observed in most publications
833 (**Table 5**). Adam et al. [45] reported a P_{cit} of 97% when SS ashes are treated at 1000 °C with 150 g
834 Cl/kg as MgCl₂. Vogel et al. [46] showed an increase in P_{NAC} from 14% for raw ashes to 37% when a
835 mixture of PVC (150 g Cl/kg) and MgO (95 g/kg) is used for thermochemical treatment at 950 °C.
836 Finally, Xia et al. [62] observed a shift in P_{NAC} from 15% for raw SS to 74% for the ashes after pyrolysis
837 at 700 °C with 80 g Cl/kg SS as CaCl₂.

838 Interestingly, the various Cl-donors used to promote TME vaporization seem to have different
839 impacts on P solubility after thermochemical treatment (**Table 5**). In the work of Jeon et al. [53], the
840 obtained P_{cit} are of 72, 63, 52, 28 and 45% when MgCl₂, CaCl₂, NaCl, KCl and AlCl₃ are respectively
841 used as Cl-donors in the same amounts. Vogel et al. [48] reported a P_{cit} of 71, 64, 53 and 71% with
842 MgCl₂, CaCl₂, HCl and a mixture of MgCO₃ and HCl respectively. It therefore seems that to increase P
843 solubility, MgCl₂ is the best Cl-donor, followed by CaCl₂. It is due to the presence of Mg and its
844 reaction with P to form highly soluble P forms such as Mg₃(PO₄)₂ (below 1000 °C) and Ca₄Mg₅(PO₄)₆
845 (above 1000 °C) [45]. It also explains why, when mixtures of MgCO₃ and HCl or of MgO and PVC are
846 used as additive, high P solubility is also reported by Vogel et al. [46,48] (**Table 5**). When CaCl₂ is
847 involved during thermochemical treatment, Ca-P-Cl species such as Ca₅(PO₄)₃Cl, Ca₅(PO₄)₃F_{0.09}Cl_{0.88}
848 and Ca₂PO₄Cl are detected (**Table 5**) [53,63]. Finally, the other Cl-donors (NaCl, KCl, PVC, AlCl₃) do not
849 seem to have a significant impact on P solubility [46,48,53].

850 High P_{NAC} are observed in the work of Xia et al. [63], during pyrolysis treatments with Mg-free
851 additives (72, 74 and 74% with NaCl, PVC and CaCl₂ respectively). Furthermore, the highest P_{NAC} are
852 observed in the work of Herzel et al. [78], when additives without Cl are used. P_{NAC} of 95, 90 and 85%
853 were thus reported with Na₂SO₄, Na₂CO₃ and NaOH respectively, leading to a fertilizing effect
854 comparable to triple superphosphate. Unfortunately, no mechanism is proposed to explain how
855 these additives react with the phosphate species in the SS ashes to form new P-containing mineral
856 species with high solubility. Furthermore, the reported TME removal rates are not as high as when Cl-
857 donor are used for thermochemical treatment, especially for Cu, Cr, Ni, Pb and Zn [78]. However,
858 MgCl₂ and Na₂SO₄ mixtures and/or reductive treatment conditions may be interesting to test, to
859 combine high impacts on TME and P.

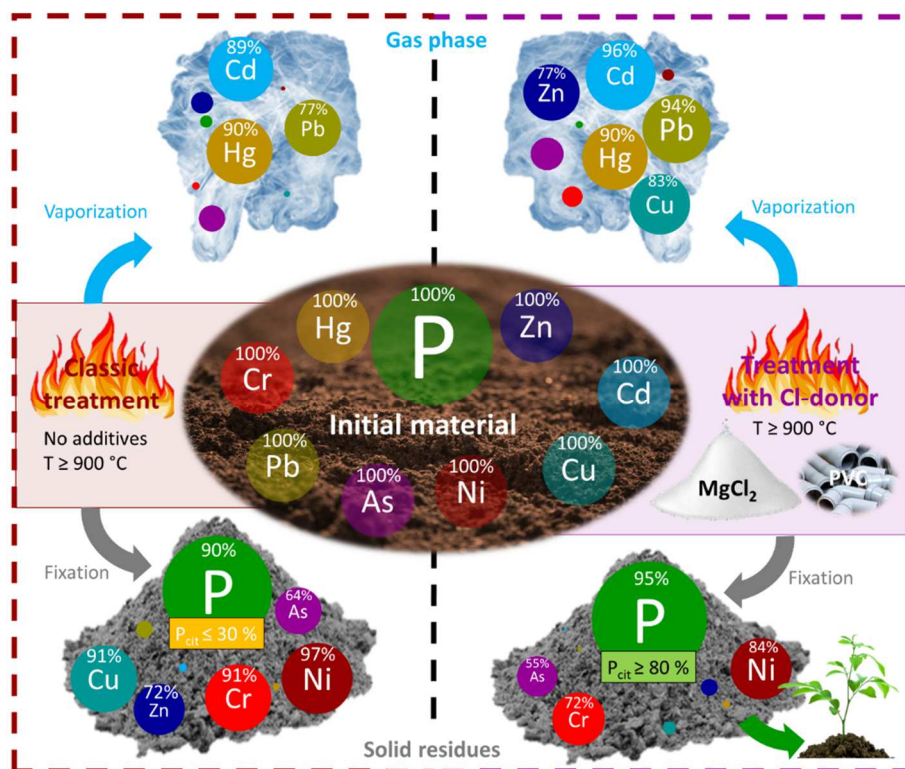
860 7. Conclusion and research perspectives

861 Phosphorus is a non-substitutable element necessary for plant growth whose supply is increasingly
862 limited and currently controlled by very few countries. The EU Commission has classified P as a
863 critical raw material in 2014 and recovery processes need to develop in the coming decades.
864 According to Schnell et al. [38], in Germany, with upcoming regulations on P recovery restricting SS
865 co-incineration disposal route, the most expected strategy is the development of new capacities for
866 SS mono-incineration plants with downstream P recovery from produced ashes.

867 To that extend, SS ashes thermochemical treatment with Cl-donor may be a particularly relevant
868 solution. Indeed, it allows an efficient removal of TME by the gas phase while enriching P in the solid
869 residues in highly soluble forms. Metal chlorides such as MgCl₂, CaCl₂ and NaCl are mostly used as Cl-
870 donors, offering the advantages of low costs, easy availability, low toxicity and trouble-free handlings

871 during the chlorination process. $MgCl_2$ appears to be the most interesting Cl-donor because it has a
 872 combined impact on TME vaporization and P solubility. SS ashes thermochemical treatment under air
 873 with 100-150 g Cl/kg as $MgCl_2$ at 950-1000 °C thus allows, in average, removal rates of 40-50, >90,
 874 10-20, >80, >90, 10-20, >90 and >80% for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn respectively and a P_{cit}
 875 around 80-90%. For the downstream recovery of P from SS ashes, the development of such
 876 thermochemical treatments may therefore be particularly relevant.

877 As discussed in detail in this review, the studied TME have different vaporization properties. **Fig.**
 878 **7** summarizes the present results and compares the impact on TME vaporization and P bioavailability
 879 of a conventional SS thermochemical treatment without additives and a thermochemical process
 880 with $MgCl_2$ (for Cd, Cu, Hg, Pb and Zn) or PVC (for As, Cr and Ni) as Cl-donor. Thus, for materials with
 881 high Hg, Cd and/or Pb contents (and low contents for the other TME), a conventional
 882 thermochemical treatment without additives at a temperature above 900 °C is most of the time
 883 satisfying to produce P-rich solid residues that may be directly recovered as fertilizers or soil
 884 conditioners. High Zn and/or Cu contents require chlorine addition, preferentially in the form of
 885 $MgCl_2$ and a thermochemical treatment above 900 °C. It is interesting to mention that the use of
 886 $MgCl_2$ generally enhances the bioavailability of P in the solid residues obtained. For materials
 887 containing high As, Cr or Ni contents, thermochemical treatments may not be the best technical
 888 solutions at this time.



889 **Figure 7** – Summary graph comparing the impact on TME vaporization and P bioavailability of a classic SS thermochemical
 890 treatment (no additives) and a thermochemical process with $MgCl_2$ and/or PVC (for As, Cr and Ni removal) as Cl-donors. The
 891 circle size is related to the content in the different phases and was build thanks to the median removal rates compiled in
 892 Tables 3 and 4.
 893

894 Some limitations require further research and discussions. First the reported removal rates for
 895 Cr, Ni and As are so far below 50%. Therefore, other additives and treatment conditions need to be
 896 investigated with a focus on these three elements. Another limitation is the high Cl-contents used to
 897 achieve high removal rates. They are mostly above 100 g Cl/kg SS ashes which is a large excess (50 to

898 100 times more) compared to the TME concentrations in SS ash. Not many works trying to optimize
899 the Cl-TME contacts in order to minimize Cl addition were reported. Finally, few studies have
900 addressed on the impact of mixtures with different Cl-donors during thermochemical treatment,
901 when this could be a solution to improve As, Cr and Ni removal while preserving high vaporization
902 properties for the other TME. Moreover, despite many advantages (single industrial installation,
903 higher energy yields, combined P and energy recovery, high TME removal rates), direct SS
904 thermochemical treatments by incineration, pyrolysis or gasification with Cl-donors are currently
905 only poorly studied.

906 Therefore, many questions need to be addressed such as the impact of the Cl-rich gases produced
907 during the treatment process (corrosion issue on the reactor and pipes), the overall energy
908 efficiency, the TME removal rates and P solubility under various unexplored operating conditions, the
909 fate of the TME and their possible treatment after removal by the gas phase, the leachability of the
910 remaining TME in the solid residues, the organic matter influence, the impact of scaling up (batch to
911 continuous mode, lab to pilot and industrial scale), etc.

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917

918 Conflicts of interest

919 There are no conflicts to declare.

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Graphical abstract

