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## ► To cite this version:

Basile Galey, Boram Kim, Denise Blanc, Gaëlle Ducom, Elodie André, et al.. Sewage sludge thermochemical treatment with MgCl<sub>2</sub>: Preparation conditions impact on trace metal elements vaporization and phosphorus recovery. Sustainable Chemistry and Pharmacy, 2022, 27, pp.100652. 10.1016/j.scp.2022.100652 . hal-03776323

**HAL Id: hal-03776323**

**<https://hal.science/hal-03776323v1>**

Submitted on 22 Jul 2024

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1           **Sewage sludge thermochemical treatment with MgCl<sub>2</sub>: preparation conditions impact**  
2           **on trace metal elements vaporization and phosphorus recovery**

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11   **Abstract**

12   Phosphorus (P) plays an essential role in crops growth. Due to the overexploitation of non-renewable  
13   phosphate rock deposits and their uneven distribution worldwide, P has turned into a strategic  
14   resource for the modern agricultural system. Finding sustainable ways to secure P for fertilizer  
15   applications has become critical. Sewage sludge (SS) is a waste material containing P in high amounts.  
16   Among several options, SS thermochemical treatment with Cl-donors addition such as MgCl<sub>2</sub>, CaCl<sub>2</sub> or  
17   NaCl allows to separate P from inorganics pollutants such as trace metal elements (TME). The  
18   additives goal is to help fix and form bioavailable P species in solid residues while promoting TME  
19   vaporization through the gas phase via chlorination mechanisms. This paper studies the impact of  
20   MgCl<sub>2</sub> addition on TME vaporization and P speciation during SS direct calcination treatment at 1000  
21   °C for 4 hours. Four different preparation methods for the “SS + MgCl<sub>2</sub>” mixtures were compared,  
22   with a variation of either the SS (raw or crushed) or the MgCl<sub>2</sub> form (powder or solution). The  
23   samples were characterized by ED-XRF, FTIR, XRD, TGA/DSC and the P speciation was obtained  
24   thanks to Williams-Saunders method. The use of 0.06 g MgCl<sub>2</sub> / g SS as a Cl-donor divides the TME  
25   contents in the solid residues by a factor of more than 10 for Zn and Pb, about 2 for As and Ni but  
26   less than 1.25 for Cu. Concerning P, Ca associated P species (mostly Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>) are formed with  
27   MgCl<sub>2</sub> addition. The results showed that the impact of different preparation methods on the  
28   obtained solid residues characteristics is limited.

29   **Key words**

30   Phosphorus recovery, Trace metal elements, Sewage sludge, Thermochemical treatment,  
31   Vaporization, Chlorination

## 32 1. Introduction

33 Phosphorus (P) is a vital non-substitutable element for life and food production (Ruttenberg, 2003). It  
34 is also a strategic resource as the modern agricultural system has become highly dependent on  
35 massive application in the fields of industrial P-based fertilizers. These fertilizers are however mostly  
36 produced by exploiting non-renewable phosphate rock (PR) deposits (Cordell et al., 2009; Cordell and  
37 White, 2011). Even if the scientific community is split about whether or not the reserve depletion will  
38 occur within 50 or 300 years, there is a general consensus on (i) the uneven distribution of PR  
39 deposits around the world, (ii) the remaining PR decreasing quality and (iii) the increasing extraction  
40 processing and shipping costs (Daneshgar et al., 2018). Consequently, finding alternative ways with  
41 circular economy approach to secure P for fertilizer applications has become one of the major  
42 challenges for the next decades.

43 Among several options, P recovery from sewage sludge (SS) has gathered the interest of many  
44 scientists (Raheem et al., 2018). Indeed, SS is the waste material containing the second greatest  
45 amounts of P after bone meal and has the main advantage of being abundantly produced worldwide.  
46 However, due to trace metal elements (TME) and the presence of microbiologic and organic  
47 pollutants, SS is most of the time incinerated for energy production and not further valued as a  
48 secondary P resource (Schnell et al., 2020). Indeed, in such thermochemical processes, the TME (Cr,  
49 Ni, Cu, Pb, Zn, etc.) are concentrated with P in the solid residues. European legislation will thus  
50 evolve. In 2026 in Switzerland, it will be mandatory to recover at least 80% of the P contained in SS  
51 before final disposal. Germany, France and the EU may follow before 2030 (in 2029 or 2032 for  
52 Germany, depending on the plant size). Simple SS incineration processes will therefore no longer be  
53 possible. Finding a way to recover both P and energy during SS thermochemical treatment is  
54 therefore highly desirable (Gao et al., 2020).

55 Alternative SS thermochemical treatments with additives may be a solution. The idea is to treat  
56 SS with chemical additives to produce energy and P-rich solid residues that may be directly used as  
57 fertilizers or soil conditioners (Meng et al., 2019). Cl-based compounds such as  $MgCl_2$ ,  $CaCl_2$ , PVC,  
58 NaCl and KCl are the most frequently used (Adam et al., 2009; Vogel et al., 2013). The role of these  
59 additives is to help fix P under bioavailable forms in solid residues (interaction with Mg, Ca, Na, K,  
60 etc.) while promoting TME (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) vaporization through the gas phase  
61 (chlorination mechanisms). Current existing thermochemical treatments with Cl-donors can be  
62 performed either in one (Xia et al., 2020) or two steps (Vogel et al., 2013). In the two step processes,  
63 SS are first incinerated (leading to energy production and waste volume reduction), then the  
64 obtained ashes are further thermochemically treated with additives for P recovery (Nowak et al.,  
65 2010). The two step processes have been extensively studied during the last decades due to existing  
66 widespread SS incinerators (Adam et al., 2007; Herzel et al., 2016; Jeon and Kim, 2018; Kuboňová et  
67 al., 2013; Li et al., 2015; Nowak et al., 2012; Schnell et al., 2020; Vogel et al., 2016; Vogel and Adam,  
68 2011; Yu et al., 2016). In single step SS thermochemical processes, the sludge is directly treated with  
69 additives either by incineration, pyrolysis or gasification, with the dual purpose of recovering energy  
70 and P. Despite advantages of single industrial installation, only few studies focus on the single step SS  
71 thermochemical treatments with Cl-based compounds (Liu et al., 2015; Saleh Bairq et al., 2018; Xia et  
72 al., 2020; Yang et al., 2019). Galey et al. recently wrote a review article on the topic (Galey et al.,  
73 2022).

74 Magnesium chloride ( $MgCl_2$ ) has been extensively studied in the literature due to a high  
75 efficiency for TME removal (indirect chlorination pathway) combined with a high solubility of the P  
76 species formed during treatment (interaction Mg-P) (Adam et al., 2009, 2007; Jeon and Kim, 2018; Li

77 et al., 2015; Nowak et al., 2012, 2010; Xia et al., 2020; Yu et al., 2016, p. 2). Most of the time,  $\text{MgCl}_2$  is  
78 used in powder hexahydrate form ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and mixed with SS (or SS ashes) before  
79 thermochemical treatment (Nowak et al., 2012, 2010; Xia et al., 2020; Yu et al., 2016). The Cl-donor  
80 can also be solubilized in water before being added to the SS (Adam et al., 2009, 2007). The  
81 preparation method for the “ $\text{MgCl}_2 + \text{SS}$ ” mixtures is however only poorly detailed in most papers.  
82 Furthermore, to our knowledge, no work compared different preparation methods impact on trace  
83 metal elements vaporization and phosphorus recovery from sewage sludge yet.

84 The present study therefore aims to present and compare different preparation methods for one-  
85 step SS thermochemical treatments with  $\text{MgCl}_2$ . Five different SS-based mixtures were thus prepared  
86 by varying either the form of SS (raw or crushed) or the form of  $\text{MgCl}_2$  (powder or in solution with  
87 water). They were treated in a tubular furnace at 1000 °C with air excess and with a 4 h residence  
88 time. The objectives were to highlight the role of  $\text{MgCl}_2$  addition and to evaluate the influence of the  
89 particle size of the SS and of the water content during the incineration process with chloride addition  
90 notably regarding the TME removal and the phosphorus distribution in ashes. The obtained ashes  
91 were characterized by XRD to identify the principal crystalline forms and by ED-XRF to determine the  
92 inorganics contents. Additional thermogravimetry analyses coupled with differential scanning  
93 calorimetry and Fourier-transform infrared spectroscopy analyses were also performed. A special  
94 focus was also done on phosphorus, which was fractioned into four operationally defined fractions:  
95 organic, inorganic, Ca associated and non Ca associated, thanks to Williams-Saunders method (Kim et  
96 al., 2015).

## 97 2. Materials and methods

### 98 2.1. Materials

99 All the thermochemical experiments were carried out with a SS from a Swiss wastewater treatment  
100 plant, using Fe salts to precipitate phosphates from wastewater. The sludge was dehydrated (using a  
101 centrifugation process), dried to reach a water content of around 6 wt% and stored in a freezer up to  
102 treatment. In the following, this sludge is referred to as raw SS “**r-SS**”. Commercial hexahydrate  
103 magnesium chloride (pure  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , powder form, Chimie Plus Laboratory) salt was used as  
104 additive.

### 105 2.2. Samples preparations

106 Five different SS-based mixtures were prepared. For some samples, a ball mill from Retsch was used  
107 to perform a grinding at 30 RPM during 5 min with a zirconium ball. When  $\text{MgCl}_2$  was added to SS, it  
108 is important to note that, irrespective of the preparation method, the amount of  $\text{MgCl}_2$  added was  
109 always 0.06 g  $\text{MgCl}_2$  / g SS (i.e. 44.7 g Cl/kg SS).

- 110 1. The first prepared mixture is called “**m-SS**”. It is the reference sample and corresponds to raw  
111 SS milled during 5 min as detailed above.
- 112 2. Raw SS was also co-milled with 0.06 g  $\text{MgCl}_2$  / g SS of  $\text{MgCl}_2$  under  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  powder form.  
113 It is the most classic preparation method. This sample is denoted as “**m-(SS+ $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )**”.
- 114 3. For the third preparation method, SS was first milled and then mixed with  $\text{MgCl}_2$  in solution  
115 concentrated at 32 wt%. In this mixture, the water amount involved is of 17 wt% and not  
116 enough to moisturize all SS. This mixture is called “**m-SS +  $\text{MgCl}_2$ .32%**”.
- 117 4. For the fourth mixture, SS was also first milled and then mixed with  $\text{MgCl}_2$  in solution  
118 concentrated at 12 wt%. In this mixture, the water content is of 35 wt% and allows to

119 moisturize all SS. This sample is denoted as “m-SS + MgCl<sub>2</sub>.12%”. Along with the third  
120 mixture, it may allow to study water impact on MgCl<sub>2</sub> dispersion in SS during preparation.

121 5. Finally, raw SS was used (without milling) and directly mixed with MgCl<sub>2</sub> in solution  
122 concentrated at 12 wt%. This mixture is called “r-SS + MgCl<sub>2</sub>.12%”. The water content is also  
123 of 35 wt%. With this sample, the goal is to investigate the impact of not milling the SS prior to  
124 thermochemical treatment.

### 125 2.3. Thermochemical treatment

126 After preparation, the 5 mixtures were thermochemically treated in a horizontal tube furnace from  
127 Thermolyne, under the same operating conditions. Four ceramic crucibles were used (for each  
128 mixture, in order to obtain enough ashes for sample characterization), filled with 20 g of samples (5 g  
129 in each crucible) and placed in the furnace. The treatment temperature was set to 1000 °C with a  
130 residence time of 4 h. Considering the heating time of 1 h and the cooling time of 2 h, each  
131 treatment lasts 7 h, of which 4 h at 1000 °C. Air was used in high excess as treatment gas. The  
132 obtained solid residues (ashes) were collected and milled 30 s at 30 RPM to ease subsequent  
133 analyses. Hereafter, ash from the calcination of m-SS is referred to as “m-SS ash”, ash from the  
134 calcination of m-(SS+MgCl<sub>2</sub>.6H<sub>2</sub>O)” is referred to as “m-(SS+MgCl<sub>2</sub>.6H<sub>2</sub>O) ash”, etc.

### 135 2.4. Samples characterization

136 The characterizations were performed either on the mixtures before thermochemical treatment or  
137 on the obtained solid residues (ashes). The produced gases during treatment were unfortunately not  
138 monitored.

139 Energy Dispersive X-ray Fluorescence (ED-XRF) with Xepos (AMETEK, FX EDXRF model XEPOS V  
140 HE) method was used to determine the inorganics contents (majors and minors) in the different  
141 samples. ED-XRF was also used to determine the TME and the total P contents in the solid residues  
142 obtained after the calcination experiments.

143 A thermogravimetric analyser coupled with a differential scanning calorimeter (TG-DSC, Mettler  
144 Toledo TGA 2) was used to study the mixtures decomposition. The mass of the samples was  
145 approximately 20 mg. The decomposition experiments were performed under 50 ml/min air, from 30  
146 to 1000 °C, with a heating rate of 10 °C/min and in an Al<sub>2</sub>O<sub>3</sub> crucible. A second heating ramp under  
147 the same conditions was performed after the first one, in order to see if the decomposition is  
148 complete.

149 Fourier Transform InfraRed spectroscopy (FTIR, Perkin Elmer Spectrum One FTIR spectrometer)  
150 experiments were performed on the raw SS and the produced ashes, with the Attenuated Total  
151 Reflectance method (ATR). X-ray diffraction experiments (XRD, Bruker D8 Advance instrument  
152 equipped with a copper anticathode) were also performed to determine the different crystalline  
153 forms in the produced ashes.

154 Finally, P was fractioned in organic, inorganic, Ca associated and non Ca associated, and the  
155 various liquid extracts were quantified by inductively coupled plasma with atomic emission  
156 spectroscopy (ICP-AES, Ultima 2 Horiba Jobin Yvon SAS) thanks to Williams-Saunders method, as  
157 described elsewhere by Kim et al. (Kim et al., 2015).

## 158 3. Results and discussion

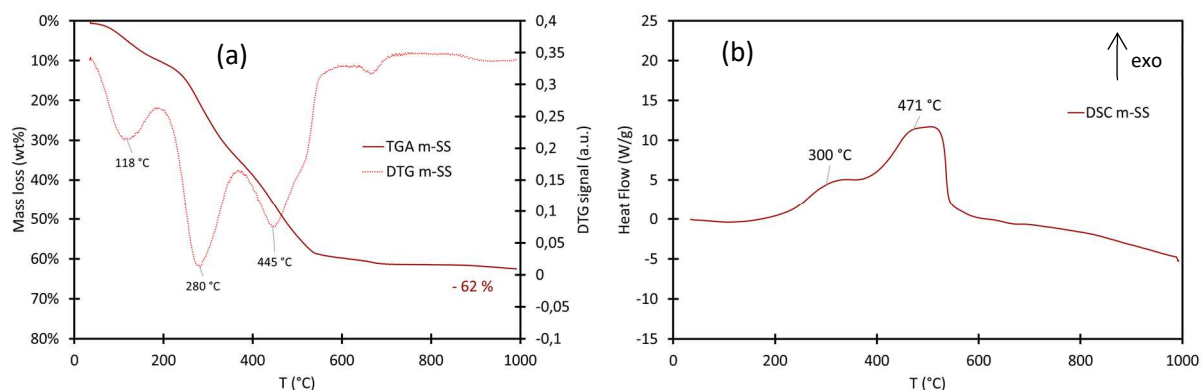
159 3.1. Samples characterization

160 The composition (majors and TME contents) of the sewage sludge used in this work is given in **Table**  
 161 **1**, as obtained by ED-XRF. The SS is Fe rich, which is in good agreement with the fact that Fe salts  
 162 were used to precipitate phosphates during the wastewater treatment process. Phosphorus content  
 163 is 2.8 wt%. The other majors contents are in the typical range of SS in Europe (Ronda et al., 2019).  
 164 Concerning the trace metal elements, the sludge is mostly rich in Cu and Zn (content of 399 and 855  
 165 mg/kg respectively) while only 80, 36, 35, 13, 1 and 1 mg/kg of Cr, Pb, Ni, As, Cd and Hg were  
 166 detected by ED-XRF respectively (**Table 1**).

**Table 1 – r-SS composition: majors (wt%) and TME (mg/kg), as obtained by ED-XRF**

Majors	Si	Al	Fe	Ca	Mg	K	S	P
wt%	2.7 ± 0.3	2.5 ± 0.2	5.4 ± 0.5	3.2 ± 0.3	0.5 ± 0.1	0.2 ± 0.1	2.1 ± 0.5	2.8 ± 0.3
TME	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
mg/kg	13 ± 3	1 ± 1	80 ± 37	399 ± 30	1 ± 1	35 ± 4	36 ± 6	855 ± 50

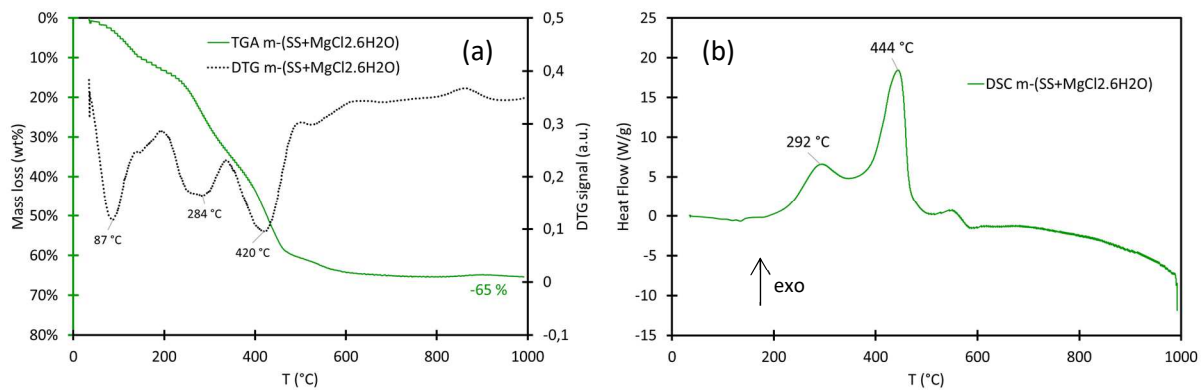
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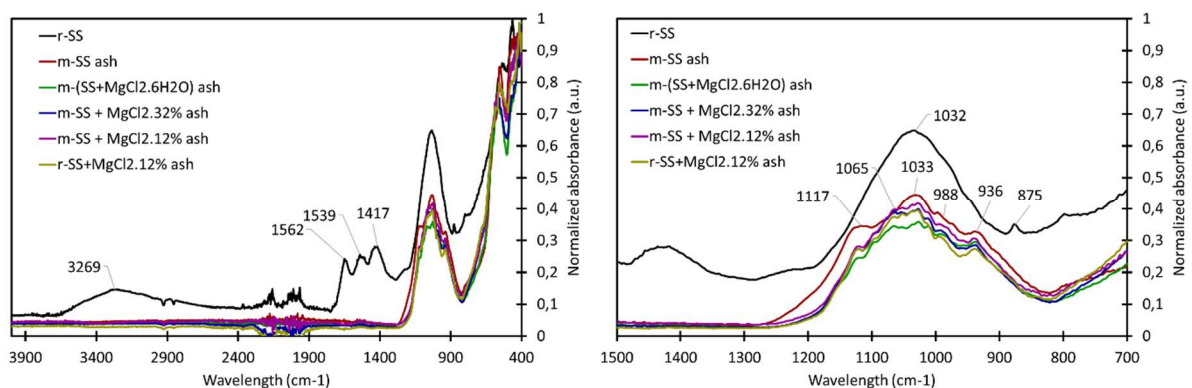
169 Figure 1 – Thermochemical decomposition of the reference system “m-SS” heated under air from 30 to 1000 °C (10 °C/min):  
 170 (a) mass loss (TGA) and derivative (DTG) (b) heat flow as a function of the temperature.

171 **Fig. 1** presents the thermal analyses performed on the reference system (m-SS), allowing to  
 172 study its decomposition pathway. As visible in the thermogravimetric analyses of **Fig. 1 (a)**, the  
 173 decomposition of the sludge starts as early as 40 °C with a first mass loss of approximately 10 wt% up  
 174 to 190 °C. It is likely to correspond to the vaporization of water present in the sludge. Above 200 °C  
 175 (with 2 DTG maxima at 280 and 445 °C), the organic carbon species are decomposed, as confirmed by  
 176 the two exothermic peaks visible in the DSC experiment of **Fig. 1 (b)**. At the end of the thermal  
 177 treatment, a plateau is visible from 600 to 1000 °C with no more significant decomposition.  
 178 According to the performed TG-DSC experiment, the volatile content in the sewage sludge is 62 w%,  
 179 with 10 wt% of water. No thermal decomposition is visible during the second heating ramp as visible  
 180 in **Fig. S1**.



181  
 182 *Figure 2 – Thermochemical decomposition of a mixture of SS and  $MgCl_2 \cdot 6H_2O$  in powder form “m-(SS+ $MgCl_2 \cdot 6H_2O$ )” heated*  
 183 *under air from 30 to 1000 °C (10 °C/min): (a) mass loss and derivative (b) heat flow as a function of the temperature.*

184 When  $MgCl_2$  is added to the SS, few differences can be noticed. Fig. 2 presents the thermal  
 185 analyses performed on the mixture m-(SS+ $MgCl_2 \cdot 6H_2O$ ). 0.06 g  $MgCl_2$  / g SS of  $MgCl_2$  was thus added  
 186 to the SS before grinding, under  $MgCl_2 \cdot 6H_2O$  powder form. The thermogravimetric analysis of Fig. 2  
 187 (a) shows three mass losses with DTG maxima at 87, 284 and 420 °C. The first one corresponds to  
 188 water evaporation and is slightly higher than for m-SS (14 against 10 wt%) due to the presence of  
 189 water in the  $MgCl_2 \cdot 6H_2O$  used to prepare the mixture. The two other mass losses correspond to the  
 190 organic carbon species decomposition (as confirmed in Fig. 2 (b) by the two exothermic peaks). In  
 191 comparison with the thermal decomposition of m-SS in Fig. 1, the second exothermal peak observed  
 192 for m-(SS+ $MgCl_2 \cdot 6H_2O$ ) mixture is thinner and happens at a lower temperature (444 against 471 °C).  
 193 As visible in Fig. S2 (thermal decomposition of the  $MgCl_2 \cdot 6H_2O$  powder used for the experiments),  
 194 when  $MgCl_2$  is heated up to 1000 °C, HCl gas is likely to be produced from 400 to 800 °C (as also  
 195 reported in (Yu et al., 2016)). HCl presence and interaction with the SS may therefore explain the  
 196 difference of the peak shape between Fig. 1 (b) and 2 (b). At 1000 °C, about 65 wt% of the mixture is  
 197 decomposed, with 14 wt% of water. No further thermal decomposition is visible during the second  
 198 heating ramp, Fig. S1. Vogel et al. investigated the treatment of sewage sludge ashes with  $MgCl_2$  by  
 199 thermogravimetry (Vogel et al., 2011a). Without organic matter, they observed a nearly constant  
 200 mass loss in the range 400–1000 °C, which is consistent with these results.

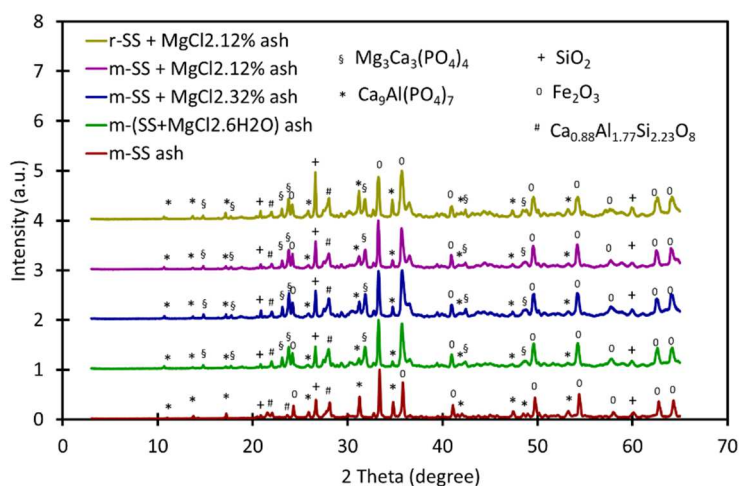


201  
 202 *Figure 3 – FTIR experiments performed on the raw SS and on the obtained ashes after the calcination experiments for*  
 203 *the five prepared mixtures.*

204 Fig. 3 presents the FTIR experiments performed on the raw SS and on the ashes obtained after  
 205 the calcination treatment at 1000 °C for the five mixtures. First, it is important to note that the  
 206 absorption bands corresponding to water at 3269  $cm^{-1}$  and to carbon species present at 1562,  
 207 1539, 1417 and 875  $cm^{-1}$  in the raw SS are not present anymore in the ashes after the calcination



208 treatment, mainly due to water vaporization and organic matter degradation. The mixture  
 209 decomposition is therefore complete under the chosen operating conditions (1000 °C – 4 h residence  
 210 time – air). The IR bands between 900 and 1200 cm<sup>-1</sup> visible in the ashes samples result from several  
 211 contributions which overlap. These wavelengths are characteristic of Si–O–Si vibrations and  
 212 therefore to quartz and silica based minerals (Vogel et al., 2011a). In the range 1000-1100 cm<sup>-1</sup> some  
 213 P-O stretching bands characteristic of Mg/Ca-P compounds can also be observed (Kim et al., 2013;  
 214 Vogel et al., 2011b). The high content in iron in raw sludge would also suggest the presence of P–O  
 215 stretching bands associated to small amount of iron phosphate (Palacios et al., 2012). No significant  
 216 differences are visible between the 5 ashes except the presence of an IR bound at 1065 cm<sup>-1</sup> for the 4  
 217 mixtures containing MgCl<sub>2</sub>, which may be attributed to P-O bound stretching of Mg-P compounds  
 218 (Vogel et al., 2011b).



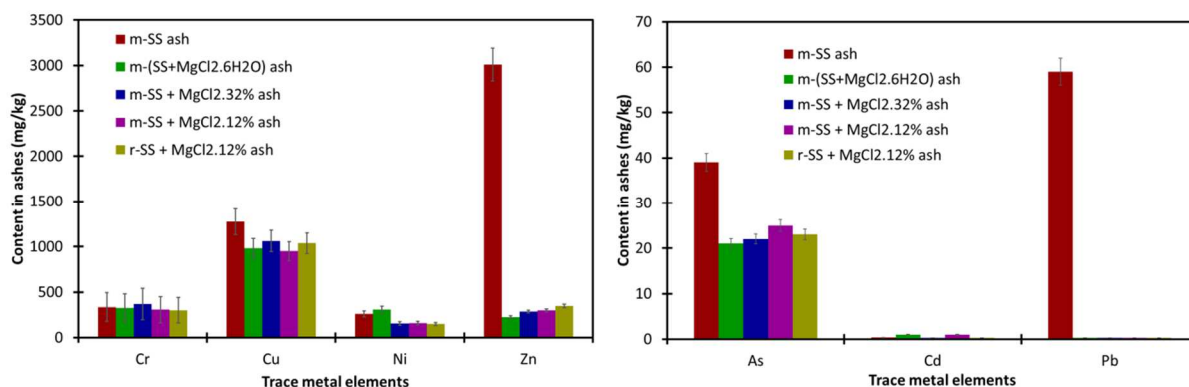
219  
 220 *Figure 4 – X-ray diffraction patterns of the obtained ashes after the calcination experiments for the five prepared*  
 221 *mixtures.*

222 XRD experiments were also performed on the produced ashes after calcination experiments.  
 223 The obtained results are presented in Fig. 4. Classical inorganic compounds are detected in the 5  
 224 solid residues, corresponding to SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Ca-Al-Si species. No significant differences  
 225 concerning these species are visible between the samples. Interestingly, for the P based species:  
 226 Ca<sub>9</sub>Al(PO<sub>4</sub>)<sub>7</sub> is detected in all mixtures while Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> is only present in the samples containing  
 227 MgCl<sub>2</sub>. It means that MgCl<sub>2</sub> addition prior to thermochemical treatment leads to the formation of  
 228 Mg-Ca-P species when treated at high temperature, as also observed in other works (Adam et al.,  
 229 2009; Vogel et al., 2013; Yang et al., 2019).

### 230 3.2. TME removal

231 The primary goal of sewage sludge thermochemical treatment with Cl-based additives is to promote  
 232 TME vaporization in order to obtain TME-free solid residues (for further use as fertilizer). The  
 233 European regulation focuses on 8 TME: arsenic, cadmium, chromium, copper, lead, mercury, nickel  
 234 and zinc. Their contents in the solid residues obtained after the calcination of the 5 prepared  
 235 mixtures were therefore measured thanks to ED-XRF. The results are presented in Fig. 5.





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Figure 5 – TME contents in the obtained ashes after the calcination experiments for the five prepared mixtures as obtained by ED-XRF.

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First, it is interesting to compare the ashes obtained from the sample without MgCl<sub>2</sub> (m-SS ash) with the ashes from the mixtures containing 0.06 g MgCl<sub>2</sub> / g SS of MgCl<sub>2</sub> (the four other samples):

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It appears that the contents of Zn and Pb in the ashes are greatly decreased thanks to MgCl<sub>2</sub> addition (from 3011 to less than 350 mg/kg for Zn and from 59 to less than 1 mg/kg for Pb, Fig. 5). Cl addition therefore promotes Zn and Pb removal thanks to ZnCl<sub>2</sub> (boiling point of 732 °C) and PbCl<sub>2</sub> (boiling point of 950 °C) volatile compounds formation, as reported elsewhere (Fraissler et al., 2009; Galey et al., 2022; Liu et al., 2015; Xia et al., 2020). According to (Galey et al., 2022), the chosen calcination conditions (combustion under air, at 1000 °C, 4 h residence time and with MgCl<sub>2</sub> as chlorine donor) are the best to promote both Zn and Pb removal through the gas phase. It probably explain the low contents observed in the ashes after calcination.

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Cadmium is a volatile compound which was initially present in low amounts in the SS (1 mg/kg, see Table 1) and was observed in amounts lower than 1 mg/kg in the obtained ashes after the calcination experiments, Fig. 5. Because of these very low amounts, the influence of MgCl<sub>2</sub> on Cd vaporization properties in these experiments are complicated to discuss.

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Arsenic removal seems to be enhanced by MgCl<sub>2</sub> addition, with a decrease of the contents in the ashes from 39 mg/kg without MgCl<sub>2</sub> to around 25 mg/kg in the 4 “MgCl<sub>2</sub> + SS” mixtures. It is difficult to conclude if the vaporization is due to chlorination mechanisms and/or by a remobilization of the element due to the acidic condition created by MgCl<sub>2</sub> addition. However, according to the data compiled by (Galey et al., 2022), arsenic hardly interacts with Cl during thermochemical treatment of SS. The authors also reported that arsenic mostly interacts with the major inorganic elements initially present in SS to form As-based stable compounds such as Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>, KAsO<sub>2</sub> and AlAsO<sub>4</sub>. The decomposition temperatures of these species are above 1000 °C. It may explain why arsenic is not completely vaporized during the calcination experiments.

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Copper vaporization properties seem to be only slightly enhanced in presence of MgCl<sub>2</sub> (1274 mg/kg of Cu in m-SS ashes against around 1050 mg/kg in the ashes treated with MgCl<sub>2</sub>). If higher removal rates are often reported in literature for copper when SS are treated with MgCl<sub>2</sub> (Adam et al., 2009; Xia et al., 2020), some authors also highlighted lower Cu removal rate (Galey et al., 2022; Jeon and Kim, 2018; Nowak et al., 2012). A competition between Cl<sup>-</sup> and other anions may occur and limit Cu-Cl interaction. For example the high sulphur content in the used SS (2.1 wt%, Table 1) could lead to the formation of CuS, which is a stable compound under the chosen operating conditions, limiting Cu-Cl interaction and therefore Cu vaporization as CuCl, CuCl<sub>2</sub> or (CuCl)<sub>3</sub> (Galey et al., 2022).

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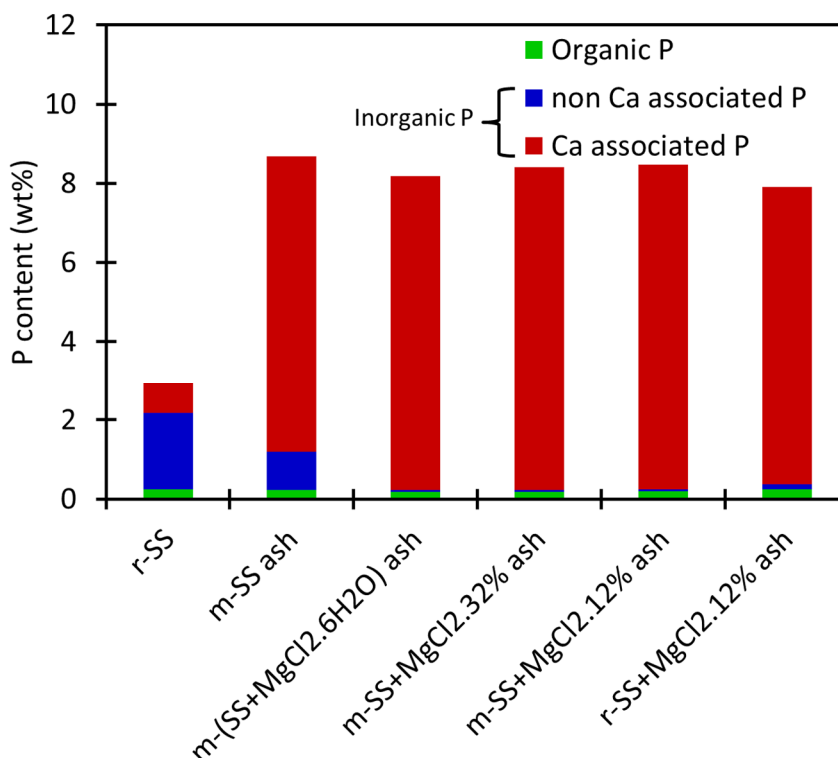
270 The amount of Cl addition, the limiting interaction of gas phase with solid and the residence time  
271 were also factors which were identified as limiting for Cu removal (Galey et al., 2022).

272 The observed mercury contents in the ashes are surprisingly high (between 29 and 22 mg/kg),  
273 especially regarding the initial content in the SS of only 1 mg/kg and the high volatility of the element  
274 (Cheng et al., 2019; Sun et al., 2020). The observed contents are therefore likely to be due to an  
275 external contamination, probably coming from the furnace used to perform the calcination  
276 treatments. This element was therefore not further studied.

277 No significant changes in the chromium contents are visible for the five ashes, meaning that  
278  $MgCl_2$  has no impact on its vaporization under the chosen treatment conditions. It is in good  
279 agreement with what is observed in literature, Cr being considered as a low volatile TME with low  
280 interaction with Cl and whose removal is particularly challenging (Fraissler et al., 2009; Galey et al.,  
281 2022; Vogel and Adam, 2011).

282 The comparison between the 4 samples containing  $MgCl_2$  (added with different preparation  
283 methods) with each other shows no significant difference concerning the obtained TME contents in  
284 the produced ashes except for nickel. Indeed, when  $MgCl_2 \cdot 6H_2O$  in powder form is co-milled with dry  
285 SS, the Ni content in the obtained solid residues after calcination is of 309 mg/kg, while when more  
286 water is involved in the preparation process (use of  $MgCl_2$  in solution), the obtained contents are  
287 below 160 mg/kg. It means that the presence of water in the mixtures prior to treatment may  
288 enhance nickel removal, probably by promoting HCl formation and interaction with Ni to form  $NiCl_2$   
289 gas phase. To our knowledge, such Ni vaporization properties were however not observed elsewhere  
290 in literature.

### 291 3.3. P recovery



292  
293 Figure 6 – Phosphorus speciation in the raw SS (no calcination) and on the ashes after the calcination experiments for the  
294 five prepared mixtures, as obtained by Williams-Saunders method.

295 The second goal of sewage sludge thermochemical treatment with Cl-based additives is to help form  
296 P species that are bioavailable, in order to use the obtained ashes directly as fertilizers. A special  
297 focus on the behaviour of phosphorus during treatment was therefore done. Fig. 6 presents the  
298 speciation of P in the raw SS and in the ashes obtained after the calcination experiments for the five  
299 prepared mixtures. “Organic P” corresponds to phosphorus associated with organic compounds,  
300 “non-Ca associated P” to P associated with oxides and hydroxides of Al, Fe and Mn and “Ca  
301 associated P”.

302 In the raw SS, phosphorus is mostly under non-Ca associated forms, Fig. 6. It is in good  
303 agreement with the fact that Fe salts were used to precipitate phosphates during the wastewater  
304 treatment process and the observed high Fe content in the sludge (5.4 wt%, Table 1). Organic P is  
305 also detected in the raw sludge as well as Ca associated P. The P in the ashes obtained after the  
306 calcination treatment without MgCl<sub>2</sub> involved (m-SS ash) is mostly under Ca associated forms (mostly  
307 Ca<sub>9</sub>Al(PO<sub>4</sub>)<sub>7</sub>, as detected by XRD in Fig. 4) but with significant amounts of non-Ca associated P as well.  
308 When 0.06 g MgCl<sub>2</sub> / g SS of MgCl<sub>2</sub> is added to the mixtures prior to calcination, the P in the obtained  
309 ashes is almost 100% under Ca associated forms. MgCl<sub>2</sub> addition therefore allows to convert non-Ca  
310 associated P into Ca associated P, with the predominant crystalline form being Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> as  
311 detected by XRD in Fig. 4. Mg-Ca-P species formation thanks to MgCl<sub>2</sub> addition is also widely  
312 observed in literature (Adam et al., 2009; Galey et al., 2022; Vogel et al., 2013; Yang et al., 2019).  
313 Interestingly, these Mg-Ca-P species are considered highly bioavailable, notably in acidic soils (Vogel  
314 et al., 2018), and therefore particularly interesting for further use of the ashes as recycling fertilizers.

315 Concerning the 4 different preparation methods for MgCl<sub>2</sub> addition to SS, no significant  
316 differences are visible for the P speciation (Fig. 6), as well as for the P crystalline forms in XRD (Fig. 4)  
317 and the total P contents (Fig. 6). It means that the preparation method has a negligible impact on the  
318 P forms in the obtained solid residues.

#### 319 4. Conclusion

320 This study investigated the effect of MgCl<sub>2</sub> addition and the addition method on TME vaporization  
321 during sewage sludge direct thermochemical treatment at 1000 °C for 4 hours and the forms of P  
322 species in the solid residues. The use of 0.06 g MgCl<sub>2</sub> / g SS MgCl<sub>2</sub> as a Cl-donor (44.7 g Cl/kg SS)  
323 divides the TME contents in the solid residues by a factor of more than 10 for Zn and Pb, about 2 for  
324 As and Ni (when water is involved during preparation) but less than 1.25 for Cu (due to the high S  
325 content in the SS). No Cr removal was observed while Cd was vaporized even without MgCl<sub>2</sub> addition.

326 Concerning phosphorus, the obtained speciation and XRD analyses show the formation of Ca  
327 associated P forms in the solid residues obtained after SS calcination with MgCl<sub>2</sub>, mostly under the  
328 Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> form. SS direct thermochemical treatment at high temperature (1000 °C) with MgCl<sub>2</sub> is  
329 therefore particularly interesting to form bioavailable P species (notably in acidic soils) for further use  
330 of the ashes as recycling fertilizers.

331 Concerning the 4 different preparation methods for the “SS + MgCl<sub>2</sub>” mixtures explored in this  
332 work, no significant differences were observed between the produced ashes for the P speciation and  
333 forms and for the TME removal rates, except for nickel. Indeed, lower Ni contents in the solid  
334 residues were observed when water is involved in the “SS + MgCl<sub>2</sub>” mixtures preparation method,  
335 meaning that the presence of water promotes Ni-Cl interaction. The comparison of the different  
336 preparation methods allows to conclude that the co-milling of the SS and MgCl<sub>2</sub> is not required to  
337 obtain a good interaction between the SS and MgCl<sub>2</sub>, at least under the studied conditions. The  
338 simple mixing of SS (dewatered form thanks to a centrifugation process for example) with MgCl<sub>2</sub> in

339 solution (the preparation method noted “r-SS + MgCl<sub>2</sub>.12%”) thus allows to obtain solid residues with  
340 similar TME contents (even lower for Ni) and P forms.

#### 341 **Conflicts of interest**

342 There are no conflicts to declare.

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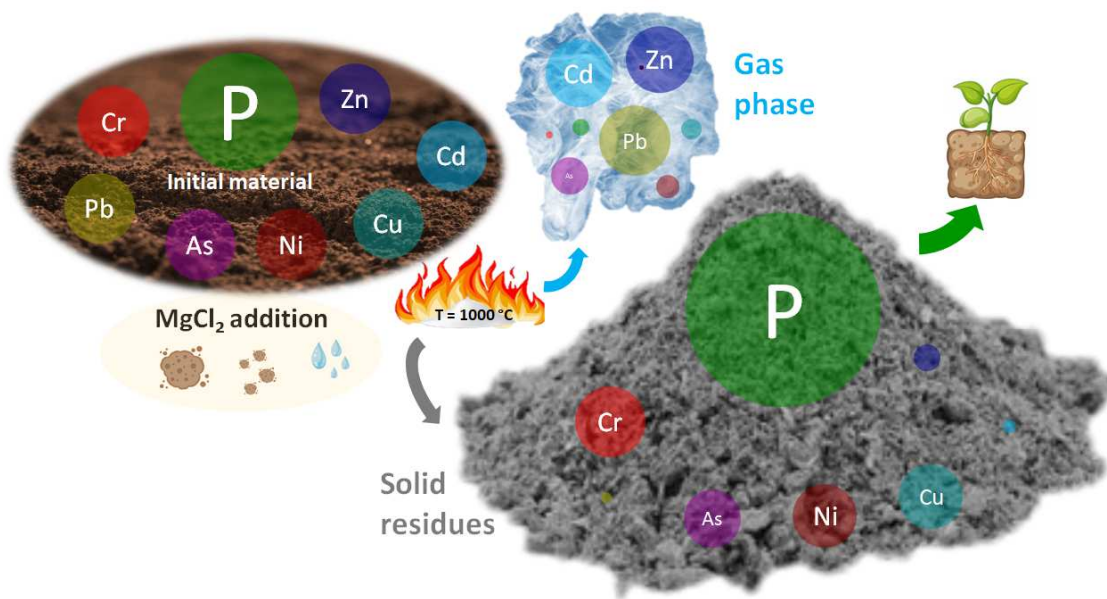
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455 **Graphical abstract**

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