

Behavior of phosphorus in catalytic supercritical water gasification of dewatered sewage sludge: The conversion pathway and effect of alkaline additive

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4 **1 Title Page**
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4 17 **Abstract:** This paper describes the behavior of phosphorus during the gasification of
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6 18 dewatered sewage sludge in supercritical water with an alkaline additive. Dewatered
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9 19 sewage sludge was treated in the autoclave at 400 °C for 30 min. Without additives,
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12 20 phosphorus is enriched in solid residue. The phosphorus transferred from the solid
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14 21 residue to the liquid product and the phosphorus content in the liquid product
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16 22 increased from 41.0 mg/L to 2214.5 mg/L in the presence of 2 wt% -8 wt% alkaline
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18 23 additive. The pathway of phosphorus under the catalytic condition is proposed.
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20 24 Analysis of the distribution of phosphorus forms in the solid residue and XRD results
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22 25 indicate that the alkaline additive combines with solid phase phosphate to form
23
24 26 analcime and kalsilite, which releases phosphate into the liquid phase. The
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26 27 concentration of phosphorus in the liquid product of supercritical water gasification
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28 28 with the alkaline additive was close to that obtained by chemical extraction.
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30 29 **Key Words:** dewatered sewage sludge, phosphorus, supercritical water, alkaline
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32 30 additive, Olsen phosphorus, dissolve reactive phosphorus
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43 32 **1. Introduction**

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45 33 Phosphorus is an essential element for all life forms and it is estimated that the
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47 34 remaining accessible reserves of phosphate rock on the earth will run out in 50 years,
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49 35 if the growth of demand for fertilizers remains at 3% per year ¹. For this reason, the
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51 36 recovery of phosphorus is very necessary. Dewatered sewage sludge (DSS) is an
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53 37 inevitable by-product of sewage treatment. It is difficult to dispose of, and is a source
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55 38 of environmental pollution risks because of its high moisture content and complex
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4 39 organic components. However, due to the large amount of phosphorus enriched in
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6 40 sludge during the sewage treatment process ², it has a high phosphorus recovery
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9 41 potential.

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11 42 Supercritical water gasification (SCWG) of sewage sludge has been receiving
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14 43 widespread attention in recent years ³, because it is a method that can decompose
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17 44 pollutants in sewage sludge and, at the same time, produce syngas (hydrogen,
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20 45 methane, carbon monoxide and so on), a clean energy resource ⁴. However, DSS
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22 46 contains many macromolecular substances such as lignin and humus, which inhibit
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25 47 gasification to some degree. In addition, the reaction conditions of SCWG are harsh,
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28 48 requiring a significant amount of energy for the water to reach a supercritical state.
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30 49 Thus, it is difficult to justify the high cost of operation if the only product obtained
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33 50 from the process is syngas. However, if large amounts of phosphorus can be
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36 51 recovered simultaneously with syngas, then the product value of SCWG of DSS will
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38 52 be improved effectively.

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40 53 To achieve high phosphorus recovery from DSS, it is necessary to study the regulation
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43 54 of the transformation of phosphorus during the gasification of DSS in supercritical
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46 55 water. In our previous work ⁵, the DSS was treated in autoclave at a reaction
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49 56 temperature of 400-500 °C without adding a catalyst. The organic phosphorus in the
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52 57 sludge was almost completely converted into inorganic phosphorus after the reaction,
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54 58 yielding a large amount of phosphorus that reached 20 mg/g in the solid residue .

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56 59 Other scholars have carried out experiments using different temperatures and types of
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59 60 reactors. For example, Feng et al. ⁶ reported that non-apatite inorganic phosphorus in
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4 61 sewage sludge tended to be converted into apatite phosphorus with the increase in pH
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6 62 after hydrothermal treatment at temperatures ranging from 220 °C to 240 °C;
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9 63 Amrullah and Matsumura⁷ used a continuous reactor to gasify sludge at 500-600 °C
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11 64 and established the reaction kinetics of phosphorus transformation. They found that
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13 65 organic phosphorus in the liquid products are converted into inorganic phosphorus
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15 66 within 5-10 seconds, and this conversion process proceeds according to first order
16
17 67 reaction kinetics. In addition, the recovery of phosphorus from other types of biomass
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19 68 has also been reported. Zhang et al.⁸ analyzed the distribution of phosphorus in the
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21 69 product of SCWG of cyanobacteria from Taihu Lake and found that even though
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23 70 solids comprise only 3.85% of cyanobacteria, approximately 80% of the phosphorus
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25 71 reside in the solid residues and approximately 75% of the phosphorus is combined
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27 72 with calcium. Alkaline additives are a form of homogeneous catalyst that are widely
28
29 73 used in hydrothermal gasification, as they can improve hydrogen production⁹. Chen
30
31 74 et al.¹⁰, employing algae mud and four alkaline additives in supercritical water at
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33 75 250-400 °C, found the phosphorus enriched in the solid residues was transferred to
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35 76 the liquid products under the influence of alkaline additives, but the mechanism of
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37 77 this phenomenon was not discussed.
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39 78 Therefore, knowledge based on the current research rests on two common areas of
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41 79 understanding. The first is that after hydrothermal treatment, organic phosphorus will
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43 80 be converted into inorganic phosphorus. The second is that inorganic phosphorus is
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45 81 mainly enriched in the solid phase products after hydrothermal treatment. However,
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47 82 the regulation of phosphorus transformation and the pathway it takes under catalytic
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4 83 conditions in the SCWG of DSS are still poorly understood. In this work, Na_2CO_3 and
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6 84 K_2CO_3 were used as homogeneous alkaline catalysts to further study (1) the
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9 85 transformation of phosphorus during sludge gasification in supercritical water and (2)
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12 86 the effects of alkali additives on phosphorus behavior and the mechanism involved in
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15 87 such effects. Based on our results, we propose a strategy for the recovery of
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17 88 phosphorus from gasification products of DSS in supercritical water.

19 89 **2. Material and Method**

22 90 **2.1 Material.** The DSS samples were collected from a sewage treatment plant in
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24
25 91 Nanjing, China, and refrigerated at a temperature below 4 °C. The properties of the
26
27 92 DSS are shown in Table 1. Moisture content was measured by differential weight after
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29
30 93 drying overnight in a 105 °C oven. Then, a certain amount of dried DSS was burned
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32 94 in muffle furnace at 550 °C for 4 hour to obtain the organic matter content.

35 95 [Insert Table 1 here]

38 96 Two alkali additives, Na_2CO_3 and K_2CO_3 , were purchased from Sinopharm
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40 97 Chemical Reagent Co., Ltd.

43 98 **2.2 Experimental procedures.** The experiments were performed in a batch
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46 99 autoclave purchased from the Songling Chemical Instrument Co. (China), and has
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48 100 been described in detail in a previous study¹¹. In the experiments, 41.1 g DSS and
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51 101 different amount alkaline additives were added to the reactor (containing 33 mL water,
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53 102 ensuring that the pressure reached 23 MPa at 400 °C), and then the reactor was placed
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56 103 into a salt bath furnace for heating. When the temperature reached 400 °C, it was held
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58 104 30 minutes, then the reactor was removed and cooled rapidly to room temperature
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6 106 **2.3 Separation and analysis of products.** After the completion of the reaction,
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9 107 the products were separated using a process of separation that was described in our
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11 108 previous paper ¹². Liquid products and solid residues were obtained after separation.
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14 109 Total phosphorus, composed of dissolved reactive phosphorus in the liquid product,
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17 110 and Olsen phosphorus in the solid residue, were determined by GB/T11893-1989 and
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19 111 HJ704-2014, respectively, and were measured by an ultraviolet spectrophotometer
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21 112 (UV2450; Shimadzu, Japan). The continuous chemical extraction method ¹³ was used
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24 113 to determine the total phosphorus content and the phosphorus form in the solid
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27 114 residue. Furthermore, phase analysis of the solid residues was carried out using X-ray
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29 115 diffraction (X'ATR, ARL, Switzerland).
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31 116 **3. Result**

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35 117 **3.1 Effect of alkaline additive on the distribution of phosphorus.** The total
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37 118 phosphorus content in the liquid products produced with different amounts alkaline
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39 119 additives in the reaction is shown in Fig. 1, and the distribution of total phosphorus in
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41 120 the solid residues and the liquid products is shown in Fig. 2. All experiments were
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43 121 repeated three times and the results are presented with standard deviations.
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47 122 Without alkaline additives, the content of phosphorus in the liquid product was very
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49 123 low (41.0 mg/L) with 98.9% of phosphorus concentrated in the solid residue. This
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51 124 result is consistent with previously reported experimental results. After adding 2
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53 125 wt%-8 wt% alkaline additives, the phosphorus content of the liquid products
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56 126 increased significantly when the alkaline additive was above 4 wt%. The increase in
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4 127 phosphorus content of the liquid phase is due to the transfer of phosphorus from the
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6 128 solid residue to the liquid product. The proportion of phosphorus in the liquid product
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9 129 reached 10.1% to 55.7% with the addition of alkaline additive (4 wt% to 8 wt%); and
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11 130 the phosphorus in the liquid product reached the highest concentration of 2214.5 mg/L
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14 131 when 8 wt% K_2CO_3 was added. This level is 54 times higher than that achieved
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17 132 without an alkaline additive.

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19 133 In addition, when we compared the effect of the same amount of different basic
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21 134 additives (Na_2CO_3 and K_2CO_3) on the liquid phase phosphorus content, we found that
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24 135 potassium salt was more effective than sodium salt in promoting the transformation of
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27 136 phosphorus from the solid to the liquid phase. This shows that the types of alkali
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30 137 metals also have an effect on the behavior of phosphorus in SCW. How alkali metals
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32
33 138 affect the transformation of phosphorus will be discussed in section 4.1.

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35 139 [Insert Figure 1 here]

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37 140 [Insert Figure 2 here]

38 39 40 141 **3.2 Effect of alkaline additive on the form of phosphorus in the solid residue.**

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42 142 Phosphorus in the solid residue exists in either organic or inorganic forms. The
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45 143 inorganic phosphorus includes exchangeable phosphorus (Ex-P), aluminum-combined
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48 144 phosphorus (Al-P), iron-combined phosphorus (Fe-P), occluded phosphate (Oc-P),
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51 145 self-ecological phosphorite and debris phosphorus. Self-ecological phosphorite and
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54 146 debris phosphorus both belong to calcium-combined phosphorus (Ca-P). The
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57 147 respective contents of the various forms of phosphorus in dry raw sludge and solid
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59 148 residues after SCWG with different alkaline additives were determined. The results
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4 149 are shown in Fig. 3. In the raw sludge, phosphorus was mainly in the form of
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6 150 inorganic phosphorus, and the content of organic phosphorus was only 0.14 mg/g. The
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9 151 value we obtained for the content of organic phosphorus in raw sludge is lower than
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11 152 values measured by other scholars^{5,7}, which may be mainly due to the difference in
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13 153 sludge properties and sewage treatment processes. Therefore, due to the much low
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15 154 content of organic phosphorus, we think that the change of organic phosphorus in our
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17 155 experiment condition is not the main pathway of transformation of phosphorus during
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19 156 SCWG of DSS. However, before and after the reaction, the change of organic
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21 157 phosphorus content was consistent with the results of previous studies. After the
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23 158 reaction, the content of organic phosphorus decreased gradually, regardless of whether
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25 159 alkali catalysts were added or not. After supercritical water gasification, the content of
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27 160 Ca-P in the solid residues increased significantly. The source for this increase in Ca-P
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29 161 is likely the transformation of other forms of phosphorus in the solid phase (mainly
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31 162 Al-P and Fe-P). However, we also found that the levels of reduction of the other
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33 163 forms of phosphorus were lower than the increases in Ca-P, indicating that
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35 164 water-soluble phosphate radicals are also combined with Ca^{2+} and then concentrated
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37 165 in the solid residue at the same time.

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39 166 After adding alkaline additive, phosphorus begins to transfer from the solid residue to
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41 167 the liquid product, reflected by an obvious decrease in the phosphorus level of the
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43 168 former. This is due to the combination of carbonate in alkaline additives with calcium,
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45 169 which produces a more stable calcium carbonate, because the different types of alkali
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47 170 metals do not significantly affect the reduction of Ca-P. However, when K_2CO_3 was
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4 171 added, the decrease in Al-P was more obvious compared to the situation when
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6 172 Na_2CO_3 was added. This may be due to the fact that compared to sodium ions,
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9 173 potassium ions combine with more aluminum. For this reason, the solid residues
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12 174 obtained by the experiments with different types of alkaline additives were further
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14 175 analyzed by X-ray diffraction, and the results are shown in Fig. 4.

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17 176 Quartz (SiO_2) was mainly detected in raw sludge and in the solid residues without
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19 177 alkaline additive. When Na_2CO_3 was added, the sodium ions combined with
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22 178 aluminum ions and SiO_2 to form analcime ($\text{NaAlSi}_2\text{O}_6$). On the other hand, when
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24 179 K_2CO_3 was added, the potassium ions combined with aluminum ions and SiO_2 to
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27 180 form kalsilite (KAlSiO_4). Aluminum ions tend to combine with alkali metal ions, and
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29 181 the phosphate ions that were originally bound to the aluminum ions are released into
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32 182 liquid products. The results of XRD indicate that the reduction of Al-P is related to the
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35 183 addition of alkali metal ions. Moreover, the addition of K_2CO_3 is related to a weaker
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38 184 detection peak signal of SiO_2 compared to the addition of Na_2CO_3 . This confirms our
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41 185 previous speculation that the potassium salt can more effectively combine with
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43 186 aluminum ions, resulting in a greater release of phosphate ions from Al-P.

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45 187 [Insert figure 3 here]

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47 188 [Insert figure 4 here]

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49 189 **3.3 Effect of alkaline additive on the Olsen phosphorus and dissolved**
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52 190 **reactive phosphorus.** Olsen-phosphorus (Olsen-P, is the result of available
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54 191 phosphorus determination by sodium bicarbonate extraction method) in solid residues
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57 192 and dissolved reactive phosphorus (DRP) in liquid products are forms of phosphorus
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60 193 that can be directly utilized by plants or easily extracted by chemical reagents.

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4 194 Therefore, the contents of these forms of phosphorus are very important for
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7 195 subsequent phosphorus recovery and utilization.

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9 196 The concentration of Olsen-P in the solid residue after adding different alkaline
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12 197 additives is shown in Fig. 5 (a). The red line in the figure represents the content of
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15 198 Olsen-P (455.42 ug/g) measured from dried raw sludge before the reaction. After
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18 199 SCWG, the Olsen-P in the solid residue rose, indicating that phosphorus in the solid
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21 200 residue was transformed into another form during SCWG, and the new forms of
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24 201 phosphorus were more easily and directly utilized or extracted. The concentration of
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27 202 Olsen-P decreased gradually with the addition of alkaline additive, which is mainly
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30 203 caused by the decrease in the total phosphorus content in the solid residue.

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33 204 Fig. 5 (b) shows the concentration of DRP and the ratio of DRP to total phosphorus in
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36 205 the liquid product after the addition of different amounts of alkaline additive. DRP is
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39 206 operationally defined as the colorimetrically detected orthophosphate and various
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42 207 ion-pairs with contributions from organophosphorus compounds and inorganic
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45 208 polyphosphates that are hydrolyzed to reactive phosphate during the analytical
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48 209 procedure ¹⁴. The addition of alkaline additive increased the ratio of DRP in liquid
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51 210 products, reaching 830.0 mg/L and 2006 mg/L, respectively, when Na₂CO₃ and
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54 211 K₂CO₃ were added at a concentration of 8 wt%. These concentrations are much higher
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57 212 than those achieved without Na₂CO₃ (21.6 mg/L). In addition, when the alkaline
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60 213 additive was added at a concentration of 2 wt%, although the resulting concentration
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215 214 of DRP was low, its proportion relative to total phosphorus in the liquid product
increased significantly. This shows that when Na₂CO₃ and K₂CO₃ were added at a

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4 216 concentration of 2 wt%, the proportion of active phosphorus in liquid phase increased
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6 217 significantly, indicating that the addition of alkaline additive can promote the release
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9 218 of phosphorus from the solid to the liquid phase, and that this released phosphorus
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11 219 basically exists in the form of DRP, such as phosphate. Comparing the results from
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14 220 the two alkaline additives, the concentration of DRP was higher when K_2CO_3 was
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17 221 added, which is consistent with the experimental results described in Section 3.1.

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21 22 223 **4. Discussion**

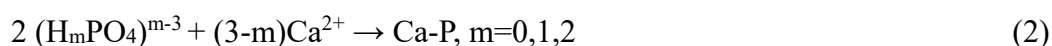
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25 224 **4.1 Transformation pathway of phosphorus during catalytic gasification of**
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27 225 **sludge in supercritical water.** Based on our experimental data and the research
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30 226 results of other scholars^{5, 15, 16}, the possible transformation pathways of phosphorus in
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33 227 SCWG of DSS are summarized below:

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35 228 a, Conversion of phosphorus without alkaline additive addition

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38 229 Without an alkaline additive, phosphorus was enriched in the solid residue, and the
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41 230 content of phosphorus in the liquid product was very low. Under these conditions, the
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43 231 transformation of phosphorus occurs through the different form phosphorus in the
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46 232 solid phase as shown in equation 1.



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51 233 Our experimental results also indicate that some phosphorus is transferred from the
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54 234 liquid product to the solid residue (as showed in equation 2), which is mainly due to
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57 235 the combination of phosphate ions and calcium in the liquid phase to form Ca-P.



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4 236 b, Conversion of phosphorus with alkaline additive addition

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6 237 In the presence of alkaline additives, the transformation of phosphorus occurs not
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9 238 only in the solid phase, but also between solid and liquid phases. The conversion of
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11 239 phosphorus in the solid residue follows the same pathway that operates without
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14 240 alkaline additives; and the pathway between solid and liquid phases mainly follows
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17 241 two routes:

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19 242 In the first, as shown in equation 3, the phosphorus that was originally combined
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22 243 with calcium releases into liquid product under action with alkaline additive



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27 244 In the second route, as showed in equation 4, alkali metal ions combine with Al to
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30 245 form analcime or kalsilite; and phosphorus, which was originally combined with
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33 246 aluminum, is released into the liquid phase.



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37 247 A summary of all the above pathways is presented in Figure 6.

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40 248 [Insert figure 6 here]

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43 249 In the previous results, we found that potassium salts were more effective than sodium
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46 250 salts in promoting the phosphorus from the solid residue to the liquid phase. Fig. 7
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48 251 shows the phosphorus balance with different alkali additives. It is worth noting that
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51 252 potassium salt can promote the transformation of Al-P and Ca-P to liquid phase more
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54 253 than sodium salt. The promotion of Al-P by potassium salts can be explained by XRD
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57 254 results, but the mechanism of potassium salt promoting Ca-p transformation is
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60 255 difficult to explain with data at present. This may be attributable to the promotion of

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4 256 the dissolution of hydroxyapatite under the action of potassium salts¹⁷. Besides, the
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6 257 addition of alkaline additive may directly inhibit the formation of Ca-P due to the low
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9 258 content of Ca-P in raw sludge.

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12 259 [Insert figure 7 here]

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14 260 **4.2 Phosphorus recovery and utilization analysis.** The SCWG, as well as other
15
16 261 hydrothermal treatments, of DSS results in phosphorus becoming enriched in solid
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18 262 residues. This type of phosphorus is often difficult to utilize directly (e.g. as
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20 263 phosphorus fertilizer), because of the complex properties of DSS itself. For example,
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22 264 DSS contains a variety of pollutants that may be effectively degraded by SCWG but
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24 265 are still associated with some environmental risks. Therefore, the common method of
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26 266 phosphorus recovery is by extracting from solid residues, followed by further
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28 267 recycling. For example, Acelas et al.¹⁸ used oxalic acid and sulfuric acid to extract the
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30 268 solid residues from sewage sludge gasified in supercritical water at 400-600 °C for 8
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32 269 hours. This process recovered between 80% to 95.5% of the phosphorus. Yu et al.¹⁹
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34 270 combined the hydrothermal pretreatment of sludge with the Magnesium Ammonium
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36 271 Phosphate (MAP) Precipitation method to recover the phosphorus in sewage sludge;
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38 272 this resulted in the recovery of 91.6% of the phosphorus.

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40 273 The first step in these recovery methods is the transfer of phosphorus enriched in the
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42 274 solid phase to the liquid phase by extraction. During this process, a large amount of
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44 275 extracting agent, often strong acid-based, is typically consumed. This is not
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46 276 compatible with subsequent processes such as the MAP methods that often require an
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48 277 alkaline environment. In this study, we found that alkaline additives can effectively
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4 278 promote the transfer of phosphorus from solid residues to liquid products. The liquid
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7 279 products containing high concentrations of phosphorus can be directly used in
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10 280 subsequent processes without extraction, which greatly simplifies the process and
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12 281 reduces the cost associated with the use of chemical reagents.

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14 282 Similar experimental results have been found in the SCWG of algae mud, however,
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16
17 283 the phosphorus content of algae mud is much lower than that of DSS. Using different
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20 284 types of alkaline additives, the highest concentration of phosphorus in liquid products
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22 285 obtained from algae mud was only 599 mg/L, which is only a quarter that of the liquid
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25 286 products of DSS gasification under the same conditions. Ekpo et al.²⁰ used a variety
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28 287 of chemical reagents to extract hydrothermally treated products of pig manure. The
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30 288 maximum phosphorus concentration in the extract reached 2200 mg/L, a standard that
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33 289 was reached during the SCWG of DSS with an alkaline additive.

34 35 290 **5. Conclusion**

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38 291 The behavior of phosphorus during sludge catalytic gasification with alkaline additvie
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41 292 in SCW were studied. Without an alkaline additive, the dominant reaction process is
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44 293 the conversion of different forms of phosphorus in solid phase, and 98.9% of the
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47 294 phosphorus enrich in the solid residues. Adding an alkaline additive can effectively
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50 295 promote the transfer of phosphorus from the solid phase to the liquid phase. Alkaline
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53 296 additives combine with Ca^{2+} and Al^{3+} to form calcium carbonate, analcime and
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56 297 kalsilite, and the phosphorus that was originally combined with Ca^{2+} or Al^{3+} is
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59 298 released to the liquid phase in the form of phosphate. The highest content of
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299 phosphorus in the liquid product reached 2214.5 mg/L, which is equivalent to the

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4 300 yield of other phosphorus recovery methods by chemical extraction. Direct production
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6 301 of liquid products with a high phosphorus concentration can simplify the exaction
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9 302 steps during subsequent phosphorus recovery. Therefore, the recovery of phosphorus
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11 303 from municipal sewage sludge by supercritical water gasification has great potential.
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4 380 **Figure captions**

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6 381 **Figure 1** Effect of the amount of alkaline additive on the phosphorus content of the
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9 382 liquid product, 400 °C, 30 min.

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11 383 **Figure 2** Distribution of total phosphorus in solid residue (S-TP) and liquid product
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14 384 (L-TP), 400 °C, 30 min.

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16 385 **Figure** Effect of the amount of (a) Na₂CO₃ (b) K₂CO₃ on phosphorus form in solid
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19 386 residue, 400 °C, 30 min.

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22 387 **Figure 4** XRD patterns of (1) raw dry sludge and solid residue (2) without additive (3)
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25 388 with 4 wt% Na₂CO₃ (4) with 4 wt% K₂CO₃, 400 °C, 30 min.

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27 389 **Figure 5** (a) Olsen phosphorus (Olsen-P) content of the solid residue and (b) amount
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30 390 and proportion of dissolved reactive phosphorus (DRP) in the liquid product, 400 °C,
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32 391 30 min.

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35 392 **Figure 6** Proposed pathway of phosphorus transformation in the supercritical water
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38 393 gasification of sewage sludge with alkaline additive, M⁺ represents the Na⁺ or K⁺,
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40 394 m=0,1,2.

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43 395 **Figure 7** Phosphorus balance in liquid product (L-TP) and solid residue with different
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46 396 alkaline additive, additive amount 4wt%.

397 **Tables****Table 1.** Properties of the tested dewatered sewage sludge.

Moisture content (wt%)	Organic matter (wt%) ^a	Ash (wt%) ^a	Ultimate analysis (wt%) ^a					HHV (MJ/kg) ^c	treatment process
			C	H	N	S	O ^b		
80.3	40.8	59.2	19.5	3.7	3.18	0.17	14.25	9.45	domestic sewage

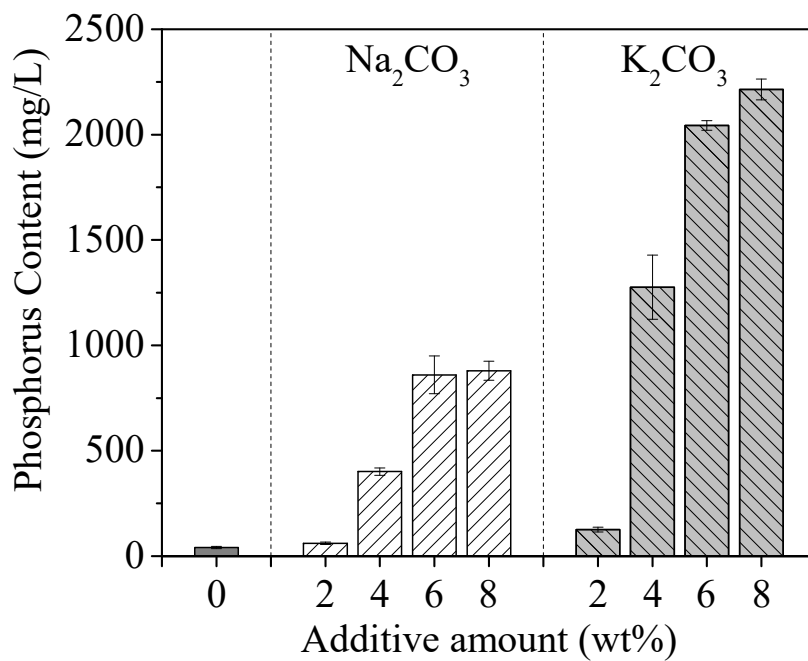
^a On an air-dried basis

^b By difference (O% = 100% - Ash% - C% - H% - N% - S%)

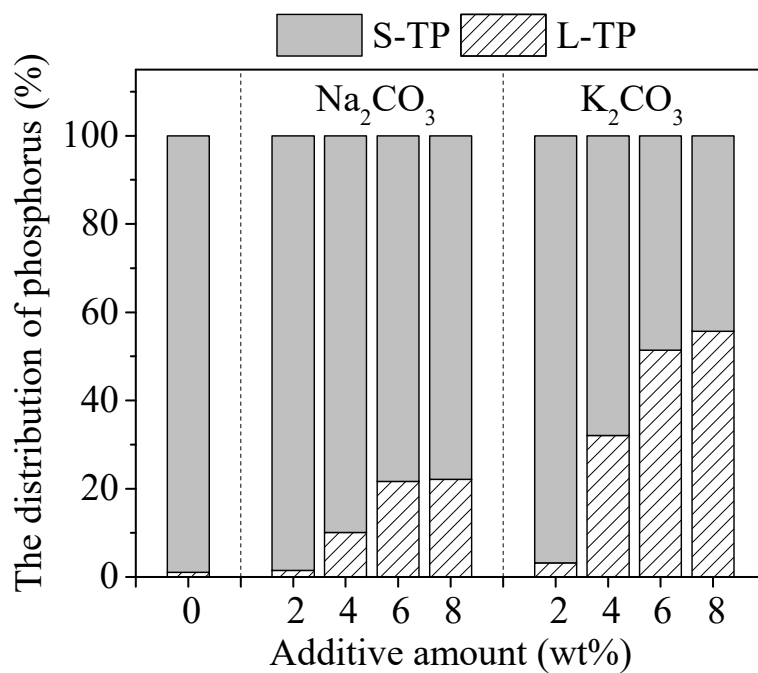
^c Higher heating value (HHV) calculated by the Dulong Formula: $HHV(KJ/kg) = 0.3393C + 1.443(H - O/8) + 0.0927S + 0.01494N$

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399 **Figure**
400 **Figure 1**



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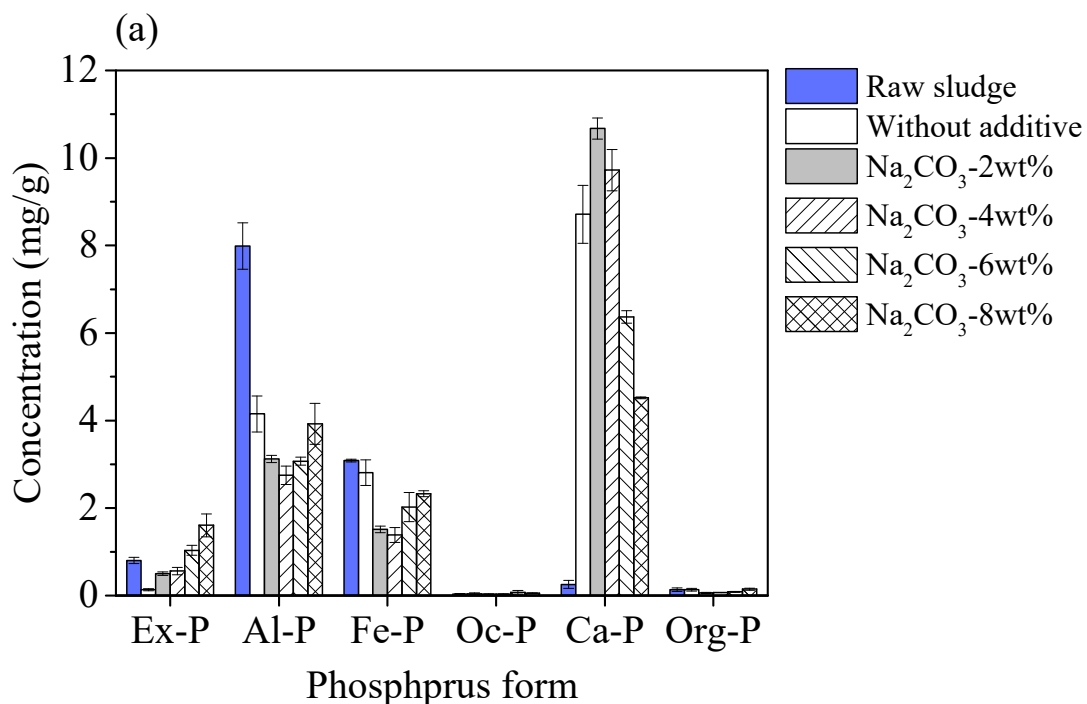
402 **Figure 2**

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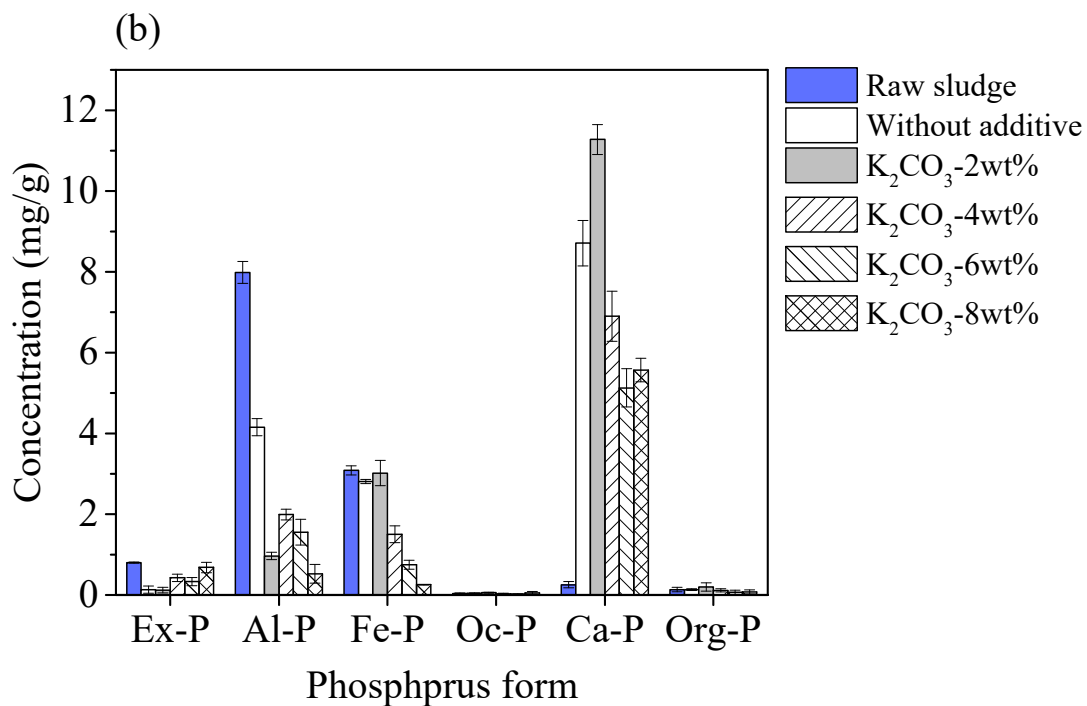
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404 **Figure 3**

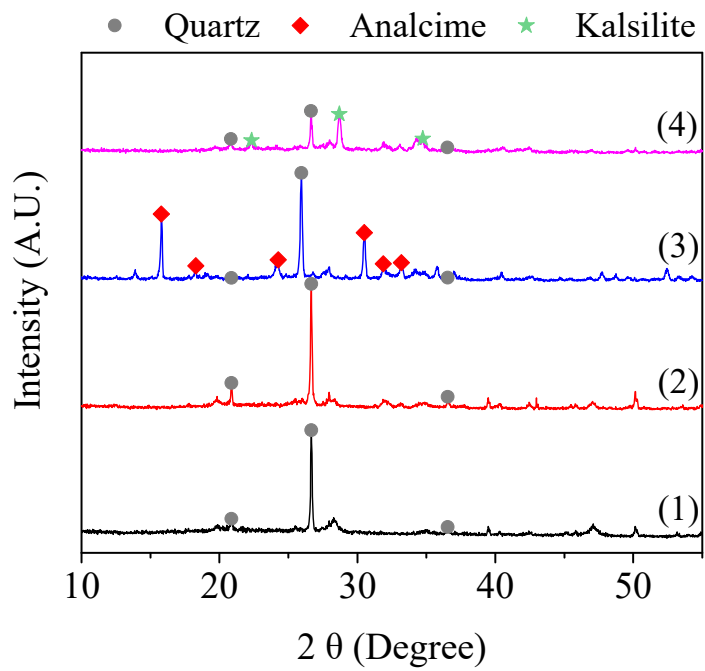
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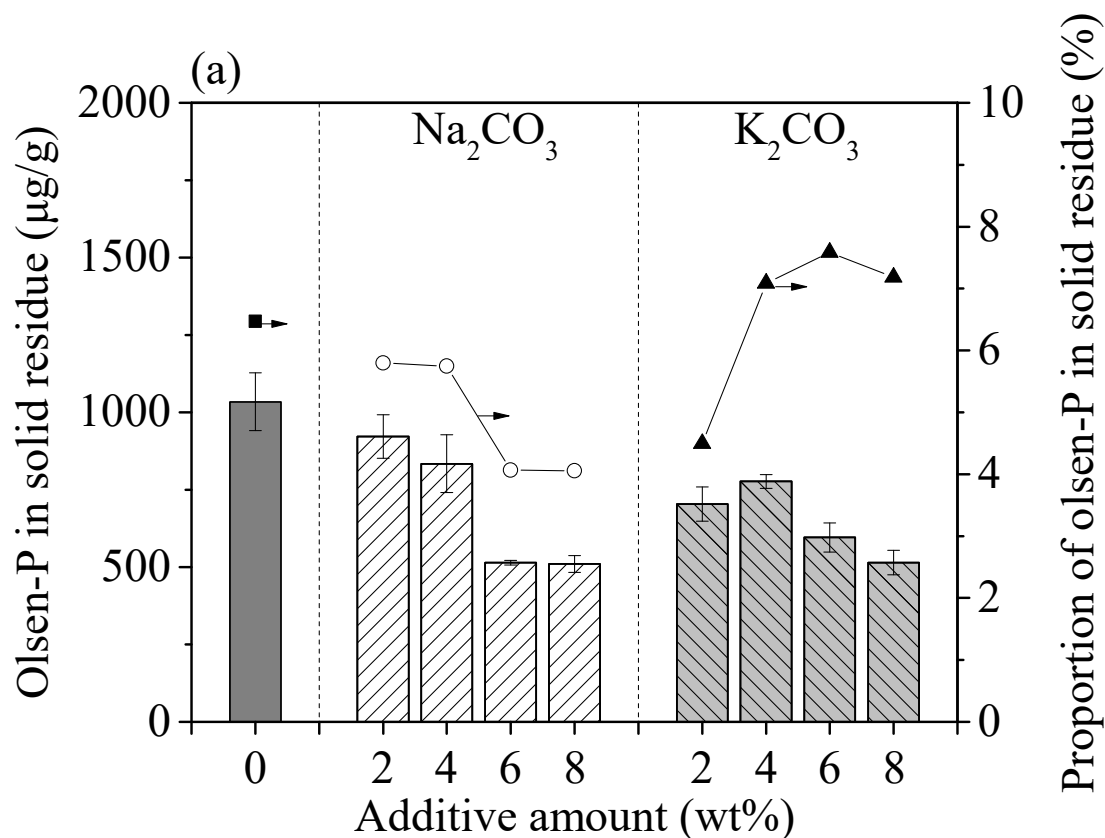
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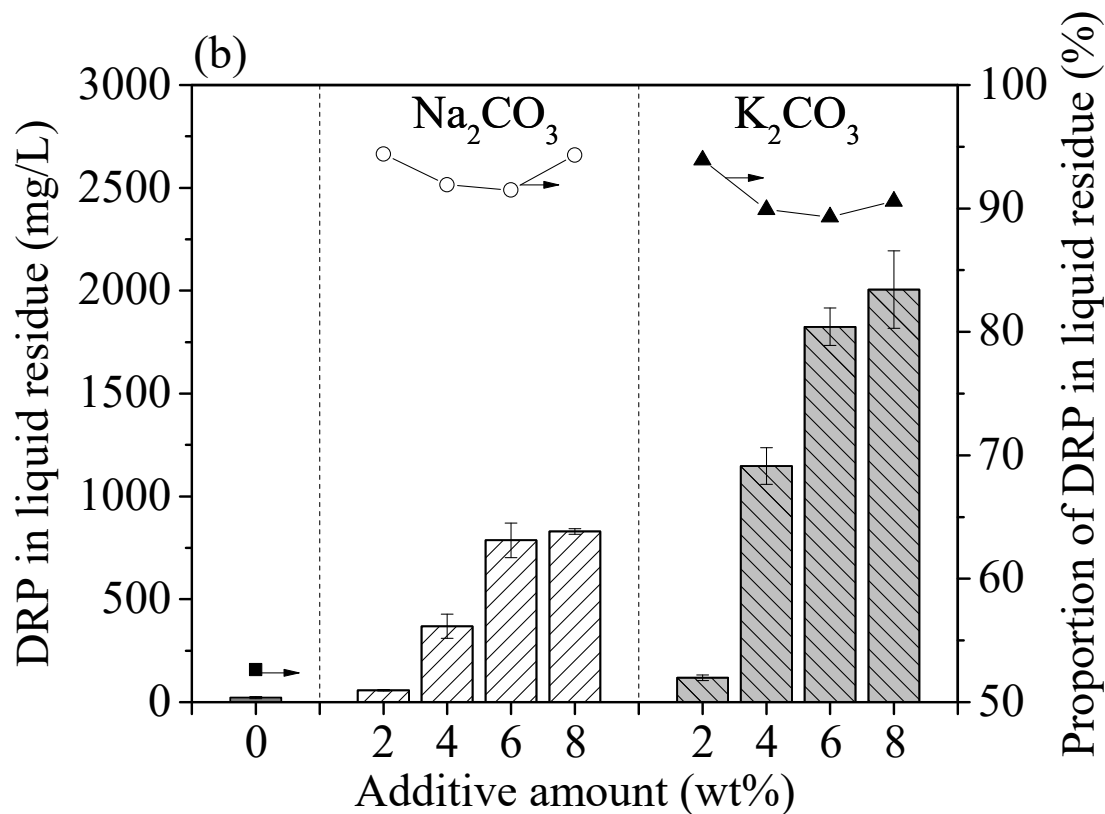
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408 **Figure 4**

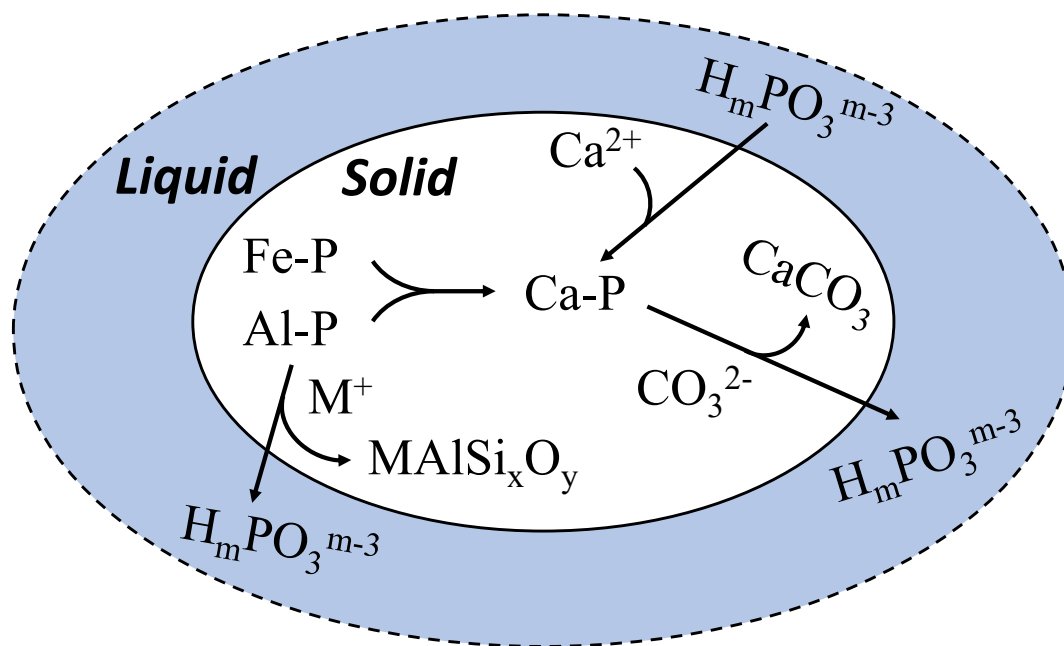
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410 **Figure 5**

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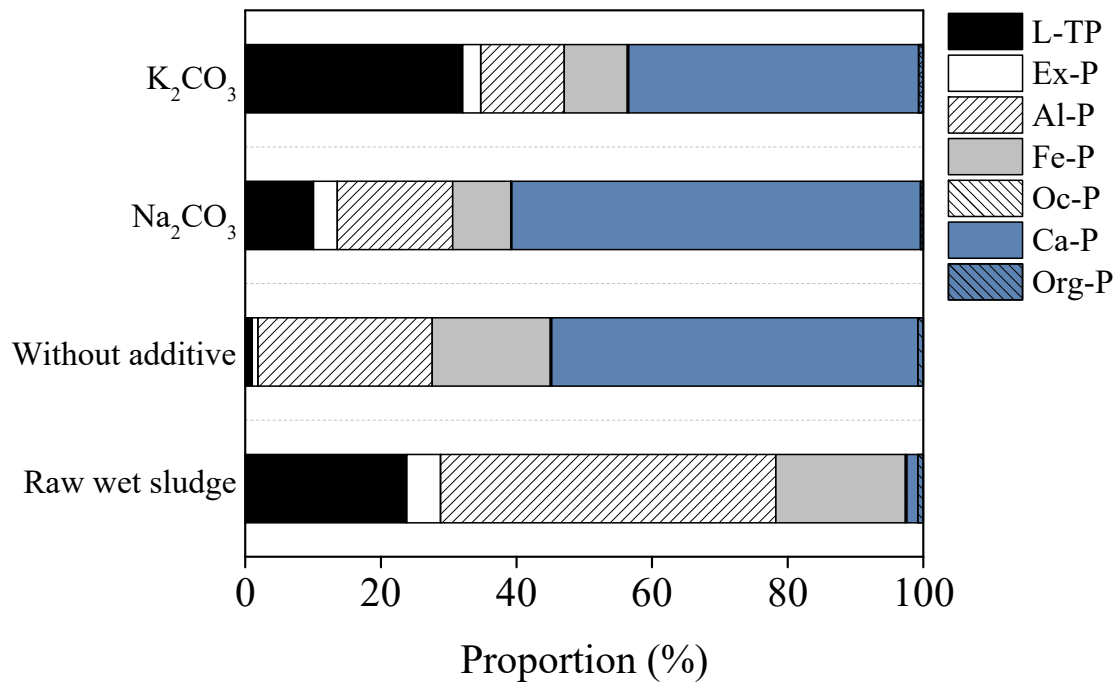
413 **Figure 6**

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415 **Figure 7**

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