Emission control of NO\textsubscript{x} precursors during sewage sludge pyrolysis using an integrated pretreatment of Fenton peroxidation and CaO conditioning

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\textbf{ABSTRACT}

In order to control the emissions of NO\textsubscript{x} precursors during sewage sludge pyrolysis, we proposed a novel integrated pretreatment method based on Fenton peroxidation and CaO conditioning. Nitrogen transformation was investigated using a self-designed drop-tube/fixed-bed furnace, and the mechanism of influence of residual conditioners was further clarified by employing model compounds. According to the results, the conversion of sludge-N to gas-N at 873–1273 K was strengthened by composite conditioning during the pyrolysis process. The remaining iron salts prevented some nitrogenous organic matter from deamination, whereas calcium compounds promoted the decomposition of proteins and amine to release NH\textsubscript{3}. Active iron atoms derived from an Fe-bearing conditioner reacted with NH\textsubscript{3} through the formation of Fe\textsubscript{a}N. Furthermore, combined conditioning hampered the conversion of amine-N/pyridine-N, pyrrole-N and nitrile-N to HCN, therefore enhancing their yields in char. The residual Ca compounds, which presented as Ca(OH)\textsubscript{2}, facilitated the hydrolysis of HCN and hampered HCN generation from amine-N, nitrite-N and heterocyclic-N in tar. Both residual iron and calcium conditioners were capable of reacting with protein-N in sludge and char to form Fe\textsubscript{a}N and CaC\textsubscript{x}Ny, respectively. The formation of complex Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} facilitated the decomposition of these intermediates, thus facilitating the conversion of sludge-N and NO\textsubscript{x} precursors (tar-N, NH\textsubscript{3}, HCN) to N\textsubscript{2}, achieving a highest non-polluting gas yield of 80.5%.

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\textbf{1. Introduction}

Thermal disposal is an efficient process to realize sewage sludge management with a potential benefit of energy recovery [1–3]. In
the development of this technology, NOx emissions, one of the leading causes of acid rain and photochemical smog, becomes a critical issue. This is due to the fact that the sludge nitrogen level tops off at 9.0%, which is far higher than that of traditional solid fuel [4,5]. It is widely accepted that NOx generation strongly depends on the NOx precursors yielded in the initial devolatilization (pyrolysis) stage, predominantly NH3 and HCN [6]. At temperatures below 1073 K, NH3 emissions are primarily a consequence of the deamination of amine-N compounds from sludge proteins, and the ring-opening of heterocyclic-N and nitrile-N from dehydrogenation and polymerization of amine-N contributes to the release of HCN [7,8]. When sludge is pyrolyzed in a microwave, a fixed bed or fluidized/fixed-bed reactor, these two main NOx precursors represent up to 30–80% of total nitrogen [4,5,7–10], which aggravates the risk of NOx pollution during subsequent combustion or gasification processes. Alternatively, if sludge-N can be efficiently converted to N2 rather than the precursors, this problem might be readily solved.

According to the literature [11–14], many kinds of metal materials possess a catalytic ability in N2 formation during solid fuel pyrolysis, especially for Fe- and Ca-containing compounds. Iron minerals hamper the formation of HCN, tar-N, NH3 and char-N, while calcium catalysts only reduce the production of HCN and tar-N [15,16]. This tendency is applicable to a variety of low rank coal [13]. On solid particles, iron compounds are likely to convert from the ion-exchangeable state into fine metallic particles which might be readily solved. Coincidentally, in the sludge pretreatment process, several iron and calcium salts are commonly applied to improve dewaterability and drying performance, for example, in the advanced composite conditioning method using Fenton’s reagent (Fe2+/H2O2) and CaO previously developed by the current authors [22–25]. Additional papers of this series [26–28] demonstrate that Fenton peroxidation and CaO conditioning can also cooperatively alter element evolution, promoting the generation of H2-rich fuel gas, as well as the cracking of tar molecules during sludge thermal disposal. Furthermore, the residual Fe- and Ca-compounds jointly capture liberated sulfur, realizing efficient sulfur fixation [27–29]. This Fe/Ca based conditioner thus plays an important role in sludge thermochemical conversion. However, it is uncertain whether additional capacity to affect nitrogen transformation exists.

In order to address this, we have recently investigated the individual role of CaO [5]. On that basis, the present study focused on: (1) quantifying the individual effect of Fenton’s reagent as well as the synergy of Fenton peroxidation and CaO conditioning on nitrogen distribution in three-phase pyrolysates; (2) clarifying the evolutionary mechanism by analyzing nitrogen functionalities and using model compounds; (3) providing the theoretical basis for an emission control strategy of NOx precursors during sewage sludge pyrolysis.

2. Experimental section

2.1. Sample preparation and sludge properties

Raw sludge (RS) was gathered from the dewatering chamber of an urban wastewater treatment plant in Wuhan, China. The RS collected contained 84.5 wt% of moisture after centrifugal dewatering using polyacrylamide as a conditioner. To ensure consistency and comparability of the tests, all treated samples were prepared using the RS. The optimized procedure (the rationale is given in our previous works [22,23]) can be found in Table 1. The RS underwent Fenton oxidation and/or CaO conditioning, deep dewatering, drying, grinding and sieving, and were accordingly labeled as S-Fenton, S-CaO and S-Fenton-CaO. According to the main characteristics listed in Table 2, four samples contained a content of volatile matter above 46% with a proportion of fixed carbon below 6%. For this type of fuel, studying devolatilization is essential in understanding any

### Table 1
Sample preparation procedure.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conditioning</th>
<th>Deep dewatering</th>
<th>Drying and sieving</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>Control</td>
<td>Filter press dewatering (40 min,</td>
<td>Thermal drying (273 K, 24 h) →</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6–0.9 MPa; 5 min, 1.0–1.1 MPa)</td>
<td>Grinding and sieving (180–250 μm)</td>
</tr>
<tr>
<td>S-Fenton</td>
<td>Mixing with H2O2 → Mixing with H2SO4 → Mixing</td>
<td>Filter press dewatering (40 min,</td>
<td>Thermal drying (273 K, 24 h) →</td>
</tr>
<tr>
<td></td>
<td>with FeSO4 (40 mg g−1 DS) → Mixing with H2O2 (32</td>
<td>0.6–0.9 MPa; 5 min, 1.0–1.1 MPa)</td>
<td>Grinding and sieving (180–250 μm)</td>
</tr>
<tr>
<td>S-CaO</td>
<td>Mixing with H2O2 → Mixing with CaO (300 mg g−1</td>
<td>Filter press dewatering (40 min,</td>
<td>Thermal drying (273 K, 24 h) →</td>
</tr>
<tr>
<td></td>
<td>DS)</td>
<td>0.6–0.9 MPa)</td>
<td>Grinding and sieving (180–250 μm)</td>
</tr>
<tr>
<td>S-Fenton-CaO</td>
<td>Mixing with H2O2 → Mixing with H2SO4 → Mixing</td>
<td>Filter press dewatering (40 min,</td>
<td>Thermal drying (273 K, 24 h) →</td>
</tr>
<tr>
<td></td>
<td>with FeSO4 (40 mg g−1 DS) → Mixing with H2O2 (32</td>
<td>0.6–0.9 MPa; 5 min, 1.0–1.1 MPa)</td>
<td>Grinding and sieving (180–250 μm)</td>
</tr>
<tr>
<td></td>
<td>(32 mg g−1 DS) → Mixing with CaO (300 mg g−1</td>
<td>Filter press dewatering (40 min,</td>
<td>Thermal drying (273 K, 24 h) →</td>
</tr>
<tr>
<td></td>
<td>DS)</td>
<td>0.6–0.9 MPa)</td>
<td>Grinding and sieving (180–250 μm)</td>
</tr>
</tbody>
</table>

### Table 2
Main physicochemical characteristics of raw sludge and the three conditioned samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Proximate analysis (wt%, dry basis)</th>
<th>Ultimate analysis (wt%, dry basis)</th>
<th>Ash analysis (wt%)</th>
<th>Iron speciation (At%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile matter</td>
<td>Ash</td>
<td>Fixed carbon</td>
<td>C</td>
</tr>
<tr>
<td>RS</td>
<td>52.10</td>
<td>41.94</td>
<td>5.96</td>
<td>28.27</td>
</tr>
<tr>
<td>S-Fenton</td>
<td>56.38</td>
<td>42.26</td>
<td>1.36</td>
<td>26.72</td>
</tr>
<tr>
<td>S-CaO</td>
<td>46.04</td>
<td>53.70</td>
<td>0.26</td>
<td>20.73</td>
</tr>
<tr>
<td>S-Fenton-CaO</td>
<td>46.13</td>
<td>53.69</td>
<td>0.18</td>
<td>19.60</td>
</tr>
</tbody>
</table>
thermal conversion process. Table 2 also implies that Fenton’s reagent had no discernible effect on sludge nitrogen level, whereas CaO significantly reduced the ratio from 5.36% to 3.40%. This reduction might be connected with additional inorganic solids and NH₃ emissions during the sludge conditioning stage [29]. Ash analysis and Mossbauer data included in Table 2 demonstrates that pretreatment resulted in high proportions of the iron and calcium remaining in the sludge matrix. Following oxidation, 100% of the iron was presented as Fe³⁺ rather than Fe²⁺ (Eq. (1) [30]).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^-  \tag{1}
\]

### 2.2. Sludge pyrolysis procedure

A self-designed drop-tube/fixed-bed reactor was used to perform sludge pyrolysis and product separation. The detailed configuration is displayed in Fig. 1a. Briefly, the reactor consists of an injector, an intermediate reaction tube, an outer quartz tube and two special U-shaped tubes. In a single run, three streams of ultra-pure argon were continuously injected as the carrier gas. Firstly, the main parts of the reactor were heated to the expected temperatures of 873 K, 1073 K and 1273 K using an electrical furnace. Secondly, sludge particles were fed (0.2 g min⁻¹) from the screw feeder into the water-cooled injector, preventing the sample from being pyrolyzed before entering the reaction zone. As the sludge dropped into the intermediate tube, it was rapidly heated and then devolatilized, accompanied by the falling of particles. Thus, this system enjoys the features of a drop-tube furnace.

Thirdly, within 10 min of feeding time, as shown in Fig. 1b, nascent char gathered at the bottom plate of the intermediate tube, while volatiles escaped through a circle of quartz frit nearby, achieving efficient separation of gas-solid products. Afterwards, condensable volatiles passed via the outer tube and flask into the U-shaped tube (labeled 1# in Fig. 1a) immersed in a low temperature environment (see Fig. 1c, liquid nitrogen for tar collection). In a parallel experiment, non-condensable volatiles escaped from the system (changing liquid nitrogen with ice water for gas analysis), and were collected using a gasbag. As a result, the perfect separation of gas-liquid products was achieved. Therefore, this reactor also embodies the features of a fixed bed. Finally, the system was quenched to room temperature by turning the furnace power off and opening its door, providing a continuous supply of argon. All parts of the reactor were washed and burned before commencing the next run.

### 2.3. Quantification of the pyrolysates

When the reactor returned to room temperature, it was disassembled into four parts. The production of the solid residue was obtained by weighing the intermediate reaction tube before and after sludge pyrolysis. The tar yield was estimated by calculating the weight difference of the U-shaped tubes in the test employing a liquid nitrogen bath. Subsequently, the nitrogen content of the collected char and tar were determined using a Vario Microcube analyzer (Elementar Company, Germany). The yields of N-containing gases, including N₂, NH₃ and HCN, were measured by means of a Micro Gas Chromatograph (Agilent 3000A) and a FT-
IR gas analyzer (Gasmet DX4000). Then, the gas-N production was estimated by adding them together. To clearly illustrate the balance, nitrogen yields in each phase as different functionalities were expressed as the percentage of nitrogen in the corresponding sludge sample. The production of other-N (HNCO, soot-N, etc.) was calculated from the difference.

2.4. N-functionalities analysis of tar and char

The nitrogen functionalities in tar were determined using Gas Chromatography-Mass Spectrometry (GC–MS, Agilent 7890 A/5975 C). A 30 m × 250 µm × 0.25 µm capillary column (HP-5 MS) was employed with 5% phenyl methyl silox. Septum purge flow was set as 3 mL min⁻¹, while the split ratio and flow were controlled at 2:1 and 50 mL min⁻¹, respectively. Initially, the oven temperature was kept at 313 K for 5 min, then increased to 453 K at a rate of 5 K min⁻¹, and finally programed to 553 K at 20 K min⁻¹ with an isotherm hold of 10 min. The results were analyzed using the NIST mass spectral database.

The nitrogen species in the sludge and char were identified by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000). The peak area represented the relative ratio of different nitrogen speciation. Assuming that the nitrogen forming on the surface is the same as that in bulk, semi-quantitative results of a certain species could be obtained via the nitrogen level of the sample and its relative content.

2.5. Pyrolysis procedure of model compounds

Sludge is known to be a highly complex material, and verification using model compounds should be used in conjunction with sludge pyrolysis experiments. Therefore, highly representative model compounds, including protein (bovine serum albumin), proline, phenylalanine, aniline, quinoline, and benzonitrile, were respectively pyrolyzed with or without pure catalysts. As our former work [26] demonstrated, conditioner CaO was presented as Ca(OH)₂, while Fe³⁺ was the predominant form of iron in S-Fenton and S-Fenton-CaO (Table 2). Thus, analytical grade Ca(OH)₂ and Fe₂(SO₄)₃ were utilized. Considering the liquid compounds involved, pyrolysis experiments were conducted by using a fixed bed furnace, depicted in Fig. 2.

To ensure an excess of catalysts, the amount of each reagent was set as 0.3 g. The pyrolysis procedure lasted for 10 min with 100 N mL min⁻¹ high purity Ar as the carrier gas. The production of NH₃ and HCN in the model compounds pyrolysis with, or without simulated catalysts was measured using a FT-IR gas analyzer (Gasmet DX4000), which would provide verification of the effects of the two conditioners on sludge nitrogen transformation. Finally, the nitrogen associated mineral forms in the residues were analyzed using X-ray diffraction (XRD, X'Pert PRO, PANalytical. B. C.).

3. Results and discussion

3.1. Effects on nitrogen distribution

Fig. 3 lists the nitrogen distribution results in three-phase products during the pyrolysis of the four sludge samples at 873–1273 K. With regards to RS, char-N accounted for 1.9–13.2% of the total sludge nitrogen (S-N), and tar-N yield was in the range of 13.4–36.6%. Additionally, 25.3–70.5% of RS nitrogen was converted to gas. When the sludge was treated with Fenton’s reagent and/or CaO, more nitrogen was fixed in char at 873 K, and the retention rate remained almost unchanged at higher temperatures. Conversely, tar-N yield decreased sharply after separate conditioning, and the minimum value was observed with the co-usage of two conditioners. The maximum gas-N production was then detected during S-Fenton-CaO pyrolysis. This indicates that composite conditioning promoted S-N conversion to gas-N, whereas it inhibited the conversion to tar-N.

3.2. Effects on nitrogen species evolution

Generally, S-N is presented as protein-N (an important component of microorganisms [31,32], including its decomposition product amino acid), amine-N and inorganic-N [6,26]. Our previous study found [29] that, during the pretreatment process, Fenton’s reagent oxidized organic-N (including protein-N and...
amine-N), leading to the increased relative content of inorganic-N in dry sludge. When adding CaO to form an alkaline environment, most of the ammonia-N converted to NH₃, and a portion of the nitrates-N and nitrites-N dissolved in the filtrate. To further investigate the influence of conditioners on nitrogen transformation during the devolatilization process, its functionality in solid residues was firstly examined by XPS. Fig. 4 depicts chars generated at 1073 K; RS char-N included quaternary-N (peak value = 401.5 eV), pyrrole-N (peak value = 400.3 eV), amine-N/pyridine-N (peak value = 398.6 eV) and nitrile-N (peak value = 398.0 eV). The peaks of quaternary-N and amine-N/pyridine-N for S-Fenton-1073 were slightly higher than that for RS-1073. Furthermore, the N 1s spectra of S-Fenton-CaO-1073 is similar to that of S-CaO-1073, demonstrating that CaO played a substantial role in the char-N evolution of co-treated sludge.

![Fig. 4. N 1s XPS spectra of (a) RS char, (b) S-CaO char, (c) S-Fenton char and (d) S-Fenton-CaO char generated at 1073 K.](image-url)

![Fig. 5. Effects of Fenton peroxidation and CaO conditioning on the evolution of nitrogen species in (a) char, (b) tar, and (c) gas.](image-url)
The semi-quantitative results summarized in Fig. 5a provide more detailed information. It is apparent that protein-N only presented in char generated at 873 K. After Fenton’s reagent was used singly, the protein-N yield decreased by 0.4% of the total sludge nitrogen. In contrast, when using CaO alone, the relative ratio of protein-N increased from 2.3% to 6.5%. Therefore, with the combination of their promoting and inhibitory effects on protein-N disintegration, 3.4% of sludge nitrogen was presented as proteins in char at 873 K. Fig. 5a also indicates that the pretreatment process was conducive to the generation of quaternary-N and amine-N/pyridine-N in char at any temperature used in this study, regardless of the two conditioners being used singly or in combination. For nitrile-N production at 873 K, the increment might be attributed to the inhibitory effect of residual iron salts on nitrile decomposition. When the temperature increased to 1073 K, the nitrile-N content of S-CaO char was essentially equal to that of S-Fenton-CaO char, which was higher than the nitrile-N content of RS char and S-Fenton char. It can be deduced that, in the composite conditioned sludge pyrolysis, calcium compounds hindered the cracking of nitrile-N at higher temperatures. Furthermore, Fig. 5a illustrates that Fenton peroxidation promoted the formation of pyrrole-N significantly at 873 K. Even with the negative influence of calcium, combined conditioning still enhanced the pyrrole-N yield by 1.4%. When temperatures increased, Fe-/Ca-bearing compounds began to play a role in its catalytic cracking. At this point, less pyrrole-N remained in char.

Fig. 5b indicates the nitrogen species in the tar. Compared with RS tar, S-Fenton tar contained more nitrile-N and amine-N. This indicates that residual iron salts facilitated the generation of these two condensed volatile matters. Alternatively, the salts inhibited their thermal decomposition. When CaO participated in sludge conditioning, the fraction of amine-N in tar probably decreased as a result of the catalytic deamination reactions. Thus with co-treatment, tar amine-N yield during S-Fenton-CaO pyrolysis was at the same level as that during RS pyrolysis. Unlike amine-N, at 873 K the relative ratio of nitrile-N in tar increased after using Fenton’s reagent and/or CaO, demonstrating that the most unsaturated N-containing tar is most easily generated with Fe-/Ca-catalyst at low temperatures. At 1073 K, CaO began to catalyze the denitrification of condensed volatile matter, resulting in less nitrile-N forming in S-CaO and S-Fenton-CaO tar. Similarly, residual iron and calcium compounds cooperatively promoted the decomposition of heterocyclic-N in tar at a wide temperature range from 873 K to 1273 K.

The effects of composite conditioning on the generation of major gaseous nitrogen compounds are depicted in Fig. 5c. It was revealed that NH3 yields during sludge pyrolysis are on the order of S-CaO > RS > S-Fenton. Fenton peroxidation reduced NH3 might occur via three pathways: (1) ammonia-N was lost in oxidation conditions during the pretreatment process, reducing a major source of NH3; (2) remaining Fe catalyst was able to prevent some nitrogen organics from deamination in sludge pyrolysis; (3) residual Fe salts converted to form active iron atoms, which could react with NH3 (Eq. (2) [33]).

\[
8\text{Fe} + 2\text{NH}_3 \rightarrow 2\text{Fe}_2\text{N} + 3\text{H}_2 \quad (2)
\]

It is possible that CaO can also facilitate the dissolving or emission of inorganic-N in the conditioning and dewatering process [27]. Thus, a certain degree of increase in NH3 yield probably occurred as calcium significantly promoted the deamination of proteins (including amino acids) and amine. In the pyrolysis of S-Fenton-CaO, lower NH3 production was detected at above 1073 K.

For HCN, the effects of these two conditioners were the opposite of NH3 at 873 K and 1073 K (Fig. 5c). Specifically, iron compounds facilitated some HCN formation reactions, while calcium salts hindered some HCN formation reactions, for example, the thermal cracking of nitrile-N (Eq. (3)). Moreover, both newly formed CaO and H2O (Eq. (4)) could consume HCN (Eqs. (5) and (6) [34,35]). The reaction of HCN hydrolysis catalyzed by CaO (Eq. (6)) also happens to be a source of NH3. When the temperature increased to 1273 K, a clear decrease in HCN occurred after any conditioning, suggesting that high temperatures favor the Fe-/Ca-catalyzed reduction of HCN.

\[
\text{R} = \text{C} = \text{N} \rightarrow \text{HCN} + \text{R}' \quad (3)
\]

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (4)
\]

\[
\text{CaO} + 2\text{HCN} \rightarrow \text{CaCN}_2 + \text{CO} + \text{H}_2 \quad (5)
\]

\[
\text{HCN} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO} \quad (6)
\]

Additionally, satisfactory results regarding non-polluting gas are indicated in Fig. 5c. Separate use of Fenton’s reagent and CaO enhanced N2 yields by 13.0–24.4% and 16.0–22.0%, respectively. Composite conditioners possessed much stronger catalytic ability, contributing to the highest N2 production (38.3%, 67.1%, 80.5%) in S-Fenton-CaO pyrolysis. Many coal-related literatures [20,36] reported that metallic Fe and CaO derived from Fe-/Ca-containing RS tar, S-Fenton tar contained more nitrile-N and amine-N, which will further decompose to yield N2 (Eqs. (9) and (10)). Therefore, it was inferred that the remaining conditioners improved by this non-precursor might form some intermediates by reacting with sludge-N.

\[
\alpha\text{-Fe} + \text{Pyrrole-N/Pyridine-N} \rightarrow \text{Fe}_x\text{N} \quad (7)
\]

\[
\text{CaO} + \text{Pyrrole-N/Pyridine-N} \rightarrow \text{Ca}_x\text{N}_y + \text{CO} \quad (8)
\]

\[
\text{Fe}_x\text{N} \quad (\text{or Fe}_x\text{C}_y\text{N}) \rightarrow \alpha\text{-Fe} + \text{N}_2 \quad (9)
\]

\[
\text{Ca}_x\text{N}_y \rightarrow \text{Ca}_x + y/2 \text{N}_2 \quad (10)
\]

### Table 3

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Emissions (mL g⁻¹)</th>
<th>Protein</th>
<th>Proline</th>
<th>Phenylalanine</th>
<th>Aniline</th>
<th>Quinoline</th>
<th>Benzonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>+Fe₂(SO₄)₃</td>
<td>−10.00</td>
<td>−1.54</td>
<td>−5.90</td>
<td>−0.36</td>
<td>−0.14</td>
<td>−0.11</td>
</tr>
<tr>
<td></td>
<td>+Ca(OH)₂</td>
<td>* 3.34</td>
<td>* 1.16</td>
<td>* 1.03</td>
<td>* 0.81</td>
<td>* 0.29</td>
<td>* 0.03</td>
</tr>
<tr>
<td>1073</td>
<td>+Fe₂(SO₄)₃ + Ca(OH)₂</td>
<td>* 10.27</td>
<td>* 6.50</td>
<td>* 21.08</td>
<td>* 3.27</td>
<td>* 0.07</td>
<td>* 1.92</td>
</tr>
<tr>
<td></td>
<td>+Fe₂(SO₄)₃</td>
<td>−9.94</td>
<td>−2.60</td>
<td>−6.06</td>
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<td>−0.90</td>
<td>−0.59</td>
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<tr>
<td></td>
<td>+Ca(OH)₂</td>
<td>+1.40</td>
<td>+3.01</td>
<td>+3.91</td>
<td>+8.28</td>
<td>−0.31</td>
<td>+0.32</td>
</tr>
<tr>
<td>1273</td>
<td>+Fe₂(SO₄)₃</td>
<td>−28.17</td>
<td>−5.14</td>
<td>−10.85</td>
<td>−4.56</td>
<td>−0.53</td>
<td>−2.90</td>
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<td></td>
<td>+Ca(OH)₂</td>
<td>−7.64</td>
<td>−3.74</td>
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<td>+Fe₂(SO₄)₃ + Ca(OH)₂</td>
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<td>+1.14</td>
<td>+12.76</td>
<td>−0.99</td>
<td>+0.02</td>
</tr>
<tr>
<td></td>
<td>+Fe₂(SO₄)₃ + Ca(OH)₂</td>
<td>−21.11</td>
<td>−5.86</td>
<td>−14.85</td>
<td>−7.59</td>
<td>−3.28</td>
<td>−2.24</td>
</tr>
</tbody>
</table>

* * indicates the corresponding gas yield increased when adding Fe₂(SO₄)₃ and/or Ca(OH)₂.

* − indicates the corresponding gas yield decreased when adding Fe₂(SO₄)₃ and/or Ca(OH)₂.
3.3. Clarification of the evolutionary mechanism

Low contents of nitrogen and high fractions of complex minerals in the sludge char pose technical challenges in locating the intermediates. To solve this problem, nitrogenous model compounds were used to provide verification of the mechanisms. In view of the XPS analysis, protein (bovine serum albumin), proline and phenylalanine were employed to represent solid-N species. Meanwhile, based on the GC–MS data, the most abundant components, i.e. aniline, quinoline, and benzonitrile, were used to represent three types of tar-N forms.

Table 3 shows the influence of Fe$_2$(SO$_4$)$_3$ and Ca(OH)$_2$ on NH$_3$ emissions during the model compound pyrolysis. It can be seen that, generally, NH$_3$ production declined in the presence of Fe$_2$(SO$_4$)$_3$. On the contrary, the emissions of this pollutant gas increased with the addition of Ca(OH)$_2$ for the majority of model compounds, especially at lower temperatures. Negative values in the case of Fe plus Ca were only detected above 1073 K, which is in accordance with the results in Fig. 5c. This proved that the residual iron salts, which presented as Fe$_2$(SO$_4$)$_3$ in sludge, indeed hamper the deamination of proteins, amino acids and tar-N substances, thus offsetting the promoting effects of residual calcium compounds.

The results on the other important NO$_x$ precursors are listed in Table 4. It was shown that HCN emissions were reduced by Ca(OH)$_2$ in all cases of this study, indicative of the significant catalytic ability of conditioner CaO on HCN conversion. However, Fe$_2$(SO$_4$)$_3$ only prevented HCN generation at 1273 K. Co-usage showed no

![Figure 6](image_url)  
**Fig. 6.** XRD spectrum of solid residuals produced in the pyrolysis of protein with Ca(OH)$_2$ and/or Fe$_2$(SO$_4$)$_3$ at 1073 K.

![Figure 7](image_url)  
**Fig. 7.** Effects of Fenton oxidation and CaO conditioning on nitrogen transformation during sludge pyrolysis.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Emissions (mL g$^{-1}$)</th>
<th>Protein</th>
<th>Proline</th>
<th>Phenylalanine</th>
<th>Aniline</th>
<th>Quinoline</th>
<th>Benzonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>+Fe$_2$(SO$_4$)$_3$</td>
<td>-1.06</td>
<td>+0.13</td>
<td>-5.35</td>
<td>-0.52</td>
<td>+0.04</td>
<td>+1.98</td>
</tr>
<tr>
<td></td>
<td>+Ca(OH)$_2$</td>
<td>-0.95</td>
<td>-0.04</td>
<td>-0.17</td>
<td>-0.05</td>
<td>-0.03</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>+Fe$_2$(SO$_4$)$_3$ + Ca(OH)$_2$</td>
<td>-11.32</td>
<td>+0.48</td>
<td>+0.44</td>
<td>+0.67</td>
<td>+0.17</td>
<td>+0.18</td>
</tr>
<tr>
<td>1073</td>
<td>+Fe$_2$(SO$_4$)$_3$</td>
<td>-3.08</td>
<td>+1.92</td>
<td>-8.83</td>
<td>-0.61</td>
<td>-1.44</td>
<td>+0.29</td>
</tr>
<tr>
<td></td>
<td>+Ca(OH)$_2$</td>
<td>-1.86</td>
<td>-0.29</td>
<td>-4.46</td>
<td>-0.25</td>
<td>-0.13</td>
<td>-0.15</td>
</tr>
<tr>
<td></td>
<td>+Fe$_2$(SO$_4$)$_3$ + Ca(OH)$_2$</td>
<td>-23.41</td>
<td>+5.02</td>
<td>+2.76</td>
<td>+0.99</td>
<td>+1.76</td>
<td>+0.84</td>
</tr>
<tr>
<td>1273</td>
<td>+Fe$_2$(SO$_4$)$_3$</td>
<td>-9.41</td>
<td>-13.15</td>
<td>-6.06</td>
<td>-1.67</td>
<td>-2.05</td>
<td>-2.48</td>
</tr>
<tr>
<td></td>
<td>+Ca(OH)$_2$</td>
<td>-0.57</td>
<td>-3.08</td>
<td>-5.19</td>
<td>-0.61</td>
<td>-0.01</td>
<td>-4.61</td>
</tr>
<tr>
<td></td>
<td>+Fe$_2$(SO$_4$)$_3$ + Ca(OH)$_2$</td>
<td>-14.21</td>
<td>-16.20</td>
<td>+1.82</td>
<td>+1.12</td>
<td>+2.12</td>
<td>+4.39</td>
</tr>
</tbody>
</table>

$^a$ "+" indicates the corresponding gas yield increased when adding Fe$_2$(SO$_4$)$_3$ and/or Ca(OH)$_2$.

$^b$ "-" indicates the corresponding gas yield decreased when adding Fe$_2$(SO$_4$)$_3$ and/or Ca(OH)$_2$. 

Table 4 Difference in HCN emissions during model compounds pyrolysis with and without the presence of Fe$_2$(SO$_4$)$_3$ and/or Ca(OH)$_2$.
obvious regularity on HCN emissions from the pyrolysis of six types of nitrogenous model compounds, at least suggesting that the co-effect of residual iron and calcium is not a simple superposition of their behavior. Although composite conditioning promoted the cracking of some amino acids and nitrogenous tar-N to release HCN, adding Fe2(SO4)3 and Ca(OH)2 simultaneously exhibited strong hindrance on HCN production from protein, which is the predominant nitrogen form in sludge. Thus it can be deduced that during S-Fenton-CaO pyrolysis, the reduction in HCN yields (see Fig. 5c) is mainly associated with the synergies of residual iron and calcium on protein-N conversion.

The XRD analysis (Fig. 6) suggests that FeN0.0589 and Ca(CN)2 were respectively formed in solid residues when protein was pyrolyzed with Fe2(SO4)3 or Ca(OH)2, indicating that residual Fe-/Ca-conditioners were capable of reacting with protein-N to produce Fe2N and CaC2N2 (Eqs. (11) and (12)). As a consequence, the transformation of the majority of sludge-N, HCN and NH3 to N2 can be realized (Eqs. (5), (9)-(13)). Additionally, another interesting phenomenon that can be deduced from Fig. 6 is that Ca2Fe2O5 formed when Fe2(SO4)3 and Ca(OH)2 simultaneously participated in protein pyrolysis. Here, weaker diffraction peak intensity for FeN0.0589 and Ca(CN)2 was observed. According to the reports of Berggren [37], in the crystal structure of Ca2Fe2O5, Fe is both octahedrally and tetrahedrally coordinated by O, with Ca in the holes between the polyhedra. Briefly, Ca2Fe2O5 is a complex and stable oxide. Thus, it can be inferred that in the composite conditioned sludge devolatilization process, the formation of complex oxides containing Fe and Ca facilitated the thermal decomposition of some intermediates (e.g. Fe2N and CaC2N2), thus further enhancing N2 production.

Residual Fe-conditioner + Protein-N → Fe2N
Residual Ca-conditioner + Protein-N → CaC2N2
CaC2N2 + y NH3 → CaC2N2y + 3/2y H2

4. Conclusions

The nitrogen transformation routes affected by Fenton peroxidation and CaO conditioning during sewage sludge pyrolysis were studied in this work. The results demonstrated that, as depicted in Fig. 7, Fenton’s reagent oxidized inorganic-N during the pretreatment process, and then prevented some nitrogen organics from deamination during sludge pyrolysis. Active iron atoms derived from this conditioner reduced NH3 emission through the formation of Fe2N. Although CaO facilitated the deamination of proteins and amine, less NH3 was eventually generated in S-Fenton-CaO pyrolysis at above 1073 K. Additionally, composite conditioning enhanced the yields of amine-N/pyridine-N, pyrrole-N and nitrile-N in char, but hampered their conversion to HCN. The remaining Ca compounds promoted the hydrolysis of HCN to form NH3 and inhibited the cracking of all types of tar-N, thus further decreasing HCN emissions. Both residual iron and calcium conditioners were able to react with protein-N. The formation of Ca2Fe2O5 facilitated the thermal decomposition of some intermediates (e.g. Fe2N and CaC2N2), thus further enhancing N2 production. Briefly, the emission control of NOx precursor can be realized during sewage sludge pyrolysis with an integrated pretreatment method of Fenton peroxidation and CaO conditioning.

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