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SIMULTANEOUS OXIDATION OF CYANIDE AND THIOCYANATE

AT HIGH PRESSURE AND TEMPERATURE

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Abstract

Thiocyanate and cyanide are important contaminants that frequently appear mixed in industrial efflu-ents. In this work the wet oxidation of mixtures of both compounds, simulating real compositions, wascarried out in a semi-batch reactor at temperature between 393 K and 483 K and pressure in the range of 2.0–8.0 MPa. The presence of cyanide (3.85 mM) increased the kinetic constant of thiocyanate degrada-tion by a factor of 1.6, in comparison to the value obtained for the individual degradation of thiocyanate ,$(5.95 \pm 0.05) \times 10^{-5} \text{ s}^{-1}$. On the other hand, the addition of thiocyanate (0.98 mM) decreased the degrada-tion rate of cyanide by 16%. This revealed the existence of synergistic and inhibitory phenomena betweenthese two species. Additionally, cyanide was identified as an intermediate in the oxidation of thiocyanate,and formate, ammonia and sulfate were found to be the main reaction products. Taking into account theexperimental data, a reaction pathway for the simultaneous wet oxidation of both pollutants was pro-posed. Two parallel reactions beginning from cyanate as intermediate were considered, one yieldingammonia and formate and the other giving carbon dioxide and nitrogen as final products.

Keywords

Cyanide, Kinetics, Reaction pathway, Synergistic phenomena, Thiocyante.

1. Introduction

According to the European Pollutant Release and Transfer Register (E-PRTR) of 2011, European annual emissions of total cyanide (free cyanide, cyanide complexes and thiocyanate) contained in industrial wastewaters are above 148 tons and Spain is responsible for 6% of this amount [1]. The presence of cyanide in industrial efflu- ents is an important environmental issue due to the acute toxicity of cyanide for living organisms, even at low concentrations [2,3].

Although thiocyanate is a less toxic form than cyanide, many harmful effects of thiocyanate on human health and the aquatic ecosystem have also been reported [4]. Moreover, several authors have reported that cyanide can be formed by the incomplete oxidation of thiocyanate [5,6].

Different biodegradation techniques have been proposed for the simultaneous treatment of these cyanide pollutants, including the use of bacterial co-culture, activated sludge and biofilm processes [7–10]. However, high concentrations of cyanide and thiocyanate and/or their simultaneous presence can cause inhibition of the biodegradation [9]. Hence, other treatments have been proposed, such as ferrate oxidation [5], hydrogen peroxide oxidation [11], photochemical oxidation [11], ozonation [12], coagulation–flocculation–sedimentation, Fenton oxidation and adsorption on activated carbon [13].

Wet oxidation is a well-established technique which involves the liquid-phase oxidation of organics and oxidizable inorganic compounds under high temperature (453–588 K) and pressure conditions (2.0–15.0 MPa) using a gaseous source of oxygen. The effectiveness of this technique for the treatment of wastewaters containing only cyanide [14–19], thiocyanate [20,21] or metal–cyanide complexes [22–24] has been proved. However, as far as we know, studies on the simultaneous wet oxidation of cyanide and thiocyanate do not exist, although these compounds are important pollutants in various industrial wastewaters and they commonly appear together. Besides, cyanide was proposed as an intermediate during thiocyanate oxidation [5]. The existence of synergistic and inhibitory effects is common in aqueous-phase oxidations, such as wet oxidation, and may affect the overall oxidation rate of the process significantly.

Synergism involves the simultaneous reaction of two species, one being easily oxidized and the other more refractory to oxidation, with the easily oxidized component effectively increasing the oxidation rate of the refractory compound [25]. Hence, the values of the kinetic constants for the simultaneous degradation of thiocyanate and cyanide may be different from those obtained in the individual degradation of both pollutants. Moreover, the study of the simultaneous wet oxidation of these compounds could also be useful for clarifying the degradation pathway.

Consequently, the aim of this work was to investigate the kinetics that govern the wet oxidation of effluents containing a mixture of cyanide and thiocyanate and to propose a complete reaction pathway for the wet oxidation of these cyanide compounds, paying special attention to the synergistic and inhibitory effects. With this aim, a wide range of temperatures, pressures, initial concentrations of cyanide and thiocyanate were studied, and final reaction products and some intermediates were identified. This knowledge will allow a better evaluation of the applicability of this treatment for the oxidation of industrial cyanide wastewaters.

2. Experimental

2.1. Apparatus and procedure

Experiments were performed in a 1 L capacity semi-batch reac- tor (Parr T316SS) equipped with two six-bladed magnetically driven turbine agitators. A more detailed description of the experimental set up can be found in Oulego et al. [14]. In each run, the reactor was loaded with 0.7 L of distilled water and pH was adjusted to a suitable value using NaOH, so that after the addition of the cyanide and thiocyanate solution, the medium had a pH value of 11. This basic pH was used in order to prevent the formation of hydrocyanic acid (pKa = 9.21 at 298 K) [26]. Once the desired conditions of pressure and temperature were achieved, 10 mL of a concentrated cyanide and thiocyanate solution (both sodium salts) was injected into the reactor.

The concentration of this solution was calculated to give the desired concentration inside the reactor (in most cases 3.85 mM of cyanide and 2.20 mM of thiocyanate). These concentrations were selected taking into account the typical concentration of these pollutants in industrial effluents. Three bubblers filled with a concentrated sulfuric acid solution and two bubblers filled with a concentrated sodium hydroxide solution were installed at the end of the gas line with the purpose of absorbing ammonia and hydro- cyanic acid, in case it was formed. All experiments were performed in triplicate.

2.2. Analytical methods

Concentrations of thiocyanate (SCN^-), sulfate (SO_4^{2-}), cyanate (CNO^-), formate ($HCOO^-$), nitrite (NO_2^-) and nitrate (NO_3^-), were monitored by using an ion exchange chromatograph (Dionex DX-120 Ion Chromatograph) and a suppressed conductivity detector (ASRS-ULTRA Autosuppresion Recycle Mode). The eluent employed was a solution of 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$, with a flow rate of 1.04 mL/min; the precolumn was IonPac AG23 (4 mm x 50 mm), and the column was IonPac AS23 (4 mm x 250 mm). Cyanide concentration was measured by means of a cyanide ion-selective electrode (ISE Crison 9653) together with a double-junction reference electrode (Crison 5044) and an ISE-meter (Crison pH and Ion-Meter GLP 22). Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were measured using a TOC analyzer (Shimadzu TOC-VCSH). Ammonia concentration was determined using the Nessler method [27] and pH was measured employing a selective electrode (pH Meter JEN- WAY 3510). All analytical measurements were made at least in triplicate, and the standard deviation was found to be below 5% in all cases. A portable gas detector (Gasman Crowcon detection) situated at the end of the gas line was used to determine the presence of hydrogen in the gas outflow.

3. Results and discussion

3.1. Composition Simultaneous wet oxidation of cyanide and thiocyanate and reaction products

Fig. 1 compares the simultaneous wet oxidation of cyanide and thiocyanate with the individual wet oxidation of both pollutants. These runs were performed under 8.0 MPa of oxygen at 453 K, with an initial cyanide and thiocyanate concentration of 3.85 mM and 2.20 mM, respectively. The initial pH decreased as the reaction proceeded, its value being in the range of 11.0–10.6. This can be explained by the formation of protons (H+) in the reaction medium as will be explained in Section 3.3. The same behavior was observed in all the experiments in this study. The concentration of thiocyanate and cyanide plotted in Fig. 1a and b are divided by the initial concentration of each pollutant, respectively. The concentrations of ammonia and formate plotted in Fig. 1c are divided by the sum of the concentrations of cyanide and thiocyanate, and sulfate concentrations are only divided by thiocyanate concentration since cyanide oxidation cannot produce it. During both individual and simultaneous wet oxidation, the cyanide degradation rate was considerably greater than that of thiocyanate. Hence, in both oxidations, cyanide was completely degraded within 20 min whereas at the same reaction time the degradation of thiocyanate was found to be lower than 10%. The presence of cyanide improved the degradation rate of thiocyanate appreciably. Thus, during the individual wet oxidation of thiocyanate, 85% conversion was reached in approximately500 min. However, in the presence of cyanide, the same conversion was achieved in approximately 300 min. The opposite effect was observed for cyanide, although this effect was less pronounced. In all cases, the data were successfully fitted to pseudo-first order kinetic model with respect to the pollutants ($r^2 > 0.99$).

This is in agreement with Bharghava et al. who stated that the kinetic order with respect to the pollutant in wet oxidation processes is usually one [28]. Thus, the kinetic constant for the degradation of cyanide in the presence of thiocyanate, $k_2 = (5.42 \pm 0.07) \times 10^{-3}$ s^{-1}, was found to be approximately 16% lower than in the absence of thiocyanate, $k_2 = (6.42 \pm 0.07) \times 10^{-3}$ s^{-1}. These results suggest an interaction between the two species during the oxidation process, cyanide being easily oxidizable and thiocyanate being more refractory to oxidation [29]. Synergism phenomena has been frequently reported by several authors during the wet oxidation of different compounds such as: mixtures of simple alcohols and acetic acid [30], low molecular mass carboxylic acids [31], phenol, cellobiose and low molecular weight acids [32], nitrobenzene and phenol [25], and dinitrophenol and trinitrophenol [33]. During a synergistic mechanism, one of the species (cyanide in this case) is a better radical generator than the less easily oxidizable species(thiocyanate). However, this last one is a better radical scavenger. Thus, the presence of a compound susceptible to be easily oxidized (such as cyanide), when it is degraded individually by wet oxidation, improves the degradation of compounds more refractory than itself (such as thiocyanate). With regard to the reaction products (Fig. 1c), formate and ammonia were identified as the main products in the individual wet oxidation of cyanide and thiocyanate as well as in the simultaneous process. Besides, sulfate (Fig. 1d) was determined as another main reaction product in the wet oxidation of thiocyanate, both in the presence or absence of cyanide. In the individual wet oxidation of cyanide, the conversion of this pollutant to ammonia and for-mate after 15 min was found to be approximately 65%. However, in the simultaneous wet oxidation, the conversion of cyanide to ammonia and formate was lower, 45%, at the same reaction time.

This drop in conversion is due to the slow kinetics of thiocyanate degradation and the lower cyanide degradation rate in the presence of thiocyanate. In the individual wet oxidation of thiocyanate, the conversion of this contaminant to ammonia and formate in approximately 300 min was found to be 51%, while the conversion of sulfate was 68%. The enhancement in thiocyanate degradation due to the presence of cyanide yielded greater conversions, 68% and 82%, respectively, at the same reaction time.

Figure 1

3.2. Effect of the operating variables

The influence of operating variables such as the initial concentration of thiocyanate and cyanide, pressure and temperature wasstudied in order to explain their effect on the oxidation process.

3.2.1. Effect of the initial concentration of thiocyanate

Fig. 2 shows the effect of initial thiocyanate concentration on the degradation rate of cyanide and thiocyanate and the formation rate of ammonia, formate and sulfate. Wet oxidation runs at 453 Kand 8.0 MPa were conducted with initial concentrations of thiocyanate between 0.98 mM and 8.62 mM, since they resemble the common concentrations of this pollutant in industrial wastewaters [5,34]. As can be observed, the degradation rate of cyanide was lower for higher initial concentrations of thiocyanate, although this effect was not very marked. A conversion of 84% was achieved in 5 min when the initial concentration of thiocyanate was 0.98 mM, whereas a 71% conversion was obtained at the same reaction time when the initial concentration was 8.62 mM. The highest removal efficiency of cyanide was observed in the absence of thiocyanate, reaching a conversion above 99% in only 13 min. A possible explanation would be that thiocyanate competes with cyanide for the free-radicals generated beginning from the oxygen in the reaction medium, decreasing the degradation rate of cyanide.

However, this effect is not very noticeable, since cyanide degradation rate has little dependence on the oxygen concentration as will be seen in Section 3.4. For thiocyanate degradation, the reaction showed the typical pattern of radical systems, i.e., when the initial concentration of the pollutant is lower, fewer free radicals are generated and the reaction time is longer [28]. Thus, the constant rate of thiocyanate degradation was $(7.60 \pm 0.05) \times 10^{-5}$ s^{-1} when the initial thiocyanate concentration was 0.98 mM, whereas this constant was two times higher, $(1.49 \pm 0.03) \times 10^{-4}$ s^{-1}, when the initial concentration of thiocyanate was 8.62 mM (see Fig. 2b).The behavior of the reaction products was as expected. Regarding the formation of ammonia and formate, it can be observed two stages (Fig. 2c). In the first stage, the evolution of reaction products was practically not affected by the initial thiocyanate concentration. In the second stage, beginning from 30 min, the influence of initial thiocyanate concentration was more noticeable. This is due to the fact that during the first stage, reaction products are mainly formed from cyanide oxidation, which is quite faster than thiocyanate oxidation. On the opposite, during the second stage, products are formed from thiocyanate oxidation. Regarding the production of sulfate (Fig. 2d), the higher the initial concentration of thiocyanate the higher was the conversion rate to sulfate, yielding a final conversion of nearly 100% when thiocyanate concentration was 8.62 mM. This behavior confirmed that the degradation of thiocyanate took place by a free-radical pathway as previously commented.

Figure 2

3.2.2. Effect of the initial concentration of cyanide

The influence of initial cyanide concentration on the degradation rate of cyanide and thiocyanate and the formation rate of ammonia, formate and sulfate is shown in Fig. 3.

A set of runs were conducted at 453 K, 8.0 MPa, an initial thiocyanate concentration of 2.20 mM and an initial cyanide concentration in the range 3.85–15.38 mM.

Again, cyanide concentrations were selected so that they resemble the typical concentration found in various industrial effluents [35]. An analysis of the data reveals that the degradation rate of thiocyanate increased significantly when cyanide/thiocyanate molar ratios were higher. Hence, a removal efficiency of thiocyanate of 95% was obtained in 525 min, 480 min and 390 min when the cyanide/thiocyanate molar concentration ratios were 1.75, 3.5 and 7, respectively. The initial cyanide concentration had a very slightly effect onits own degradation rate. For example, when working at 3.85 mM, a 79% conversion was obtained in 5 min, and when the initial cyanide concentration was 15.38 mM an 81% conversion was achieved at the same reaction time. This behavior is similar to that observed during the individual wet oxidations of cyanide, where conversions between 87% and 86% were obtained in 5 min when the initial cyanide concentration was in the range of 3.85–25 mM [14]. this case, two stages can also be distinguished during the formation of ammonia and formate. In the first stage, the conversion of cyanide to ammonia and formate showed a slight delay when the initial concentration of cyanide was lower. In the second stage, the initial cyanide concentration had the opposite effect (after 150 min of reaction), higher conversions to ammonia and formate being obtained when the initial concentration was lower. Increases in the initial cyanide concentration enhanced the degradation rate of thiocyanate to sulfate. Hence, a conversion of 82% was obtained in 300 min when the initial cyanide concentration was 3.85 mM, whereas a conversion of 90% was obtained at the same reaction time when the initial cyanide concentration was increased by a factor of four. To sum up, it was observed that the higher the initial concentration of thiocyanate, the lower the degradation rate of cyanide.

Nevertheless, the higher the initial concentration of cyanide, the higher the degradation rate of thiocyanate. Similar behavior has been found by other authors, who reported an enhancement in the oxidation of the more refractory compound (i.e. nitrobenzene or acetic acid) in the presence of easily oxidizable compounds (phenol or ethanol, respectively) [25,30].

Figure 3

3.2.3. Effect of oxygen pressure

A plot of the evolution of cyanide, thiocyanate and the concentration of the reaction products for runs performed at 453 K, with an initial cyanide concentration of 3.85 mM, an initial thiocyanate concentration of 2.20 mM, and an oxygen pressure varying in the range 2.0–8.0 MPa, is shown in Fig. S1 of the SI. The oxygen flow rate, 2.33×10^{-5} Nm^3/s, provided sufficient oxygen transfer to guarantee oxygen saturation during the reaction. The value of the oxygen concentration varied from run to run as the oxygen pressure was changed. The increase in the operating pressure leads to higher reaction rates for thiocyanate, reducing the time needed to oxidize this pollutant. Thus, when the working pressure was 8.0 MPa, a conversion of 95% was achieved in approximately 500 min, whereas, at the same reaction time, only 30% conversion was obtained when working at 2.0 MPa. However, the degradation rate of cyanide was only slightly affected by this parameter. Thus, when working at 2.0 MPa,5 min were necessary to achieve a cyanide conversion of 73%, and at 8.0 MPa a conversion of 80% was reached at the same reaction time. This behavior is similar to that observed during the individual wet oxidation of cyanide and thiocyanate in which oxygen pressure exerted practically no effect on cyanide removal and greatly accelerated thiocyanate degradation [14,21].

On viewing Fig. S1c and d of the SI, it can be concluded that higher oxygen pressure led to a higher formation rate of ammonia, formate and sulfate, in agreement with the behavior observed for thiocyanate degradation. Hence, when the working pressure was 8.0 MPa, the conversion of cyanide and thiocyanate to ammonia and formate in around 500 min was found to be 74%, whereas at 2.0 MPa, the conversion was considerably lower, 50%.

For the conversion to sulfate, the values were 94% and 31% at the same reaction time and pressure values. For the highest pressure, the conversion of thiocyanate to sulfate was almost complete in 500 min.

3.2.4. Effect of temperature

The influence of temperature on thiocyanate and cyanide degradation and on the distribution of the reaction products was studied in the range of 393–483 K. Fig. S2 of the SI shows the result of a set of runs carried out with an oxygen pressure of 8.0 MPa, an initial thiocyanate concentration of 2.20 mM and an initial cyanide concentration of 3.85 mM. The concentration of oxygen was constant for a given run but varied from run to run as temperature changed. Results showed that a small increase in temperature implied an important increase in the reaction rate of both thiocyanate and cyanide. For example, when the working temperature was 393 K, the time needed to attain a cyanide removal of up to 99% was about 500 min, whereas only 100 min were required to reach the same conversion when working at 423 K. In the case of thiocyanate removal, a conversion of 75% was obtained in 225 min when the temperature was 453 K, while a conversion of 99% was achieved at the same reaction time when the temperature was 483 K. As expected, the formation rates of ammonia, formate and sulfate were greater as temperature increased, since the degradation rates of cyanide and thiocyanate also increased.

Nevertheless, for the highest assayed temperature (483 K), the concentration of for-mate began to decline after 75 min of reaction, which suggested hat formate was oxidized at this temperature but not at lower temperatures. Shende and Mahajani [36] have also reported that formate was oxidized almost completely during a non-catalytic process at 513 K and 0.69 MPa.

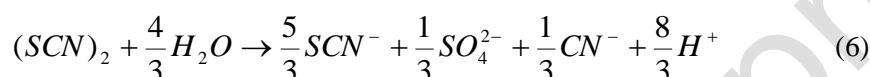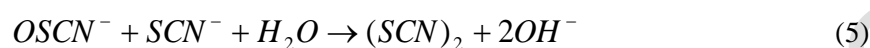### 3.3. Reaction pathway and elemental balances

Based on the experimental results and bibliographic informa-tion, we propose the following pathway for the degradation ofthiocyanate in the presence of cyanide (Fig. 4). The first step of the pathway implies the oxidation of thio-cyanate by the free-radicals generated in the reaction medium,which leads to the formation of cyanide as reaction intermediateand sulfate as final product (Eq. (1)):

$$\frac{1}{3}SCN^- + \frac{1}{2}O_2 + \frac{1}{3}H_2O \xrightarrow{k_1} \frac{1}{3}SO_4^{2-} + \frac{1}{3}CN^- + \frac{2}{3}H^+ \qquad (1)$$
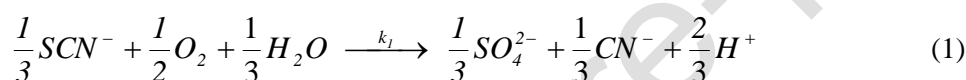
Numerous free-radical reactions can occur during the wet oxidation of thiocyanate due to the high reactivity and unspecified nature of free-radicals. It is possible the formation of a unimolecular reaction in which O_2 forms $O^\bullet$ radicals (Eq. (2)), which would react with H_2O to give $OH^\bullet$ radicals (Eq. (3)) [28,37]. These radicals would react with thiocyanate through a chain reaction mechanism in which various free radicals, such as $OOS(O)CN^\bullet$ and $OS(O)CN^\bullet$, actively participate, yielding finally hypothiocyanite ($OSCN^-$) (Eq.(4)) [38,39]. This is in agreement with the experimental results in which the reaction rate of thiocyanate increased as the initial concentration of thiocyanate did. This behavior has been reported by several authors in radical systems [28]. Next, $OSCN^-$ would react with SCN^- present in the medium to form thiocyanogen $(SCN)_2$ (Eq.(5)). Various authors have proposed the formation of $(SCN)_2$ and $OSCN^-$ as reaction intermediates in different works of oxidation of thiocyanate [40,41].

Because of the severe operating conditions used, the hydrolysis of $OSCN^-$ and $(SCN)_2$ is very fast, obtaining thiocyanate, cyanide and sulfate (Eq. (6)) [38,42]. Nevertheless, the presence of these intermediates could not be experimentally proved due to their extremely short residence time in the reaction bulk [41].

$$\frac{1}{2}O_2 \to O^{\bullet} \tag{2}$$

$$O^{\bullet} + H_2O \to OH^{\bullet} + OH^{\bullet} \tag{3}$$

$$SCN^- + 2OH^{\bullet} \to OSCN^- + H_2O \tag{4}$$

$$OSCN^- + SCN^- + H_2O \to (SCN)_2 + 2OH^- \tag{5}$$

$$(SCN)_2 + \frac{4}{3}H_2O \to \frac{5}{3}SCN^- + \frac{1}{3}SO_4^{2-} + \frac{1}{3}CN^- + \frac{8}{3}H^+ \tag{6}$$

It can be considered that Eq. (1) is the slowest reaction and therefore the rate-determining one for thiocyanate oxidation. This would explain the increase in the thiocyanate degradation rate observed for higher pressures that gave place to higher oxygen concentrations in the reaction medium. A final yield of thiocyanate to sulfate of 1.08 mmol SO_4^{2-}/mmol SCN^- was obtained from the experimental data (see Fig. 5a). This value, which is similar to the maximum theoretical yield (1.00), proves that sulfate is the only product with sulfur in its composition.

The formation of cyanide as a reaction intermediate has already been suggested in previous studies on wet oxidation of acid wastewaters containing thiocyanate [20]. In the second step of the pathway, the oxidation of cyanide either present as pollutant in the initial wastewaters or formed from thiocyanate is initiated byt he free-radicals generated from the molecular oxygen, obtaining cyanate (CNO^-) as reaction intermediate (Eq. (7)) [43].

$$\frac{1}{3}CN^- + \frac{2}{3}OH^{\bullet} \to \frac{1}{3}CNO^- + \frac{1}{3}H_2O \tag{7}$$
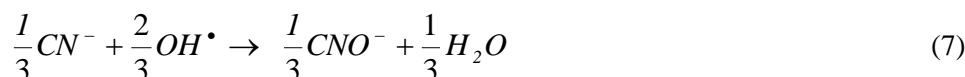
As this reaction progresses, it becomes increasingly complex as the oxygen and radicals formed from cyanide can also react with oxidation intermediates. Several authors have reported the presence of $CN^\bullet$ as free radicals in the oxidation of cyanide [43–45].

Thus, it is possible that high initial concentrations of cyanide favor the formation of more free radicals, which can participate in the oxidation of thiocyanate improving it. It seems obvious that if these free radicals from cyanide participate in the thiocyanate oxidation, they are not available for cyanide oxidation. This would explain the slight decreased observed in the cyanide oxidation rate when the initial concentration of thiocyanate increased and the negative initial concentration order obtained for the initial thiocyanate concentration during cyanide individual degradations. As a consequence, Eq. (8) is considered here as the second step of the reaction pathway:

$$\frac{1}{3}CN^- + \frac{1}{6}O_2 \xrightarrow{\quad k_2 \quad} \frac{1}{3}CNO^- \tag{8}$$

The presence of cyanate was tested at different reaction times, but this compound was found to be present only during the first minutes of the reaction (around 10 min) (see Fig. S3 of the SI). Next, cyanate is hydrolyzed, giving place to different final products. The products experimentally measured in the reaction medium were ammonia and formate. Elemental balances for nitrogen and carbon were carried out in order to determine the evolution of the reaction products and clarify the reaction pathway (Fig. 5b and c). The final yield of thiocyanate and cyanide to ammonia was 0.63 mmol NH_3 per mmol of CN^- or SCN^- degraded, respectively (see Fig. 5b). The production of $HCOO^-$ went in parallel with the production of ammonia with a final yield of 0.62 mmol per mmol of CN^- or SCN^-. Theoretically, 1 mmol of NH_3 and 1 mmol of $HCOO^-$ can be formed from each mmol of CN^- or SCN^- reacted.
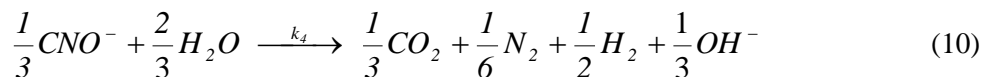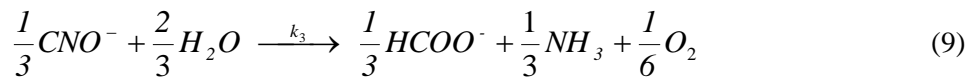
The difference observed between experimental and theoretical yields indicates that ammonia and formate are the principal N-compound and C-compound formed, but not the only ones, the existence of other nitrogenous and carbonaceous products being likely.

The presence of NO_3^- and NO_2^- was tested in samples taken at different reaction times, but these compounds were not found to be present at any moment (detection limits: 7.3×10^{-4} mM for nitrate and 5.4×10^{-4} mM for nitrite). Besides, three bubblers filled with a concentrated acid solution were placed at the end of the gas line in order to soak up the ammonia lost by desorption (pKa= 9.25 at 298 K). Only 5% of the initial nitrogen was absorbed as ammonia in the bubblers, which did not justify the difference between the observed and the theoretical yield of cyanide and thiocyanate to ammonia. However, it could be explained by the formation of molecular nitrogen as the final product of cyanide oxidation (see Fig. 4), which seems quite probable. Moreover, TOC was measured in samples withdrawn at different reaction times, which showed that the amount of carbon due to formate is approximately the same as the TOC value (Fig. 5c). Therefore, the presence of other organic compounds dissolved in the medium was ruled out and it was very likely that carbon dioxide would be obtained as a reaction product. Various authors have also put forward N_2 and CO_2 as the final reaction final reaction products of the oxidation of cyanide species by different oxidative techniques [46–49]. Hence, the difference between the theoretical total nitrogen and carbon and the experimental values are considered to be due to N_2 and CO_2 formation. The evolution of these compounds, N_2 and CO_2 (calculated by difference), is shown in Fig. 5b and c. Analyzing these figures it can be concluded that the evolution of N_2 coincided with the evolution of CO_2. In the same way, the evolution of NH_3 coincided with the evolution of $HCOO^-$.

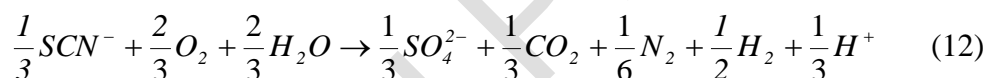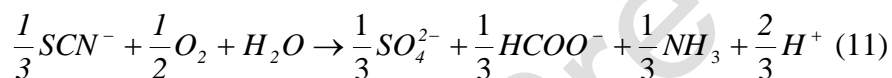**Figure 4 and Figure 5**

This indicates the existence of two parallel routes for CNO^- oxidation. On viewing the results, the following equations have been proposed (Eqs. (9) and (10)):

$$\frac{1}{3}CNO^- + \frac{2}{3}H_2O \xrightarrow{k_3} \frac{1}{3}HCOO^- + \frac{1}{3}NH_3 + \frac{1}{6}O_2 \qquad (9)$$

$$\frac{1}{3}CNO^- + \frac{2}{3}H_2O \xrightarrow{k_4} \frac{1}{3}CO_2 + \frac{1}{6}N_2 + \frac{1}{2}H_2 + \frac{1}{3}OH^- \qquad (10)$$

The presence of hydrogen in the gas outflow was determined by a hydrogen gas detector situated at the end of the gas line. The maximum concentration of hydrogen measured was 16 ppm, the highest value being registered during the first minutes of the experiments (see Fig. S4 of the SI).

The overall reactions are shown as follows:

$$\frac{1}{3}SCN^- + \frac{1}{2}O_2 + H_2O \rightarrow \frac{1}{3}SO_4^{2-} + \frac{1}{3}HCOO^- + \frac{1}{3}NH_3 + \frac{2}{3}H^+ \quad (11)$$

$$\frac{1}{3}SCN^- + \frac{2}{3}O_2 + \frac{2}{3}H_2O \rightarrow \frac{1}{3}SO_4^{2-} + \frac{1}{3}CO_2 + \frac{1}{6}N_2 + \frac{1}{2}H_2 + \frac{1}{3}H^+ \qquad (12)$$

Besides, when temperature was 483 K, it was observed that formate concentration decreased (Figure S2c of the SI). This indicates that formate can be partially oxidized to carbon dioxide (Eq. 13). The same was pointed out by other authors during the wet air oxidation of formic acid [50].

$$\frac{1}{3}HCOO^- + \frac{1}{3}H^+ + \frac{1}{6}O_2 \xrightarrow{k_5} \frac{1}{3}CO_2 + \frac{1}{3}H_2O \qquad (13)$$
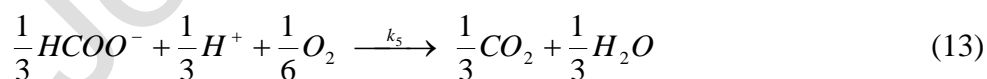
3.4. Kinetic model

Based on the reaction pathways for the oxidation of thiocyanate in presence of cyanide, the following kinetic equations can be proposed for each compound:

$$\frac{dC_{SCN^-}}{dt} = -k_1 C_{SCN^-} \tag{14}$$

$$\frac{dC_{CN^-}}{dt} = k_1 C_{SCN^-} - k_2 C_{CN^-} \tag{15}$$

$$\frac{dC_{CNO^-}}{dt} = k_2 C_{CN^-} - k_3 C_{CNO^-} - k_4 C_{CNO^-} \tag{16}$$

$$\frac{dC_{SO_4^{2-}}}{dt} = k_1 C_{SCN^-} \tag{17}$$

$$\frac{dC_{HCOO^-}}{dt} = k_3 C_{CNO^-} - k_5 C_{HCOO^-} \tag{18}$$

$$\frac{dC_{NH_3}}{dt} = k_3 C_{CNO^-} \tag{19}$$

$$\frac{dC_{CO_2}}{dt} = k_4 C_{CNO^-} + k_5 C_{HCOO^-} \tag{20}$$

$$\frac{dC_{N_2}}{dt} = 0.5 \cdot k_4 C_{CNO^-} \tag{21}$$

All the experimental data were successfully fitted to the proposed kinetic model (Eqs. 14 to 21) using Micromath Scientist 3.0, with a regression coefficient greater than 0.99 (see solid lines in Figs. 1-3 and Figure S1 and S2 of the SI).

The values of the kinetic constants obtained in the experiments at different pressures, temperatures and initial concentrations of thiocyanate and cyanide are shown in Table S1. Using these constants, kinetic orders for oxygen (α_i), initial concentration of thiocyanate (β_i), initial concentration of cyanide (γ_i) and activation energies (E_{ai}) for the degradation of thiocyanate and cyanide have been calculated (see Table 1). The calculation method for the determination of the kinetic orders and activation energies is shown in section 6 of the SI.

These results confirm that an increase in pressure had an appreciable effect only on the degradation rate of thiocyanate, since the value of α_1 (1.06 ± 0.02) is significantly higher than α_2 (0.20 ± 0.02). The oxygen reaction orders for the oxidation of other inorganic compounds are generally in the range of 0.3-1 [51-53], which are very similar to those obtained in this work. As the value of α_3 and α_4 is zero, the effect of pressure on cyanate degradation was negligible, which demonstrates that cyanate is degraded via hydrolysis and not oxidation, as we indicated in the reaction pathway proposed above.

Additionally, the activation energy obtained for thiocyanate degradation (Eq. 1) is higher than that obtained for cyanide degradation (Eq. 8), 112 ± 7 and 88 ± 2 kJ/mol, respectively. This indicates that the effect of temperature was more marked in thiocyanate oxidation than in cyanide oxidation (see Table 1). Several authors have reported activation energies between 25.8 and 150 kJ/mol for the oxidation of other inorganic compounds [52-54]. The activation energy of formate and ammonia formation (Eq. 9) was found to be greater than the activation energy of carbon dioxide and nitrogen formation (Eq. 10). This indicates that the formation of formate and ammonia is much more favored by high temperatures. Besides, high initial concentration of thiocyanate or cyanide improved the degradation of thiocyanate considerably, as indicated by the positive values of β_1 and γ_1. On the other hand, high initial thiocyanate concentration hindered somewhat the degradation of cyanide. Regarding the reaction products, the formation of carbon dioxide and nitrogen was hampered as the initial thiocyanate concentration increased (see Fig. S5a and b of the SI). This is indicated by the negative value of β_4 (see Table 1). However, an increase in the initial cyanide concentration had the opposite effect (see Figure S5c and d of the SI).

The formation of formate and ammonia was always favored by the rise in the concentration of thiocyanate and cyanide, since both β_3 and γ_3 are positive values, although the effect of thiocyanate concentration was more noticeable since $\beta_3 > \gamma_3$ (see Table 1).

Taking into account the above-mentioned experimental data, the kinetic model for the degradation of thiocyanate and cyanide can be expressed through the following equations (time in seconds, temperature in Kelvin, concentrations in molarity):

$$-r_{SCN^-} = 9.50 \times 10^{12} e^{-13462/T} C_{O_2}^{1.06} C_{CN_0^-}^{0.18} C_{SCN_0}^{0.29} C_{SCN^-} \tag{22}$$

$$-r_{CN^-} = 9.50 \times 10^{12} e^{-13462/T} C_{O_2}^{1.06} C_{CN_0^-}^{0.18} C_{SCN_0}^{0.29} C_{SCN^-} - 4.67 \times 10^9 e^{-10577/T} C_{O_2}^{0.20} C_{CN_0^-}^{-0.100} C_{SCN_0^-}^{0.030} C_{CN^-} \tag{23}$$

The kinetic model for the reaction intermediate (cyanate) and the reaction products (formate, ammonia, carbon dioxide and nitrogen) is shown in section 8 of the SI. The experiments on the degradation of thiocyanate and cyanide were simulated using Eqs. 22 and 23 and equations S1 to S6 of the SI with a good degree of concordance ($r^2 > 0.98$).

4. Conclusions

A synergistic effect between thiocyanate and cyanide was observed during the simultaneous wet oxidation of these com-pounds .Oxygen concentration has a marked effect on thiocyanate degra-dation, as proven by the oxygen reaction order, $\alpha_1 = 1.06 \pm 0.02$,in the reaction rate equation. For cyanide, this dependence was much less significant, the reaction order being $\alpha_2 = 0.20 \pm 0.02$. The degradation of both pollutants presents an Arrhenius-type temperature dependence, obtaining values of $E_{a1} = 112 \pm 7$ kJ/mol and $E_{a2} = 88 \pm 2$ kJ/mol, for thiocyanate and cyanide, respectively. A free-radical pathway has been proposed for thiocyanate degradation in which cyanide and cyanate are the reaction intermediates. Their final degradation takes place by two parallel routes, one giving formate and ammonia as reaction products and the other one forming carbon dioxide, nitrogen and hydrogen.

The first route was favored at higher temperature whereas the second one occurred to a greater extent at lower temperature. The kinetic model obtained validates the pathway here proposed, as demonstrated by the good correlation between the experimental and theoretical concentrations.

Acknowledgements

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Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
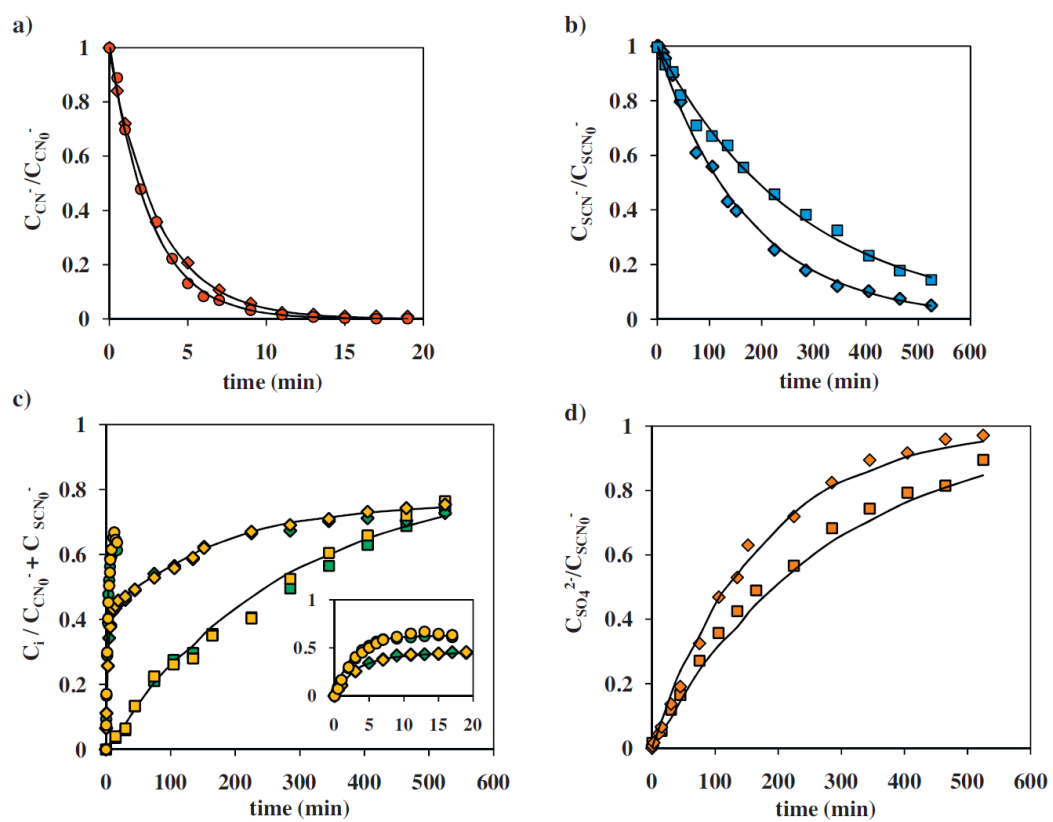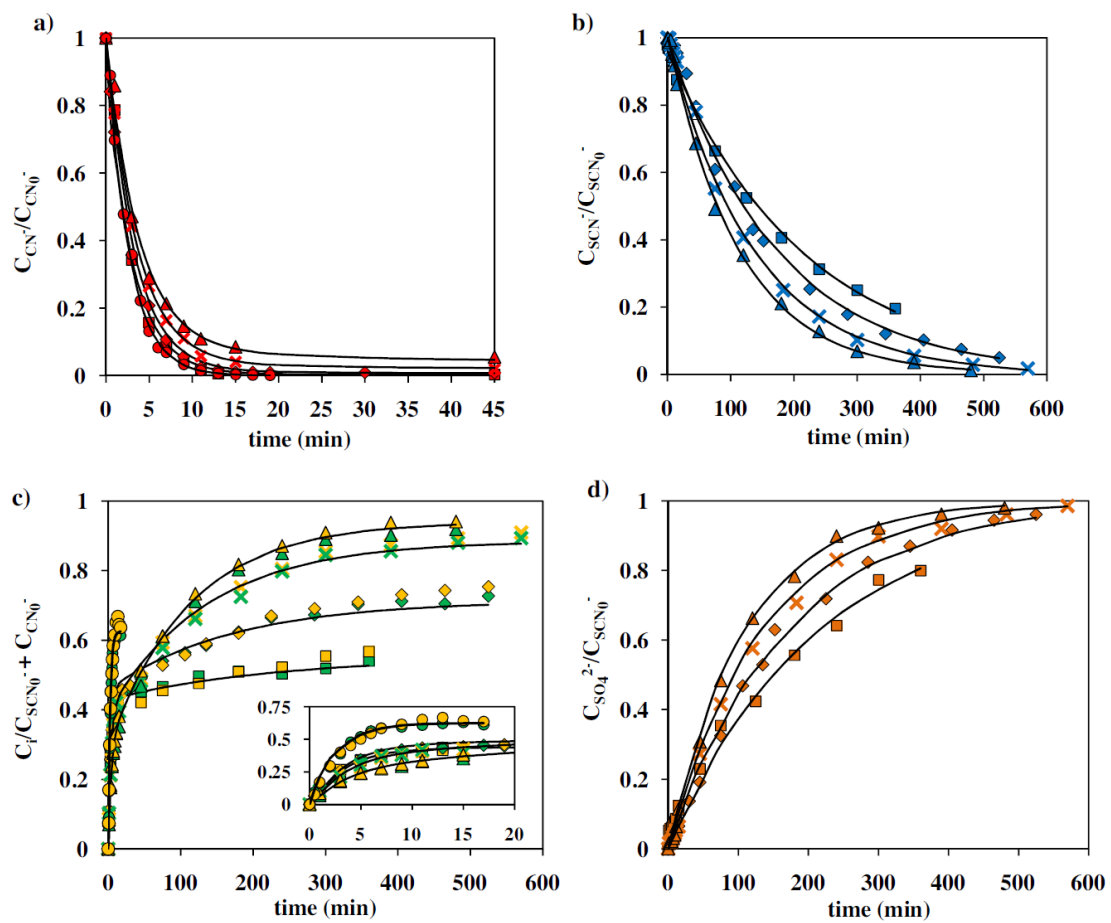
Figure 1

Figure 2

Figure 3
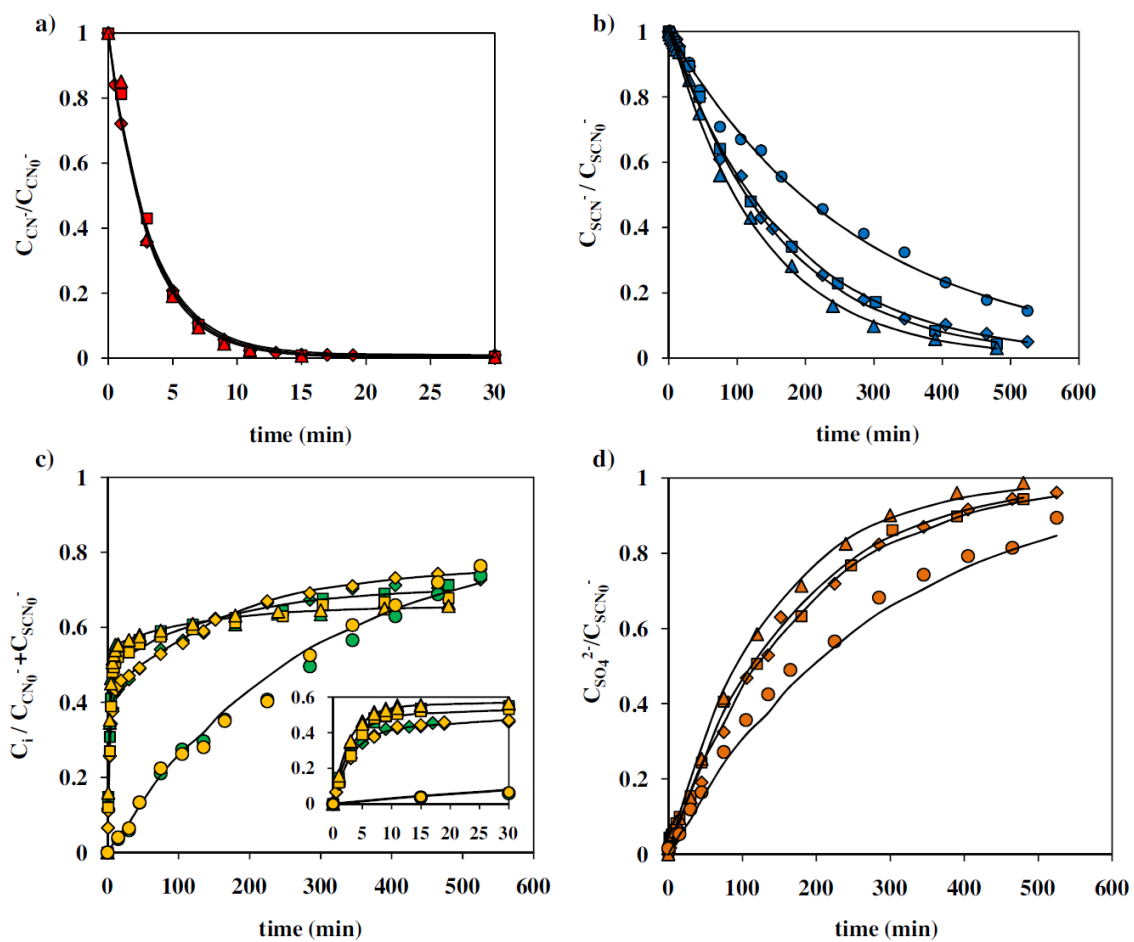
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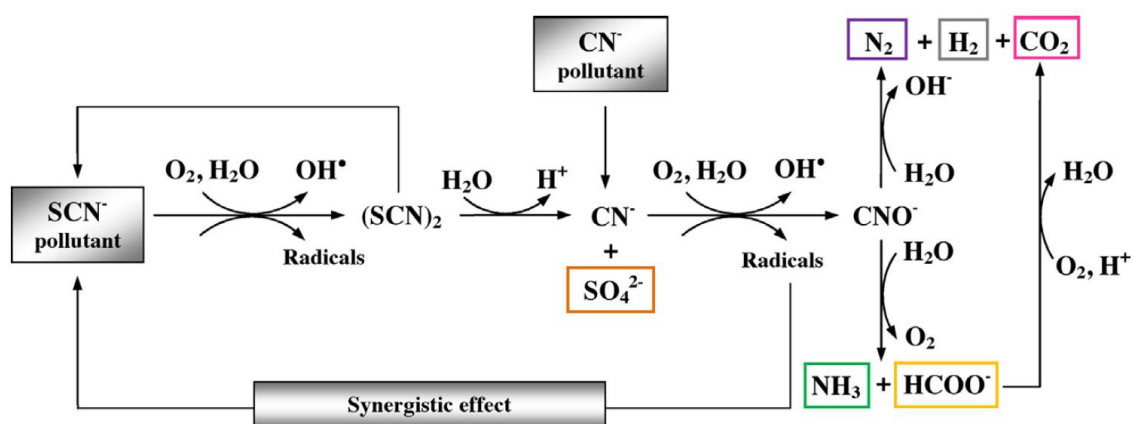
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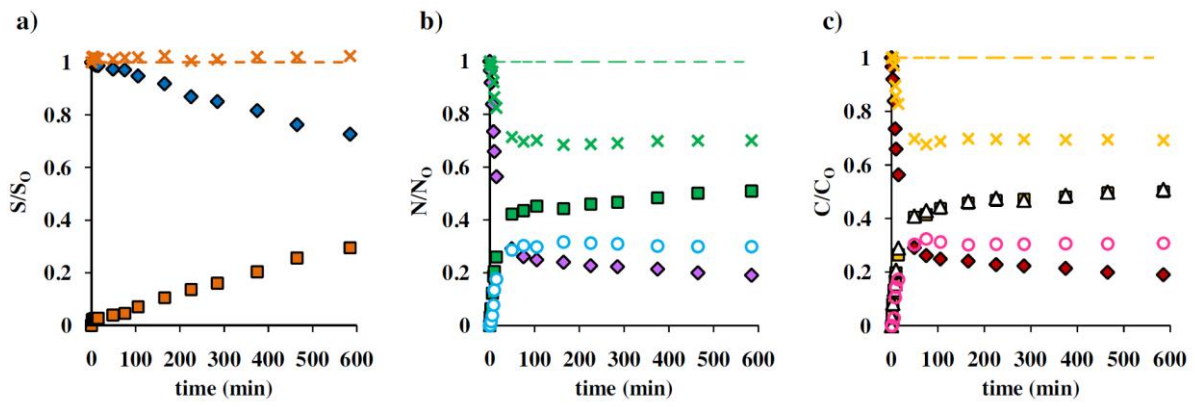
Figure captions

Fig. 1. Evolution of the concentration of cyanide (a), thiocyanate (b), formate (yellow) and ammonia (green) (c), and sulfate (d), during the individual degradation of cyanide (•), the simultaneous degradation of cyanide and thiocyanate (♦), and the individual degradation of thiocyanate (■). The graph shown in (c) has been enlarged for a better visualization of the data during the first 20 min. Operating conditions: initial cyanide concentration = 3.85 mM, initial thiocyanate concentration = 2.20 mM, T = 453 K, P = 8.0 MPa, and pH 11. Solid lines denote models according to Table S1.

Fig. 2. Evolution of the concentration of cyanide (a), thiocyanate (b), formate (yellow) and ammonia (green) (c) and sulfate (d), during the simultaneous wet oxidation of cyanide and thiocyanate performed at different initial thiocyanate concentrations: 0 mM (•), 0.98 mM (■), 2.20 mM (♦), 5.17 mM (×) and 8.62 mM (▲). The graph shown in(c) has been enlarged for a better visualization of the data during the first 20 min. Operating conditions: initial cyanide concentration = 3.85 mM, T = 453 K, P = 8.0 MPa, and pH 11. Solid lines denote model data according to Table S1.

Fig. 3. Evolution of the concentration of cyanide (a), thiocyanate (b), formate (yellow) and ammonia (green) (c), and sulfate (d), during the simultaneous wet oxidation of cyanide and thiocyanate performed at different initial cyanide concentrations: 0 mM (•), 3.85 mM (♦), 7.69 mM (■) and 15.38 mM (▲). The graph shown in (c) has been enlarged for a better visualization of the data during the first 30 min. Operating conditions: initial thiocyanate concentration = 2.20 mM, T = 453 K, P = 8.0 MPa, and pH 11. Solid lines denote model data according to Table S1 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.).

Fig. 4. Reaction pathway for the degradation of thiocyanate in the presence of cyanide.

Fig. 5. Sulfur (a), nitrogen (b) and carbon (c) elemental balance during the simultaneous wet oxidation of cyanide and thiocyanate: S, N or C as SCN^- ($\blacklozenge$), S as SO_4^{2-}, N as NH_3 or C as $HCOO^-$ ($\blacksquare$), total measured S (SO_4^{2-} plus SCN^-), total measured N ($NH3$ plus CN^- plus SCN^-), or total measured C ($HCOO^-$ plus CN^- plus SCN^-) ($\times$), N as theoretical N_2 or C as theoretical CO_2 ($\bigcirc$), C as TOC ($\triangle$). Broken lines indicate theoretical total S, theoretical total N or theoretical total C. Operating conditions: initial cyanide concentration = 3.85 mM, initial thiocyanate concentration = 2.20 mM, T = 423 K, P = 8.0 MPa and pH 11.

Tables

Table 1. Kinetic Orders and Activation Energies for the Degradation of Thiocyanate and Cyanide at Different Operating Conditions.

	Eq 1 (k_1)	Eq 2 (k_2)	Eq 3 (k_3)	Eq 4 (k_4)
α_i	1.06 ± 0.02	0.20 ± 0.02	0.000	0.000
$r^{2,a}$	0.9997	0.989	N/A	N/A
E_a (kJ/mol)	112 ± 7	88 ± 2	18.4 ± 0.5	0.34 ± 0.02
$r^{2,b}$	0.993	0.9993	0.998	0.996
β_i	0.29 ± 0.02	-0.100 ± 0.004	0.54 ± 0.030	-0.90 ± 0.07
$r^{2,c}$	0.989	0.997	0.994	0.987
γ_i	0.18 ± 0.02	0.030 ± 0.001	0.185 ± 0.007	0.44 ± 0.02
$r^{2,d}$	0.989	0.998	0.998	0.998

[a,b,c,d] refer to the goodness of fit for α, Ea, β and γ, respectively.

Graphical abstract
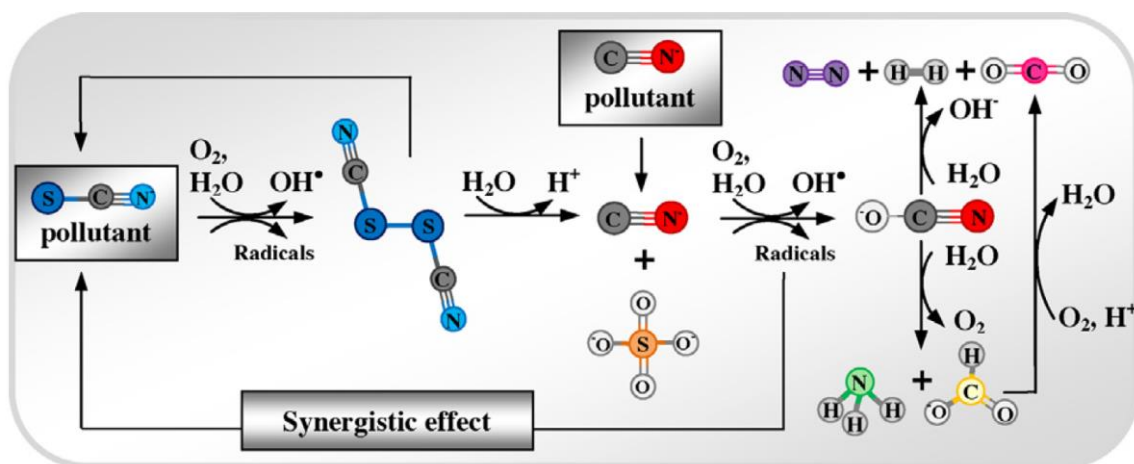
Highlights

- The oxidation rate of SCN^- was greatly enhanced by the presence of CN^-.

- The degradation of mixtures was significantly affected by temperature and pressure.

- A free-radical pathway was proposed, CN^- and CNO^- being the reaction intermediates.

- The principal reaction products were found to be $HCOO^-$, NH_3 and SO_4^{2-}.

- One of the parallel routes gives the found products and the other N_2, CO_2 and H_2.

Supplementary Information for

Simultaneous Oxidation of Cyanide and Thiocyanate at High Pressure and Temperature

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(12 Pages, 5 Figures, 1 Table)

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8. Kinetic model for the reaction intermediate (cyanate) and the reaction products (sulfate, formate, ammonia, carbon dioxide and nitrogen).

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1. Effect of the oxygen pressure on the simultaneous wet oxidation of thiocyanate and cyanide (Figure S1).

Figure S1. Simultaneous wet oxidation of cyanide and thiocyanate performed at different pressures: ($\square$) 2.0 MPa, ($\triangle$) 5.0 MPa and ($\diamond$) 8.0 MPa: a) Concentration of cyanide (red symbols). b) Concentration of thiocyanate (blue symbols). c) Concentration of ammonia (green symbols) and formate (yellow symbols). The area of the graph that shows the first 30 min has been enlarged for a better visualization of the data. d) Concentration of sulfate (orange symbols). Operating conditions: initial cyanide

concentration = 3.85 mM, initial thiocyanate concentration = 2.20 mM, T = 453 K, and

pH = 11. In all cases, solid lines denote model data according to Table S1.

2. **Effect of the temperature on the simultaneous wet oxidation of thiocyanate and cyanide (Figure S2).**

a)

b)

c)

d)
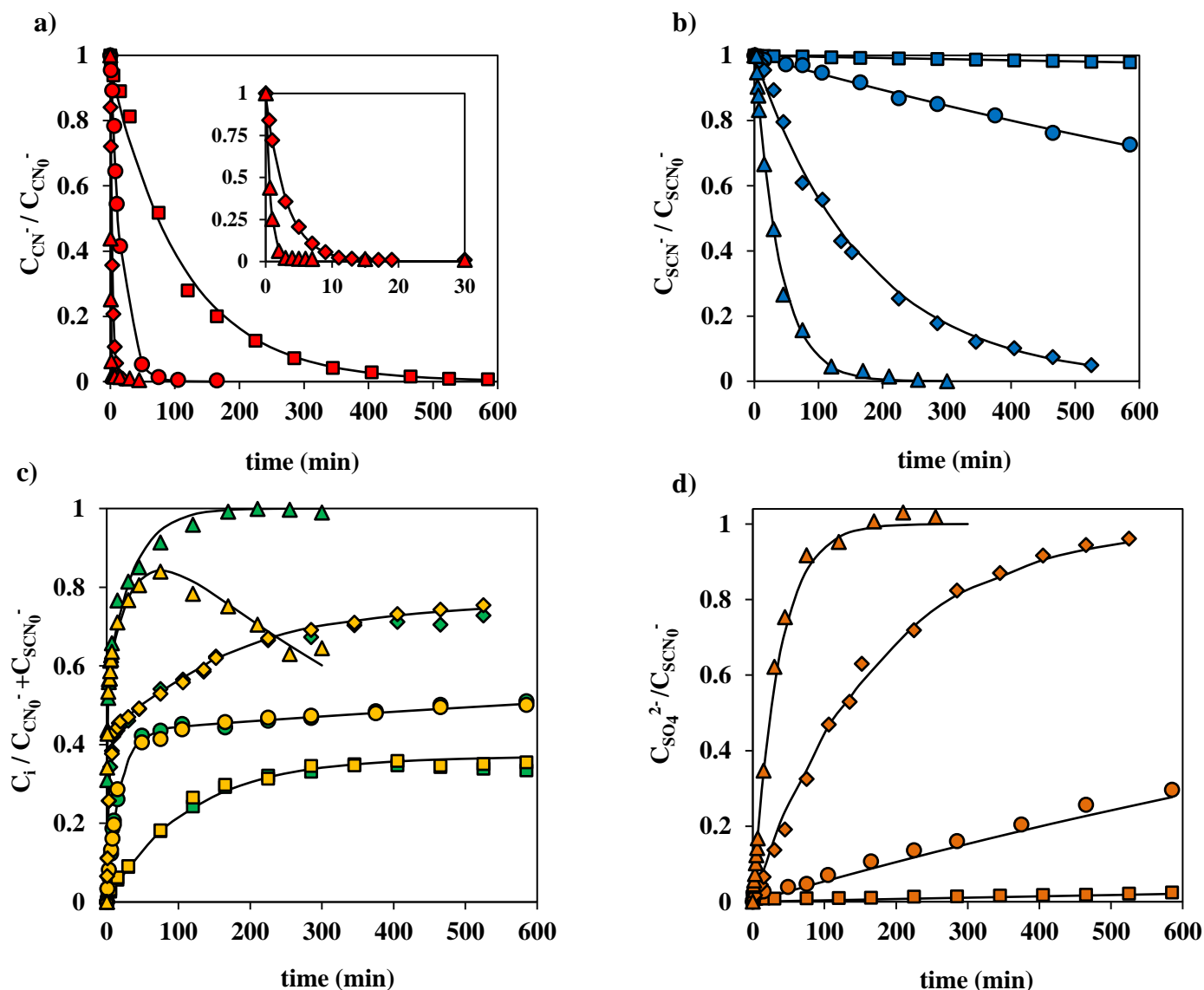
Figure S2. Simultaneous wet oxidation of cyanide and thiocyanate performed at different temperatures: ($\square$) 393 K, ($\bigcirc$) 423 K, and ($\diamond$) 453 K and ($\triangle$) 483 K: a) Concentration of cyanide (red symbols). The area of the graph that shows the first 30 min has been enlarged for a better visualization of the data. b) Concentration of thiocyanate (blue symbols). c) Concentration of ammonia (green symbols) and formate (yellow symbols). d) Concentration of sulfate (orange symbols). Operating conditions: initial cyanide concentration = 3.85 mM, initial thiocyanate concentration = 2.20 mM, P

= 8.0 MPa, and pH = 11. In all cases, solid lines denote model data according to Table S1.

3. Comparison between the experimental data of cyanate and the results calculated by Micromath Scientist 3.0 (Figure S3).
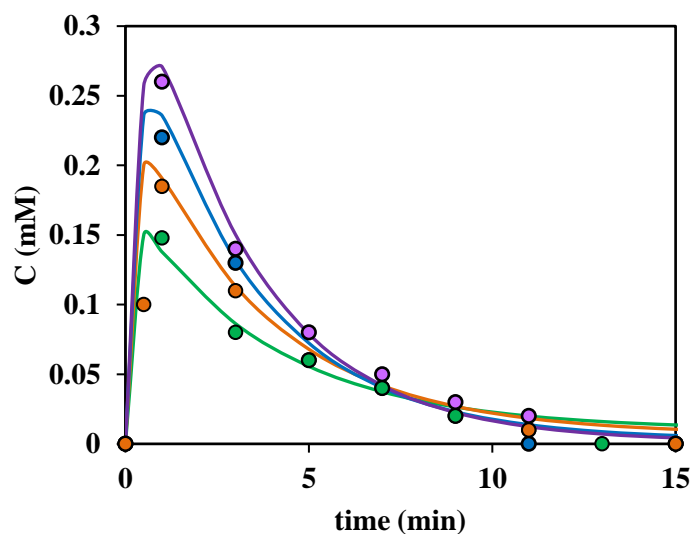
Figure S3. Experimental (circles) and simulated (lines) concentrations of cyanate during the degradation of thiocyanate and cyanide conducted at different initial thiocyanate concentrations; (—) 0.98 mM, (—) 2.20 mM, (—) 5.17 mM and (—) 8.62 mM. Operating conditions: initial cyanide concentration = 3.85 mM, T = 453 K, P = 8.0 MPa, and pH = 11.

4. Values of hydrogen concentration for the simultaneous wet oxidation of thiocyanate and cyanide (Figure S4).
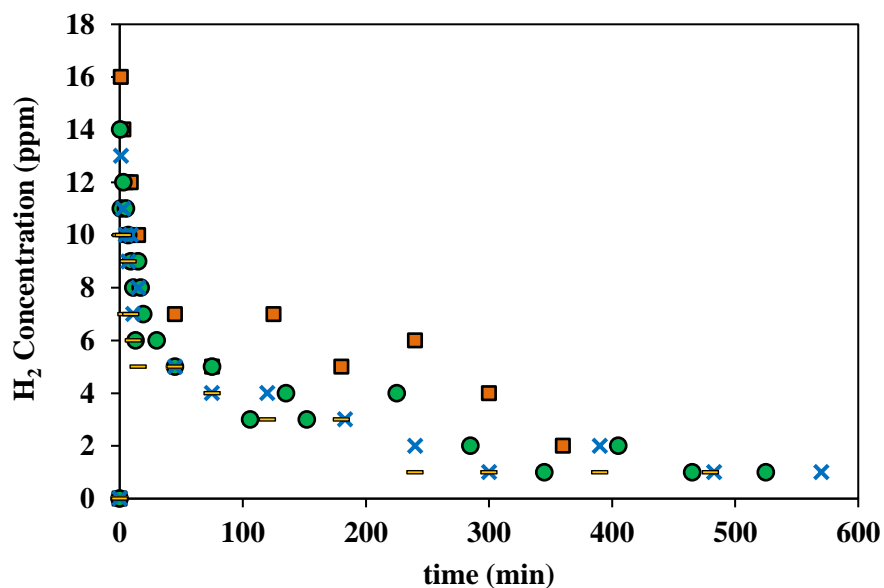
Figure S4. Concentration of hydrogen during the degradation of thiocyanate and cyanide conducted at different initial thiocyanate concentrations: (■) 0.98 mM, (●) 2.20 mM, (×) 5.17 mM, (−) 8.62 mM. Operating conditions: initial cyanide concentration = 3.85 mM, T = 453 K, P = 8.0 MPa, and pH = 11.

5. Relevant Kinetic Data Results for the Degradation of Thiocyanate and Cyanide at Different Operating Conditions (Table S1).

Table S1. Relevant Kinetic Data Results for the Degradation of Thiocyanate and Cyanide at Different Operating Conditions.

Effect of pressure					
T(K)	453				
P(MPa)	2.0	5.0	8.0		
C_{SCN0^-} (mM)	2.20 ± 0.01	2.20 ± 0.01	2.20 ± 0.02		
C_{CN0^-} (mM)	3.85 ± 0.02	3.85 ± 0.03	3.85 ± 0.02		
C_{O2} (M)	1.0×10^{-2}	3.8×10^{-2}	6.7×10^{-2}		
k_1 (s^{-1})	$(1.20 \pm 0.20) \times 10^{-5}$	$(5.12 \pm 0.08) \times 10^{-5}$	$(9.63 \pm 0.02) \times 10^{-5}$		
k_2 (s^{-1})	$(3.50 \pm 0.08) \times 10^{-3}$	$(4.50 \pm 0.20) \times 10^{-3}$	$(5.20 \pm 0.05) \times 10^{-3}$		
k_3 (s^{-1})	$(1.31 \pm 0.01) \times 10^{-1}$	$(1.31 \pm 0.02) \times 10^{-1}$	$(1.31 \pm 0.03) \times 10^{-1}$		
k_4 (s^{-1})	$(5.55 \pm 0.02) \times 10^{-2}$	$(5.55 \pm 0.02) \times 10^{-2}$	$(5.55 \pm 0.03) \times 10^{-2}$		
k_5 (s^{-1})	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$		
Effect of temperature					
P(MPa)	8.0				
T(K)	393	423	453	483	
C_{SCN0^-} (mM)	2.20 ± 0.01	2.20 ± 0.02	2.20 ± 0.02	2.20 ± 0.03	
C_{CN0^-} (mM)	3.85 ± 0.01	3.85 ± 0.03	3.85 ± 0.02	3.85 ± 0.02	
C_{O2} (M)	5.7×10^{-2}	6.0×10^{-2}	6.7×10^{-2}	7.2×10^{-2}	
k_1 (s^{-1})	$(5.91 \pm 0.08) \times 10^{-7}$	$(9.20 \pm 0.20) \times 10^{-6}$	$(9.63 \pm 0.02) \times 10^{-5}$	$(4.33 \pm 0.03) \times 10^{-4}$	
k_2 (s^{-1})	$(1.54 \pm 0.05) \times 10^{-4}$	$(9.41 \pm 0.01) \times 10^{-4}$	$(5.05 \pm 0.07) \times 10^{-3}$	$(2.43 \pm 0.03) \times 10^{-2}$	
k_3 (s^{-1})	$(7.63 \pm 0.03) \times 10^{-2}$	$(1.09 \pm 0.01) \times 10^{-1}$	$(1.59 \pm 0.02) \times 10^{-1}$	$(2.16 \pm 0.02) \times 10^{-1}$	
k_4 (s^{-1})	$(6.55 \pm 0.02) \times 10^{-2}$	$(6.59 \pm 0.03) \times 10^{-2}$	$(6.63 \pm 0.03) \times 10^{-2}$	$(6.67 \pm 0.04) \times 10^{-2}$	
k_5 (s^{-1})	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$	$(1.79 \pm 0.05) \times 10^{-3}$	
Effect of initial thiocyanate concentration					
P(MPa)	8.0				
T(K)	453				
C_{SCN0^-} (mM)	0.00	0.98 ± 0.02	2.20 ± 0.02	5.17 ± 0.03	8.62 ± 0.03
C_{CN0^-} (mM)	3.85 ± 0.02	3.85 ± 0.01	3.85 ± 0.02	3.85 ± 0.03	3.85 ± 0.02
k_1 (s^{-1})	---	$(7.60 \pm 0.05) \times 10^{-5}$	$(9.63 \pm 0.08) \times 10^{-5}$	$(1.22 \pm 0.07) \times 10^{-4}$	$(1.49 \pm 0.03) \times 10^{-4}$
k_2 (s^{-1})	$(6.42 \pm 0.07) \times 10^{-3}$	$(5.42 \pm 0.07) \times 10^{-3}$	$(5.20 \pm 0.20) \times 10^{-3}$	$(4.63 \pm 0.05) \times 10^{-3}$	$(4.35 \pm 0.03) \times 10^{-3}$
k_3 (s^{-1})	$(5.10 \pm 0.20) \times 10^{-3}$	$(3.16 \pm 0.03) \times 10^{-2}$	$(4.66 \pm 0.05) \times 10^{-2}$	$(7.49 \pm 0.06) \times 10^{-2}$	$(1.08 \pm 0.01) \times 10^{-1}$
k_4 (s^{-1})	$(2.94 \pm 0.07) \times 10^{-3}$	$(3.75 \pm 0.05) \times 10^{-2}$	$(1.87 \pm 0.03) \times 10^{-2}$	$(9.20 \pm 0.08) \times 10^{-3}$	$(3.70 \pm 0.04) \times 10^{-2}$
k_5 (s^{-1})	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$
Effect of initial cyanide concentration					
P(MPa)	8.0				
T(K)	453				
C_{SCN0^-} (mM)	1.72 ± 0.03	1.72 ± 0.02	1.72 ± 0.03	1.72 ± 0.01	
C_{CN0^-} (mM)	0.00	3.85 ± 0.02	7.69 ± 0.01	15.38 ± 0.03	
k_1 (s^{-1})	$(5.95 \pm 0.05) \times 10^{-5}$	$(9.63 \pm 0.08) \times 10^{-5}$	$(1.06 \pm 0.01) \times 10^{-4}$	$(1.24 \pm 0.06) \times 10^{-4}$	
k_2 (s^{-1})	$(3.60 \pm 0.06) \times 10^{-3}$	$(5.15 \pm 0.02) \times 10^{-3}$	$(5.25 \pm 0.02) \times 10^{-3}$	$(5.38 \pm 0.03) \times 10^{-3}$	
k_3 (s^{-1})	$(3.47 \pm 0.05) \times 10^{-2}$	$(5.83 \pm 0.03) \times 10^{-2}$	$(6.67 \pm 0.03) \times 10^{-2}$	$(6.59 \pm 0.04) \times 10^{-2}$	
k_4 (s^{-1})	$(6.31 \pm 0.09) \times 10^{-3}$	$(2.33 \pm 0.02) \times 10^{-2}$	$(3.18 \pm 0.03) \times 10^{-2}$	$(4.27 \pm 0.05) \times 10^{-2}$	
k_5 (s^{-1})	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$	$< 10^{-10}$	

6. Calculation method for the determination of the kinetic orders (α, β and γ) and activation energies (Ea).

Over the range of pressures studied, the experimental data were successfully fitted to a pseudo-first order model (see Table S1). Solid lines in Figure S1 denote the model curve according to the calculated pseudo-first order kinetic constants. The oxygen reaction order (α_i) was calculated by correlating the oxygen concentration and the reaction rate constant at different working pressures ($k_i = k_i' C_{O_2}^{\alpha_i}$) yielding two values, α_1 and α_2, for k_1 and k_2, respectively. The values for α_3 and α_4 were zero, which indicates that pressure had no influence on cyanate degradation.

Regarding the effect of temperature, the experimental data were also successfully fitted to a pseudo-first order kinetic model (see Table S1). New kinetic constants k_{SCN^-}' and k_{CN^-}' were calculated taking into account the effect of the oxygen concentration ($k_{SCN^-}' = k_{SCN^-} / C_{O_2}^{1.06}$; $k_{CN^-}' = k_{CN^-} / C_{O_2}^{0.20}$) at the operating conditions of each run. Nevertheless, $k_{HCOO^-,\ NH_3}$ and $k_{CO_2,\ N_2}$, were exactly the same as the value of $k_{HCOO^-,\ NH_3}'$ and $k_{CO_2,\ N_2}'$, since α_3 and α_4 values were zero. All constants were assumed to have an Arrhenius-type temperature dependence, $k_i' = A \cdot \exp(-Ea/RT)$, and four values of activation energies (for k_1', k_2', k_3' and k_4') were determined.

Regarding the effect of initial thiocyanate and cyanide concentration, again the experimental data were fitted with success to a pseudo-first kinetic model (see Table S1). Solid lines in Figure 2 and 3 denote the model curve according to the calculated pseudo-first order kinetic constants. The reaction orders for the initial thiocyanate concentration (β_i) and the initial cyanide concentration (γ_i) were calculated correlating the initial concentration of each pollutant and the kinetic constants at different initial thiocyanate and cyanide concentrations, respectively: $k_i^{II} = k_i'' C_{SCN^-}^{\beta_i}$, $k_i^{III} = k_i''' C_{CN^-}^{\gamma_i}$.

7. Comparison between carbon dioxide and nitrogen concentrations calculated from experimental data and data obtained by solving the equation system, equations 14 to 21 (Figure S5).
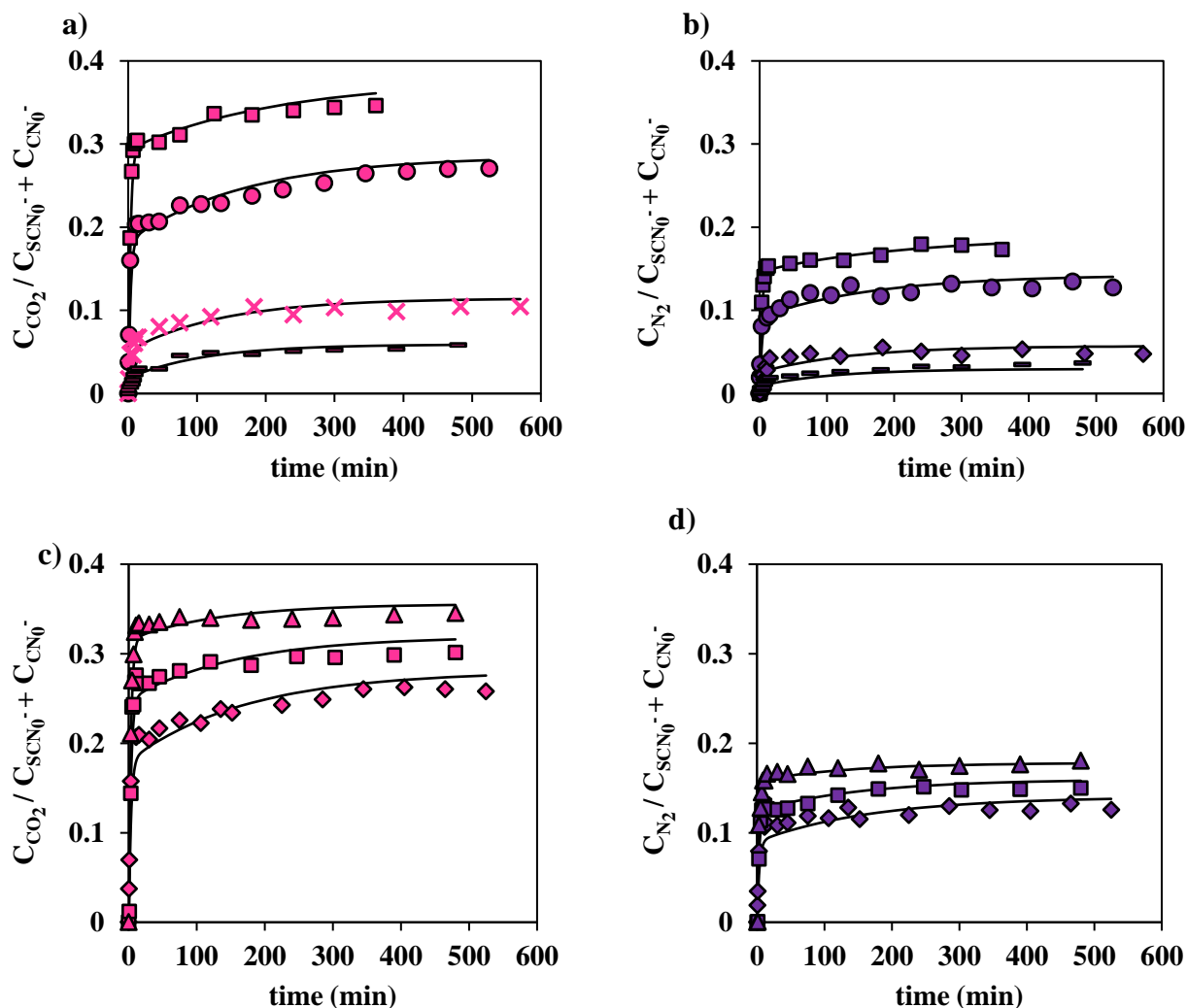
Figure S5. Calculated (symbols) and simulated (lines) concentrations of carbon dioxide (magenta) and nitrogen (purple) during the degradation of thiocyanate and cyanide conducted at different: initial thiocyanate concentrations (a and b): (□) 0.98 mM, (○) 2.20 mM, (×) 5.17 mM and (▱) 8.62 mM. Initial cyanide concentration (c and d): (◇) 3.85 mM, (□) 7.69 mM and (△) 15.38 mM. Operating conditions in all cases: T = 453 K, P = 8.0 MPa, and pH = 11. Solid lines denote models according to Table S1.

8. Kinetic model for the reaction intermediate (cyanate) and the reaction products (sulfate, formate, ammonia, carbon dioxide and nitrogen).

The kinetic model for the reaction intermediate (cyanate) and the reaction products (formate, ammonia, carbon dioxide and nitrogen) is shown as follows:

$$r_{CNO^-} = 4.67 \times 10^9 e^{-10577/T} C_{O_2}^{0.20} C_{CN_0^-}^{0.030} C_{SCN_0^-}^{-0.100} C_{CN^-} - 1.30 \times 10^{-1} e^{-41/T} C_{CN_0^-}^{0.44} C_{SCN_0^-}^{-0.90} C_{CNO^-}$$
$$- 4.28 \times 10^4 e^{-2217/T} C_{CN_0^-}^{0.185} C_{SCN_0^-}^{0.54} C_{CN^-} C_{CNO^-} \tag{S1}$$

$$r_{SO_4^{2-}} = 9.50 \times 10^{12} e^{-13462/T} C_{O_2}^{1.06} C_{CN_0^-}^{0.18} C_{SCN_0^-}^{0.29} C_{SCN^-} \tag{S2}$$

$$r_{HCOO^-} = -4.28 \times 10^4 e^{-2217/T} C_{CN_0^-}^{0.185} C_{SCN_0^-}^{0.54} C_{CN^-} C_{CNO^-} \tag{S3}$$

$$r_{NH_3} = -4.28 \times 10^4 e^{-2217/T} C_{CN_0^-}^{0.185} C_{SCN_0^-}^{0.54} C_{CN^-} C_{CNO^-} \tag{S4}$$

$$r_{CO_2} = 1.30 \times 10^{-1} e^{-41/T} C_{CN_0^-}^{0.44} C_{SCN_0^-}^{-0.90} C_{CNO^-} \tag{S5}$$

$$r_{N_2} = 0.65 \times 10^{-1} e^{-41/T} C_{CN_0^-}^{0.44} C_{SCN_0^-}^{-0.9} C_{CNO^-} \tag{S6}$$