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Polythionic Acids in the Wackenroder Reaction

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Cite This: *ACS Omega* 2021, 6, 26140−26149

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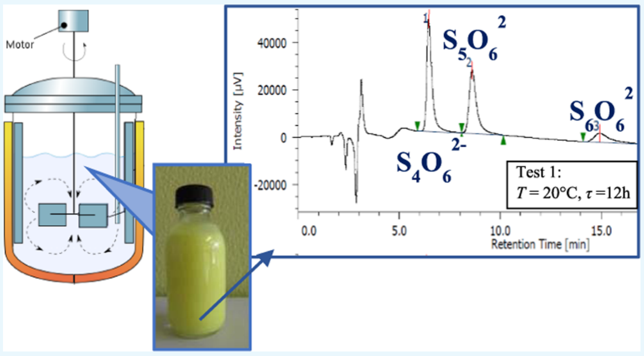
ABSTRACT: Polythionic acids, whose general formula is $H_2S_nO_6$, with n greater than 2, were discovered in the aqueous solution of SO_2 and H_2S, known as the Wackenroder liquid. Their reactions with each other and with other reagents are, mostly, difficult to characterize, since such compounds readily decompose and interconvert, especially in solution. Nevertheless, they play an important role in technical applications (e.g., gold leaching, magnesium milling, cooling in metal processing) and in reactions of inorganic chemistry of sulfur. A few years ago, Shell−Paques/Paqell patented the first industrial process for the biological conversion of H_2S into a colloidal mixture of sulfur and polythionates. Such hydrophilic sulfur can be used as a fertilizer and soil improver in agriculture in all but alkaline soils. Recently, Eni S.p.A. has developed to bench plant scale a new process, the HydroClaus process for the conversion of H_2S into an acidic hydrophilic slurry of sulfur and polythionate ions. Such a slurry can be used as a soil improver where the very alkaline soil pH hinders the cultivation. The aim of this work is to study the laboratory-scale production of polythionates in view of the novel HydroClaus process scale-up at the industrial level. After the literature related to polythionates and their characterization has been revised, the sulfur-based mixture has been synthesized and the polythionate ions concentration has been determined. Also, the effect of the reaction operating conditions has been investigated to assess how they can influence the nature and the distribution of products in solution.



1. INTRODUCTION

Polythionic acids are of great interest in the technical processes since they can find application in several fields. Indeed, they can be used[1]

- in solutions for chemical milling of magnesium and its alloys, by the method of immersion, that allows us to carry out deep etching of large-size parts of a complicated profile;
- as lubricants and coolants for metal machining, where a solution of polythionates allows us to improve the durability of the cutting tool and the surface roughness;
- as fertilizers and soil improvers for agriculture;[2−5]
- as eluting agents in gold leaching processes, allowing the sorption of gold complexes on a high basic anion exchanger, to obtain faster leaching, higher gold yield, and lower consumption of leaching agent.

Despite their disparate applications, these are not so widespread due to their instability and their tendency to form complex mixtures, the characterization of which is a challenging task.

Their flexibility, together with their lack of abundance, make polythionic acids significantly valuable products.

From the chemical point of view, polythionic acids are sulfur-rich compounds whose structures can be represented as unbranched sulfur chains terminated by sulfonate groups. These sulfur-rich compounds, of composition $H_2S_nO_6$, with n ranging from 3 (trithionic acid) to probably more than 50 (polythionic acids), show a peculiar characteristic of being soluble in water.

Although the acid sulfur chain can be quite long ($H_2S_nO_6$ with n more than 50), the most widely known and spread compounds are $H_2S_nO_6$ with n between 3 and 6: trithionic acid, tetrathionic acid, pentathionic acid, and hexathionic acid, respectively.[6]

Trithionic acid ($H_2S_3O_6$) is the least stable of the polythionic acids.[7,8] The aqueous solution of the free acid slowly decomposes, even at the ordinary temperature, with the formation of sulfur (S_8) and sulfates (SO_4^{2-}) as the end

Received: June 15, 2021
Accepted: September 14, 2021
Published: September 28, 2021

ACS Publications

https://doi.org/10.1021/acsomega.1c03139

products. The free acid is known only in the form of its aqueous solution, which is colorless and odorless.

On the other hand, tetrathionic acid ($H_2S_4O_6$) is the most stable of the polythionic acids. Considering its heat of neutralization with dilute sodium hydroxide and the electrical conductivity of the solution, it can be stated that tetrathionic acid is a fairly strong acid, comparable with dithionic acid in this respect.[7,9,10]

Pentathionic ($H_2S_5O_6$) and hexathionic ($H_2S_6O_6$) acids are quite stable in acid solution but undergo decomposition in nearly neutral, alkaline solutions with the formation of sulfur and a lower polythionate ($S_4O_6^{2-}$ for the penthathionic acid, $S_5O_6^{2-}$ for the hexathionic acid).[11−14]

The stability of polythionates in an aqueous solution has been investigated many times in the previous literature.[10,13−15]

Recently, Pan and co-workers have studied the alkaline decomposition of hexathionate[13] and pentathionate,[14] while the kinetics and mechanism of tetrathionate decomposition were analyzed by Varga and Horváth.[10] In the case of hexathionate decomposition, a significant amount of sulfur deposition was observed, with heptathionate as a key intermediate in detectable amounts. On the other hand, thiosulfate, tetrathionate, and hexathionate appear in significant amounts during the pentathionate decomposition reaction. Regarding tetrathionate, thiosulfate and trithionate have been identified as major decomposition products. In all cases, the decomposition reactions are faster at increased temperatures and higher pH.

The most important property of polythionate anions is the tendency of forming hydrophilic sulfur water solutions, even at very high sulfur contents. Elemental sulfur is an extremely hydrophobic material, and the same holds for sulfur-rich compounds $R{-}S_n{-}R$ with hydrophobic organic terminal groups. However, strongly hydrophilic groups like SO_3 are able to turn these hydrophobic substances into hydrophilic materials. Polythionate anions are such species that show amphiphilic behavior in water.[16]

Long-chain polythionate anions in water, together with elemental sulfur, form emulsions called hydrophilic sulfur sols. Depending on how these anions are synthesized, two types of sols are known. Raffo sols result from the acid decomposition of sodium thiosulfate by concentrated sulfuric acid, while Selmi sols are obtained by the reaction of H_2S with an excess of SO_2 in water.

In both cases, the solution appears as a yellow liquid of low viscosity. Its density depends on the sulfur content in solution: for Raffo sols, a density of about 1.24 g/cm^3 has been measured when the temperature is fixed at 16 °C and when the sulfur content is about 450 g/L.

The dispersion can be classified as a sulfur micellar colloid because long-chain polythionates ions aggregate in water by self-organization to form micelles, whose structure is reported in Figure 1.

In these micelles, the hydrophobic sulfur chains are stored in the core of the globule, while the hydrophilic sulfonic acid groups are concentrated on the surface, giving the overall hydrophilic character.[17]

As can be clearly understood, the micellar stability is strongly related to the stability of the polythionate ions: owing to the decomposition of polythionates, sulfur sols suffer from the aging phenomenon.

In general, operating conditions such as temperature and pH can significantly affect the micellar stability, but probably the most impactful factor is the $S_n/S_mO_6^{2-}$ sol ratio: the polythionates keep the elemental sulfur in solution, so Selmi sols are usually less stable than Raffo sols, with lower polythionate content and higher sulfur content.[16]

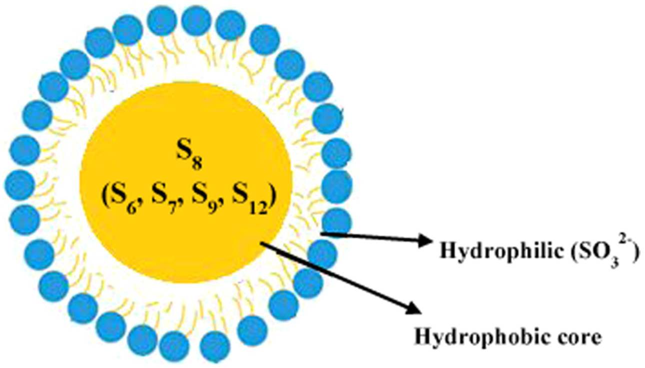


Figure 1. Micelle structure in hydrophilic micellar colloids.

In the literature, the sulfur micelles are reported to be metastable and slow to decompose, with the formation of lower polythionates and elemental sulfur,[16] which precipitates from the solution, according to

$$S_nO_6^{2-} \rightarrow S_{n-x}O_6^{2-} + \frac{x}{n}S_n; \quad n > 5 \tag{1}$$

The short-chain polythionates are soluble in water and do not form micelles. Therefore, the elemental sulfur content of the sol drops and part of the sulfur precipitates both as rings S_n and as insoluble polymeric sulfur.

Polythionates, the ions of polythionic acids, were first found in an aqueous solution of sulfur dioxide and hydrogen sulfide, known as the Wackenroder solution, the product of the Wackenroder reaction.

Wackenroder[18] observed that, when H_2S and SO_2 react in an aqueous solution, polythionates are formed as well as sulfur. H_2S, fed to the system in the gas phase, diffuses from the bulk of the gas phase to the liquid phase to contact the aqueous solution of SO_2.

The global general reaction that takes place in the aqueous phase can be schematized through eq 2, with typical operating conditions reported in the literature[19] being ambient pressure, ambient temperature, and variable pH from 3 to 2.

$$\begin{aligned}&(2n-5)H_2S + (n+5)SO_2\\&\quad \rightarrow 3S_nO_6^{2-} + 6H^+ + (2n-8)H_2O\end{aligned} \tag{2}$$

The exact analytical characterization of polythionates is difficult since such compounds readily decompose, especially in solution. In addition, individual polythionates are very similar in their chemical and physical properties. Several investigations are available in the literature.[11,12,20] The most outdated studies were based on the determination of polythionates in solution by reaction with cyanide or sulfonic acid, forming thiocyanate or thiosulfate.

Nietzel and De Sesa[21] proposed a spectrophotometric method for the determination of low concentrations of tetrathionate ions. This method is based on the stoichiometric formation of thiocyanate from tetrathionate by reaction with cyanide in an alkaline medium, and the subsequent formation of a red ferric thiocyanate complex with excess ferric chloride. The drawback of this method is that it is not suitable for determining higher polythionate concentrations (mainly, pentathionate and hexathionate) because of the partial decomposition experienced by these species.

This problem, according to the authors, can be overcome by working at a specific pH, which however results strictly related to the sulfur quantity available in the samples. Iwasaki and Suzuki[22] evaluated the tetrathionate concentration by means of its decomposition with sulfite through a photometric method. It is based on the formation of thiosulfate equivalent to the tetrathionate and on the photometric determination of thiosulfate by measuring its decoloration of an iodine solution. The specified reaction, however, does not allow to obtain thiosulfate selectively due to interference by sulfites and sulfides and is applicable at specific pH intervals only.

More recent studies are based on liquid chromatography. Chapman and Beard[23] used high-speed liquid chromatography to evaluate the polythionate concentration through an activated carbon column and a UV detector. Wolkoff and Larose[24] suggested an ion-exchange column, while the detection system employed involved reaction of the polythionate anions with a base and then oxidation with cerium(IV) sulfate, followed by fluorometric detection of cerium(III). Also, this method does not allow the exact determination of polythionates in solution due to the decomposition of the species.

None of these procedures was found satisfactory or easily adaptable for the purposes of the present analysis. The most modern analysis techniques to determine the polythionate concentration in solution are based on ion-pair chromatography.[25−27]

Ion chromatography (IC) has recently been proposed for the determination of polythionic acids $H_2S_xO_6$ ($x = 3-5$) using UV detection in several works.[26]

Among them, the method proposed by Steudel and Holdt[25] was based on ion-pair liquid chromatography, with ammonium salts as ion-pair reagents and UV detection. The problem associated with the proposed methodology is the very high retention time for species with more than six sulfur atoms.

As a result of the analysis of the related literature, in this paper, high-pressure liquid chromatography (HPLC) has been selected as the analytical method to quantify the polythionate concentration, with tetrabutylammonium ($TBA\cdot H_2SO_4$) as the ion-pair reagent and UV detection.

The polythionate mixture has been synthesized according to the procedure described in Section 6. After the mixture was produced, the available polythionate standard samples were collected and both qualitative and quantitative analyses were performed to characterize the HydroClaus reaction products.

2. PREPARATION OF THE HYDROCLAUS MIXTURE

The HydroClaus reaction mixture was produced according to the experimental procedure described in Section 6. The selected operating conditions strongly affect the type and the distribution of products formed. It was found experimentally[19] that working at pH > 1 causes the preferential formation of polythionate ions with respect to sulfur. The pH increase corresponds to a reduction in sulfur production and an increase in polythionate ion formation whose sulfur chains become shorter and shorter, up to the formation of thiosulfate ($S_2O_3^{2-}$) only. At pH 8, the reaction seems incomplete and proceeds slowly: a considerable portion of H_2S remains unconverted.

In addition to the pH, the initial H_2S/SO_2 ratio can significantly influence the nature of reaction products. When excess H_2S is fed into the reactor, sulfur and short-chain polythionates are preferentially produced (mainly $S_4O_6^{2-}$). On the other hand, when SO_2 is the most abundant reagent, $S_nO_6^{2-}$, with n ranging from 4 to 8, is essentially formed.[19,28]

For this reason, the assessment of the effect of the reaction operating condition on the HydroClaus reaction product is one of the crucial issues of the process scale-up, which is part of the aim of this work.

The fresh product appears as a yellow milky dispersion (see Figure 2a). During the aging of the solution, two phases can be clearly distinguished after 3−7 days: one solid, which is deposited at the bottom of the storage tank, and another liquid, which disperses the solid (Figure 2b).

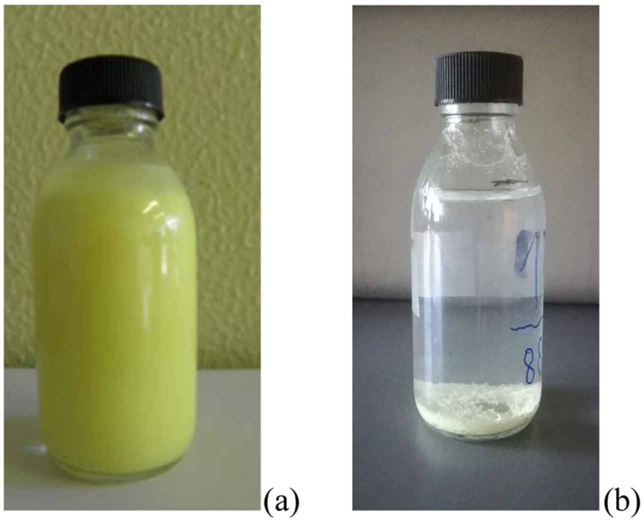


Figure 2. Fresh (a) and aged (b) Wackenroder reaction product.

Depending on the operating conditions selected in the reactor, different slurries are produced, which appear more or less stable and homogeneous. The liquid−solid separation experienced by the aging of the slurries can be also achieved instantaneously by flocculation of the mixture: part of the liquid−solid dispersion produced is sampled and added with about 2000 ppm of nitrate-based polyelectrolyte flocculant (EstFloc 175, by Est Chemie Srl) to force the phase separation. Few minutes after the polyelectrolyte addition, a solid appears at the bottom of the sampler as in Figure 2b.

When the liquid−solid separation is completed, the liquid is collected separately from the solid to analyze the two different phases and determine their compositions.

3. CHARACTERIZATION OF THE HYDROCLAUS REACTION PRODUCT

3.1. Qualitative Analysis. The qualitative analysis of the produced slurry allows a preliminary identification of the species formed in the Wackenroder reaction.

This analysis was performed after aging for 3−7 days from the synthesis, and two separate solid and liquid phases were then clearly distinguished.

The separation of the water-soluble and insoluble species was completed by gently rinsing the deposited solid with additional water and then added to the surnatant. The UV−vis and Raman spectroscopies were applied to perform the preliminary characterization of the soluble and insoluble phases, respectively.

3.1.1. Surnatant Product: UV–Vis Analysis. The spectrum shows a characteristic absorption band with the maximum at 213.5 nm (Figure 3), which is assigned to thionates by comparison with the water solutions of the reference standards.

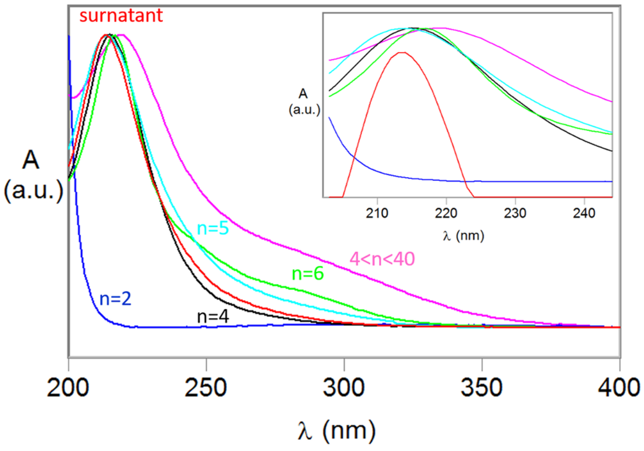


Figure 3. UV spectrum of the surnatant solution and the reference thionate standards.

The reference standards molar extinction coefficient (ε) and the wavelength corresponding to the maximum absorbance (λ_{max}) are reported in Table 1.

Table 1. Reference Standards Molar Extinction Coefficient (ε) and Wavelength Corresponding to the Maximum Absorbance (λ_{max})

species	λ_{max} (nm)	ε (M/cm)	notes
$K_2S_2O_6$			no absorption in the analyzed range; it cannot be detected by UV due to its chromophore behavior
$Na_2S_4O_6{\cdot}2H_2O$	215.5	9411	
$K_2S_5O_6{\cdot}1.5H_2O$	213.9	14 583	
$K_2S_6O_6$	216.6		shoulder at 285 nm
$S_nO_6^{2-}$, $15 < n < 40$	218.9		strong shoulder at 250–350 nm

The spectra of the surnatant and the tetrathionate solution are very similar, suggesting that the four-sulfur-atom thionate is the most abundant species; the higher absorption queue at $\lambda \geq 230$ nm suggests the presence of some higher-order thionates, most likely penta- and hexathionates in small quantity.

The absorption band at about 213 nm is due to the electronic excitation of the S–S bond, with a molar extinction coefficient increasing with the number of S atoms in the chain. The high value of ε (ε of the order of 10^4 were measured on the commercial $Na_2S_4O_6$ and $K_2S_5O_6$ standards) makes the analysis very sensitive. The drawback of this technique is that the position and shape of the rather broad absorption band change very little with the number of S atoms in the molecule so that the contribution of thionates differing by chain length cannot be spectroscopically distinguished. Neither the single nor the overall thionate concentration in a mixture of different species can be exactly determined. Therefore, this analysis was applied to check the thionate formation and merely estimate the order of magnitude of their concentration in solution.

3.1.2. Solid Product: Raman Spectroscopy. The solid phase separated by sedimentation was analyzed after rinsing with Milli-Q water and drying at room temperature to prevent any degradation.

A typical average Raman spectrum of the solid product is reported in Figure 4, showing the characteristic peaks at 148, 214, and 470 cm^{-1}. Figure 4 clearly indicates the predominant presence of pure sulfur in the form of α-S_8, whose spectrum, obtained on the commercial Sigma-Aldrich product, is also reported for comparison with the relative assignments.

Raman peaks up to 700 cm^{-1} are assigned to the S–S bond, with the S_nO_m species at $1/\lambda > 600$ cm^{-1}.[29] In particular, the band visible at about 470 cm^{-1} is due to the symmetric S–S stretching, at 220 cm^{-1} to the symmetric S–S bending, and at 151 cm^{-1} to the asymmetric bending.

In the case of the solid reaction product, the S–S symmetric stretching of S_8 at 470 cm^{-1} is flanked by a new component at 455 cm^{-1}. This red-shifted peak is due to the same S–S mode but in polymeric sulfur,[30] where S atoms are arranged in an open chain, unlike S_8 that shows a ring configuration. The same occurs in the S_n chain of the reference potassium polythionate, whose spectrum is also shown in Figure 4.

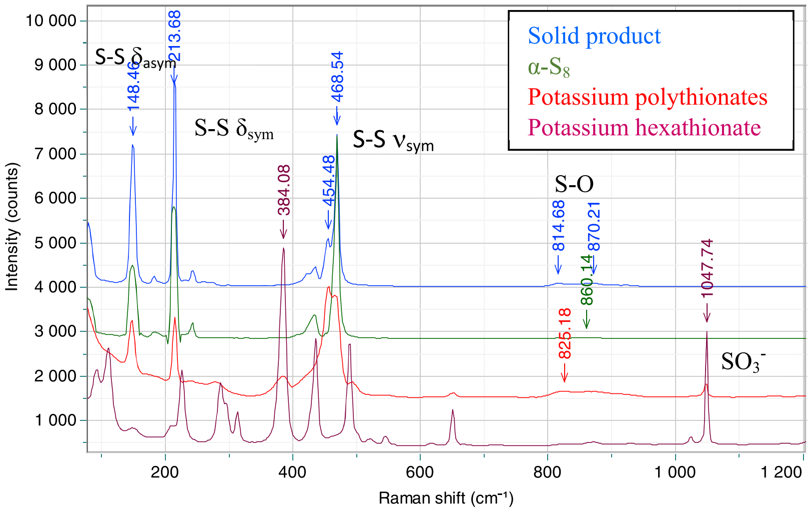


Figure 4. Raman spectra of the solid reaction product, α-S_8, potassium hexathionate, and potassium polythionates.

The ratio between the integrated areas $A(472)/A(455)$ is about 3, depending on the synthesis conditions. Considering the proximity of the two signals, it could be hypothesized that the absorption coefficient is similar and that this value is representative of the concentration ratio between α S_8 and polymeric sulfur in the sample.

Concerning the presence of thionates, the terminal SO_3 moiety should contribute with the characteristic S−O stretching at about 1047 cm^{-1}, observed in all of the reference standards, obviously with lower relative intensity in the polythionate ($n > 6$) with respect to shorter species (see in Figure 4 the Raman spectra of potassium hexathionate and polythionate, solid powders).

No absorption is observed at $1/\lambda > 1000$ cm^{-1}; therefore, the thionates, if present, should have an S−S chain much longer than the soluble five- to six-sulfur atom species present as minor components in solution. In the region of S−O stretching, the only signals are in the 750−950 cm^{-1} region, as in α-S_8, but with higher relative intensity. This agrees with a fine texture of the solid precipitated from the pristine slurry, with the large surface area exposed to oxidative atmospheric conditions.

As expected, the solid product can be considered mainly as α-S_8, with a smaller amount of polymeric sulfur. Although this is quite an obvious result, the characterization of the solid phase was the fundamental prerequisite for the system kinetic analysis, which is the object of further future developments of the present work.

3.2. Quantitative Analysis. Once the presence of polythionates in the reaction product was assessed, the polythionate concentration in the solution was quantified according to high-pressure liquid chromatography (HPLC).

3.2.1. Potassium Hexathionate Purity. Since potassium hexathionate of standard purity was not bought from the supplier, several analyses were performed to determine its actual composition: inductive coupled plasma-optical emission spectroscopy (ICP-OES), CHNS analysis, HPLC-UV−vis analysis, and ionic chromatography (IC).

The ICP-OES analysis allowed us to determine the total amount of potassium and sulfur in the sample, while the CHNS analysis was useful to quantify the H concentration, related to the total water content, as well as the amount of S in the sample.

The results of these two analyses are reported in Table 2.

Table 2. ICP-OES and CHNS Analyses Results[a]

	K (wt %)	S (wt %)	H (wt %)
ICP-OES	21.33	30.10	
CHNS		30.08	0.44

[a] Standard deviation: ±5%.

The amount of sulfur in Table 2 is intended as a global sulfur concentration in the sample due to $S_6O_6^{2-}$, $S_5O_6^{2-}$, and $S_4O_6^{2-}$ in the solution.

The concentrations of $S_4O_6^{2-}$ and $S_5O_6^{2-}$ in the hexathionate sample were quantified by the developed HPLC technique and that of $S_6O_6^{2-}$ in the solution was estimated as the difference between their concentrations and the total sulfur concentration.

Stoichiometric count allowed us to assert S as the limiting agent with respect to K: the maximum $K_2S_6O_6$ concentration (and that of $S_6O_6^{2-}$ anion) has been evaluated starting from the S amount.

The IC analysis revealed traces of chloride ions; hence, the K excess with respect to S is due to the presence of KCl, which is a precursor of the hexathionate synthesis reaction.

On the other hand, the CHNS analysis allowed us to estimate the total amount of water in the sample: the water concentration was recalculated from the H value and turned out to be equal to 3.96 wt %.

With this methodology, the purity of the heaxathionate sample was determined. The evaluated sample composition in terms of polythionates is reported in Table 3 (the difference to 100% being KCl and H_2O).

Table 3. Hexathionate Sample Composition[a]

	$S_6O_6^{2-}$	$S_5O_6^{2-}$	$S_4O_6^{2-}$
composition (wt %)	50.07	1.82	0.37

[a] Standard deviation: ±5%.

3.2.2. Calibration Plots. The commercially available standards (i.e., tetrathionate and pentathionate) were diluted in water with different ratios and injected into the liquid chromatograph.

Also, hexathionate response factor was determined, starting from the evaluated sample composition reported in Table 4.

Table 4. Calibration Factor for the Considered Polythionate Species

species	response factor (μV·L/mg)	R^2
$S_4O_6^{2-}$	36 025	0.9992
$S_5O_6^{2-}$	50 044	0.9987
$S_6O_6^{2-}$	73 307	0.9997

Since the species were hydrated, the actual acid sample concentration was determined considering its dry concentration together with its related purity.

Moreover, to quantify the polythionates in solution loose from the cation with which are bounded, results were provided in terms of $S_nO_6^{2-}$ anion mass concentration.

The resulting chromatogram for a mixture of standard samples in water is reported in Figure 5.

When peak area vs sample concentration is plotted, each calibration graph shows a linear behavior, whose slope, as determined through the linear regression of experimental points, is the response factor.

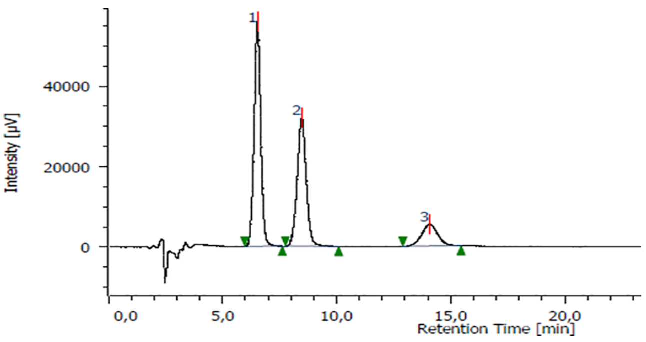


Figure 5. HPLC chromatogram of a mixture of tetrathionate (peak 1), pentathionate (peak 2), and hexathionate (peak 3).

Table 4 gives the evaluated response factors, which are related to the instrumental sensitivity only, together with the associated correlation indexes, for different polythionate species tested.

The limit of quantification (LOQ) associated with the three polythionate species is reported in Table 5 and was determined according to eq 3, where s is the instrument bias when no analytes are tested.

$$\text{LOQ} = 10 \cdot s \tag{3}$$

Table 5. LOQ for Polythionates

species	LOQ (mg/L)
$S_4O_6^{2-}$	0.50
$S_5O_6^{2-}$	0.40
$S_6O_6^{2-}$	0.30

4. RESULTS AND DISCUSSION

The developed analytical method was used to determine the concentration of polythionates in the synthesized Wackenroder solution samples.

A sample of each test was injected into the chromatograph and its concentration was determined.

Results for each performed test are reported in Figures 6–8. Table 6 provides the detail of the operating conditions used in the sample preparation phase described in Section 3.

From the diluted sample concentrations reported in Figures 6–8, the corresponding polythionate concentration in the outlet reaction slurry was evaluated and is reported in Table 7, together with solid sulfur concentration for each sample and elemental sulfur distribution between liquid and solid products.

4.1. Effect of Reaction Temperature. The effect of reaction temperature was investigated to determine how it affected the nature and distribution of products in the analyzed samples.

Sample 1 and sample 2 were produced at a fixed residence time τ of 12 h but at variable temperatures T of 20 and 30 °C, respectively.

Samples 3 and 4 were produced at residence time τ of 9.6 h and temperatures of 25 and 35 °C, respectively.

Two opposite trends can be observed in Table 7: while for tetrathionic acid, an increase in reaction temperature results in a decrease in acid concentration, the concentrations of higher homologues increase with increasing temperature.

Based on these results, the distribution of sulfur between soluble (thionates) and insoluble (α-S_8, polymeric sulfur) products decreases with increasing temperature.

4.2. Effect of Residence Time. The residence time, similar to temperature, affects the nature and distribution of products in the analyzed samples.

Samples 2, 5 and 3, 6 were obtained at fixed temperature but variable residence time, as reported in Table 6 (T = 30 °C for the first two and T = 25 °C for the last two).

From the results reported in Table 7, it is clear that residence time results in an increase in longer-chain polythionates (i.e., hexathionate and penthathionate) and a decrease in shorter-chain polythionates (i.e., tetrathionate).

Considering sulfur distribution among S_g and polythionates products, increasing residence time determines a reduction of the liquid products, promoting solids formation.

4.3. Aging of the Samples. As already mentioned in Section 1, polythionates are not stable but they decompose with the formation of shorter-chain homologues and sulfur.

For this reason, it is of great interest to analyze the composition of the produced samples at different times to determine how the system tends to evolve with time. Toward this aim, analyses of samples 2 and 5 were repeated after about 2 months, with the samples kept at about 5 °C.

The results of the tests performed on samples 2 and 5 at different times are reported in Figures 9 and 10.

Table 8 reports the acid concentration in the samples as it is, considering their dilution in water.

A comparison of the concentrations of polythionates in the fresh and aged samples shows a slight change in the polythionate concentrations; this is more evident in sample 2, where the tetrathionate concentration increased while those of pentathionate and hexathionate decreased.

This behavior proves that the system tends to evolve toward a more thermodynamically stable configuration, promoting the decomposition/disproportion reactions as described in Section 1.

The samples were kept at low temperatures, so these reactions were not preponderant.

5. CONCLUSIONS

In this work, a novel H_2S valorization technology developed by Eni S.p.A. is presented, that is, the HydroClaus process. A mixture of polythionate and sulfur slurry was prepared experimentally according to the HydroClaus reaction at different operating conditions, i.e., temperature T and residence time τ in the reactor. Both qualitative and quantitative analyses have been performed on reaction products. The UV–vis and Raman spectroscopies were applied to perform a preliminary identification of the soluble and insoluble phases, respectively.

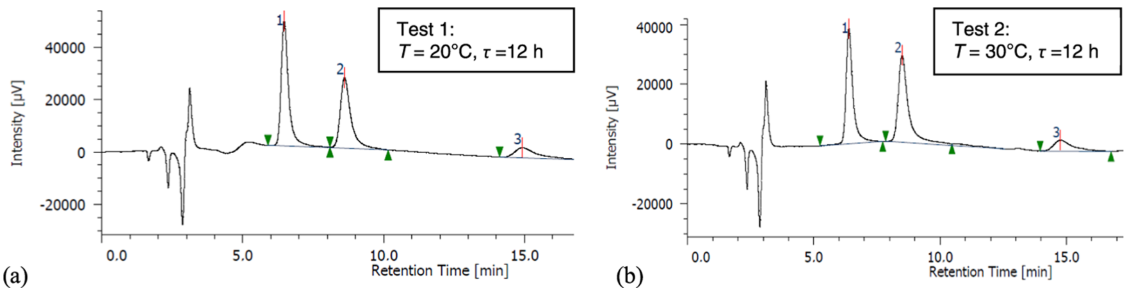


Figure 6. Chromatograms for (a) test 1 and (b) test 2.

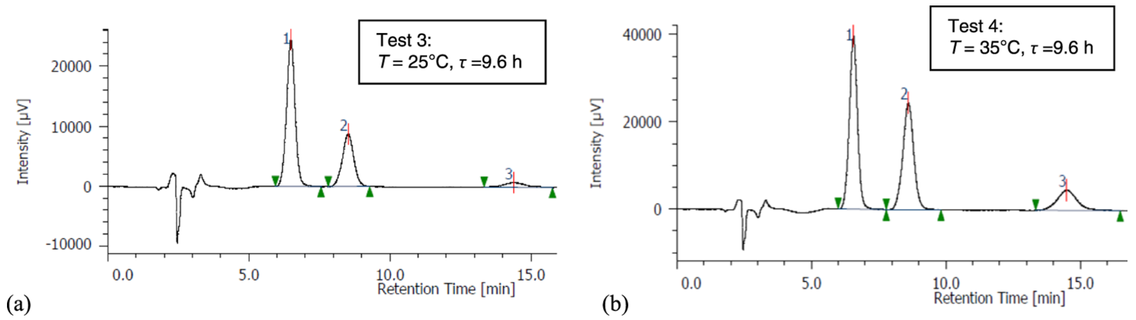


Figure 7. Chromatograms for (a) test 3 and (b) test 4.

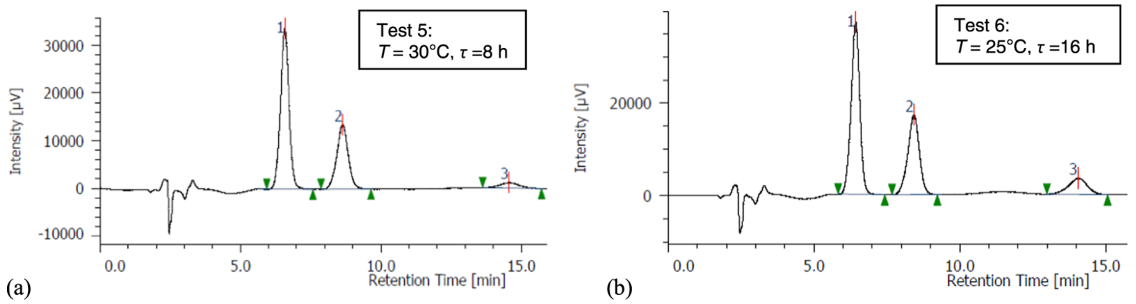


Figure 8. Chromatograms for (a) test 5 and (b) test 6.

Table 6. Operating Conditions Used in the Sample Preparation Phase

test no.	T (°C)	τ (h)
1	20	12
2	30	12
3	25	9.6
4	35	9.6
5	30	8
6	25	16

High-pressure liquid chromatography (HPLC), on the other hand, allows us to quantify the polythionate concentration in a solution.

The standards of sodium tetrathionate dihydrate ($Na_2S_4O_6 \cdot 2H_2O$) and potassium pentathionate sesquihydrate ($K_2S_5O_6 \cdot 1.5H_2O$) were purchased commercially, while potassium hexathionate was synthesized elsewhere[23] with no defined purity, that was determined in the present work. These standards were useful for calibrating the chromatograph and calculating the pure species retention factor.

Once tuned the analytical method, the effect of reaction temperature and residence time and aging phenomenon have been investigated, proving that the HydroClaus reaction operating conditions can significantly affect the nature and distribution of the polythionates produced. The assessment of the effect of the operating conditions on the nature and the distribution of polythionates in a mixture is one of the key aspects for the HydroClaus process scale-up at the industrial level.

6. EXPERIMENTAL SECTION

The experimental apparatus used for tests is reported in Figure 11.

A solution of saturated SO_2 (6 wt %) in water was fed continuously into a stainless steel tank (AISI 316L); its behavior was proved to be a CSTR one, with volume V of 2.4 L, together with the flow rates of gaseous streams of H_2S and N_2 of 2 and 1 N L/h, respectively.

The reactor pressure was fixed at 3 bar, while the reaction temperature was maintained constant by means of a cooling water jacket; the reaction was fairly exothermic. The reacting zone was kept continuously agitated to ensure good mixing. As soon as H_2S was fed into the reactor, it started to diffuse into the liquid mixture so that the liquid phase reaction could occur. The reaction temperature was varied between 20 and 50 °C to verify its effect on product distribution. The residence time in the reactor (τ) depended on the flow rate of the SO_2 aqueous solution. The test was stopped at time $t = 3\tau$ to ensure that the reactor worked in steady-state conditions; after that, the product was collected and stored in specific tanks.

Table 7. Polythionates Concentration for Each Performed Test

test no.	T (°C)	τ (h)	$S_4O_6^{2-}$ (mol/L)	$S_5O_6^{2-}$ (mol/L)	$S_6O_6^{2-}$ (mol/L)	S_{solid} (mol/L)	$\sum S_{polithionates}$ (mol/L)	$\sum S_{polithionates}/S_{solid}$ (mol/mol)
1	20	12	0.1002	0.0617	0	0.2936	0.7093	2.4
2	30	12	0.0830	0.0629	0.0057	0.4241	0.6807	1.6
3	25	9.6	0.0890	0.0300	0.0048	0.2635	0.5348	2.0
4	35	9.6	0.0589	0.0343	0.0107	0.4313	0.4713	1.1
5	30	8	0.0915	0.0358	0.0047	0.3101	0.5732	1.8
6	25	16	0.0680	0.0535	0.0158	0.4357	0.6343	1.5

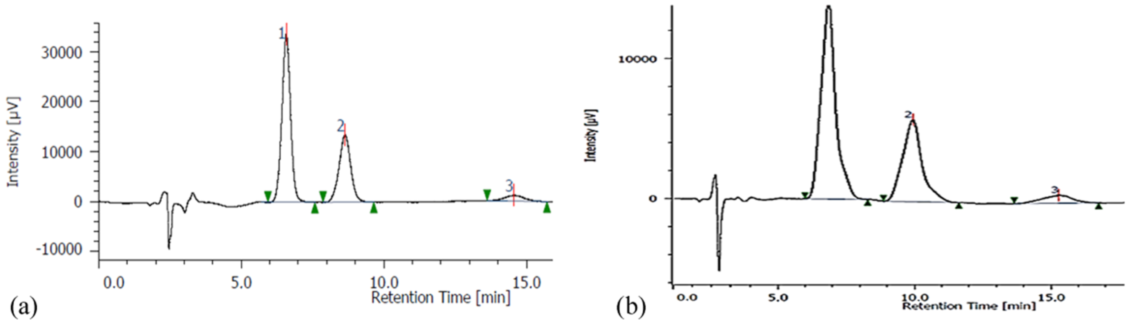


Figure 9. Chromatograms for test 5 performed on (a) fresh sample and (b) aged sample.

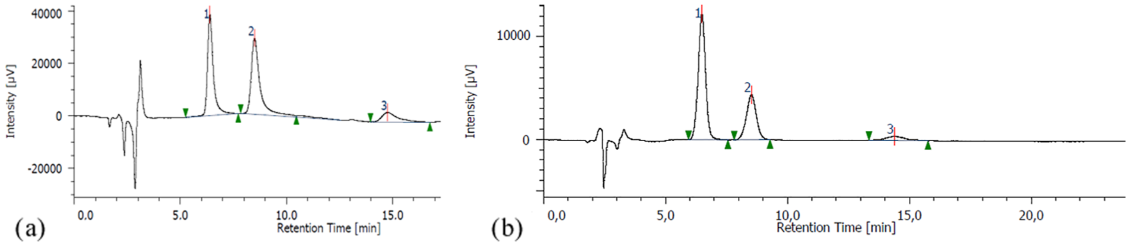


Figure 10. Chromatograms for test 2 performed on (a) fresh sample and (b) aged sample.

Table 8. Polythionates Concentration for Tests 2 and 5 in the Aged Samples

test no.	$S_4O_6^{2-}$ (mol/L)	$S_5O_6^{2-}$ (mol/L)	$S_6O_6^{2-}$ (mol/L)
2	0.0915	0.0410	0.0056
5	0.0916	0.0338	0.0046

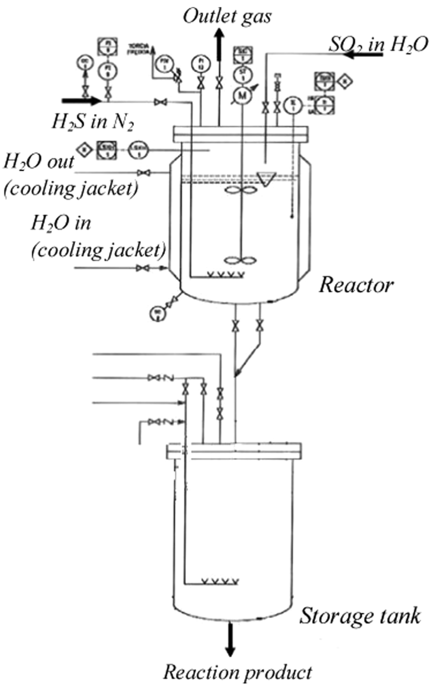


Figure 11. Experimental apparatus for the preparation of the Wackenroder solution (arrows not specified refer to pipeline and instrumentation).

The apparatus used for high-pressure liquid chromatography was a Jasco HPLC system, consisting of a PU-2089 model intelligent solvent delivery pump, an AS-2057 autosampler model with a 10−100 μL injection loop, a computerized system controller, and a MD-2018 UV−vis diode array (200−600 nm) detector. Chromatographic separation was performed using a Hamilton PRP-1 reversed-phase column (150 × 4.1 mm^2, 10 μm particle size, Restek, U.K.) heated at 25 °C. The mobile phase consisted of the TBA·HSO_4 solution (0.006 M)/acetonitrile (64/36 v/v) at pH 5.0 ± 0.1. The mobile phase was eluted at a flow rate of 0.6 mL/min, and the effluent was monitored at 230 nm for 24 min.

The UV−vis analyses were performed with a PerkinElmer 950-S spectrophotometer after filtering with cellulose acetate membranes (0.45 μm pore size) and suitable dilution in Milli-Q H_2O.

Raman spectra were acquired with a MicroRaman HORIBA Evolution equipped with 532 nm laser excitation and calibrated at every use with a pure Silicon specimen ($1/\lambda_{max}$ = 520.7 cm^{-1}).

The laser power was limited to 1 mW to avoid the possible degradation of the sample. The adopted 50× objective yields an illuminated area with a diameter of about 2 μm; therefore, to improve the statistical reliability of the measurement, the acquisition was repeated at 10 × 10 equally spaced points in a 25 × 25 μm^2 area and the average spectrum was calculated.

The standards of the only two commercial polythionates, sodium tetrathionate dihydrate ($Na_2S_4O_6 \cdot 2H_2O$) and potassium pentathionate sesquihydrate ($K_2S_5O_6 \cdot 1.5H_2O$), were purchased from Sigma-Aldrich (Buchs, Switzerland) and Toronto Research Chemicals (North York, Ontario), respectively, and were of analytical grade. The polythionates not available commercially (potassium dithionate, potassium hexathionate, and potassium polythionate mixture, $S_nO_6^{2-}$ with 15 < n < 40) were synthesized elsewhere.[31] The purity of potassium hexathionate was not provided by the supplier. The technique used to determine its composition is discussed in Section 3.2.1.

All of the standard solutions were prepared by dissolving the samples in filtered Milli-Q water. Sulfur α-S_8 was purchased from Sigma-Aldrich, too. Lastly, tetrabutylammonium hydrogensulfate 97% (TBA·H_2SO_4), acetonitrile HPLC grade, and

NaOH 1 M standard solution were purchased from Sigma-Aldrich.

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Notes

The authors declare no competing financial interest.

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