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1	Competitive kinetics study of sulfide oxidation by chlorine using sulfite
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12	Graphical abstract
	Aim of Unknown (CIOH/CIO ⁻) known



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14 Abstract

15 To design and optimize hydrogen sulfide scrubbers working with chlorine, the 16 knowledge of the kinetics of the hydrogen sulfide oxidation is necessary. In this work, the 17 kinetics of the hydrogen sulfide oxidation by sodium hypochlorite was experimentally 18 investigated using a reactor without headspace (100 mL gas-tight syringe) and the 19 competitive kinetics method. The sulfite ion was selected as the reference compound. First, 20 the apparent stoichiometries of sulfite anion and hydrogen sulfide chlorinations were 21 determined performing single-compound experiments. Then, the kinetics of the hydrogen 22 sulfide chlorination was studied in the pH range 6-12 performing simultaneous sulfite and 23 sulfide chlorinations. The results demonstrated that sulfide and sulfite oxidation kinetic rates 24 have the same order of magnitude, which validates the choice of the sulfite anion as the 25 reference compound. Kinetic simulations emphasized that the kinetic rates of the oxidation 26 of both compounds were limited by acid base reactions. The sulfide oxidation in the pH 27 range 6-12 is mainly due to the hydrosulfide (HS-) oxidation by the hypochlorous acid (CIOH) with an associated kinetic constant of 1.2×10^9 L mol⁻¹ s⁻¹ at 25°C. 28

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Keywords: Chlorine, sulfide, sulfite, sodium hypochlorite, kinetics, competitive method

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32 **1. INTRODUCTION**

Hydrogen sulfide (H₂S) is a toxic compound involved in emissions from many industries such as waste water treatment or pulp industry (Gostelow et al., 2001; Kangas et al., 1984; Rappert and Müller, 2005). Several processes are currently used to remove H₂S : biofiltration, absorption in chlorine solution, absorption in alkanolamine solutions, absorption using the Claus process or catalysts to recover elemental sulfur, etc. (Busca and Chiara, 2003; Kohl and Nielsen, 1997).

Chemical scrubbing, which provides high and reliable efficiencies, is widely used for hydrogen sulfide removal. The process involves mass transfer in an aqueous solution using a gas-liquid contactor. At acid pH, H₂S is poorly soluble in water. However, hydrogen sulfide apparent solubility increases with the pH. Indeed, H₂S is a weak diacid which dissociates into hydrosulfide (or bisulfide) HS⁻ (pK_{a,1} = 7.0 at 25°C) and sulfide anions as showed by Eqs (1) and (2) (Roustan, 2003):

45

$$H_2S + H_2O \xrightarrow{k_1} HS^- + H_3O^+ K_{a,1} = k_1/k_{-1}$$
 (1)

$$HS^{-} + H_2 O \xrightarrow{K_2} S^{2^-} + H_3 O^+ \qquad K_{a,2} = k_2 / k_{-2}$$

$$46 \qquad (2)$$

Authors' results diverge about the value of pK_{a,2}, reported from 12 to 17 (Giggenbach, 1971;
Licht et al., 1990; Meyer et al., 1983; Migdisov et al., 2002; Stephens and Cobble, 1971).
However, the most recent articles are all concordant and confirm a value around 17.
Consequently, S²⁻ can be neglected in most aqueous media. Oxidants are often added to
regenerate the scrubbing solution and to enhance mass transfer. The most frequently
oxidants used are chlorine (Biard et al., 2010; Biard et al., 2009; Bonnin, 1991; Cadena and

- 3/3 -

53 Peter, 1988; Chen et al., 2001), ozone (Kerc and Olmez, 2010) and hydrogen peroxide
54 (Couvert et al., 2006; Féliers et al., 2001).

Proving an excellent efficiency at rather low cost, chlorine is widely used for H₂S chemical scrubbing. Chlorine has attracted significant commercial attention for its wide scope in the fields of bleaching, oxidation, and disinfection. Gaseous chlorine (Cl₂) or sodium hypochlorite (NaOCl) are commonly used for chlorination processes (Deborde and Von Gunten, 2008). Due to the complex chlorine chemistry in water, various species may be present in the solution. Indeed, chlorine gas is hydrolyzed into hypochlorous acid (ClOH) according to the following reaction (Eq. 3):

$$Cl_{2} + H_{2}O \xrightarrow{k_{3}} ClOH + Cl^{2} + H^{+} \qquad K_{3} = k_{3}/k_{-3} \qquad (3)$$

$$Wang and Margerum (1994) demonstrated that K_{3} is equal to 5.1 10-4 L2 mol-2 at 25°C and for a negligible ionic strength (Wang and Margerum, 1994). Hypochlorous acid is a weak acid which dissociates in turn into hypochlorite anions (Eq. 4):$$

CIOH + H₂O
$$\xrightarrow{k_4}_{k_{-4}}$$
 CIO⁺ + H₃O⁺ $K_{a,4} = k_4/k_{-4} = K_{a,CIOH}$ (4)
Deborde and Von Gunten (2008) reported a value of the acid dissociation constant Ka₄ of
2.9×10⁻⁸ (pK_{a,4} = 7.54) at 298 K. Consequently, the chlorine speciation depends on several
parameters including the pH, the temperature, the chloride concentration and, with a lower
importance, the ionic strength. Cl₂, CIOH and CIO⁻ are called the free chlorine species. Other
reactive chlorine species can be formed upon various conditions (Cl₃⁻, Cl₂O, etc.) but their
formation are not favored at low chloride concentrations (Doré, 1989). In most chemical
conditions applied in water treatment, Cl₂ is negligible in solution for pH > 6.

CIOH is more electrophilic and usually more reactive than CIO⁻ (Deborde and Von Gunten, 2008). The chlorine reactivity with organic or inorganic compounds depends on the chlorine and target compounds speciation; so a great pH dependence of the apparent kinetic rate constants is expected in many cases. The oxidation reactions usually follow a secondorder kinetic law with partial first-orders for both the free active chlorine concentration and for the total compound concentration (Deborde and Von Gunten, 2008).

80 The oxidation of hydrogen sulfide occurs by a complex mechanism which involves 81 many by-products: colloidal sulfur, sulfites, thiosulfates, or sulfates depending on the pH, the 82 temperature and the advancement of the reaction (Bonnin, 1991; Cadena and Peter, 1988; 83 Choppin and Faulkenberry, 1937). Sulfide (oxidation degree -2) is firstly oxidized into sulfur 84 (degree of oxidation 0) which can be further oxidized into thiosulfate (degree of oxidation 85 +2) sulfite (degree of oxidation +4) and sulfate (degree of oxidation +6) depending on the pH 86 and the residual chlorine concentration (Choppin and Faulkenberry, 1937). Sulfite is directly 87 oxidized in sulfate which requires one equivalent of chlorine for one equivalent of sulfite 88 (Fogelmann et al., 1989). Consequently, at least one equivalent of chlorine is required for 89 the production of sulfur as end-product (Eq. 5) whereas 4 equivalents are necessary for the 90 production of sulfate (Eq. 6):

$$Na_2S + NaOCI + H_2O \longrightarrow S + NaCI + 2 NaOH$$
(5)

$$Na_2S + 4 NaOCI \xrightarrow{\text{complete oxidation}} 4 NaCI + Na_2SO_4$$
(6)

Few studies focus on hydrogen sulfide chlorination due to the high kinetic rates observed, the complex chemistry of these species and the difficulty to analyze sulfur compounds properly. The kinetics of the H₂S oxidation in alkaline solutions has been investigated by Bonnin (1991) through reactive absorption. Using a gas-liquid contactor and

97 an excess of sodium hypochlorite in solution, Bonnin determined an apparent kinetic constant of 1.8×10^8 L mol⁻¹ s⁻¹ between pH 9 and 11 and confirmed that the kinetics is very 98 99 fast. This determination did not take both chlorine and sulfide speciations into account. 100 Moreover, Biard et al. (2010) demonstrated that Bonnin used a wrong assumption when he 101 neglected the gas-phase resistance to simplify the absorption rate. In 2010, considering the 102 results of field chemical scrubbing experiments, Biard et al. assessed that the apparent kinetic constant at alkaline pH below 10.5 could reasonably range between 10⁶ and 10⁹ L 103 mol⁻¹ s⁻¹. Deborde and Von Gunten (2008) proposed a kinetic constant for the specific 104 reaction of HS⁻ with ClOH very close to that of sulfite ions in the range 10^8 - 10^9 L mol⁻¹ s⁻¹. This 105 106 determination was based on the HS⁻ nucleophilicity assuming a chlorine electrophilic attack similar to those previously described for halides or other anionic inorganic compounds (SO₃²⁻ 107 , I⁻, Br⁻, Cl⁻ and CN⁻). The specific kinetic constants of H_2S reactions with ClO⁻ (k = 6.75 10^6 L 108 $mol^{-1} s^{-1}$) and ClOH (k = 1.62 $10^5 L mol^{-1} s^{-1}$) have been studied by reactive absorption in a 109 110 gas-liquid contactor (Vilmain et al., 2014). The surprising larger value found with ClO⁻ was 111 justified by a two steps mechanism (acid base reaction between H₂S and ClO⁻ followed by 112 direct oxidation between CIOH + HS⁻). Therefore, these kinetic constants are apparent and 113 probably overestimate the true values.

To satisfactorily design and understand chemical scrubbers applied to H_2S treatment, a good knowledge of the kinetics and mechanism of oxidation is necessary. Due to the absence of accurate kinetic data, the scrubbers' design is largely based on the feedback from existing plants more than on a precise demonstration. The goal of this study is then to extend the study of Vilmain et al. (2014) through the determination of the kinetic constant between HS⁻ and ClOH/ClO⁻ and to be able to calculate the kinetic rate of hydrogen sulfide chlorination in a rather large pH range at T = 298 K. The competitive kinetics method has

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121 been selected. This method has been successfully applied to determine large kinetic 122 constants, especially in the ozonation field (Beltrán, 2004; Biard et al., 2011; Hoigne and 123 Bader, 1983) and is based on the comparison of the consumptions by free chlorine of the target compounds (H₂S) and a reference compound whose kinetic constant is known. The 124 sulfite anion $SO_3^{2^-}$ was selected as the reference compound since its kinetic rate should be 125 126 close to sulfide kinetic rate in a rather large pH range considering that their nucleophilicities 127 (i.e. their kinetic constants) are similar (Deborde and Von Gunten, 2008). Moreover, the 128 sulfite oxidation mechanism is very simple since 1 equivalent of chlorine is consumed to 129 oxidize directly 1 equivalent of sulfite into sulfate and its oxidation kinetics has been deeply 130 investigated at T = 298 K (Fogelman et al., 1989).

131

2. MATERIALS AND METHODS 131

132 2.1. Experimental method

The competitive kinetics method was applied to determine the H₂S chlorination 133 kinetics using the sulfite anion $SO_3^{2^2}$ as the reference compound. The chlorination of both 134 pure compounds (sulfite and sulfide) was carried out previously to find out the apparent 135 136 stoichiometries for each compound depending on the initial concentrations. Both 137 chlorinations were performed in a 100 mL gas-tight syringe (Hamilton) whose needle was 138 replaced by a septum allowing to quickly withdraw and inject samples. A stir bar was placed 139 in the syringe for the subsequent mixing. As mentioned by Biard et al. (2011), this kind of reactor is headspace free to avoid H₂S volatilization as well as oxygen dissolution which can 140 consume sulfite anions. Moreover, its volume varies when sampling due to the plunger 141 142 course which enables to keep a constant pressure inside the reactor.

143

- 144
- 145

Fig. 1: Presentation of the experimental method.

A schematic representation of the protocol is illustrated in Fig. 1. All solutions were 146

147 prepared using Ultra Pure Water (UPW) prepared by reverse osmosis using an Elga lab purification unit (resistivity > 18 M Ω cm). UPW was deoxygenated by N₂ (99,999% with 148 maximum 2 ppmv of residual O₂, provided by Air Liquide) bubbling. To avoid SO₃²⁻ oxidation 149 150 by O₂, the sulfite solution was prepared directly in the reactor by adding sodium sulfite. Then 100 mL of UPW was added to dissolve it. 90 mL of this solution were drained to keep only 10 151 152 mL. Then, 3mL of a sulfide solution, a buffer solution and UPW until 98.4 mL were added 153 with gas-tight glass syringes (SGE, Australia). Reaction solutions were buffered for experiments at pH 6, 7, 7.5 and 8. For pHs 9-12, the initial pH was set by adding NaOH. The 154

syringe was held horizontally in a thermostatic bath regulated at 25 °C ± 0.2. After 20 min, 1
mL of chlorine solution was injected in the reactor using a gas-tight syringe (from SGE). Then,
after 2 min of stirring (assuming oxidation is achieved) and complete chlorine consumption,
0.6 mL of ethanol (99% purity) was injected in the reactor to stabilize the sulfite ions in the
aqueous solution before analyses (de Carvalho and Schwedt, 2000).

We note that sulfite and sulfide can react together to form thiosulfate. This reaction
is slow and does not happen during the short time between the mixture preparation and the
chlorine injection.

163

2.2. Analytical methods

164 The pH was controlled directly after each experiment by a pH-meter type Eutech 165 Instruments Cyberscan 510 (\pm 0.01 pH unit tolerance) equipped with a Fisher Scientific probe. 166 The pH variation due to chlorine addition was found negligible in all cases. The sulfite anions 167 were analyzed using ion chromatography (§ 2.2.2). Since HS⁻ and SO₃²⁻ have the same 168 retention time, H₂S was previously stripped from a sample of the solution set at neutral pH 169 by N₂ bubbling.

170 2.2.1. Hydrogen sulfide analysis

The methylene blue spectrophotometric method has been evaluated and recommended by various researchers for sulfide quantification (Fogo and Popowsky, 1949; Reese et al., 2011). N,N-Dimethyl-1,4-phenylenediamine (DMPD) reacts with hydrogen sulfide to form a compound which changes into blue leucomethylene. This compound, oxidized under acidic conditions in the presence of an oxidant (usually Fe(III)), forms methylene blue. This method was used in combination with the standard addition method for a higher accuracy of H₂S measurement. The limit of quantification and detection are

approximately 0.3 ppm and 0.1 ppm. Statistic methods validated the repeatability,reproducibility and the reliability of the method.

180 2.2.2. Determination of the sulfite and sulfate anions' concentrations by ionic
 181 chromatography

Dionex-DX 120 Ion Chromatography, equipped with IonPac[®] AG 18 (4 mm × 50 mm) 182 guard column and AS18 analytical column (4mm \times 250 mm), was used for SO₃²⁻ 183 quantification. Filtered samples (syringe filter with prefilter Minisart from Sartorius, 184 membrane: cellulose acetate; threshold: 0.45 µm) were injected (250 µL samples). KOH 185 eluent (flow rate of 1.06 mL min⁻¹) was degassed by vacuum and produced electrochemically 186 in-line. Ramped eluent concentration was used with 10 mmol L⁻¹ (0-10 min), 10-45 mmol L⁻¹ 187 (10-25 min) and 45 mmol L⁻¹ (25-35 min). Data acquisition was performed by Chromeleon 188 software. The resolution between sulfate and sulfite peaks was equal to 1.6. 189

190 Sulfite is easily oxidizable and is particularly unstable in the presence of oxygen. This oxidation was prevented before the reaction step by preparing the sulfite solution in the 100 191 192 mL syringe with deoxygenated water. Only a small amount of O_2 can dissolve in the solution 193 during the sample preparation prior to ionic chromatography. Therefore, ethanol was 194 selected to stabilize the sulfite anions immediately after the reaction (de Carvalho and Schwedt, 2000). Using non-deoxygenated UPW, the sulfite anion concentration decreases 195 196 quickly (38.0% of recovery after 350 min) whereas using deoxygenated UPW in the syringe enabled this phenomenon to be limited. An ethanol concentration of 0.1 mol L⁻¹ is necessary 197 to achieve a negligible sulfite consumption (99.4% of recovery after 350 min). 198

199

- 10/10 -

199 200

2.2.3. Chlorine analysis

201 Chlorine was measured after sampling using the iodometric method. 5 mL of glacial 202 acetic acid and 1 g of potassium iodide was added to the sample. Thereafter, the sample was 203 titrated with 0.1 M or 0.001 M sodium thiosulfate (Normadose[®] VWR).

204 **2.3. Reagents**

205 All chemical products had an analytical grade. Sodium sulfide nonahydrate, sodium 206 sulfite, sodium thiosulfate, sodium hypochlorite, potassium hydrogen phtalate, potassium 207 sulfate, acetic acid, absolute ethanol and acetone were purchased from Acros Organics 208 (Belgium). Sodium hydroxide was purchased from Fischer Scientific, potassium iodate from 209 Labogros, potassium dihydrogen phosphate from Panreac Quimica, and tris-210 (hydroxymethyl)aminomethane from Merck. Hydrochloric acid was obtained from Prolabo. 211 Hydrochloric acid (0.01, 0.1, 1 M) was prepared using Analar Normapur[®] solutions. The 212 hydrogen sulfide solutions were prepared daily by serial dilutions.

Buffer solutions were prepared by dissolving appropriate amounts of three chemical products in Ultra Pure Water: potassium hydrogen phthalate, potassium dihydrogen phosphate and (hydroxymethyl)aminomethane completed with HCl or NaOH.

216

216 **3. RESULTS AND DISCUSSION**

217**3.1.** Chlorination of the pure compounds: determination of the apparent218stoichiometries219The apparent stoichiometric coefficients,
$$\delta$$
 and γ , of the reactions between sulfite220and sulfide anions with chlorine at 25°C were determined through the chlorination of each221pure compound:222Na₂S+ δ NaOCl \longrightarrow products223Na₂SO₃+ γ NaOCl \longrightarrow products224 δ and γ were calculated from the Na₂S and NaOCl consumptions by chlorine:225 $\delta = \frac{[NaOCl]_{t=0} - [NaOCl]_{finot}}{[Na_2S]_{t=0} - [Na_2S]_{finot}}$ 226 $\gamma = \frac{[NaOCl]_{t=0} - [NaOCl]_{finot}}{[Na_2SO_3]_{t=0} - [Na_2SO_3]_{finot}}$ 227 δ and γ were determined for different pH and different ratio of the initial228reagents' concentrations, Ra_{sulfide} and Ra_{sulfite}, defined as:229 $Ra_{sulfide} = \frac{[Na_2S]_{1=0}}{[NaOCl]_{t=0}}$ 230 $Ra_{sulfide} = \frac{[Na_2SO_3]_{1=0}}{[NaOCL]_{t=0}}$ 241(12)

In the one hand, in excess of oxidant (low Ra_{sulfide}), the oxidation was almost complete and around 4 equivalents of chlorine were consumed for 1 equivalent of sulfide whatever the pH in agreement with the reaction 5 (Fig. 2). Sulfate was the end-product of

234 the oxidation (Choppin and Faulkenberry, 1937) which was confirmed by the detection of 235 sulfate anions by ionic chromatography. In the other hand, when sulfide was in sufficient excess ($Ra_{sulfide} > 3$), the oxidation was restricted to the parent compound. One equivalent of 236 237 chlorine was consumed for one equivalent of sulfide ($\delta = 1$) improving the selectivity of the 238 reaction. Indeed, in this case, the end-product should be only sulfur which is in agreement 239 with the literature (Choppin and Faulkenberry, 1937). Moreover, no sulfite and sulfate anions were detected by ionic chromatography. Consequently, to ensure no sulfite anions 240 241 produced during sulfide anion oxidation and no interaction during mixture experiments, 242 Ra_{sulfide} must be larger than approximately 3. The pH seems to have a slight effect only when 243 the initial chlorine concentration was larger than the sulfide anion concentration.

Otherwise, since sulfite anions is directly oxidized into sulfate anions, which cannot be further oxidized by chlorine (Fogelmann et al., 1989), one equivalent of chlorine was consumed for one equivalent of sulfite ($\gamma = 1$), whatever the value of $Ra_{sulfite}$ applied (Fig. 2). The rather large dispersion of the points around 1 is due to the quite low sulfite anion analytical methods precision (sulfite instability in solution). This low precision has no influence in the competitive kinetics method results analysis (section 3.2).

250

Fig. 2: Evolution of δ and γ vs. respectively $Ra_{sulfide}$ and $Ra_{sulfite}$

3.2 Chlorination of sulfide/sulfite anion mixtures: determination of the relative
 apparent kinetic constant

253 Chlorination of the sulfide/sulfite mixture was performed between pH 6 and 12. Each 254 experiment was triplicated with $Ra_{sulfite} \approx 1.5$ and $Ra_{sulfide} \approx 2.7$. These ratios were optimal to 255 accurately measure the sulfite and sulfide consumptions and to optimize the sulfide 256 oxidation selectivity. Chlorine was the limiting reagent and was not detected at the end of 257 each experiment.

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258 Since the consumptions of the three species were measured, the mass balance could 259 be checked. According to Eqs 9 and 10:

260
$$[NaOCI]_{t=0} - [NaOCI]_{final} = \delta ([Na_2S]_{t=0} - [Na_2S]_{final}) + \gamma ([Na_2SO_3]_{t=0} - [Na_2SO_3]_{final})$$
(13)

261

Figure 3: Sulfite and sulfide consumptions (
$$\Delta$$
[i]) during competitive kinetics trials

262

The oxidation removal efficiencies of sulfite and sulfide were in the range 10-25% and were significantly measurable. Figure 3 presents a histogram of the average consumed concentrations ($\Delta[i]$) of hydrogen sulfide and sulfite for each pH studied. The mass balance was well respected by taking γ and δ = 1, except at pH 10 at which a lower sulfide and/or sulfite consumption was measured.

Assuming that partial orders are equal to 1 (Deborde and von Gunten, 2008), the ratio of the kinetic constants $k_{relative}$, can be written as (Beltrán, 2004; Biard et al., 2011):

$$270 k_{relative,1} = \frac{k_{app}^{sulfide}}{k_{app}^{sulfite}} = \frac{\delta}{\gamma} \times \left(\frac{Ln \frac{[Na_2S]_{t=0}}{[Na_2S]_{final}}}{Ln \frac{[Na_2SO_3]_{t=0}}{[Na_2SO_3]_{final}}} \right)$$
(14)

Equation 14 can be used by knowing just the concentrations of the two target compounds (*i.e* the initial oxidant concentration is not required). In this study, the oxidant concentration was also measured, enabling to calculate $k_{relative}$ by two additional equations deduced from the mass balance equation (Biard et al., 2011):

275
$$k_{relative,2} = \frac{k_{app}^{sulfide}}{k_{app}^{sulfite}} = \frac{\delta}{\gamma} \times \left(\frac{Ln \frac{[Na_2S]_{t=0}}{[Na_2S]_{final}}}{Ln \frac{[Na_2SO_3]_{t=0}}{[Na_2SO_3]_{t=0} - [NaOCI]_{t=0} + [Na_2S]_{t=0} - [Na_2S]_{final}}} \right)$$
(15)

276
$$k_{relative,3} = \frac{k_{app}^{sulfide}}{k_{app}^{sulfide}} = \frac{\delta}{\gamma} \times \left(\frac{Ln \frac{[Na_2S]_{t=0}}{[Na_2S]_{t=0} - [NaOCI]_{t=0} + [Na_2SO_3]_{t=0} - [Na_2SO_3]_{final}}}{Ln \frac{[Na_2SO_3]_{t=0}}{[Na_2SO_3]_{t=0}}} \right)$$
(16)

k_{relative} obtained with the three methods and the average value at constant 277 temperature (25±0.2 °C) is shown in Fig. 4. Except at pH = 10, the values of $k_{relative}$ found 278 279 were close whatever the equation used since the mass balance was well respected. At pH = 280 10, a stronger dispersion was observed but the average value was consistent with the value obtained by Eq. 14 like the other values of pH. Consequently, the average value of $k_{relative}$ is 281 282 reliable. Depending on the pH, k_{relative} is in the range 1-2 confirming that sulfite and sulfide 283 oxidation kinetic rate are close, even at pH close to the neutrality, at which acidic species 284 (H₂S, HSO₃⁻) are present and can bias this observation. Indeed, according to Deborde and Von Gunten (2008), HS⁻ and SO₃²⁻ oxidation kinetic rates are expected to be similar but no 285 286 data are available for H₂S and HSO₃⁻ ones. The trend of Fig. 4 remains complicated to justify 287 since many chemical reactions are *a priori* involved. The next section focuses on sulfite 288 oxidation kinetic rate analysis prior to sulfide kinetic rate determination.

289 Figure 4: Effect of pH on the $k_{relative}$ values determined with equations 14-16 and the average value of 290 $k_{relative}$. The error bars represent the standard deviations

291 **3.3 Sulfite oxidation kinetics**

The sulfite anion is a basic species in equilibrium with the hydrogen sulfite (HSO_3^{-}) . The apparent pK_a value is included in the range 6.91-7.2 at 298 K, depending on the hydrogen sulfite concentration since HSO_3^{-} exists in two tautomeric forms (Rhee and Dasgupta, 1985). At low sulfite concentration (< 10^{-4} L mol⁻¹ s⁻¹), pK_{a,5} = 6.91. H₂SO₃ (H₂O + SO₂) is present only at very acidic pH and is neglected in this discussion. The oxidation mechanism of the sulfite anion with chlorine involves *a priori* several acid-base (Reactions 17

298 to 21) and oxidation reactions (Reactions 22 to 24) synthesized Table 1. The potential 299 reaction between ClO⁻ and HSO₃⁻ has not been considered since it involves a weak base and 300 a weak acid whose coexistence in solution is unlikely. Moreover, the kinetic rate of this reaction should be low since CIO⁻ and HSO₃⁻ are respectively poorer electrophile and 301 nucleophile than ClOH and SO_3^{2-} (Fogelman et al., 1989). Fogelman et al. determined the 302 303 kinetic constants of reactions 22 and 23 using the stopped-flow method at 298 K (Fogelman et al., 1989). Even if hypochlorous acid (CIOH) does not predominate at pH > 7.54, since k_{23} 304 >> k_{22} , sulfite anion is more oxidized by CIOH than CIO⁻ for pH < 12-12.1. Their study was 305 306 conducted at pH > 9.5, at which reaction 24 which involves two acids is unexpected and 307 unfortunately k₂₄ is unknown. For the rest of the discussion, this reaction was neglected since HSO_3^- should be less reactive than SO_3^{2-} and the study was mainly conducted in the pH 308 range (> 6.91-7.2) at which SO_3^{2-} is predominant. This assumption will be confirmed in the 309 section 3.2.5. Kinetic constants of bimolecular proton transfer reactions (Eqs 17 to 21) are 310 311 not precisely known. According to Eigen (1964), the orders of magnitude of the kinetic constants for recombination of a base with H^{+} (reverse reactions 18 and 20) and of an acid 312 with HO⁻ (Reactions 17 and 19) are respectively typically 10^{10} - 10^{11} and 10^{9} - 10^{11} L mol⁻¹ s⁻¹ 313 314 (Eigen, 1964). The ratio of them for a given acid/base couple is between 2 and 3 in many cases. Fogelman et al. used with a good agreement a value of $k_{17} = 3 \times 10^9$ L mol⁻¹ s⁻¹ in their 315 316 simulations (Fogelman et al., 1989). Taking this into consideration, k₁₇, k₋₁₈, k₁₉ and k₋₂₀ are 317 respectively set to the values presented in Table 1. The rather large value of k₋₂₀ has been chosen equal to k_{30} by analogy (H₂S dissociation, Table 5). Considering that $pK_{a,4}$ - $pK_{a,5} \approx 0.5$, 318 k_{21} can be set to 3×10^8 L mol⁻¹ s⁻¹ according to Eigen (1964). 319

In a batch reactor, at constant temperature and volume, the kinetic law of totalsulfite consumption can be written:

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$$\frac{d\left[SO_{3}^{2^{-}}\right]_{T}}{dt} = -\frac{d\left[SO_{3}^{2^{-}}\right]}{dt} - \frac{d\left[HSO_{3}^{-}\right]}{dt} = -\frac{d\left[CIO^{-}\right]}{dt} - \frac{d\left[CIOH\right]}{dt}$$
(25)

$$-\frac{d\left[SO_{3}^{2^{-}}\right]_{T}}{dt} = k_{22}\left[SO_{3}^{2^{-}}\right]\left[CIO^{-}\right] + k_{23}\left[SO_{3}^{2^{-}}\right]\left[CIOH\right]$$
(26)

The kinetic rate of this reaction was expected to decrease with the pH since the hypochlorous acid concentration decreased. The temptation is high to consider that both acid/base couples are in equilibrium to introduce the total sulfite and hypochlorite concentrations and the pK_a values:

$$\frac{d\left[SO_{3}^{2^{-}}\right]_{T}}{dt} = k_{app,cal}^{sulfite} \times \left[SO_{3}^{2^{-}}\right]_{T} \left[ClO^{-}\right]_{T}$$

$$\text{with } k_{app,cal}^{sulfite} = \frac{k_{22}}{\left(1+10^{pK_{a,5}-pH}\right)\left(1+10^{pK_{a,5}-pH}\right)} + \frac{k_{23}}{\left(1+10^{pH-pK_{a,4}}\right)\left(1+10^{pK_{a,5}-pH}\right)}$$

$$(27)$$

With this assumption, at a constant pH, the kinetics is second-order with a calculated apparent kinetic constant $k_{app,cal}^{sulfite}$ (whose evolution versus the pH is represented in Fig. 5). The subscripts "cal" means that k_{app} has been calculated through Eq 27. Then, the chlorine and the sulfite concentration-time profiles can be determined by Eq. 28, which is the classical solution of the differential equation for a second-order kinetics in a batch reactor:

334
$$T = k_{app}^{sulfite} \times t \text{ with } T = \frac{1}{\left[ClO^{-}\right]_{T,0} - \left[SO_{3}^{2^{-}}\right]_{T,0}} \ln \left[\frac{\left[SO_{3}^{2^{-}}\right]_{T,0}\left[ClO^{-}\right]_{T}}{\left[SO_{3}^{2^{-}}\right]_{T}\left[ClO^{-}\right]_{T,0}}\right]$$
(28)

Table 1

335

Fig. 5: Effect of pH on $k_{app,cal}$ for sulfite and sulfide oxidations. $k_{app,cal}$ was calculated with Eq. 27 and 38 whereas $k_{app,sim}$ was calculated through the numerical simulations (using the conditions of Table 2). The blue and green areas delimit zones where k_{app} for respectively sulfite and sulfide should be located for a wide range of experimental conditions.

340 Equation 27 implies that proton transfer reactions (reactions 17 to 21) are 341 instantaneous compared to oxidation reactions to maintain sulfite and chlorine species 342 equilibrium over all times. This assumption can be controversial, especially at pH close to the 343 neutrality, where the kinetic rate is maximal. To assess it, the concentration-time profile of 344 each species involved in reactions 17 to 23 has been determined using the software COPASI 345 developed by the Virginia Bioinformatics Institute (USA) and the universities of Heidelberg 346 (Germany) and Manchester (UK). This open-source software is dedicated to the numerical resolution of differential equations systems found in biological and chemical kinetics. 347 348 Examples of concentration-time and reaction rate-time profiles returned by COPASI are 349 presented in appendix. An analytical solution is not possible, especially since steady-state 350 approximations (Bodenstein) are not possible. HO^{-} and H^{+} concentrations have been fixed to 351 their initial values since a buffer is added to maintain a constant pH (except at pH \ge 9 at 352 which it is not necessary). Different operating conditions (pH, total sulfite and chlorine 353 concentrations) have been applied to assess their influence. For each simulation, the time 354 course is discretized into 500 intervals until a degree of advancement of 90% is reached (t_{90}) 355 is the corresponding time). The term T (Eq. 28) can be calculated during the data post 356 processing. Then a linear regression model using the time series data is applied (using the "Linest" function of Excel[®]) : 357

to check if the kinetic rate is second-order (using appropriated statistic criteria such as
 the determination coefficient R² and the F-test value);

• if so, to determine the apparent 2^{nd} order kinetic constants (called $k_{app,sim}$) from the slope;

362 • to compare $k_{app,sim}$ and $k_{app,cal}$.

- 18/18 -

363 Tables 2, 3 and 4 synthesize the results to assess respectively the influence of the pH 364 (at the chlorine and sulfite initial concentrations used in the section 3.2.2), the order of magnitude of the initial concentrations and the initial concentrations ratio (Tables 3 and 4 365 366 simulations were performed at pH 8 since it is the pH which presents the largest discrepancy 367 between $k_{app,cal}$ and $k_{app,sim}$). Except for a few limited cases (Simulations #11 and #15), the 368 reaction was predicted to follow second-order kinetics. At pH lower than 10, $k_{app.sim}$ was always lower than $k_{app,cal.}$ (Table 2), which emphasizes that the kinetic rate was limited by 369 proton transfer reactions. Fig A.2 clearly highlights that the CIOH consumption rate by 370 371 reaction 23 was larger than its reformation rate due to reactions 17, 18 and 21. Even if CIOH 372 and CIO⁻ were in equilibrium at the beginning of the simulation, the ratio [CIOH]/[CIO⁻] 373 decreased with time whereas the pH stayed constant. Consequently, using Eq. 27 can lead to 374 severe overestimations of the kinetic rate and by the way bias the results of the competitive 375 study. For example, with the initial conditions of simulation #4, the time necessary to 376 achieve a degree of advancement of 90 % using $k_{app,cal}$ was 0.46 ms, whereas the time 377 simulated was 0.98 ms. This observation is particularly true for pH ranging between 7 and 9 378 where the kinetic rate is maximal. When the pH exceeds 10, the oxidation kinetic rate 379 decreased and the CIOH consumption was more easily compensated, which enabled to maintain more easily the species equilibrium. In this case, the apparent kinetic constant 380 381 calculated by Equation 27 was exact and the reaction time necessary to consume 90% of the 382 limiting reagent (chlorine) increased beyond 1 s.

Even if the kinetic rate of the reaction increases with the initial concentrations (t₉₀ decreases), the value of $k_{app,sim}$ decreases (Table 3). Indeed, with larger initial concentrations, the HSO₃^{-/}SO₃²⁻ equilibrium is more difficult to maintain since the kinetic rate is larger. By the way, $k_{app,sim}$ tends towards $k_{app,cal}$ when the initial concentration decreases. When sulfite

- 19/19 -

387	is the limiting reagent (simulation #13), sulfite equilibrium is more difficult to maintain. The
388	apparent kinetic constant is rather poorly influenced by the initial concentrations ratio
389	(Table 4) except when chlorine is added in great excess. In this case, the kinetic rate is
390	pseudo first-order, the chlorine species stay obviously at the equilibrium and the simulated
391	apparent kinetic constant tends towards the calculated one.
392	Table 2
393	Table 3
394	Table 4

395 3.4 Sulfide oxidation kinetics 396 Table 5 397 As for the sulfite anions, the sulfide oxidation (Table 5) a priori involves several acidbase reactions (17, 18 and 29 to 31) and pure oxidation reactions (32 to 34). Only the first 398 oxidation step which leads to elemental sulfur was considered since the initial 399 concentrations ratio (Ra_{sulfide}) was carefully selected. Moreover, in the pH range studied (6-400 12), S²⁻ can be neglected. Based on these assumptions, the kinetic law of total sulfide 401 402 consumption can be written: $-\frac{d[H_2S]_{\tau}}{dt} = -\frac{d[H_2S]}{dt} - \frac{d[HS^-]}{dt} = -\frac{d[CIO^-]}{dt} - \frac{d[CIOH]}{dt}$ 403 (36) $-\frac{d[H_2S]_{T}}{dt} = k_{32}[H_2S][CIO^-] + k_{33}[H_2S][CIOH] + k_{34}[HS^-][CIO^-] + k_{35}[HS^-][CIOH]$ 404 (37) 405 If chlorine and sulfide species are in equilibrium with their respective conjugated 406 species, then: $-\frac{\mathsf{d} \left[H_2 S\right]_{\tau}}{\mathsf{d} t} = k_{app,cal}^{sulfide} \times \left[H_2 S\right]_{\tau} \left[ClO^{-}\right]_{\tau}$ With $k_{app,col}^{sulfide} = \frac{k_{32}}{(1+10^{pK_{o,A}-pH})(1+10^{pH-pK_{o,1}})} + \frac{k_{33}}{(1+10^{pH-pK_{o,A}})(1+10^{pH-pK_{o,A}})}$ 407 (38) $+\frac{k_{34}}{(1+10^{pH-pK_{o,4}})(1+10^{pH-pK_{o,1}})}+\frac{k_{35}}{(1+10^{pH-pK_{o,4}})(1+10^{pK_{o,1}-pH})}$ 408 For the sulfite oxidation, $k_{app,cal}$ and $k_{app,sim}$ are equal only for pH 11 and 12 (Table 2). 409 Consequently, $k_{relative}$ should be used to study the sulfide oxidation only at these pH. $k_{app,exp}$ for the sulfide oxidation can be extrapolated from $k_{relative}$ (Eqs 14-16) and $k_{app,cal}^{sulfite}$ (Eq. 27): 410

411
$$k_{app,exp}^{sulfide} = k_{relative} \times k_{app,cal}^{sulfite}$$
(39)

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412 At these pHs, it is quite obvious that reactions 32 and 34 are unlikely. Then, k₃₃ and 413 k₃₅ can be determined by numerical resolution trying to minimize the following least square 414 objective function:

415
$$\operatorname{Min}(F_{i} \text{ at pH} = 11 + F_{i} \text{ at pH} = 12) \operatorname{With} F_{i} = \left(\frac{k_{app,cal}^{sulfide} - k_{app,exp}^{sulfide}}{k_{app,exp}^{sulfide}}\right)^{2}$$
(40)

An excellent agreement is obtained with $k_{35} = 1.2 \times 10^9$ L mol⁻¹ s⁻¹ when the value of k₃₃ can be set between 0 and 10⁴ L mol⁻¹ s⁻¹ with a very restricted influence (Table 6). In Table 6, R₃₃ represents the following ratio:

419
$$R_{33} = \frac{k_{33}}{(1+10^{\rho H - \rho K_{o,1}})(1+10^{\rho H - \rho K_{o,1}})} / k_{app,cal}^{sulfide}$$
(41)

420 It confirms the order of magnitude proposed by Deborde and von Gunten (2008) but 421 invalidated, as expected, the value determined by Bonnin (1991). The very weak sensitivity 422 of the model to k_{33} emphasizes that reaction 33 (sulfide oxidation by hypochlorite anion) is 423 unlikely or very limited, at least at pH \leq 12, even if the ClOH concentration is low at basic pH. 424 Consequently, the value of k_{33} cannot be determined with a sufficient confidence degree. It 425 justifies why $k_{relative}$ is larger than 1 at pH 11 but lower than 1 at pH 12. Indeed, at pH 12, 426 sulfite is oxidized simultaneously by ClO- and ClOH.

Using the same methodology than for sulfite (section 3.2.3), it is possible to determine $k_{app,sim}$ for sulfide and to try to compare it to $k_{app,cal}$ (Table 7 and Fig. 5). The same main conclusions apply for both compounds. The sulfide oxidation is limited by acid-base reactions (17, 18, 29-31) at pH lower than 10, especially when pH ranges between 6 and 9. Therefore, it confirms that it was pertinent to use only the results obtained at pH 11 and 12 to determine k_{35} by numerical resolution. The simulation at pH 6 (simulation #16) demonstrates that reactions 32 and 34 can be neglected whatever the pH. Indeed, the

434 reaction rate of reaction 32 does not exceed 2% of the reaction rate of reaction 35 (obtained

435 through simulations) when reaction 34 is absolutely negligible.

436 Table 6 437 Table 7

438 **3.5 Discussion**

↓^{sulfide}

439 k_{35} was calculated using $k_{relative}$ at pH 11 and 12. When the pH ranges between 6 and 440 11, the experimental value of $k_{relative}$ follows a very special trends. Using the values of $k_{app,cal}$ 441 (Eqs 27 and 38) and $k_{app,sim}$ (Tables 2 and 7), $k_{relative}$ can be recalculated twice and compared 442 to the experimental value ($k_{relative,exp}$):

$$k_{relative,cal} = \frac{k_{app,cal}^{sulfide}}{k_{app,cal}^{sulfite}}$$
(42)

$$k_{relative,sim} = \frac{\kappa_{app,sim}}{k_{app,sim}^{sulfite}}$$
(43)

445

446 Figure 6: Comparison between the experimental k_{relative} values and the calculated and simulated ones. 447 On the one hand, the value of $k_{relative,cal}$ is totally in disagreement with $k_{relative,exp}$ (Fig. 448 6). This results was expected since $k_{app,cal}$ is determined assuming that acid-base species 449 stays at the equilibrium, which is not valid at pH lower than 10. On the other hand, the value 450 of $k_{relative.sim}$ follows the same trend than $k_{relative}$ at basic pH which is probably not a 451 coincidence. The agreement remains imperfect but one has to consider that $k_{relative}$ suffers 452 from experimental uncertainties whereas $k_{app,sim}$ is calculated with estimated values of the 453 kinetic constants of numerous acid-base reactions. Moreover, there is a potential uncertainty concerning pK_{a,5}. 454

455

456

Table 8

457 Before going further, several questions need to be discussed and assumptions have 458 to be confirmed:

459 $k_{relative,sim}$ and $k_{relative,exp}$ present an interesting correlation. However, the values of $k_{app,sim}$ are determined with estimated values of the different acid-base reactions (17-21) 460 and 29-31). What is the sensitivity of the values of $k_{app,sim}$ to these estimated kinetic 461 constants? To answer to this question, $k_{app,sim}$ for sulfite and sulfide have been 462 recalculated at pH 6 with underestimated and overestimated values of the kinetic 463 constants (Table 8). On the one hand, the results demonstrate that $k_{app,sim}$ is not so 464 465 sensitive to theses values (especially for sulfide). At least, it does not change the conclusions of the numerical resolutions. The most influential kinetic constants are those 466 467 of reactions 21 and 31. On the other hand, the influence on k_{relative,sim} is rather important $(k_{relative.sim} = 1.81 \text{ and } 1.26 \text{ respectively using simulations } 24+26 \text{ and } 25+27)$ and can justify 468 the disagreement observed at this pH between $k_{relative,exp}$ and $k_{relative,sim}$. 469

The potential reactions between CIOH and CIO^{-} and S^{2-} were neglected; this hypothesis 470 required to be discussed more deeply. A possible influence of these two reactions is 471 expected only at very basic pH. Concerning the reaction between CIOH and S²⁻, their 472 respective predominance domains are far apart. By the way, assuming a probably 473 overestimated kinetic constant of 5×10^9 L mol⁻¹ s⁻¹, $k_{ann cal}$ at pH 12 goes from 4.2 10^{-4} to 474 4.4 10^{-4} L mol⁻¹ s⁻¹ which confirms that this reaction can be neglected at pH lower than 12. 475 The potential reaction between S²⁻ and ClO⁻ involves species whose coexistence domains 476 477 are concomitant. However, it would imply a collision between two weak bases whose one 478 of them carries two negative charges and consequently which requires exceeding an important electrostatic repulsion force. With a probably overestimated value of the 479 kinetic constants of 5 10⁵ L mol⁻¹ s⁻¹ (maximal order of magnitude encountered between 480

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481	CIO ⁻ and any species), $k_{app,cal}$ goes from 4.2 10 ⁴ to 5.0 10 ⁴ L mol ⁻¹ s ⁻¹ at pH 12. It confirms
482	that the reaction between ClO^{-} and S^{2-} is unlikely at least at pH lower than 12. Moreover,
483	a low pK_a has been considered in this calculation (13.78 according to Stephens and Cobble
484	(1971)) even if the most recent studies seem to confirm that this value is up to 17 at 298K
485	(Migdisov et al., 2002).
486 •	Reaction 24 was neglected between pH=6 and pH=12. This assumption must be
487	demonstrated. It involves two weak acids with compatible predominance domains.
488	Simulation #1 (pH=6) performed with this additional reaction provides the following
489	results:
490	✓
491	f k = 10^7 L mol ⁻¹ s ⁻¹ , the kinetic rate due to this reaction remains lower than 10%
492	compared to the kinetic rate of the reaction between CIOH and SO_3^{2-} .
493	✓ ()
494	$f k = 10^8 L mol^{-1} s^{-1}$, the kinetic rate due to this reaction exceeds the kinetic rate of
495	the reaction between ClOH and SO_3^{2-} . However, this order of magnitude remains
496	unexpected regarding the value between SO_3^{2-} and CIOH and considering that
497	HSO_3^- is less electrophilic. Moreover, in this case, a huge drop of $k_{relative}$ in Fig. 6
498	would have been observed at pH 6. Therefore, we can assume that the potential
499	reaction between HSO_3^- and ClOH can be neglected at pH larger than 6-7.
500	

500

501 CONCLUSIONS

Finding a reliable chemical oxidation method requires the knowledge of the reaction kinetics. The objective of this research was to assess the kinetics of sulfide oxidation by chlorine in a wide pH range (6-12). There are few reliable studies of this reaction studied in the literature, mainly because the large observed kinetic rates makes such studies difficult. The competitive kinetics method using sulfite as the reference compound has been selected. Speciations of chlorine, sulfite and sulfide is rather complex since it involves several acidic or basic compounds.

The results enable to determine the kinetic constant of the reaction between the hydrosulfide anion (HS⁻) and the hypochlorous acid (ClOH): $k_{35} = 1.2 \ 10^9 \ Lmol^{-1} \ s^{-1}$ at 298 K. This reaction is prevalent in the pH range 6-12 even if ClO⁻ is predominant over ClOH at pH > 7.54. The potential reactions between the hypochlorous acid and the conjugated acid (H₂S) and base (S²⁻) are unlikely. Moreover, the reaction between the hypochlorite anion (ClO⁻) and HS⁻ was confirmed as negligible. However, we cannot confirm that the reaction between ClOH and S²⁻ is unlikely at pH > 12.

516 Numerical simulations focused on both sulfite and sulfide oxidations demonstrated 517 that oxidation rates are limited by the various acid base reactions whose kinetic rates are 518 not sufficient to maintain the acid base pairs equilibria. Consequently, in the range pH=6-519 pH=10, the true kinetic rate should be lower than the kinetic rate determined assuming that 520 acid and base equilibriums are maintained during the oxidation.

521 The results of these simulations enable to correlate the result of the competitive 522 method. Additionally to sulfide kinetics investigation, the results allowed to affirm that the 523 potential reaction between HSO_3^- and CIOH is unlikely at least at pH > 6.

524Study of the chlorination process at pH lower than 6 is even more complicated since,525depending on the total chloride concentration, Cl2 can be found in solution which excludes526the possibility of working at such pH in chemical scrubbing to avoid Cl2 desorption in the527treated gas.528In future, the influence of the sulfide oxidation kinetic rates in chemical scrubbing will

be assessed to develop a tool for scrubbers design as well as to understand deeper themechanism involved.

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610

610 Appendix: concentration-time and reaction rate-time profiles

examples with the Software COPASI



612

611

613

Fig A.1: Concentration profile versus time for simulation 1 obtained with Copasi (Virginia

614 Bioinformatics Institute (USA) and the universities of Heidelberg (Germany) and Manchester (UK)).

615





618 (USA) and the universities of Heidelberg (Germany) and Manchester (UK)). Negative fluxes are permitted for

619 reversible reactions when the reverse reaction rate is larger than the forward one. Only the most significant

620 reactions (17, 17, 19, 21, 23) have been represented for clarity.

621 Figs A.1 and A.2 were obtained using the simulation #4 conditions (pH = 8, see Table 2)

- 622 which simulates the initial concentrations used with the competitive kinetics method.
- 623
- 624



Sulfide chlorination kinetics was studied using the competitive method Sulfite was selected as the reference compound The sulfide oxidation in the pH range 6-12 is mainly due to HS⁻ oxidation by ClOH Kinetic constants between ClOH and HS⁻ is evaluated at 1.2×10^9 L mol⁻¹ s⁻¹ Numerical resolutions are performed to check the reliability





subsident δ and γ

Figure 2



Figure 3



Figure 4





Table 1: Reactions involved in the sulfite oxidation mechanism. K_i (equilibrium constants) and k_i (kinetic constants) are reported at 298 k.

Reactio	'n	Eq (i)	K _i	k _i
CIOH + HO ⁻ $\frac{k_{17}}{k_{-17}}$	= CIO ⁻ + H ₂ O	(17)	$^{1}10^{pKw-pK_{a,4}} = 2.88 \times 10^{6}$	${}^{2}k_{17} = 3 \times 10^{9} \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{.17} = 1.0 \times 10^{3} \text{ s}^{-1}$
	CIO ⁻ + H ⁺	(18)	$10^{-pK_{a,4}} = 2.88 \times 10^{-8}$	$k_{18} = 288 \text{ s}^{-1}$ ${}^{3}k_{-18} = 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
$HSO_{3}^{-} + HO - \frac{k_{19}}{k_{-19}}$	$SO_3^{2-} + H_2O$	(19)	$10^{pKw-pK_{a,5}} = 1.23 \times 10^7$	${}^{b}k_{19} = 2.5 \times 10^{10} \text{ L mol}^{\circ} \text{ s}^{-1}$ $k_{.19} = 2.3 \times 10^{3} \text{ s}^{-1}$
HSO ₃ ⁻ k_{20}	$- SO_3^{2-} + H^+$	(20)	$10^{-pK_{a,5}} = 1.23 \times 10^{-7}$	$k_{20} = 9.2 \times 10^3 \text{ s}^{-1}$ $k_{20} = 7.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
CIOH + SO ₃ ² - k_{21} k ₋₂₁	CIO ⁻ + HSO ₃ ⁻	(21)	$10^{pK_{a,5}-pK_{a,4}} = 0.23$	${}^{b}k_{21} = 3 \times 10^{8} \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-21} = 1.28 \times 10^{9} \text{ L mol}^{-1} \text{ s}^{-1}$
$CIO^{-} + SO_{3}^{2} - \frac{k_{22}}{2}$	► SO ₄ ²⁻ + Cl ⁻	(22)		$^{c}k_{22} = 2.3 \times 10^{4} \text{ L mol}^{-1} \text{ s}^{-1}$
CIOH + SO ₃ ² k_{23}	$SO_4^{2-} + Cl^- + H^+$	(23)		${}^{c}k_{23} = 7.6 \times 10^{8} \text{ L mol}^{-1} \text{ s}^{-1}$
$CIOH + HSO_3 \xrightarrow{k_{24}}$	$SO_4^{2-} + CI^- + 2H^+$	(24)	\mathcal{O}	Assumed to be negligible at pH > 6-7

_

 $^{^{1}}$ K_w is the water dissociation constant = 10^{-14} at 298 K. ² (Eigen, 1964)

³ (Fogelman et al., 1988)

 3.69×10^{11} 4.93×10^{4} Always 1.55 Always 1.000100.0 Yes 12 ∞ Always 2.69× 10^{-1} 1.32×10^{9} 2.84×10⁵ Always 1.000Yes 99.3 11 3.10×10^{-2} 2.47×10⁶ 1.44×10^{7} Always Mainly 1.000Yes 93.4 10 و 4.68×10^{-3} 1.65×10^{7} 7.30×10⁵ 0.999 Always Yes No 65.1 ი ഹ 40% of the time 30% of the time 35% of the time 9.82×10^{-4} 7.58×10^{7} 0.999 4.09×10^{5} 41.9 No Yes 00 3.53×10⁵ 1.76×10⁸ 0.999 4.14×10^{-4} No Yes 55.8 7.5 2.72×10^{-4} 2.03×10^{7} 2.79×10⁸ 1.000 Yes 85.9 No 70% of the time 9.90×10^{-4} 7.56×10⁷ 1.000 1.42×10⁶ Always Yes 93.4 9 SO₃²⁻/HSO₃⁻ equilibrium CIO⁻/CIOH equilibrium k_{app,sim} (L mol⁻¹ s⁻¹) R² Simulation number kapp,sim/kapp,cal (%) F-test value t₉₀ (s) 2nd order Hq

Table 2: Simulation results with $[SO_3^2]_{T,0} = 5.0\ 10^{-5}\ mol\ L^1$ and $[CO_]_{T,0} = 3.0\ 10^{-5}\ mol\ L^1$ and various pH. The F-test value is determined with 500 degree of liberty.

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Table 3

[SO ₃ ²⁻] _{T,0} (mol L ⁻¹)	5.0×10 ⁻⁶	5.0×10⁻⁵	5.0×10 ⁻⁴	5.0×10 ⁻³
[ClO ⁻] _{T,0} (mol L ⁻¹)	3.0×10 ⁻⁶	3.0×10 ⁻⁵	3.0×10 ⁻⁴	3.0×10 ⁻³
Simulation number	9	4	10	11
SO ₃ ²⁻ /HSO ₃ ⁻ equilibrium	Always	35% of the time	No	No
ClO ⁻ /ClOH equilibrium	No	No	No	No
<i>t₉₀</i> (s)	5.48×10 ⁻³	9.82×10 ⁻⁴	2.66×10⁻⁴	1.75×10 ⁻⁴
2 nd order	Yes	Yes	Yes	Almost
$k_{app,sim}$ (L mol ⁻¹ s ⁻¹)	1.38×10^{8}	7.58×10^{7}	2.7×10 ⁷	3.96×10^{6}
R ²	1.000	0.999	0.980	0.950
F-test value	1.69×10^{6}	4.09×10^{5}	3.02×10 ⁴	1.17×10^{4}
k _{app,sim} /k _{app,cal} (%)	76.3	41.9	14.9	2.2

Table 3: Simulation results at pH = 8 and various chlorine and sulfite concentrations keeping a constant ratio. The F-test value is determined with 500 degree of liberty.

	5	5	a.a a.5	3	5
[SO ₃ ^{2*}] _{T,0} (mol L ⁻¹)	5.0×10 ⁻³	5.0×10 ⁻³	3.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³
[ClO ⁻] _{τ,0} (mol L ⁻¹)	3.0×10⁻⁵	5.0×10⁻⁵	5.0×10⁻⁵	3.0×10⁻⁵	3.0×10 ⁻³
Simulation number	4	12	13	14	15
$SO^{\frac{2}{2}}/HSO^{\frac{1}{2}}$ aquilibrium	35% of the	40% of the	Almost	Always	almost
SO ₃ /HSO ₃ equilibrium	time	time	never	Always	never
CIO ⁻ /CIOH equilibrium	No	No	No	No	Always
<i>t₉₀</i> (s)	9.82×10 ⁻⁴	1.90×10 ⁻³	7.52×10 ⁻⁴	6.68×10^{-6}	4.46×10 ⁻⁶
2 nd order	Yes	Yes	Yes	Yes	Almost
$k_{app,sim}$ (L mol ⁻¹ s ⁻¹)	7.58×10 ⁷	9.50×10 ⁷	9.76×10 ⁷	6.61×10 ⁷	1.73×10 ⁸
R ²	0.999	0.975	0.993	0.985	0.949
F-test value	4.09×10^{5}	6.57×10^{4}	1.22×10^{5}	7.05×10^{5}	2.51×10^{7}
k _{app,sim} /k _{app,cal} (%)	41.9	52.5	53.9	36.5	95.8

Table 4: Simulation results at pH = 8 and various chlorine and sulfite concentrations. The F-test valueis determined with 500 degree of liberty.

Reaction	Eq (i)	K _i	k _i
Reaction 17 and 18 are sh	ared between both	mechanisms with su	fite and sulfide.
$H_2S + HO^- = \frac{k_{29}}{k_{-29}} HS^- + H_2G$	(29) O	$10^{pK_{W}^{-}pK_{a,1}} = 10^{7.0}$	${}^{1}k_{29} = 2.5 \times 10^{10} \text{ L mol} \text{ s}^{-1}$ $k_{-29} = 2500 \text{ s}^{-1}$
H_2S k_{30} $HS^- + H^+$	(30)	$10^{-pK_{a,1}} = 10^{-7.0}$	$k_{30} = 7500 \text{ s}^{-1}$ ${}^{a}k_{-30} = 7.5 \ 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
CIOH + HS ⁻ $\frac{k_{31}}{k_{-31}}$ CIO ⁻ + H ₂	(31) 2 ² S	$10^{pK_{a,1}-pK_{a,4}} = 0.29$	^a $k_{31} = 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-31} = 1.04 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
$CIO^{-} + H_{2}S \xrightarrow{k_{32}} S + H_{2}O +$	(32) Cl ⁻	${}^{2}k_{32} = 6.7$	75×10 ⁶ L mol ⁻¹ s ⁻¹
$k_{33} = \frac{k_{33}}{5} + HO^{-} +$	(33) Cl ⁻		k ₃₃
CIOH + H ₂ S $\xrightarrow{k_{34}}$ S + H ₃ O ⁺ +	(34) · Cl⁻	^b k ₃₄ = 1.	62×10 ⁵ L mol ⁻¹ s ⁻¹
CIOH + HS ² k_{35} S + H ₂ O +	(35) Cl ⁻	k ₃₅ expected	close to 10^9 L mol ⁻¹ s ⁻¹

Table 5: Reactions involved in the sulfide oxidation mechanism. K_i (equilibrium constants) and k_i (kineticconstants) are reported at 298 K. S can be further oxidized. We consider it as negligible since we used $Ra_{sulfide}$ such as elemental sulfur oxidation would remain marginal.

² (Vilmain et al., 2014)

рН	1	1	12	
k _{relative}	1.	55	0.3	82
k _{app,exp} (L mol ⁻¹ s ⁻¹)	4.4×10 ⁵		4.0>	<10 ⁴
k ₃₃ value (L mol ⁻¹ s ⁻¹)	0	10^{4}	0	10^{4}
k ₃₅ value (L mol ⁻¹ s ⁻¹)	1.23×10 ⁹	1.05×10 ⁹	1.23×10 ⁹	1.05×10^{9}
<i>k_{app,cal}</i> (L mol ⁻¹ s ⁻¹)	4.2×10 ⁵	3.7×10 ⁵	4.2×10 ⁴	4.6×10^{5}
F _i (%)	0.23	2.51	0.19	2.09
Error (%)	5	16	4	14
k ₃₃ /k _{app,cal} (%)	0	2.7	0	21.6

Table 6: Numerical resolution results for k_{35} value determination.

Table 7: Simulation results with $[H_2S]_{T,0} = 10.0 \ 10^5 mol \ L^1$ and $[ClO_]_{T,0} = 3.0 \ 10^{-5} mol \ L^1$ and various pH. The F-test value is determined with 500 degree of liberty

2	y	-	7 5	٥	a	01	11	10
	D	, r,	0.7	0				77
Simulation number	16	1/	18	19	70	21	77	23
SO ₃ ²⁻ /HSO ₃ ⁻ eq.	80% of the time	Almost no	30% of the time	Almost no	Always	Always	Always	Always
CIO ⁷ /CIOH eq.	No	No	No	No	No	No	Always	Always
t ₉₀ (s)	2.99E×10 ⁻⁴	7.68×10 ⁻⁵	1.30×10^{-4}	3.65×10^{-4}	1.92×10^{-3}	8.82×10^{-3}	6.93×10^{-2}	6.75×10^{-1}
2 nd order	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
k _{app,sim} (L mol ⁻¹ s ⁻¹)	9.49×10^{7}	3.64×10^{8}	2.02×10 ⁸	7.30×10^{7}	1.48×10^{7}	3.24×10 ⁶	4.09×10^{5}	4.22×10^{4}
R ²	0.999	1.000	0.993	0.999	1.000	1.000	1.000	1.000
F-test value	4.92E+05	1.49×10^{6}	7.25×10^{4}	4.77×10 ⁵	$1.89{\times}10^{6}$	7.91×10 ⁶	2.62×10^{8}	3.43×10^{10}
K _{app,sim} /K _{app,cal} (%)	88.0	76.9	41.6	25.6	36.6	77.1	97.1	100
	0000							

Simulation number	24 (k _i understimations for sulfite)	25 (k _i overestimations for sulfite)	26 (k _i underestimations for sulfide)	27(k _i overestimations for sulfide)
k _i values (L mol ⁻ 1 s ⁻¹)	$k_{17} = 10^9$ $k_{-18} = 3 \times 10^9$ $k_{19} = 5 \times 10^9$ $k_{-20} = 10^{10}$ $k_{21} = 10^8$	$k_{17} = 10^{10}$ $k_{-18} = 5 \times 10^{10}$ $k_{19} = 2.5 \times 10^{10}$ $k_{-20} = 7.5 \times 10^{10}$ $k_{21} = 10^{9}$	$k_{17} = 10^9$ $k_{-18} = 3 \times 10^9$ $k_{29} = 5 \times 10^9$ $k_{-30} = 7.5 \times 10^{10}$ $k_{31} = 10^8$	$k_{17} = 10^{10}$ $k_{-18} = 5 \times 10^{10}$ $k_{19} = 2.5 \times 10^{10}$ $k_{-20} = 7.5 \times 10^{10}$ $k_{21} = 10^{9}$
k _{app,sim} (L mol ⁻¹ s ⁻¹)	5.17×10 ⁷	7.58×10 ⁷	9.35×10 ⁷	9.53×10 ⁷
t ₉₀ (s)	1.47×10^{-3}	1.00×10^{-3}	3.00×10 ⁻⁴	2.99×10 ⁻⁴
k _{app,sim} /k _{app,cal} (%)	63.9	93.7	86.7	88.28
R ²	0.991	1.000	0.999	0.999

Table 8: Simulation results with underestimated and overestimated kinetic constants of acid-basereactions. The operating conditions are those of simulations #1 and #16.