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1 **Competitive kinetics study of sulfide oxidation by chlorine using sulfite**  
 2 **as reference compound**

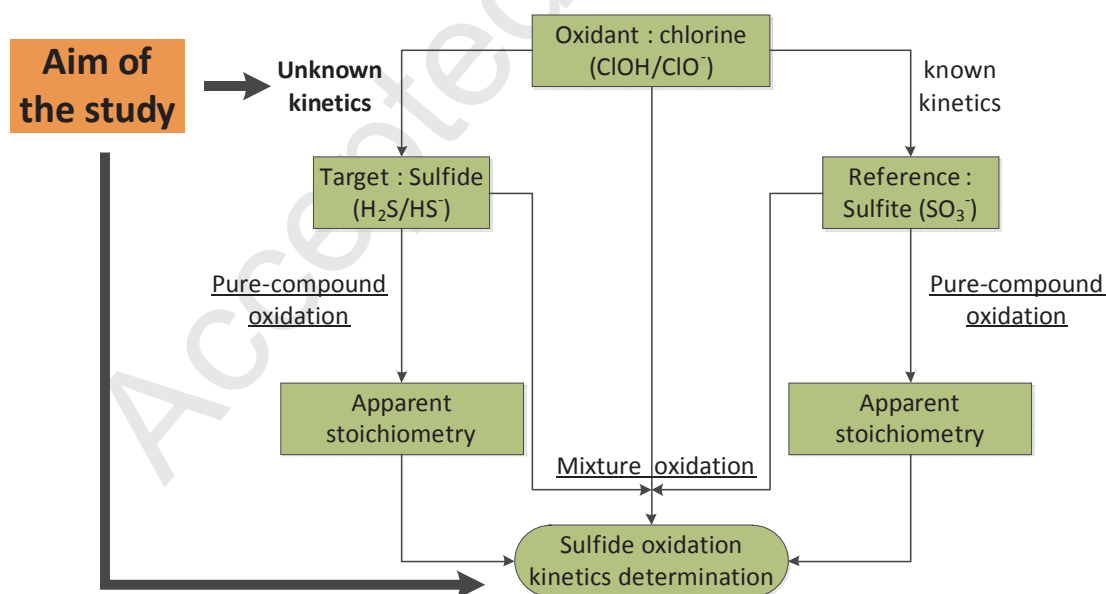
3  
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12 **Graphical abstract**



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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<sup>-</sup>) oxidation by the hypochlorous acid (ClOH)  
28 with an associated kinetic constant of  $1.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  at 25°C.

29

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

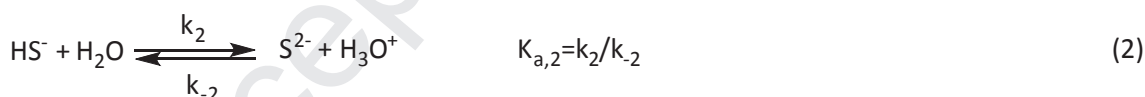
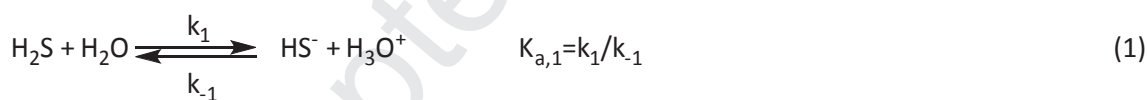
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32

32 **1. INTRODUCTION**

33 Hydrogen sulfide (H<sub>2</sub>S) is a toxic compound involved in emissions from many  
 34 industries such as waste water treatment or pulp industry (Gostelow et al., 2001; Kangas et  
 35 al., 1984; Rappert and Müller, 2005). Several processes are currently used to remove H<sub>2</sub>S :  
 36 biofiltration, absorption in chlorine solution, absorption in alkanolamine solutions,  
 37 absorption using the Claus process or catalysts to recover elemental sulfur, etc. (Busca and  
 38 Chiara, 2003; Kohl and Nielsen, 1997).

39 Chemical scrubbing, which provides high and reliable efficiencies, is widely used for  
 40 hydrogen sulfide removal. The process involves mass transfer in an aqueous solution using a  
 41 gas-liquid contactor. At acid pH, H<sub>2</sub>S is poorly soluble in water. However, hydrogen sulfide  
 42 apparent solubility increases with the pH. Indeed, H<sub>2</sub>S is a weak diacid which dissociates into  
 43 hydrosulfide (or bisulfide) HS<sup>-</sup> (pK<sub>a,1</sub> = 7.0 at 25°C) and sulfide anions as showed by Eqs (1)  
 44 and (2) (Roustan, 2003):



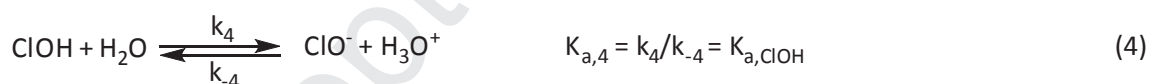
47 Authors' results diverge about the value of pK<sub>a,2</sub>, reported from 12 to 17 (Giggenbach, 1971;  
 48 Licht et al., 1990; Meyer et al., 1983; Migdisov et al., 2002; Stephens and Cobble, 1971).  
 49 However, the most recent articles are all concordant and confirm a value around 17.  
 50 Consequently, S<sup>2-</sup> can be neglected in most aqueous media. Oxidants are often added to  
 51 regenerate the scrubbing solution and to enhance mass transfer. The most frequently  
 52 oxidants used are chlorine (Biard et al., 2010; Biard et al., 2009; Bonnin, 1991; Cadena and

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

55 Proving an excellent efficiency at rather low cost, chlorine is widely used for H<sub>2</sub>S  
 56 chemical scrubbing. Chlorine has attracted significant commercial attention for its wide  
 57 scope in the fields of bleaching, oxidation, and disinfection. Gaseous chlorine (Cl<sub>2</sub>) or sodium  
 58 hypochlorite (NaOCl) are commonly used for chlorination processes (Deborde and Von  
 59 Gunten, 2008). Due to the complex chlorine chemistry in water, various species may be  
 60 present in the solution. Indeed, chlorine gas is hydrolyzed into hypochlorous acid (ClOH)  
 61 according to the following reaction (Eq. 3):



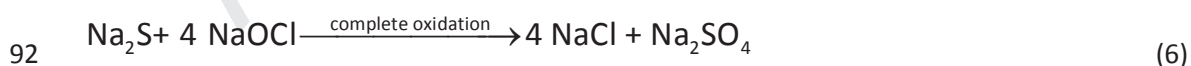
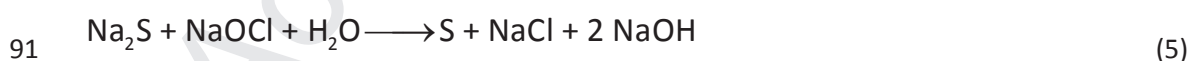
62 Wang and Margerum (1994) demonstrated that  $K_3$  is equal to  $5.1 \cdot 10^{-4} \text{ L}^2 \text{ mol}^{-2}$  at 25°C and  
 63 for a negligible ionic strength (Wang and Margerum, 1994). Hypochlorous acid is a weak acid  
 64 which dissociates in turn into hypochlorite anions (Eq. 4):  
 65



66 Deborde and Von Gunten (2008) reported a value of the acid dissociation constant  $K_{a,4}$  of  
 67  $2.9 \cdot 10^{-8}$  ( $\text{p}K_{a,4} = 7.54$ ) at 298 K. Consequently, the chlorine speciation depends on several  
 68 parameters including the pH, the temperature, the chloride concentration and, with a lower  
 69 importance, the ionic strength. Cl<sub>2</sub>, ClOH and ClO<sup>-</sup> are called the free chlorine species. Other  
 70 reactive chlorine species can be formed upon various conditions (Cl<sub>3</sub><sup>-</sup>, Cl<sub>2</sub>O, etc.) but their  
 71 formation are not favored at low chloride concentrations (Doré, 1989). In most chemical  
 72 conditions applied in water treatment, Cl<sub>2</sub> is negligible in solution for pH > 6.  
 73

74 ClOH is more electrophilic and usually more reactive than ClO<sup>-</sup> (Deborde and Von  
 75 Gunten, 2008). The chlorine reactivity with organic or inorganic compounds depends on the  
 76 chlorine and target compounds speciation; so a great pH dependence of the apparent kinetic  
 77 rate constants is expected in many cases. The oxidation reactions usually follow a second-  
 78 order kinetic law with partial first-orders for both the free active chlorine concentration and  
 79 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):



93 Few studies focus on hydrogen sulfide chlorination due to the high kinetic rates  
 94 observed, the complex chemistry of these species and the difficulty to analyze sulfur  
 95 compounds properly. The kinetics of the H<sub>2</sub>S oxidation in alkaline solutions has been  
 96 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  
98 constant of  $1.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  between pH 9 and 11 and confirmed that the kinetics is very  
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  
103 kinetic constant at alkaline pH below 10.5 could reasonably range between  $10^6$  and  $10^9 \text{ L}$   
104  $\text{mol}^{-1} \text{ s}^{-1}$ . Deborde and Von Gunten (2008) proposed a kinetic constant for the specific  
105 reaction of  $\text{HS}^-$  with  $\text{ClOH}$  very close to that of sulfite ions in the range  $10^8$ - $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . This  
106 determination was based on the  $\text{HS}^-$  nucleophilicity assuming a chlorine electrophilic attack  
107 similar to those previously described for halides or other anionic inorganic compounds ( $\text{SO}_3^{2-}$   
108 ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{CN}^-$ ). The specific kinetic constants of  $\text{H}_2\text{S}$  reactions with  $\text{ClO}^-$  ( $k = 6.75 \cdot 10^6 \text{ L}$   
109  $\text{mol}^{-1} \text{ s}^{-1}$ ) and  $\text{ClOH}$  ( $k = 1.62 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ) have been studied by reactive absorption in a  
110 gas-liquid contactor (Vilmain et al., 2014). The surprising larger value found with  $\text{ClO}^-$  was  
111 justified by a two steps mechanism (acid base reaction between  $\text{H}_2\text{S}$  and  $\text{ClO}^-$  followed by  
112 direct oxidation between  $\text{ClOH} + \text{HS}^-$ ). Therefore, these kinetic constants are apparent and  
113 probably overestimate the true values.

114 To satisfactorily design and understand chemical scrubbers applied to  $\text{H}_2\text{S}$  treatment,  
115 a good knowledge of the kinetics and mechanism of oxidation is necessary. Due to the  
116 absence of accurate kinetic data, the scrubbers' design is largely based on the feedback from  
117 existing plants more than on a precise demonstration. The goal of this study is then to  
118 extend the study of Vilmain et al. (2014) through the determination of the kinetic constant  
119 between  $\text{HS}^-$  and  $\text{ClOH}/\text{ClO}^-$  and to be able to calculate the kinetic rate of hydrogen sulfide  
120 chlorination in a rather large pH range at  $T = 298 \text{ K}$ . The competitive kinetics method has

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  
124 target compounds ( $\text{H}_2\text{S}$ ) and a reference compound whose kinetic constant is known. The  
125 sulfite anion  $\text{SO}_3^{2-}$  was selected as the reference compound since its kinetic rate should be  
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  $T = 298 \text{ K}$  (Fogelman et al., 1989).

131



## 131 2. MATERIALS AND METHODS

### 132 2.1. Experimental method

133 The competitive kinetics method was applied to determine the H<sub>2</sub>S chlorination  
134 kinetics using the sulfite anion SO<sub>3</sub><sup>2-</sup> as the reference compound. The chlorination of both  
135 pure compounds (sulfite and sulfide) was carried out previously to find out the apparent  
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  
140 reactor is headspace free to avoid H<sub>2</sub>S volatilization as well as oxygen dissolution which can  
141 consume sulfite anions. Moreover, its volume varies when sampling due to the plunger  
142 course which enables to keep a constant pressure inside the reactor.

143

144 *Fig. 1: Presentation of the experimental method.*

145

146 A schematic representation of the protocol is illustrated in Fig. 1. All solutions were  
147 prepared using Ultra Pure Water (UPW) prepared by reverse osmosis using an Elga lab  
148 purification unit (resistivity > 18 MΩ cm). UPW was deoxygenated by N<sub>2</sub> (99,999% with  
149 maximum 2 ppmv of residual O<sub>2</sub>, provided by Air Liquide) bubbling. To avoid SO<sub>3</sub><sup>2-</sup> oxidation  
150 by O<sub>2</sub>, the sulfite solution was prepared directly in the reactor by adding sodium sulfite. Then  
151 100 mL of UPW was added to dissolve it. 90 mL of this solution were drained to keep only 10  
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  
154 experiments at pH 6, 7, 7.5 and 8. For pHs 9-12, the initial pH was set by adding NaOH. The

155 syringe was held horizontally in a thermostatic bath regulated at  $25\text{ }^{\circ}\text{C} \pm 0.2$ . After 20 min, 1  
156 mL of chlorine solution was injected in the reactor using a gas-tight syringe (from SGE). Then,  
157 after 2 min of stirring (assuming oxidation is achieved) and complete chlorine consumption,  
158 0.6 mL of ethanol (99% purity) was injected in the reactor to stabilize the sulfite ions in the  
159 aqueous solution before analyses (de Carvalho and Schwedt, 2000).

160 We note that sulfite and sulfide can react together to form thiosulfate. This reaction  
161 is slow and does not happen during the short time between the mixture preparation and the  
162 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  $\text{HS}^-$  and  $\text{SO}_3^{2-}$  have the same  
168 retention time,  $\text{H}_2\text{S}$  was previously stripped from a sample of the solution set at neutral pH  
169 by  $\text{N}_2$  bubbling.

### 170 **2.2.1. Hydrogen sulfide analysis**

171 The methylene blue spectrophotometric method has been evaluated and  
172 recommended by various researchers for sulfide quantification (Fogo and Popowsky, 1949;  
173 Reese et al., 2011). N,N-Dimethyl-1,4-phenylenediamine (DMPD) reacts with hydrogen  
174 sulfide to form a compound which changes into blue leucomethylene. This compound,  
175 oxidized under acidic conditions in the presence of an oxidant (usually Fe(III)), forms  
176 methylene blue. This method was used in combination with the standard addition method  
177 for a higher accuracy of  $\text{H}_2\text{S}$  measurement. The limit of quantification and detection are

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

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

182 Dionex-DX 120 Ion Chromatography, equipped with IonPac® AG 18 (4 mm × 50 mm)  
183 guard column and AS18 analytical column (4mm × 250 mm), was used for  $\text{SO}_3^{2-}$   
184 quantification. Filtered samples (syringe filter with prefilter Minisart from Sartorius,  
185 membrane: cellulose acetate; threshold: 0.45  $\mu\text{m}$ ) were injected (250  $\mu\text{L}$  samples). KOH  
186 eluent (flow rate of 1.06  $\text{mL min}^{-1}$ ) was degassed by vacuum and produced electrochemically  
187 in-line. Ramped eluent concentration was used with 10  $\text{mmol L}^{-1}$  (0-10 min), 10-45  $\text{mmol L}^{-1}$   
188 (10-25 min) and 45  $\text{mmol L}^{-1}$  (25-35 min). Data acquisition was performed by Chromeleon  
189 software. The resolution between sulfate and sulfite peaks was equal to 1.6.

190 Sulfite is easily oxidizable and is particularly unstable in the presence of oxygen. This  
191 oxidation was prevented before the reaction step by preparing the sulfite solution in the 100  
192 mL syringe with deoxygenated water. Only a small amount of  $\text{O}_2$  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  
195 Schwedt, 2000). Using non-deoxygenated UPW, the sulfite anion concentration decreases  
196 quickly (38.0% of recovery after 350 min) whereas using deoxygenated UPW in the syringe  
197 enabled this phenomenon to be limited. An ethanol concentration of 0.1  $\text{mol L}^{-1}$  is necessary  
198 to achieve a negligible sulfite consumption (99.4% of recovery after 350 min).

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**2.2.3. Chlorine analysis**

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**2.3. Reagents**

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

All chemical products had an analytical grade. Sodium sulfide nonahydrate, sodium sulfite, sodium thiosulfate, sodium hypochlorite, potassium hydrogen phthalate, potassium sulfate, acetic acid, absolute ethanol and acetone were purchased from Acros Organics (Belgium). Sodium hydroxide was purchased from Fischer Scientific, potassium iodate from Labogros, potassium dihydrogen phosphate from Panreac Quimica, and tris-(hydroxymethyl)aminomethane from Merck. Hydrochloric acid was obtained from Prolabo. Hydrochloric acid (0.01, 0.1, 1 M) was prepared using Analar Normapur® solutions. The 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 **3. RESULTS AND DISCUSSION**217 **3.1. Chlorination of the pure compounds: determination of the apparent**  
218 **stoichiometries**

219 The apparent stoichiometric coefficients,  $\delta$  and  $\gamma$ , of the reactions between sulfite  
220 and sulfide anions with chlorine at 25°C were determined through the chlorination of each  
221 pure compound:



224  $\delta$  and  $\gamma$  were calculated from the  $\text{Na}_2\text{S}$  and  $\text{NaOCl}$  consumptions by chlorine:

$$225 \delta = \frac{[\text{NaOCl}]_{t=0} - [\text{NaOCl}]_{\text{final}}}{[\text{Na}_2\text{S}]_{t=0} - [\text{Na}_2\text{S}]_{\text{final}}} \quad (9)$$

$$226 \gamma = \frac{[\text{NaOCl}]_{t=0} - [\text{NaOCl}]_{\text{final}}}{[\text{Na}_2\text{SO}_3]_{t=0} - [\text{Na}_2\text{SO}_3]_{\text{final}}} \quad (10)$$

227  $\delta$  and  $\gamma$  were determined for different pH and different ratio of the initial  
228 reagents' concentrations,  $Ra_{\text{sulfide}}$  and  $Ra_{\text{sulfite}}$ , defined as:

$$229 Ra_{\text{sulfide}} = \frac{[\text{Na}_2\text{S}]_{t=0}}{[\text{NaOCl}]_{t=0}} \quad (11)$$

$$230 Ra_{\text{sulfite}} = \frac{[\text{Na}_2\text{SO}_3]_{t=0}}{[\text{NaOCl}]_{t=0}} \quad (12)$$

231 In the one hand, in excess of oxidant (low  $Ra_{\text{sulfide}}$ ), the oxidation was almost  
232 complete and around 4 equivalents of chlorine were consumed for 1 equivalent of sulfide  
233 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  
236 excess ( $Ra_{sulfide} > 3$ ), the oxidation was restricted to the parent compound. One equivalent of  
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  
240 anions were detected by ionic chromatography. Consequently, to ensure no sulfite anions  
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.

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

250 *Fig. 2: Evolution of  $\delta$  and  $\gamma$  vs. respectively  $Ra_{sulfide}$  and  $Ra_{sulfite}$*

### 251 **3.2 Chlorination of sulfide/sulfite anion mixtures: determination of the relative** 252 **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.

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

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

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

262

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

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

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

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

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

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

277  $k_{relative}$  obtained with the three methods and the average value at constant  
 278 temperature (25±0.2 °C) is shown in Fig. 4. Except at pH = 10, the values of  $k_{relative}$  found  
 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  
 281 obtained by Eq. 14 like the other values of pH. Consequently, the average value of  $k_{relative}$  is  
 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 ( $H_2S$ ,  $HSO_3^-$ ) are present and can bias this observation. Indeed, according to Deborde and  
 285 Von Gunten (2008),  $HS^-$  and  $SO_3^{2-}$  oxidation kinetic rates are expected to be similar but no  
 286 data are available for  $H_2S$  and  $HSO_3^-$  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

292 The sulfite anion is a basic species in equilibrium with the hydrogen sulfite ( $HSO_3^-$ ).  
 293 The apparent  $pK_a$  value is included in the range 6.91-7.2 at 298 K, depending on the  
 294 hydrogen sulfite concentration since  $HSO_3^-$  exists in two tautomeric forms (Rhee and  
 295 Dasgupta, 1985). At low sulfite concentration ( $< 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ ),  $pK_{a,5} = 6.91$ .  $H_2SO_3$  ( $H_2O +$   
 296  $SO_2$ ) is present only at very acidic pH and is neglected in this discussion. The oxidation  
 297 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  $\text{ClO}^-$  and  $\text{HSO}_3^-$  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  
301 reaction should be low since  $\text{ClO}^-$  and  $\text{HSO}_3^-$  are respectively poorer electrophile and  
302 nucleophile than  $\text{ClOH}$  and  $\text{SO}_3^{2-}$  (Fogelman et al., 1989). Fogelman et al. determined the  
303 kinetic constants of reactions 22 and 23 using the stopped-flow method at 298 K (Fogelman  
304 et al., 1989). Even if hypochlorous acid ( $\text{ClOH}$ ) does not predominate at  $\text{pH} > 7.54$ , since  $k_{23}$   
305  $\gg k_{22}$ , sulfite anion is more oxidized by  $\text{ClOH}$  than  $\text{ClO}^-$  for  $\text{pH} < 12-12.1$ . Their study was  
306 conducted at  $\text{pH} > 9.5$ , at which reaction 24 which involves two acids is unexpected and  
307 unfortunately  $k_{24}$  is unknown. For the rest of the discussion, this reaction was neglected  
308 since  $\text{HSO}_3^-$  should be less reactive than  $\text{SO}_3^{2-}$  and the study was mainly conducted in the  $\text{pH}$   
309 range ( $> 6.91-7.2$ ) at which  $\text{SO}_3^{2-}$  is predominant. This assumption will be confirmed in the  
310 section 3.2.5. Kinetic constants of bimolecular proton transfer reactions (Eqs 17 to 21) are  
311 not precisely known. According to Eigen (1964), the orders of magnitude of the kinetic  
312 constants for recombination of a base with  $\text{H}^+$  (reverse reactions 18 and 20) and of an acid  
313 with  $\text{HO}^-$  (Reactions 17 and 19) are respectively typically  $10^{10}-10^{11}$  and  $10^9-10^{11}$   $\text{L mol}^{-1} \text{s}^{-1}$   
314 (Eigen, 1964). The ratio of them for a given acid/base couple is between 2 and 3 in many  
315 cases. Fogelman et al. used with a good agreement a value of  $k_{17} = 3 \times 10^9$   $\text{L mol}^{-1} \text{s}^{-1}$  in their  
316 simulations (Fogelman et al., 1989). Taking this into consideration,  $k_{17}$ ,  $k_{18}$ ,  $k_{19}$  and  $k_{20}$  are  
317 respectively set to the values presented in Table 1. The rather large value of  $k_{20}$  has been  
318 chosen equal to  $k_{30}$  by analogy ( $\text{H}_2\text{S}$  dissociation, Table 5). Considering that  $\text{pK}_{a,4}-\text{pK}_{a,5} \approx 0.5$ ,  
319  $k_{21}$  can be set to  $3 \times 10^8$   $\text{L mol}^{-1} \text{s}^{-1}$  according to Eigen (1964).

320 In a batch reactor, at constant temperature and volume, the kinetic law of total  
321 sulfite consumption can be written:

$$322 \quad \frac{d[SO_3^{2-}]_T}{dt} = -\frac{d[SO_3^{2-}]}{dt} - \frac{d[H_2SO_3]}{dt} - \frac{d[ClO^-]}{dt} - \frac{d[ClOH]}{dt} \quad (25)$$

$$323 \quad -\frac{d[SO_3^{2-}]_T}{dt} = k_{22}[SO_3^{2-}][ClO^-] + k_{23}[SO_3^{2-}][ClOH] \quad (26)$$

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

$$328 \quad \frac{d[SO_3^{2-}]_T}{dt} = k_{app,cal}^{sulfite} \times [SO_3^{2-}]_T [ClO^-]_T \quad (27)$$

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

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

$$334 \quad T = k_{app}^{sulfite} \times t \quad \text{with} \quad T = \frac{1}{[ClO^-]_{T,0} - [SO_3^{2-}]_{T,0}} \ln \frac{[SO_3^{2-}]_{T,0} [ClO^-]_T}{[SO_3^{2-}]_T [ClO^-]_{T,0}} \quad (28)$$

335 *Table 1*

336 *Fig. 5: Effect of pH on  $k_{app,cal}$  for sulfite and sulfide oxidations.  $k_{app,cal}$  was calculated with Eq. 27 and 38*  
 337 *whereas  $k_{app,sim}$  was calculated through the numerical simulations (using the conditions of Table 2). The blue*  
 338 *and green areas delimit zones where  $k_{app}$  for respectively sulfite and sulfide should be located for a wide range*  
 339 *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  
347 resolution of differential equations systems found in biological and chemical kinetics.  
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.  $\text{HO}^-$  and  $\text{H}^+$  concentrations have been fixed to  
351 their initial values since a buffer is added to maintain a constant pH (except at  $\text{pH} \geq 9$  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  
357 "Linest" function of Excel®) :

- 358 • to check if the kinetic rate is second-order (using appropriated statistic criteria such as  
359 the determination coefficient  $R^2$  and the F-test value);
- 360 • if so, to determine the apparent 2<sup>nd</sup> order kinetic constants (called  $k_{app,sim}$ ) from the  
361 slope;
- 362 • to compare  $k_{app,sim}$  and  $k_{app,cal}$ .

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  
365 magnitude of the initial concentrations and the initial concentrations ratio (Tables 3 and 4  
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  
369 always lower than  $k_{app,cal}$ . (Table 2), which emphasizes that the kinetic rate was limited by  
370 proton transfer reactions. Fig A.2 clearly highlights that the ClOH consumption rate by  
371 reaction 23 was larger than its reformation rate due to reactions 17, 18 and 21. Even if ClOH  
372 and ClO<sup>-</sup> were in equilibrium at the beginning of the simulation, the ratio [ClOH]/[ClO<sup>-</sup>]  
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 ClOH consumption was more easily compensated, which enabled to  
380 maintain more easily the species equilibrium. In this case, the apparent kinetic constant  
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.

383 Even if the kinetic rate of the reaction increases with the initial concentrations ( $t_{90}$   
384 decreases), the value of  $k_{app,sim}$  decreases (Table 3). Indeed, with larger initial concentrations,  
385 the HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> equilibrium is more difficult to maintain since the kinetic rate is larger. By  
386 the way,  $k_{app,sim}$  tends towards  $k_{app,cal}$  when the initial concentration decreases. When sulfite

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 acid-  
 398 base reactions (17, 18 and 29 to 31) and pure oxidation reactions (32 to 34). Only the first  
 399 oxidation step which leads to elemental sulfur was considered since the initial  
 400 concentrations ratio ( $Ra_{sulfide}$ ) was carefully selected. Moreover, in the pH range studied (6-  
 401 12),  $S^{2-}$  can be neglected. Based on these assumptions, the kinetic law of total sulfide  
 402 consumption can be written:

$$403 \quad -\frac{d[H_2S]_T}{dt} = -\frac{d[H_2S]}{dt} - \frac{d[HS^-]}{dt} = -\frac{d[ClO^-]}{dt} - \frac{d[ClOH]}{dt} \quad (36)$$

$$404 \quad -\frac{d[H_2S]_T}{dt} = k_{32} [H_2S][ClO^-] + k_{33} [H_2S][ClOH] + k_{34} [HS^-][ClO^-] + k_{35} [HS^-][ClOH] \quad (37)$$

405 If chlorine and sulfide species are in equilibrium with their respective conjugated  
 406 species, then:

$$407 \quad -\frac{d[H_2S]_T}{dt} = k_{app,cal}^{sulfide} \times [H_2S]_T [ClO^-]_T \quad (38)$$

$$+ \frac{k_{32}}{(1+10^{pK_{a,4}-pH})(1+10^{pH-pK_{a,1}})} + \frac{k_{33}}{(1+10^{pH-pK_{a,4}})(1+10^{pH-pK_{a,1}})}$$

$$+ \frac{k_{34}}{(1+10^{pH-pK_{a,4}})(1+10^{pH-pK_{a,1}})} + \frac{k_{35}}{(1+10^{pH-pK_{a,4}})(1+10^{pK_{a,1}-pH})}$$

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.  $k_{app,exp}$

410 for the sulfide oxidation can be extrapolated from  $k_{relative}$  (Eqs 14-16) and  $k_{app,cal}^{sulfite}$  (Eq. 27):

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

412 At these pHs, it is quite obvious that reactions 32 and 34 are unlikely. Then,  $k_{33}$  and  
 413  $k_{35}$  can be determined by numerical resolution trying to minimize the following least square  
 414 objective function:

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

416 An excellent agreement is obtained with  $k_{35} = 1.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  when the value of  
 417  $k_{33}$  can be set between 0 and  $10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  with a very restricted influence (Table 6). In  
 418 Table 6,  $R_{33}$  represents the following ratio:

$$419 \quad R_{33} = \frac{k_{33}}{(1 + 10^{pH - pK_{a,1}})(1 + 10^{pH - pK_{a,2}})} / k_{app,cal}^{sulfide} \quad (41)$$

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  $\text{pH} \leq 12$ , 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<sup>-</sup> and ClOH.

427 Using the same methodology than for sulfite (section 3.2.3), it is possible to  
 428 determine  $k_{app,sim}$  for sulfide and to try to compare it to  $k_{app,cal}$  (Table 7 and Fig. 5). The same  
 429 main conclusions apply for both compounds. The sulfide oxidation is limited by acid-base  
 430 reactions (17, 18, 29-31) at pH lower than 10, especially when pH ranges between 6 and 9.  
 431 Therefore, it confirms that it was pertinent to use only the results obtained at pH 11 and 12  
 432 to determine  $k_{35}$  by numerical resolution. The simulation at pH 6 (simulation #16)  
 433 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

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 ( $k_{relative,exp}$ ):

$$443 \quad k_{relative,cal} = \frac{k_{app,cal}^{sulfide}}{k_{app,cal}^{sulfite}} \quad (42)$$

$$444 \quad k_{relative,sim} = \frac{k_{app,sim}^{sulfide}}{k_{app,sim}^{sulfite}} \quad (43)$$

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  
454 uncertainty concerning  $pK_{a,5}$ .

455 *Table 8*

456



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  
460  $k_{app,sim}$  are determined with estimated values of the different acid-base reactions (17-21  
461 and 29-31). What is the sensitivity of the values of  $k_{app,sim}$  to these estimated kinetic  
462 constants? To answer to this question,  $k_{app,sim}$  for sulfite and sulfide have been  
463 recalculated at pH 6 with underestimated and overestimated values of the kinetic  
464 constants (Table 8). On the one hand, the results demonstrate that  $k_{app,sim}$  is not so  
465 sensitive to these values (especially for sulfide). At least, it does not change the  
466 conclusions of the numerical resolutions. The most influential kinetic constants are those  
467 of reactions 21 and 31. On the other hand, the influence on  $k_{relative,sim}$  is rather important  
468 ( $k_{relative,sim} = 1.81$  and  $1.26$  respectively using simulations 24+26 and 25+27) and can justify  
469 the disagreement observed at this pH between  $k_{relative,exp}$  and  $k_{relative,sim}$ .
- 470 • The potential reactions between ClOH and ClO<sup>-</sup> and S<sup>2-</sup> were neglected; this hypothesis  
471 required to be discussed more deeply. A possible influence of these two reactions is  
472 expected only at very basic pH. Concerning the reaction between ClOH and S<sup>2-</sup>, their  
473 respective predominance domains are far apart. By the way, assuming a probably  
474 overestimated kinetic constant of  $5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $k_{app,cal}$  at pH 12 goes from  $4.2 \cdot 10^{-4}$  to  
475  $4.4 \cdot 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$  which confirms that this reaction can be neglected at pH lower than 12.  
476 The potential reaction between S<sup>2-</sup> and ClO<sup>-</sup> involves species whose coexistence domains  
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  
479 important electrostatic repulsion force. With a probably overestimated value of the  
480 kinetic constants of  $5 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  (maximal order of magnitude encountered between

481 ClO<sup>-</sup> and any species),  $k_{app,cal}$  goes from  $4.2 \cdot 10^4$  to  $5.0 \cdot 10^4$  L mol<sup>-1</sup> s<sup>-1</sup> at pH 12. It confirms  
482 that the reaction between ClO<sup>-</sup> and S<sup>2-</sup> is unlikely at least at pH lower than 12. Moreover,  
483 a low pK<sub>a</sub> 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<sup>-1</sup> s<sup>-1</sup>, the kinetic rate due to this reaction remains lower than 10%  
492 compared to the kinetic rate of the reaction between ClOH and SO<sub>3</sub><sup>2-</sup>.

493 ✓ |  
494 f  $k = 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>, the kinetic rate due to this reaction exceeds the kinetic rate of  
495 the reaction between ClOH and SO<sub>3</sub><sup>2-</sup>. However, this order of magnitude remains  
496 unexpected regarding the value between SO<sub>3</sub><sup>2-</sup> and ClOH and considering that  
497 HSO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> and ClOH can be neglected at pH larger than 6-7.

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**CONCLUSIONS**

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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.

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The results enable to determine the kinetic constant of the reaction between the hydrosulfide anion ( $\text{HS}^-$ ) and the hypochlorous acid ( $\text{ClOH}$ ):  $k_{35} = 1.2 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  at 298 K. This reaction is prevalent in the pH range 6-12 even if  $\text{ClO}^-$  is predominant over  $\text{ClOH}$  at  $\text{pH} > 7.54$ . The potential reactions between the hypochlorous acid and the conjugated acid ( $\text{H}_2\text{S}$ ) and base ( $\text{S}^{2-}$ ) are unlikely. Moreover, the reaction between the hypochlorite anion ( $\text{ClO}^-$ ) and  $\text{HS}^-$  was confirmed as negligible. However, we cannot confirm that the reaction between  $\text{ClOH}$  and  $\text{S}^{2-}$  is unlikely at  $\text{pH} > 12$ .

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

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The results of these simulations enable to correlate the result of the competitive method. Additionally to sulfide kinetics investigation, the results allowed to affirm that the potential reaction between  $\text{HSO}_3^-$  and  $\text{ClOH}$  is unlikely at least at  $\text{pH} > 6$ .

524 Study of the chlorination process at pH lower than 6 is even more complicated since,  
525 depending on the total chloride concentration,  $\text{Cl}_2$  can be found in solution which excludes  
526 the possibility of working at such pH in chemical scrubbing to avoid  $\text{Cl}_2$  desorption in the  
527 treated gas.

528 In future, the influence of the sulfide oxidation kinetic rates in chemical scrubbing will  
529 be assessed to develop a tool for scrubbers design as well as to understand deeper the  
530 mechanism involved.

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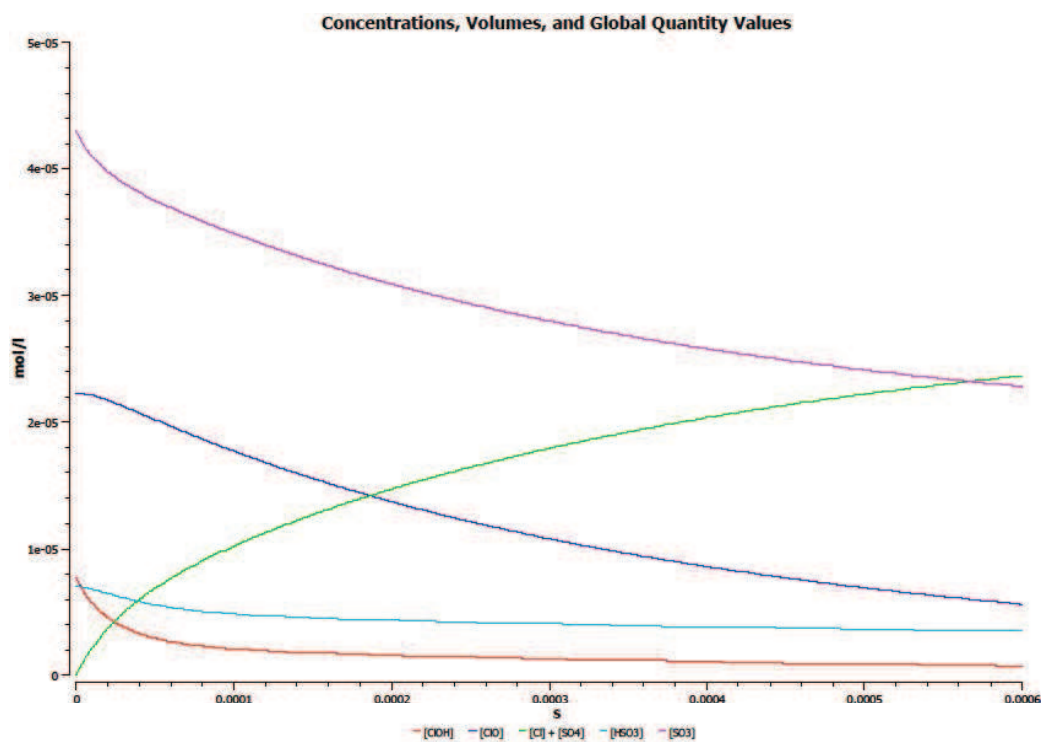
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610 **Appendix: concentration-time and reaction rate-time profiles**

611 **examples with the Software COPASI**

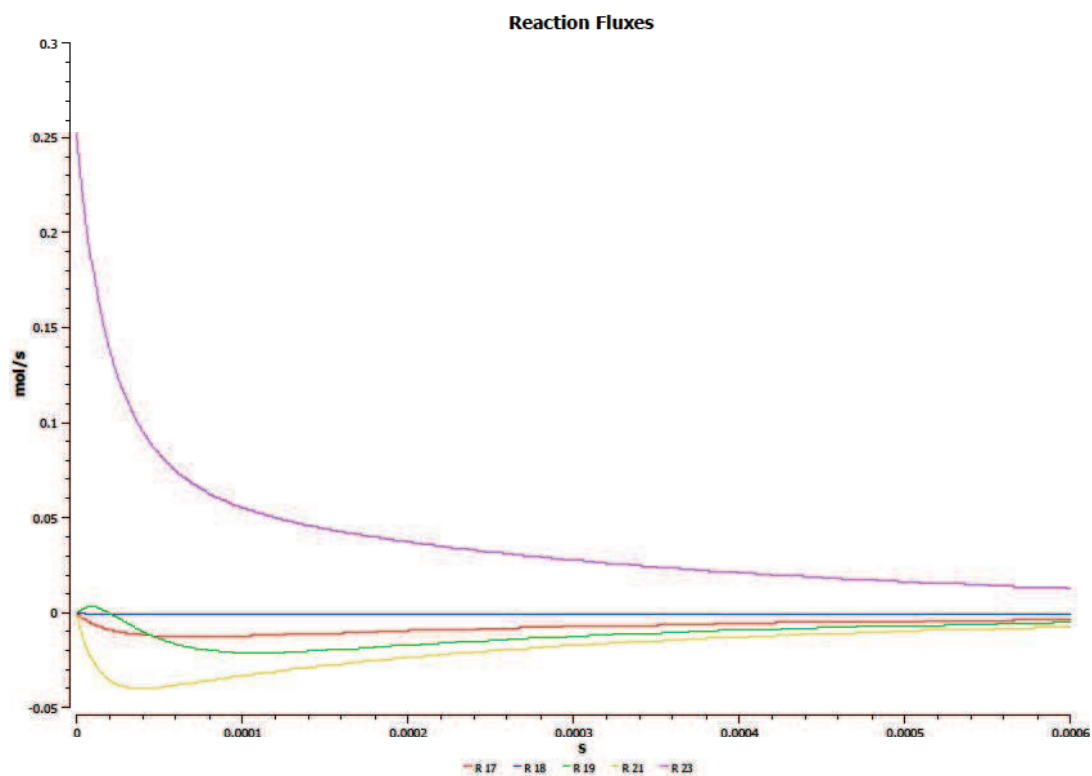


612

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



616  
 617 Fig A.2: Reaction rate profile versus time for simulation 1 obtained with Copasi (Virginia Bioinformatics Institute  
 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.

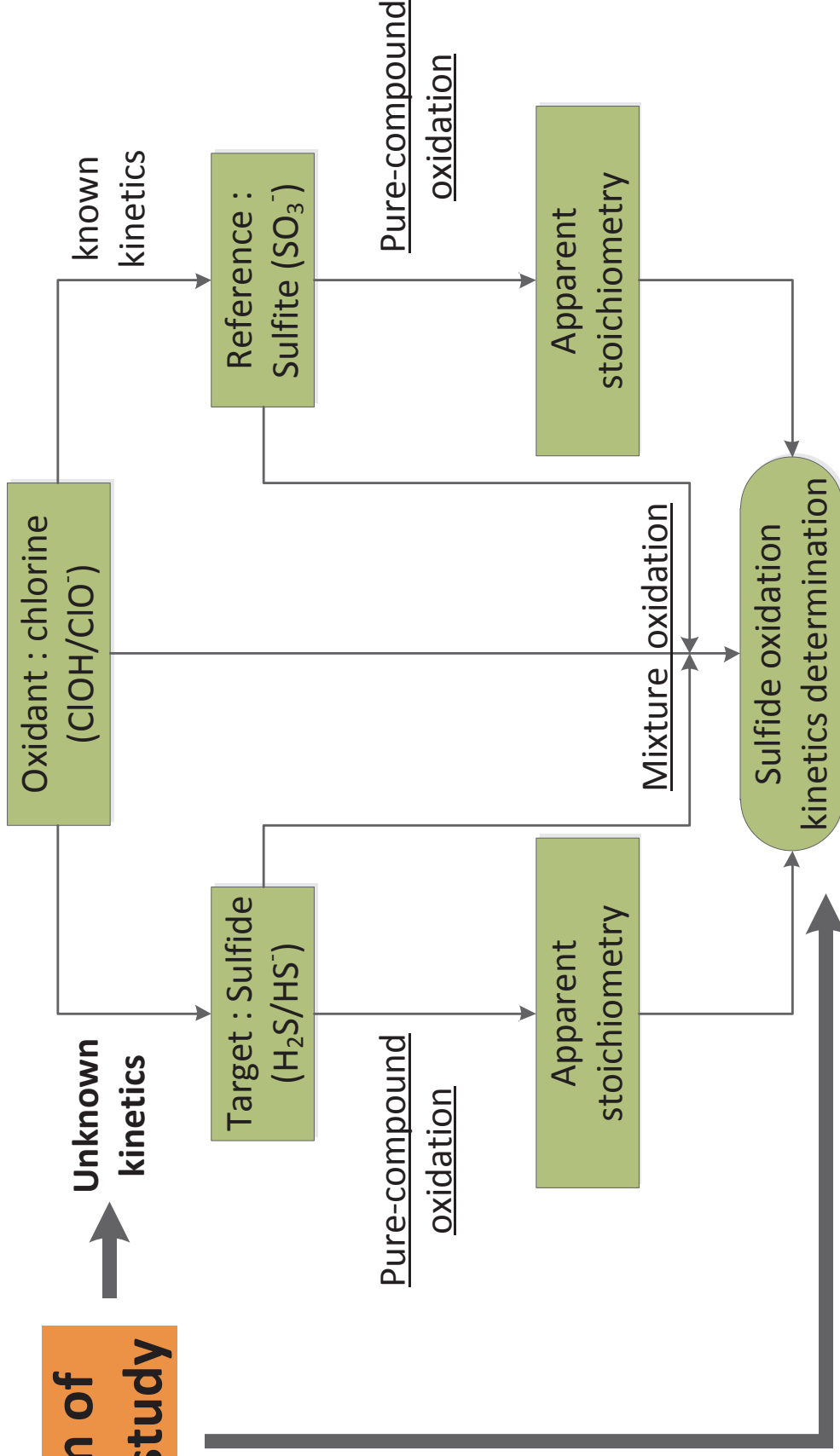
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624



# Aim of the study

Unknown kinetics



Sulfide chlorination kinetics was studied using the competitive method

Sulfite was selected as the reference compound

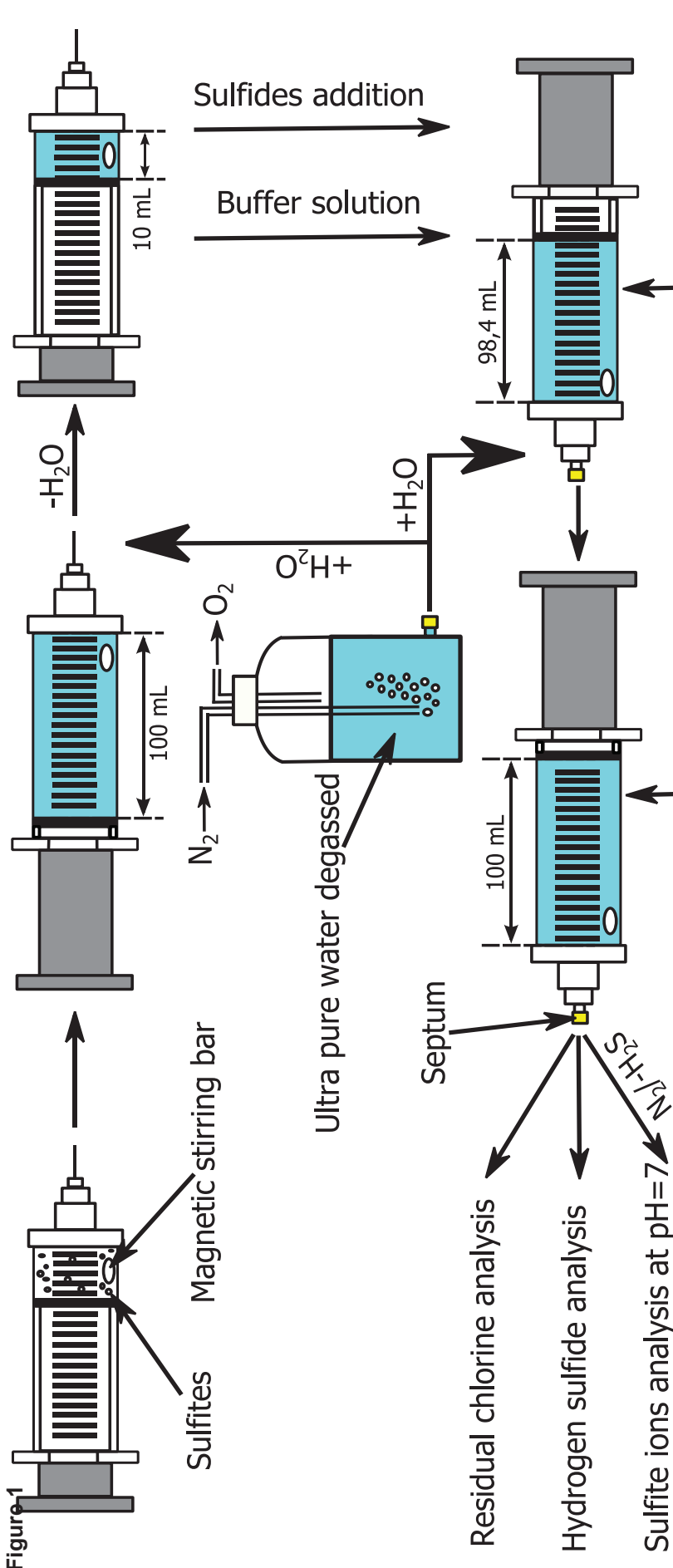
The sulfide oxidation in the pH range 6-12 is mainly due to  $\text{HS}^-$  oxidation by  $\text{ClOH}$

Kinetic constants between  $\text{ClOH}$  and  $\text{HS}^-$  is evaluated at  $1.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$

Numerical resolutions are performed to check the reliability

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Figure 1



Placed in a thermostated bath at 25 °C

Figure 2

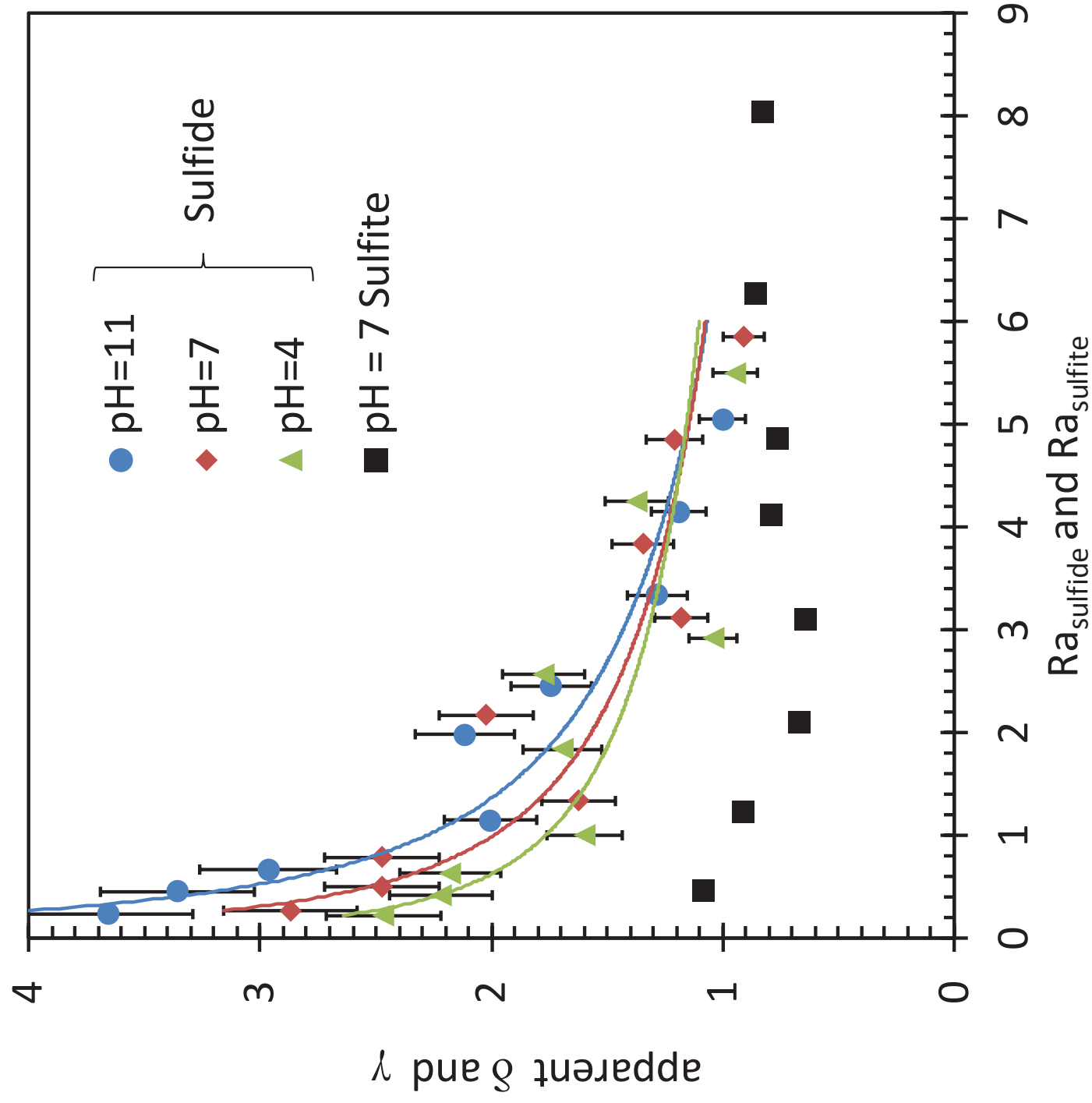


Figure 3

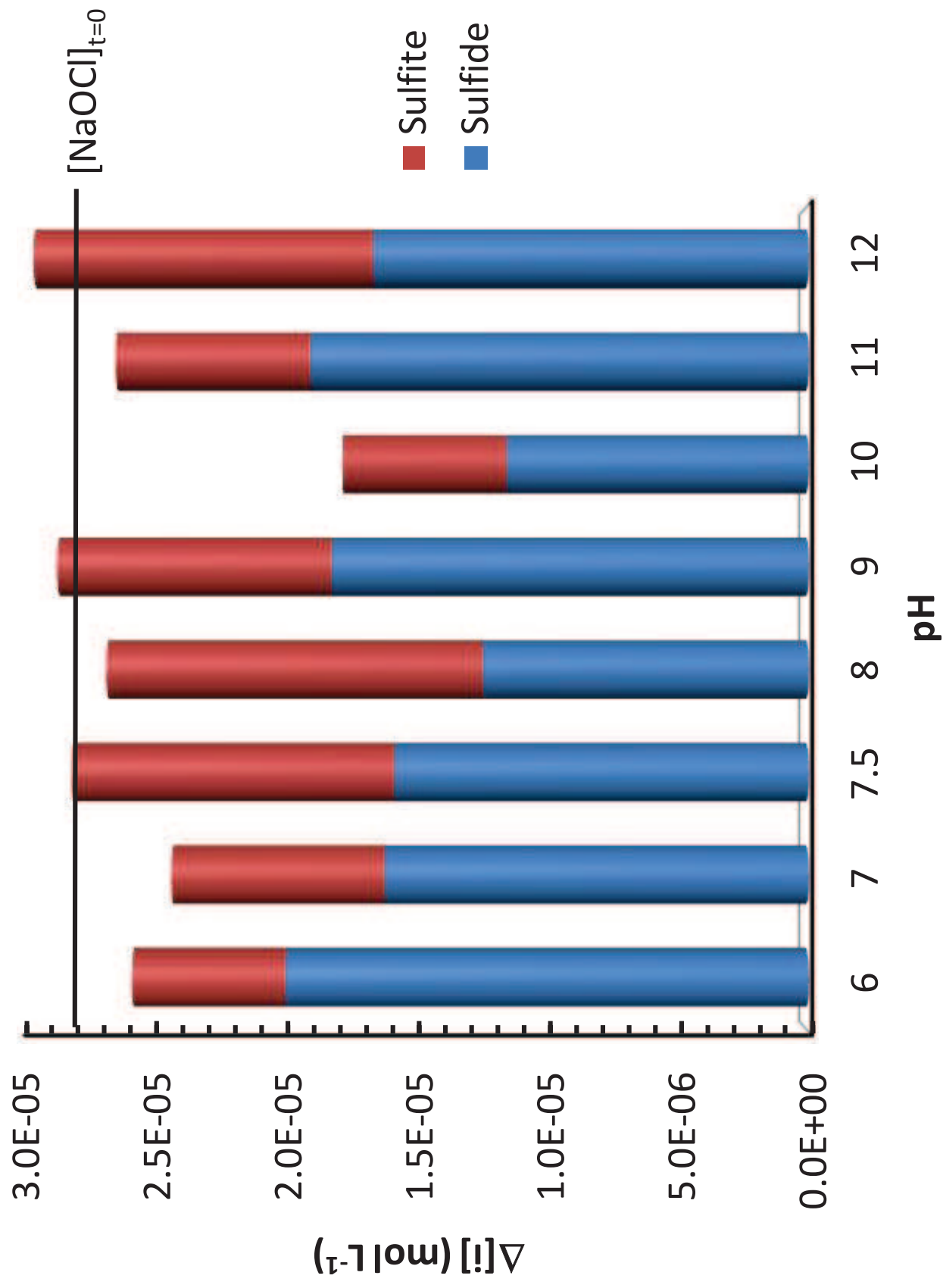


Figure 4

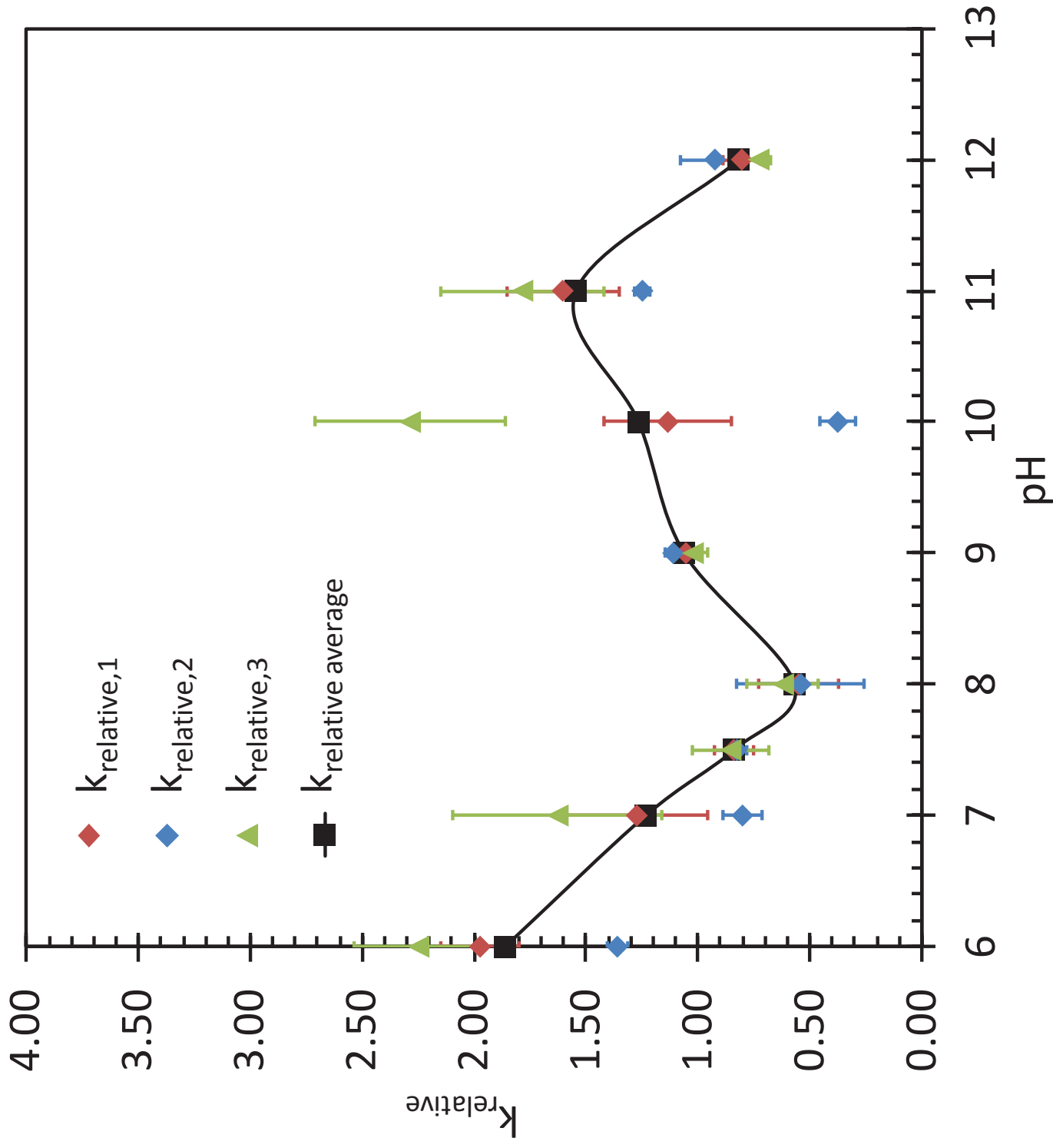


Figure 5

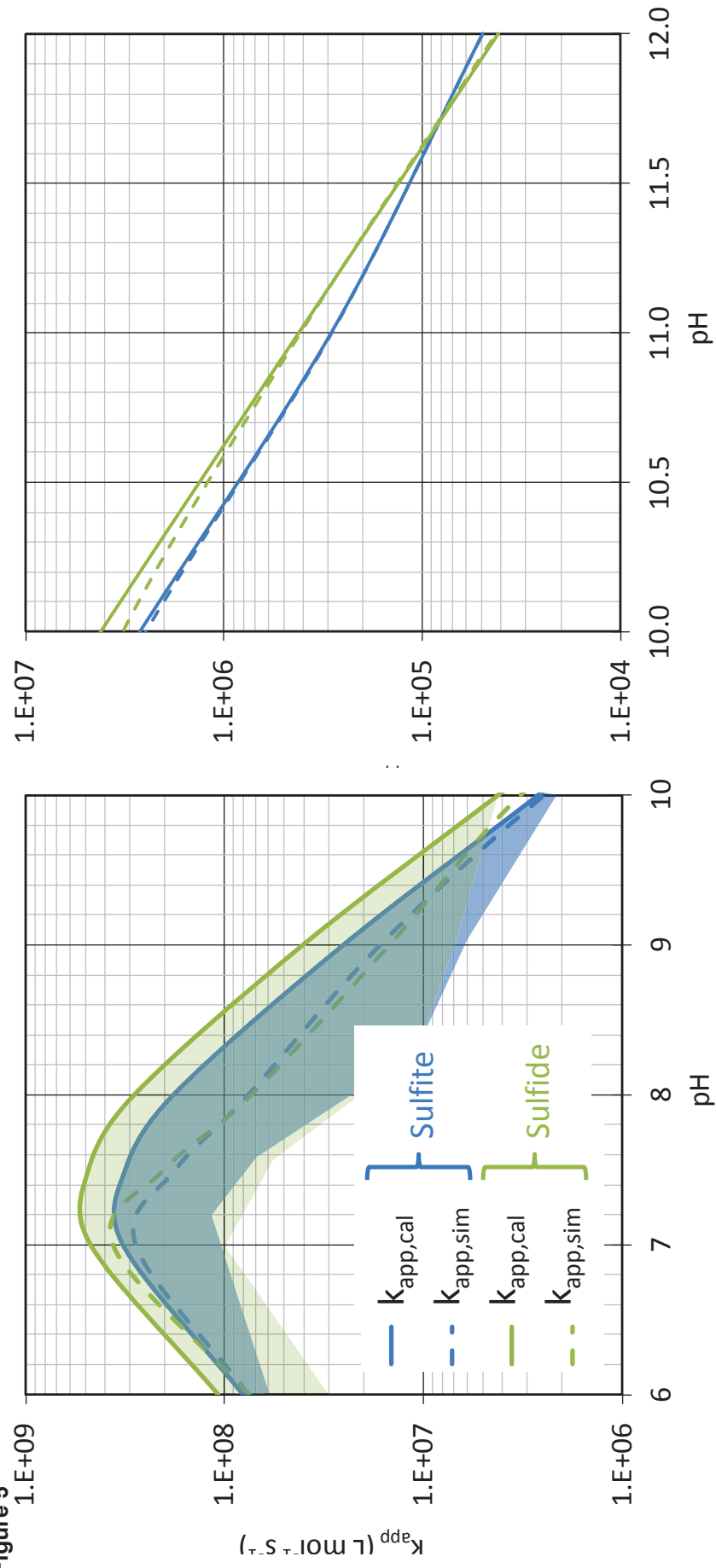


Figure 6

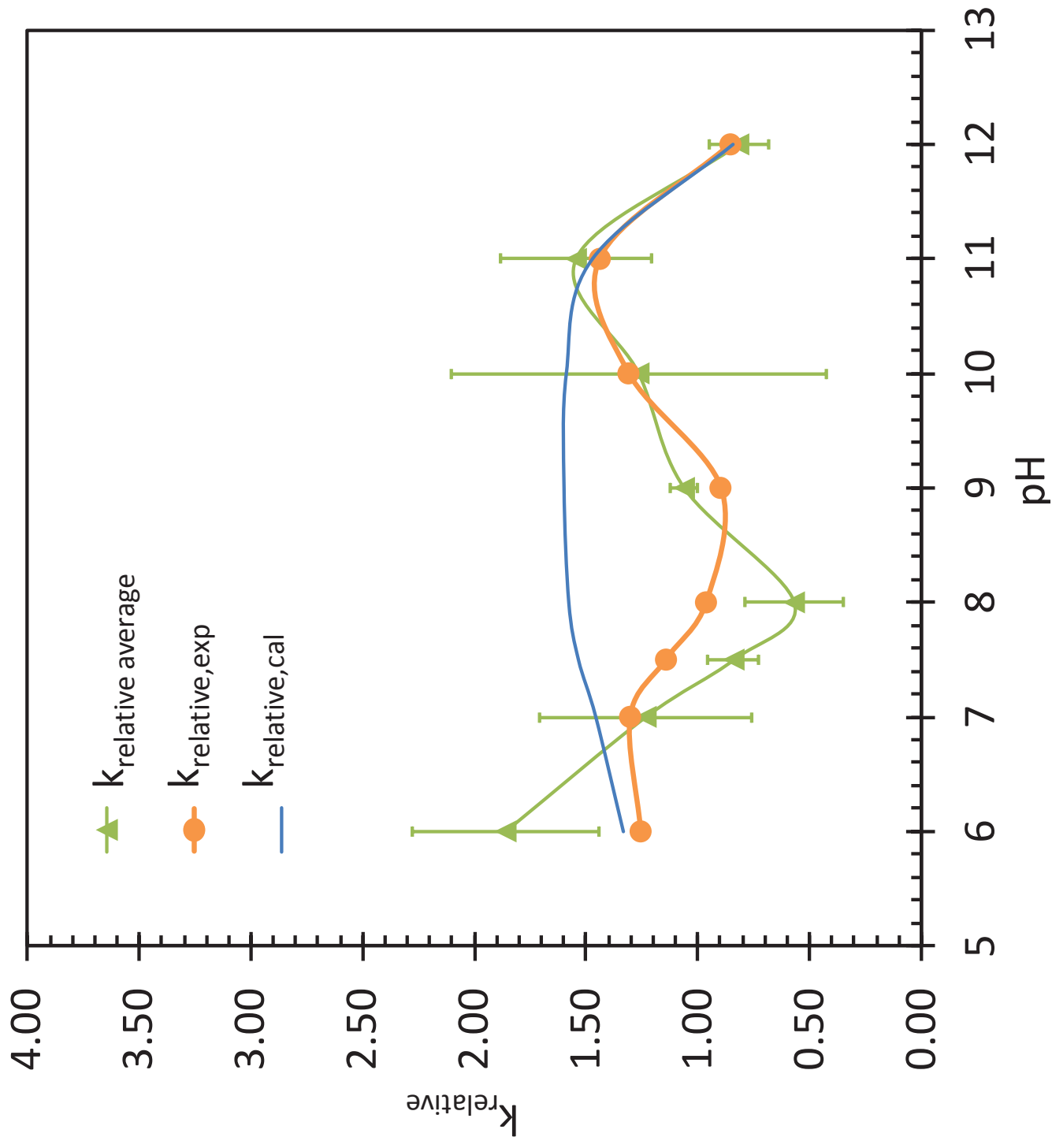




Table 1: Reactions involved in the sulfite oxidation mechanism.  $K_i$  (equilibrium constants) and  $k_i$  (kinetic constants) are reported at 298 K.

Reaction	Eq (i)	$K_i$	$k_i$
$\text{ClOH} + \text{HO}^- \xrightleftharpoons[k_{-17}]{k_{17}} \text{ClO}^- + \text{H}_2\text{O}$	(17)	$10^{\text{p}K_w - \text{p}K_{a,4}} = 2.88 \times 10^6$	${}^2k_{17} = 3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-17} = 1.0 \times 10^3 \text{ s}^{-1}$
$\text{ClOH} \xrightleftharpoons[k_{-18}]{k_{18}} \text{ClO}^- + \text{H}^+$	(18)	$10^{-\text{p}K_{a,4}} = 2.88 \times 10^{-8}$	$k_{18} = 288 \text{ s}^{-1}$ ${}^3k_{-18} = 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{HSO}_3^- + \text{HO}^- \xrightleftharpoons[k_{-19}]{k_{19}} \text{SO}_3^{2-} + \text{H}_2\text{O}$	(19)	$10^{\text{p}K_w - \text{p}K_{a,5}} = 1.23 \times 10^7$	${}^b k_{19} = 2.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-19} = 2.3 \times 10^3 \text{ s}^{-1}$
$\text{HSO}_3^- \xrightleftharpoons[k_{-20}]{k_{20}} \text{SO}_3^{2-} + \text{H}^+$	(20)	$10^{-\text{p}K_{a,5}} = 1.23 \times 10^{-7}$	$k_{20} = 9.2 \times 10^3 \text{ s}^{-1}$ ${}^b k_{-20} = 7.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClOH} + \text{SO}_3^{2-} \xrightleftharpoons[k_{-21}]{k_{21}} \text{ClO}^- + \text{HSO}_3^-$	(21)	$10^{\text{p}K_{a,5} - \text{p}K_{a,4}} = 0.23$	${}^b k_{21} = 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-21} = 1.28 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClO}^- + \text{SO}_3^{2-} \xrightarrow{k_{22}} \text{SO}_4^{2-} + \text{Cl}^-$	(22)		${}^c k_{22} = 2.3 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClOH} + \text{SO}_3^{2-} \xrightarrow{k_{23}} \text{SO}_4^{2-} + \text{Cl}^- + \text{H}^+$	(23)		${}^c k_{23} = 7.6 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClOH} + \text{HSO}_3^- \xrightarrow{k_{24}} \text{SO}_4^{2-} + \text{Cl}^- + 2\text{H}^+$	(24)		Assumed to be negligible at pH > 6-7

<sup>1</sup>  $K_w$  is the water dissociation constant =  $10^{-14}$  at 298 K.

<sup>2</sup> (Eigen, 1964)

<sup>3</sup> (Fogelman et al., 1988)

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

pH	6	7	7.5	8	9	10	11	12
Simulation number	1	2	3	4	5	6	7	8
$SO_3^{2-}/HSO_3^-$ equilibrium	70% of the time	40% of the time	30% of the time	35% of the time	Always	Always	Always	Always
$ClO^-/ClOH$ equilibrium	Always	No	No	No	No	Mainly	Always	Always
$t_{90}$ (s)	$9.90 \times 10^{-4}$	$2.72 \times 10^{-4}$	$4.14 \times 10^{-4}$	$9.82 \times 10^{-4}$	$4.68 \times 10^{-3}$	$3.10 \times 10^{-2}$	$2.69 \times 10^{-1}$	1.55
2 <sup>nd</sup> order	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
$k_{app,sim}$ ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )	$7.56 \times 10^7$	$2.79 \times 10^8$	$1.76 \times 10^8$	$7.58 \times 10^7$	$1.65 \times 10^7$	$2.47 \times 10^6$	$2.84 \times 10^5$	$4.93 \times 10^4$
$R^2$	1.000	1.000	0.999	0.999	0.999	1.000	1.000	1.000
F-test value	$1.42 \times 10^6$	$2.03 \times 10^7$	$3.53 \times 10^5$	$4.09 \times 10^5$	$7.30 \times 10^5$	$1.44 \times 10^7$	$1.32 \times 10^9$	$3.69 \times 10^{11}$
$k_{app,sim}/k_{app,cal}$ (%)	93.4	85.9	55.8	41.9	65.1	93.4	99.3	100.0

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.

$[\text{SO}_3^{2-}]_{T,0}$ (mol L <sup>-1</sup> )	$5.0 \times 10^{-6}$	$5.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$5.0 \times 10^{-3}$
$[\text{ClO}^-]_{T,0}$ (mol L <sup>-1</sup> )	$3.0 \times 10^{-6}$	$3.0 \times 10^{-5}$	$3.0 \times 10^{-4}$	$3.0 \times 10^{-3}$
Simulation number	9	4	10	11
$\text{SO}_3^{2-}/\text{HSO}_3^-$ equilibrium	Always	35% of the time	No	No
$\text{ClO}^-/\text{ClOH}$ equilibrium	No	No	No	No
$t_{90}$ (s)	$5.48 \times 10^{-3}$	$9.82 \times 10^{-4}$	$2.66 \times 10^{-4}$	$1.75 \times 10^{-4}$
2 <sup>nd</sup> order	Yes	Yes	Yes	Almost
$k_{app,sim}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$1.38 \times 10^8$	$7.58 \times 10^7$	$2.7 \times 10^7$	$3.96 \times 10^6$
R <sup>2</sup>	1.000	0.999	0.980	0.950
F-test value	$1.69 \times 10^6$	$4.09 \times 10^5$	$3.02 \times 10^4$	$1.17 \times 10^4$
$k_{app,sim}/k_{app,cal}$ (%)	76.3	41.9	14.9	2.2

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

$[\text{SO}_3^{2-}]_{T,0}$ (mol L <sup>-1</sup> )	$5.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-3}$	$5.0 \times 10^{-5}$
$[\text{ClO}^-]_{T,0}$ (mol L <sup>-1</sup> )	$3.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	$3.0 \times 10^{-3}$
Simulation number	4	12	13	14	15
$\text{SO}_3^{2-}/\text{HSO}_3^-$ equilibrium	35% of the time	40% of the time	Almost never	Always	almost never
$\text{ClO}^-/\text{ClOH}$ equilibrium	No	No	No	No	Always
$t_{90}$ (s)	$9.82 \times 10^{-4}$	$1.90 \times 10^{-3}$	$7.52 \times 10^{-4}$	$6.68 \times 10^{-6}$	$4.46 \times 10^{-6}$
2 <sup>nd</sup> order	Yes	Yes	Yes	Yes	Almost
$k_{app,sim}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$7.58 \times 10^7$	$9.50 \times 10^7$	$9.76 \times 10^7$	$6.61 \times 10^7$	$1.73 \times 10^8$
R <sup>2</sup>	0.999	0.975	0.993	0.985	0.949
F-test value	$4.09 \times 10^5$	$6.57 \times 10^4$	$1.22 \times 10^5$	$7.05 \times 10^5$	$2.51 \times 10^7$
$k_{app,sim}/k_{app,cal}$ (%)	41.9	52.5	53.9	36.5	95.8

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

Reaction	Eq (i)	$K_i$	$k_i$
<b>Reaction 17 and 18 are shared between both mechanisms with sulfite and sulfide.</b>			
$\text{H}_2\text{S} + \text{HO}^- \rightleftharpoons \text{HS}^- + \text{H}_2\text{O}$	(29)	$10^{\text{p}K_w - \text{p}K_{a,1}} = 10^{7.0}$	$^1k_{29} = 2.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-29} = 2500 \text{ s}^{-1}$
$\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$	(30)	$10^{-\text{p}K_{a,1}} = 10^{-7.0}$	$k_{30} = 7500 \text{ s}^{-1}$ $^a k_{-30} = 7.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClOH} + \text{HS}^- \rightleftharpoons \text{ClO}^- + \text{H}_2\text{S}$	(31)	$10^{\text{p}K_{a,1} - \text{p}K_{a,4}} = 0.29$	$^a k_{31} = 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ $k_{-31} = 1.04 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClO}^- + \text{H}_2\text{S} \xrightarrow{k_{32}} \text{S} + \text{H}_2\text{O} + \text{Cl}^-$	(32)		$^2 k_{32} = 6.75 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClO}^- + \text{HS}^- \xrightarrow{k_{33}} \text{S} + \text{HO}^- + \text{Cl}^-$	(33)		$k_{33}$
$\text{ClOH} + \text{H}_2\text{S} \xrightarrow{k_{34}} \text{S} + \text{H}_3\text{O}^+ + \text{Cl}^-$	(34)		$^b k_{34} = 1.62 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$
$\text{ClOH} + \text{HS}^- \xrightarrow{k_{35}} \text{S} + \text{H}_2\text{O} + \text{Cl}^-$	(35)		$k_{35}$ expected close to $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$

<sup>1</sup> (Eigen, 1964)

<sup>2</sup> (Vilmann et al., 2014)

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

pH	11		12	
$k_{\text{relative}}$	1.55		0.82	
$k_{\text{app,exp}} (\text{L mol}^{-1} \text{s}^{-1})$	$4.4 \times 10^5$		$4.0 \times 10^4$	
$k_{33}$ value ( $\text{L mol}^{-1} \text{s}^{-1}$ )	0	$10^4$	0	$10^4$
$k_{35}$ value ( $\text{L mol}^{-1} \text{s}^{-1}$ )	$1.23 \times 10^9$	$1.05 \times 10^9$	$1.23 \times 10^9$	$1.05 \times 10^9$
$k_{\text{app,cal}} (\text{L mol}^{-1} \text{s}^{-1})$	$4.2 \times 10^5$	$3.7 \times 10^5$	$4.2 \times 10^4$	$4.6 \times 10^5$
$F_i$ (%)	0.23	2.51	0.19	2.09
Error (%)	5	16	4	14
$k_{33}/k_{\text{app,cal}}$ (%)	0	2.7	0	21.6

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

pH	6	7	7.5	8	9	10	11	12
Simulation number	16	17	18	19	20	21	22	23
$SO_3^{2-}/HSO_3^-$ eq.	80% of the time	Almost no	30% of the time	Almost no	Always	Always	Always	Always
$ClO^-/ClOH$ eq.	No	No	No	No	No	No	Always	Always
$t_{90}$ (s)	$2.99E \times 10^{-4}$	$7.68 \times 10^{-5}$	$1.30 \times 10^{-4}$	$3.65 \times 10^{-4}$	$1.92 \times 10^{-3}$	$8.82 \times 10^{-3}$	$6.93 \times 10^{-2}$	$6.75 \times 10^{-1}$
2 <sup>nd</sup> order	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
$k_{app,sim}$ ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )	$9.49 \times 10^7$	$3.64 \times 10^8$	$2.02 \times 10^8$	$7.30 \times 10^7$	$1.48 \times 10^7$	$3.24 \times 10^6$	$4.09 \times 10^5$	$4.22 \times 10^4$
$R^2$	0.999	1.000	0.993	0.999	1.000	1.000	1.000	1.000
F-test value	$4.92E+05$	$1.49 \times 10^6$	$7.25 \times 10^4$	$4.77 \times 10^5$	$1.89 \times 10^6$	$7.91 \times 10^6$	$2.62 \times 10^8$	$3.43 \times 10^{10}$
$k_{app,sim}/k_{app,cal}$ (%)	88.0	76.9	41.6	25.6	36.6	77.1	97.1	100

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

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