

Electrochemical oxidation of sulfide ion at a Ti/IrO₂–Ta₂O₅ anode in the presence and absence of naphthenic acids

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Abstract Electrochemical oxidation of sulfide ion at a Ti/IrO₂–Ta₂O₅ anode followed partial order kinetics (between current and mass transport control) in the absence and presence of chloride ion and of naphthenic acids, at sulfide concentrations typical of sour brines. The desired outcome was to promote the 2-electron oxidation of sulfide to elemental sulfur rather than the 8-electron oxidation to sulfate. Although elemental sulfur accumulated to some extent at low conversion of sulfide, sulfate ion became the principal product as the reaction progressed. At high conversion, the overall current efficiencies were typically higher than 50%, with material balance about 90%. However, this anode material was gradually poisoned by sulfide in long term use.

Keywords Sulfide ion · Electrochemical oxidation · Ti/IrO₂–Ta₂O₅ anode · Naphthenic acids · Geothermal sour brine

1 Introduction

Sulfide ion is a significant contaminant in the geothermal brines that accompany oil and gas extraction, as well as in certain oil refinery waste streams. Hydrogen sulfide is highly toxic and odorous; in addition, sulfide solutions are corrosive towards metal pipes [1–4]. Chemical methods of

remediation of sour brines [5, 6] by precipitation (e.g., as ZnS) and oxidation (e.g., with chromates) are unsatisfactory in terms of both cost of chemicals used and disposal of the resulting toxic sludge. Biological oxidation is slow and applicable only to low concentrations of sulfide [7, 8]. Consequently, there is interest in possible remediation technologies involving electrochemical oxidation to either elemental sulfur or sulfate ion [9–11].

Ateya and Al-Kharafi [1, 12] found that electrochemical oxidation of sulfide at graphite anodes led to deposition of sulfur on the anode. The same group also achieved oxidation of sulfide in synthetic geothermal brine that contained 3.5% by mass of NaCl. They confirmed the deposition of sulfur by X-ray photoelectron spectroscopy [9], and argued that further oxidation of elemental sulfur to sulfur oxyanions did not occur under these conditions, because they observed no other species sorbed to the anode. However, no material balance for sulfur was reported. Sulfur did not deposit on a titanium anode [13], but pitting occurred at a stainless steel anode [14], suggesting the intervention of electrocoagulation under the latter conditions, as had previously been observed at iron or aluminum sacrificial anodes [6, 15].

We recently reported that the oxidation of sulfide ion to sulfate at a boron-doped diamond (BDD) anode occurred with near quantitative chemical yield and current efficiency, in both the absence and presence of chloride ion [16]. However, there are certain disadvantages in developing this chemistry into a prospective technology. First, BDD is still a rather exotic material that is not available in large format at low cost. Second, the formation of sulfate as the chief product carries the risk of precipitation of calcium sulfate when the treated sour brine is pumped into a reinjection well. Third, the 8-electron oxidation of sulfide to sulfate is four times as energy intensive as the 2-electron

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oxidation to elemental sulfur. These limitations prompted us to investigate other anodes for the oxidation of sulfidic brines. Because dimensionally stable anodes based on iridium dioxide are known for their exceptional longevity for oxidation of chloride in the chlor-alkali industry, we selected a commercially available Ti/IrO₂-Ta₂O₅ anode.

2 Materials and methods

Sodium sulfide nonahydrate (ACS reagent, 98%), sodium sulfate (anhydrous, 99.9%), sodium thiosulfate, and starch indicator for iodometry were supplied by Sigma-Aldrich (Oakville, ON). Chloroform (reagent grade), sodium chloride, sodium hydroxide, barium chloride, and hydrochloric acid were supplied by Fischer Scientific (Toronto, ON). Naphthenic acids were supplied by Acros Organics (Geel, Belgium). Iodine (sublimed) was supplied by Caledon Labs (Georgetown, ON).

The anode (IrO₂-Ta₂O₅ on titanium mesh, often described as a mixed metal oxide anode Ti/IrO₂-Ta₂O₅) was supplied by Eltech Company (Fairport Harbour, OH). A stainless steel plate with dimensions of 3.7 × 2 cm, supplied by the University of Guelph machine shop, was used as the cathode. Both electrodes were cut to dimensions 15 × 2 cm, with 3.7 × 2 cm immersed in the solution.

Electrolyses were performed at constant current in a 100 mL Pyrex beaker with power supplied by an EG&G Model 363 potentiostat/galvanostat. Electrical connections were made to the electrodes with alligator clips. The reactor was operated in batch mode with 80 mL of solution under stirring. The solutions contained sodium sulfide (15–45 mM) with 0.25 M sodium hydroxide supporting electrolyte, and sodium chloride concentrations from 0 to 5% (w/v). The electrolyses were performed at currents from 50 to 400 mA for up to 8 h. The change in the concentration of sulfide with time was determined by iodometry.

The concentration of sulfate was determined by turbidimetry at 420 nm using a Pharmacia LKB Novaspec II UV/Vis spectrophotometer [17]. For samples containing naphthenic acids, a 1 mL sample was acidified with two drops of conc. HCl and the naphthenic acids were extracted with 1 mL of chloroform prior to analyzing for sulfate turbidimetrically.

The concentration of sulfur was determined by an HPLC method modified from reference [18]. Sulfur was extracted from the reactor and electrodes by first rinsing the electrodes with 25 mL of CHCl₃. The whole reactor solution (80 mL) was then acidified to precipitate naphthenic acids (when relevant) by addition of 10 mL of conc. HCl. The supernatant was extracted with the 25 mL of rinse CHCl₃ prior to analysis by HPLC. Separation was carried out

with a reverse-phase Phenomenex Spherisorb column with dimensions of 4.6 × 150 mm, a silica precolumn, a Gilson 305 pump, and detection at 254 nm with a Waters 441 UV-visible detector. The mobile phase was 90% methanol and 10% Milli-Q water (v/v) at a flow rate 1 mL min⁻¹.

X-ray photoelectron spectroscopy was carried out using a Kratos Axis Ultra X-ray photoelectron spectrometer at the Surface Science Western laboratories of the University of Western Ontario, London, ON. Survey scan analyses were carried out with an analysis area of 300 × 700 microns and pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 × 700 microns and a pass energy of 20 eV.

3 Results and discussion

3.1 Electrolyses in the absence of naphthenic acids

Miller and Chen [19] observed that the oxidation of sulfide at Ti/IrO₂-Ta₂O₅ anodes gave galvanic voltammograms whose potential showed large periodic excursions that were explained in terms of deposits of elemental sulfur. These repeatedly formed on the anode surface and either flaked off [19] or dissolved as polysulfide by the action of excess sulfide ion [20]. Similar behaviour occurs at platinum anodes [13]. The deposition of solid sulfur onto the anode and its subsequent descaling made some of our kinetic data irreproducible, as discussed below.

The first kinetic experiments were carried out with 30 mM sodium sulfide, with concentrations of NaCl of 0, 1, and 5% w/v. In order to prevent volatilization of H₂S(g), 0.25 M NaOH was used as the supporting electrolyte—under these conditions S²⁻ was the major sulfide species (H₂S has pK_a values 7.04 and 11.96). The disappearance of sulfide was followed titrimetrically. Visually, we noted (a) the evolution of gas at the anode (in our earlier experiments at BDD, there was almost none, because the current efficiency for conversion of sulfide was so high); and (b) the presence of suspended solid particles at all but the longest electrolysis times. The solid deposited on the anode was identified as sulfur by dissolution into chloroform followed by evaporation of the solvent, giving a yellow solid with m.p. (113 °C) and mixture m.p. (113 °C) with authentic material (m.p. 115–116 °C). The yield of sulfur was quantitated by extraction into chloroform from both the anode surface and the bulk solution. The literature method [18] was unsuited to the analysis of sulfur in the presence of naphthenic acids, as required later. The amended method involved extraction into chloroform and separation using a reverse-phase Phenomenex Spherisorb HPLC column with a mobile phase composition of 90:10 methanol:water in order to achieve separation.

In the absence of chloride, the rate of loss of sulfide ion was approximately proportional to current density (Fig. 1). We examined kinetic models based on both current control (rate independent of the concentration of sulfide) and diffusion control (rate first order in sulfide). A partial order model [21]—rate proportional to $[\text{SH}^-]^n$ ($0 < n < 1$)—gave the best fit to the data: Eq. 1 and its integrated form Eq. 2.

$$\text{rate} = k \cdot [\text{S}^{2-}]^n \cdot i^m \quad (1)$$

$$[\text{S}^{2-}]_{(t)}^{1-n} - [\text{S}^{2-}]_{(0)}^{1-n} = k \cdot i^m \cdot t \quad (2)$$

Plots of $[\text{S}^{2-}]^{1-n}$ versus time at constant current over the whole time course of the reactions were constructed with values of n varying by steps of 0.1. The best fit was the value of n that had the highest R^2 value, although there was little difference in R^2 over two or three steps around the optimum. For a series of experiments at 100 mA at varying initial concentrations of sulfide, the optimum values of n were 0.6, 0.7, and 0.9 for initial concentrations of 15, 30 and 45 mM, respectively (Supplementary Figure S1). For nominal current densities of 13.5 mA cm^{-2} (100 mA), 27.0 mA cm^{-2} (200 mA), and 54.0 mA cm^{-2} (400 mA) and initial concentration of sulfide 30 mM, the optimal values of n were 0.7, 0.5, and 0.9 respectively (Supplementary Figure S2). These results suggest a kinetic order with respect to sulfide concentration near 0.7, showing that in the concentration range of our experiments (which are typical of the sulfide concentrations in sour brine), the overall rate of oxidation was influenced by both the rate of

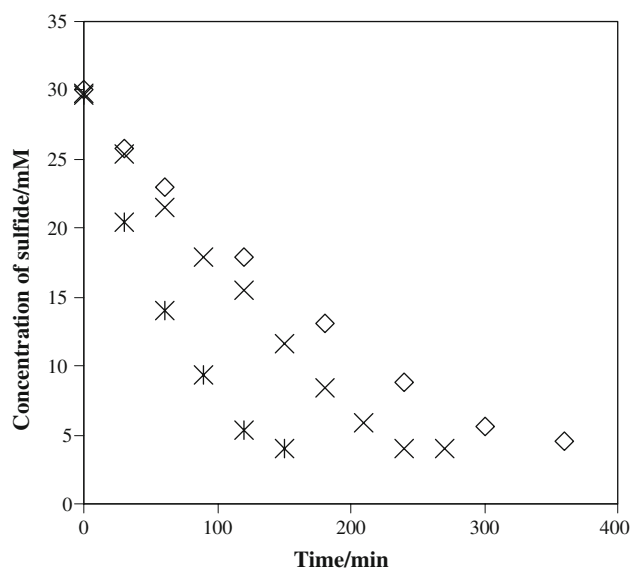


Fig. 1 Electrolysis of sulfide solutions at various current densities of 13.5 mA cm^{-2} (100 mA) (rhomb), 27.0 mA cm^{-2} (200 mA) (\times), and 54.0 mA cm^{-2} (400 mA) (asterisks)

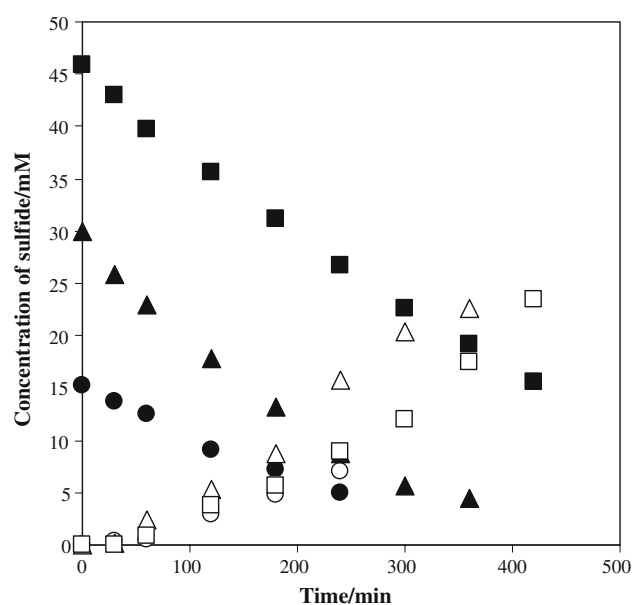


Fig. 2 Electrolysis of sulfide solutions of initial concentrations of 15 mM (full circles), 30 mM (full triangles), and 45 mM (full squares) with a current density of 13.5 mA cm^{-2} . The sulfate concentrations corresponding to the initial sulfide concentrations of 15, 30, and 45 mM are shown as empty circles, triangles and squares respectively

diffusion of the substrate to the anode and the rate of oxidation once it arrived there.

Figure 2 suggests a gradual change towards higher order in sulfide as the concentration falls. The initial rates of oxidation of sulfide were similar for 30 and 45 mM sulfide at 100 mA (13.5 mA cm^{-2}), but the initial rate was less for a starting concentration of 15 mM.

There was little dependence in the rate of loss of sulfide when the current and the initial sulfide concentration were kept constant but the concentration of $[\text{NaCl}]$ varied, a similar result to our earlier observations at BDD [16] (Fig. 3).

Changes were noted after the $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode had been used several times. Less anode gas and fewer flakes of solid sulfur were observed; instead, the partly electrolyzed solution became coloured yellow due to the formation of polysulfide, whose presence was confirmed by UV/Vis spectroscopy. In these cases, the kinetic curves usually followed a “staircase” pattern, which seemed to correlate with the formation and detachment of solid sulfur (Supplementary Figure S3).

XPS analysis was consistent with gradual poisoning of the anode by sulfur species. The S 2p spectrum of an anode that had been used several times and then thoroughly rinsed with water indicated the presence of sulfate ion (33%), sulfite (52%), bisulfide (8%) and either polysulfide or elemental sulfur (8%). The corresponding effect is well known at Pt anodes, at which the PtO_x layer formed under

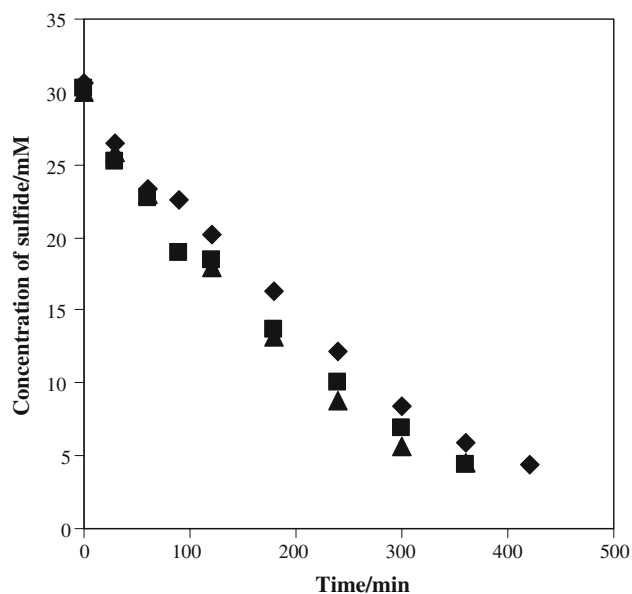


Fig. 3 Electrolysis of sulfide solutions containing NaCl at 0% (triangles), 1% (rhombs), and 5% (squares). A current density of 13.5 mA cm^{-2} (100 mA) was used in 80 mL of solution

anodic polarization is converted to an insoluble Pt sulfide when the electrolyte contains sulfide ions [22]—although there is a report [23] that elemental sulfur deposited on a Pt anode at potentials $<0.2 \text{ V}$ versus SCE; this redissolved as polysulfide in the presence of excess sulfide ion. Similar behaviour is observed at gold [24]; sulfur deposition hinders the further oxidation of sulfide, except at high potentials when the sulfur is oxidized further to sulfate [25].

Product analysis of the electrolyte revealed the formation of sulfate ion, which was analyzed turbidimetrically—as noted above, it is unclear whether this product is formed at carbon anodes [1, 9]. In both the absence (Fig. 4a) and presence (Fig. 4b) of chloride ion there was a lag in the production of sulfate ion, consistent with formation of elemental sulfur, which was detected as the major product early in the reaction. In the construction of Fig. 4, the concentrations of sulfide and sulfate were obtained in the usual manner by removing small aliquots from the electrolyte, but separate electrolyses were needed at each time point in order to analyze for sulfur, because we needed to extract the whole electrolyte with chloroform. The material balance, starting with 30 mM sulfide, was 25, 22, and 27 mM at time points 60, 180, and 360 min, respectively, representing 90% at the end of the reaction (Fig. 4a). The amount of sulfur produced was slightly greater the presence of 1% NaCl than in the absence of NaCl and the material balances were 33, 30, and 30 mM at times 60, 180, and 360 min (Fig. 4b). In our earlier work at BDD [16], we had found losses of up to 5% each through

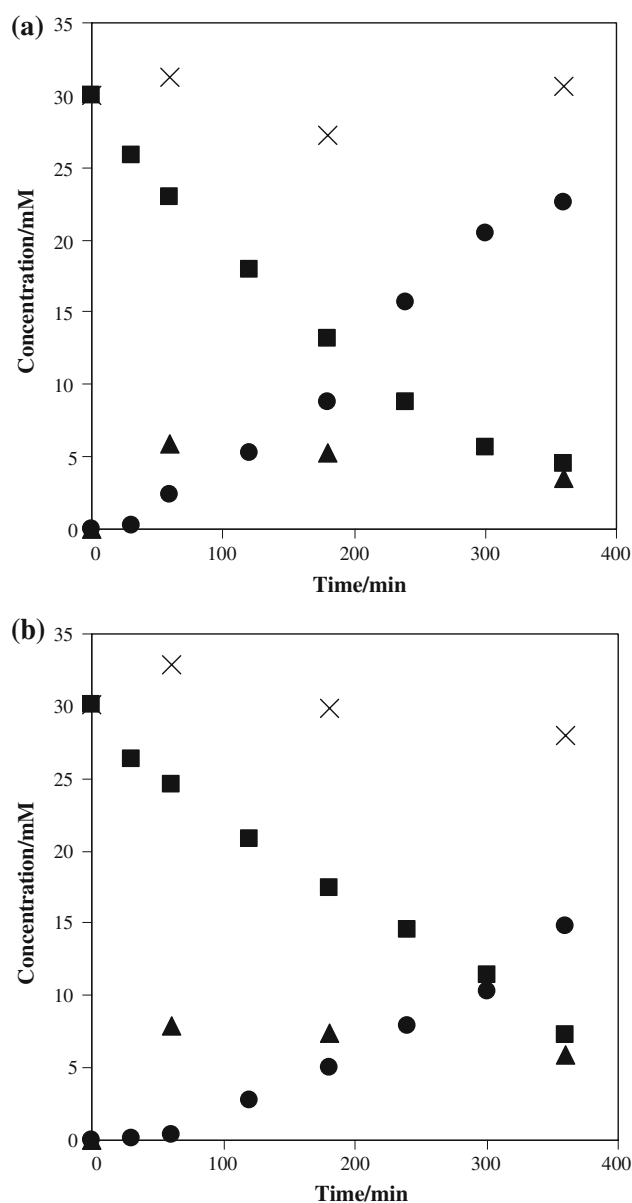


Fig. 4 Electrolysis of 30 mM sulfide at pH 11 with current density of 13.5 mA cm^{-2} , showing sulfide (squares), sulfate (circles), sulfur (triangles), and mass balance (×). **a** No NaCl; **b** 1% NaCl (w/v)

volatilization of H_2S and disproportionation of polysulfide and its conversion to tetrathionate ion. These results at Ti/IrO₂-Ta₂O₅ anodes contrast with our observations at BDD [16], at which we observed a near-quantitative material balance between S^{2-} and SO_4^{2-} at all stages of the reaction. Elemental sulfur was never released from the BDD anode as a discrete intermediate (and no solid particles of sulfur were seen).

Current efficiencies were calculated on the basis of the experimental concentrations of residual sulfide, sulfur, and sulfate in solution at times 60, 120, and 180 min using Eq. 3.

CE

$$= \frac{\{n(\text{SO}_4^{2-}) \times 8 + n(\text{S}) \times 2\} \text{mole}^- \times 96,500 \text{ C (mole)}^{-1}}{I \cdot t} \quad (3)$$

The current efficiencies in the absence of NaCl at 60, 180, and 360 min were 41, 50, and 65% respectively; in the presence of 1% NaCl the corresponding values at the same time points were 40, 39 and 46%. Although these current efficiencies are lower than those observed at BDD, they are still high enough to be encouraging from the perspective of environmental remediation.

The complication of the observed kinetics for loss of S^{2-} is explained by the competition between 2-electron oxidation of sulfide and 6-electron oxidation of elemental sulfur. Otherwise, we would have expected a monotonic trend from current control at low conversion towards diffusion control as the concentration of S^{2-} falls [21].

3.2 Electrolyses with naphthenic acids

Naphthenic acids are complex mixtures of polycyclic aliphatic carboxylic acids that are ubiquitously present in sour brines [26]; they exist as their conjugate bases in solutions above about pH 5. We wished to determine whether the surfactant properties of naphthenate anions would mitigate the deposition of sulfur on the anode surface. This would be important from the perspective of the efficiency of environmental remediation. Previously Shih and Lee [27] had suggested the use of an organic solvent to remove sulfur from the anode surface as it formed, but this approach increased the cell resistance and reduced the current efficiency.

Previous work at BDD in the presence of naphthenic acids (unpublished) showed that over-oxidation of sulfide solutions led to the production of an oily film on the anode, which we explained by parasitic Kolbe decarboxylation of the naphthenate anions [28]. At Ti/IrO₂-Ta₂O₅, 100 mA, the rate of oxidation of sulfide was similar in both the presence and absence of 3% naphthenic acids. At 400 mA, oxidation of sulfide was somewhat slower and less efficient when naphthenic acids were present, due to the competing Kolbe reaction at the correspondingly higher anode potential (Supplementary Figure S4).

We could not demonstrate a surfactant effect by the naphthenic acids; fouling of the anode was evidenced by the irregular kinetics that we termed the “staircase effect”. By contrast, the use of sodium dodecyl sulfate as a model surfactant avoided the staircase kinetics and gave a modest increase in the rate of oxidation of sulfide. The lack of a significant surfactant effect is presumably because of the poor solubility of elemental sulfur in hydrocarbon (and

hence hydrocarbon-like) media. The role of anode fouling as a cause of the staircase kinetics was demonstrated by cleaning the anode surface with acetone at regular intervals (Supplementary Figure S5), or by using two identical anodes, one of which was in service while the other was being cleaned.

The simple turbidimetric method for the quantitation of sulfate ion with BaCl₂(s) [17] was unsuccessful in the presence of naphthenic acids due to co-precipitation of barium naphthenate salts. Some success was achieved by ion exchange chromatography followed by the use of a “reactor column” filled with barium chloranilate [29], but the most effective method was acidification and precipitation of the free naphthenic acids, followed by the conventional turbidimetry.

Although we had contemplated a higher yield of elemental sulfur in the electrolyses by sequestration of sulfur in the presence of surfactant naphthenic acids, product analysis showed that the yield of sulfur was lower upon electrolysis of 30 mM sulfide solution containing 1% NaCl and 3% naphthenic acids at pH 11 at a current density of 13.5 mA cm⁻² compared with similar experiments when naphthenic acids were not present (Supplementary Figure S6). The current efficiencies at 60, 180, and 360 min were 54, 88, and 58%, respectively—higher than in the absence of naphthenic acids but with the same 1% NaCl.

4 Conclusions

Our objectives were to investigate whether the electrochemical oxidation of sulfide ion at a commercial Ti/IrO₂-based anode would occur with comparable efficiency as was previously obtained with the more exotic BDD anode. We also hoped to promote the 2-electron oxidation of sulfide to elemental sulfur over the 8-electron oxidation to sulfate ion, anticipating that naphthenic acids, which occur ubiquitously in sour brines, would exhibit surfactant behaviour and sequester elemental sulfur.

Although sulfur was indeed formed at the Ti/IrO₂-Ta₂O₅ anode, and identified both qualitatively and quantitatively, it was oxidized further as the electrolyses proceeded, and at high conversion the main product was sulfate ion. Our results parallel work done by Rajalo and Petrovskya [30] who oxidized the sulfide ion in tannery wastewater at a Ti/MnO₂ anode; when they increased the current density, the yield of sulfate increased at the expense of sulfur deposited on the anode.

Mechanistically, the system under investigation has a number of complexities. Besides the electrochemical oxidations of sulfide to sulfur and sulfur to sulfate, chloride ion, which is isoelectronic with S^{2-} , is oxidized (although at more positive potentials than the oxidation of sulfide) to

hypochlorite. Hypochlorite is itself able to oxidize sulfide to sulfate ion, and the high oxidizing power of hypochlorite undoubtedly contributes to increasing the relative yield of sulfate as concentration of starting material declines during the reaction. A minor complication is that sulfur dissolves in excess sulfide solution to form polysulfide ion, which can either act as a reservoir of elemental sulfur, or can disproportionate to thiosulfate, especially at elevated temperatures, with the eventual formation of tetrathionate ion [10]. From the perspective of environmental remediation, tetrathionate is not regarded as a major pollution problem, being used in recent technologies as a replacement for cyanide in the extraction of gold [31].

Finally, the surface of the Ti/IrO₂-Ta₂O₅ anode was changed chemically (sulfurated) in long term use—i.e., this material is slowly poisoned by sulfide ion. The combination of the foregoing factors suggests that Ti/IrO₂-based anodes are unlikely to be useful materials for the remediation of sour brines.

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